Chapter 1

Introduction

1. General introduction

This chapter discusses the current rate of energy consumption and the demand for renewable sources. It discusses the role of sustainable sources like fuel cells and hydrogen cars and the key reactions taking place in them, emphasizing oxygen electrochemistry. It gives a bird eye view of current trends in green energy research, in emphasis to interfacial heterogeneous electrocatalysis. The role of different interfaces like oxide-oxide, oxide-hydroxide have been discussed in detail with an extensive literature study. Some research gaps and research questions have been identified and discussed and the objectives of the thesis work are presented.

1.1 A brief overview of hydrogen cars, fuel cells, and oxygen electrochemistry

We all know that with the increase in the global human population, the energy demand increases manifold. This demand shall keep on rising with time as industrialization has taken over the earth. The mother source of this energy production is, currently, fossil fuels. But the burning of fossil fuels emits a lot of hazardous gases like carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), etc. These gases are responsible for all kinds of environmental issues like global warming, drastic climate changes, melting of icebergs, and glaciers, to name a few. Also, there is a major concern that there might not be enough fossil fuel left in the earth-crust for the future. A major portion of these greenhouse gases come from automobile emission. In this regard, the concept of '*hydrogen car*' is a greener technology choice that takes up hydrogen from a pre-filled H_2 cylinder and oxygen (O_2) directly from the air [1,2]. Both the gases combine within a fuel cell (FC) setup to produce water as the only by-product with the generation of a large amount of electrical energy sufficient to run the vehicle. The production cost of H_2 gas is cheaper than gasoline per unit energy, and such vehicles can exhibit higher mileage at a more affordable rate. And with H_2 generated from biomass, the cost would be even cheaper; this, in turn, benefits the farmers and agro-based sectors too. With unitized regenerative FCs, there shall be no requirement for frequent battery replacement as in conventional cars, thereby demanding low maintenance. Hence, with a view to switching towards sustainable energy domain, switching from conventional petrol/diesel vehicles to greener hydrogen cars can bring upon a revolutionary change. However, such automobiles are currently manufactured on an experimental basis only and have not yet achieved proper commercialization. Despite that, in 1960, NASA's Apollo journey to the moon deployed

H_2-based FC powerhouse to its onboard electrical circuit successfully. The major bottleneck for practical application of hydrogen automobiles is that the cathode reaction ‘oxygen reduction reaction’ (ORR) in the FC set-up occurs at a very sluggish rate than the anode reaction ‘hydrogen oxidation reaction’ (HOR) [2,3]. The basic anatomy of an FC is shown in Figure 1.1.

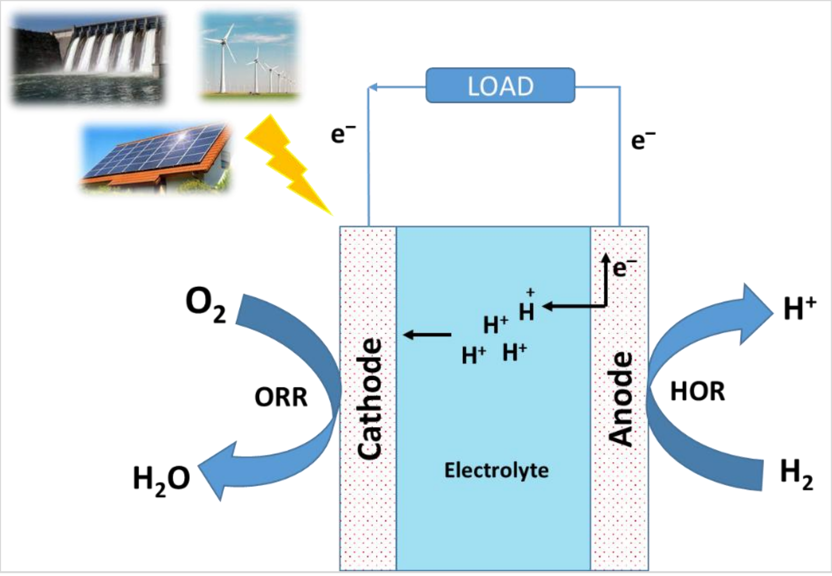

Figure 1.1. The anatomy of a typical hydrogen-based fuel cell.

In 1839, the first successful operation of traditional FC was carried out by Sir William Grove [4] using Pt electrode as the EC. ORR is generally associated with its reversible reaction, oxygen evolution reaction, abbreviated as OER which is a half-reaction of water-splitting and finds application in rechargeable metal-air batteries [5]. This reaction is of major importance because green plants perform water-splitting during photosynthesis, giving out oxygen via OER [6]. These two reactions *viz.* ORR and OER, are the main oxygen reactions involved in most energy-efficient devices like super-capacitors, FCs, metal-air batteries, etc.

1.2 Reaction kinetics and mechanism of ORR and OER

The fundamental reaction mechanism for ORR and OER is somewhat ambiguous. It is difficult to find a clear explanation of the elementary steps involved in these reactions. Unlike the anodic HOR that involves only one intermediate (H*), the oxygen electrode reactions involve multiple intermediates *viz.* O_2*, O*, OH*, OOH*. Although ORR and

OER are oppositely directed reactions, they do not follow proper microscopic reversibility and require different experimental platforms to occur. In general, ORR occurs at pure metal surfaces while OER needs metal oxides (MOs). Figure 1.2 shows a volcano plot of the electrochemical activities of different metals towards ORR at various applied potentials.

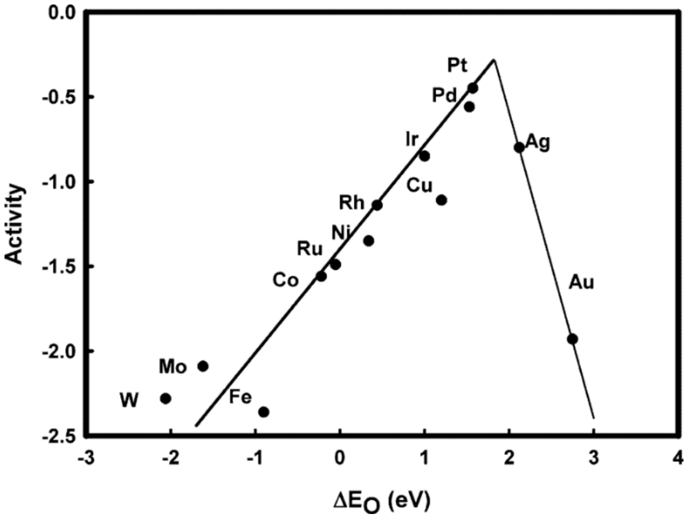

Figure 1.2. Volcano plot for ORR (Reproduced with permission from [7]).

From Figure 1.2, it is seen that noble metals like Pt, Pd, Ir race towards the peak of the volcano with Pt sitting almost at the summit. For OER, on the other hand, noble MOs such as IrO_2 [8], RuO_2 [8], $IrO_x/SrIrO_3$ [9], PtO_2 [10], various lanthanum-based perovskites of the type $LaMO_3$ [11,12] as well as a few non-noble transition MOs like CoO_x, $NiCoO_x$, $CoFeO_x$ [13], FeMoW [14], NiO_x [15] act as catalyst materials.

