

Chapter – 1

INTRODUCTION

Introduction

Search for alternative energy sources is not a new thinking for mankind. Wood fire was the primary source of energy for cooking and heating until around 1500 AD, and later, the use of charcoal and fossil fuels as a source of primary energy.

Today in the 21st century, energy has become the most important issue in world. Increasing population and industrialization have increased the demand for energy. In the present era, the fossil fuels are most important source of energy. Approximately 82% of total primary energy which we are using now a days comes from fossil fuels. The deposits of fossil fuels are limited and it is expected that these fossil fuels and oils will be exhausted by the mid-21st century [1] also the gases which are being produced on combustion of these fuels is creating an adverse effect in environment. Some important environmental issues are green house effect, acidic rain, climate change etc., due to these all negative impacts our future could not be with fossil fuels and use of fossil fuels is expected to decline.

In view of above discussion, today the challenge is greater than ever to find new alternative efficient and low cost technologies to convert the renewable energy sources into electrical energy, which could be more sustainable and eco-friendly. Fuel cell is one of the efficient technology in our present and for future, it converts chemical energy of fuels like hydrogen directly into electrical energy through electrochemical process without creating any negative impact on our environmental. Fuel cells have properties to be an interesting and very promising alternative tool for clean electric power generation with high efficiency [2]. Today there are various types of fuel cells have been invented and classified on the basis of their design and the type of fuel consume in them. A Hydrogen-Oxygen fuel cell (alkaline fuel cell) is an important type of fuel cell and it has efficiency of about 60-70%, while some other like Magnesium-Air fuel cell has efficiency up to about 90%.

Introduction

The future era is based on hydrogen economy. Hydrogen is being become an important part of our future energy systems. There are four main sources to produce the hydrogen gas at commercial scale and these are natural gas, oil, coal, and water electrolysis; which account for 48%, 30% 18% and 4% of the world's hydrogen production respectively [3]. Out of these all sources the hydrogen produced by the electrolysis of water exhibits maximum purity (which is a necessary requirement for the use of hydrogen in fuel cells) also this process of hydrogen production does not create any negative impact in environmental.

It is a cyclic process to produce the hydrogen gas via electrolysis of water or alkaline water by consuming available electrical energy at one place and use the produced hydrogen gas in fuel cells to produce electrical energy at another place. We may say that “Hydrogen is not an energy source, but an energy carrier because it takes a great deal of energy to extract it from water. It is useful as a compact energy source in fuel cells and batteries”.

Electrolysis in electrolytic cell → consumes electrical energy to produce hydrogen gas.

Oxidation of hydrogen in fuel cells → consumes hydrogen gas to produce electrical energy.

In this cycle, the main challenge however is to produce maximum hydrogen gas with minimum consumption of electrical energy in electrolytic cell and to produce maximum electrical energy by the minimum consumption of hydrogen gas in fuel cells. One of the important solution for this challenge is the application of efficient electrocatalyst for both reduction and oxidation process of hydrogen in electrolytic cells as well as in fuel cells, respectively by aiming to reduce the value of anodic as well as cathodic overpotentials. The efficiency and performance of an electrolytic cell can be improve by using a more suitable electrocatalyst. Consequently the search for those materials (electrocatalysts) which can reduce both anodic and cathodic overpotentials has been increased considerably.

1.1 Water Electrolysis

Water electrolysis is the process of decomposition of water molecule into Oxygen (O_2) and Hydrogen (H_2) by consuming electric current being passed through the water in presence of suitable substance, called electrolyte. It was in 1800 when Alessandro Volta invented the voltaic pile and a few weeks later Nicholson and Carlisle used it for the electrolysis of water. By 1902 more than 400 industrial water electrolyzers were in operation and in 1939 the first large water electrolysis plant with the capacity of $10,000 \text{ Nm}^3 \text{ Hz/h}$ went into operation and in 1948 the first pressurized industrial electrolyzer was built. The history ends up in our days with the creation of proton exchange membranes, usable for water electrolysis and fuel cell [4] However, on industrial scale, the production of hydrogen by water electrolysis commenced before the beginning of 19th century [5-7]. Later this process became obsolete when the cheaper hydrogen began to produce from fossil fuel.

Water electrolysis is the straight forward and the simplest electrochemical route at present for storing electricity in the form of the non-pollutant hydrogen and it considered as the cleanest way to produce hydrogen, when the required electricity is derived from renewable energy sources. In those countries where a lot of waterfalls are present, hydroelectricity can be used as the energy source for water electrolysis. Other renewable sources like solar, aeolic and geothermal energy can also be use in electrolysis. In photoelectrolysis the photovoltaic cells are also the electrodes that decompose water to hydrogen and oxygen gas, could be used for the production of hydrogen. Above mentioned technologies could be used to store energy in the form of hydrogen and which can be use to generate electricity through fuel cells.

Due to sudden hikes in the price of oil and other fossil fuel in the year 1970 vis-à-vis growing interests in water electrolysis, the production of hydrogen from

non-conventional energy sources has become interesting task aiming at especially to improve its efficiency; so that the cost of electrocatalytically produced hydrogen could be made comparable to that of hydrogen obtained by fossil fuels.

Now a days in commercial electrolyzer 15-30 wt% KOH is used as electrolyte, nickel or plated nickel as anode and mild steel or nickel as cathode [8]. The commercial electrolytic production of H₂ is more costly than that produced by the fossil fuels. Thus, the production of H₂ is preferred only in those countries where cheap electrical powers, such as, nuclear (France and Belgium) and hydroelectric (Canada, Brazil, Zaire etc) are available. The list of commercial electrolyzers along with their operating conditions which are available in the market is shown in Table 1.1.1. These electrolyzers consist of either monopolar or bipolar cells. Bipolar cells are energetically more effective comparative to older and technically simpler monopolar cells. Therefore, monopolar cells have been gradually replaced worldwide by the energetically more effective bipolar cells.

Table 1.1.1: Typical commercial water electrolyzers and their operating conditions.

Manufacturer	Electrolyser Corp. Ltd	Brown Bovert& Cle	Norsk Hydro A. S	DeNora S.P.A.	LURGI Gmbl I	Krebskosmo Berlin
Cell Type	Monopolar tank	Bipolar Filter press				
Operating pressure	0.1Mpa	0.1Mpa	0.1Mpa	0.1Mpa	3Mpa	0.1Mpa
Operating temperature	70°C	80°C	80°C	80°C	90°C	80°C
Electrolyte	28% KOH	25% KOH	25% KOH	29% KOH	25% KOH	25% KOH
Current density kAm ²	1.34	2.0	1.75	1.5	2.0	2.5-3.0
Cell volt, V	1.90	2.04	1.75	1.85	1.86	1.85
Current efficiency %	99.9	99.9	98.0	98.5	98.75	98.5
Oxygen purity %	99.7	99.6	99.3-99.7	99.6	99.3-99.5	99.5
Hydr. Purity %	99.9	99.8	98.8-99.9	99.9	98.8-99.9	99.9
Power consumption DC kwh/Nm ³ H ₂	4.9	4.9	4.3	4.6	4.5	4.5
Current required for 1 Nm ³ hydrogen =2393 A hr.						
This table has been printed from “Electrochemical Hydrogen Technologies” H. Wendt (Ed) Elsevier, Amsterdam. 1990						

1.1.1. Thermodynamic aspect of water electrolysis:-

Electrolysis of water is a well-known principle to produce oxygen and hydrogen gas. The basic electrolysis unit consist an electrochemical cell, filled with pure water and has two electrodes which are connected with an external electric power source. At a certain potential, called critical potential, between both electrodes, at negatively biased electrode hydrogen gas liberates and at the positively biased electrode oxygen gas. The volume of gases produced per unit time depends on the current that passes through the electrochemical cell. In pure

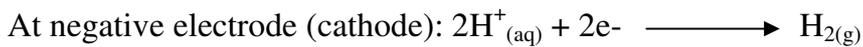
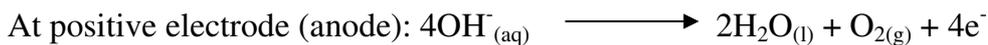
water, there is always a certain percentage found as ionic species; H^+ and OH^- but still it is poor conductor of electricity so in practice, always an electrolyte must be added so that the reaction can proceed at a technologically acceptable cell voltage.

Electrolysis of water can be carried out in both acidic as well as alkaline medium.

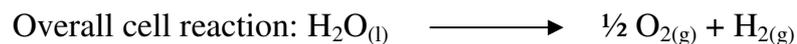
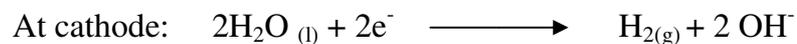
In pure water, there is always a certain percentage which is found as ionic species; H^+ and OH^- represented by the equilibrium equation:



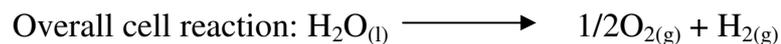
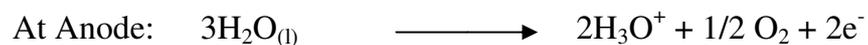
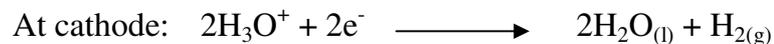
On electrolysis of water at noble metal electrodes, following reactions takes place at electrodes.



In alkaline medium reactions are as following:



In acidic medium reactions are as following:



To split the water in to hydrogen and oxygen gases the minimum energy required or cell voltage can be calculated by the relation;

$$\text{Electrical energy} = nFE_{\text{cell}} \quad (1)$$

Where, E_{cell} = cell voltage

F = Faraday constant

n = total no of electrons involved in the cell reaction

In thermodynamics, the cell voltage is related with free energy change (ΔG) for the cell reaction.

$$-\Delta G = nFE_{\text{cell}} = 2FE_{\text{cell}} \quad (n=2)$$

$$\text{But } \Delta G = (\mu_{\text{H}_2} + \frac{1}{2}\mu_{\text{O}_2}) - (\mu_{\text{H}_2\text{O}})$$

$$\text{or } \Delta G = (\mu_{\text{H}_2}^{\circ} + RT \ln a_{\text{H}_2} + \frac{1}{2}\mu_{\text{O}_2}^{\circ} + \frac{1}{2}RT \ln a_{\text{O}_2}) - (\mu_{\text{H}_2\text{O}}^{\circ} + RT \ln a_{\text{H}_2\text{O}})$$

$$= (\mu_{\text{H}_2}^{\circ} + RT \ln P_{\text{H}_2} + \frac{1}{2}\mu_{\text{O}_2}^{\circ} + RT \ln P_{\text{O}_2}^{\frac{1}{2}}) - (\mu_{\text{H}_2\text{O}}^{\circ} + RT \ln a_{\text{H}_2\text{O}})$$

$$= (\mu_{\text{H}_2}^{\circ} + \frac{1}{2}\mu_{\text{O}_2}^{\circ} - \mu_{\text{H}_2\text{O}}^{\circ} + RT \ln \left[\frac{P_{\text{H}_2} P_{\text{O}_2}^{\frac{1}{2}}}{a_{\text{H}_2\text{O}}} \right])$$

$$\Delta G = \Delta G^{\circ} + RT \ln \left[\frac{P_{\text{H}_2} P_{\text{O}_2}^{\frac{1}{2}}}{a_{\text{H}_2\text{O}}} \right] \quad (2)$$

Where, terms μ , μ° , P and a , have their usual meanings.

