

Chapter – 3

EXPERIMENTAL

3.1 Starting Materials and Experimental Techniques

This chapter deals the specifications of chemical and reagents used for the synthesis of oxide materials and the solution used in the electrochemical study. Different methodologies used in the preparation of electrode materials and various techniques used for the physicochemical and electrochemical study of synthesized materials are also mentioned in this chapter.

3.1.1 Starting Materials

Chemicals and reagents used in the preparation of oxide materials as well as in electrochemical study of prepared electrode materials were either AR-grade or purified grade. Such chemicals and reagents are listed below,

Fe(NO₃)₃.9H₂O (Merck, 98%), Co(NO₃)₂.6H₂O (Merck, 97%), Ni(NO₃)₂.6H₂O (Merck, 97%), Oxalic acid (Merck, 99%), Citric acid (Merck, 99.5%), NH₄OH (25%, Fischer), NaOH (Merck, 98%) DL-Malic acid (Merck, 98%), Sr(NO₃).6H₂O (Merck, 99%) Egg for egg-white (purchased from local market), Chloroform (Merck, 99%), HCl (Qualigen, 36.46%), HNO₃ (Merck), Acetone (Merck, 99%), Emery paper (grade-4/0), Triton X-100 (Merck, 98%), KCl (Merck, 99%), Agar-Agar (Merck), KOH (Merck, 98%), KNO₃(Merck, 98%), Silver paste (SPI supplies, USA), Commercial grade Copper wire (1 mm thick) and Araldite (Huntsman Advanced Materials Ltd, India). Ni-plate (0.5 mm thick, 99.9%, Aldrich, USA) and Pt-plate (0.25 mm thick, Sigma-Aldrich, 99.9% USA) were taken as conducting support for the oxide films.

3.2 Preparation of Solutions

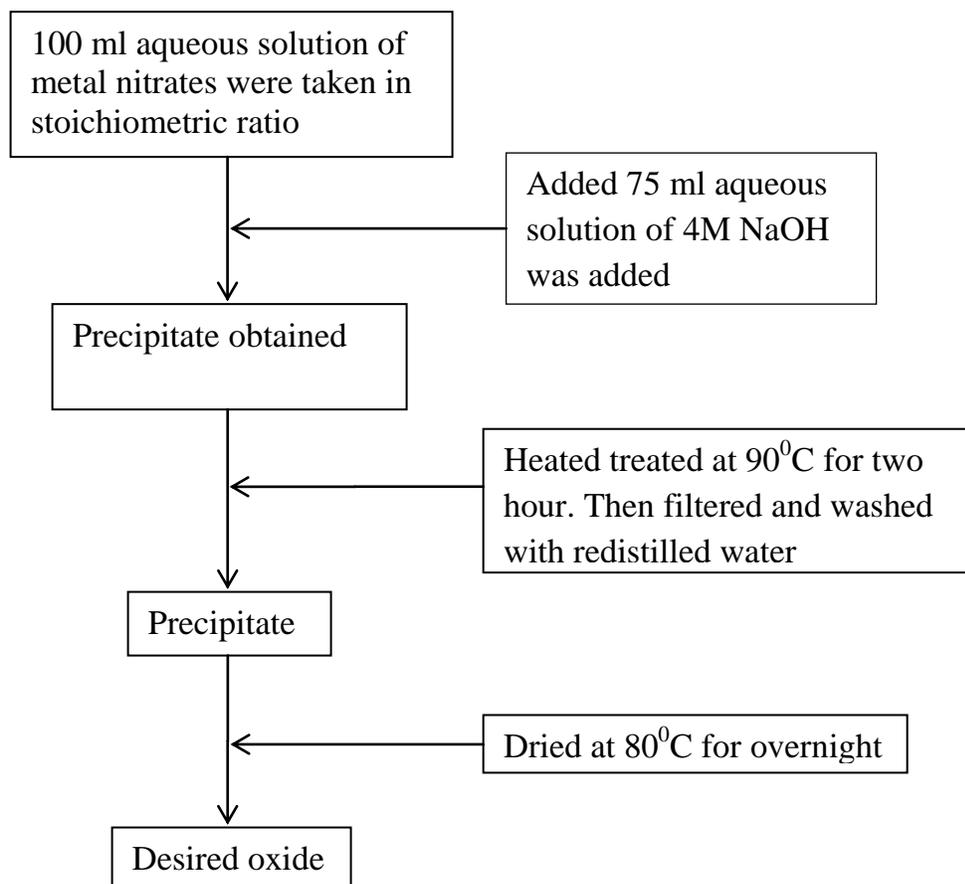
All the solution were prepared in aqueous medium using double distilled water. KOH solution was prepared by titrating against standard oxalic acid solution using phenolphthalein indicator. KCl + Agar-Agar gel was used in