The kinetics of ORR is regulated by binding energies of the attaching/detaching mode of the adsorbed O_2. A facile reaction is possible only when the energies of adsorption/desorption on the catalyst surface are optimum. A surface that binds oxygen too tightly or too loosely is likely to exhibit slow kinetics. The overpotential (generally not less than 0.3 V) [16] that limits facile ORR presumably arises from the fact that the binding energies for all the intermediates involved (O_2*, O*, OH*, OOH*) fall in a narrow range and are difficult to deconvolute. This, in turn, makes probing into the reaction mechanism difficult.

The O_2 molecule can hold on to the catalyst surface by either bidentate mode or monodentate mode. Obviously, bidentate O_2 binding makes the reduction process faster as more units of O_2 are reduced, with a lesser number of bonds to be broken. Again, since it is a complex proton-coupled electron-transfer reaction, the number of electrons transferred plays a significant role in influencing its rate. The overall ORR in acidic and alkaline media can be represented as shown in Table 1.1.

Table 1.1. ORR mechanism

Pathway	Acidic media	Alkaline media
$4e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
$2e^-$	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ $H_2O + HO_2^- + 2e^- \rightarrow 3OH^-$

ORR can occur in acidic as well as in alkaline media. However, it is practically more feasible to carry it out under alkaline conditions because of the critical stability of non-noble metal-based ECs [17]. Note that the $2e^-$ mechanism is an indirect process that involves the formation of peroxide intermediate HO_2^- and consecutively leading to reduced oxygen products. On the contrary, the $4e^-$ pathway does not form any such unwanted intermediate; it directly forms water or hydroxide ions which is why, it is often called as '*direct 4e⁻ pathway*' and the $2e^-$ pathway is called 'indirect $2e^-$ pathway'. For a material to be called a good oxygen EC, it should undoubtedly favour the direct $4e^-$ pathway. Benchmark catalysts like Pt/C favors the direct $4e^-$ pathway [18].

In the case of OER, elementary steps include adsorption of OH^-, formation of active oxygen intermediates like O* and OOH*, and subsequent desorption of oxygen molecule [19]. The simplest depiction of this reaction in alkaline media is:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

It is a half-reaction of water splitting reaction, which is one of the most important ones since the world survives on oxygen. Plants perform water splitting by photosynthesis and deliver oxygen to the biosphere. The other half-reaction associated with OER in water-splitting is the hydrogen evolution reaction (HER) which is also equally important since hydrogen gas is a cleaner and potential substitute for conventional fossil fuel. However, OER, due to its highly sluggish kinetics (generally not less than 1.23 V overpotential) [16], has gained more importance than HER in terms of studying design principles and developing ECs.

1.3 Benchmark catalysts and recent advancements

Since the invention of Pt EC by Sir William Grove, the scientific community has been tirelessly involved in designing cost-effective ECs by alloying Pt with non-noble metals and MOs as well as Pt-free ECs. Figure 1.3 gives a summary of developments and modifications of Pt-based ECs over time.

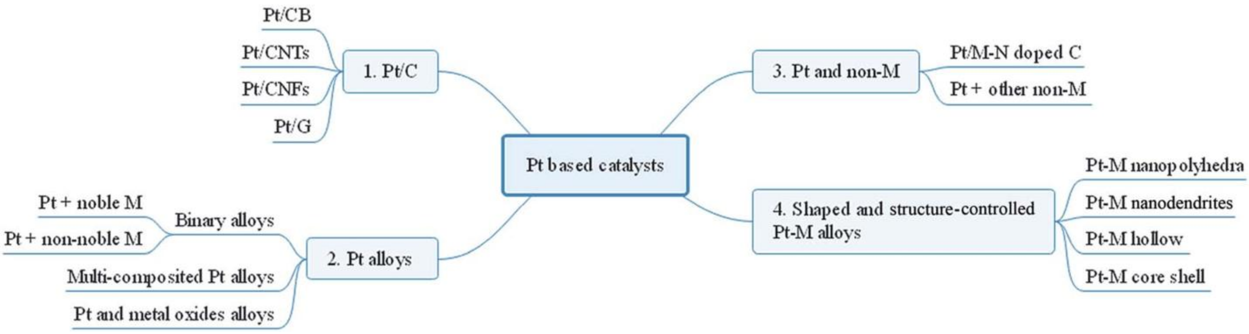

Figure 1.3. A schematic of recent developments to Pt-based ECs (Adapted with permission from [20]).

By far, Pt nanoparticles (NPs) supported on multi-dimensional carbon networks like nanosheets, nanotubes, core-shell structures, broadly represented as Pt/C, have served as the benchmark catalysts required for satisfactory ORR kinetics in FCs [21–23]. However, its low natural abundance and expensive nature limit it from being the most accessible ECs. Moreover, there are certain intrinsic demerits of Pt-based ECs; the carbonaceous support undergoes corrosion due to electro-oxidation, leaving the Pt-NPs agglomerated [17]. Hence, all Pt-based catalysts are undoubtedly the best ECs for oxygen electrode reactions, but only under the best-operating conditions. To bring down the dependency on such precious metals, designing other budget-friendly and competent alternatives became a hotspot of research for electrochemists.

Since the past few decades, rational engineering of interfaces is regarded as an efficient strategy to fine-tune the electronic and catalytic properties of the materials. It also helps prevent quick agglomeration, which is common to all pure-metallic ECs. Today we have numerous literature works reported on the successful synthesis of noble as well as non-noble, intermetallic ECs hybridized with oxidic and/or hydroxidic hetero phases, mostly supported on a highly conductive carbonaceous bed. Metal oxyhydroxides, in the form of vacancy-modified layered double hydroxides (LDHs) are an established class of oxygen ECs [24–26]. The carbonaceous bed, such as graphitic carbon-nitride (g-C_3N_4) and reduced graphene oxide (rGO) provide a smooth platform to ensure even distribution of the catalyst [27]. This helps in improving proton-electron conductivity and reduces intrinsic Ohmic resistance. Further modifications such as surface-etching, de-lamination, sulfurization, introducing oxygen vacancies into MO structures add to the decrease in Ohmic resistance and increase proton-electron conductivity of the electrolyte media (acidic or alkaline). The details in this regard shall be discussed in later sections of the chapter. Owing to promising ORR and OER functionalization, non-noble MOs are considered as potential candidates for cost-effective electrocatalysis. Transition MOs of all types of crystallinities (rock-salt MO, rutile MO_2 or M_2O_3, perovskite ABO_3, spinel AB_2O_4) are efficient oxygen ECs. Grimaud and co-workers experimented upon various MOs for OER by *in-situ* ^{18}O isotope labelling mass spectrometry and found that the O_2 generated comes from lattice-oxygen oxidation [28]. There are reports of electronic perturbation (hot electron dynamics) at inverse metal/oxide interface sites that promote catalytic activity [29]. Also, metal/oxide/oxyhydroxide heterogeneous and inverse interface sites have reports of being outstanding catalytic performance in running important reactions like water-gas shift reactions [30], CO oxidation [31,32], and water splitting [33]. A prompt and effective way of enhancing the electrocatalytic activity is by hybridizing its structural network by adding dopants or creating interfaces by forming oxygen vacancies and interstitial defects. Modification or hybridization at the molecular level brings about electronic changes to the architecture of the catalyst material. For example, rock-salt oxides like MnO, CoO, NiO have good intrinsic OER tendency. However, when these are intermixed to form MnO-CoO having oxide/oxide heterophases, the intrinsic activity is further enhanced [34].