Under standard state conditions i.e.

Temperature = 25 °C

Pressure = 1 atmosphere

$$\Delta G = \Delta G^{\circ} \text{ and } -\Delta G^{\circ} = nFE_{\text{cell}}^{\circ} \quad (3)$$

Where, E_{cell}° is standard cell voltage.

To split the liquid water (at 25 °C and 1 atmospheric pressure) thermally into its constituent gaseous H₂ and O₂ the values of ΔH°, ΔS° and ΔG° are 286.86 KJ mol⁻¹, 164.22 J deg⁻¹ and -237.178 kJmol⁻¹ respectively.

$$E_{cell}^{\circ} = \frac{-\Delta G^{\circ}}{nF} = \frac{-\Delta G^{\circ}}{2F} = \frac{237178 \text{ J mol}^{-1}}{2 \times 96485 \text{ Coulombs}}$$

$$= 1.229 \text{ V} \approx 1.23 \text{ V}$$

Thus, at 25 °C and 1 atmospheric pressure the minimum cell voltage required for electrolysis of water is 1.23V. From Eq. (2), it is clear that E_{cell} is a function of pressure. At high pressure the value of cell voltage is also high, therefore at high pressure a higher cell voltage will be required to split the water. Thus, higher pressure will disfavor water splitting.

Due to modification in the activity of water on changing the electrolytic concentration, E_{cell}^o also depends over the concentration of electrolyte, but this effect is only considerable at high level.

According to equation ΔG° = ΔH° - TΔS° the value of ΔG° is a function of temperature, so the temperature also affects the value of E_{cell} and it decreases with increase in temperature. In terms of enthalpy (ΔH°) and entropy (ΔS°) changes, Eq. (2) can be written as:

$$E_{cell}^{\circ} = \frac{-\Delta G^{\circ}}{2F} = \frac{\Delta H^{\circ} - T\Delta S^{\circ}}{2F} = \frac{\Delta H^{\circ}}{2F} - \frac{T\Delta S^{\circ}}{2F}$$

$$= \frac{286860 \text{ J mol}^{-1}}{2 \times 96485 \text{ Coulombs}} - \frac{T \times 164.22 \text{ J deg}^{-1} \text{ mol}^{-1}}{2 \times 96485 \text{ Coulombs}}$$

$$E_{cell}^{\circ} = 1.48 - 0.85 \times 10^{-3} T \quad (4)$$

Where, T is the temperature in Kelvin.

It means that with per degree rise in temperature the value of cell voltage decrease by 0.85 mV. It concludes that the water electrolysis is more favorable and economical at relatively high temperature and low pressure. However, high temperature electrolysis seems to be impractical unless a considerable pressure is increased to suppress the water evaporation. By using the water in vapor state and solid oxide electrolyte like Ytria-doped Zirconia as an oxygen ion conductor in place of aqueous KOH electrolyte, this problem of solvent evaporation can be avoided and efficiency of the process can be enhanced. Use of solid electrolyte prevents from the corrosion due to KOH at high temperature. The applied capability of this high temperature vapor electrolysis is under active investigation during recent years [9].

1.1.2. Kinetic Aspects

The value of theoretical (thermodynamic) cell voltage is 1.23 volt vs. standard hydrogen gas electrode for the electrolysis of water, but practically process takes place at a considerably higher cell voltage (1.8–2.1 V vs. NHE). From this, it is evident that along with the thermodynamic cell voltage, the internal cell voltage is contributed by some other factors also. Therefore, the amount of energy spent in the electrolysis is more than required theoretically.

Following are the factors which influence the value of cell potential:

- (i) The values of reversible anodic (E_a) and cathodic (E_c) potentials in the electrolytic cell.
- (ii) The over potentials for the oxygen evolution reaction (OER) at the anode (η_a) and hydrogen evolution reaction at the cathode (η_c).
- (iii) Increase in the overpotential with time during cell operation due to the deterioration of the electrode materials (ΔV_t).

- (iv) The iR drop (where R is the total resistance of the circuit) in the electrolyte (interelectrode gap), in the electrode structure and in the connecting circuit.

Thus, the overall cell voltage becomes

$$\Delta V = E_a - E_c + \eta_a + \eta_c + iR + \Delta V_t$$

$$\text{Energy efficiency} = \frac{\text{Thermodynamic cell voltage}}{\text{Practical applied cell voltage}}$$

$$= \frac{E_a - E_c}{\Delta V_{\text{app}}} = \frac{1.23}{\Delta V_{\text{app}}}$$

Thus, electrolysis cell with high energy efficiency can be achieved by minimizing the contribution of η_a , η_c , iR to the cell potential to a possible extent. The contribution of iR to the cell potential can be minimized by using electrode and electrolyte of high conductance and keeping the minimum possible gap between the electrodes. ΔV_t is related to the stability of the electrode materials. However, η_a and η_c represents the surplus energy necessary to overcome the concentration gradients and to activate the reaction of hydrogen and oxygen evolution at the electrodes. The overpotential can be minimized by developing the more efficient electrocatalysts with gradually enhanced surface area. The value of overpotential of electrode reaction has been observed to vary with the electrolysis current density.

As, according to Tafel's law,

$$\eta = \frac{RT}{\alpha F} \ln \left(\frac{j}{j_o} \right)$$

$$j = j_o e^{\frac{\alpha F \eta}{RT}}$$

Similarly,

$$j = j_o e^{\frac{\alpha F \eta}{RT}}$$

$$\text{Where } \frac{RT}{\alpha F} = \pm \left(\frac{\partial \eta}{\partial \log j} \right)_{T,P} = b \text{ (Tafel slope)}$$

η is the overpotential, it is the difference between the reversible potential $E_r = (E_a \text{ or } E_c)$, corresponding to the system at equilibrium with no current passing and the potential (E) measured when a current density j is passed across the interface, j_0 is the exchange current density and α is an empirical parameter called transfer coefficient.

$$\eta = E - E_r$$

The exchange current density (j_0) is the current density at zero overpotential or can say it is the current density in the absence of net electrolysis. The exchange current can be thought of as a background current to which the net current observed at various overpotentials is normalized i.e., when anodic current is balanced by the cathodic current. This ongoing current in both directions is called the exchange current density. When the potential at any electrode (either at cathode or anode) is set more than the formal potential, the net current density is observed which is the difference between the cathodic and anodic current densities.

To determine the experimental value of exchange current density the linear portion of the plot of η vs. $\log j$ is extrapolated to the reversible potential, where $\eta = 0$. When two or more electrocatalysts exhibit similar Tafel slope under this situation, exchange current density plays an important role to compare their catalytic activities. Thus, both the exchange current density and the Tafel slope for the reaction depend on the nature of the electrode materials. Therefore η can be minimized by development of suitable electrode materials. In fact, this is the task of electrocatalysis, where in relationship between the physicochemical properties of the electrode materials and the mechanism and rate of the electrode reactions are studied.

On the basis of theoretical data earlier reported in literature, values of various electrode kinetic parameters such as Tafel slope (b), exchange current density (j_0) and order of reaction (p) can be evaluated. The slope of the linear portion of the curve, η (or E) vs. $\log j$ gives the Tafel slope.

Mathematically Tafel slope is defined as

$$b = \left(\frac{\partial E}{\partial \log j} \right)_{T,C}$$

The numerical value of Tafel slope is expressed in Volts (or millivolts) per decade of current density.

Only the value of Tafel slope cannot decide the mechanism of electrochemical reaction because several different mechanisms can produce the similar numerical value of Tafel slope.

In chemical kinetics following partial derivative defines the reaction order (p),

$$p = \left(\frac{\partial \log v}{\partial \log C_j} \right)_{T,P,C_{j \neq i}}$$

Above expression determines the dependence of the rate of reaction (v) on the concentration of one chemical species in the solution, keeping the concentration of all other species constant at a constant temperature and pressure. In electrochemistry order of reaction (p) is defined in a similar way as in chemical kinetics here along with keeping temperature and pressure at a constant value, the potential or overpotential must be maintain constant, resulting two reaction orders in electrochemistry, one (p_1) at constant potential and other (p_2) at constant overpotential.

$$p_1 = \left(\frac{\partial \log j}{\partial \log C_i} \right)_{E, T, P, C_{j \neq i}}$$

and

$$p_2 = \left(\frac{\partial \log j}{\partial \log C_i} \right)_{\eta, T, P, C_{j \neq i}}$$

Reversible potential as well as the overpotential of the cell changes when we change the concentration of reactant due to the dependency of the reversible potential on the concentration of the reactant. Therefore, the order of reaction should always be determined by keeping the potential constant across the electrode electrolyte interface, and if the order is to be determined at constant overpotential the result will be erroneous.

To evaluate the order of reaction, first we get a series of j/E plots at different concentrations of the electroactive species 'i' at a constant temperature and from the data obtained; we construct $\log j$ vs. $\log C_i$ plot at different constant potentials across the electrode-electrolyte interface. The slope $\left[= \left(\frac{\partial \log j}{\partial \log C_i} \right)_E \right]$ of these linear plots, give the value for the order of the reaction with respect to C_i .

While determining the order of reaction to avoid any error, the ionic strength of the medium should be constant and must be sufficiently high because in the determination of order different concentrations of electrolyte are used. So, the electrical double layer structure may change particularly at lower concentrations of the electrolyte resulting the change in electrode kinetics and erroneous order.

1.1.3. Electrocatalysis

A catalyst used to catalyses an electrochemical reaction occurring at the electrodes by increasing the rate of electrochemical reaction (oxidation or reduction) without being consumed in the process is known as electrocatalyst. It may be in the form of a coating at any substrate material or may be the itself as electrode. The main function of electrocatalyst is to decrease the value of reaction overpotential for a electrochemical reaction.

For the production of hydrogen and oxygen gas by the electrolysis of alkaline water various types of electrocatalysts like metals, metallic oxides, metallic mixed oxides etc. are being used. The main task among the researchers is to develop cost efficient (should not contain precious metals) electrocatalysts with long term stability to corrosion and greatly enhanced real surface area.

In electrolysis, materials are synthesized, characterized for their physicochemical surface properties and also for their electrocatalytic activities. Mainly, following three scales have been reported in literature for the comparison of electrocatalytic activity of materials:

- (i) Based on the current density values at constant potential (or overpotential).
- (ii) Based on the overpotential (or potential) values at constant current density value.
- (iii) Based on the exchange current density values (meaningful only when the reaction has the same Tafel slope on electrodes to be compared).

