

Review article

Recent advances in cobalt based heterogeneous catalysts for oxygen evolution reaction



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ABSTRACT

The future of the world energy lies in clean and renewable energy sources. Many technologies, such as solar cells, wind turbines, etc., have been developed to harness renewable energies in different forms of fuel. Amongst them, electrolysis of water to produce oxygen and hydrogen is one of the paramount developments towards achieving clean energy, which has attained significant attention due to its green and simple method for the production of fuels. In electrolysis of water, the half-reaction containing the oxygen evolution reaction (OER) is a reaction that is kinetically sluggish, which requires higher overpotential to produce O₂, when compared to the other half-reaction, i.e. hydrogen evolution reaction (HER). Many electrocatalysts are studied extensively to be used in the OER process to get an economical yield out of it. Noble metal-based catalysts are the state-of-the-art catalyst used for OER currently. But due to their high cost and scarcity, they cannot be applied in a large-scale manner to be used in the future. The non-noble metals (transition metals and perovskites) are gaining interest by exhibiting on par or better OER performance compared to the noble metal used. Due to their low cost, ample resources, and several metals available, they have opened up a variety of areas with a different combination of metals to be used as a catalyst for OER. Amongst these metals, cobalt has received massive appreciation for performing as an excellent OER catalyst. Multi metals, multimetal mixed oxides, multimetal phosphides, perovskites, and carbon-supported catalysts containing cobalt have shown low overpotential with high long-term stability. Therefore, in this review, we go through different cobalt-based electrocatalysts for OER, the general mechanism governing the OER process, the challenges that we are facing today to enhance the catalytic performance, and future aspects to overcome such challenges.

1. Introduction

We, as humans, consume energy in different forms in our day to day

life. Most of it is in the form of electrical energy that comes from the burning of finite fossil fuels. Combustion of fossil fuels harms our environment due to large scale carbon emission and alternative solutions

Abbreviations: OER, Oxygen evolution reaction; HER, Hydrogen evolution reaction; RDS, Rate-determining step; ITO, Indium tin oxide; RDC, Rotating disc carbon electrode; RHE, Reversible hydrogen electrode; DFT, Density functional theory; SEM, Scanning electron microscopy; CV, Cyclic voltammetry; FBNW, Fishbone-like nanowires; ORR, Oxygen reduction reaction; HEA, High entropy alloys; np-HEA, Nanoporous high entropy alloys; NHE, Normal hydrogen electrode; KB, Ketjenblack; NW, Nanowire; ICP-AES, Inductively coupled plasma atomic emission spectroscopy; TOF, Turn over frequency; LDH, Layered double hydroxide; XAS, X-ray absorption spectrum; LSV, Linear sweep voltammetry; FTO, Fluorine-doped tin oxide; EIS, Electrochemical impedance spectroscopy; ECSA, Electrochemical active surface area; NC, Nanocrystal; ML, Monolayer; BET, Brunauer-Emmett-Teller; PBS, Phosphate buffered saline; PBA, Prussian blue analog; MOF, Metal-organic framework; DOS, Density of states; HNB, Hollow nano brick; rGO, Reduced graphene oxide; EDS, Energy dispersive X-ray spectroscopy; NF, Nickel foam; CNF, Carbon nanofibre; HNS, Hollow nanospheres; CCS, Conductive carbon-shelled; CC, Carbon cloth; ONS, Oxide nanosheet; XPS, X-ray photoelectron spectroscopy; HNTAs-NF, Hybrid nanotube arrays-nickel foam; GC, Glassy carbon; PNSAs/CFC, Porous nanosheets arrays/carbon fiber cloth; XAFS, X-ray absorption fine spectra; R_{CT}, Charge transfer resistance; 3DGN, 3-D graphene network; TEOS, Tetraethoxysilane; NrGO, Nitrogen-doped reduced graphene oxide; CNTs, Carbon nanotubes; SWCNTs, Single-walled carbon nanotubes; MWCNTs, Multi-walled carbon nanotubes; mMWCNT, Mildly oxidized multi-walled carbon nanotube; PC, Porous carbon; CCHH, Cobalt carbonate hydroxide hydrate; DETA, Diethylenetriamine; NPCNTs, N, P dual doped carbon nanotubes; ALD, Atomic layer deposition; FESEM, Field emission scanning electron microscopy; TEM, Transmission electron microscopy; NP, Nanoparticle; PCP, Porous carbon polyhedron; GO, Graphene oxide; ZIF, Zeolitic imidazolate-framework; NBGHs, N- and B-doped graphene hollow spheres; N-csCNT-GNR, Nitrogen-doped, core-shell structured carbon nanotube-graphene nanoribbon; CCH, Cobalt carbonate hydroxide; OBA, 4,4'-Oxybis (benzoic acid); ND, Nanodiamond

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with clean and sustainable energy are required to overcome our dependency on fossil fuels. Solar energy and wind energy are the most exploited among renewable energies. The amount of solar energy reaching the surface of the earth is several folds greater than that required for human progress so even a low conversion performance would be satisfactory to fulfill the energy requirements. [1] However, wind and solar energy generation are not constant and need efficient and economical storage facilities and conversion to better fuels. Energy conversion to hydrogen releases no carbon dioxide (CO_2) and it can also generate clean discharge (water) on combustion. [2,3] This has attracted much attention due to its green nature and high energy density. Water splitting is amongst the many promising technologies that enable the production of hydrogen and oxygen, which converts sustainable renewable energy into ideal chemical energy using electricity or sunlight. [4,5] This energy conversion technology has amassed worldwide attention owing to its high energy conversion efficiency, a potentially wide range of applications, and negligible environmental pollution. [6–8] Integrated solar water-splitting systems that integrate light-capturing semiconductors with electrocatalysts to effectively split water display specific promise as a means of direct sunlight to fuel production. [9] Thus generated fuels can be used in various applications to reduce carbon emission dramatically. For example, the hydrogen used in a hydrogen driven engine does not burn the fuel like in the conventional internal combustion engine. Instead, it fuses with the oxygen from the air to form H_2O instead of CO_2 . No primary wastes are produced in the electrochemical splitting of water when the electricity is used from solar cells. As a result, it is considered to be a clean process for producing H_2 and O_2 gases.

Electrochemical water splitting can be classified into two half-reactions and they are OER and HER. These reactions are kinetically inactive and require an overpotential to occur at a practical rate. The overpotential loss due to OER is generally much greater than HER. Therefore, OER is generally viewed as the bottleneck of water splitting. [9,10] As a consequence, water electrolysis requires effective catalysts to expedite these reactions smoothly and unhindered. Presently, carbon-based platinum is the most efficient catalyst for HER [11–14] while the standard catalysts for OER are ruthenium- and iridium- based oxides. [15] The first reported work on the OER catalyst was by Meyer and co-workers [16] on the so-called “blue dimer” a binuclear oxo-bridged ruthenium complex. Even though these are excellent electrocatalysts, scarcity in nature and high cost make it difficult to administer them into large scale applications. This gave rise to the widespread study of different non-precious earth-abundant catalysts that have high efficiency for both OER and HER. Considerable progress has been made in using transition metals for better efficiency in OER. Intellectual studies of Co, Ni, Fe, and Mn-based oxides in OER dates back to more than half a century ago. [17–20] Among these metals, special mention goes to cobalt-based compounds for OER and HER reactions. Although cobalt has no biological relevance in water splitting, and although it is significantly less abundant than Fe, Mn, or Ni, it is now emerging as a fascinating metal due to its catalytic power for OER and HER. [21] Cobalt compounds, either as molecular species or as three-dimensional materials, seem to be attractive multi-electron catalysts for both HER and OER in the water-splitting process.

Since OER is considered to be kinetically sluggish, researchers have done extensive studies to overcome this drawback in overall water splitting. Cobalt seems to be an effective catalyst for enhanced and fast OER. Herein, we discuss recent developments regarding characterization, design, and evaluation in the field of cobalt-based electrocatalyst based on noble metals, noble metal alloys, transition metal compounds, perovskite, and functional nanocarbon structures. Further, we share the challenges faced and our outlook on this topic. We also consider future aspects as well.

2. Mechanism of OER

A classic electrolyzer consists of three components, i.e. anode, cathode, and an electrolyte. The electrocatalysts are coated on the electrodes for a speedy activity. In such a system the electrocatalysts used are different on the anode and the cathode which facilitates OER and HER, respectively. But recent studies have come up with new electrocatalysts which are bifunctional for both OER and HER. Ruthenium- and iridium- based compounds had been considered as the novel catalysts for OER due to their high performance in a wide range of pH. [15] Since these precious metals are scarce and expensive, earth-abundant transition metal catalysts are studied to replace them. Generally, electrolyzers operate under high conductive media, i.e. either acidic or alkaline. One drawback of these transition metals is that they degrade in an acidic condition due to high oxidative potential which, in turn, hinders the activity of the catalyst. So, to overcome this, most of the transition metal-based OER catalysts are studied under alkaline medium.

We can find many proposed mechanisms for OER in literature. [22–25] Let us denote “M” to be the active site of a catalyst. In the first step, a hydroxyl radical (OH^-) is adsorbed onto the active site (M) to give M–OH by an electron (e^-) oxidation on OH^- . Then another OH^- reacts with M–OH to give M–O by removing a proton and electron pair. M–OH and M–O are common intermediates in most of the proposed mechanisms. The dissimilarities start after the formation of M–O. Generally, there are two reaction mechanisms to form oxygen gas (O_2) from M–O. In the first (green pathway), it is the direct combination of two M–O intermediates to produce oxygen gas and free active site M. In the second (white pathway), there is a formation of M–OOH intermediate (hydroperoxide intermediate) by the nucleophilic attack of OH^- on M–O, paired with an e^- oxidation. A further proton paired electron transfer results in the decomposition of M–OOH into $\text{O}_{2(g)}$ and the free active site M. This forms the basis for the majority of the mechanisms proposed with the change in the number of electron transfer in individual steps (single/multiple electron reaction). The bonding interaction within the intermediates (M–O, M–OH, and M–OOH) is decisive for the overall electrocatalytic ability. [26] A brief schematic explanation is given in Fig. 1.

The mechanisms are proposed based on certain electrocatalytic kinetic parameters like overpotential (η) and Tafel slope (b). These are also used to evaluate the electrocatalyst’s catalytic performance.

2.1. Overpotential (η)

Overpotential is defined as, the difference between the potential

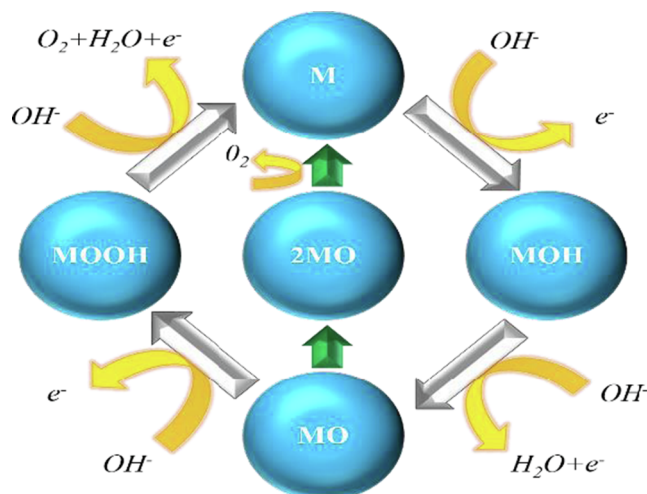


Fig. 1. Mechanism of OER in alkaline medium.

required to practically run the reaction and the theoretically found out equilibrium potential of the reaction. It is one of the important factors for assessing the performance of an OER catalyst. But, it is difficult to get the exact value of the overpotential. So, the potential value at a constant current density is taken as the overpotential. Normally, a 10 mA cm^{-2} current density value is set to find the overpotential of the target reaction.

For OER, the overpotential is calculated as the potential difference between the potential reaching a current density (i) of 10 mA cm^{-2} and the equilibrium potential of 1.23 V. Generally, an electrocatalyst with an overpotential in the range of 0.3–0.4 V is considered to be of excellent catalytic activity for OER.

2.2. Tafel slope (b)

Tafel slope is usually drawn to evaluate the reaction kinetics and mechanism. It is also used to contrast the catalytic activity of different catalysts. As stated by the Butler-Volmer equation,

$$i = i_0 \left\{ \exp\left(\frac{\alpha_a n F E}{RT}\right) + \exp\left(\frac{\alpha_c n F E}{RT}\right) \right\} \quad (1)$$

where “ i ” is the current density, “ i_0 ” is the exchange current density, “ α_a ” the anodic charge transfer coefficient, “ α_c ” the cathodic charge transfer coefficient, “ R ” the universal gas constant, “ F ” the Faraday’s constant (96485 C mol^{-1}), “ n ” the number of electrons involved in the electrode reaction, “ E ” applied potential, and “ T ” absolute temperature (K).

When there is very high overpotential for the anodic electrode, in the above equation the overall current is largely due to the anodic electrode. Therefore the equation can be simplified as,

$$i \approx i_0 \exp\left(\frac{\alpha_a F \eta}{RT}\right) \quad (2)$$

The above equation is known as the Tafel equation. [27] This can be further reduced as,

$$\log(i) = \log i_0 + \frac{\eta}{b} \quad (3)$$

$$b = \frac{\sigma \eta}{\sigma \log(i)} = \frac{2.303 RT}{\alpha F} \quad (4)$$

Tafel slope (b) defines how swiftly the current increases with the overpotential applied. It also helps in finding the rate-determining step (RDS) and formulating a mechanism for the reaction. In an OER, the RDS can be either a single electron reaction or multiple electron reaction. In a single electron reaction mechanism, the transfer coefficient, designated by “ α ”, becomes the symmetry factor (β) which is given by the equation below,

$$\alpha = \beta = \frac{1}{2} + \frac{\eta}{\lambda} \quad (5)$$

where λ is the re-organization energy. From this, the Tafel slope shows a value of 120 mV dec^{-1} . In other words, if the Tafel slope of an electrocatalyst is 120 mV dec^{-1} then the RDS is a single electron reaction and accordingly, a mechanism can be proposed. Whereas in multiple electron reaction, according to Bockris and Reddy, the transfer coefficient is formulated as

$$\alpha_a = \frac{\eta_b}{\nu} + \eta_r \beta \quad (6)$$

where η_b is the number of electrons that transfer back to the electrode before RDS, ν is number of RDS that have occurred in the overall reaction and η_r is the number of electrons that are involved in the RDS. The Tafel slope and transfer coefficient are therefore related to the number of electrons participating in the reaction. Therefore, different Tafel slope defines different RDS and hence different mechanisms for the reaction. In order for an OER catalyst to be considered good in

catalytic activity, it should possess a low Tafel slope.

To obtain a low Tafel slope, various cobalt-based catalysts have been reported in the literature by different teams of researchers. Mainly on noble metals, transition metals, perovskites, and carbon-based cobalt compounds. We will discuss the recent developments in the above-mentioned categories.

3. Noble metals

In an electrolyzer, the OER reaction is kinetically sluggish and requires higher overpotential than the HER reaction. Therefore, catalysts with enhanced activity are required to overcome this drawback. Noble metals are among the catalysts that show high activity as well as durability in a vast range of pH for OER reactions. Iridium, ruthenium, gold, and silver are some commonly used noble metals for this purpose. However, because these elements are scarce and expensive, researchers have tried to use them optimally or replacing them in many ways by synthesizing catalysts consisting of cost-effective alternatives while maintaining equal or better performance. Here we discuss mainly the cobalt-based noble metals used for improved OER activity. Since cobalt has high activity for OER, it can be doped with another active catalyst to better the performance.

3.1. Iridium

Iridium has been used as a novel catalyst for OER due to its high stability and activity in both acidic and alkaline medium. Cobalt linked with iridium for OER has been reported by many research groups. Eunju Lee Tae *et al.* have studied crystalline cobalt oxides nanoparticles (nc-CoO_x) on ITO (indium tin oxide) glass substrate doped with $\sim 5 \text{ mol} \%$ crystalline iridium oxide nanoparticles (nc-IrO_x). [28] It displayed a much lower overpotential (η) and Tafel slope (b) in comparison to the nc-CoO_x electrode and nc-IrO_x electrode. Under a buffer solution of 0.1 M phosphate, the η at 1 mA cm^{-2} values of $[\text{nc-CoO}_x]_{\text{ITO}}$ were 0.37 V at pH 7 and 0.34 V at pH 13, whereas for $[\text{nc-IrO}_x/\text{nc-CoO}_x]_{\text{ITO}}$ were 0.22 V at pH 7 and 0.19 V at pH 13. A drop of 0.15 V can be seen regardless of the pH condition. The Tafel slope for $[\text{nc-IrO}_x/\text{nc-CoO}_x]_{\text{ITO}}$ was 29 to 34 mV dec^{-1} and for $[\text{nc-IrO}_x]_{\text{RDC}}$ (rotating disc carbon electrode) was 38 to 44 mV dec^{-1} . A work performed by Youkui Zhang *et al.* saw the development of a self-assembled 3-dimensional Cobalt-Iridium (CoIr-x) hierarchical structures using a one-step reduction path with NaBH_4 as a reducing agent. [29] The Ir species were incorporated into the irregular surfaced cobalt-based hydroxide nanosheets (3D CoIr-x) as clusters and single atoms. It showed enhanced activity in the neutral and alkaline medium compared to the commercially available IrO_2 electrocatalyst. [29] In the neutral media (1.0 M phosphatic buffer solution, pH@7), the CoIr-0.2 (0.2 is the molar ratio of Ir to Co in precursor or CoIr with 9.7 wt% Ir content) showed a η of 0.373 V@ 10 mA cm^{-2} current density, which is relatively lower when compared to the IrO_2 (0.431 V@ 10 mA cm^{-2}). Regarding the Tafel slope, CoIr-0.2 exhibited a value of $117.5 \text{ mV dec}^{-1}$, which is also below the value for IrO_2 of $132.1 \text{ mV dec}^{-1}$. Whereas in the basic media (1.0 M potassium hydroxide (KOH), pH@14), CoIr-0.2 needed an η of 0.235 V to achieve 10 mA cm^{-2} and Tafel slope of 70.2 mV dec^{-1} . From the above-mentioned electrocatalyst studies, we can understand that the OER activity is favored more by the alkaline medium. This is possible because the rate-determining step of the OER reaction is the accelerated OH^- discharge process for the aforementioned catalysts. [30] Recent studies indicate that by enabling electrochemical oxidation of metallic electrocatalysts in basic media one can considerably enhance the behavior of OER in neutral electrolytes as compared to the direct activation in neutral media without pre-oxidation of metallic electrodes. [31] Taehyun Kwon and co-workers fabricated hollow octahedral nanocages of Co-doped on IrCu alloy (Co-IrCu ONC/C) on carbon support [32], which showed excellent OER activity in addition to prolonged stability in acidic medium. The catalyst exhibited an η value of 0.293 V

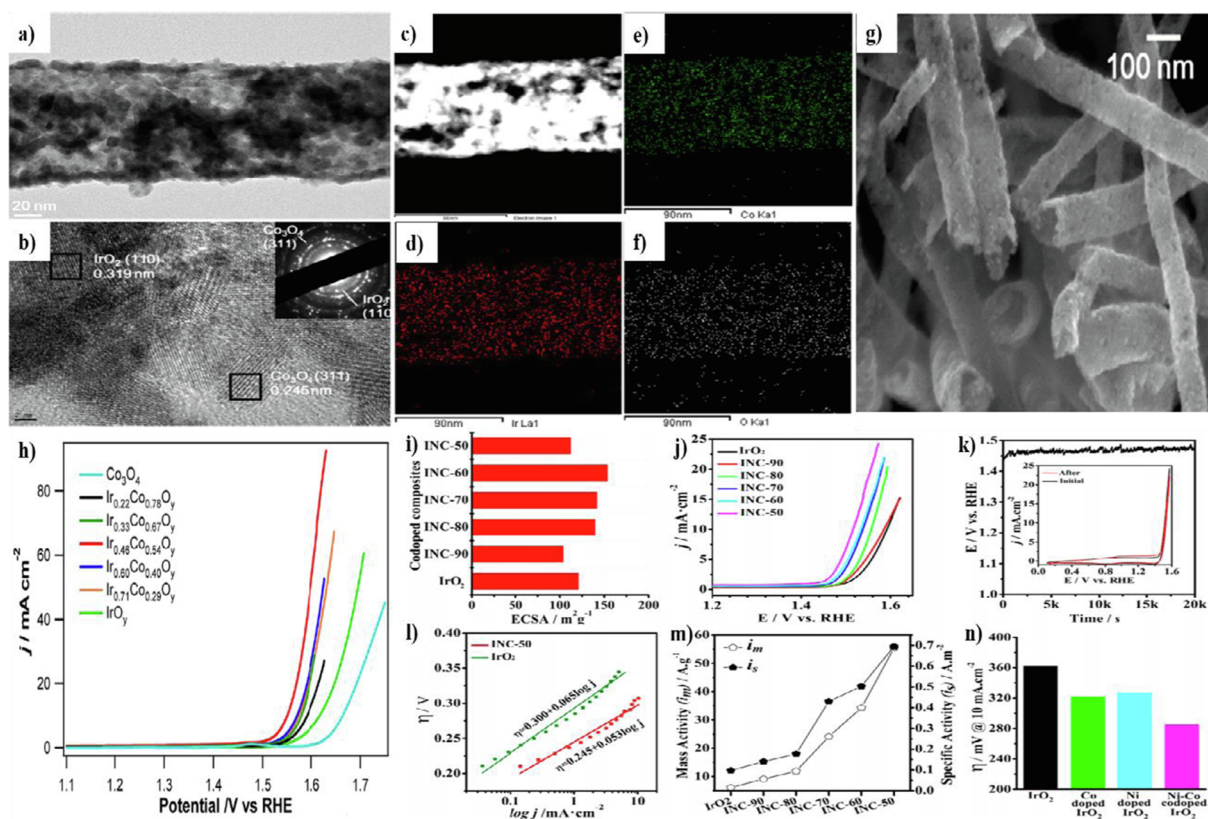


Fig. 2. Ir_{0.46}Co_{0.54}O_y nanotubes' (a) TEM image and (b) high-resolution TEM image (Inset: selected area electron diffraction patterns), (c) Ir_{0.46}Co_{0.54}O_y nanotubes' TEM image used for elemental mapping. (d-f) Elemental mapping study of Ir, Co, and O atoms existing in Ir_{0.46}Co_{0.54}O_y nanotubes, (g) SEM image of Ir_{0.46}Co_{0.54}O_y, (h) iR-compensated RDE voltammograms for the OER in 1 M NaOH aqueous solution saturated with argon at 10 mV s⁻¹ scan rate with 1600 rpm rotating speed, (i) Electrochemically active surface area for all the codoped composites by extracting the double layer capacitance, C_d, (j) iR corrected linear sweep voltammetry curves for the OER process of all codoped composites relative to IrO₂ in the acidic solution of 0.1 M HClO₄, (k) Chronopotentiometric curves at the constant 10 mA cm⁻² current density. The inset displays the polarization curves for INC-50 before and after the chronoamperometry (CA) experiments, (l) Tafel plots of INC-50 and IrO₂, (m) Mass and area-specific activity of IrO₂ and all codoped composites at 1.5 V vs. RHE, (n) A graph representing the overpotential needed to acquire a current density of 10 mA cm⁻² for IrO₂, codoped IrO₂, and for Ni and Co individually doping in IrO₂ [33–34].