Luggin capillary and the gel was prepared by boiling the KCl and Agar-Agar in 10:1 ratio in double distilled water.

3.3.1 Preparation methods of Spinel type oxides

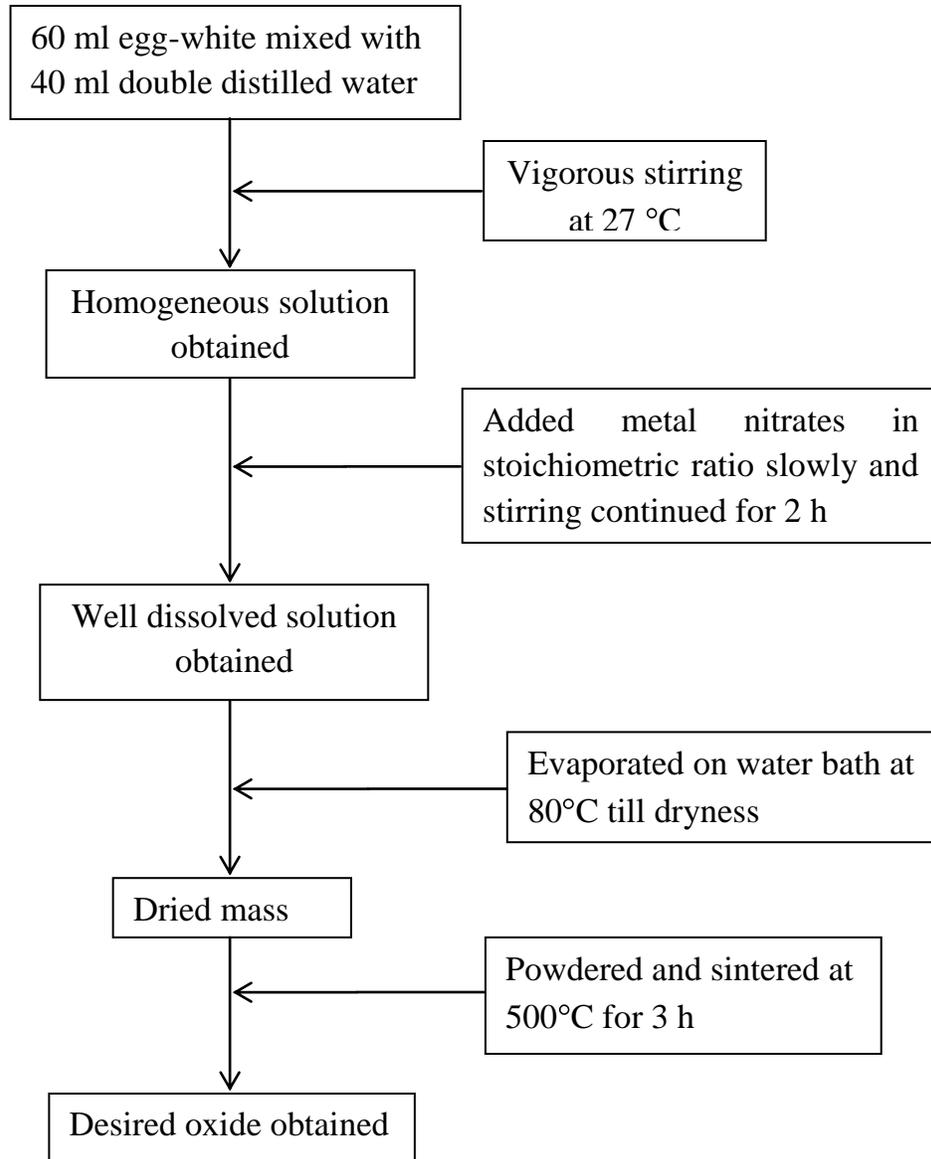
The binary spinel type of oxide material was prepared by using novel low temperature Co-precipitation and Egg white sol-gel methods. The used methods are described here with the help of block diagram.