Electrocatalysts are investigated for the technologically important reactions such as hydrogen and oxygen evolution reaction in alkaline medium. Electrocatalytic activity is to be determined by using Tafel plots. These plots are also used to determine the electrode kinetic parameters such as tafel slope (b), the

order of reaction (p) and activation energy etc. The later parameters are required to understand the mechanism of the reactions at the electrode surface. Thus, the enhancement of reaction rate is achieved through the decrease of the activation energy of the required reaction, at constant Gibbs energy change.

The electrocatalytic activity of electrocatalysts are can be best compare by knowing the values of the overpotential or current density at a fixed current density or overpotential. The electrode which shows the maximum current density at a fixed overpotential becomes the highest active one and vice-versa.

The comparative scale discussed above is based on the geometrical area of the electrode and the current density measured is designated as apparent current density (j_a):

$$\text{Current density}(j_a) = \frac{\text{Observed current density}}{\text{Geometrical area of the electrode}}$$

For the same geometrical area different electrocatalysts materials may have different roughness (electrochemically active areas). It is found the generally that with increase in the roughness of the electrocatalyst material rate of electrochemical reaction increases. Thus, electrocatalytic activity of two electrodes should be normalized by the roughness factor. The current so obtained, is referred as real (true) current density.

$$\text{real current density} = \frac{\text{Current density based on geometrical surface area}}{\text{Roughness factor}}$$

For the reactions in which gas molecules are produced as a product of reaction at the electrode, from the technological application point of view for these types of reactions an ideal electrode should essentially have the properties such as large specific surface area, good electrical conduction, good electrocatalytic properties, enhanced selectivity, long-term stability, minimized gas bubble problems, good mechanical properties, low cost and large availability.

At present the alkaline water electrolysis is not economical to produce the oxygen and hydrogen gases because in case of the alkaline water electrolysis, it is found that the cells have normally 0.57-0.58 V higher practical cell voltage than the theoretical cell voltage (1.23 V & NHE) so large amount of electrical energy is consumed in the process. A major fraction of the electrical energy is, in fact, wasted to overcome the internal cell resistance and anodic and cathodic overpotential. Further it has been observed that in the process of electrolysis for oxygen evolution at nickel electrode the value of overpotential increases with the passage of operational time, the increase being more at higher anodic potentials. In an analysis, it has been observed that the initial activity of the electrode was decreased from 2.0 to 0.7 kA cm⁻² in 40h [10]. The decrease in activity has been attributed to a gradual formation of the resistive NiO-film [11] on the nickel anode. As the rate of electrolysis is based on the catalytic efficiency of both the electrodes, any change in activity of either of electrodes will certainly influence the overall production of hydrogen. In view of above, worldwide efforts have recently been made to reduce the practical cell voltage so as to make the cost of electrolytically produced hydrogen comparable to that prepared by other methods. All works carried out were mainly in the following three directions.

- (i) To Reduce internal cell resistance
- (ii) To improve the efficiency of the traditional nickel anode &
- (iii) To develop low cost and corrosion resistant new electrocatalysts.

The internal resistance of the cell can be reduced by decreasing the distance between the electrodes, for this purpose several suitable membranes have been invented [12] using these the inter-electrode distance could be reduced to 1-2 mm. Some of these membranes are polymer reinforced asbestos, Sintered nickel, PTFE bonded zirconia, nickel net backed porous cermet membrane etc. By the application of these membranes in the cells, it has now been possible to bring down the specific resistance [12] as low as 0.4 Ωcm. The older cells have specific

cell resistance of the order of 1 Ωcm . To reduce the ohmic losses and hence the voltage further, the zero gap electrolyzer design has recently been proposed [12] and adopted by the majority of electrolyzer manufacturer. In this configuration the particulate electrode materials are pressed on either side of the porous membrane so that, hydrogen and oxygen gases are forced to leave the electrodes at the rear and that they do not interfere with the current passage through the electrolytes between the electrodes. To avoid the complications due to blockage of pores of membrane as a result of the gas precipitation, the radius of pores of the membrane is kept smaller than the radius of the smallest gas bubbles contained in the electrolyte.

Under anodic polarization conditions it has been found the nickel is unstable, nevertheless researchers are working on to minimize the overpotential on the inexpensive electrode material and also on its alloys. In order to increase the porosity and the surface area of the nickel electrodes various techniques, such as powder coating [13], Raney nickel coating [14, 15], electrodeposition [16-18], plasma spraying [19], etc. are being used. The materials other than Nickel such as spinels (ex. Co_3O_4 and NiFe_2O_4) and perovskites (ex. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ etc.) have been developed and considered to be very promising because of their low cost, stability in strong basic medium [20] and are easily available.

1.2. Earlier work on oxygen Evolution

The oxygen evolution is one of the most technologically important anodic reactions in electrolytic production of H_2 by alkaline water electrolysis. Water electrolysis is the simplest and well known technology for the storage of electricity in the form of non-pollutant hydrogen.

Generally, materials with low overvoltage are required for electrochemical evolution of O_2 . However, in processes like ozone production [21] and organic oxidation in aqueous solutions, material of high oxygen overpotential are sought

which adversely affects the economy of the process. Various types of materials have been investigated for oxygen evolution reaction in order to improve the overall efficiency of water electrolysis cell and extensive researches for new electrode materials with better electrolytic properties have been carried out for several decades. Materials which are often employed in the form of finely divided powders having considerable surface area are attractive for O₂ evolution [22]. Various metals Pt, Ni [23-25] and their pure (RuO₂, IrO₂) [26-28] as well as mixed oxides [29-31] particularly possessing spinel (Co₃O₄, NiCo₂O₄ etc.) and perovskite [LaCoO₃, La_{1-x} Sr_xCoO₃, LaNiO₃ etc] type structures have extensively been studied and reviewed in books [32-34] and Journals [35-43]. Some oxides having delafossite structure [44] (CuFeO₂) and pyrochlorals [45, 46] (Pb₂Ru₂O₇) were also investigated. The oxides such as RuO₂ and IrO₂ are good in acid solutions [47] whereas spinels and perovskites are recommended for alkaline solutions due to their corrosion resistance property [48]. Among the catalyst materials investigated for the OER, transition metal mixed oxides with spinel [29, 49-76] and perovskite type [37, 77-85] structures are considered as very promising ones. Literature shows that some of the binary and ternary metal substituted ferrites [86, 87] and cobaltites [88, 89] having a spinel crystallographic structure and LaNiO₃, LaCoO₃ and their metal substituted products with perovskite [90, 38] structure are found to be potent electrocatalytic materials for their use as anodic OER in alkaline solutions. Although, a very huge literature on the OER have been published so far but we have confined our self to the literature of the study of the oxygen evolution (OE) on mixed transition metal oxides particularly belonging to Spinel family.

1.2.1. Oxygen evolution on spinel type oxides

Mixed oxides having general formula [91, 92] AB_2O_4 are called spinel type oxides where A and B are generally the transition metal ions. A is a bivalent cation such as Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Cd etc. while b is a trivalent cation such as Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni etc. the bivalent (A) cations occupy the tetrahedral void and the trivalent (B) ions occupy the octahedral void in the face centered cubic arrangement of oxygen ions. Spinel type oxides are classified as (i) normal, (ii) inverse and (iii) intermediate depending on the position of 'A' and 'B' ions in the 8a or 16d positions. In a normal spinel (AB_2O_4), all the 8a position and all the 16d positions are occupied by A and B cations, respectively. Examples of normal spinel are aluminates [93], MgV_2O_4 , ZnV_2O_4 [94] and Co_3O_4 [95]. In the inverse spinel, $[B(AB)O_4]$, the 8 'B' cations and 8 'A' cations occupy the 16d positions in a statistically disordered manner. $CoFeO_4$, $NiCo_2O_4$ and certain titanates [96, 97] are examples of inverse spinels. In intermediate spinels $[B_{1-x}A_x(A_{1-x}B_{1+x})O_4]$, the A & B cations are arranged in a disordered manner in both 8a and 16d positions. The quantity X is a measure of the degree of inversion of the spinel. It is rather a difficult problem to find this parameter.

Spinel type of oxides are being used as catalyst in various branches of chemistry. For the oxygen evolution reaction in alkaline medium Co_3O_4 [29, 98-103] and $NiCo_2O_4$ [29, 54, 102, 103] were the most widely used electrocatalysts. In acidic solutions OE is invariably followed by the dissolution of the spinel lattice [104]. Spinel type oxide materials are being synthesized now a days using various techniques which include co-precipitation of nitrates of corresponding metals [99] followed by thermal decompositions, freeze drying [105] and synthesis of catalysts on carriers such as dispersed carbon [106, 107] and nickel screen [99, 108]. For their application as electrocatalyst the various prepared oxide materials are transformed in the form of thin films on the conductive supports such as Ni, Ti, Pt, conducting glass etc. and generally dip-coating, sequential

solution coatings, oxide-slurry paintings spray pyrolysis, plasma-jet spraying methods have been employed to obtain the catalytic films. In some cases, the uses of conductive carriers as well as promoters [109] were also made. In order to obtain large specific surface area and better homogeneity, Co_3O_4 have been prepared following low temperature synthetic routes such as sol-gel [60, 110].

Singh et al [111-114] formed the thin films of Co_3O_4 and NiCo_2O_4 on glass / CdO, Titanium and Nickel by the spray pyrolysis method and sequential solution coatings method [114]. The sprayed films have found to be homogeneous and adherent and their electrical conductivities were many times higher than the similar films prepared by other methods. Films of NiCo_2O_4 electrocatalyst on glass / CdO support [111] showed a Tafel slope of 60 mVd^{-1} in 0.5-4 M KOH at 25°C , while on Ti support, $62\text{-}67 \text{ mVd}^{-1}$ in 1-3 M KOH and at higher concentrations of KOH value was 40 mVd^{-1} [112]. On Ni-substrate similar films by spray method [113] provide two Tafel slopes ~ 40 and $\sim 120 \text{ mVd}^{-1}$ at low and high over potentials, respectively. Electrocatalytic study shows that among all, the sprayed films on Ni-support were more active as compared to the films obtained on other supports. At Ni-support sprayed NiCo_2O_4 films reduced the oxygen overpotential by 150 mV compared to the pure Ni [115] at 100 mA cm^{-2} in 1 M KOH. For oxygen evolution reaction the film of Co_3O_4 on Ni, constructed by spray and solution coating methods [114] were also quite active. The electrochemically active area increases following by a constant value with increase in oxide loading. The electrocatalyst film of Co_3O_4 constructed by solution coatings was found to be more active than the sprayed one in 1 M KOH but in 30 wt. % KOH at 70°C , at the current density of 1 A cm^{-2} these electrodes produced approximately similar overpotential ($\eta_{\text{O}_2} = 402 \pm 5 \text{ mV}$). At low overpotential the tafel slope ranged over $51\text{-}58 \text{ mVd}^{-1}$ and at higher $120\text{-}140 \text{ mVd}^{-1}$. The reaction order for Co_3O_4 was found 'first order' with film prepared by solution coating technique while found 'second order' for sprayed with respect to

[OH]. On the basis of these parameters a suitable mechanism for the electrochemical reaction has been proposed for oxygen evolution.