at a current density of 10 mA cm⁻², as compared to Ir/C catalyst that showed an η of 0.315 V. A Tafel slope value of 50 mV dec⁻¹ was reported for Co-IrCu ONC/C, and the catalyst also demonstrated high durability with a reduction of only 3 percent after 2000 cycles of CV analysis. In comparison, the Ir/C catalyst dramatically deactivated with a 50% decrease in current density. The outstanding performance of Co-IrCu ONC/C is credited to the 3D integrated structure. In another work, Waqas Qamar Zaman and the team constructed a multimetallic IrO₂ catalyst by co-doping with two different 3d transition metals (nickel and cobalt) to atomically replace 50% of the precious metal. [33] It was developed by the hydrothermal method to make sure composite homogeneity is achieved and later crystallized at 400 °C. The lower crystal formation energy (calculated using DFT (density functional theory) studies) for co-doping was the main factor for the significant dopant penetration. The synthesized co-doped IrO₂ (Ir-NC-50) demonstrated η at 10 mA cm⁻² current density of 0.285 V which was significantly lower than individually doped IrO₂ by cobalt and nickel. The Tafel data of Ir-NC-50 was 53 mV dec⁻¹ lower than the classic IrO₂ (65 mV dec⁻¹). Therein, they also establish a linear correlation between the decreasing onset potential and the decreasing iridium concentration. This helps in reducing the iridium doping by replacing it with transition metals without any decrease in activity. Stability studies were carried out by mounting the prepared material (Ir-NC-50) on the Ti plate in an acidic medium at a constant current of 10 mA cm⁻² for 5 hrs. It showed negligible differences in activity, pre and post chronopotentiometry tests. Areum Yu *et al.* fabricated a crystalline one-dimensional (1D) tubular nanocomposite of iridium and cobalt (Ir_xCo_{1-x}O_y)

through electrospinning and successive calcination. [34] The Nanocomposite with various Ir to Co ratios was created to test the efficiency and find the optimum loading of Ir to maximize the activity for OER reaction. Ir_{0.46}Co_{0.54}O_y nanotubes demonstrated the best activity for OER as well as high stability in alkaline medium. Scanning electron microscopy (SEM) images showed that Co₃O₄ had a smooth tubular structure and IrO₂ a fiber morphology. The simple creation of Co₃O₄ shell in Ir_xCo_{1-x}O_y probably offers a prototype of the tubular structure, promotes the development of IrO₂ by combining precursors with Ir, and ultimately creates the mixed IrCo oxide nanotubes. To assess the electrochemical properties of the optimum catalyst (Ir_{0.46}Co_{0.54}O_y), cyclic voltammetry (CV) was carried out in 1 M KNO₃ aqueous solution. The CV curves possessed a rectangular shape, showing the swift charging and discharging processes. Electrocatalytic measurements were conducted on a rotating disc electrode (RDE) voltammetry in an aqueous solution of 1 M NaOH at 1600 rpm electrode rotation speed. Ir_{0.46}Co_{0.54}O_y nanotubes had a η value of 0.310 V at a current density of 10 mA cm⁻² and a Tafel slope of 58.6 mV dec⁻¹, which was lower compared to IrO_y nanofibers and Co₃O₄ nanotubes. The Stability test did not show much change in the potential used to generate 10 mA cm⁻² after 1000 repetitive scans. Transition-metal oxides could demonstrate greater stability during OER when compared to metals, possibly due to metal oxides being already present at higher oxidation state and further oxidation shifts is less likely to take place. [35] In a recent work by Yingjun Sun *et al.*, they reported a new material of Pt-rich PtCo/Ir-rich IrCo trimetallic fishbone like nanowires, denoted as PtCo/Ir FBNWs. [36] The optimized Pt₆₂Co₂₃/Ir₁₅ FBNWs only needed

an overpotential of 0.308 V, much lower than the commercial Ir/C (0.380 V), to reach a current density of 10 mA cm⁻². The catalyst also displayed great activity in a broad pH range. DFT calculations reported that the catalyst's high activity was because of the modulation of highly electron active Ir-5d orbital on the Pt-based hetero-d-band-junction. It also acts as an outstanding trifunctional (ORR, OER, and HER) catalyst in a wide range of pH levels. Alloys containing five or more metal elements in a single phase are categorized as high entropy alloys (HEAs) [37], which provides ample possibilities to alter alloys' catalytic activities and surface electronic properties. [38–41] Recently, Zeyu Jin and coworkers worked on nanoporous HEA (np-HEA) of AlNiCoIrMo alloy, which showed high activity towards both OER and HER in acidic medium. [42] They were synthesized by incorporating Ir with other four metals into one single nanostructure phase of de-alloyed Al-based precursor alloys with merely 20 atomic % of Ir. The composition effect showed that the as-synthesized np-HEA had a nano ligament size of about 2 nm. An overpotential value of 0.233 V was needed to attain the current density of 10 mA cm⁻² and a mass current density of about 115 mA mg⁻¹ in an acidic medium. Seung Woo Lee *et al.* achieved a highly active and stable 3D mesoporous binary oxide of Ir and Ru (MS-IrO₂/RuO₂) with an optimum Ir to Ru molar ratio of 1:10 via nano-replication followed by Adams method. [43] When compared with conventional IrO₂/RuO₂ (0.340 V), MS-IrO₂/RuO₂ had a lower overpotential of 0.300 V at 10 mA cm⁻². After the accelerated stability test for over 2 h, the increase in overpotential was found to be 0.022 V for MS-IrO₂/RuO₂, whereas 0.044 V for IrO₂/RuO₂, demonstrating a better stability for MS-IrO₂/RuO₂ (Fig. 2).

3.2. Ruthenium

A ternary compound with iridium, ruthenium, and cobalt was studied by J.L. Corona-Guinto and co-workers. [44] They developed a RuIrCoO_x powder by chemical reduction method, followed by a thermal oxidation process. Cyclic and linear voltammetry at 20 mV s⁻¹ scan rate and 900 rpm in 0.5 M H₂SO₄, was utilized to analyze the electrochemical properties of the electrocatalysts. The RuIrCoO_x specimens revealed a Tafel slope value of 70 mV dec⁻¹ at low current densities and 108 mV dec⁻¹ at high current densities. When compared to RuIrO_x, Tafel slopes of RuIrCoO_x were lower in both the high and the low current densities. Whereas, the overpotential of RuIrCoO_x was found to have a value of 0.410 V at a current density of 18 mA cm⁻². Chronopotentiometry experiments were performed in a current pulse of 0.25 mA cm⁻² to 75 mA cm⁻² in 300 s. The pulse length of the currents was found to be long enough to keep the voltage constant. This result shows that the use of mixed metals can contribute to synergetic effects that may increase the stability and selectivity of OER kinetics. Lei Wang *et al.* reported an active hollow Ru-modulated Co_xP polyhedral structure (Ru-RuP_x-Co_xP) by adopting a facile solid-liquid-phase chemical method. [45] Catalytic activity measured the value of η@10 mA cm⁻² as 0.291 V and a Tafel slope of 85.4 mV dec⁻¹ in an electrolyte of 0.1 M KOH. The obtained value was low compared to RuO₂ (η₁₀ = 0.312 V) and IrO₂ (η₁₀ = 0.393 V). They found that Ru modulation can cause unstable surface termination, improve the electron transfer and promote the reaction kinetics by enhancing the density of states at the Fermi level to improve the electron transfer which further reduces the adsorption energy gap between the intermediates. Youngmin Kim *et al.* synthesized RuO₂/Co₃O₄ nanowires by electrospinning process [46], which showed an η of 0.410 V at 10 mA cm⁻² when subjected to 1600 rpm in 0.1 M KOH solution saturated with oxygen. In comparison to Co₃O₄ and Ketjenblack (KB), RuO₂/Co₃O₄ NWs showed a relatively greater OER current density and lower onset and overpotentials. The study established that the addition of highly active and conductive RuO₂ onto the 1-D Co₃O₄ nanowire enhances the bifunctional performance of catalyst to a larger extent when compared to pure 1-D Co₃O₄. Caiyan Gao *et al.* reported ruthenium-cobalt nanoalloys encapsulated in carbon layers doped with nitrogen fabricated through incipient wetness

impregnation pyrolysis process (RuCo@NC-750 °C, 1.56 wt% Ru). [47] It showed great stability and activity towards OER. ICP-AES test of RuCo@NC-750 °C after 10 h of CA test showed unchanged Ru and Co content compared to the initial sample. It exhibited an η value at 10 mA cm⁻² of 0.308 V and a TOF value of 0.35 s⁻¹ at η₃₀₀ for OER. They related the enhanced activity to the introduction of Ru into the Co lattice matrix, which can significantly increase the transfer of an electron from the alloys to the carbon surface and increase the defects on the carbon surface. In a recent work by Pengsong Li *et al.*, a monoatomic Ru attached on the surface of CoFe-LDH (Ru/CoFe-LDH), with an optimized wt% of 0.45 Ru, displayed an excellent OER activity with a η@10 mA cm⁻² as low as 0.198 V, significantly lower Tafel slope of 39 mV dec⁻¹ and high stability in basic solution when compared to CoFe-LDH and commercial RuO₂ catalysts. [48] In-situ and operando XAS measurements along with DFT + U calculation indicated an electronic coupling that is strong between LDH and Ru support, which acts as a cocatalyst to reduce the kinetic energy barrier to form *OOH from *O intermediate and avoided the formation of the high oxidation state of Ru. A comparison of catalytic activity of different transition metal LDH as cocatalysts revealed a trend as η₁₀ (Ru/CoFe-LDHs) (~0.198 V) < η₁₀ (Ru/NiFe-LDHs) (~0.220 V) < η₁₀ (Ru/NiCo-LDHs) (~0.240 V) < η₁₀ (Ru/MgAl-LDHs) (~0.290 V). Shaoyun Hao and coworkers modified the electronic properties of NiCo-LDH by incorporating Ru cations by one-step chlorine (Cl⁻¹) corrosion of Ni foam (NiCoRu-LDH@NF). [49] Due to the high adsorption energy and improved active sites, the catalyst showed η@100 mA cm⁻² of 0.270 V, a low Tafel slope of 40 mV dec⁻¹ (Fig. 3), and continued stability (55 Hours at 100 mA cm⁻²) in basic solution. As in the previous results, here also, Ru reduced the energy barriers from *OH to *OOH which accelerated the reaction kinetics of OER. Juan Wang and the team fabricated a Co-doped RuO₂ NWs (molar ratio, Ru:Co = 19:1) by combining a facile wet-chemical process and post-annealing treatment. [50] They demonstrated an η@10 mA cm⁻² as low as 0.2 V under acidic medium. First-principle calculations estimating the adsorption free energy of intermediates indicate a modulation in d-band center after metal doping, which is thought to be the cause of the enhancement in the OER activity. Jieqiong Shan *et al.* performed the generation of an alloy of RuIr nanocrystal with Co metal (Co-RuIr). [51] Addition of Co gave way to an enhancement of electronic structure of Co-RuIr alloy resulting in 0.235 V overpotential at 10 mA cm⁻² and a Tafel slope value of 66.9 mV dec⁻¹ in 0.1 M HClO₄ media. This improvement was due to the expected Co leaching which results in increased concentration of O²⁻ species, which further favors OER catalytic activity.

3.3. Silver

Ruohao Dong *et al.* designed a 2-D layered double hydroxide (LDH) structure comprising of silver (Ag) decorated Co(OH)₂ nanosheets (Ag@Co(OH)₂) via a selective reduction-oxidation technique from metal nitrates. [52] In the field of electrocatalysis, cobalt compounds are granted close attention, among the 2-D materials community. Ag@Co(OH)₂ showed excellent performance for OER and a yield of gram-scale, possibly because the near-surface oxygen vacancies in the Co(OH)₂ nanosheets have the capacity to improve the electrophilic ability of O being absorbed, promote the adsorption of -OH on active sites, and shape the -OOH adsorbed species. [53–54] In addition, the Co(OH)₂ interlayer spacing is greater than the typical transition metal hydroxides, resulting in a high ion transfer tendency and improved OER kinetic capability. [55] The electrochemical measurements were performed in an electrochemical workstation that has a three-electrode system in a solution of 1 M KOH (pH ~ 13.85) at room temperature. CV measurements were performed by sweeping the potential from a value of 1.3 to 1.7 V (vs RHE) at 10 mV s⁻¹ sweep rate and LSV with a 5 mV s⁻¹ scan rate. From the LSV curves η@10 mA cm⁻² of Ag@Co(OH)₂ was found to be as low as 0.270 V, whereas a pure Co(OH)₂ synthesized using the same technique showed an η@10 mA cm⁻² of

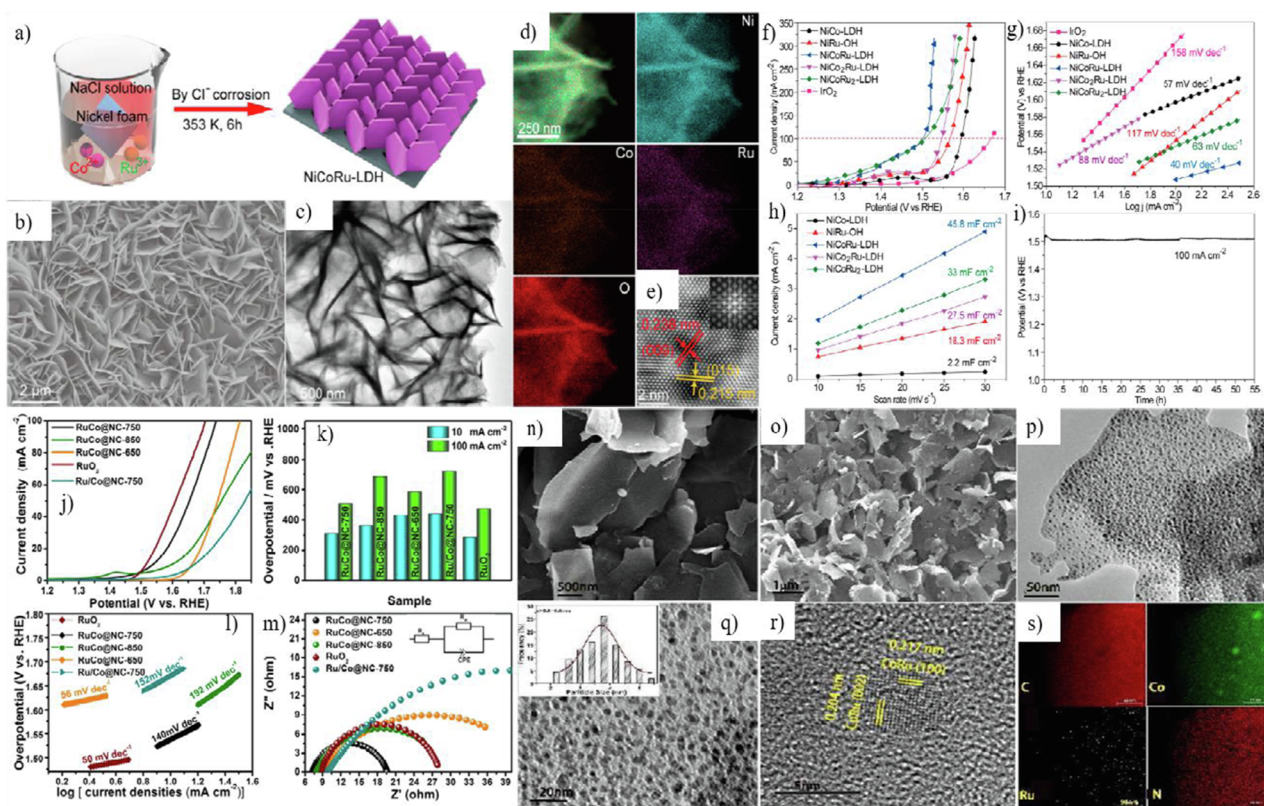


Fig. 3. (a) A schematic diagram representing the synthesis of NiCoRu-LDH by Cl⁻ corrosion technique, (b) SEM images for NiCoRu-LDH. (c) TEM image for NiCoRu-LDH, (d) Elemental maps for NiCoRu-LDH. (e) HAADF-STEM image with FFT analysis for NiCoRu-LDH, (f) LSV curve for the synthesized NiCo-LDH, NiRu-OH, NiCoRu-LDH, NiCo₂Ru-LDH, NiCoRu₂-LDH, and IrO₂/C (g) SEM image of Co-based MOF's, (h) Ru doped Co-based MOF's SEM image. (i, j) TEM images of RuCo@NC-750 and alloy particle size distribution diagram of RuCo@NC-750. (k) HRTEM image and (l) the EDS mappings of C, Co, Ru, and N of RuCo@NC-750 sample. (m) Polarization curves of OER, (n) The corresponding histogram of overpotential vs. RHE at 10 and 100 mA cm⁻² current density, (o) the Tafel slope and (p) the EIS spectra of RuCo@NC-Temp and RuO₂ [47,49].

0.350 V. [56–57] They also prepared ternary materials comprising of cobalt, silver, and other transition metal elements (Ag@Co-Ni LDH and Ag@Co-Fe LDH), which showed better performance than the original Co LDH. This explained how silver doping on the LDH can enhance its efficiency by intensifying the catalyst's electrical conductivity. During the chronopotentiometry analysis (about 8 hrs.), the catalytic performance of Ag@Co(OH)₂ faded only faintly with time. Ag@Co(OH)₂ showed the greatest value of current density of 37.6 mA cm⁻² @ 0.350 V that was threefold more than that of pure Co(OH)₂ nanosheets. In the case of Tafel slope Ag@Co(OH)₂ exhibited a value of 67 mV dec⁻¹. Kai-Li Yan *et al.* synthesized an Ag-doped Co₃O₄ nanowire array reinforced FTO (Ag-Co/FTO) via a facile electrodeposition-hydrothermal process in acidic media (0.5 H₂SO₄), which presented 1.91 V vs RHE onset potential and 0.680 V overpotential. [58] The results indicate that the vertical growth of Co₃O₄ nanowire was a result of Ag film deposition on the FTO substrate, and the formation of the mesoporous nanostructure can be attributed to Ag₂O in Ag-Co hydroxide precursors. In a similar work, B. Jansi Rani *et al.* reported Ag-doped Co₃O₄ nanorods via hydrothermal method at different temperatures (90, 120, 150, and 180 °C). [59] The sample synthesized at 150 °C showed a good activity towards OER with 0.344 V overpotential to achieve a current density of 9.45 mA cm⁻². Conducting an EIS study and following the Nyquist plot, they concluded that the product synthesized at 150 °C had a low resistance of 13 Ω and a narrow arc radius indicating quicker interfacial electron transfer. The enhancement in activity could have been due to the incorporation of Ag into Co₃O₄ crystal lattice which enhances the electrical conductivity and reduces the catalyst's internal resistance. It is also reported that Ag metal enhances the kinetic reversibility, specific capacitance, and redox reaction

of pristine Co₃O₄. [60] In a different work, Xiaoyun Li *et al.* fabricated Ag loaded Fe-Co-S embedded on nitrogen-doped carbon composite (CISC-Ag) via calcination method and subsequent simple dipping route (Ag). [61] When they compared the electrocatalytic activity with pristine CISC, they found that CISC-Ag-3% (0.329 V) exhibited a lower overpotential at 10 mA cm⁻² than pristine CISC (0.366 V). The measured photocurrent density of Hematite photoanode covered with CISC-Ag-3% (with catalyst loading mass of 0.06 mg cm⁻²) was found to be 0.527 mA cm⁻² that was 7 times that the bare hematite photoanode (0.075 mA cm⁻²) at a bias voltage of 1.23 V vs. RHE. They elucidated that this activity was the result of the presence of metallic Ag in the catalyst, which suppresses the surface electron-hole recombination and endorses electron-hole formation. The electrical conductivity of Ag is mainly attributed to the loosely bonded outer electrons of Ag atoms. Therefore, adding Ag to any catalyst increases its electrical conductivity. Xu Zhao and coworkers worked on engineering the electrical conductivity of lamellar Ag-CoSe₂ nanobelts (width 300–500 nm) via partial cation exchange method. [62] About 1% of Ag⁺ cations enhanced the catalyst's OER stability and activity when compared to CoSe₂ nanobelts. 1% Ag-CoSe₂ demonstrated 0.320 V overpotential at 10 mA cm⁻², 22.36 mA cm⁻² current density at an η of 0.350 V and low Tafel slope of 56 mV dec⁻¹. They interpreted that the introduction of Ag⁺ had two effects on the catalyst. Firstly, they found that Ag⁺ caused a 5.6% decrease in the electrochemical active surface area (ECSA) which hinders the activity; and secondly, due to the improved electron transport, there was an increase in Co⁴⁺ sites which promotes the OER activity. The small decrement in ECSA was compensated by a more active generation of Co⁴⁺ active sites.