1.4 Role of interfaces in nano-electrocatalysis

At this point of discussion, the role of the interface (or the concept of surface hybridization) demands sincere attention. The presence of interface and surface boundaries seem to directly influence the material properties of an EC. To begin with the simplest instances, single perovskites like $LaFeO_3$, $LaCoO_3$, $CaMnO_3$ that are an established class of oxygen ECs are predicted to be good because of intermetallic boundaries of A/B, A/O, and B/O (A, B = metal, O = oxygen) [35–37]. Also, the crystal structure with distorted [AO_{12}] and [BO_6] conjoint units have a direct impact upon its enhanced catalytic properties [38]. Again, spinel oxides such as $NiCo_2O_4$ also show improved activity towards ORR and OER compared to their monologues Co_3O_4 and NiO [39–41]. This added electro-activity can be attributed to the development of interfaces in the nanostructure of the $NiCo_2O_4$ hybrid EC. Likewise, numerous reports in the scientific research database are found to acknowledge the importance of hybrid ECs and defects or interface engineering that has shown extra-ordinary soar than their intrinsic electro-activity towards oxygen redox reactions.

After understanding the immense influence of proper interfacial hybridization into a catalyst framework, the next task *i.e.,* to incorporate dopants like nitrogen, sulfur, phosphorous (N/S/P) or generate anion vacancies in a controllable manner, remains somewhat complicated to accomplish. Not only that, but there also isn’t yet a unanimous agreement among the research fraternity around the globe as to what mechanism is followed that leads to an increased extent of the catalyst performance [42]. Hence, it is an established fact that all kinds of MOs have gained supreme importance as potential oxygen ECs due to their inherent anionic oxygen defects, which can be further elevated by doping and interface tuning. Defect generation methods like thermal annealing under a reducing environment can be a very effective strategy as it creates oxygen vacancies maintaining the original crystallinity of the material. Kim *et al.* reported that the oxygen-deficient double perovskite $Ca_2Mn_2O_5$ generated by thermal annealing showed a higher OER rate compared to $CaMnO_3$. They attribute this enhanced OER to the vacancy-originated porosity for the conducting ions like OH^- [43]. Thermal annealing can sometimes effectively bring about transformation of phases into more active secondary phases. Chen *et al.* reported remarkably enhanced oxygen electrocatalysis by thermally annealed pristine $Pr_{0.5}Ba_{0.5}MnO_{3-\delta}$, which is attributed to the newly transformed mix-phase catalyst comprising of pristine and layered $PrBaMn_2O_{5+\delta}$ (H-PBM) [44]. Besides this, cationic doping with strontium [45], anionic doping [46,47] with N/P/S, strain-induced oxygen vacancy can also be an effective strategy in enhancing the ORR/OER activity. In fact, the coupling of strain and anion defects has a great role to play. Techniques such as vacuum annealing impose strain into the crystal structure and shuffle the electronic configuration of the material [48]. The bandgap, which is a key factor in influencing electrocatalytic properties, gets squeezed, thereby filling up the e_g levels of the metal. Often, the electro-neutrality after oxygen vacancy generation is maintained by concurrent reduction of multivalent cations. After understanding the positive influences of oxygen vacancy concentration towards ORR/OER, a similar observation is expected from another closely related oxygen-vacant oxide/hydroxide inter-phasic ECs. Cai and group reported that DFT+U study suggests performance enhancement of ultrathin Co_3O_4 EC towards OER due to increased oxygen vacancy concentration and concurrent charge balance by surface reduction of Co sites from +3 to +1 state [49].

Moving one step forward, introducing H-atoms into some of the oxygen voids can be thought of as another modified version of a hybrid EC *i.e.*, exploring metal oxy-hydroxides as oxygen ECs. Oxide/hydroxide is also a type of oxygen vacancy interface under a reduced atmosphere. There are reports of successful vacancy engineering at the oxide/hydroxide interface developing due to the local electron potential at the interface of oxide/hydroxide [50]. Pt alloyed Bi-oxyhydroxide can enhance the anti-poisoning nature of pure Pt EC. With the development of oxide/hydroxide interface into its molecular framework, the unwanted adsorption of CO, which previously led to CO-poisoning of the Pt catalyst decreased. On the contrary, the OH adsorption increased, which enhanced the overall efficiency of the catalyst. In this regard, LDH has attracted tremendous attention in different electrochemical reactions. Their composition and ion exchangeability can be tuned to get better results in different applications.

1.4.1 Oxide/oxide interfaces

As the regulation of catalysts functionalities through oxide/oxide interface modulating seems optimistic; many researchers have been working on tailoring oxide/oxide interface to design advanced electrode catalysts for ORR/OER. For instance, Goswami *et al.* reported highly rich and well-dispersed oxide/oxide interfacial $CuO_x{-}CeO_2$/C hetero nanostructured EC for ORR/OER [51]. The HRTEM image as shown in Figure 1.4 clearly displays the interfacial structures between different facets of $CuO_x{-}CeO_2$, $CeO_2{-}CeO_2$ and oxide−carbon. The white dotted line indicates the oxide/oxide interface between monoclinic CuO-002 planes (d spacing; 0.25 nm) and fcc CeO_2-111 planes (d spacing; 0.31 nm), while the yellow dotted line indicates the oxide/oxide interface between CeO_2 phases.