Srinivasan et al [56] performed the electrode kinetic study for oxygen evolution first time on NiCo_2O_4 in strong basis medium at 80 °C. They observed a Tafel slope of 40 mVd^{-1} and on the basis of their analysis they suggested that a step following the first electron transfer step is the rate determining step. Jasem and Tseung [101] performed the analysis of the NiCo_2O_4 film electrode for oxygen evolution reaction. They found the Tafel slope of about 120 mVd^{-1} in 5 M KOH at 25 °C which is consistent with the discharge of OH⁻ ions being rate determining and is contrary to Srinivasan et al [56]. Efremov and Tarasevich [103] also observed similar Tafel slope value on NiCo_2O_4 .

Shalaginov et al [116] observed that how the synthesis temperature of Co_3O_4 film affects the Electrocatalytic activity for oxygen evolution reaction on Ti support and observed that the electrolytic activity of the film increased with decrease in the preparation temperature from 450 ° to 300 °C. They reported that electrocatalytic activity of Co_3O_4 electrode depends over structural defects of film material and attributed to the influence of structural defects on the electrocatalytic activity.

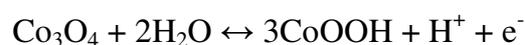
Orehotsky et al [117] studied $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($0.9 \leq x \leq 1.68$) film electrodes for oxygen evolution reaction and examined the influence of magnetic properties on oxygen evolution. They analyzed that for OER transfer coefficient was not depend on the room temperature saturation magnetism of the $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ spinel series. Iwakura et al [118, 119] also studied the similar ferrite film electrodes on Fe substrate with composition MFe_2O_4 (M = Mg, Cu, Ni, Co and Mn) and observed that at a fixed current density the oxygen overpotential linearly decreased with increase in effective Bohr magneton (μ_B) which is contrary to the experimental finding of Orehotsky et al [117]. Iwakura et al [120] studied the effect of substrate

material in oxygen evolution reaction, using Co_3O_4 film electrode on several conductive supports namely Ti, Co, Nb, Ta and Fe and found that the polarization characteristic of the Co_3O_4 film strongly influenced by the nature of the substrate material. The Electrocatalytic film electrodes on substrate Co, Ti, Ta and Ni exhibited the Tafel slope of $\sim 60 \text{ mVd}^{-1}$, while the film of same catalyst material on Fe substrate showed an average Tafel slope of $\sim 45 \text{ mVd}^{-1}$. They also analyzed the doping effect of Rh, Ir and Ru in the Co_3O_4 oxide film and found reduction in oxygen overpotential considerably. However, the value of anodic Tafel slope was not affected and remained practically constant ($\sim 45 \text{ mVd}^{-1}$). The low Tafel slope values were explained by a mechanism similar to that proposed by O'Grady et al [121] for OE on Ti / RuO_2 electrodes.

Nadesan and Tseung [98] and Rasiyah and Tseung [29] analyzed the Li-doped Teflon-bonded Co_3O_4 film electrodes for oxygen evolution and observed that the doping increases activity as well as conductivity of electrode substantially, however, the anodic Tafel slope was not affected for OE (60 mVd^{-1}). They explained the experimental data by considering a mechanism [29] involving the formation of higher valence oxides on the surface of oxide electrodes and also performed long term stability tests for NiCo_2O_4 and 10% Li-doped Co_3O_4 electrodes [122, 123] in 45% KOH at 80°C . Observation resulted current density of 1 A cm^{-2} at 1.60 (DHE) over a period of $\sim 6000 \text{ h}$ with only about 0.04 V increase in the oxygen overvoltage.

Trasatti et al [124] studied the effect of synthesis temperature, precursor and methodology and the nature of substrate material on the physicochemical surface properties of the Co_3O_4 film electrode. They constructed the film electrode by using spray and sequential solution coating methods to obtained Co_3O_4 in thick film form onto Ti and quartz plates. An aqueous solution of cobalt nitrate was used in spray method, while cobalt nitrate in isopropanol was used in sequential solution coating method. Along with explained films electrodes they also

synthesized Co_3O_4 in powder form by thermal decomposition method, for the purpose, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in air were used as precursors. Physicochemical studies (XRD, TGA and SEM) indicated the formation of a single spinel phase in the temperature range (250 °-700 °C) and observed that the oxide material synthesized by using cobalt nitrate precursor was found smaller in crystallite size than synthesized by using cobalt chloride. Further, the nature of substrate, as well as solvent also influenced morphology of the films. Coatings on quartz were appeared to be less rough than on Titanium. Film prepared by spray technique. exhibited cracks and were less adherent. On the other hand, the catalytic films obtained by coating of the precursor solution in alcohol were relatively compact, homogeneous and porous. Synthesis temperature also considerably influenced the morphology of the catalytic film. Further they observed [124] that the open-circuit potential (E_{OCP}) of the electrodes prepared at temperature between 200 ° and 700 °C indicated a break at about pH 5 in the E_{OCP} - pH curve at the point when the solution was changed from alkali to acidic. The Open circuit Potential (OCP) was not affected by calcination temperature up to a temperature of 500 °C. As the pH value of solution decreased from alkaline to pH 5 during this the OCP was observed to enhanced at the rate of about 60 mV per pH unit, the effect was explained by considering the surface equilibrium equation.



The electrocatalyst film synthesized by the sequential coating method gets equilibrated more rapidly than the sprayed ones. Trasatti et al [101] have prepared Co_3O_4 film electrodes also on Titanium support and in it a layer of RuO_2 was sandwiched and analyzed the formed electrode by cyclic voltammetry, Chronoamperometry and potential step experiments in alkaline solutions. Electrochemical analysis showed that the Co_3O_4 surface is reversibly oxidized and

reduced prior to onset of oxygen evolution due to the establishment of the following diffusion controlled surface reaction.



For the above reaction, the slope of the plot of linear peak potential vs. pH has been found ~ 80 mV per pH unit, this value is greater than the expected value of slope for the above reaction. The higher slope has been attributed to the formation of surface oxyanions. The sandwiched layer of RuO_2 between the Titanium substrate and the Co_3O_4 oxide prevents the formation of an insulating layer of TiO_2 . In the absence of sandwich layer of Ruthenium(IV) oxide the actual feature of the cyclic voltammogram of the Co_3O_4 film in KOH solution distorted due to the formation of the insulating TiO_2 layer at the $\text{Ti-Co}_3\text{O}_4$ interface during the oxide sintering process, which has already been demonstrated [125]. A spectroscopic investigation of Co_3O_4 deposited on Ti / RuO_2 revealed [126] that Ru penetrates the Co_3O_4 layer and approaches the surface but it does not reach the surface in the temperature range 200°C - 400°C . The Co(III) ratio on the surface has been increased by increasing the oxide annealing temperature.

Chartier et al [127, 128] used the non-conducting glass as substrate material and deposited the films of Co_3O_4 and NiCo_2O_4 with an interlayer of CdO by the method of spray hydrolysis at 400°C and performed the physicochemical analysis namely, XRD, SEM, Conductivity, roughness [127] and also electrochemical surface properties [128]. It has been found that the catalyst films were adherent, homogeneous and the electrical conductivity was $10^2 - 10^4$ times more than the similar films obtained by other methods. It have been reported by Trasatti et al [129] that they found the existence of the quasi - reversible Co (IV) / Co (III) redox couple on the cobaltite surface before the onset of O_2 evolution in 1 M KOH. However, on the NiCo_2O_4 electrode film surface Ni (III) / Ni (II) redox couple forms. Similar catalytic films on Ti-support were also synthesized by Singh

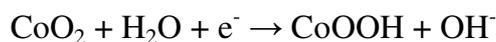
et al [112] and were found similar results of electrode kinetic study and cyclic voltammetry as those found for the sprayed film on glass/ CdO.

Rios et al [130] formed catalytic film electrodes of a series of manganese Cobalt spinel oxides of $Mn_XCo_{3-X}O_4$ ($0 \leq X \leq 1$) general formula using conductive glass (glass/ SnO_2) as substrate material at 150 °C and performed analysis of film electrode for electrocatalytic properties in alkaline medium. They found anodic tafel slope value in between 67-69 mV and the reaction order ranging from 1 to 1.2. It has been observed that the increase of content of Co by Mn in Co_3O_4 lattice decreased the electrocatalytic activity of the anode. Kinetic data were interpreted by a mechanism involving a Temkin type of electrosorption of OH^- followed by an electrochemical rate determining step.

Chialvo et al [131] studied the $Ni_XCo_{3-X}O_4$ ($0.6 \leq X \leq 1.3$) film electrodes for their electrocatalytic properties for oxygen evolution reaction in alkaline medium to establish a relationship between electrocatalytic activity and surface composition and / or the bulk oxide structure. To confirm the spinel structure above oxides were characterized by physicochemical techniques namely, XRD, IR, XPS and SEM. They observed that the oxide film electrode, with cobalt-nickel atomic surface ratio equal to two has the maximum catalytic activity.

Chartier et al prepared Co_3O_4 [60] and $NiCo_2O_4$ [108] through novel sol-gel technique using propionic acid as precursor. By this technique Co_3O_4 (at 280 °C) and $NiCo_2O_4$ (at 350 °C) spinel oxides were prepared in powder form. BET analysis showed the surface area as high as $29 \text{ m}^2\text{g}^{-1}$ and $46 \text{ m}^2\text{g}^{-1}$, for Co_3O_4 and $NiCo_2O_4$ respectively. The physiochemical characterization of the oxide was carried out by using IR, TGA-DTA, BET measurements, CV, XRD and SEM. To construct the electrode film a suspension of oxide in isopropanol were coated on conductive supports (graphite polyisobutylene and Ni-foil) followed by thermal treatment at 200 °C for 1 hr. it has been observed that the doping of Ni in Co_3O_4

lattice obtained at 300°C increased the roughness factor as well as apparent electrocatalytic activity at 0.7 V vs. Hg / HgO. Co₃O₄ oxide film electrodes on a Ni - substrate were also synthesized by Trasatti et al [132] using the similar method with slight modification and analyzed by physicochemical techniques (TGA, XRD and SEM) and electrochemical (open circuit potentials, CV). In Trasatti's method the Cobalt propionate gel was not treated with liquid N₂, but it was dissolved in ethanol and resulting solution was applied onto the support and then decomposed thermally in the temperature range 200 ° - 600 °C. Observation showed that the open circuit potential (E_{OCP}) first increased with a maximum at around 300 °C and then decreased. Cyclic voltammetric curve exhibited a pair of redox peaks prior to onset of oxygen evolution reaction, and influenced by any uncompensated ohmic drop [133] as well as by the reversibility of the surface redox reaction



Cu_xCo_{3-x}O₄ film electrodes on Ni and Ti substrates were synthesized by Marsen et al [134] using sequential solution coating at temperatures ranging between 250 ° and 400 °C. The electrocatalytic analysis of Cu_{0.9}Co_{2.1}O₄/ Ni film electrode prepared at 275 °C with the oxide loading 3.3 mg cm⁻² showed fairly low overpotential for oxygen evolution (η_{O₂} = 280 mV and 320 mV at 10 and 100 mA cm⁻²) and very high roughness factor (1400) in 1 M KOH. Further observation showed that higher oxide loading (> 3.3 mg cm⁻²) and higher sintering temperature (> 300 °C) creates detrimental effect on the oxide roughness as well as on the electrolytic activity. Fatih and Marsan [135] used a highly porous lanthanum phosphate bonded nickel support (LPBN) as substrate for the same copper-cobalt spinel electrocatalyst film electrode and analyzed for oxygen evolution reaction in alkaline solution. Film electrodes showed the highest electrocatalytic activity at a catalyst loading of 52 mg cm⁻². It has been found that the electrocatalytic activity

decreased when an excess of either Co or Cu was present in the spinel oxide film beyond the stoichiometric ratio of the precursors.