3.4. Gold

Aolin Lu and team worked on a core-shell structure of gold (Au)-cobalt nanoparticles, with the core being Au nanoparticle and shell being Co_3O_4 supported by carbon (AuCo/C). [63] They developed the structure by two different methods i.e. a facile one-pot synthesis and an injection synthesis. Due to the synergistic interaction between the shell and the core, core-shell nanocrystals (NCs) exhibit exceptional catalytic activity in comparison to single-component NCs. [64–65] Oxygen and nitrogen saturated solutions were used for OER activity measurements. Electrochemical polarization curves were analyzed at 5 mV s^{-1} scan rate after the CV test with the working electrode subjected to a rotation of 2000 rpm. They found that the optimal ratio of Au:Co to be 2:3 ($\text{Ag}_{40}\text{Co}_{60}/\text{C}$), which showed the highest value of current density of 428.6 and 366.9 mA mg^{-1} respectively, at 1.67 V, for OER in N_2 and O_2 saturated solutions when prepared by one-pot synthesis. A Tafel slope value of 65 mV dec^{-1} was exhibited by $\text{Au}_{40}\text{Co}_{60}/\text{C}$, which was lower than bulk Au and bulk Co_3O_4 . Boon Siang Yeo *et al.* reported cobalt oxide (CoO_x) deposited onto the surface of rough gold (Au) substrate as monolayers for better performance for OER reaction. [66] They reported the OER activity of 0.4 monolayer (ML) of CoO_x on Au to be approximately 3 times greater than that of bulk iridium and 40 times greater than that of bulk CoO_x under the same electrochemical conditions. The turn over frequency (TOF) of 0.4 ML CoO_x on Au was found to be 1.8 s^{-1} . This was mainly due to the growth in the surface Co^{IV} population confirmed by Raman spectroscopy. Xunyu Lu *et al.* reported Au nanoparticles-doped mesoporous Co_3O_4 structure (Au/ mCo_3O_4) synthesized via a nano casting process using mesoporous silica KIT-6 as a hard template. [67] An enhanced OER activity was obtained with 2.5% Au doped mCo_3O_4 which displayed a lower onset potential of 1.53 V (vs. RHE) and overpotential of $\eta_{10} = 0.440 \text{ V}$ when compared to mCo_3O_4 (onset potential = 1.56 V (vs. RHE), $\eta_{10} = 0.520 \text{ V}$). This superior performance was ascribed to the doping of electronegative Au nanoparticles, highly exposed active sites, and large Brunauer–Emmett–Teller (BET) surface area. In a different work, Xu Zhao and associates developed CoSe_2 nanobelts decorated with a trace amount (0.1 wt%) of isolated Au atom ($\text{Au}_1\text{-CoSe}_2$). [68] They probed from the study that the trace amounts of isolated Au atoms enhanced the exposure of cobalt active sites, limited the use of Au, shifted up the d-band center, and thereby reduced the H_2O adsorption energy of active sites. An η of 0.303 V at 10 mA cm^{-2} and a Tafel slope of 42 mV dec^{-1} was calculated from the LSV curve of $\text{Au}_1\text{-CoSe}_2$ in O_2 saturated alkaline medium (Fig. 4).

4. Transition metal

To elevate a catalyst's activity, synthesis of specific catalyst morphologies and nanostructures has been practiced for a long time. [69] Based on Mott–Schottky's effect, Zhong-Hua Xue and his team created a Janus particle based on cobalt. [30] A Janus Co/CoP nanoparticle was created by a controllable vacuum-diffusion method for continuous phosphidation of carbon-coated metallic cobalt nanoparticle. In Janus particle, one plane was metallic (Co) and the other was semi-conductive (CoP). Co/CoP had a high ECSA than that of pure Co sample which resulted in an enhanced activity for Co/CoP. Co/CoP-x showed OER activity in a wide range of pH which makes it different from other conventional electrocatalysts. Overpotential of Co/CoP-5 ($\eta = 0.340 \text{ V}$, where 5 indicates the weight ratio of NaH_2PO_2 and Co elements) @ 10 mA cm^{-2} was significantly less than Co (0.430 V) and CoP (0.380 V) species in 1.0 M KOH basic media. In the neutral media (1.0 M PBS), Co/CoP-5 attained a current density of 2.6 mA cm^{-2} at a potential of 1.8 V (vs. RHE) and in acidic media (0.5 M H_2SO_4) it achieved a current density of 1.3 mA cm^{-2} at 1.8 V (vs. RHE) potential. The preparation of aligned cobalt-based $\text{Co}@/\text{CoO}_x$ nanostructures was performed by Qi and team that was achieved by the pyrolysis of cobalt oxalate precursors. [70] The 2-dimensional alignment of the derived

cobalt nanoparticles was guided by the precursor's 2-dimensional morphology. To obtain a current density of 10 mA cm^{-2} the resulting electrocatalyst needs a significantly low overpotential value of 0.298 V. They performed the OER experiment in an aqueous solution of 1 M KOH on a simple glassy carbon electrode. The nanoparticles' compact alignment as well as the metallic nature of the bulk of the catalyst is capable of assisting with the inner- and inter-particulate transfer of charge. In addition, the particles' 2-dimensional alignment can, in general, intercept the dissolution and ripening of cobalt metal nanoparticles, as compared with isolated nanoparticles that is produced via traditional techniques. [71] The resulting electrocatalyst could also demonstrated a superior stability for electrolysis of 24 h at 1.55 V vs RHE. Jing *et al.* performed the synthesis of an oriented assembly constructed by hexagonal $\text{Co}(\text{OH})_2$ nanosheets. [72] A solvothermal technique in a mixture of methanol, water, and ethanol were first carried out to achieve single-crystalline CoC_2O_4 micro rods having ultra-high aspect ratio. The CoC_2O_4 was then converted into $\text{Co}(\text{OH})_2$ from anion-exchange by immersing the CoC_2O_4 precursor in a solution of alkali. The 1-dimensional microrod single crystals were converted into 2-dimensional nanosheets assembly and 3-dimensional structural voids were generated in the oriented assembly. The resulting materials combined the qualities of both 2-dimensional and 3-dimensional arrangements, displaying improved water oxidation activity in comparison to the freely isolated nanosheets. The assembly's magnified performance is primarily due to two reasons. The first is that the anisotropic 2-dimensional nanosheet substructure possesses intrinsic high charge transfer capacity. [73–74] The fabricated ultra-long structure provides a directed pathway for the transfer of charge. The second reason is that the 3-dimensional structural voids elevate the accessible surface area and assist with mass transport. [75] The assembled arrangement can also prevent the aggregation and ripening that takes place during electrolysis for enhanced durability. [71] Relative to the isolated nanosheet counterpart the nanosheet assembly demonstrated a greater activity for OER at similar mass loading. The nanosheet assembly could achieve 10 mA cm^{-2} current density at an overpotential of 0.359 V, and to achieve the same current density, the isolated nanosheet displayed an overpotential of 0.394 V. In addition, the nanosheet assembly has a Tafel slope of 76 mV dec^{-1} when determined by LSV at 5 mV s^{-1} . This value is comparatively smaller than that shown by the isolated nanosheets (95 mV dec^{-1}). Wu's group carried out a facile preparation of cobalt metal thin films through physical vapor deposition (PVD) on different nonconductive substrates. [76] These substrates include polyimide, mica sheet, regular and quartz glass, and polyethylene terephthalate (PET). When the group performed surface electrochemical modification using cyclic voltammetry, the films became active for electrocatalytic water oxidation. This activity was demonstrated by the film as it achieved 10 mA cm^{-2} current density at a low overpotential value of 0.330 V in a solution of 1 M KOH. This is also the value required for a photovoltaic equipment to achieve 12.3% solar-to-hydrogen efficiency. [77] The electrodes were also sturdy, and their activity remained unchanged during chronopotentiometry analysis of long durations. Furthermore, no other energy or time consuming treatments (e.g., annealing, aging, or anodic oxidation, are necessary to reach the achieved activity with the resulting catalyst film. Wan and team developed a new electrocatalyst of $\text{Co}(\text{OH})\text{F}$ for OER. [78] The 3-dimensional $\text{Co}(\text{OH})\text{F}$ microspheres were constructed by building blocks of 2-dimensional nanoflake, which are then woven by 1-dimensional nanorod foundations. Weaving and constructing the substructures of 1-dimensional nanorods and 2-dimensional nanoflakes could deliver high structural void porosity with abundant interior space in the 3-dimensional material synthesized. The $\text{Co}(\text{OH})\text{F}$ material's hierarchical structure merges the merits of all material dimensions in heterogeneous catalysis. The advantages being possessed by the anisotropic low-dimensional (1-dimensional and 2-dimensional) substructures include swift charge transport and high surface-to-volume ratio. Furthermore, the nanorods' interconnectivity

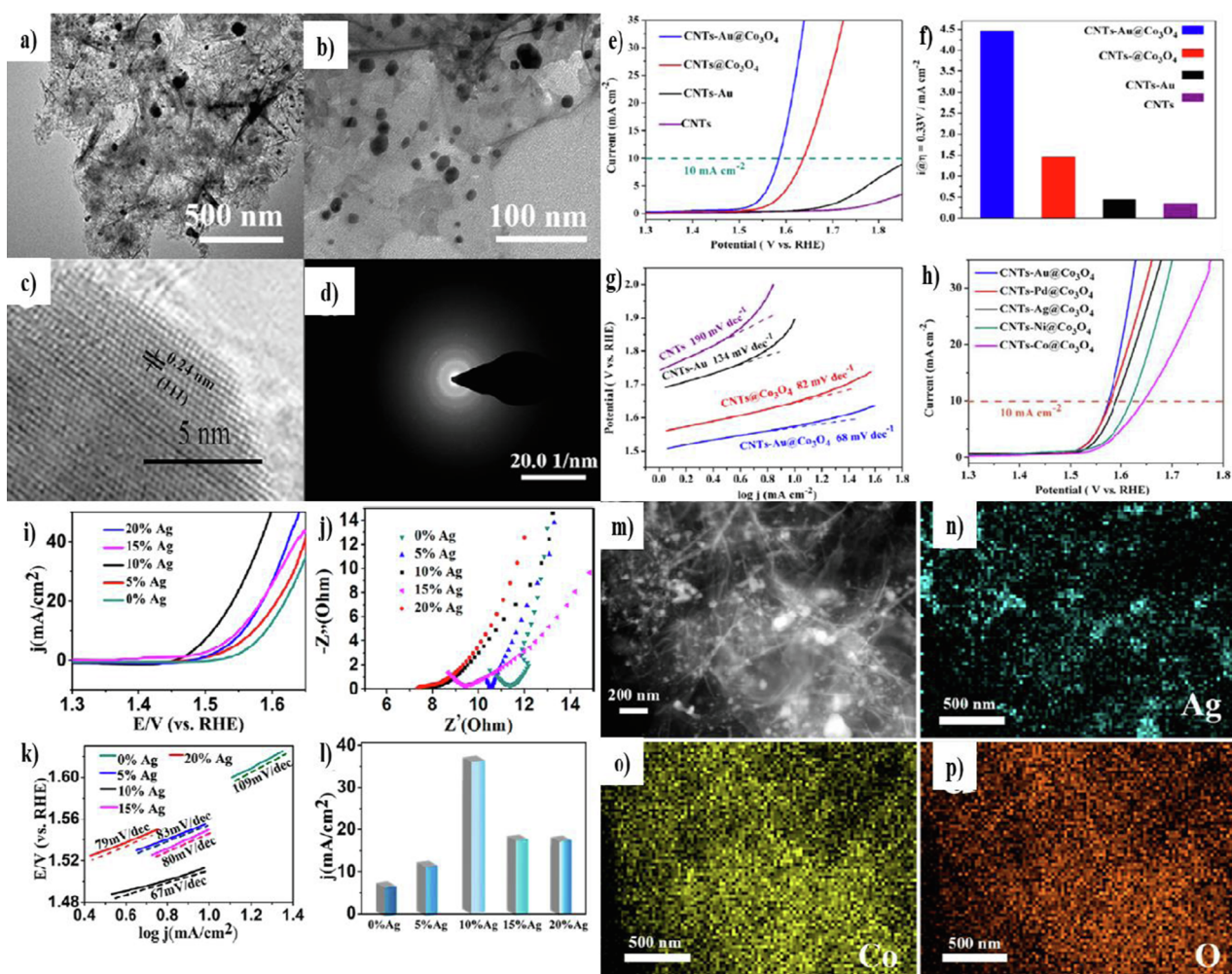


Fig. 4. TEM image of (a-b) CNTs-Au@Co₃O₄, HRTEM of (c-d) CNTs-Au@Co₃O₄ (e) Polarization curves of CNTs, CNT-Au, CNTs@Co₃O₄ and CNTs-Au@Co₃O₄ in a 1 M KOH solution saturated with oxygen (at 5 mV s⁻¹ scan rate), (f) The catalysts' activity at an overpotential of 0.33 V, (g) The catalysts' Tafel plots, (h) Polarization curves of CNTs-Au@Co₃O₄, CNTs-Pd@Co₃O₄, CNTs-Ag@Co₃O₄, CNTs-Ni@Co₃O₄ and CNTs-Co@Co₃O₄ in a 1 M KOH solution saturated with oxygen (at 5 mV s⁻¹ scan rate), (i-j) 10% Ag-decorated Co(OH)₂ nanosheets' TEM images, (k) 10% Ag-decorated Co(OH)₂ nanosheets' HRTEM images and (l) selective area electron diffraction (SAED) of 10% Ag-decorated Co(OH)₂, (m) LSV curves, (n) EIS curves, (o) Tafel slope, and (p) current densities at the overpotential of 0.35 V of different ratios of Co(OH)₂ nanosheets decorated with silver [52,181].

is valuable for charge transport. The 3-dimensional arrangement generates adequate number of active sites per surface area and is useful for efficient mass diffusion during catalysis. With the synthesized material a low overpotential value of 0.313 V was required to drive an OER current density of 10 mA cm⁻² in 1 M aqueous solution of KOH. Guo's team employed a facile 2-phase protocol to synthesize an α -Co(OH)₂ by utilizing sodium oleate as a phase-transfer surfactant. [79] The team regulated the structure and crystallinity of the α -Co(OH)₂ by heat treatments toward improved electrocatalytic OER activity. Calcination of the synthesized α -Co(OH)₂ at a temperature of 200 °C produced a networked and well-dispersed nanoparticles of CoO (Co-200). The CoO sample synthesized displayed an OER current density of 10 mA cm⁻² under a low overpotential value of 0.312 V in a 1 M KOH aqueous solution. The improved activity could be described by the presence of ultra-small particle size and ample open spaces, both of which can deliver many surface catalytic sites. In addition, the onset potential for OER was 0.290 V and the Tafel slope was 75 mV dec⁻¹. Zhao *et al.* successfully produced a unique hollow and porous CoO tetragonal prism-like structure through performing a facile and efficient co-precipitation technique. [80] With this technique, Co₃(OAc)₅OH particles of uniform size were synthesized using cobalt acetate in presence of polyvinylpyrrolidone (PVP K30). PVP itself possesses a strong

coordination capability to metal ions through the N and/or C=O functional groups. The Co₃(OAc)₅OH being produced has a highly uniform and discrete tetragonal prism-like system. The produced material was then calcinated at a temperature of 200 °C for a duration 3 h, in the presence of argon, and at a heating rate of 2 °C/min to obtain the porous CoO structure (CoO-200). High activity as well as high stability could be demonstrated by the porous and hollow CoO microprisms in 1 M KOH solution. A low overpotential of 0.280 V was needed to achieve 10 mA cm⁻² current density. A Tafel slope of 70 mV dec⁻¹ was also displayed by the Co-based catalyst that indicates a fast water oxidation kinetics. The high performance observed could be due to the synergistic effect that exists between 2 different but finely-distributed CoO crystalline phases, ameliorative crystallinity, uniform particle size, low mass transfer resistance, and high surface area exploited from the unique porous arrangement. Liang's research team synthesized β -Co(OH)₂/Co(OH)F hierarchical hexagrams with a six-fold symmetrical arrangement. [81] During the synthesis, hexagonal β -Co(OH)₂ plates were first produced that behave as templates for the growth of Co(OH)F nanorods. An intermediate of β -Co(OH)₂/Co(OH)F hybrid was then generated that consists of plate-like β -Co(OH)₂ hexagonal cores appended with 6 rod-like Co(OH)F branches. Long reaction durations could lead to the complete conversion of β -Co(OH)₂ hexagons that

resulted in the formation of authentic six-branched Co(OH)F nanorods. As a result, nanorods of Co(OH)F were ordered into a six-fold symmetry. Another point to note is that along β -Co(OH)₂ hexagon edges the growth of Co(OH)F nanorods could be observed as lateral branches in place of perpendicular to hexagons. The unusual epitaxial growth mechanism is regarded to be because of the matching between a-axis of β -Co(OH)₂ crystals and the b-axis of Co(OH)F crystals, which is advantageous for electrocatalysis. Relative to pure Co(OH)F and β -Co(OH)₂, the hybrid material could demonstrate enhanced water oxidation activity such as lower overpotential of 0.329 V to deliver 10 mA cm⁻² current density. Liang *et al.* performed a polyvinylpyrrolidone (PVP)-assisted pyrolysis to carry out the transformation of ZIF-67 into *meso*/microporous cobalt-embedded nitrogen-enriched carbon (Co-NC) material for both OER and ORR. [82] During pyrolysis, PVP was enclosed within ZIF-67 in one-pot and remained in it. With this technique, the breakdown of the porous structure at low temperatures could be avoided. The group chose PVP for a number of reasons. The first one was that PVP could be encapsulated because of the strong coordination interaction between the C=O groups in PVP and the metal ion sites in metal-organic frameworks. [83] The second reason was due to the findings by Lai *et al.* in which they found that a PVP derived carbon//ZIF derived carbon interfacial structure could be generated in PVP/ZIF nanocomposites. [84–85] The interfacial arrangement may lead to the improved electrocatalytic activities. Therefore, the group proposed that the *meso*/microporous Co-NC material could modify the pyrolysis functioning of ZIF-67, producing large electrochemical surface area. In addition, the presence of PVP could cause an increase in N content and the generation of the interfacial structure that could further contribute to the enhanced OER and ORR electrocatalytic activities. The group synthesized a number of materials and amongst them P-Co-NC-4 (4 being the synthetic PVP/Co²⁺ molar ratio) demonstrated the best activity. Analysis of the sample using LSV showed that it displayed an onset potential of 0.90 V. Its overpotential value at 10 mA cm⁻² current density was 0.315 V and it displayed a Tafel slope of 75.7 mV dec⁻¹. Liang and group prepared quasi-single-crystalline CoO hexagons that was characterized by structural long-range ordering and plentiful oxygen vacancies as defects. [86] The material was synthesized at β -Co(OH)₂/Co(OH)F hexagons' critical phase transition point. The matching between the a-axis of β -Co(OH)₂ crystals and the b-axis of Co(OH)F crystals is vital for the generation of CoO hexagon single crystals. The resulting material, specifically P-400 (400 = pyrolysis temperature, P = pyrolysis step), possessing abundant defects were very efficient for the oxidation of water as it demonstrated a low overpotential value of 0.269 V to deliver a current density of 10 mA cm⁻² in 1 M KOH aqueous solution. Liang and team used a simple preparation technique to produce 2-dimensional ultrathin α -Co(OH)₂ nanosheets. [87] The technique involved mixing cobalt salt aqueous solution with a methanolic solution of 2-methylimidazole at room temperature. The products synthesized were of nanosheets form that were micrometer in size and possessed an average thickness of approximately 2.5 nm. The ultrathin structure provided the α -Co(OH)₂ nanosheet with the ability to perform greatly for OER. An overpotential value 0.267 V was displayed by the resulting material at $j = 10$ mA cm⁻². With this strategy it is also possible to synthesize other 2-dimensional cobalt-based layered double or triple hydroxides. Furthermore, the α -Co(OH)₂ nanosheets demonstrated a Tafel slope of 64.9 mV dec⁻¹. This value is comparatively lower than that of commercial RuO₂ (78.7 mV dec⁻¹) and hexagonal α -Co(OH)₂ plates (81.2 mV dec⁻¹). Quentin Daniel *et al.* established that when cobalt porphyrins were deposited on FTO glasses (via spin coating), they decompose into thin film of CoO_x on the surface during electrochemical water oxidation under borate buffer (pH 9.2, 0.1 M). [88] The thin film was only detectable by XPES using low photon energies (1000 eV). The newly formed catalyst showed advanced activity for OER with a high TOF value of the order of 10 s⁻¹. Huiling Sun *et al.* reports the synthesis of four Cobalt corroles attached with different acid/base pendants in

neutral aqueous solution. [89] The working electrode used was catalyst loaded on FTO glass. Complex LCH [2]PO(OH) [2] -Co showcased higher performance for both OER and HER compared to other complexes. The LCH [2]PO(OH)₂ -Co complex showed an overpotential of 0.45 V. Samaneh Sohrabi and team worked on a composite 3D porous coordination network (PCN) with 3D nanochannels via solvothermal method with the help of Zr₆ clusters and tetrakis (4-carboxyphenyl) porphyrin cobalt (MOF). [90] Because of the presence of porphyrins and ultrastable Zr₆ clusters on the backbone of the MOF, it was an easy access for the reactants. The catalyst developed showcased an overpotential of 0.4 V.