3.3.1(a) Method-I: Co-precipitation: Co and Ni substituted ferrites were synthesized by using this method based on the method reported in literature [244].



Oxides prepared: Fe_3O_4 , $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$, CoFe_2O_4 , $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$, $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$, NiFe_2O_4 and $\text{Ni}_{1.5}\text{Fe}_{1.5}\text{O}_4$

3.3.1(b) Method-II: Egg-white sol-gel method: Oxides were prepared by using the method given by Maensiri et al [245].

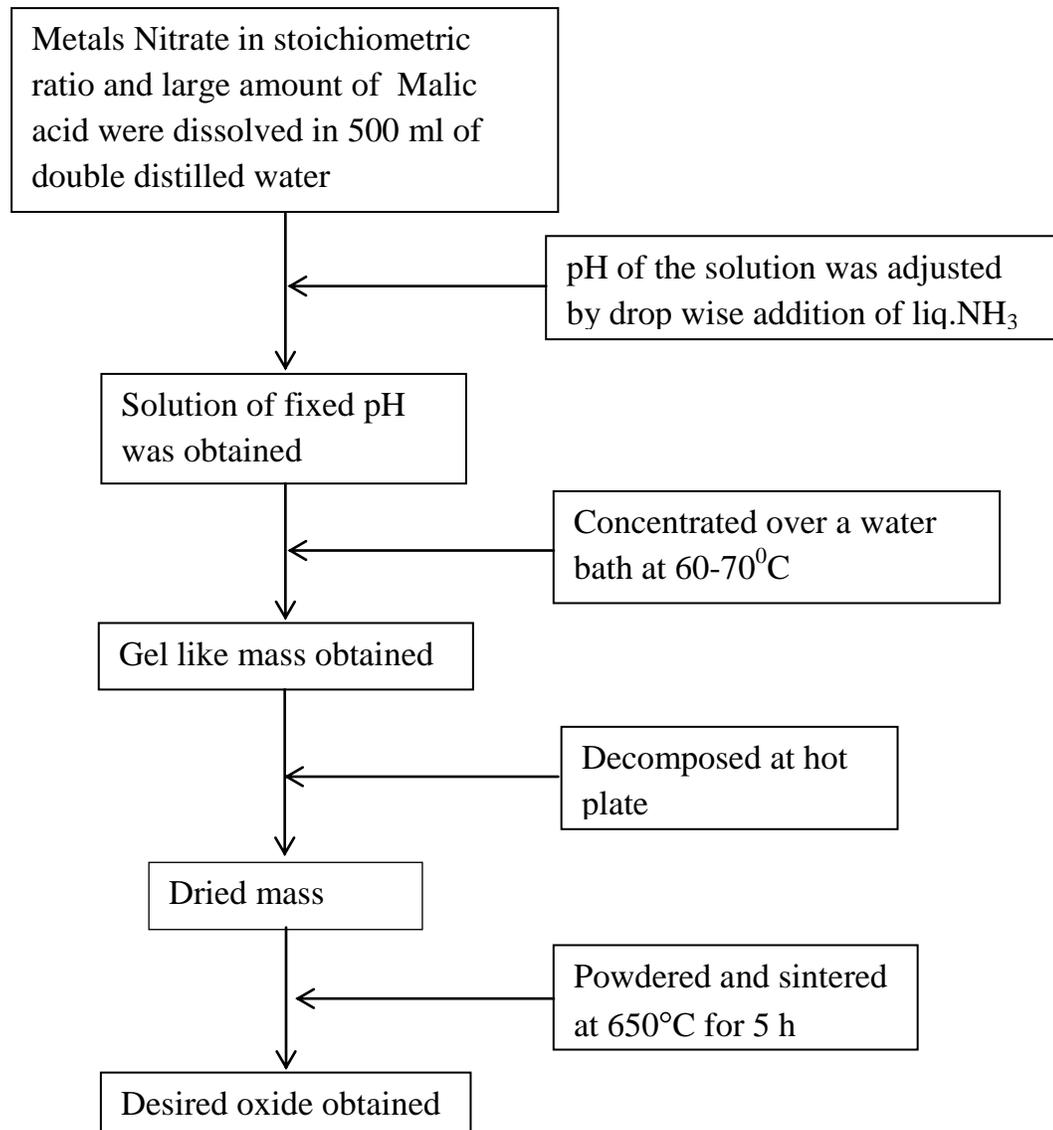


Oxides prepared Fe_3O_4 , $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$, CoFe_2O_4 and $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$

3.3.2 Preparation methods of Perovskite type oxides

The block diagram for the preparation of perovskite type of oxide is given below:

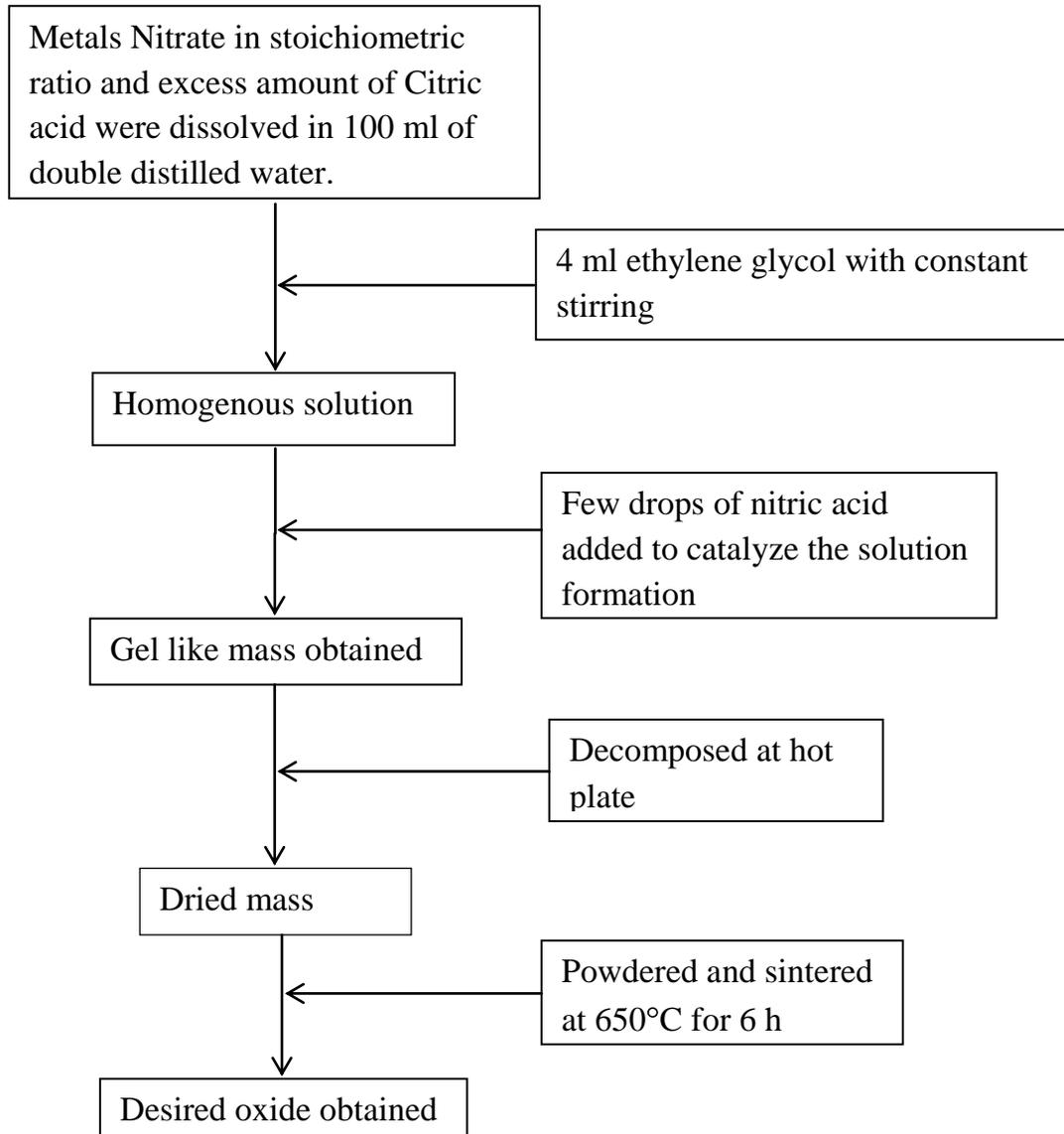
3.3.2(a) Method-III: Malic acid sol-gel method (MA-SG): Oxide materials were synthesised by the method reported by Teraoka et al [246]