Bocca et al [136] prepared the Co_3O_4 and Li-doped Co_3O_4 electrocatalysts using different methods the form of a layer film on chemically pickled nickel plates, on observation they found two tafel slopes for oxygen evolution reaction in alkaline medium one at low and the other at high overpotential in 15 wt. % KOH at 60 °C. They also found that the catalytic efficiency of oxide material strongly depends upon the preparation method. The observed two tafel slopes were explained by considering a change in valence state of the oxide surface. Bocca et al [137] also prepared Ni-Co oxides using different techniques such as: oxalate and hydroxide Co-precipitation, evaporation freeze drying techniques and studied the OER on NiCo_2O_4 electrodes (Ni-substrate) in 15 wt. % NaOH solution at 60°C. The Teflon bonded electrocatalysts synthesized through oxalate and hydroxide Co-precipitation method showed remarkable activity towards oxygen reaction. It was also noticed that the galvanostatic ageing especially increased the electrochemical performance of the electrode obtained by the hydroxide Co-precipitation method.

Hamdani et al were synthesized Li-doped Co_3O_4 thin film electrodes by thermal decomposition [57] and spray pyrolysis at 300°C [138]. Electrocatalytic study of electrodes towards OE showed that the roughness and catalytic activity both have been increased with increasing Li - content (up to 3% Li) in the oxide. They observed value of tafel slope was $\sim 60 \text{ mVd}^{-1}$ and the order of reaction was 1.7 in OH^- concentration. Results have been explained by considering one electron transfer reaction in a quasi-equilibrium condition prior to a rate determining step which involves peroxide ion.

Svegl et al [49] were synthesized Co_3O_4 and Li doped Co_3O_4 thin films on Pt or ITO/ glass adopting sol-gel route using dip - coating technique and Co (II) sulphate as precursor. Stoichiometry study showed that in both pure and Li-doped

(upto 10 mol % of Li^+) Co_3O_4 film structure a deficiency of Cobalt (III) ions have been found. They also found that the film electrodes synthesized at low temperature ($300\text{ }^\circ\text{C}$) showed high surface area ($R_F \sim 700$). Values of the Tafel slope and reaction order with respect to the $[\text{OH}^-]$ were found to be $55\text{-}60\text{ mVd}^{-1}$ and ~ 1.2 , respectively

Singh et al [68] prepared spinel type pure and substituted Co_3O_4 oxides by n-butyl amine sol-gel route, Substitution of Cobalt in Co_3O_4 oxide material have been done from Copper and Nickel to get the derivatives products. Observation showed that the substitution of Cu or Ni in the Co_3O_4 lattice improved both oxide roughness as well as electrocatalytic activity. However, Mn-substitution showed detrimental effect on electrocatalytic properties. Singh et al [139] also synthesized the Cu, Ni and Mn substituted cobalties using hydroxide precipitation method and investigated their electrocatalytic properties. Analysis showed that the substitution of 0.5-1.0 mol Cu/or Ni in the base oxide increased the oxide roughness as well as apparent electrocatalytic activity greatly. The R_f value was found to be the highest ($R_f = 2382$) and the lowest ($R_f = 63$) with 0.5 mol Ni substitution and base oxide, respectively. Regardless to the nature and the ratio of foreign metal has been substituted in base oxide, the value of tafel slope and the order of reaction were found similar for each oxide electrocatalyst for OER.

Tavares et al [140] have synthesized the $\text{NiCo}_{2-x}\text{Rh}_x\text{O}_4$ ($0 \leq X \leq 0.5$), $\text{Ni}_{1-x}\text{Cu}_x\text{Co}_2\text{O}_4$ and $\text{NiCo}_{2-x}\text{Cu}_x\text{O}_4$ [141, 142] catalytic oxide film electrodes on Ni mesh, for the purpose aqueous solution of mixed metal nitrates were coated on Ni mesh followed by thermal decomposition at 350 ° and $500\text{ }^\circ\text{C}$, respectively. Study showed that initial tafel slope have been found similar ($46\text{-}48\text{ mVd}^{-1}$) for oxygen evolution for each electrode film in 5 M KOH. The presence of Rhodium in the Ni-Co oxide spinel for $X \leq 0.25$ improved significantly the performance of electrodes towards oxygen evolution. They also have been found that the substitution of nickel and cobalt by Cu (II) ions in the NiCo_2O_4 spinel lattice

produced significant notifications in the electrode surface composition and activity.

Pereira et al [143] were synthesized Co_3O_4 and $\text{Co}_{2.9}\text{Rh}_{0.1}\text{O}_4$ electrocatalytic film electrodes on Ni-support and $\text{Co}_{2.4}\text{Rh}_{0.05}\text{O}_4$ [144] on Ti-support by solution technique, for the purpose they coated the aqueous solution of mixed metal nitrates followed by thermal decomposition at 400°C . They observed that two Tafel slopes ($48\text{-}51 \text{ mVd}^{-1}$) and ($144\text{-}180 \text{ mVd}^{-1}$) for OER on the catalytic films in 5 M KOH. They found that the electrocatalytic activity towards OER increased by the presence of small amount of Rh in Co_3O_4 spinel coating, because of Rh in the spinel structure influence the oxide surface morphology and the electrical resistance of the substrate coating interface.

Co_3O_4 oxide powder has been also synthesized by Cannas et al [145] via sol-gel auto combustion method. During quasi-steady state current potential process they observed two distinguishable tafel slopes at low and high overpotentials. The observed value of tafel slope at high overpotential was $\sim 190 \text{ mVd}^{-1}$ while lower tafel slope are reported in the literature [57, 114, 135] for oxygen evolution reaction at cobalt oxide film electrodes in alkaline medium.

The effect of synthesis temperature on the electrocatalytic properties of NiCo_2O_4 oxide material have been analyzed by Chi et al [146]. They prepared the oxide using hydroxide Co-precipitation method and were characterized by TGA, XRD, BET, SEM, EDS, cyclic voltammetry, Tafel curves and stability test. They observed that the preparation temperature significantly affects the electrocatalytic properties of NiCo_2O_4 oxide catalyst. With increase in preparation temperature it has found that the BET surface area and surface roughness factor of electrodes decreased with increase in temperature, whereas the crystallinity of oxide increased. NiCo_2O_4 prepared at 300°C showed better electrocatalytic activity ($j = 201.2 \text{ mA cm}^{-2}$ at $E = 700 \text{ mV vs. SCE}$) in 1M KOH than those prepared & at

other temperatures. They also synthesized ZnCo_2O_4 [147] and $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ [148] film electrodes on Ni-support using electrophoretic deposition and coating technique. Electrocatalytic analysis showed that for oxygen evolution reaction the value of Tafel slope was found to be $\sim 70 \text{ mVd}^{-1}$ in 1 M KOH. Also the performance of electrode towards OER improved significantly by the substitution of 0.9 mol Copper in the oxide matrix.

Mondonca et al [149] synthesized $\text{CoFe}_{2-x}\text{Mn}_x\text{O}_4$ ($0.0 \leq X \leq 2.0$) and $\text{CoFe}_{2-x}\text{Ni}_x\text{O}_4$ ($0.0 \leq X \leq 1.8$) oxides using standard ceramic powder method. Physicochemical characterization of the solid oxide material showed that the iron is more easily substituted by Mn than by Ni and that the cubic phase was maintained till 60% of Mn substitution in base oxide while a two phase system was found with Ni substitution $>15\%$. The substitution of Ni in $\text{CoFe}_{2-x}\text{M}_x\text{O}_4$ increased activity of electrode more than that was produced by Mn substitution. Godinho et al [150] also prepared partially Ni and Mn-substituted CoFe_2O_4 by adopting similar method and found similar electrocatalytic activity.

Palmas et al [151, 152] were synthesized Co_3O_4 oxide by adopting sol gel auto combustion method. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid, respectively were used as source of metal ions and chelating fuel agent. Teflon suspension in water has been used as binder to transform the powdered oxide material into film on Titanium support. The formed film electrode was studied for oxygen evolution reaction in alkaline medium analysis involved cyclic voltammetry, impedance spectroscopy and Tafel polarization techniques. Cyclic voltammetric analysis showed different redox transitions during the oxidative process leading to Co(III) and Co(IV) containing phases which constituted specific sites for OER. The impedance data have also been used to estimate the kinetic parameters, Tafel slope (115 mVd^{-1}) and exchange current density ($3 \times 10^{-5} \text{ A cm}^{-2}$). The steady state polarization produced the higher Tafel slope $\sim 185 \text{ mVd}^{-1}$. They have studied oxygen evolution reaction at Teflon bonded $\text{Ti}/\text{Co}_3\text{O}_4$ electrode [153] through impedance

spectroscopy. Also an equivalent circuit fitting method and mathematical model based on the Faradic impedance of the reacting system have been used to simulate the experimental data. The correlation between the auxiliary electrochemical parameters and the elements of the equivalent circuit was derived and the lumped kinetic parameters of the different steps involved during oxygen evolution were evaluated. The method was validated by comparing experimental and model predicted data.