4.1. Nickel

Bangan Lu and co-workers synthesized a nanowire array of nickel and cobalt oxides freely standing on nickel foam substrate (Ni_xCo_{3-x}O₄-1:1). [91] They reported that Ni doping on the Co₃O₄ increased the roughness and in turn increased the activity of the catalyst. The Ni doped Co₃O₄ (Ni:Co = 1:1) and pure Co₃O₄ had the same nanowire array structure when SEM image analysis was conducted. When the atomic ratio of Ni:Co was larger than 1:1, a change in morphology into nano flake structure was seen. Electrochemical studies showed an overpotential value at 5 mA cm⁻² mg⁻¹ of 0.56 V and 0.65 V for Ni_xCo_{3-x}O₄-1:1 and Co₃O₄ respectively. At 0.6 V the current density of Ni_xCo_{3-x}O₄-1:1 was about 5 times in magnitude than that of pure Co₃O₄. There was also a 5-fold difference in the roughness factor between Ni_xCo_{3-x}O₄-1:1 and Co₃O₄, which proves that an increase in roughness increases the activity of the catalyst. Ni doping is assumed to increase the electrocatalytic activity of Co₃O₄, either by increasing its roughness factor and surface area (geometrical effect) or by enhancing its conductivity (electronic effect) or both. [92] The stability test studied showed a negligible change in potential after 10 h in an alkaline medium. Small Tafel slopes, lower overpotential, and high current density are due to the presence of large active electrochemical surface area (ECSA) as well as 1-D morphology for better charge conduction. Siwen Li *et al.* had a similar approach to develop a Co-Ni based 1-D nanotube with adjustable Co:Ni ratios by a cation-exchange method to build hydroxides (CoNi(OH)_x) grown on a conductive Cu substrate for OER. [93] The nanotube morphology of the catalyst aided in forming a conductive structure with a large surface area, and therefore producing ample catalytic reaction sites. It is also reported that the Co²⁺ at octahedral sites (O_h) gives a better result for OER than Co²⁺ at tetrahedral sites (T_h). [94–95] When X-ray absorption spectroscopy (XAS) was carried out, a peak at 781.1 eV in the Co L-edge XAS spectra correlates to the characteristic peak of Co²⁺ ions at O_h. [96] The LSV showed an onset potential value of 1.48 V (vs. RHE) and an η as low as 0.280 V at 10 mA cm⁻² with a Tafel slope of ≈ 77 mV dec⁻¹. EIS analysis revealed that CoNi(OH)_x nanotube retains a considerably lower charge transfer resistivity which is due to the reaction between the O* intermediate and different hydroxides on the surface of the catalyst. [97] Xuehui Gao *et al.* synthesized hierarchical NiCo₂O₄ hollow micro cuboids constructed by 1-D porous nanowire subunits. [98] It exhibited a small onset potential of 1.46 V (vs. RHE) to reach 1 mA cm⁻², 1.52 V (vs. RHE) at 10 mA cm⁻² and a Tafel slope of 53 mV dec⁻¹. OER activity of NiCo₂O₄ is accredited to its unique hollow mesoporous structure composed of 1-D nanowires, which provides easy access for electrolytes to the active sites. Substituting a second metal into monometallic phosphides could efficiently alter the electronic structure of the parent compounds and further enhance the OER activity. Lei Han *et al.* prepared Ni-Co mixed oxide nanocages from Ni-Co Prussian blue analog (PBA) cubes metal-organic framework (MOF) precursors through an anisotropic chemical etching route. [99] Due to their complex 3-D cage-like hollow structure in addition to the high surface area to volume ratio, they exhibited low overpotential (0.380 V@10 mA cm⁻²) and Tafel slope (50 mV dec⁻¹) under basic medium. Wook Ahn and co-workers fabricated a multivoid nanocuboidal MOF catalyst with multiple

mesosized and microsized pores synthesized from a ternary Ni-Co-Fe MOF (NCF-MOF) by a facile co-precipitation and post heat treatment method. [100] Altering ion exchange rates of the transition metals in the MOF are used to produce heteroatom doping, interconnected internal voids, and favorably tuned electronic structure by combining the outer electrons of active Co and Fe metal ions, which leads to reduced adsorption strength with the intermediates. All these aids in bringing about enhanced activity of OER with low overpotential ($\eta_{10} = 0.320$ V) and Tafel slope (49 mV dec^{-1}) for the catalyst. Bocheng Qiu *et al.* reported Ni-Co bimetallic phosphide nanocages (NiCoP) with constant dispersion of Ni and Co atoms by using Cu_2O cubes as sacrificial templates. [101] $\text{Ni}_{0.6}\text{Co}_{1.4}\text{P}$ nanocages derived from $\text{Ni}_{0.6}\text{Co}_{1.4}(\text{OH})_2$ nanocages exhibited notable activity towards OER ($\eta_{10} = 0.3$ V, 80 mV dec^{-1}) when compared to Ni_2P ($\eta_{10} = 0.420$ V, 128 mV dec^{-1}) and CoP ($\eta_{10} = 0.370$ V, 100 mV dec^{-1}). The stability test at 1.53 V for 10 h proved that $\text{Ni}_{0.6}\text{Co}_{1.4}\text{P}$ had the least current density loss (10%) compared to CoP(20%) and Ni_2P (30%) nanocages. The authors elucidated that appropriate doping of Co atoms can significantly lower the activation barrier of the catalyst and increase the density of states (DOS) at the Fermi level, resulting in low intermediate adsorption energy and high charge carrier density. Enlai Hu *et al.* presented a template-assisted strategy to organize 2-D nanosheets of Ni-Co precursors into an oriented stacking of 3-D anisotropic Ag_2WO_4 cuboid particles. [102] After successive heating, etching, and phosphorization treatments, Ni-Co precursors are converted to open and hierarchical Ni-Co-P hollow nano bricks (HNBs). Overpotential value of 0.270 V to achieve 10 mA cm^{-2} current density and a Tafel slope of 76 mV dec^{-1} was observed. The extended stability was tested by a CA measurement and only about 6.5% of the initial current was lost in 20 h time period. Micropores and mesopores among the oriented stacking and macropores due to the open and hollow interior promote exposure of active sites as well as penetration of electrolytes into the catalyst which further eases the OER activity. [98,103] Xin Liang and coworkers formed $\text{Ni}_2\text{P-CoP}$ bimetallic phosphides via low-temperature phosphorization of Ni-Co organic frameworks. [104] Enhanced catalytic activity was achieved by controlled formation of interfaces of $\text{Ni}_2\text{P-CoP}$, which reduced the bandgap and promoted faster electron transport. LSV curves showed onset potential (1.50 V (vs. RHE)) and overpotential ($\eta_{10} = 0.320$ V) to be lower than Ni_2P and CoP. Jiayuan Li *et al.* came up with a facile synthesis of single-phase ternary $\text{Ni}_{2-x}\text{Co}_x\text{P}$ ($x \leq 1.0$) rGO hybrids with well-regulated Co doping concentration. [105] It is noted that the presence of rGO increases the number of surface-active sites and enhances the hybrid electrodes' activity. Co doping controls the active sites' catalytic activity and accelerates the charge transfer process of the catalyst. Onset potential of 0.251 V (vs. RHE), η of 0.270 V at 10 mA cm^{-2} and a small Tafel slope of 65.7 mV dec^{-1} were reported for the NiCoP/rGO hybrids ($x = 1$) in an electrolyte of 1.0 M KOH. Long-term catalytic stability proved stable OER current density of 50 mA cm^{-2} at 0.360 V overpotential for 18 h. Hanfeng Liang and coworkers fabricated ternary a NiCoP nanostructure from hydrothermally formed NiCo hydroxides via PH_3 plasma-assisted approach, supported on nickel foam, for the first time (NiCoP/NF). [106] The plasma-assisted process promoted low-temperature reaction and fast preparation of the catalyst. From energy-dispersive X-ray spectroscopy (EDS) mapping, they found the ratio of Ni:Co:P to be 1.106:1:1.138, which was close to NiCoP . Electrocatalytic studies measured an η of 0.28 V to obtain a current density of 10 mA cm^{-2} , which was lower than $\text{Ni}_2\text{P/NF}$ (0.34 V) and NiCo-OH/NF (0.404 V). They attributed the enhanced OER activity to the Co addition which lowered the activation barrier, altered the electronic structure, and synergistic effect between Ni and Co. Junyuan Xu *et al.* worked on tri-metallic equimolar FeCoNiP on carbon nanofiber (CNF) pre-catalyst prepared by chemical reduction followed by phosphorization treatment. [107] Overpotential as small as 0.2 V at 10 mA cm^{-2} current density and a high TOF of 0.94 s^{-1} at an η of 0.35 V was measured from the LSV data under alkaline medium. Also, a greater mass activity of 5000 mA mg^{-1} was obtained at $\eta = 0.330$ V. CNFs aided in the

improved charge transfer and increased the nucleation sites during wet chemical reduction. The authors interpreted that Co helps in reducing the overpotential in the low potential region and Ni boosts the anodic current in the high potential region. Jingchao Zhang *et al.* fabricated mesoporous Ni-Co sulfide nanotubes via template-free solvothermal method followed by anion-exchange process. [108] Due to the synergistic effect between Ni and Co, altered electronic structure, and increased surface area, $\text{Ni}_{0.13}\text{Co}_{0.87}\text{S}_{1.097}$ nanotube exhibited improved performance for OER with lower onset potential (0.262 V at 1 mA cm^{-2}), overpotential (0.316 V at 10 mA cm^{-2}) and Tafel slope ($54.72 \text{ mV dec}^{-1}$) in comparison to $\text{CoS}_{1.097}$ ($\eta_{10} = 0.280$ V, $\eta_{10} = 0.331$ V and Tafel slope = $55.54 \text{ mV dec}^{-1}$). A 3-D structure promotes OER activity by contributing to the high specific surface area, more defects as exposed active sites, accelerated H_2O adsorption, and easy gas permeability. Chengzhou Zhu *et al.* designed a 3D bimetallic Ni-Co oxide hollow nanosponges (HNS) by a sodium borohydride reduction strategy ($\text{Ni-Co}_2\text{-O HNS}$). [109] Due to the hollow structure, synergistic effect between Ni-Co and high specific surface area, the catalyst exhibited a superior OER activity. $\text{Ni-Co}_2\text{-O HNS}$ had a porous and interconnected network and an ultra-low density of around 0.08 g cm^{-3} . LSV curve showed an onset potential of as low as 1.501 V (vs. RHE) and an η of 0.362 V in 0.1 M O_2 saturated KOH solution. In a different work, Seok-Hu Bae and co-workers shaped a 3D conductive carbon-shelled Ni-Co nanowire structure (CCS Ni-Co NWs) (Fig. 5). [110] The Ni-Co nanowires grown on the carbon fiber woven fabric (hydrothermal method) were coated with conductive carbon shell via glucose carbonization followed by annealing processes. The granular and porous structure of Ni-Co nanowires aids in the rapid release of O_2 and provides an enlargement in the number active of sites. Whereas the carbon shell aids in fast electron transmission from the active site to the current collector (carbon fiber fabric) and avoids the dispersion of catalytic particles during active O_2 evolution. These properties of the structure helps in enhancing the catalyst's OER activity. A 0.302 V overpotential @ 10 mA cm^{-2} with a Tafel slope of 43.6 mV dec^{-1} in KOH solution of 1 M concentration was reported. When compared with Ni-Co NWs, the charge transfer resistance of CCS Ni-Co NWs was lower, implying increased current access and enhanced charge transport efficiency. [111] Another notable merit of this catalyst is that it acts as a catalytic electrode, which can be deposited directly on the working electrode without any binders. Cheng Du *et al.* reported a continuous hydrothermal, oxidation, and phosphidation process using NaH_2PO_2 to synthesize a 3-D nest-like ternary NiCoP supported on carbon cloth (CC) electrocatalyst. [112] In alkaline medium, η of 0.242 V @ 10 mA cm^{-2} with a Tafel slope of 64.2 mV dec^{-1} was reported. They concluded that the addition of urea, carbon cloth, and the coexistence of Ni and Co precursors to be the main reason for the 3-D nest-like structure. Furthermore, the carbon cloth acts as a current collector to improve the conductivity and charge transferability. [105]

4.2. Iron

Linzhou Zhuang and coworkers reported Fe-Co oxide nanosheet ($\text{Fe}_x\text{Co}_y\text{-ONS}$, x/y indicates the molar ratio of Fe/Co) synthesized by a solution reduction process using NaBH_4 reducing agent to improve oxygen vacancies and the catalyst's active sites. [113] The optimized $\text{Fe}_1\text{Co}_1\text{-ONS}$ had a high specific surface area of about $261 \text{ m}^2 \text{ g}^{-1}$ which resulted in an η of only 0.308 V @ 10 mA cm^{-2} and Tafel slope as low as 36.8 mV dec^{-1} in an alkaline solution (0.1 M KOH). The results obtained were superior to those of commercial RuO_2 . At $\eta = 0.350$ V, $\text{Fe}_1\text{Co}_1\text{-ONS}$ showed a current density of 54.9 A g^{-1} , which is 5.8 times larger than that of RuO_2 available commercially. A detailed characterization using X-ray photoelectron spectroscopy (XPS) and Photoluminescence spectroscopy confirmed that the excellent OER performance of the catalyst was due to abundant oxygen vacancies which result in an easy excitation of the delocalized electrons into the conduction band near the oxygen-deficient sites. Jin-Xian Feng *et al.*

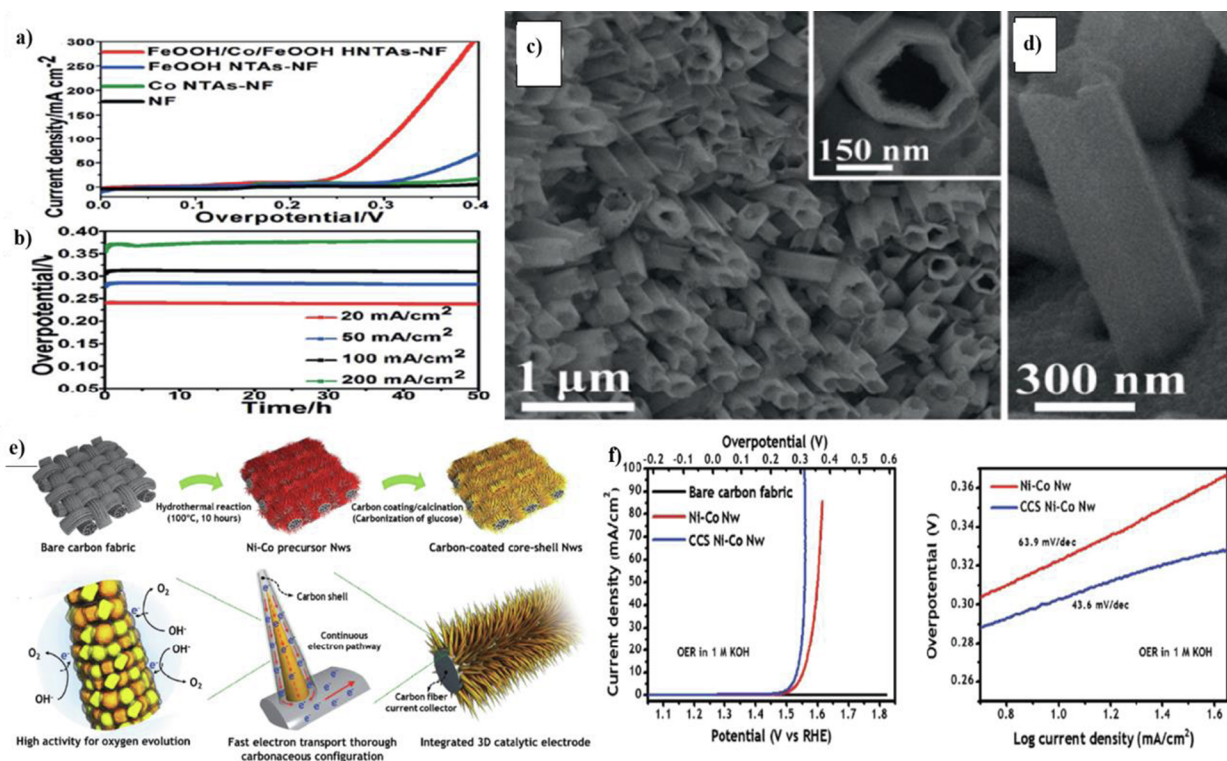


Fig. 5. (a) Polarization curves of NF, FeOOH NTAs-NF and FeOOH/Co/FeOOH HNTAs-NF for OER at 5 mV/s scan rate, (b) CA measurements of the FeOOH/Co/FeOOH HNTAs-NF at different current densities, (c) SEM images of FeOOH/Co/FeOOH HNTAs-NF, (d) SEM image of a typical FeOOH/Co/FeOOH HNT, (e) fabrication procedure of CCS Ni-Co NWs, (f) LSV Curve of CCS Ni-Co NWs and its corresponding Tafel plot [110,114].

designed a FeOOH sandwiched cobalt hybrid nanotube arrays supported on nickel foam (FeOOH/Co/FeOOH HNTAs-NF). [114] Co and FeOOH were loaded as 0.28 mg cm^{-2} and 0.22 mg cm^{-2} , respectively. EIS studies confirmed that FeOOH/Co/FeOOH HNTAs-NF has a significantly smaller electronic resistance when compared to FeOOH NTAs-NF. This result confirms that the Co metal layer enhances electron transmission because of its high electrical conductivity and Ni foam acts as a current collector which together overcomes the poor electric conductivity of FeOOH. The optimum thickness of 25 nm for FeOOH showed the highest OER activity.

FeOOH/Co/FeOOH HNTAs-NF showed an overpotential of just 0.250 V (Fig. 5) to reach 20 mA cm^{-2} current density and a Tafel slope as low as -32 mV dec^{-1} in an alkaline medium. Chronopotentiometric studies performed for 50 h showed no negligible change in overpotential to maintain the current density values of 20, 50, 100, and 200 mA cm^{-2} . Theoretical studies suggest that the energy of OER intermediates can be modulated with the inclusion of metal elements for a given metal oxide. Bo Zhang *et al.* fabricated a gelled FeCoW (oxy) hydroxides (G-FeCoW) using a sol-gel procedure that would include incorporation of W^{6+} into FeCo (oxy) hydroxides, which is hydrolyzed at a controlled rate to achieve atomic homogeneity. [115] Here, tungsten (W) modulated 3d metal oxide (CoOOH), provided excellent adsorption energies for OER intermediates which in turn enhanced catalytic activity. When the G-FeCoW catalyst underwent electrocatalytic studies, it exhibited surprising results compared to the FeCo LDH and NiFe LDH. It presented an η of 0.191 V at 10 mA cm^{-2} current density when deposited on a gold-plated Ni foam. This is significantly lower than the precious metal-based electrocatalyst used for OER previously. The stability test showed no appreciable increase in potential under 30 mA cm^{-2} current density for 550 h. When the catalytic measurements were conducted on glassy carbon (GC) electrode, the catalyst showed an η of 0.223 V at 10 mA cm^{-2} current density, a TOF of 0.46 s^{-1} and mass activity of 1175 A g^{-1} . Similar work has been reported by Peng Fei Liu *et al.* where they used molybdenum (Mo^{6+}) to

modulate 3d metal (oxy) hydroxides (FeCoMo) to attain better adsorption energy for the OER intermediates and provide rich active sites for OER. [116] FeCoMo displayed an η of 0.277 V at 10 mA cm^{-2} current density on GC and no evidence of degradation was reported for about 40 h at constant 10 mA cm^{-2} current density. It exhibited a bulk mass activity of 177.35 A g^{-1} at 0.3 V overpotential, which is approximately 7 times larger in comparison to IrO_2 . Harshad A. Bandal and coworkers prepared a composite electrode of high activity for water splitting by placing ordered spinel FeCo oxide (50 nm thickness) on the surface of Ni foam (FeCoO-NF). [117] When compared to CoO-NF ($\eta_{10} = 0.268 \text{ V}$), FeCoO-NF ($\eta_{10} = 0.244 \text{ V}$) revealed advanced performance for OER activity. Tafel slope of FeCoO-NF (57 mV dec^{-1}) was also lower than the compared CoO-NF (67 mV dec^{-1}), which indicates that the incorporation of iron into Co_3O_4 has a positive effect on enhancing the OER activity. When compared to conventional RuO_2 , FeCoO-NF required comparatively less overpotential to reach the 50 and 100 mA cm^{-2} current density marks. The 3-D white fungus-like structure of FeCoO-NF aided in the effective transport of electrons between the catalyst and electrolyte, easy dissipation of O_2 , and reduced solution and charge transfer resistance. Wei Liu *et al.* fabricated an amorphous Co-Fe hydroxide (CoFe-OH) nanosheets (20–30 nm thickness) via facile electrodeposition for 20 min grown homogeneously on a graphite substrate's surface. [118] Due to their hierarchical network formed by the nanosheets, it resulted in a high electrochemically active surface area which exhibited a low η (0.280 V at 10 mA cm^{-2}) and low Tafel slope (28 mV dec^{-1}) when compared to Fe-OH and Co-OH samples in alkaline medium. In a different work; Hui Xu, Jingjing Wei, and coworkers created a 2-D CoFe oxyhydroxide nanosheet doped with phosphorous (2D-CoFeP NS) in alkaline medium (1 M KOH), which delivered 0.305 V overpotential at 10 mA cm^{-2} current density with a low Tafel slope of 49.6 mV dec^{-1} . [119] 2D-CoFeP NSs electrode maintained long term stability with a negligible decrease in potential at the 10 mA cm^{-2} current density for 24 h. The doped phosphorous played a critical part in modifying the surface-active sites of the catalyst. To