Oxides prepared: (A) At pH 4.00: LaCoO_3 , $\text{La}_{0.8}\text{Cu}_{0.2}\text{CoO}_3$, $\text{La}_{0.6}\text{Cu}_{0.4}\text{CoO}_3$, $\text{La}_{0.4}\text{Cu}_{0.6}\text{CoO}_3$, $\text{La}_{0.2}\text{Cu}_{0.8}\text{CoO}_3$

(B) At pH 3.75: LaCoO_3 , $\text{La}_{0.8}\text{Cu}_{0.2}\text{CoO}_3$, $\text{La}_{0.6}\text{Cu}_{0.4}\text{CoO}_3$, $\text{La}_{0.4}\text{Cu}_{0.6}\text{CoO}_3$, $\text{La}_{0.2}\text{Cu}_{0.8}\text{CoO}_3$

3.3.2(b) Method-IV: Citric acid sol-gel method (CA-SG): Oxide materials were synthesized by the method reported by Vassiliou et al [247]



Oxides prepared : LaCoO_3 , $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$, $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_3$

3.4 Preparation of the oxide film electrodes

The oxide materials so prepared were used as electrocatalyst in the form of film electrode on a conductive support for the purpose polished pre-treated Ni or Pt-plate were taken as conductive support and performed following steps to get the oxide film electrode.

1. Pre-treatment of conductive metal support
2. Film preparation
3. Electrical contact

3.4.1 Pre-treatment of the conductive support

In the treatment of conductive support, the metallic plates (Ni or Pt) of area approximately 1.5 cm^2 were first polished mechanically by using fine emery paper and washed with double distilled water to remove previously deposited material on the plate. In the treatment of Ni plate it was first it dipped in concentrated HCl for 20 minutes, washed thoroughly using double distilled water followed by treating in acetone for 5 minutes to degrease it and finally washed 4-5 times with double distilled water and dried in open air. The treatment of Pt-plate was done in the same manner as mentioned in the case of Ni-plate. The only difference was that an aqua regia was used in place of HCl.

3.4.2 Film Preparation

Mainly oxide slurry painting technique [84] was used to convert the oxide powder in the form of film on conductive support. In this technique, small amount of oxide material was taken in agate pastel mortar along with few drops of Triton X-100 and crushed until homogeneous paste was obtained. This paste was coated on one side of pre-treated conductive support with the help of a fine brush and then heat treated at 380°C for one and half hour in an electrical furnace (ASCO). The plate was removed when furnace attained the temperature $< 80^\circ\text{C}$ for better

adherence of the oxide film. The process was repeated 2-3 times to get the desired oxide loading (in mg/cm^2).