Singh et al [73, 74] prepared substituted $M_xFe_{3-x}O_4$ ($M = Mn$ and Ni , $0 \leq X \leq 1.5$) ferrites using a precipitation method and transformed powdered oxide into film electrode by adopting oxide slurry painting technique ($T = 380\text{ }^\circ\text{C}$) on Ni-substrate. Observation showed that the oxide roughness as well as the apparent electrocatalytic activity both have increased by the doping of Mn and Ni in Fe_3O_4 lattice. The optimum value of the apparent electrocatalytic activity strongly affected by the nature of metal doped oxide. For instance, at 100 mA cm^{-2} in 1 M KOH at $25\text{ }^\circ\text{C}$, Fe_3O_4 , $MnFe_2O_4$, $NiFe_2O_4$ and $CoFe_2O_4$ obtained by this method produced the oxygen over potential 524 , 338 , 379 and 395 mV , respectively. Further, they also partially substituted Cr or Fe in $CoFe_2O_4$ [72], $NiFe_2O_4$ [75], $MnFe_2O_4$ [76] to improve the electrocatalytic activity. Observation showed that electrocatalytic activity of the oxide enhance greatly by the partial substitution of Cr. Among Cr-substituted ferrites, $NiFeCrO_4$ produced the greatest electrocatalytic activity. Singh et al [154] synthesized nano sized ternary ferrites $CuFe_{2-x}Cr_xO_4$ ($0 \leq X \leq 1$) by adopting a precipitation method and analyzed for its electrocatalytic activity in the form of film electrodes for oxygen evolution reaction in 1 M KOH at $25\text{ }^\circ\text{C}$. Analysis has found two Tafel slopes $50\text{-}77\text{ mV}$ at low and $80\text{-}120\text{ mV}$ at higher potentials. The reaction order w.r.t $[OH^-]$ was found to be 1. It has been found that the substitution of Fe by Cr in the $CuFe_2O_4$ matrix improved both geometrical and electronic properties of the substituted products. Using microwave assisted synthesis Singh et al [155] also prepared pure and La-

doped Co_3O_4 spinel oxides. Electrocatalytic characterization was carried out in 1 mol dm^{-3} KOH at 25°C . They observed that the pure Co_3O_4 oxide film electrode (oxide loading $3.4 \pm 0.3 \text{ mg cm}^{-2}$ on Ni) and La doped Co_3O_4 oxide film electrode (oxide loading $2.8 \pm 0.4 \text{ mg cm}^{-2}$ on Ni) produced very low potentials, 235 ± 7 and $224 \pm 8 \text{ mV}$, respectively. X-Ray Diffraction study of powdered oxides denotes that both pure and lanthanum doped cobaltites crystallized in a single phase regardless of La – substitution.

Singh et al. also formulated iron [156], Nickel [157] and cobalt [158] molybdates by applying precipitation method and studied their physicochemical and electrocatalytic properties. Among all oxide film electrodes the iron molybdate with Mo/ Fe = 1.0 ratio exhibited the maximum catalytic activity towards the oxygen evolution in alkaline medium. At a constant current density of 100 mA cm^{-2} , the oxide electrode produced $E = 674$ (Mo/ Fe = 1.5), 678 (Mo/ Fe = 3.0), 790 (NiMoO_4) and 731 mV (CoMoO_4) in 1 M KOH at 25°C .

Laouini et al prepared Fe- Co_3O_4 (Fe = 0.5 and 10%) [159] and Co_3O_4 [160] coated film electrodes by using thermal decomposition technique on stainless steel substrate. Electrochemical study of the film electrodes involved cyclic voltammetry and impedance spectroscopy 1 M KOH solution. Analysis of cyclic voltamogram shows that prior to onset of oxygen evolution; the catalytic film is reversibly oxidized and reduced due to the establishment of $\text{Co}^{4+}/\text{Co}^{3+}$ redox couple. A high tafel slope value $\sim 156 \text{ mV}$ was found with Co_3O_4 film while Fe substituted Co_3O_4 film exhibited tafel slope of only $45\text{-}70 \text{ mV}$. Study showed that doping of Fe in Co_3O_4 oxide matrix enhanced the electrocatalytic activity of cobaltites.

Anindita et al [161] prepared spinel type ternary oxides of theoretical formula $\text{NiFe}_{2-x}\text{V}_x\text{O}_4$ ($0 \leq X \leq 1$) via hydroxide precipitation method. The formed oxide materials were transformed as film electrodes and studied towards oxygen

evolution reaction in alkaline medium. They have been found that the substitution of Vanadium from 0.25 to 1.0 mol in place of Iron in spinel oxide matrix greatly enhance the electrocatalytic activity of oxide materials and found maximum for 0.5 mol Vanadium substitution. The polarization curve showed two Tafel slopes, 35-40 mVd^{-1} at low and 65-73 mVd^{-1} at higher potentials. However, the Tafel slopes for base oxide (NiFe_2O_4) were observed $\sim 75 \text{ mVd}^{-1}$ and $\sim 100 \text{ mVd}^{-1}$ respectively at low and high potentials. Electrode kinetic study showed that the order of reaction was found ~ 1 for base oxides and ~ 2 for substituted products with respect to the hydroxide ion concentration. XRD data showed that $\text{NiFe}_{2-x}\text{V}_x\text{O}_4$ ($0 \leq X \leq 1$) oxides crystallized in almost a single phase.

Jingshu et al [162] reported $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq X \leq 1.5$) spinel oxides, they synthesized materials by using thermal decomposition method and for electrochemical study transformed the powdered oxide materials in the form of thin film electrodes on Titanium support and analyzed towards oxygen evolution reaction in 1 M KOH solution at 35 °C. Observation showed that the electrocatalyst with $x = 0.3$ showed highest activity. By the analysis of cyclic voltammograms of Ti/ $\text{Cu}_{0.3}\text{Co}_{2.7}\text{O}_4$ they have been found that there exist one anodic and two cathodic peaks before commencement of oxygen evolution.

Bangan et al [163] reported the study of nanowire arrays of mixed oxides of Ni and Co ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ with Ni : Co ratio 0: 1, 1: 1, 1: 4, 2: 3, 3: 2 and 4: 1) freely standing on Ni foam, synthesized by using template free growth method. It have been observed that among all prepared oxide electrocatalysts, electrode which was obtained by taking 1:1 molar ratio of Ni and Co in the preparation solution exhibits the highest catalytic activity and a good stability towards oxygen evolution reaction in aqueous sodium hydroxide solution. The observed order of reaction for $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ electrodes with respect to hydroxide ion concentration was close to 2 and 1 at low and high overpotential, respectively.

Spinel type mixed oxides of theoretical formula $\text{Ru}_{0.3}\text{Co}_{0.7-x}\text{Ce}_x$ ($0 \leq X \leq 0.7$) have been synthesized and characterized by Hongjun et al [164]. They have used sol-gel technique to prepare the oxide catalysts. Electrochemical characterization was carried out in 1.0 mol dm^{-3} KOH at room temperature. They observed that Tafel plots exhibit two linear regions for each analyzed electrode. At low overpotential, Tafel slope was observed at about 50 mV whereas at high overpotential, Tafel slope was observed at about 120 mV. The order of reaction with respect to the hydroxide ion concentration was found to be 1 at both overpotential. XRD data showed well defined Ti peaks for all the investigated samples. Rutile RuO_2 and spinel Co_3O_4 phases were also detected. Different values of the crystallographic parameters between RuO_2 rutile and Co_3O_4 spinel structures refers to a low probability of forming a solid solution.

Zhang et al [165] have recently synthesized the Cu substituted cobalt oxides with Co/Cu ratio from 0.5 to 3.4 by adopting reacting magnetron sputtering technique and transformed in the form of thin film electrodes on Ti substrate. The SEM images indicated that the Cu-doping not only made the grain size reduced, but also favored the formation of the fine grain. XRD data did not show any peaks of CuO phase due to its too small size, even when the copper content exceeded the stoichiometric amount of Cu in the CuCo_2O_4 spinel. However, the UV absorption was also observed by them that catalytic activity of Cu-Co oxide electrodes changed with Cu-content. The Cu-rich Cu_2CoO_4 with segregated CuO phase showed better performance for the OER than that of the spinel Cu-Co oxide, indicating the CuO phase may be homogeneously distributed in the oxide bulk resulting in an enhanced active surface area.

Recently, spinel type oxides of theoretical formula $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.0$) were synthesized by Al-Mayouf et al [166] using hydrothermal method and transformed the powdered oxide material in to film on Ni-support by using an oxide slurry painting technique. They analyzed the film electrodes using

physicochemical technique namely, SEM, IR, XRD and electrochemical characterization was carried out by cyclic voltammetry, Tafel polarisation curves study and EIS. In spite of doping of Ni in base oxide matrix the Tafel slope value was observed to be $41 \pm 6 \text{ mVd}^{-1}$ for each electrocatalysts and the order of reaction was found ~ 2 for oxygen evolution reaction.

1.2.2 Oxygen evolution on perovskite type oxides

Perovskite are the compounds having general formula ABO_3 , where 'A' is a large sized cation typically lanthanide or alkaline earth metal and can be monovalent, bivalent or trivalent while 'B' is a transition metal cation. The name perovskite comes from a naturally occurring mineral perovskite, CaTiO_3 . The CaTiO_3 has cubic structure and each unit cell contains calcium ions at the corners of the cube and Titanium ions at the body centre and oxygen ions at the centre of the face. Later it was observed that the CaTiO_3 follow the orthorhombic structure [167], but the simple cubic structure has retained the name perovskite. Through years it has been observed that very few perovskite oxides have simple cubic structure at the room temperature, but many assumed this ideal structure at higher temperatures. Goldschmidt has shown that the cubic perovskite structure is stable [168] only if the tolerance factor 't' defined by $R_A + R_B = t \sqrt{2} (R_B + R_O)$, has an approximate value in the range of $0.8 < t < 0.9$, and the distorted perovskite structure would otherwise result. R_A , R_B , and R_O are the ionic radii of A, B and O elements. The ABO_3 composition can be modified, in many cases, by partial substitution of either A ion with another similar type of A' to give $\text{A}_{1-x}\text{A}'\text{BO}_3$ or B ion with another similar type B' to give $\text{AB}_{1-x}\text{B}'\text{O}_3$. The substitution modifies the composition as well as the physical properties such as resistivity and magnetism of the oxides. The changes in these properties may considerably influence their chemical and electrochemical interfacial properties. There are large number of perovskite compounds, but, to our knowledge, only those compounds in which

cation A is a lanthanide element and B is a transition metal cation (B = Ni, Co, Sr, Mn etc.) have been used in electrocatalysis of oxygen evolution or reduction.

Generally perovskite type oxides were prepared by high temperature thermal decomposition of a mixture of metal salts taken in stoichiometric ratio [169] or solid state reaction of approximate oxides [170]. In order to improve homogeneity and specific surface area, oxides were also synthesized by the modified thermal decomposition such as freeze-drying [171-172] precipitation [173], plasma jet spraying [174], electrodeposition [175-178] etc. Recently some novel low temperature methods based on knowledge of solution chemistry such as solid hydroxide solution precursor [179], sol-gel [180-182] etc. have also been reported to produce highly dispersed oxide powders. These new low temperature methods generally produced oxide with relatively more homogenous oxides.