add to the phosphorization, and synergetic effect between Co and Fe, the unique structure provides a great surface area and ample inter-linked channels for O₂ release and mass transport. In a similar work, Xiao Zhang and team introduced a novel CoFeP multi-void nanocages (CoFeP-NC) that were derived from CoFe-PBA (Prussian blue analog) nanocubes via a self-template phosphorization process with uniform size ranging from 250 nm to 350 nm. [120] From the XPS spectra, it was clear that both Co and Fe acted as active sites in the catalyst, and the synergism induced between them improved the electronic structure as well. In alkaline medium, CoFeP-NC showed an η as low as 0.180 V at 10 mA cm⁻² current density, superior stability, and a turnover frequency of 0.93 s⁻¹ at 0.270 V overpotential. This enhanced OER activity could be explained by the porous hollow system with large surface area, high effective active sites, and reduced charge transfer distance. The pyridinic N doped in the CoFeP catalyst provided an added synergistic effect to OER activity. The catalyst exhibited a fast-current density increase within a small change in overpotential ($\eta_{100} = 0.280$ V). Yuan *et al.* developed a hierarchical hollow nanocube structure that was based on ultrathin CoFe-layered double hydroxide (CoFe-LDH) nanosheets. [121] The group first prepared Cu₂O nanocubes as the self-sacrificing template. They employed a template-assisted route for the production of hollow nanocubes based on CoFe-LDH nanosheets through coordinating etching. The performance of the resulting material was demonstrated when it displayed a low overpotential of 0.270 V for 10 mA cm⁻² current density for water oxidation. A low Tafel slope value of 58.3 mV dec⁻¹ as well as a long-term stability was also displayed in an aqueous solution of 1 M KOH. DFT study was also performed by the research group and the analysis revealed that Fe addition provided a metallic identity with Co(OH)₂, assisting in electron transfer. Qian Zhou *et al.* reported a facile cation-exchange process for creating iron-doped Co(OH)₂ nanosheets with the augmented active site. [122] Iron-doped Co(OH)₂ nanosheets showed lower Tafel slope and overpotential (53 mV dec⁻¹, $\eta_{10} = 0.320$ V) when compared to pristine Co(OH)₂ nanosheets (69 mV dec⁻¹, $\eta_{10} = 0.370$ V). After the cation exchange process, Fe³⁺/Co²⁺, the Fe-doped Co(OH)₂ nanosheets had substantial grain boundaries, rougher surface, improved hydrophilicity, and enhanced electronic properties which resulted in an enhanced activity for OER. In recent work, Lei Zhong and coworkers produced Fe doped CoTe (Fe-CoTe) by a one-step solvothermal process, which showed excellent activity and stability without any activation process. [123] A 0.300 V overpotential at 10 mA cm⁻² current density and 45 mV dec⁻¹ Tafel slope value were observed from the electrocatalytic measurements. The authors elucidated that Fe-CoTe had the maximum Fe-Co synergy and the catalytic performance was due to intrinsic properties of Fe-CoTe, and not from the Fe impurity adsorbed from the electrolyte. The improved amount of lattice oxygen also aided to the enhanced OER activity. The charge transfer resistance of Fe-CoTe was only 1/6th of the pristine CoTe catalyst, representing the Fe-doping effect. Sheng-Hua Ye *et al.* fabricated Fe substituted CoOOH porous nanosheets arrays developed on a cloth of carbon fiber (Fe_xCo_{1-x}OOH PNSAs/CFC, 0 ≤ x ≤ 0.33) with 3-D structures via in-situ anodic oxidation of α-Co(OH)₂ NSAs/CFC. [124] Fe_{0.33}Co_{0.67}OOH PNSAs/CFC showed enhanced activity towards OER with a low η_{10} of 0.266 V and a Tafel slope value of 30 mV dec⁻¹. X-ray absorption fine spectra (XAFS) studies indicated a partial substitution of CoO₆ octahedral structures in CoOOH by FeO₆ octahedral during the conversion from α-Co(OH)₂ to Fe_xCo_{1-x}OOH. Detailed DFT calculations indicated that such substitution can reduce the energy levels of the intermediates and products as FeO₆ octahedron is a highly active site for OER. Li-Ming Cao and team proposed a concrete pathway for the hierarchical fabrication of a novel self-supporting 3-D porous sulphur-doped NiCoFe LDH nanosheets (S-NiCoFe LDH) on carbon cloth. [125] The EIS measurements revealed that the charge transfer resistance (R_{CT}) value of S-NiCoFe LDH was smaller than those of undoped LDH (NiCoFe LDH and NiFe LDH), which indicates that sulphur doping helped in improving the catalyst's electrical conductivity. A low η of

0.206 V at 10 mA cm⁻² current density as well as a Tafel slope of 46 mV dec⁻¹ was reported from the electrocatalytic measurements. The XPS results supported that the Co-S bonds and Ni-S bonds were altered into Ni/Co oxyhydroxides that further enhanced the OER activity.

4.3. Other transition metals

Jingrui Han *et al.* developed an amorphous Mn-Co-P layer on MnCo₂O₄ supported on a titanium mesh (Mn-Co-P@MnCo₂O₄/Ti) through a cathodic polarization in NaPO₂H₂ solution. [126] Under alkaline medium, the catalyst demonstrated an η of 0.269 V at a current density of 10 mA cm⁻², Tafel slope of 102 mV dec⁻¹ which was lower compared to MnCo₂O₄/Ti ($\eta_{10} = 0.362$ V, 210 mV dec⁻¹). XPS results revealed that the Mn-Co-P layer was produced on the surface of the MnCo₂O₄ as a shell that boosts the OER activity. Xijun Liu *et al.* reported hierarchical Zn_xCo_{3-x}O₄ nanoarrays which had secondary nanoneedles grown on primary rhombus-shaped pillar arrays supported on titanium (Ti) foil prepared by the co-deposition of zinc and cobalt precursors followed by calcination in air. [127] A 0.320 V overpotential @ 10 mA cm⁻² was detected for Zn_xCo_{3-x}O₄-1:3 (1:3 is the ratio of Zn and Co precursor used) nanoarrays with a low Tafel slope value of 51 mV dec⁻¹. Zn_xCo_{3-x}O₄ can be directly used as electrodes for OER. [128] The close contact of the 3-D porous structure to Ti foil ensured long term stability and gave way for the conduction of electrons. [127,129] The enhanced performance of Zn_xCo_{3-x}O₄ is attributed to the unique hierarchical 3-D nanostructure which brings about high porosity, large surface area, more active sites, increased roughness factor, and improved gas permeability. Jianfeng Ping and team prepared a 3-D porous CoAl-layered double hydroxide (LDH) nanosheets (CoAl-NS) onto a 3D graphene network (3DGN) by electrostatic self-assembly (3DGN/CoAl-NS). [130] Here to obtain the CoAl-NSs, the CoAl-LDH (NO³⁻) crystal with the largest interlayer area was made use for exfoliation. The electrochemical activity was studied in 1 M KOH with a loading mass of CoAl-NSs on 3DGN as about 0.05±0.01 mg cm⁻². The results revealed an η at 10 mA cm⁻² current density to be 0.252 V and a 36 mV dec⁻¹ Tafel slope value. At $\eta = 0.300$ and 0.350 V, the current densities values were 45.37 and 91.74 mA cm⁻², respectively. Stability tests confirmed a nearly constant current density for 18 h at $\eta = 0.250$ and 0.280 V. The exposed active edge sites of the CoAl-NSs made it easy for the proton paired electron transfer process during OER. [131–132] Also a constant coating of single layer CoAl-NSs on the 3DGN by electrostatic self-assembly is an effective way by which it can expedite the reaction kinetics and accelerate the electron transfer. [133–134] Furthermore, the unique structure of 3DGN aids for the access of ions to the catalysts and prevents the restacking of CoAl-NSs [135–137].

5. Perovskite-based

Perovskites exhibit an ABO₃ type of empirical formula with A generally being a rare-earth or alkaline earth metal while B being commonly a transition metal. It has been stated that doping of A- or B- site cations in the perovskites structures is an effective way to improve OER activity. [138–139].

Denis Kuznetsov *et al.* introduced a high electronegative (Bi³⁺) element into the A-site of the strontium cobalt perovskites to sustain high Co-O covalency through the inductive effect. [140] An exceptionally low Tafel slope of 25 mV dec⁻¹ was obtained for the bismuth substituted strontium cobalt perovskites. This was attributed to the potentially increased hydroxide kinship on the catalyst's surface by the introduction of Bi³⁺ ions. Xi Cheng *et al.* analyzed the influence of Sr substitution into the A- site of LaCoO₃ perovskites. [141] The surface composition, bulk electronic structure, electrochemical activity, and conductivity for the La_{1-x}Sr_xCoO₃ perovskite series (0 ≤ x ≤ 1.0) were investigated experimentally and theoretically. A phase transition from rhombohedral (LaCoO₃) to cubic structure (La_{1-x}Sr_xCoO₃) was observed after the gradual replacement of La by Sr. They found that Sr

substitution has the effect of aligning along the Co-O-Co axis, straightening the octahedral cage, and rising the average oxidation state of Co ions. DFT calculations proved that the above merits improve the overlap between the unoccupied Co 3d conduction bands and the occupied O 2p valence bands which further improved the catalyst's OER activity.

To understand the influence of B-site substitution in perovskites, Maria A. Abreu-Sepulveda *et al.* investigated an organized substitution of Co by Fe in $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskites ($\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$) under alkaline medium via a facile glycine-nitrate synthesis. [142] A rise in the surface concentration of different Co oxidation states by the incorporation of Fe was showcased by the XPS results. Specific activity trend of the substitution followed the trend: $\text{Fe}_{0.9} > \text{Fe}_{0.8} > \text{Fe}_0 > \text{Fe}_{0.1} > \text{Fe}_{0.2} > \text{Fe}_{0.5} > \text{Fe}_{1.0}$. Iron incorporation decreased the barrier for electron transfer and facilitated the generation of cobalt-hydroxides. A Tafel slope value of 49 mV dec^{-1} was determined for $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.1}\text{Fe}_{0.9}\text{O}_3$ ($x = 0.9$). They found that Fe complexes are significant for OER by enabling the interaction of Co-OH bond and CoOOH are responsible for the electronic conductivity. Under alkaline medium layered double hydroxide perovskites $\text{PrBaCo}_2\text{O}_{6-\delta}$ (PBC) has been found to be very active. The addition of Fe further enhances the activity. Xiaomin Xu *et al.* reported $\text{BaCo}_{0.9-x}\text{Fe}_x\text{Sn}_{0.1}\text{O}_{3-\delta}$ (BCFSn) perovskites oxides through doping Fe and Sn in $\text{BaCoO}_{3-\sigma}$ parent oxide via solid-state reaction under alkaline medium. [143] BCFSn-721 ($x = 0.2$) displayed a low value of onset potential ($\approx 1.53 \text{ V vs. RHE}$), overpotential ($\approx 0.420 \text{ V}$ at 10 mA cm^{-2} current density) and a Tafel slope value of 69 mV dec^{-1} . They established that the catalyst's OER activity can be tuned by simply altering the concentration of Fe and Sn. The mass activity of the catalyst can be further enriched by reducing their particle size or creating pore structures with a large surface area. [144] Bae-Jung Kim *et al.* doped iron into the B-site of PBC with different ratios to synthesize $\text{PrBaCo}_2(1-x)\text{Fe}_{2x}\text{O}_{6-\delta}$ (x is 0.2 or 0.5; designated as PBCF82 and PBCF55, respectively) nanoparticles in the size range of 5–30 nm. [145] PBCF82 and PBCF55 exhibited the same Tafel slope value of 50 mV dec^{-1} which was lower than PBC (72 mV dec^{-1}) and greater current densities at 1.55 V vs. RHE (17.1 and 19.7 A g^{-1}) (Fig. 6, A-E). When stability tests were conducted, PBCF55 lost only 32% of its starting current density, while PBC lost approximately 74% of its initial current density. They elucidated from their studies that Fe incorporation stabilizes cobalt in the lower oxidation state by delivering finer distribution of charge, encouraging the emergence of oxygen vacancies, and improving the structural stability of the layered double perovskites catalyst by supporting the formation of oxy(hydroxide) layer. Yinlong Zhu and coworkers fabricated $\text{SrNb}_{0.1}\text{Co}_{0.7}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SNCF) under alkaline medium. [146] SNCF was ball milled to increase its surface area, which further increases the OER activity. Advanced OER ability with low onset potential (1.49 V vs. RHE), overpotential ($\eta_{10} = 0.420 \text{ V}$), and Tafel slope of 76 mV dec^{-1} was observed due to excellent ionic and charge-transfer capabilities along with optimized e_g orbital filling, and high O_2 desorption and OH^- adsorption abilities. It also exhibited good stability for the long term due to the incorporation of Nb^{5+} cations on the B-site of the catalyst. The catalytic performance of conventional $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskites (BSCF) is limited by a low specific surface area ($0.5 \text{ m}^2 \text{ g}^{-1}$). Yisu Yang *et al.* developed porous BSCF perovskites with ordered pore structure (3–10 nm) via a novel in-situ tetraethoxysilane (TEOS) template technique to increase the specific surface area (reaching a value of $32.1 \text{ m}^2 \text{ g}^{-1}$) of the conventional BSCF perovskites. [147] This method increased the specific surface area of the nonporous BSCF by 60 times. An optimum ratio of 3.4 for TEOS to BSCF was found to have the highest performance for OER. Under alkaline conditions, BSCF-3.4 exhibited the highest current density of 35 A g^{-1} at 1.63 V vs. RHE (η of 0.4 V) (Fig. 6, f-j), which was 5.3 times higher than nonporous BSCF (6.6 A g^{-1}), and a Tafel slope value of 62 mV dec^{-1} . They concluded from their studies that silica-containing impurities reduce the conductivity of the electrodes and the enhanced activity was strictly

related to the microstructural properties of the catalyst.

Chao Su *et al.* synthesized perovskites oxides with the composition of $\text{SrM}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ ($M = \text{Co, Fe}$) via the sol-gel method. [148] $\text{SrCo}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ (SCT) showed better functioning stability in comparison to $\text{SrFe}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ (SFT), BSCF, and IrO_2 . Such OER activity could be accredited to the low average bond energy of Co-O, optimal e_g electron filling, and good charge transferability. Xiaoming Ge *et al.* designed a novel $\text{La}(\text{Co}_{0.55}\text{Mn}_{0.45})_{0.99}\text{O}_{3-\delta}$ (LCMO) nanorods (diameter of 45–55 nm and aspect ratio of 3–10) using a hydrothermal method followed by heat treatment. [149] The 1% B-site lattice vacancy offers an added advantage for good OER activity of oxides. [150] The further synergetic covalent coupling that exists between LCMO and reduced graphene oxide doped with nitrogen (NrGO) exhibited exceptional bi-functional activity for OER and ORR. The OER onset potential of LCMO/NrGO was about 0.45 V vs RHE and the potential to reach 10 mA cm^{-2} was 0.787 V vs. RHE, which was lower compared to Ir/C. The coupling between the NrGO and LCMO, NrGO's permeating electrical conduction, and the intrinsic activity of LCMO perovskites resulted in the advanced OER activity. Anchu Ashok *et al.* investigated on lanthanum based electrocatalytically active LaMO_3 ($M = \text{Cr, Mn, Fe, Co, Ni}$) perovskites produced through a single-step solution combustion method. [151] Results from the study showed enhanced OER for LaCoO_3 that is because of the optimum stabilization of reaction intermediates present in the RDS of OER. The stability test proved LaCoO_3 to be the most stable among the perovskites studied in the report. Taking inspiration from a previous work by Mohamed A. Ghanem [152] on the mixed anion perovskites (ABO_xX_y , X is a non-oxygen anion), Yuto Miyahara and co-workers studied the bi-functionality, for OER and ORR, of layered cobalt perovskite oxychlorides, namely $\text{Sr}_2\text{CoO}_3\text{Cl}$ and $\text{Sr}_2\text{Co}_2\text{O}_5\text{Cl}_2$, synthesized through a solid-state reaction that utilizes $\text{Sr}_2\text{Co}_2\text{O}_5$ as a precursor. [153] The catalyst was found to be highly active, which was because of the upshift of the O p-band center compared to the Fermi level caused by the incorporation of Cl^- into the oxygen sites. The onset potential of the oxychlorides was exhibited to outperform the state-of-the-art BSCF perovskites. Tafel slope also reveals the same outcome about the activity of oxychlorides (60 and 62 mV dec^{-1} , respectively) when compared to BSCF perovskites (72 mV dec^{-1}).

6. Cobalt supported on carbon materials

Over the past few decades, carbon materials have received substantial attention as a support in various electrocatalyst due to their high thermal stability, environmental friendliness, good conductivity, chemical inertness, high specific surface area, corrosion-resistant, tunable surface function, and higher stability in both acidic and alkaline medium. [154–155] Based on the crystal structure, carbon atoms can be of various allotrope forms with distinct and unique physical and chemical properties. Various carbonaceous nanomaterials such as carbon nanofiber (CNF), carbon nano coil (CNC), nano carbon black (CB), single/multi-walled carbon nanotubes (SWCNT/MWCNTs), carbon mesoporous (CMS) and graphene/graphene oxides (G/GOs) are possibly incorporated with the cobalt-based catalyst in order to enhance the electronic conductivity and electrochemical performance. [156] Here we discuss various cobalt-based catalysts supported on carbon materials towards oxygen evolution reaction.

6.1. Carbon nanotube

Carbon nanotubes (CNTs) have received significant attention in the area of fuel cells as effective support because of the large surface area, high electronic conductivity, thermal stability, and durability that they offer. CNTs are rolled-up sheets of single (SWCNTs) or multi-layer (MWCNTs) carbon atoms (graphene) in cylindrical form.