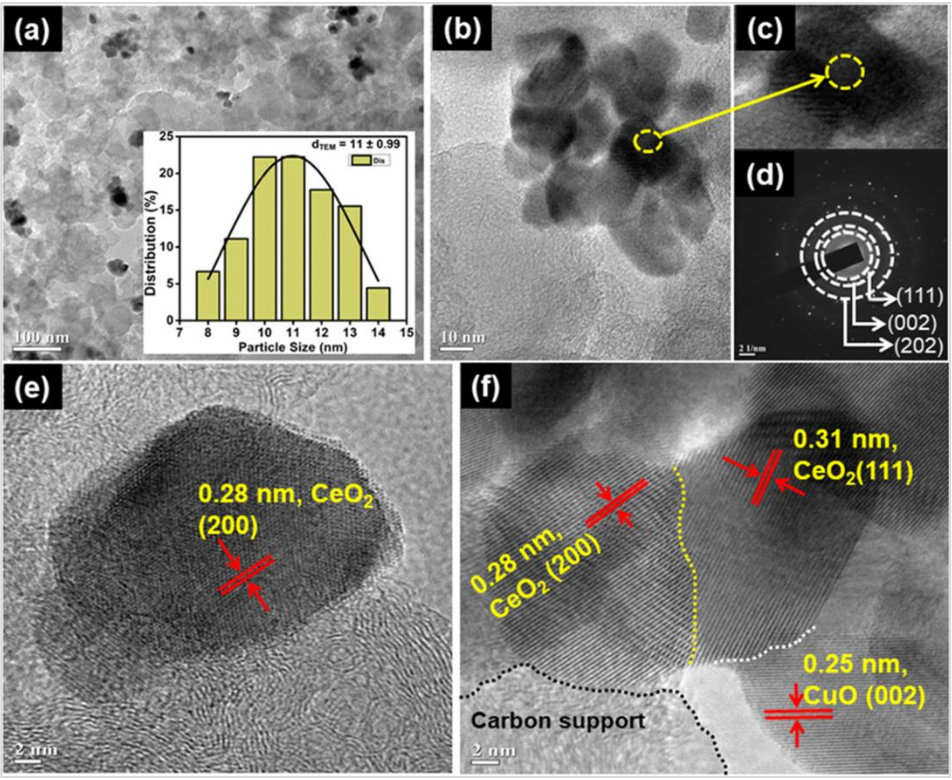

Figure 1.4. (a–c, e, f) TEM and HRTEM images with distinguished lattice fringes, particle size distribution curve (inset image (a)), and (d) SAED pattern for the CuO_x–CeO_2/C EC (Reproduced from [51]).

The EC exhibits a direct $4e^-$ ORR pathway demonstrating higher current density (−5.03 mA cm^{-2}) and a smaller Tafel slope (65 mV dec^{-1}) with onset potential (−0.10 V vs Ag/AgCl), which is comparable to benchmark Pt/C. In addition, it shows better stability with a loss of 23% of its initial current after 6h compared to 28% observed for Pt/C. The EC also exhibited significant OER activity in alkaline media with a less positive onset potential (0.20 V) and a lower Tafel slope (177 mV dec^{-1}). The strong oxide/oxide interfacial contact between CuO and CeO_2 and the favorable electronic perturbation at their interface is primarily reported for the observed enhanced activity. Chen *et al.* have synthesized a hybrid of MnO_x–CeO_2/KB (KB: Ketjen Black) by a continuous two-step process. The observed electrocatalytic ORR performance of the catalyst is better than MnO_x/KB and CeO_2/KB. Thus, non-noble metal based-hybrid EC displayed comparable ORR activity and significantly higher durability to the benchmark Pt/C [52].

Cabot and co-workers reported an interface modulated $Mn_3O_4@CoMn_2O_4–Co_xO_y$ (with [Co]/[Mn] =1) NPs entailing the cation exchange between Mn and Co in preformed Mn_3O_4 NPs via a one-pot two-step synthesis method (Figure 1.5) and explored for ORR/OER. It exhibited a lower Tafel slope of 52 mV dec^{-1} and low overpotential of 0.31 V at −3 mA cm^{-2} for ORR. A remarkable OER performance has also been observed with a Tafel slope of 81 mV dec^{-1} and overpotential of 0.31 V at 10 mA cm^{-2}. The overall activity of the catalyst was observed to be superior to commercial Pt-, IrO_2-based, and previously reported TMO-based catalysts. This cation exchange-based interfacial modification strategy offers an insightful strategy for designing novel heterostructure NPs as efficient bifunctional oxygen ECs [53].

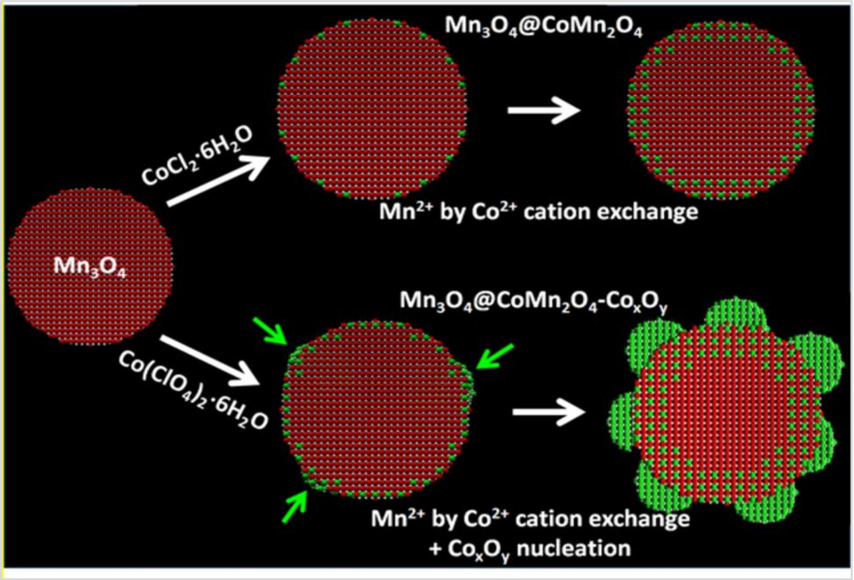

Figure 1.5. Scheme of the formation of the $Mn_3O_4@CoMn_2O_4$ and $Mn_3O_4@CoMn_2O_4–Co_xO_y$ nano-heterostructures when using either a cobalt chloride or a cobalt perchlorate solution. Green arrows in the bottom cartoon point at Co_xO_y nanocrystal nucleation sites (Adapted with permission from [53]).

Zhang *et al.* have reported porous $NiO/NiCo_2O_4$ nanofibers containing rich oxide/oxide interfacial active sites via an electro-spinning strategy, which exhibited superior electrocatalytic activity. DFT calculations have established the feasibility of chemical bonds in the oxide/oxide heterostructure, which may accelerate the charge transfer process. XPS analysis of the interface organized reveals the existence of enormous Ni^{3+} and Co^{3+} species coupling with the oxide/oxide interface. Consequently,

$NiO/NiCo_2O_4$ heterostructure exhibit outstanding and durable performances toward OER and ORR in KOH solution. Figure 1.6 displays the electrochemical activities exhibited by the catalyst. The catalyst possesses an ORR half-wave potential of 0.73 V and a lower OER overpotential of 357 mV at 10 mA cm^{-2}. Besides, testing for zinc-air battery the $NiO/NiCo_2O_4$ shows remarkable specific capacities of 814.4 mA h g^{-1}, and reliable cycling stability of 175 h. This new strategy towards modifying oxide/oxide interface over MMO heterostructure could optimize them as potential EC for energy converting devices [54].