Electrocatalysis of oxygen evolution

The perovskite type oxide as oxygen electrode materials was first commenced since the beginning of 1970. The activity of LaCoO_3 was first reported by Meadcroft [183] comparable to that of platinum in relation to oxygen reduction reaction (ORR) in concentrated KOH solution. However, systematic investigation of oxygen evolution reaction on perovskite oxide NiM_2O_4 (M = La, Pr and Nd) [184] as well as Ni and Co and La mixed oxide in base [185-186] was carried out first by Fiori et al. They observed that the electrocatalytic activity of oxide was little influenced by the replacement of M with La, Pr, and Nd. The Tafel slopes, 40 mv at low and 120 mV at high overpotentials were found with each oxide electrode. The oxide electrode of La with Co and Ni were found to be much active. The electrocatalytic activity towards OER were maximum with $\text{Ni}_{0.2}\text{Co}_{0.8}\text{LaO}_3$ [187]. Some deterioration of the oxide catalyst was noticed due to the La dissolution [188] under long term anodic polarization test. In these studies,

oxides were used in the form of pellets. Fiori et al. [189] also observed that the oxide in the form of thin film showed good electrocatalytic activity.

Matsumoto et. al. studied the kinetics of OER on a number of substituted perovskite oxides such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.1 \leq x \leq 0.4$) [190], $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.2, 0.4$), $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ ($0 \leq x \leq 1, 0 \leq y \leq 1$) [191] and $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ ($0 \leq x \leq 1, 0 \leq y \leq 1$) [192] in alkaline solutions. The oxide were prepared by high temperature solid state reactions and they were used in the form of compressed tablets. Their studies indicated that the activity of electrodes generally increases with increase in the degree of substitution in the oxides. They explained the kinetic results by considering the mechanism similar to that already proposed by Krasil'shchikov [193]. Depending upon the value of Tafel slope and the reaction order observed for oxygen evolution on different catalysts, the different rate controlling steps have been chosen. Later in 1985, Matsumoto and Sato [194] carried out an exhaustive investigation on the effect of multiple metal cation substitutions at the B-site of the oxide in which $A = \text{La, Sr}$ and $B = \text{Ti, V, Cr, Mn, Fe, Co, Cu}$ and Zn . Based on electrochemical measurements and lattice constant values, it was concluded that the cationic valencies at the B-site exists as M^{3+} for all the cations in LaMO_3 and that Mn exists as Mn^{5+} in $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$. These results are helpful to determine the cationic valence distribution at B-site of various perovskite oxides.

Kobussen and Mesteres [195] prepared $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ and studied detailed kinetic parameters of oxygen evolution in strongly alkaline medium. The electrode was prepared by mixing the stoichiometric amount of La_2O_3 (pre-fired at 200°C for 4h), BaCO_3 and $\text{Co}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ and pressing pellets followed by sintering in air or pure oxygen at $1100\text{-}1200^\circ\text{C}$. The reaction on this electrode showed a Tafel slope of $\sim 60\text{mV}$ and reaction order as unity in hydroxide ion concentration. Based on studies of electrode kinetics [190], impedance

measurement [195-196] and overpotential decay behavior [191], they suggested a modification over Krasil'schikov's mechanism [193] for OER.

Bockris and Otagawa [79,82,83] and Bockris and co workers [198] carried out an exhaustive study on OER on different perovskites in the form of pellet. They used high temperature solid- reactions [79, 83, 198] and hydroxide coprecipitation method [82] to prepare the perovskite oxides. They observed that the electrochemically active area of the oxide electrode prepared by hydroxide coprecipitation method was more than seven times higher than that of the same oxide obtained by high temperature solid oxide reaction. The LaNiO_3 prepared by coprecipitation technique, a low Tafel slope of 40 mV is observed in 1 M KOH at 25°C while that with the same and other perovskite oxides (LaCoO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, LaMnO_3 , $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) obtained by other methods, observed higher tafel slopes, ~ 60mV at low and 120-130 mV at high overpotentials and a first order kinetics in hydroxide ion concentration. The electrocatalytic activity of LaNiO_3 electrode obtained by coprecipitation was very high. The oxygen overpotential being only 30 mV at 100 mAcm^{-2} in 1 M KOH at 25°C. they explain the experimental findings by considering a mechanism [83] which involves the electrochemical adsorption of hydroxide ion as fast as subsequent interaction of the resulting intermediate with another hydroxide ion followed by the formation of hydrogen peroxide as intermediate as a slow step.

Wendt et al. [199, 200, 201] prepared mixed oxides of La with Co/ or Ni on the perforated Ni electrode using various methods such as painting, thermal decomposition/sintering and plasma jet spraying and studied their electrocatalytic properties in 50 wt% KOH at different temperatures (30-160°C). in 200 h continuous testing at a current density of 1 Acm^{-2} at 90°C, both $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and $\text{Ni}_{0.2}\text{Co}_{0.8}\text{LaO}_3$ electrodes produced oxygen overpotential of 330 mV. They observed that the anode activation by Raney-metals reduced the overpotential at low and high current densities by ~ 40mV at 90°C, while the activated oxide

coating reduced the oxygen overpotential by 80 – 100 mV were found to be independent of temperature. The activation energy for oxygen evolution on these oxides was ranged between 40-70kJ mol⁻¹.

Balej [202] has also tested the electrocatalytic activity of various mixed oxide anode of both spinel and perovskite families in 10 M KOH at 100°C and found similar order of activities as reported by wendt and Plzak [199], Rasiyah and Tseung [203], Davison et al. [204], Vandenborre et al. [205] and Fiori et al. [186] for similar oxide electrodes. The mixed oxide electrodes were either prepared from ready made mixed oxides or produced in the form of thin films on Ni by painting or thermal decomposition. The oxygen overpotential on most of the mixed oxide films (2-10 mg cm⁻²) on a compact Ni base was found to be ~ 40-80 mV higher than those on similar films on a Raney Nickel. This difference was reduced to ~ 10-40 mV by using sintered Ni base.

The use of La_{0.8}Sr_{0.2}Ni_{0.2}Co_{0.8}O₃ as anode in alkaline solution was investigated by Varneiren et al. [206]. Based on the electrode kinetic parameters (tafel slope = 2RT/3F, order = 1), two possible reaction mechanism have been proposed. The stability of the electrode was also explained for its application in water electrolysis cells.

A number of perovskite related ferrites have also been intensively studied from the point of view of structural and physical properties [207-2010], in relation to electrocatalytic ones [82, 83, 180, 211-213]. The non-stoichiometric strontium lanthanum ferrites, La_{1-x}Sr_xFeO_{3-y}, containing iron with mixed valencies (Fe³⁺/Fe⁴⁺) and anions were observed [212, 214, 215] to be the most active anode materials. In earlier results, several authors have already the oxygen non-stoichiometry and defects to be of great importance with regards to oxygen evolution [83, 213, 214, 216]. Wattiaux et al. [217, 218] have studied the electrocatalytic properties of La_{1-x}Sr_xFe³⁺_{1-τ}Fe_τO_{3-y} (0 ≤ x ≤ 0.5) in the form of disk

electrode in alkaline medium. Results showed that the maximum catalytic activity was found with $x = 0.90$; at this composition, value of the $\text{Fe}^{3+}/\text{Fe}^{4+}$ ratio was the highest ($\tau = 0.68$). the exchange current density values (10^{-9} - 10^{-3} Acm^{-2}), at low and high overpotentials, were observed to be lower than those previously reported by others [83, 191]. Low j_0 values were ascribed to the lower oxide roughness factors (200-300). At low overpotential, the Tafel slope and the reaction order values with respect to OH^- concentration were 66-95 mV and 1, respectively. A seven step mechanism, in which Fe^{4+} being the active site, has been proposed involving the variation of both coordination and oxidation state of iron. Attempts were also made [216] to correlate the bulk properties of the oxide with the observed electrocatalytic activity. The effect of bulk structure on the electrocatalysis of oxygen evolution on perovskite (SrFeO_3) oxides were also investigated by Carbonio et al. [219]. A mechanistic consideration based on molecular orbital theory was also given [220]. Recently, Tejuca et al. [221] have comprehensively reviewed the structure and reactivity of perovskite type oxides in catalysis and electrocatalysis.

Some perovskite type oxides were also tested (i.e. both for oxygen evolution and reduction for their use in rechargeable metal-air battery system) [222-224]. These oxides were generally PTFE-bonded carbon [222, 223] or graphitized carbon [224] loaded with large surface area perovskite oxide such as $\text{La}_{1-x}\text{Ca}_x\text{MO}_3$ ($\text{M} = \text{Co}, \text{Mn}$) [204], $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.8}\text{B}'_{0.2}\text{O}_3$ ($\text{B} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) [224] and $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ [224]. These electrodes were synthesized by amorphous citrate [222-224] or malic acid [224] precursor method. The result showed that [220] Mn-based perovskite oxides were less active than the other oxides for OE. The electrodes loaded with $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ (1 Acm^{-2} at 700 mV vs. Hg/HgO in 30wt% KOH at 25°C) [221] and $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (300 mAcm^{-2} at 620 mV vs. Hg/HgO in 7 M KOH at 25°C) [223] produced the higher electrocatalytic activity for OE. The Tafel slope values were found to be $\sim 60\text{mv}$

at low and ~ 150 mV at high current densities. Based on these electrode kinetic results, a reaction mechanism for OE similar to Bockris's oxide path [79] was also proposed on these oxide electrodes.

El Baydi et al. [131] obtained high surface area, mixed oxide powders of LaNiO_3 via sol gel route using propionic acid (PA) malic acid (MA) as precursor and studied their physicochemical and electrochemical properties oxygen evolution in KOH solution. The LaNiO_3 electrode prepared by malic acid method was in pellet form while the electrode obtained by propionic acid method was produced in the film form by painting a suspension of oxide powder in isopropanol on to a conductive support (Ni or polyethylene) followed by thermal treatment. They carried out detailed physicochemical characterization of the oxide. Morphology of the catalyst catalyst powders obtained by both methods was quite different. LaNiO_3 obtained by propionic acid method showed numerous well defined monodispersed crystal of $0.2 \mu\text{m}$, whereas LaNiO_3 obtained by malic acid method exhibited a texture of micro crystals which were intimately imbricated. The apparent electrocatalytic activity of propionic acid derived LaNiO_3 ($j = 24 \text{ mAcm}^{-2}$ at $E = 0.7 \text{ V}$) in 1 M KOH was lower than one derived by malic acid ($j = 27 \text{ mAcm}^{-2}$ at $E = 0.7 \text{ V}$) [132].

Lippert et al. [225] obtained thin film of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_{3-\delta}$, on MgO by variation of pulsed layer deposition and used them as catalysts for oxygen reduction and evolution in re-chargeable Zn/air batteries. The film composition with the higher oxygen content was characterized as an electrocatalyst for oxygen reduction and evolution reactions.