Lu and Zaho prepared crystalline cobalt oxide nanoparticle of $\sim 6 \text{ nm}$ size incorporated with mildly oxidized multiwalled carbon

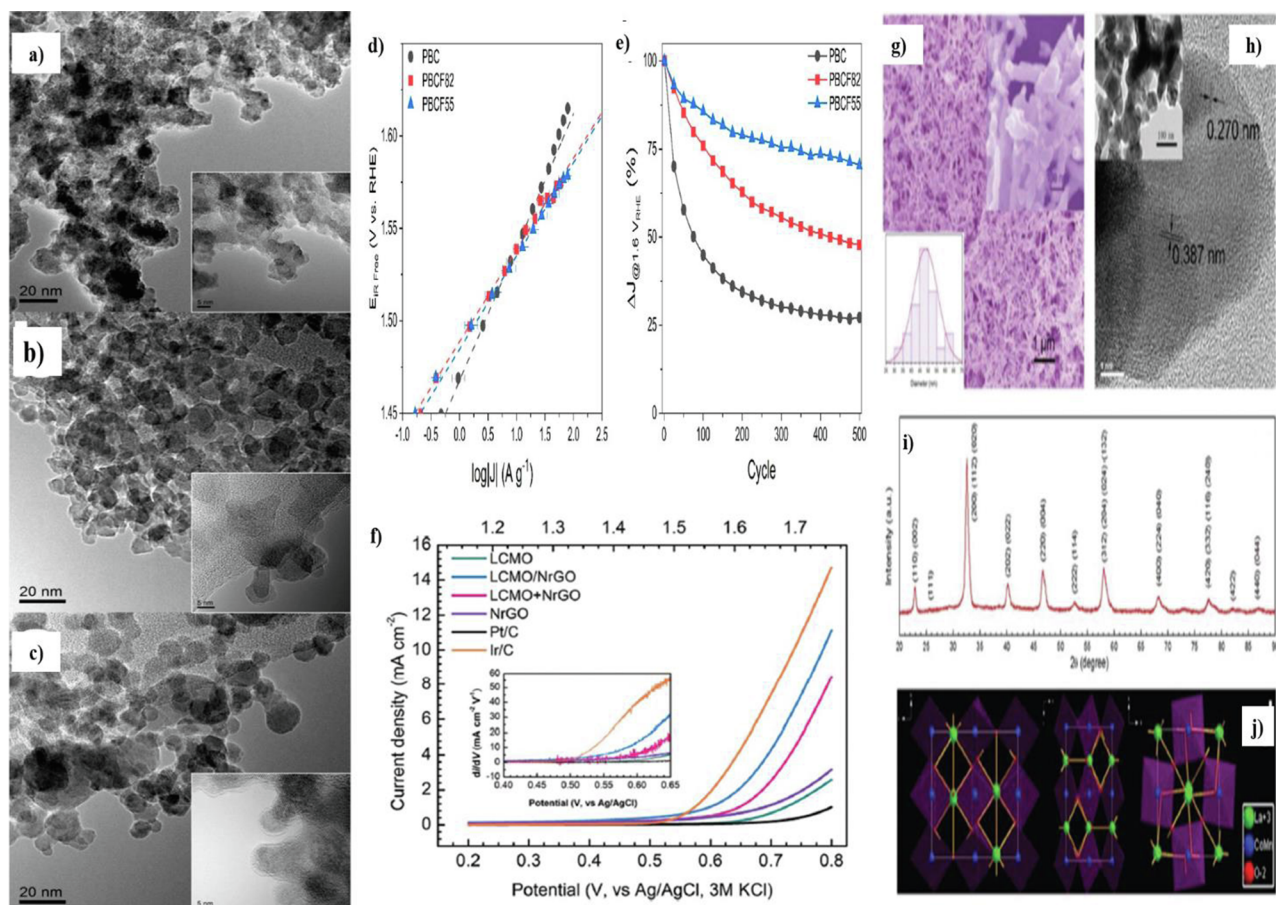


Fig. 6. Transmission electron microscopy (TEM) images of (a) PBC, (b) PBCF82, and (c) PBCF55. (Each inset display high-resolution TEM (HRTEM) images revealing fringes). Electrochemical analysis comparing (d) OER activities' Tafel plot and (e) alteration in current densities with respect to the initial current density at every 25 cycles over 500 cycles between 1.0 and 1.6 V_{RHE} of PBC (black), PBCF82 (red), and PBCF55 (blue), (f) SEM micro image of LCMO nanorods. Inset presents the high magnification of LCMO. The histogram of the diameter of LCMO nanorods (lower left inset shows). (g) HRTEM and TEM images of LCMO nanorods. (h) XRD pattern and (i) the structural representation of LCMO (j) RDE oxygen evolution polarization curves of LCMO/NrGO, LCMO + NrGO, LCMO, NrGO, Pt/C and Ir/C under a rotating rate of 2000 rpm. The inset displays the corresponding curves of di/dV , [145,149]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

nanotubes ($Co_3O_4/mMWCNT$) and used it as an effective catalyst for H_2O oxidation. They studied the correlation between various other carbon structures such as single-walled CNTs (SWCNTs), graphene, and multi-walled CNTs (MWCNTs) with different oxidation states in terms of charge transport and surface functionalization towards water oxidation reaction. The results showed that the hybrid mildly oxidized MWCNTs ($Co_3O_4/mMWCNT$) with a 0.390 V overpotential value (at 10 mA cm^{-2}) and 1.51 V vs. RHE onset potential that can sustain the electrochemical reaction even under harsh environment with minimum carbon corrosion acting as a promising electrocatalyst towards OER [157]. Zeng *et al.* reported the bifunctional cobalt (II/III) oxides strongly anchored onto a lightweight, conductive, and crosslinked aerogel film of carbon nanotubes (CNTs) as a free-standing air electrode. The LSV profile showed improved performance of crosslinked aerogel film of carbon nanotubes (CNTs) when compared with pristine CNT aerogel, N-CNT aerogel, and pure Co_3O_4 in terms of onset potential (1.45 V) and potential (1.7 V vs RHE at a current density of 10 mA cm^{-2}) (overpotential of 0.47 V) [158]. Shuo and coworkers followed the pyrolysis of metal-organic framework (MOF) encapsulated Co_3O_4 for the successful generation of Co-embedded N-doped CNTs with porous carbon (PC) that showed prolonged stability and excellent activity in alkaline solution. The polarization curve for Co-CNT/PC exhibited lower onset potential than Co-doped over porous carbon (Co-PC) that could be attributed to the improvement in the electrical conductivity for CNT. [159] Zhang and coworkers reported a superior

activity and remarkable stability for cobalt carbonate hydroxide hydrate (CCHH) nanosheets strongly adhered on the mildly oxidized MWCNTs in presence of diethylenetriamine (DETA). They found that the presence of DETA greatly influences the structure and morphology of the CCHH/MWCNT composite and thereby enhanced the resulting OER performance. Thus, prepared hybrid CCHH/MWCNT exhibited lower onset potential (approximately 1.47 V vs RHE) (overpotential of 0.285 V @ 10 mA cm^{-2}) and good kinetics that was clear from the Tafel slope analysis. [160] In 2014, the same group reported a study on Co_3O_4 nanorod-multi-walled carbon nanotube hybrid ($Co_3O_4@mMWCNT$) that exhibited 0.309 V overpotential at 10 mA cm^{-2} current density in an alkaline medium that also possess superior activity and stability. [161] Fang *et al.* analyzed the synergistic influence of Co(II), organic ligands, and CNTs that offered excellent activity and durability to sustain in a harsh environment without any carbon corrosion. The hierarchical 3-D unique system with a large surface area improved the transportation of electrons and secured the anchoring of the catalyst's active sites to the CNTs. Co-MOF@CNTs offered impressive durability and activity when compared to 20 wt% Pt/C and RuO_2 catalysts. They studied the influence of the OER performance on the amount of CNT in the overall catalyst and found that the overpotential followed an inverted volcano type trend with CNT weight percentage with increasing order of $5\% < 1\% < 10\% < 15\%$ of CNTs. [162] In order to improve the surface defect, chemically active sites, and the surface defects of CNTs; hetero atom doping with boron, phosphorous and nitrogen are

widely used. Dicobalt phosphides (Co_2P) are another category of Co-based catalyst that recently achieved wide attention owing to their catalytic and magnetic properties. Various reports are available on Co_2P anchored CNTs delivering excellent electrochemical performance. Hui *et al.* utilized N, P co-doped CNTs for the anchoring of CoP/CoP_2 nanoparticles that exhibited low overpotential, higher current density and excellent stability over 100 h. Moreover, they conducted density functional theory calculations and molecular dynamics simulations that concluded the synergetic effects of CoP and CoP_2 improved the electrocatalytic performance; also the heteroatom-doped CNTs readily diffuse out the generated O_2 molecule to help in improving the electrocatalytic oxygen evolution reaction. [163] Das and co-workers followed a novel one pot synthesis of phosphine free (PH_3) Co_2P anchored over N, P dual doped carbon nanotubes without any external carbon additive. The average diameter of prepared Co_2P was found to be 55 nm and for NPCNTs the range was between 80 and 250 nm. The hybrid $\text{Co}_2\text{P}/\text{NPCNT}$ displayed a small onset potential value of 1.293 V and an η of 0.370 V (at 10 mA cm^{-2}) that was expected for a solar water-splitting device with 10% efficiency. [164] Guo and team utilized a combination of dicobalt phosphide (Co_2P)–cobalt nitride (CoN) core–shell nanoparticles synthesized using direct pyrolysis method as double active sites for the incorporation with N doped CNTs that showed excellent trifunctional performance. The interface between CoN and N-doped CNTs was the active site for OER that has attracted applications in flexible and rechargeable Zn-air batteries. [165] Cobalt sulfides, including CoS_2 , CoS_4 , Co_3S_4 , and Co_9S_8 , have been found to be attractive and are novel electrocatalysts for the storage of energy as well as conversion applications because of the unique chemical and physical properties. [166–167] The performance of cobalt sulfides were improved by further optimization of electrode surface with carbon-based materials. Wang and co-workers prepared an integrated 3-D model of carbon-paper/carbon-tubes/cobalt-sulfide array that displayed impressively high performance towards OER. The unique hybrid structure possibly enhanced the accessibility and availability of active sites, the capacity to transport electron, and improved the release of product gases. They studied the catalyst without any CNT incorporation and found that CP/CTs/Co-S have excellent behavior in terms of potential and current density when compared to CP/Co-SN. [168] Xinwei and his team used atomic layer deposition (ALD) for the successful deposition of the thin layer of Co_9S_8 (~7 nm) onto the CNT network scaffold with a high surface area that showed remarkably great performance for rechargeable Zn-air batteries [169].

The electrical conductivity of oxidized-CNTs is lower than non-oxidized CNTs that limit their catalytic performance, nonetheless, this limitation, in some cases can be overcome by using a mildly oxidized graphene/CNTs. [170] Ting Ma *et al.* performed an in-situ synthesis of ultra-small Co–Mn–O spinel nanoparticles that have an average nanoparticle size of 4.4 nm reinforced over the non-oxidized CNTs that enabled strong coupling to aid with the transfer of electron and enhanced the activity. CMO@CNTs exhibited a lower onset potential of 2.558 V and a Tafel slope of 81.1 mV dec^{-1} that showed superior performance when compared with CMO@rGO , CMO@Vulcan , CMO@oxCNTs , and $\text{CMO} + \text{CNTs}$. [171] Fig. 7 shows the synthesis of non-spinel MnCo oxide, $\text{Co}_x\text{Mn}_{1-x}\text{O}$ (Mn^{2+} , Co^{2+}) anchored over N-doped CNTs that showed much higher OER activity than commercial IrO_2 . Co^{2+} was regarded as the active site for the evolution of oxygen because NCNT/MnO exhibited inferior performance than NCNT/CoO as reported by Liu's group. [172] Kumpeng and his team followed a two-step gas phase process for the fabrication of hierarchical hybrid Co_3O_4 – MnO_2 –CNT. The prepared spinel Mn-Co mixed oxide triggered the growth of multi-walled carbon nanotube and the active metal particles remained on the CNT surface were greatly influenced by the growth time. An HNO_3 vapor treatment was used to convert the active metals to their higher oxidation state, where MnO was oxidized to MnO_2 , and Co was converted to Co_3O_4 . Subsequently, a small amount of oxygen functional group was created on the surface of the catalyst that facilitated the

release of gases during the reaction. [173] Liu's group synthesized morphology-controlled $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{MnO}_2$ –CNTs hybrid nanocomposites which showed excellent durability and activity when compared to the commercial 20% Pt/C catalyst. The oxygen evolution reaction onset potential for $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{MnO}_2$ –CNTs, CNT, MnO_2 , $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{MnO}_2$, $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ –CNTs, $\text{Co}_3\text{O}_4/\text{MnO}_2$ –CNTs and 20% Pt/C was found to be 1.42, 1.69, 1.51, 1.70, 1.52, 1.52 and 1.67 V, respectively. This indicates that the powerful coupling effect that is present between La_2O_3 nanorod and MnO_2 nanotubes, Co_3O_4 and CNTs produces a synergy for the catalytic performance. [174] Another catalyst, Ni, showed enhanced performance in OER when alloyed with Co to form bimetallic Ni-Co. Many works have been reported on the encapsulation of NiCo with conducting CNTs in order to improve the electronic conductivity. Jie *et al.* fabricated a 3D network of NiCo encapsulated with nitrogen-doped CNTs (NiCo@NCNTs) as shown in Fig. 7e–h that showed superior activity than the bimetallic composite (Co@NCNTs and Ni@NCNTs) owing to the synergy between cobalt and nickel. They conducted a detailed study on the effect of coupling on NiCo@NCNTs in comparison with physically mixed NiCo and CNTs. The superiority of encapsulated NiCo@NCNTs caused the transfer of electrons from NiCo alloy to the walls of carbon nanotubes that reduced the local work function on the carbon surface. Also, the wrapping of CNTs over the active NiCo alloy effectively resisted the etching in harsh environment and made the catalyst active and stable for long duration. [175] Yang and co-workers fabricated ultra-small $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocrystals (~5 nm) decorated over pristine MWCNTs using the solvothermal method without destroying the CNTs. Pristine MWNTs showed an efficient electron transfer network and its incorporation with well-constructed spinel $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ led to an outstanding electrochemical performance [176]. Numerous cobalt-carbon based catalysts were reported showing extremely high activity and performance due to the hierarchical structure and synergetic effect including Co-N/CNT [177], Co-NRCNTs [178], Co(OH)_x –NCNT [179], Ni foam-supported N-CNT@ Co_3O_4 [180], CNTs–Au@ Co_3O_4 [181], CoHCF/CNT [182], Co-CNT/ Ti_3C_2 [183], CoFe/ Co_3FeS_8 /CNT. [184]

6.2. Graphene

Exceptional properties of graphene, such as great electrical conductivity, large surface area, and fine chemical and mechanical stability has led to extensive research activities, particularly utilizing them as a catalyst substrate. [185] As a result, it has also been implemented in electrical devices such as fuel cells and lithium batteries with enhanced electrochemical operation. [186–190] In terms of the use of graphene as a material for catalyst production, many graphene-based composite catalysts have been synthesized in the recent past. The resulting composites are applied on substrate electrodes, normally, using drop-casting techniques [191–192].

A composite of graphene and Co_3O_4 (G- Co_3O_4 composite) has been reported by Zhao's research team, that possesses a unique sandwich-architecture as shown in Fig. 8a. [193] Analysis of the composite using TEM and FESEM has shown that there is a homogeneous distribution of Co_3O_4 on the 2 sides of graphene nanosheet (Fig. 8, b–e). A superior catalytic behavior towards OER in an alkaline solution of 1 M KOH has been observed (Fig. 8, f–i). An onset potential of 1.454 V vs. RHE was exhibited by the composite. Furthermore, within the same alkaline solution, the achievement of 10 mA cm^{-2} current density was observed at an η of 0.313 V that is more superior than that of the mesoporous Co_3O_4 catalyst (0.525 V) and $\text{Co}_3\text{O}_4/\text{SWNTs}$ (0.593 V). In terms of stability, the composite is expected to exhibit long-term stability as it demonstrated no clear decay in current density during testing in alkaline solution after 10 h as well as an undisturbed morphology. The extraordinary behavior could be due to the synergistic influence arising from the combination of both Co_3O_4 and graphene that include swift electron transfer rate, large electroactive surface area, and better chemical and electrical coupling of the composite. In another study

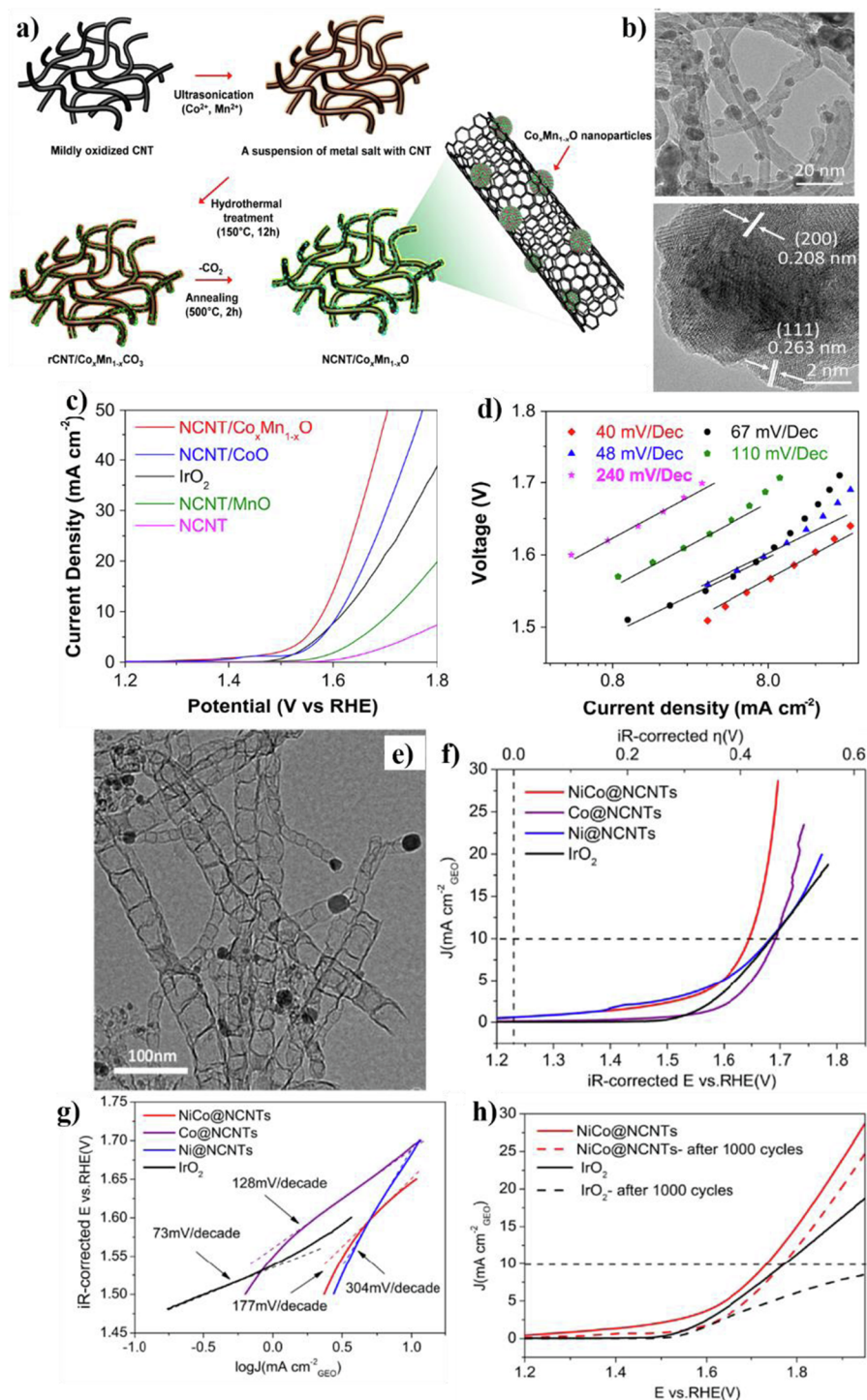


Fig. 7. (a) A representation of NCNT/Co_xMn_{1-x}O synthesis process. (b) TEM images of NCNT/Co_xMn_{1-x}O. (c) LSV profile of different Ni-Co based catalysts for OER in KOH solution of 1 M concentration and (d) its corresponding Tafel plots. (e) TEM image of NiCo@NCNTs. (f) LSV plot of NiCo@NCNTs, Ni@NCNTs, Co@NCNTs, and commercial IrO₂ in KOH solution of 0.1 M concentration at 5 mV s⁻¹ scan rate (g) Corresponding Tafel slopes and (h) the LSV profile of the NiCo@NCNTs and commercial IrO₂ after 1000 cycles in 0.1 M KOH solution saturated with oxygen at 100 mV s⁻¹ scan rate (accelerated durability test) [172,175].

performed by Zhao *et al.*, a catalyst of CoO nanoparticles wrapped by porous graphene sheets was synthesized using 1-D silica nanorods as a template to prepare the porous graphene. [194] The catalyst possessed great specific surface area and porosity and showed rapid charge transport kinetics. An improvement in catalytic activity was also seen for OER that includes large current density and a low onset potential. When the performance of the catalyst was studied in a KOH solution of 0.1 M concentration via LSVs, the PGE-CoO hybrid demonstrated a

small onset potential of 1.4934 V vs. RHE that is considerably lower than GE-CoO (1.5494 V vs. RHE) and CoO (1.5594 V vs. RHE) itself. Moreover, at 10 mA cm⁻² current density, the composite exhibited a low overpotential of 0.348 V. To measure the efficiency of the PGE-CoO catalyst Tafel plots were obtained from the LSVs and a Tafel slope value of 79 mV dec⁻¹ was determined. In comparison to the value obtained for GE-CoO and CoO this value is way smaller (GE-CoO showed 192 mV dec⁻¹ and CoO showed 354 mV dec⁻¹). The improvement in

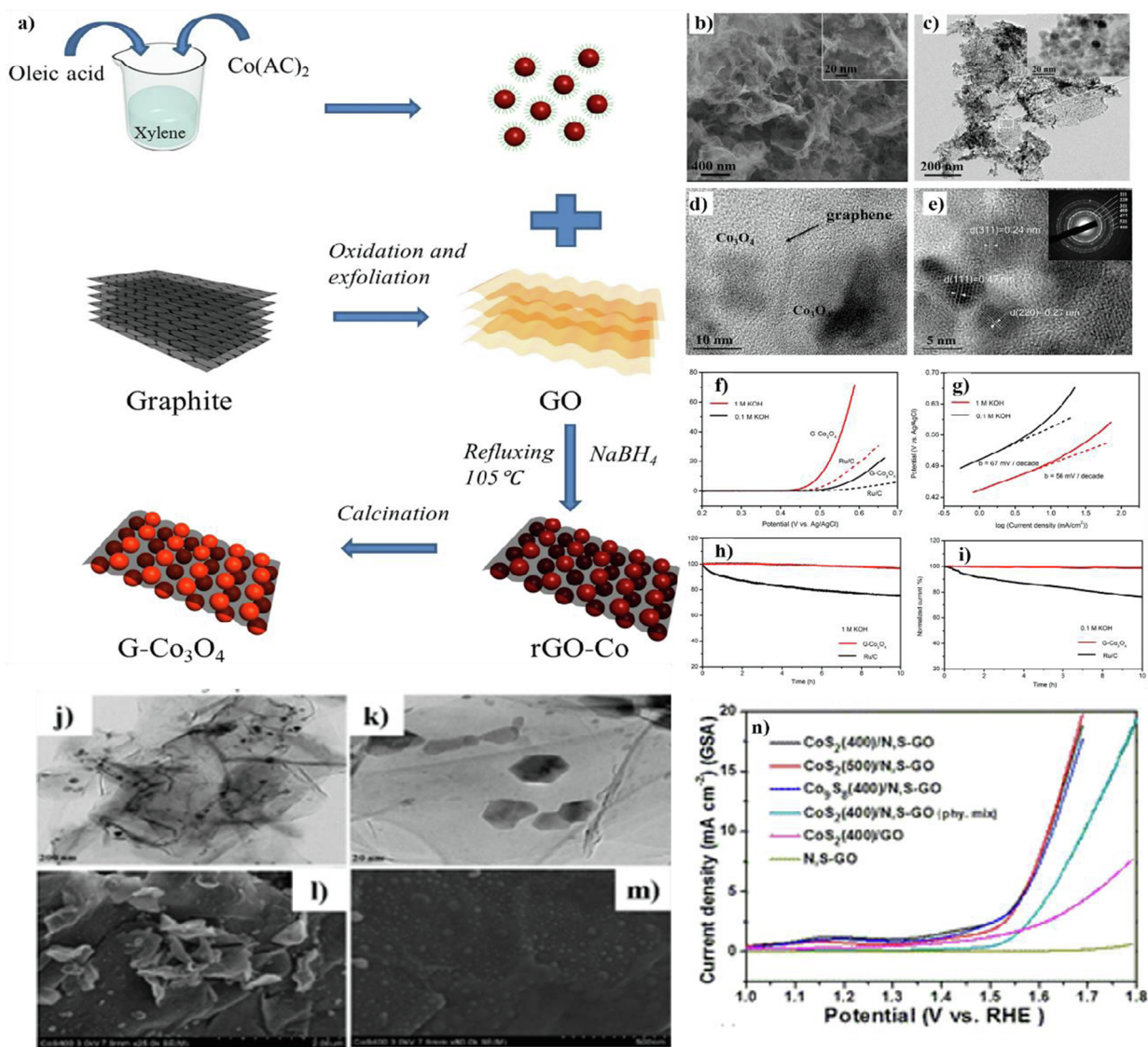


Fig. 8. (a) A diagram representing the preparation of G-Co₃O₄ nanocomposite possessing a sandwich-architecture. (b) SEM images of G-Co₃O₄ (low and high magnification). (c) TEM image of G-Co₃O₄ (low magnification). (d) HRTEM image of G-Co₃O₄. (e) Co₃O₄ nanocrystals' HRTEM image along with the SAED pattern of G-Co₃O₄. (f) Polarization curves generated from performance in 0.1 and 1 M KOH electrolytes of G-Co₃O₄ and Ru/C catalysts placed on GC electrode. (g) Tafel plots of G-Co₃O₄ catalysts in 0.1 and 1 M KOH electrolytes. (h-i) CA curves of G-Co₃O₄ and Ru/C catalysts in 1 and 0.1 M KOH electrolytes (current retained % vs. operation time). (j) Low and (k) high magnification TEM images of CoS₂(400)/N,S-GO. (l) Low- and (m) high-magnification SEM images of CoS₂(400)/N,S-GO. (n) Electrocatalytic performance of CoS₂(400)/N,S-GO, CoS₂(500)/N,S-GO, Co₉S₈(600)/N,S-GO, CoS₂(400)/N,S-GO (phy. mix), CoS₂(400)/GO, and N,S-GO for OER [193,207].

performance could be accredited to the presence of large electroactive surface area, porous structure, and a strong chemical coupling between both CoO NPs and graphene. In addition, the catalyst could maintain fine stability towards OER in an alkaline solution, possibly due to CoO NPs corrosion prevention characteristic introduced by the wrapped structure.