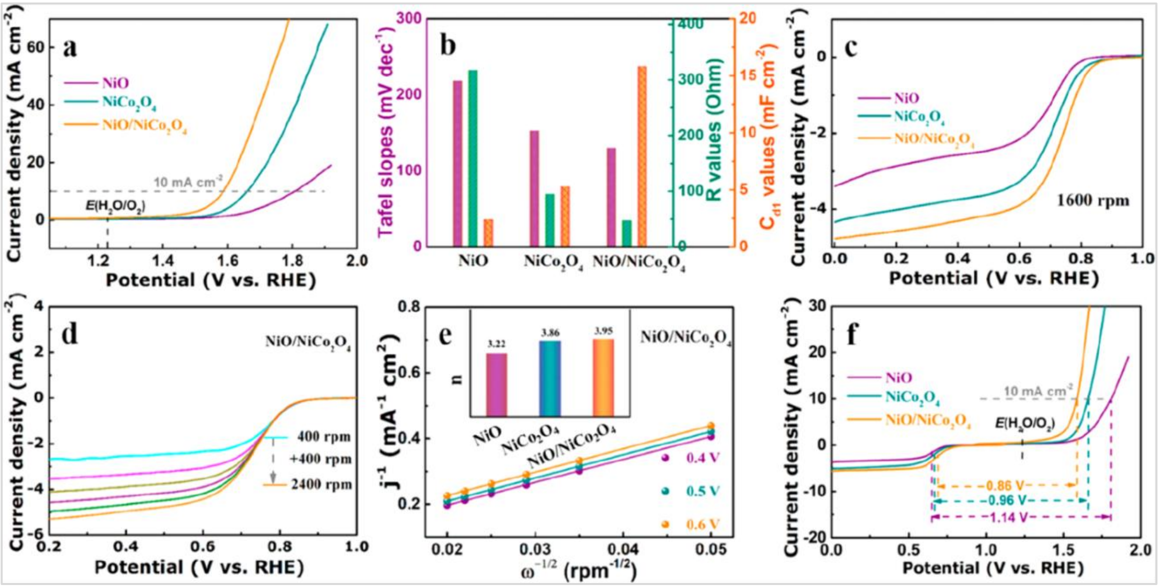

Figure 1.6. (a) LSV, and (b) Tafel slopes (purple), resistance (dark cyan), and double-layer capacitances values (orange). ORR: (c) LSV, (d) LSV of $NiO/NiCo_2O_4$ nanofibers at different rpm, and (e) corresponding K−L plots of $NiO/NiCo_2O_4$ nanofibers. Inset: n values for ORR. (f) Bifunctional ORR/OER catalytic activity (Adapted with permission from [54]).

Liu *et al.* incorporated Co and CeO_2 into KB through a facile two-step hydrothermal method and established Co_3O_4−CeO_2/KB as an advanced ORR EC for Al−air batteries. The observed ORR activity was significantly higher as compared to that of a single Co_3O_4/KB. Furthermore, along with the favorable direct 4e^- pathway, it exhibited remarkable stability than benchmark Pt/C (20 wt. %) in alkaline electrolytes. The test for the catalyst's cathodic discharge voltage is higher than that of Co_3O_4/KB and CeO_2/KB [55].

Song and co-workers have successfully constructed nano-dimensional hybrid material (with minimum particle size ~7.1 nm) with unique oxide/oxide interfacial structures by using lanthanide precursor. They designed $La_2O_2CO_3$ encapsulated La_2O_3 NPs on Vulcan carbon (Vulcan XC-72). The electrochemical activity shows that the catalyst exhibit enhanced performance in comparison to the individual counterparts. In addition to that, the stability test for the EC surpasses Pt/C. The enhanced ORR kinetics is ascribed to the sandwich-like $La_2O_2CO_3$ layer at the interface of La_2O_3 and carbon that facilitates suitable surface-adsorbed −OH substitution and endorses active O_2 adsorption at the interfaces. The characteristic −C−O−C(=O)−O−La−O− bonds, constructed at the interfaces might act as active sites on the hybrid EC, thereby opening the path towards fabrication of La-based MO hybrid as a next generation EC for ORR [56].

1.4.2 Oxide/hydroxide interfaces

Hybrid materials composed of metal oxide/hydroxides have been recently suggested as highly impressive ECs towards ORR and OER [57–59]. The physicochemical properties can be tuned by engineering their anion chemistry. Controlling the composition and morphology of these engineered nanostructures is an effective way to improve their catalytic performance [60–62]. The interactions between these constituents can lead to excellent electronic properties. Therefore, by designing multimetallic structures, the performance of the ECs can be enhanced. The performances of these materials have been further modified by using different supports. Carbonaceous materials viz. graphene sheets, carbon nanotubes, etc., are used to increase electrocatalytic activity. Moreover, carbon support provides a high BET surface area to carry out ORR/OER performances over the material [63–66]. This unique interface of metal oxide/hydroxide/support provides ample effective electron pathways through the framework.

Liu and Hu used iron oxides and oxyhydroxides to synthesize four iron oxide/oxyhydroxide/GO composites [64]. They have systemically investigated these materials for ORR in alkaline media. The synthetic procedures of these oxides are presented in Figure 1.7. These composite oxides display impressive ORR activity compared to benchmark catalysts. α-Fe_2O_3/GO shows superior ORR activity compared to other composites and benchmark catalysts. It displays better onset potential, current density, and electron transfer number in alkaline electrolyte. The composite also unveils its excellent stability and methanol tolerance ability.

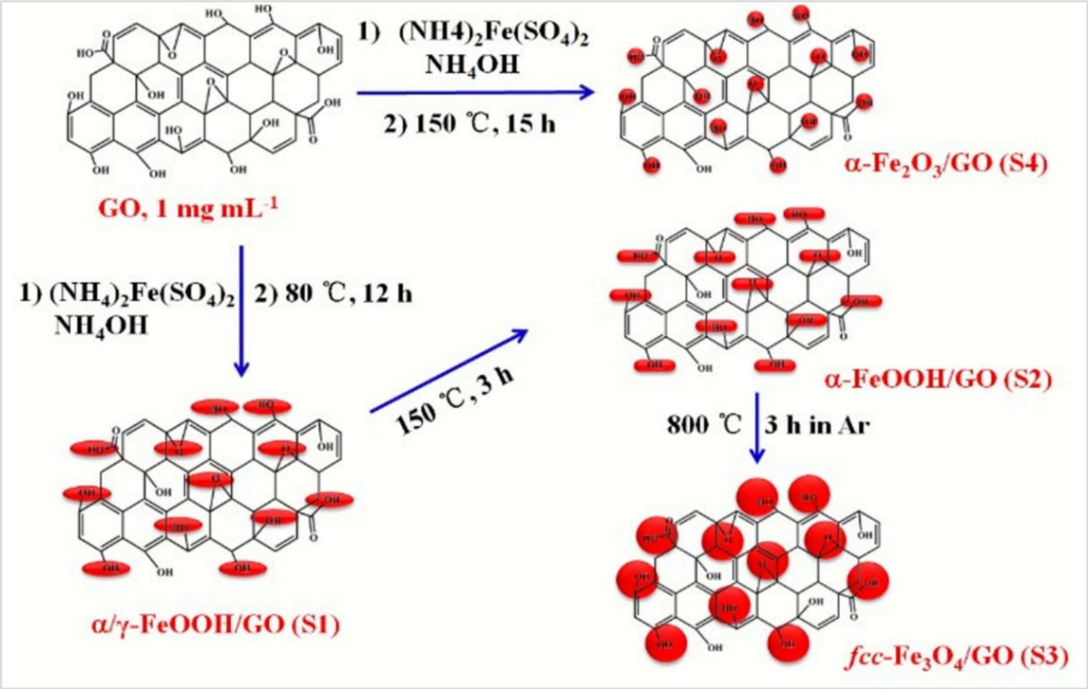

Figure 1.7. Schematic illustration of the synthesis of four iron oxide or oxyhydroxide/GO composites (Adapted with permission from [64]).