3.4.3 Electrical contact with the oxide film

The material used for electrical contact with the film were silver paste, commercial grade plastic coated copper wire (1 mm thick, length = 15 cm), and araldite epoxy adhesive. In order to make the contact proper, first the uncoated surface of plate was scratched and cleaned by blade or emery paper. The copper wire was hammered at one end to make it partially flat for better contact with film. This end of wire was kept in touch with scratched surface of Ni plate and a little amount of silver paint was applied to make the surface conducting between wire and plate. When the paint became dry small amount of epoxy adhesive was dropped over it and left untouched to become perfectly dry. Finally total area of both sides of plate was coated with epoxy adhesive except 0.5 cm^2 of the oxide film. This uncoated area was used for electrochemical study of oxide material.

3.5 PHYSICOCHEMICAL CHARACTERIZATIONS

3.5.1 Infrared Spectra (IR)

For the determination of spinel phase of prepared oxide materials Infrared (IR) spectra were recorder in the frequency range of $4000\text{-}400 \text{ cm}^{-1}$ using FT-IR Thermoscientific (Nicole-6700) instrument.

3.5.2 X-Ray Diffraction (XRD)

The powder X-Ray diffraction (XRD) pattern of sintered oxides was determined by using Philips and PANalytical Powder X-Ray Diffractometer using $\text{Cu-K}\alpha_1$ as the radiation source ($\lambda = 1.54056\text{\AA}$).

3.5.3 Scanning Electron Micrograph (SEM)

The morphology as well as topological information of the oxide powder was obtained by a scanning electron microscope (SEM) using JEOL (JSM 6490) and SEM (LEO 430) System.

3.6 ELECTROCHEMICAL CHARACTERIZATIONS:

The study of redox behaviour and Electrocatalytic activity of oxide film electrodes was carried out mainly by two techniques Cyclic Voltammetry (CV) and Tafel polarization. These are described below:

3.6.1 Electrochemical cell and electrochemical work station:

A conventional three electrode single compartment glass cell and an electrochemical Impedance system (Gamry Reference 600 ZRA) provided with potentiostat/galvanostat connected to personal computer (PC) system (hp) with corrosion and physical electrochemistry software were used for all electrochemical characterization namely, Cyclic voltammogram (CV) and anodic polarization curve. The working electrode was the prepared oxide film electrode, while the reference and auxiliary (counter) electrodes were Hg/HgO in 1 M KOH ($E^\circ = 0.098$ V vs. NHE) and pure Pt-foil with relatively large geometrical surface area (~ 2 cm²), respectively. The reference electrode was connected to the cell solution through the luggin capillary (the KCl/Agar-Agar salt bridge) to minimize the solution resistance (iR drop) between the working and the reference electrode. The potential of the working (test) electrode was measured with respect to reference electrode. Entire system for electrochemical study is shown in Fig. 3.6.1

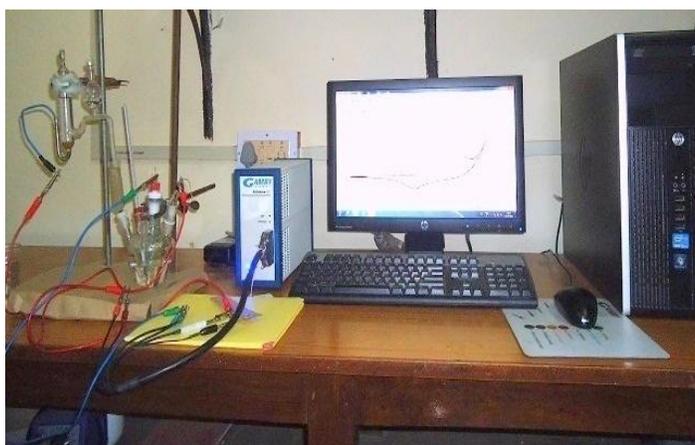


Fig. 3.6.1: Electrochemical Work station (Gamry Reference 600 Potentiostat/Galvanostat/ZRA) and hp computer.