Wang's group produced a series of electrocatalyst in which graphene and cobalt oxide NPs nano-hybrids (Co-N/G) are doped with nitrogen via a one-pot hydrothermal method. [195] A nitrogen precursor is known as 2, 4, 6-Triaminopyrimidine was also utilized to anchor cobalt oxides NPs onto the graphene oxide surface. The composites synthesized consisted of cobalt oxides in the form of Co₃O₄ and CoO as well as a high content of doped nitrogen (~6 at. %) comprising of pyrrolic, pyridinic, and graphitic types. The resulting synergistic effect generated from the coupling between Co NPs and nitrogen-doped graphene allowed the composite samples to be used as catalysts for both OER and ORR. The as-synthesized Co-N/G 600 (sample carbonized

under N₂ atmosphere at 600 °C) showed the highest potential for application in reversible electrochemical energy conversion fuel cells and metal-air batteries. This is because Co-N/G 600 demonstrated an excellent bifunctional catalytic activity with high efficiency in which high activities for oxygen evolution reaction and oxygen reduction were observed at a potential of 0.76 V (1.554 V onset potential vs RHE) and -0.2 V (0.855 V onset potential vs RHE), respectively. In addition, the Co-N/G 600 catalyst showed both fine stability and durability for both the type of reactions. Graphene-based materials doped with nitrogen have been used by Hou *et al.*, where nitrogen-doped graphene was combined with a Co-embedded porous carbon polyhedron to form N/Co-doped PCP//NRGO. [196] A simple pyrolysis of graphene oxide (GO) and zeolitic imidazolate-framework (ZIF), ZIF-67, was implemented in the preparation of the new novel hybrid electrocatalyst after which metallic cobalt was partially etched away. The utilization of ZIF-67 was performed to take advantage of the plentiful Co-N moieties and the unique dodecahedral morphologies available with ZIF-67.

[197] With these properties, ZIF-67 may be a fitting precursor for the generation of N/Co-doped PCP. The as-synthesized hybrid catalyst showed excellent performance, including great stability, not only for OER but also for ORR and HER. Such enhancement could be associated with the dual-active-site mechanisms that emerge from the synergetic influences between NRGO sheets and PCP doped with N/Co. The hybrid electrocatalyst also demonstrated a four-electron pathway, great durability, and high tolerance towards methanol. Furthermore, during the performance analysis of N/Co-doped PCP//NRGO for oxygen evolution reaction, only a small η value of 1.66 V was noticed at a current density of 10 mA cm⁻². Qiao's group co-doped graphene with both Co and nitrogen and inserted carbon nanospheres into the graphene sheets interlayers. [198] The carbon nanospheres behaved as "spacers" that enlarged the accessible surface area of graphene and provided many electrolyte channels. These two unique properties helped in promoting the diffusion of reaction species to the active sites. Enhanced conductivity could also be guaranteed as the carbon nanospheres could further act as "shortcuts" for interplanar electron transport. The synthesized catalyst possessed bifunctional stability and catalytic activity for both ORR and OER in a basic medium. When compared to Pt/C catalysts the overall oxygen electrode activity parameter (ΔE) of the bifunctional Co-N-GCI electrocatalyst was relatively lower (0.807 V). The overpotential for Co-N-GCI catalyst at 10 mA cm⁻² current density was determined to be 0.426 V, that was much lower than those obtained for Co-N-G hybrid (not intercalated with conductive carbon nanospheres, 0.472 V), and commercial Pt/C (0.621 V), at the same current density. Moreover, an excellent intrinsic OER kinetic of Co-N-GCI was confirmed by a relatively lower Tafel slope value of about 69 mV dec⁻¹ in comparison to Co-N-G (~78 mV dec⁻¹), IrO₂/C (~83 mV dec⁻¹) and Pt/C (~168 mV dec⁻¹). A strongly coupled hybrid electrocatalyst of CoO_x NPs grown on B, N-decorated graphene (CoO_x NPs/BNG) was produced by Tong *et al.* that is suitable for catalyzing both ORR and OER. [199] An abundant presence of oxygen vacancies and strong Co–N–C bridging bonds were identified in the hybrid using advanced spectroscopic techniques. These qualities promote the enhancement inability to transfer electron, a greater number of active sites, and a strong synergetic coupled effect. Towards OER in a solution of KOH with 0.1 M concentration, the hybrid electrocatalyst functioned with high efficiency by demonstrating a low η of 0.295 V (at 10 mA cm⁻² current density) and a Tafel slope of 57 mV dec⁻¹. These values are significantly lower than that for NG (0.500 V overpotential, 110 mV dec⁻¹ Tafel slope) and Co-BG (0.320 V overpotential, 70 mV dec⁻¹ Tafel slope) catalysts. Synthesis of N- and B-doped graphene hollow spheres coated with Co₃O₄ (Co₃O₄/NBGHSS) was reported by Jiang's team for use as a potential catalyst for both ORR and OER. [200] The resulting catalyst had the ability to perform with comparatively higher activities and durability for the two reactions than RuO₂/C and Pt/C. The coupling between NBGHSSs and Co₃O₄, high electrical conductivity, the strong interaction with O₂ being adsorbed, and the specific hollow design were the contributing factors in the improved performance of the catalyst. Using LSV studies in an alkaline 0.1 M solution of KOH, a value of onset potential of about 1.6 V was recorded, which is more negative than those found for pure Co₃O₄ hollow microspheres, Co₃O₄/BGHSSs, Co₃O₄/NGHSSs, Co₃O₄/GHSSs, NBGHSSs, and Pt/C. However, in comparison to the conventional RuO₂/C catalyst, the OER onset potential of Co₃O₄/NBGHSSs is greater. The η for attaining a current density of 10 mA cm⁻² was determined to be approximately 0.47 V for Co₃O₄/NBGHSSs, which is less than that of RuO₂/C with a potential of about 0.52 V. Lu *et al.* produced N-doped Co₃O₄ nanocrystals combined with core-shell structured carbon nanotube-graphene nanoribbon (N-csCNT-GNR) scaffolds. [201] A high loading of Co₃O₄ was achieved during the synthesis by utilizing a microwave-assisted controlled unzipping of MWCNTs. The high surface area of carbon nanomaterials, as well as excellent electrical conductivity, could both be achieved as the csCNT-GNR structures possess an interlinked unzipped graphene nanoribbon and an intact MWCNT core. [202–204] The composite

catalysts were also proven to be incredibly active towards both OER and ORR. OER investigation results obtained from the study in 0.1 M KOH have shown that Co₃O₄/N-csCNT-GNR could perform very actively by exhibiting an onset potential value of 1.51 V. An η of 0.360 V (iR corrected polarization curve) was also observed to obtain 10 mA cm⁻² current density. The remarkable activities demonstrated by the synthesized composite was found to be more superior in comparison to Ir/C catalyst for OER [205–206].

Ganesan's research team prepared a bifunctional hybrid electrocatalyst for ORR and OER in which cobalt sulfide NPs are grown on a nitrogen and sulfur co-doped graphene oxide surface through a solid-state thermolysis technique. [207] During the synthesis process, the size, and phase of the particle could be controlled by altering the treatment temperature. Three different treatment temperatures of 400 °C, 500 °C, and 600 °C were employed in addition to the use of cobalt thiourea and graphene oxide to successfully disperse cobalt sulfide NPs onto graphene oxide. Analysis performed using X-ray diffraction has shown that the hybrids produced at 400 °C and 500 °C consisted of pure CoS₂ phase while that synthesized at 600 °C contained Co₉S₈ phase. A simultaneous co-doping of both nitrogen and sulfur on graphene oxide was confirmed via X-ray photoelectron spectroscopy that acts as sites to strongly anchor CoS₂ NPs onto the GO surface. Amongst the catalysts synthesized CoS₂(400)/N, S-GO displayed an excellent electrode performance. It exhibited a potential of approximately 0.82 V vs. RHE in basic medium (Fig. 8n), that was far superior compared to Ir/C (0.92 V), Ru/C (1.01 V), and Pt/C (1.16 V).

In addition to the graphene-based OER electrocatalysts mentioned earlier, many other catalysts have been reported which have the potential to catalyze OER with finer electrocatalytic activity and stability. Some of these catalysts include Fe₃O₄@Co₉S₈/rGO-2 [166], Cu@GDY/Co [208], N-CG-CoO [209], and Co-B₁ NS/G. [210]

6.3. Mesoporous carbon

Many of the recent research studies that focused on the replacement of platinum-based catalysts with hybrids consisting of non-precious metal have employed mesoporous carbon in addition to graphene and nanotubes. These carbon materials are generally doped with heteroatoms (e.g., nitrogen) before they are introduced into transition metals such as cobalt, iron, manganese, and their complexes. [211–213] Doping with heteroatoms can help modify the surface electronic structure as well as develop surface hydrophilicity to adsorb O₂ species particularly in ORR. [214] Non-precious metal-supported carbon materials doped with nitrogen commonly have excellent performance for both OER and ORR when they contain cobalt oxides. This can be because of their ability of cobalt to change their valence states and maintain a steady activity [215].

Liu *et al.* prepared an efficient OER electrocatalyst in the form of 3-D mesoporous carbon-framework-encapsulated CoTe₂ nanocrystals from a metal-organic framework (MOF) precursor. [216] They also implemented tellurization and carbonization processes that aided in yielding nanocomposites of CoTe₂ and graphitic carbon doped with nitrogen (CoTe₂@N-GC) immediately from ZIF-67. The resultant catalyst demonstrated a much greater performance towards OER by exhibiting an η value of 0.300 V (at 10 mA cm⁻² current density) and value of Tafel slope of 90 mV dec⁻¹ in comparison to porous N-doped graphitic carbon powder and pristine CoTe₂. The presence of N-doped graphitic carbon matrix support provides an interaction with the confined CoTe₂ nanocrystals to enhance OER in addition to offering fully accessible active sites and better electrical conductivity. A mesoporous carbon material doped with nitrogen has previously been utilized by Hu's group along with cobalt oxide NPs enclosed in graphitic layers as a promising non-noble metal oxygen electrode catalyst. [217] A series of catalysts were produced through a facile one-pot synthesis technique that involved polymerization, centrifugation washing, and pyrolysis. Several bifunctional catalysts were developed that possess incredible

Table 1
Carbon supported cobalt-based electrocatalysts for OER reaction.

| Catalysts | Synthesis | Cobalt particle size | Onset Potential | Overpotential (at 10 mA cm ⁻²) | Tafel slope | Medium | Ref |
|---|--|--|-----------------|--|----------------------------|-----------|-------|
| Co ₃ O ₄ /mMWCNT | Hydrothermal | ~ 6 nm | 1.51 V | 0.390 V | 65 mV | 0.1 M KOH | [157] |
| Co ₃ O ₄ /N-CNT aerogel | Hydrothermal | ~ 10–50 nm | 1.45 V | – | – | 0.1 M KOH | [158] |
| Co-CNT/PC | Pyrolysis | – | –0.26 V | 0.315 V | 73.8 mV dec ⁻¹ | 0.1 M KOH | [159] |
| CCHH/MWCNT | Mild solution-phase synthesis (w/o thermal annealing treatment at high temperature) | 200 nm | 1.486 V (RHE) | 0.285 V | 51 mV dec ⁻¹ | 1 M KOH | [160] |
| Co-MOF@CNTs (5 wt%) | Self-assembly | – | 1.51 V (RHE) | 0.34 V | 69 mV dec ⁻¹ | 1 M KOH | [162] |
| CoP/CoP ₂ @NPCNTs | Calcination, phosphorization | – | – | 0.300 V (RHE) | 50 mV dec ⁻¹ | 1 M KOH | [163] |
| Co ₂ P/NPCNT | g-C ₃ N ₄ intermediated approach | Co ₂ P tips avg. diameter, 55 nm. NPCNTs diameter, 80–250 nm | 1.293 V (RHE) | 0.370 V | 53 mV dec ⁻¹ | 1 M KOH | [164] |
| CP/CTS/Co-S | Template-assisted method, wet chemical method | – | – | 0.306 V | 72 mV dec ⁻¹ | 1 M KOH | [168] |
| Co ₉ S ₈ /CNT | Atomic layer deposition | Co ₉ S ₈ layer, ~7 nm | – | 0.369 V | 58 mV dec ⁻¹ | 0.1 M KOH | [169] |
| CMO@CNTs | – | Co-Mn-O spinel NP avg. size, 4.4 nm | 2.558 V (RHE) | 0.27 V | 81.1 mV dec ⁻¹ | 1 M KOH | [171] |
| NCNT/Co ₃ Mn _{1-x} O | Hydrothermal process (w/o surfactant), annealing treatment under Ar and NH ₃ | – | – | 0.34 V | 40 mV dec ⁻¹ | 1 M KOH | [172] |
| NiCo@NCNTs | One-pot pyrolysis method | NiCo particles diameter, < 25 nm. CNTs diameter, 10–50 nm | – | ~0.041 V | 177 mV dec ⁻¹ | 0.1 M KOH | [175] |
| MWNT-PyPBLNi _x Co _{3-x} O ₄ | Solvothermal method | Ni/Co spinel oxide size, ~5 nm | – | 0.31 V (RHE) | 42 mV dec ⁻¹ | 1 M KOH | [176] |
| Co(OH) ₂ -NCNT | Solution immersion process | – | – | 0.35 V (RHE) | 36 mV dec ⁻¹ | 1 M KOH | [179] |
| Ni foam-supported N-CNT@Co ₃ O ₄ | One-step chemical vapour deposition (CVD), electrodeposition | – | 1.47 V (RHE) | 0.310 V | 84 mV dec ⁻¹ | 1 M KOH | [180] |
| CNTs-Au@Co ₃ O ₄ | – | Co ₃ O ₄ layer thickness, ~ 2 nm. CNTs diameter, ~40 nm. Au particle avg. diameter, ~3.86 nm | 1.56 V (RHE) | 0.350 V | 68 mV dec ⁻¹ | 1 M KOH | [181] |
| CoHCF/CNT (CCFC-2) | One-pot co-precipitation method | CoHCF nanosphere size, ~40 nm | 0.152 V (RHE) | 0.274 V | 62.43 mV dec ⁻¹ | 1 M KOH | [182] |
| CoFe/Co ₉ Fe ₈ /CNT | Microwave-assisted sulfidation and annealing process | – | – | 0.290 V | 38 mV dec ⁻¹ | 1 M KOH | [184] |
| G-Co ₃ O ₄ nanocomposite | – | – | 1.454 V (RHE) | 0.313 V | 56 mV dec ⁻¹ | 1 M KOH | [193] |
| PGE-CoO | – | – | 1.4934 V (RHE) | 0.348 V | 79 mV dec ⁻¹ | 0.1 M KOH | [194] |
| Co-N/G 600 | Hydrothermal process | Cobalt oxide NPs size, 20–50 nm | 1.554 V (RHE) | – | 121.8 mV dec ⁻¹ | 0.1 M KOH | [195] |
| Co-N/G 500 | Hydrothermal process | Cobalt oxide NPs size, 20–50 nm | 1.544 V (RHE) | – | 149.1 mV dec ⁻¹ | 0.1 M KOH | [195] |
| Co-N/G 400 | Hydrothermal process | Cobalt oxide NPs size, 20–50 nm | 1.554 V (RHE) | – | 167.8 mV dec ⁻¹ | 0.1 M KOH | [195] |
| N/Co-doped PCP//NRGO | Pyrolysis | Cobalt NPs diameter, ~12 nm | – | 1.66 V | 292 mV dec ⁻¹ | 0.1 M KOH | [196] |
| Co-N-GC1 | – | – | – | 0.426 V | ~69 mV dec ⁻¹ | 0.1 M KOH | [198] |
| CoO _x NPs/BNG | Modified Hummers method, ultrasonication, simple room temperature method | – | – | 0.295 V | 57 mV dec ⁻¹ | 0.1 M KOH | [199] |
| Co ₃ O ₄ /NBGHS | – | – | ~1.6 V | ~0.47 V | 63 mV dec ⁻¹ | 0.1 M KOH | [200] |
| [Co ₃ O ₄ /N-cCNT-GNR] | Controlled partial longitude unzipping of MWNTs | – | 1.51 V | 0.360 V | 44 mV dec ⁻¹ | 0.1 M KOH | [201] |
| CoS ₂ (400)/N,S-GO | Solid-state thermolysis | Avg. particle size, ~42 nm | – | 0.38 V | 75 mV dec ⁻¹ | 0.1 M KOH | [207] |
| CoS ₂ (500)/N,S-GO | Solid-state thermolysis | Avg. particle size, ~67 nm | – | 0.39 V | 80 mV dec ⁻¹ | 0.1 M KOH | [207] |
| Co ₉ S ₈ (600)/N,S-GO | Solid-state thermolysis | Avg. particle size, ~81 nm | – | 0.4 V | 96 mV dec ⁻¹ | 0.1 M KOH | [207] |
| Fe ₃ O ₄ @Co ₉ S ₈ /rGO-2 | Solvothermal treatment, annealing in N ₂ | Cobalt sulfide particles size, 350–500 nm | ~1.48 V | 0.320 V | 54.5 mV dec ⁻¹ | 1 M KOH | [166] |
| Cu@GDY/Co | Chemical reduction of Co ²⁺ salt precursor in aqueous solution, acetylenic coupling reaction with Cu foam | Co NPs avg. diameter, ~4 nm | ~1.53 V | 0.35 V | 148 mV dec ⁻¹ | 0.1 M KOH | [208] |
| N-CG-CoO | Aerolization/high-temperature-induced GO crumpling and nanocrystal growth method | CoO nanocrystal size, 10–30 nm | 1.30 V | ~0.34 V (standard reaction potential) | 71 mV dec ⁻¹ | 1 M KOH | [209] |
| Co-B ₁ NS/G | Room temperature synthesis approach | – | – | 0.290 V | 53 mV dec ⁻¹ | 1 M KOH | [210] |
| CoTe ₂ @N-GC | Tellurization & carbonization | CoTe ₂ nanocrystals diameter, 10–30 nm | – | 0.300 V | 90 mV dec ⁻¹ | 1 M KOH | [216] |
| Co-N/C 800 | One-pot synthesis (polymerization, centrifugation washing, & pyrolysis) | Cobalt oxide NPs size, 30–50 nm | – | 0.51 V | 130.2 mV dec ⁻¹ | 0.1 M KOH | [217] |
| Co _{0.5} Fe _{0.5} S@N-MC | Soft-templated mediated approach | Sulfide nanocrystal diameter, 20–40 nm | ~1.57 V | 0.41 V | 159 mV dec ⁻¹ | 1 M KOH | [218] |

(continued on next page)