Li *et al.* have synthesized NiFe LDH over reduced graphene oxide nickel foam (NiFe-LDH/rGO/NF) for OER in alkaline media. The material shows higher catalytic activity with a current density of 10 mA cm^{-2} and a lower overpotential of 150 mV. The higher activity is due to the surface-active groups of rGO and also the improved interface conductivity [67]. Cao *et al.* designed a flower-like three-dimensional NiFe-LDH over graphene oxide (NiFe-LDH/GO) by a one-step hydrothermal method and used for ORR in alkaline electrolyte. The designed material has a large BET surface area, good conductivity, and more active sites [68]. It has a smaller Tafel slope value of 82 mV dec^{-1} with an early onset potential. The interaction between the LDH and the GO was responsible for the excellent electrocatalytic activity of the material for ORR.

Garcia *et al*. synthesized a nickel oxyhydroxide (NiOOH) EC by the precipitation of $Ni(OH)_2$ on polycrystalline gold by an electrochemical method for OER. The effect of various alkali cations, e.g., Na^+, K^+, $Li^{+,}$ and Cs^+ with and without impurities of Fe were investigated for boosting the OER activity of NiOOH. The OER activity was affected when Fe impurities were present. The better OER activity is due to the interactions of the cation with the produced charged intermediates. However, further works are necessary to confirm their proposal [69]. Jia *et al.* have designed a ternary CoNiMn- LDH/polypyrrole (PPy)/rGO composite by a one-step method and explored for ORR/OER in alkaline media. The prepared composite also shows remarkable durability towards both reactions [65].

A coralloid-like trimetallic oxyhydroxide was synthesized over nickel foam or carbon nanotubes by Huang and co-workers [70]. A series of trimetallic WCoFe-oxyhydroxides was synthesized by a wet-chemical method. They optimized the trimetallic structures depending on the Fe content. The optimized catalyst ($W_{0.5}Co_{0.4}Fe_{0.1}$/NF) exhibits excellent OER activity. The OER activity is directly dependent on the Fe content with a lower Tafel slope of 32 mV dec^{-1}. They correlated the OER activity with the ratio of $Co^{2+}/Co^{3+}$and amount of Fe added, thus $W_{0.5}Co_{0.4}Fe_{0.1}$ showing highest activity. The

Recent works also focused on trifunctionality that is being observed with certain two-dimensional layered materials. Lim *et al.* have studied the trifunctionality of layered transition metal for HER, OER, and ORR [71]. The electrocatalytic properties of several first-row transition-metal oxyhydroxides with the general formula MO(OH), where M represents the transition metal, e.g., CoO(OH), MnO(OH), FeO(OH), NiO(OH), and CrO(OH) for the three reactions. Their electrochemical studies show that the cobalt and nickel oxyhydroxides display superior OER and HER activity compared to other oxyhydroxides. A NiFe LDH supported over rGO was reported by Lee and co-workers and studied for electrochemical OER and photoelectrochemical H_2O splitting reactions [66]. It displays superior OER activity and stability compared to pristine-NiFe LDH and benchmark IrO_2 catalyst. The material shows 97% Faradaic efficiency for OER. In another study, Zhan *et al.* have reported the synthesis of a NiFe LDH supported on rGO, which tested successfully as a bifunctional catalyst for ORR and OER in alkaline media. The detailed ORR polarization curves are presented in Figure 1.8. They compared among pristine NiFe-LDH, NiFe-LDH/GO, and NiFe-LDH/rGO. From Figure 1.8 (A), it is clearly seen that the oxygen reduction peak appears at ~0.78 V for all three catalysts. However, more positive onset potential and higher current densities (Figure 1.8 (B)) are exhibited by NiFe-LDH/rGO, rendering it the best among the three catalysts. NiFe-LDH/rGO follows a $4e^{-}$ pathway for ORR in 0.1 M KOH (inset of Figure 1.8 (D)). Additionally, it is observed that pristine NiFe-LDH showed the least favorable output for all parameters involved. This puts into light the importance of a strong and conductive carbon support and also proper vacancy modulation induced by the presence of rGO. The excellent bifunctionality was due to the synergistic effect and the porous structure of the nanohybrid, which was beneficial for fast electron transfer [72].

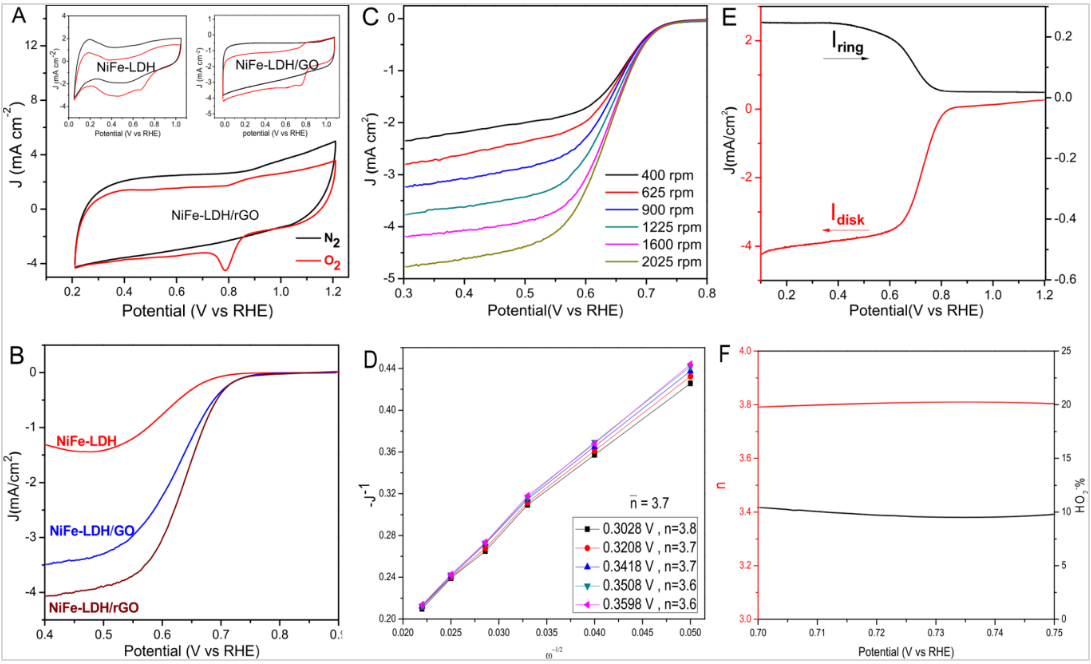

Figure 1.8. (A) CVs in N_2- and O_2-saturated, (B) LSV in O_2-saturated 0.1 M KOH for NiFe-LDH, NiFe-LDH/GO and NiFe-LDH/rGO composites with 1600 rpm. (C) RDE voltammograms of rGO-LDH in O_2-saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} at different rotating speed, (D) the corresponding K-L plot of J^{-1} vs. $\omega^{-1/2}$. The inset shows the electron transfer number (n), and (E) RRDE voltammograms of NiFe-LDH/rGO in O_2-saturated 0.1 M KOH. The disk potential is scanned at 10 mV s^{-1} and the ring potential is constant at 1.3 V. (F) The electron transfer number n and percentage of HO_2^- at certain potentials are based on the corresponding RRDE results (Adapted with permission from [72].