3.6.2 Cyclic voltammetry (CV)

To know the redox behaviour of oxide film electrode, cyclic voltammograms of each oxide film electrode were recorded in the potential region of 0.0-0.7 V in 1 M KOH at 25°C. Before recording the final CV curve, each electrode was first cyclic voltammograms were cycled for 4 times in the said potential region at the 20 mV sec⁻¹ scan rate. CV curve of each oxide electrode was analyzed for its anodic peak potential (E_{pa}), cathodic peak potential (E_{pc}), anodic peak current density (j_{pa}), cathodic peak current density (j_{pc}), formal redox potential (E°) and peak separation potential (ΔE_p). To know the effect of scan rate at the nature of voltammograms, CV curves were also recorded at varying scan rate from 20 to 120 mV sec⁻¹. The voltammetric charge (q) was estimated by integrating the CV curve between potential 0.0 V and the potential just prior to the start of oxygen evolution using Gamry Echem analyst software. The plot of voltammetric charge (q) vs (scan rate)^{-1/2} determined the diffusion controlled property of the surface redox reaction.

In order to determine the electrochemically active area, cyclic voltammograms were recorded in a small potential region (0.0-0.1 V) at varying potential scan rate from 20 to 120 mV sec⁻¹. The charging current density (j_{cap}) was measured at the middle of potential range (i.e. 50mV). Double layer capacitance (C_{dl}) was determined by the slope of straight line plots of j_{cap} vs. scan rate. Assuming that the double layer capacitance 60 $\mu\text{F cm}^{-2}$ for smooth oxide surface, roughness factor for oxides was calculated by using the following formula.

$$R_f = \frac{C_{dl} \text{ of the test oxide}}{C_{dl} \text{ of the smooth oxide surface}}$$

3.6.3 Tafel Polarization studies

The electrocatalytic activity for Oxygen evolution reaction of oxide film electrode at Ni support was determined by recording iR-compensated anodic polarization curve (E vs. log j or E vs. j) at a slow scan rate of 0.2 mV sec⁻¹ in 1 M KOH at 25°C. The Tafel slope was estimated by measuring the slope of the linear part of the Tafel polarization curve. To determine the order of reaction with respect to the concentration of OH⁻, polarization curves were recorded in varying KOH concentrations (0.25 M KOH, 0.50 M KOH, 1.00 M KOH and 1.50 M KOH) by maintaining the ionic strength ($\mu = 1.5$) constant using KNO₃ as inert electrolyte. The plot of log j vs. log [OH⁻] was constructed and the order was determined by measuring the slope of straight line at different constant applied potentials. The effect of temperature on oxygen evolution reaction and other thermodynamic parameters for the electrochemical reaction were determined by recording the anodic polarization curve at varying temperature (20-50 °C) in 1 M KOH. During the experiment the temperature of reference electrode was kept constant (at 25± 2 °C). Arrhenius plot (log j vs. 1/T) was constructed. The slope of straight line plot gives the value of activation energy for the reaction. Standard entropy of activation ($\Delta S^{o\ddagger}$) and standard enthalpy of activation ($\Delta H^{o\ddagger}$) were calculated by using the relations [250].

$$\Delta S^{o\ddagger} = 2.3R \left[\log j + \frac{\Delta H_{el}^{o\ddagger}}{2.3RT} - \log(nF\omega C_{OH^-}) \right] \quad (1)$$

Where, $\omega \left(= \frac{k_B T}{h} \right)$ is the frequency term and n = 2.

$$\Delta H_{el}^{o\ddagger} = \Delta H^{o\ddagger} - \alpha F \eta \quad (2)$$

Where, $\alpha \left(= \frac{2.303RT}{bF} \right)$ is the transfer coefficient

All the other terms appeared have their usual meanings.