Brusel et al. [226] synthesized $\text{La}_{0.1}\text{Ca}_{0.9}\text{MnO}_3$ (by precipitation method), $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ and LaNiO_3 (by drip pyrolysis) and investigated their physicochemical (TEM, BET) and electrochemical (CV, Tafel) properties for oxygen reduction and evolution in 6 M KOH . TEM micrographs were composed

by crystalline network-like structure with particle size ranging between 30-160 nm and BET surface area between 12 and 35 m²g⁻¹. The tafel slopes and apperent activation energies for respective catalysts were 123 & 17.5 for La_{0.6}Ca_{0.4}CoO₃, 122 & 17.3 for La_{0.1}Ca_{0.9}MnO₃ and 125 mV and 19.1 kCal mol⁻¹ for LaNiO₃.

Kahoul et al. [227] prepared La_{1-x}Ca_xCoO₃ (x = 0, 0.2, 0.4 & 0.6) by amorphous citrate method. Their study indicated the optimum electrode activity and stability of the electrode with x = 0.4. Using similar amorphous citrate precursor method. Wu et al. [228] also synthesized La_{0.6}Ca_{0.4}CoO₃. the oxides were annealed at temperature decending from 800-100°C. the study showed that the catalytic activities of the oxides towards oxygen reduction and evolution were influenced by two mechanisms. Annealing above 300°C showed an increase in oxygen content and concurrently a decrease in the activities. On the other hand, annealing below 300°C led to maximum activities, which likely results from changes in the surface chemistry/structure.

Singh et al. [82, 229, 230] synthesized La_{1-x}Sr_xCoO₃ (0 ≤ x ≤ 0.5) by three different non-conventional precursor routes such a malic acid (MA) [229], hydroxide solid solution (HSS) [230] and polyacrylic acid (PAA) [84]. They obtained the electrodes in the form of Ni (or Pt) by the oxide slurry painting technique. The cyclic voltammetric curves recorded on the catalytic films did not indicate any oxidation-reduction of the surface films prior to the oxygen evolution in 1 M KOH. Values of the Tafel slope were ranged between 59 to 72 mV. In each preparative method, 0.2 mol Sr substitution, was found to be the most active from electrocatalysis stand point. The order of reaction with respect to the hydroxide ion concentration was observed to be ~ 1, regardless to the method of preparation. In the case of MA precursor method, the influence of partial replacement of Co by some transition metal ion in the active La_{0.8}Sr_{0.2}CoO₃ lattice enhanced the electrochemically active area as well as electrocatalytic activity significantly. In contrast, the Cu or Cr substitution has detrimental effects on the electrocatalytic

activity. Following similar precursors they also prepared lanthanum nickelate and investigated the electrocatalytic properties towards oxygen evolution in alkaline solution [231-234, 38]. Additionally, the lanthanum nickelate films were also obtained by spray pyrolysis and sequential solution coating methods using an aqueous solution of mixed metal nitrates. SEM micrographs of the catalytic films showed that the morphology of the oxide film is strongly influenced by the preparation method and also on the nature of support used. The roughness of the LaNiO_3 film was also markedly influenced by the methodology adopted in the catalyst preparation. Value of roughness factor (R_F) as determined by cyclic voltammetry, was minimum with sprayed- LaNiO_3 film ($R_F = 170$) and the highest with the film obtained by the HSS method ($R_F = 1820$). With the exception of the sprayed LaNiO_3 film ($b = 45 \text{ mV}$, $p = 2.2$), all other catalytic films of LaNiO_3 had approximately the same Tafel slope ($b = -73 \text{ mV}$) and the reaction order with respect to the hydroxide ion concentration ($p = 1$). Based on apparent current values at $E = 0.74 \text{ V}$ vs. Hg/HGO in 1 M KOH at 25°C , the electrocatalytic activity of the electrode prepared by PPA method was the highest ($j = 150 \text{ mAcm}^{-2}$, $R_F = 1025$). Substitution of 0.25 mol Fe for Ni in the LaNiO_3 lattice obtained by HSS method reduced the oxygen overpotential. The electrodes prepared by these nonconventional routes were also observed to be quite stable (30 wt\% KOH) under galvanostatic static polarization condition (i.e. 0.05 or 0.1 Acm^{-2}) for a period of over 50 h of the investigation.

Singh et al. [235] also investigated pure and Sr-doped lanthanum managanites synthesized by HSS method at 500°C . The oxides were produced in the film form on Ni ny slurry painting. It was observed that the roughness factor as well as the electrocatalytic activity increased with the increase in the degree of Sr-substitution for La in the LaMnO_3 lattice, the values being the greatest with 0.4 mol Sr -substitution. The OER followed approximately first order kinetics in

hydroxide ion concentration. The Tafel slope value were ranged between 90-140 mV.

Similar Sr-substituted LaMnO_3 oxides were also obtained by different sol gel routes such as malic acid [236], citric acid [237] and polyacrylic acid [238]. The PPA method appeared to be advantageous over the other two methods (MA and CA) from electrolysis stand-point as it produced LaMnO_3 with the highest electrocatalytic activity. It was noted that in the case of the oxide derived from CA and PAA, the Sr-substitution for La in the perovskite lattice did not influence the electrochemically active area significantly, in contrast, it influenced greatly in the case of catalyst obtained by the MA method. Value of the electrode kinetics parameters (Tafel slope and reaction order) for the OER in 1 M KOH were approximately the same with the pure as well as the Sr-substituted LaMnO_3 and were almost independent of the nature of the precursor used in the preparations. The apparent electrocatalytic activity of these new manganite catalysts were much higher than those obtained by ceramic method [79, 190]. Singh et al. [239] also, prepared lanthanum nickelate and its substituted products by the malic acid precursor route and investigated the electrocatalytic properties towards oxygen evolution reaction in alkaline solution. They obtained that the substitution of Fe, Co or Cu (0.05-0.5 mol) for Ni in LaNiO_3 lattice had practically no effect on the roughness, current density and reaction mechanism of the OER.

Recently, Lal et al. [240] prepared $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 \leq x \leq 0.4$) by stearic acid sol-gel method and studied their physicochemical (IR, XRD, SEM) and electrochemical (impedance, steady-state anodic polarization) properties. The oxide roughness factor and the apparent electrocatalytic activity of the Sr substituted lanthanum cobaltates were more or less similar to Sr-substituted lanthanum manganite prepared by malic acid and polyacrylic acid sol-gel route.

1.3 Mechanism of oxygen evolution

In order to explain the results of electrode kinetic studies for oxygen evolution reaction on different electrocatalysts in alkaline medium, several mechanism have been reported in the literatures [32, 84, 241-243]. A few of them which are considered in most of the publications is given in table 1.3.1:

Table: 1.3.1

Mechanism	Langmuir adsorption condition ($\theta \ll 1$)		Temkin adsorption condition ($0.2 < \theta < 0.8$)	
	b / mV	p	b / mV	p
1. Bockris's peroxide path: $S + OH^- \rightarrow SOH + e^-$ $SOH + OH^- \rightarrow S \dots H_2O_2 + e^-$	2RT/F 2RT/3F	1 1	- 2RT/F	- 1
2. Bockris oxide path: $S + OH^- \rightarrow SOH + e^-$ $2SOH \rightarrow SO + e^-$ $2SO \rightarrow 2S + O_2$	2RT/F RT/2F RT/4F	1 2 4	- ∞ ∞	- 0 0
3. Bockris Electrochemical path: $SOH + OH^- \rightarrow SO + H_2O + e^-$ $2SO \rightarrow 2S + O_2$ $2SO \rightarrow 2S + O_2$	2RT/F 2RT/F RT/4F	1 2 4	- 2RT/F ∞	- 1 0
4. Karsil'shchikov's path: $S + OH^- \rightarrow SOH + e^-$ $SOH + OH^- \rightarrow SO^- + H_2O$ $SO^- \rightarrow SO + e^-$ $2SO \rightarrow 2S + O_2$	2RT/F 2RT/F 2RT/3F RT/4F	1 2 2 4	- ∞ 2RT/F ∞	- 1 0 0
5. O'Grady's path: $S^z + OH^- \rightarrow S^zOH + e^-$ $S^zOH \rightarrow S^{z+1}OH + e^-$ $2S^{z+1}OH + 2OH^- \rightarrow 2S^z + 2H_2O + O_2$	2RT/F 2RT/3F RT/F	1 1 4	- 2RT/F ∞	- 0 2
6. Kobussen's path: $S + OH^- \rightarrow SOH + e^-$ $SOH + OH^- \rightarrow SO + H_2O + e^-$ $SO + OH^- \rightarrow SO_2H^-$ $SO_2H^- + OH^- \rightarrow SO_2^- + H_2O + e^-$ $SO_2^- \rightarrow S + O_2 + e^-$	2RT/F 2RT/3F RT/2F 2RT/5F 2RT/7F	1 2 3 4 4	- 2RT/3F ∞ 2RT/F ∞	- 1 1 1 0
Where, p = reaction order, b = Tafel slope, θ = fractional surface coverage by adsorbed species.				

Spinel ferrites of Co-, Ni- and Mn- and lanthanum based perovskite-type oxides of Ni-, Co- and Mn- are considered as potent electrocatalytic materials for the oxygen evolution (as anodes in water electrolysis cells), reduction reaction (as cathodes in fuel cells and metal air batteries). These materials are widely used as heterogeneous catalysts in catalytic converters (in automobiles) for oxidation of CO, unburnt hydrocarbons etc.

Literature of the investigation shows that the oxide catalysts obtained by conventional ceramic and thermal decomposition method, which usually require high temperatures, produce materials with low specific surface area and contain some impurities also. The interfacial properties as well as electrocatalytic properties of these materials are strongly influenced by preparation variables such as experimental conditions such as, concentration of the starting substances, pH of the solution, temperature, methodology and nature of the starting substances used. Recently, a number of low temperature methods such as co-precipitation, sol-gel (by the used of organic acids), sequential solution coatings, spray pyrolysis, freeze-drying electrodeposition etc have been reported and used in synthesis of electrocatalyst for electrocatalysis of oxygen evolution/reduction. These methods produce oxides with high specific surface area and more homogeneity. The main objective of title investigation is to synthesize the materials with high specific surface area as well as enhanced electrocatalytic properties with regard to oxygen evolution reaction in alkaline medium. Results of these low temperature synthesized materials were found to be improved significantly for electrolysis point of view.

In view of these, we adopted low temperature synthetic routes namely, citric acid, malic acid, egg-white sol-gel and NaOH co-precipitation methods for the synthesis of spinel ferrites $M_xFe_{3-x}O_4$ ($M = Ni, Co$ and $0 \leq x \leq 1.5$) and perovskite-type oxides $La_{1-x}M'_xCoO_3$ ($M' = Sr, Cu$ and $0 \leq x \leq 0.8$) with the aim to improve their physicochemical as well as the electrocatalytic properties towards oxygen evolution reaction (OER) in alkaline solutions. In physicochemical

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characterization techniques used were infrared spectroscopy, X-ray diffractometer and scanning electron microscope. Cyclic voltammetry (CV) and Tafel polarization techniques were taken to study the electrochemical measurements. Details of experimental findings are presented in 'Results and Discussion' section.