In 2017, the same group had reported nitrogen-doped NiFe LDH supported over rGO as an excellent bifunctional EC for ORR and OER. The better performance of the nanosphere in comparison to individual counterparts could be due to the hybridization of NiFe-LDH with rGO and N-doping, which in turn improved conductivity and stability [73]. Bimetallic Fe/Co double hydroxide/oxide NPs over N-doped carbon nanotubes (FeCo-DHO/NCNTs) were reported by Sun and co-workers [74]. They optimized the synthesis procedure so that FeCo-DHO uniformly anchored over the carbon nanotube surface. The ORR and OER kinetics were studied in 1.0 M KOH solution. In addition to high catalytic activity, the prepared FeCo-DHO/NCNT display very high stability. The oxide/hydroxide interfaces play an important role in boosting electrocatalytic activity. The composition, structure, and surfaces of these interfaces can be tuned to get excellent activity. The interactions between these components lead to tunable electronic properties and multi-metallic structure, which helps in enhancement of the electrocatalytic performance.

In a nutshell, hybrid and modified multi-interfacial oxide/oxide, or oxide/hydroxide, holds immense potential as revolutionary material in shifting towards sustainable energy domain, and consequently, their study is given careful note at present times.

1.5 Role of carbon support

Supported metal catalysts are one of the most extensively studied classes of electrocatalysts. Its primary role is to uniformly disperse the active metal atoms upon their extensive geometric area. Carbonaceous materials are chosen as supports because they are low-cost, have large specific surface areas, easy induction of surface groups, chemical inertness, robust nature and high electrical conductivity [75,76]. The primary forms of carbon polymorphs as catalyst-support are shown in Figure 1.9(a). Carbon black is the oldest form of carbon support for FC applications. Being amorphous, it suffers from oxidation at higher potentials [77]. Hence, nanometric carbon materials with mesopores such as single-walled and multi-walled carbon nanotubes (SWCNTs and MWCNTs), graphite, graphene, reduced graphene oxides (RGOs) doped with metals/MOs are chosen as better alternatives for application as catalysts and catalyst support [78]. The basal and edge planes of carbon materials are exposed on the surfaces [79]. Electronic interactions take place between the metal and the carbon support which influences the shape, size and dispersion. This provides good anchoring of the active metal sites onto the support material. The preferred form of carbon support for an efficient ORR catalyst is that it should have a more graphite-like 2D network. Graphene-supported iron-phthalocyanin (g-FePc) exhibited long-term stability and methanol-tolerance for ORR (Figure 1.9(b– e)), while comparable ORR features with Pt/C in terms of E_{onset} and current density. The planar macrocyclic moieties were immobilized upon planar graphene structure through π-π interactions. The obvious impact of carbon support on the catalytic ability towards ORR can be seen from LSV comparison curves of a series of carbon-supported and unsupported catalysts. It is well resolved that the carbon-supported (FePc/C) and graphene-supported (g-FePc) candidates yield maximum current-density among the series than the bare FePc analogue. Pt/Vulcan XC-72R being amorphous carbon black was proved to be inferior to Pt/CNFs (carbon nanofibres) [80].

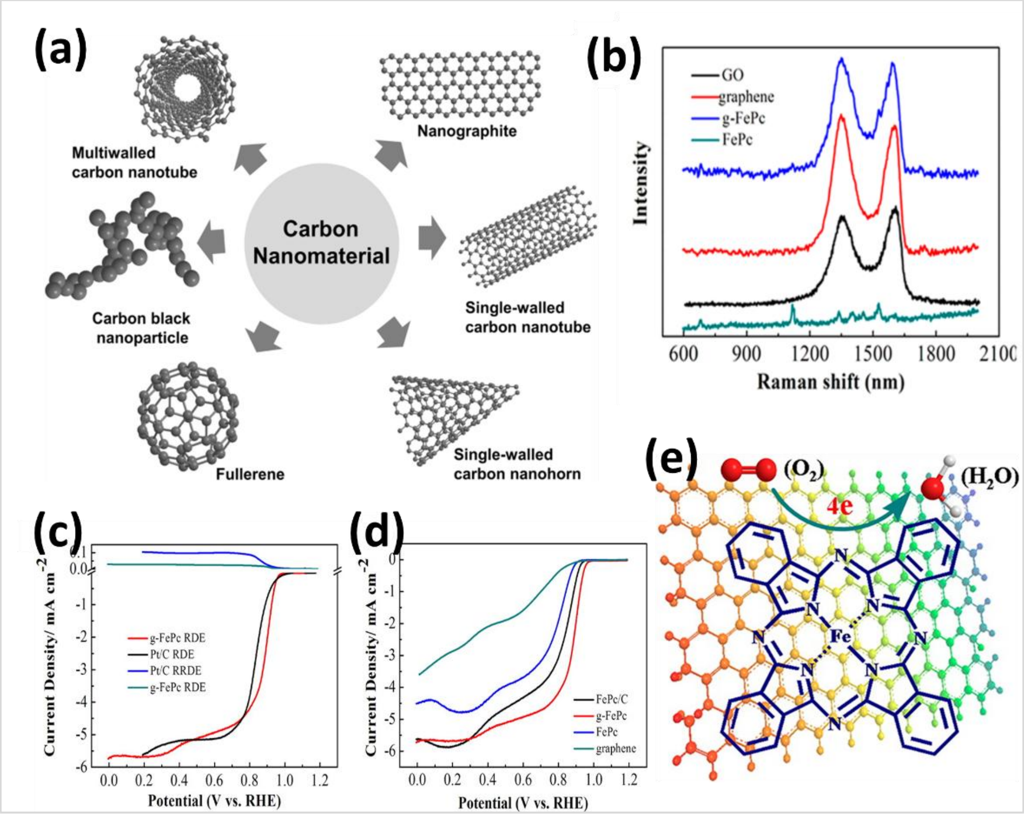

Figure 1.9. (a) Different forms of carbon as catalyst-support (Reproduced with permission from [81]), (b) Raman spectra of GO, graphene, and g-FePc, and pure FePc, (c) RDE measurements of oxygen reduction (negative current) and RRDE measurements of H_2O_2 oxidation (positive current) on g-FePc and Pt/C electrodes in O_2-saturated 0.1 M KOH, (d) Comparison of ORR curves of FePc/C, g-FePc, FePc, and graphene in O_2-saturated 0.1 M KOH at 1600 rpm, (e) Schematic illustration of the interaction between graphene and FePc and ORR process on g-FePc. (Reproduced with permission from [82])

Thus, it is evident that the effect of surface groups and graphiticity had a great role to play while determining the electrocatalytic activity. More graphiticity yielded faster kinetics and larger ECSA. The metal support interaction brings about geometric (size/shape/strain/interfacial boundary) and electronic (charge transfer) modifications crucial for a facile reaction mechanism [83]. In this thesis work, we employ graphene nanoplatelets as the carbon support for all synthesized catalysts.