Table 1 (continued)

| Catalysts | Synthesis | Cobalt particle size | Onset Potential | Overpotential (at 10 mA cm ⁻²) | Tafel slope | Medium | Ref |
|--|---|--|-----------------|--|----------------------------|-----------|-------|
| Co-NC 750 | One-pot synthesis | Cobalt NPs size, 20–50 nm | 1.574 V | – | 157.5 mV dec ⁻¹ | 0.1 M KOH | [219] |
| CoP-based nanoneedle arrays on carbon cloth | Low temperature phosphidation, modified hydrothermal approach | CoP nanoneedles avg. diameter, 200–300 nm. Length, 1–5 μm | – | 0.281 V | 62 mV dec ⁻¹ | 1 M KOH | [220] |
| Ni _{2.3%} -CoS ₂ /CC | Hydrothermal method | Ni _{2.3%} -CoS ₂ nanowires diameter, 50–100 nm | – | 0.270 V | 119 mV dec ⁻¹ | 1 M KOH | [221] |
| Co(OH) ₂ @Ni(OH) ₂ /CC | Hydrothermal process, electrodeposition | – | – | ~0.330 V | 223 mV dec ⁻¹ | 1 M KOH | [222] |
| CGH-2/C | – | – | – | 0.509 V | 117 mV dec ⁻¹ | 0.1 M KOH | [223] |
| Co-OBAC | Hydrothermal process | Nanorods avg. diameter, ~20 nm | – | 0.553 V | 85.7 mV dec ⁻¹ | 0.1 M KOH | [224] |
| NiCoP/C | Metal-organic framework-based strategy | Nanocubes size, ~750 nm | – | ~0.330 V | 96 mV dec ⁻¹ | 1 M KOH | [225] |
| Co ₂ P@NPC-1 | – | NPs' diameter, 6–8 nm. Nanorods' diameter, ~9.5 nm | – | 0.327 V | 118 mV dec ⁻¹ | 1 M KOH | [226] |
| CS-Co/C-1000 | Carbonization under argon atmosphere | Co NPs diameter, 5–15 nm | – | 0.290 V | 70 mV dec ⁻¹ | 1 M KOH | [227] |

performance through the adjustment of the carbonization temperatures. Analysis performed on the optimal and as-produced Co-N/C 800 (800 °C carbonization temperature) catalyst showed that the catalyst presented a small reversible η value of 0.96 V between OER and ORR. This value recorded is even greater than those offered by 20 wt% Pt/C (0.270 V), RuO₂ (0.390 V), and IrO₂ (0.460 V) catalysts, and indicates that the catalyst can act as a top performance non-noble metal bi-functional catalyst for reactions involving reversible oxygen electrode. A facile soft-template mediated technique was employed by Shen's research team that assisted in fabricating nanostructured Co-Fe double sulphides that are covalently enclosed within N-doped mesoporous graphitic carbon (Co_{0.5}Fe_{0.5}S@N-MC). [218] Characterization methods such as X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction were conducted during the study to unravel the connection between the structural characteristics and the composite's catalytic behavior. Based on the analysis, there was a moderate substitution as well as a fine distribution of Fe in bimetallic sulfide composites that were suspected to generate a beneficial influence on both the activation and adsorption of species containing oxygen. As a result, a unique catalyst with enhanced performance towards OER and ORR was produced that is far better than the monometallic counterparts. In addition, a covalent bridge exists between the mesoporous carbon shells and the active sulfide particles that create easy pathways for the transport of mass and electron. The features possessed by the Co_{0.5}Fe_{0.5}S@N-MC catalyst resulted in an early onset potential value of around 1.57 V and 10 mA cm⁻² current density at a low η of 0.41 V. A relatively lower Tafel slope value of 159 mV dec⁻¹ than IrO₂ (267 mV dec⁻¹) was also observed. Wang's group also described the use of mesoporous carbon to produce electrocatalysts that have the bifunctional ability in the form of Co/Co₃O₄/Co(OH)₂/N-doped mesoporous carbon (Co-NC) through a one-pot synthesis process. [219] The remarkably superior Co-NC catalyst synthesized was Co-NC 750 (750 °C carbonization temperature) that had the highest quantities of pyridinic nitrogen as well as an optimized ratio of three cobalt species. The advantage that was achieved from the presence of the strong enclosure influence between N-graphitic shell of Co-NC and Co/Co₃O₄/Co(OH)₂ core included a reduced reversible overvoltage value of 1.02 V between both OER and ORR in an alkaline medium. Table 1 presents some of the important parameters related to the carbon-supported cobalt catalysts for OER in a conveniently accessible manner.

6.4. Other types of carbon support

Various other forms of carbon supports have also been combined with cobalt-based materials to create stable and active electrocatalysts for OER. Carbon supports that include carbon cloth, carbon nanodiamond, and carbon black were some of the unique carbon-based materials that have shown improvement in reactions involving oxygen evolution. The following sections will provide reviews on some of the contemporary research works incorporating the special type of carbon supports for OER.

Wang and co-workers made use of carbon cloth as support for cobalt phosphide nanoarrays that could efficiently catalyze OER and hydrogen evolution reaction (HER) in basic media. [220] An overall potential of 1.61–1.63 V ($\eta_{\text{overall}} = 0.380\text{--}0.400$ V) was necessary for water splitting in a 2-electrode configuration at a current density of 10 mA cm⁻² over 72 h. It was found that a layer of CoO_x, the active species, covered the CoP catalyst surface during electrolysis, but the improved activity was mostly due to the presence of CoP core and the nanoarray morphology. 10 mA cm⁻² current density was obtained at an η value of 0.281 V when the synthesized catalyst was utilized for OER. The development of a bifunctional electrocatalyst for OER and HER using Ni promoted Co disulfide nanowire array and carbon cloth support (Ni_{2.3%}-CoS₂/CC) was performed in the past by Fang *et al.* [221] A simple hydrothermal method was used for the preparation of Ni_{2.3%}-CoS₂/CC that allows carbon cloth to be uniformly coated with Ni_{2.3%}-

CoS₂ nanowires of 50 to 100 nm in diameter and length of several micrometers. The OER activity of Ni_{2.3%}-CoS₂/CC was studied in a basic 1 M KOH solution and 0.270 V overpotential was needed to obtain 10 mA cm⁻² current density. This value is far more superior than previously reported catalysts that include CoMn LDH (0.324 V), Co-P (0.345 V), NiCo LDH (0.367 V), and Ni-doped Co₃O₄ (0.530 V) [131,228–230]. In addition, a Tafel slope of 119 mV dec⁻¹ was recorded and Ni_{2.3%}-CoS₂/CC retained 91% of its current density after 12 h of fixed overpotential electrolysis. Another example of electrocatalyst previously synthesized that implemented carbon support in the form of carbon cloth was Co(OH)₂@Ni(OH)₂/CC which was produced by Wang's research team. [222]. In comparison to Ni(OH)₂/CC, Co(OH)₂/CC, and commercial RuO₂ catalyst, the newly synthesized hybrid catalyst demonstrated a relatively better OER performance by showing approximately 0.330 V overpotential at 10 mA cm⁻² current density. Furthermore, the catalyst exhibited prolonged durability even after 10 h of operation. These enhanced features could be accredited to the distinctive 3-D hierarchical core-shell system present as well as the synergistic influence between Ni(OH)₂ and Co(OH)₂. Wang and co-workers supported cobalt carbonate hydroxide (CCH), a cobalt-based mineral salt, on carbon black to form a resultant catalyst, indicated as CCH/C that can catalyze OER, as well as ORR. [223]. Investigations on phase-dependent electrochemical characteristics performed during the research work, showed that extending the time of hydrothermal reaction can considerably modify the CCH's crystalline phase in CCH/C. This alteration could further influence the activity of the catalyst towards both ORR and OER. Two types of catalyst, denoted as CCH-2/C and CCH-16/C, were generated by applying thermal treatment at 170 °C for 2 h and 16 h respectively. Excellent activity and stability were observed for CCH/C in an alkaline media for ORR in comparison to a Pt/C catalyst (Vulcan XC-72 supporting 40 wt% platinum) available commercially. With regards to OER, a small η of 0.509 V was recorded for CCH-2/C to obtain 10 mA cm⁻² current density. This value is less positive than that of Pt/C and it is 0.065 V less active than that found for Ir/C catalyst. These findings provided an evidence that CCH-2/C could be a promising catalyst when utilized as a cathode material for OER. Fan's research team produced a composite catalyst of Co-OBA/C (OBA = 4,4'-Oxybis (benzoic acid)) involving carbon black. [224]. The synthesis process included an integration of a metal-organic framework of Co-OBA with black carbon through a hydrothermal process. The composite was evaluated for ORR and OER using linear sweep voltammetry (LSV) in an alkaline medium, and results indicate a potential of 0.553 V for Co-OBA/C at 10 mA cm⁻², relatively smaller than the value obtained from Co-OBA (0.758 V) and Co-OBA + C (0.691 V). In addition, the Tafel slope of Co-OBA/C was the lowest, with a value of 85.7 mV dec⁻¹, when compared to Co-OBA (110.9 mV dec⁻¹) and carbon black (178.4 mV dec⁻¹).

A special form of carbon support in the form of nanodiamond (ND) was used by Wu *et al.* to synthesize a Co-embedded nitrogen-doped graphitized carbon shell that covers an ND core (Co-N-C/ND). [231]. The final catalyst synthesized had a bifunctional property that can improve both ORR and OER. Co-N-C/ND showed an onset potential of 1.285 V (vs. RHE) for OER and better durability relative to Co-N-C catalyst obtained from carbon black. The synergistic effect of the Co-N moieties in the carbon shell is expected to have helped improve the catalytic performance while the ND core plays a critical part in maintaining the high stability of Co-N-C/ND catalyst. In addition to the electrocatalysts described earlier, various research teams have made use of other forms of carbon supports in their studies, and some of these include CoTPP/C [232], NiCoP/C [225], Co₂P@NPC [226], and CS-Co/Cs. [227]. Moreover these discussed catalysts, there were more advancement in the Co-based catalyst and the electrochemical parameters were represented in Table 2.

7. Challenges and future aspects

Water splitting is one of the most effective and green way to easily convert sustainable energies (solar, wind, and blue energies) into useful high purity fuels (H₂ and O₂). Among the two half-reactions of water splitting (HER and OER), water oxidation reaction (OER) is a kinetically sluggish reaction which hinders the easy conversion of water into H₂ and O₂, and considered a bottleneck for large scale applications. So, it is vital to develop a potent catalyst that can demonstrate both prolonged stability and low overpotential, which can further improve the OER activity and display a better overall faradaic efficiency. However, there are some challenges that we must first overcome to create such an effective electrocatalyst:

The atomic rearrangement and reaction mechanism is still not well understood due to rapid changes and multiple possibilities between the steps of the OER process. Without understanding the mechanism, we cannot predict the rate-determining step (RDS) of a reaction, and without knowing the RDS we cannot pinpoint the phenomenon regulating the activity for the catalyst, which makes it difficult to further improve it. In the case of multi-metal compound catalysts, the exact recognition of catalytically active sites is important to improve the OER activity. Because of the rapid transformation in OER process, chemical changes and restructuring of the catalyst is difficult to detect and requires advanced tools e.g. combination of in-situ spectrometric methods, electrochemical techniques, microscopy techniques and theoretical calculations for finding out the critical factors affecting a reaction and precisely determining the catalyst active sites.

Most of the precious metal-based catalysts for OER (such as Ir- and Ru-based) work efficiently under acidic medium, whereas transition metal-based catalysts work best under alkaline medium. We have only very few catalysts that show excellent behavior within a broad pH range. The search for a versatile catalyst working in a wide range of industrial electrolysis conditions (strongly acidic to strongly basic conditions) is underway. Perhaps, even a better option is to have a catalyst that operates best in the neutral media to avoid corrosion issues and increase the durability of the catalyst compared to alkaline and acidic condition systems.

The use of carbon-based support (e.g. carbon black) has a possibility of carbon corrosion and electrochemical oxidation that produces CO or CO₂ at high potentials for long-time use. This effect hinders the performance of the catalyst which is due to a reduction in the reactive surface area as well as the dissolution of the support into the electrolyte. Dilution of the doped material into the electrolyte can also disturb the accurate measurement of the activity.

In the case of soluble active catalysts, binders are needed to immobilize the catalyst onto the solid surfaces (e.g. GC). The polymer binders hinder effective charge transfer between the catalyst and electrolyte and disrupt the gas permeation from/to the catalyst. So a need exists to convert such catalysts into electrode materials by efficient and economical methods for grafting them onto a solid surface without the use of any binders.

The experimental results obtained and the DFT results vary often because the practical catalysts do not comprise of a perfect single surface as the theoretical model frequently use. DFT helps in finding the active sites of a catalyst. As the catalysts get complicated (multimetal doping or addition of support), it is more difficult to identify the exact active site of the catalyst using computational tools.

A good electrocatalyst should possess good electrical conductivity, large number of active sites, and resistance to corrosion under high anodic potential. The concept of using different metals to meet individual functional requirements in extended lattices may be useful in constructing catalysts that can follow and satisfy multiple criteria simultaneously. Integrating these high-performance catalysts on to solar cells for fuel production is admired by many as they offer clean and sustainable solutions for energy requirements. Formulation of a bifunctional or trifunctional catalyst that can work in all media is still a

Table 2
Recently reported other Cobalt-based catalysts towards oxygen evolution reaction.

| Catalysts | Medium | Over potential (η), V | Current density (j_o), mA cm ⁻² | Onset potential (V vs RHE) | Tafel slope (b), mV dec ⁻¹ | Ref |
|--|--------------------------------------|------------------------------|--|----------------------------|---------------------------------------|-------|
| Au/mCo ₃ O ₄ | 0.1 M KOH | 0.440 | 10 | 1.53 | 46 | [67] |
| Au/ NiCo ₂ O ₄ | 0.1 M KOH | 0.360 | 10 | – | 63 | [233] |
| Au@Co ₃ O ₄ NS | – | 0.378 | 10 | 1.53 | – | [234] |
| Ag-NW@ α -Co(OH) ₂ NS | 1 M KOH | 0.320 | 10 | 1.45 | 82.5 | [235] |
| IrO ₂ -CNT's | – | 0.500 | 2 | 1.45 | – | [236] |
| Co _{2-x} Rh _x P | 0.5 M H ₂ SO ₄ | 0.290 | 10 | – | 31 | [237] |
| IrO ₂ /C | 0.1 M KOH | 0.370 | 10 | – | – | [205] |
| IrO ₂ | 1 M KOH | 0.338 | 10 | – | – | [238] |
| Cu@CoS _x /CF | 1 M KOH | 0.160 | 10 | – | 61 | [239] |
| Cu _{0.3} Co _{2.7} P/NC | 1 M KOH | 0.190 | 10 | – | 44 | [240] |
| NiCo ₂ O ₄ /Ti ₄ O ₇ | 1 M KOH | 0.398 | 10 | – | 64 | [241] |
| NiCoO ₂ NW | 1 M KOH | 0.303 | 10 | – | 57 | [242] |
| Fe-NiCo ₂ O ₄ | 0.1 M KOH | 0.350 | 10 | – | 27 | [243] |
| MnO ₂ /NiCo ₂ O ₄ | 1 M KOH | 0.340 | 10 | – | – | [243] |
| Fe-Co ₃ O ₄ | 0.1 M KOH | 0.420 | 10 | – | – | [244] |
| CoFe ₂ O ₄ | 1 M KOH | 0.490 | 10 | – | 54.2 | [245] |
| ZnCo ₂ O ₄ | 0.1 M KOH | 0.306 | 10 | – | 65 | [246] |
| CoFeP | 1 M KOH | 0.267 | 10 | – | 30 | [246] |
| Fe-CoSe ₂ | 1 M KOH | 0.330 | 10 | – | 82 | [247] |
| Mn-CoN | 1 M KOH | 0.265 | 10 | – | – | [248] |
| CoFeP-1.7 NW | 1 M KOH | 0.260 | 10 | 1.43 | 58 | [249] |
| CuCo ₂ S ₄ NS | 1 M KOH | 0.310 | 10 | 1.43 | 86 | [250] |
| α -CoSe/Ti | 1 M KOH | 0.292 | 10 | – | 69 | [251] |
| Co ₉ S ₈ @NOSC-900 °C | 1 M KOH | 0.340 | 10 | 1.40 | 68 | [252] |
| CoCr ₂ O ₄ /CNS | 1 M KOH | 0.326 | 10 | 1.47 | 51 | [253] |
| CoFe LDH-F | 1 M KOH | 0.300 | 10 | – | 40 | [254] |
| Zn-CoSe ₂ NS | 1 M KOH | 0.356 | 10 | 1.34 | 88 | [255] |
| Fe ₃ O ₄ -Co ₃ S ₄ NS | 1 M KOH | 0.270 | 10 | 1.46 | 56 | [256] |
| α -NiCo hydroxides | – | 0.255 | 10 | – | 25–30 | [257] |
| CoFe ₂ O ₄ /PANIMWCNT | 1 M KOH | 0.314 | 10 | 1.50 | 30.69 | [258] |
| SrNb _{0.1} Co _{0.7} Fe _{0.2} O _{3.5} | 1 M KOH | 0.420 | 10 | 1.49 | 76 | [146] |
| α -Co ₄ Fe(OH) _x NS | 1 M KOH | 0.295 | 10 | 1.49 | 53 | [259] |
| NiCoFe LTH | 1 M KOH | 0.239 | 10 | 1.51 | 32 | [260] |
| CoSn(OH) ₆ NC | – | 0.274 | 10 | – | – | [261] |
| CoMoS ₄ / β -Co(OH) ₂ | 1 M KOH | 0.342 | 10 | – | 105 | [262] |
| Fe-Co-2.3Ni-B | 1 M KOH | 0.274 | 10 | 1.46 | 38 | [263] |
| Co-Ni-Fe511 NS | 1 M KOH | 0.288 | 10 | – | 43 | [264] |
| Co(S _{0.22} Se _{0.78}) ₂ NPs-C | 1 M KOH | 0.283 | 10 | – | 65.6 | [265] |
| 3DGN/CoAl-NS | 1 M KOH | 0.253 | 10 | – | 36 | [130] |
| FeNi ₈ Co ₂ -LDH NS | 1 M KOH | 0.224 | 10 | 1.44 | 42 | [266] |
| Ni _{0.69} Co _{0.31} -P | 1 M KOH | 0.266 | 10 | – | 81 | [267] |
| Co ₄ N | 1 M KOH | 0.330 | 10 | – | 58 | [268] |
| NiCo ₂ S ₄ | 1 M KOH | 0.337 | 10 | 1.45 | 64 | [269] |
| NiCo ₂ O ₄ NS | 1 M KOH | 0.360 | 10 | – | 50–60 | [270] |
| Fe ₁₀ Co ₄₀ Ni ₄₀ P NS | 1 M KOH | 0.250 | 10 | 1.47 | 44 | [271] |
| Mn ₃ O ₄ @Mn _x Co _{3-x} O ₄ | 1 M KOH | 0.246 | 10 | – | 46 | [272] |
| P-Co ₃ O ₄ | 1 M KOH | 0.280 | 10 | – | 51.6 | [273] |
| CoFePO | 1 M KOH | 0.2745 | 10 | – | 51.7 | [274] |
| Co ₄ Ni ₁ P NT's | 1 M KOH | 0.245 | 10 | – | 61 | [275] |
| p-Ni _{0.7} Co _{0.3} Se ₂ NS | 1 M KOH | 0.258 | 10 | – | 42.3 | [276] |
| Co ₆ Mo ₆ C ₂ /NC-rGO | 1 M KOH | 0.260 | 10 | – | 50 | [277] |
| np(Co _{0.52} Fe _{0.48}) ₂ P | 1 M KOH | 0.270 | 10 | 1.45 | 30 | [278] |
| FeCoNi-2 | 1 M KOH | 0.288 | 10 | – | 60 | [279] |
| CoSe ₂ /CF | 1 M KOH | 0.297 | 10 | – | 41 | [280] |
| Zn _x Co _{3-x} O ₄ NA | 1 M KOH | 0.320 | 10 | – | 51 | [127] |

dream to be achieved. Creative modeling and production of exclusive nanostructures to enhance the performance for OER is possible with advanced facilities. A catalyst design approach is required following systemic steps based on descriptors rather than the trial-and-error method to create good catalysts. Effective studies should focus on a comprehensive evaluation of reaction mechanism, online monitoring of chemical changes, analysis of structural transformation by applying operando, and in-situ techniques to decipher the catalyst structure that transitions into active sites during the reaction conditions. This knowledge with advanced synthesis tools could help in designing versatile catalysts that can perform outstandingly under varying industrial conditions.

8. Conclusion

World energy consumption has been increasing at a drastic rate. The energy produced from the burning of the limited fossil fuels is not sustainable and affects the environment adversely. So, the need for an energy transition towards a more sustainable and renewable form is of paramount importance for our future generations. Electrolysis of water using renewable energies has received much attention due to its clean method to produce chemical fuels that have the capability to substitute the existing carbon-emitting fossil fuels. In this review, we discussed various cobalt-based electrocatalysts for the OER. It has the capacity for large scale applications by replacing the precious-metal-based catalysts that are scarce and costly. We have discussed cobalt in presence of noble metal (Ir, Ru, Au, and Ag) as catalysts with high activity towards OER in acidic medium with a low amount of noble metals present in the

electrocatalyst. Largely the review focuses on catalysts where cobalt is present with other transition metal (such Fe, Ni, Co, and Mn) in a bi-metallic or tri-metallic form, which show outstanding OER activity in alkaline media. Furthermore, we have discussed some of the cobalt-based perovskite oxides with partial doping of A-site and B-site with other elements and anion substitution, which aided in the high activity of the perovskite catalyst. As support, we have included the effect of carbon-based compounds that enhance the OER activity in presence of cobalt catalysts. The review also includes a discussion on the mechanism of OER along with comparing the performance of OER catalysts with the help of measurement standards like the overpotential and Tafel slope.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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