1.6 Role of defects

Defects are essential in optimizing the performance of a heterogeneous catalyst. A defect-rich surface has versatile electron densities at different regions that improve the intrinsic electron-conductivity at the surface and from the surface-active sites to the adsorbate O_2. Defects can be present as dopants or impurity atoms, cation or anion vacancies, dislocations, voids, etc. For example, oxygen vacancies which are mostly observed in metal oxides.(Figure 1.10).

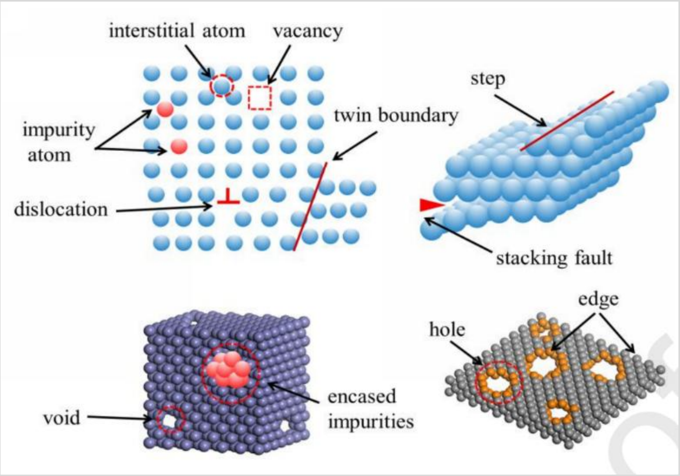

Figure 1.10. Schematic illustrating various defects and their respective features in crystals with multiple dimensions (Reproduced with permission from [84]).

Defects can be generated by various synthesis methods, viz., acid/base etching method, dopant/template removal method, plasma etching technology, intercalation/exfoliation assisted method [84]. In the case of 2D carbon sheets like graphite and graphene, doping of electron-rich and/or electron-deficient elements like O, N, B, P, S play the role of defects [78,84]. It is a consensus that the difference in electron-densities around the interfacial boundaries of defects impart catalytically active sites in its vicinity [85]. Hence, defect co-engineered nanocomposites act as even better ORR nanomaterials. For instance, a cellulose-derived NH_3- injected pyridinic-N dominated defect-enriched graphene-like nanocarbon material (ND-GLC) is superior to its pristine counterparts of the composite and comparable to Pt/C towards ORR and follows a favorable $4e^-$ pathway.

DFT calculations revealed that adsorption energies for *OH for the C-atoms near the defects were the lowest, thereby serving as the ORR active points [86].

Generally, the concentration of defects is found to be more in nano-engineered C materials than in MOs, largely because the graphitic network is flexible enough to accommodate some disorderliness by local rearrangements within the π-electron framework. In other words, defect generation is a strategy to functionalize chemically inert carbon surfaces. Oxygen atoms also serve as an important heteroatom defect. However, there is an ambiguity over the impact of oxygen defects on influencing the catalytic activity of carbon-based ORR catalysts [87–89]. There is no such co-linearity of catalytic activity and surface-functionalized oxygen-rich support. Temperature-programmed reduction and subsequent desorption (H_2-TPR/TPD) studies along with micro-calorimetry of CO and CO_2RR reveals diminished metal support interaction due to the presence of oxygen functional groups [88]. Oxygen defects are generally introduced via acid treatment, because of which functional groups like -COOH and -CO are formed on the carbon surface. While such functionalization is likely to improve ORR kinetics, some concomitant unwanted structural changes also seem to occur which might delay the ORR process [90]. In this thesis work, we have confined to introduce defects in the metal oxides/hydroxides only.

1.7 Research gap or research question:

Realizing the harmful impacts on the environment from the burning of fossil fuels and the need for an alternative sustainable energy domain, the practical utilization of fuel cell technologies is to be given supreme priority. As of now, there is enough natural stock of fossil to sustain the earth for several more years and taking this time as a period of grace, electrochemical oxygen reduction and evolution reactions shall contribute massive support towards speeding up fuel cell kinetics. But there are some hurdles on the way to complete commercialization of an easy, low-cost, high efficiency electrocatalyst. After extensive literature survey, we have come across the observation that this area has certain research gap, and the research questions are summarized here as follows:

- There is very less pioneering research into non-platinum group metal (non-PGM) based electrocatalysts. Most reported catalysts are Pt-based composites.
- Mixed oxides and oxyhydroxides display tremendous scope for interfacial electrocatalysis, outperforming their component oxides. But it is a challenging task

to synthesize intricately designed oxide/oxide or oxide/hydroxide interfacial electrocatalysts. It demands controlled redox conditions. Hence there aren't many reports on such hybrid electrocatalysts. Understanding their molecular structure and behavioral phenomena is of pivotal importance and is an integral part of this study.

- Development of practically viable electrocatalysts with minimal external input, eco-friendly starting materials, and optimum tuning of elemental compositions is expected to give an outstanding acceleration to oxygen kinetics; this is the scope of the study. In yet another perspective, oxide/hydroxides can be considered as precursors to oxide/oxide catalyst, and as such, a study of their comparison analysis can be remarkable guidance in the design-synthesis of interfacial ECs at the industrial level.
- There is no rigid explanation on how the interfacial sites render more sensitivity and activity towards enhanced electro-kinetics. There are numerous reports where it is said that there is a '*synergistic*' relationship between the non-identical interfaces. Although there is a unanimous agreement among scientists on this statement, but there is not much explanation on how this '*synergy*' works. There is not much explanation on why there is a lot of difference in the behavioral properties of mixed oxides and/or hydroxides compared to their pristine non-hybrid analogues.

1.8 Objectives of the Present Work

In line with the above-mentioned research gaps, I have focused my research work on mixed metal oxides and hydroxides of some non-precious, transitional metals and their electrocatalytic efficiency towards ORR and OER. Development of practically viable electrocatalysts with low-cost, eco-friendly materials, and optimum tuning of elemental compositions is expected to give an outstanding acceleration to ORR/OER electrokinetics; this is the aim of the study. From our extensive literature study, we believe that the feasibility of adsorption and desorption of oxygen molecules at point defects (anion vacancies, oxygen vacancies, etc.) could be a major factor behind the altered electrocatalysis of the mixed oxides and/or hydr(oxides). Studying the oxygen vacancies have been given great importance in this study. The key objectives of the study are as follows:

- ☑ To synthesize graphene supported single, bi- and tri-metallic (oxy)hydroxides of non-PGM elements of the type M_xO_y $(OH)_y$ /C where M = Co, Ni, Ce.
- ☑ To study the effect of thermal treatment temperatures for generating materials with rich oxide/hydroxide and oxide/oxide interfaces.
- ☑ To study the electrocatalytic activity of the as-synthesized oxide/oxide, oxide/hydroxides for ORR, OER.
- ☑ To employ multi-technique approaches to establish structure-activity correlation for better understanding of oxide-oxide/hydroxide interfaces.

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