

DEVELOPMENT OF MODIFIED STAINLESS-STEEL ELECTRODE FOR ALKALINE WATER ELECTROLYSIS

Submitted in partial fulfillment of the requirements for the award of
Master of Science in Chemistry

by

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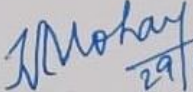
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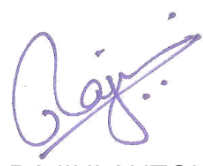
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ABSTRACT

Highly active and inexpensive electrodes are required for large scale hydrogen production using alkaline water electrolysis. To synthesize an efficient bifunctional electrocatalytic electrode of nickel deposited on stainless steel mesh by electrodeposition method. The nickel is occupied the porous present in the stainless-steel mesh. Morphological and structural characterization of nickel deposited stainless steel electrodes were correlate with electrochemical properties of the electrode. The synthesized electrode exhibits excellent electrocatalytic performance towards Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER). Because the standard overpotential for OER and HER IS 350mV and 420mV. An overpotential of 290mV for HER and 260 mV for OER at 10mAcm^{-2} in 1M KOH. A lower Tafel slope of 84.8 mVdec^{-1} for HER and 42.2 mVdec^{-1} for OER. There is no potential drop after a long-time durability test. The hydrogen generated is approximately 12ml for 100s. Therefore, the faradaic efficiency is 94.7%. The excellent activity and good stability would hopefully enable the prepared electrocatalyst to mitigate the main drawback of existing electrolysis technologies and provide possibility of developing next generation water splitting technologies.

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LIST OF ABBREVIATION

AEM - Anion Exchange Membrane Electrolyser

AWE - Alkaline Water Electrolyser

CA - Chronoamperometry

CP - Chronopotentiometry

CV - Cyclic Voltammetry

ECSA - Electro Chemical Surface Area

FESEM - Field Emission Scanning Microscopy

HER - Hydrogen Evolution Reaction

ICPAES - Inductively Coupled Plasma Atomic Emission Spectroscopy

LSV - Linear Sweep Voltammetry

OER - Oxygen Evolution Reaction

PEM - Proton Exchange Membrane Electrolyser

RHE - Reversible Hydrogen Electrode

SS - Stainless Steel

TOF - Turn Over Frequency

XRD - X Ray Diffraction

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CHAPTER 1

INTRODUCTION

The fast development of human culture has brought more genuine ecological issues and energy emergencies. As of now, with the expansion sought after for coal, oil, petroleum gas, and other non-renewable fuels, investigating and creating manageable clean energy is one of the chief inquiries went up against by specialists. Because of the spotless and productive qualities, hydrogen is viewed as the most encouraging energy and significant option in contrast to fossil energy in the future. The water splitting response gives a promising strategy for putting away discontinuous environmentally friendly power in the structure of hydrogen fuel, and the electrocatalysis of water splitting in alkaline environment for creating hydrogen has become the main focus point of current research. Hydrogen creation from electrolyzing water might be an innovation that meets the prerequisites, yet in viable applications, this innovation is still dependent upon the limitation of significant expense and low effectiveness.

For the present, to work on the productivity of the electrolysis process for the creation of hydrogen fuel, there is an overwhelming interest in reducing the overpotential of both the anode and cathode. Productive electrocatalysts with enormous explicit surface area, great electrical conductivity, and excellent stability are the way to accelerate the overall water splitting process. As of now, the noble metal based electrocatalysts, like IrO_2 , RuO_2 , and Pt group metals, are considered as the most developed and astounding electrocatalysts for both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). However, they are restricted by the low reserves and restrictive expense for large scope applications. So, it is urgent to create affordable nonprecious metal catalyst with high efficiency and durability.

Until this point in time, numerous researchers have been committed to creating compelling non-noble metal catalyst like transition metal oxides, carbides, hydroxyls, phosphates, sulfides, nitrides, and so on. Among this catalyst, the majority of the created OER catalyst show better execution in alkaline solution, while HER catalyst can function admirably in acidic media. In this way, to further develop the

overall water splitting effectiveness, rearrange the framework, and reduce cost, OER and HER catalyst ought to work in a similar electrolyte. Since acidic decomposition of water typically requires rare and expensive acid insoluble OER catalyst, alkaline water splitting has turned into a prevalent strategy for large scale hydrogen production. However, the mismatch in the electrolyte for HER and OER frequently leads to poor activity for overall water splitting. Therefore, there is as yet an extraordinary challenge to the development of highly efficient bifunctional electrocatalysts for overall water splitting in alkaline electrolyte under a viable state of alkaline electrolyte.

Lately, nickel (Ni) materials have been generally read up as electrocatalysts for OER and HER due to their abundant and superior catalytic performance in alkaline medium. However, a conductive substrate is normally expected to improve the conductivity of nickel materials. So, polymer binder [poly(tetrafluoroethylene), Nafion, etc.] are utilized to immobilize the catalyst, which not just complicate the preparation process but also covers most of the active sites, making the contact between substrate and the active sites insufficient and leading to gas accumulation on the substrate surface. On account of constant percolating, the catalyst is easily strip off from the substrate. The hydrothermal technique and electrodeposition strategy can make Ni straightforwardly develop onto a conductive substrate and try not to utilize these insulative polymer binders, thus improving the adhesion to the substrate and reducing the resistance of the electrodes. Compared with the hydrothermal method, the electrodeposition method is simpler without utilizing high pressure and high temperature and can be finished in a very short time. In addition, the electrodeposition technique can effectively control the thickness of Ni and obtain metal-modified Ni hydroxides composites to further work on the conductivity of the electrode, facilitating the electron transfer to those active sites far from the substrates.

Aside from the preparation method, the conductive substrate is essential to the microstructure and electrocatalytic preparation of Ni composites. Recently, stainless steel has been considered as superior current collector and substrates for water splitting in alkaline solution since there are an enormous number of active elements, for example, nickel, iron, and chromium in stainless steel materials, which can give all the more electrochemically active sites in different redox

responses, and hence may have better electrochemical activity. Among all the stainless-steel materials, the stainless-steel mesh has been focused more on account of its highporosity, promoting the migration of ions onto the substrate and the reduce the diffusion path and also increase the electrochemical surface area.

Motivated by the discussion above, in this, a novel electrocatalytic composite electrode created by utilizing an effortless electrodeposition method at room temperature is proposed. The electrode comprises of metal-modified nickel hydroxide exhibits in situ developed on a stainless-steel mesh conductive substrate. The pre-arranged anode has an incredible bifunctional electrocatalytic execution toward both HER and OER in alkaline electrolyte. This stir opens up an excitingavenue to extend greater chance for the optimised, cost effective, and scalablefabrication of highly efficient electrocatalysts for water electrolysis.

CHAPTER 2

LITERATURE SURVEY

2.1 RECENT PROGRESS IN ALKALINE WATER ELECTROLYSIS FOR HYDROGEN PRODUCTION AND APPLICATIONS

Alkaline water electrolysis is one of the most straightforward methods for producing hydrogen, with the benefit of simplicity. Water electrolysis faces several challenges, including lowering energy consumption, costs, and maintenance while increasing reliability, durability, and safety. This literature review examines the current state of knowledge and technology for hydrogen production by water electrolysis, as well as areas where more R&D is needed to improve the technology. An electrical circuit analogy of resistances in the electrolysis system is introduced after an overview of the fundamentals of alkaline water electrolysis. Electrical resistances, reaction resistances, and transport resistances are the three types of resistances that can be found. This is followed by a detailed examination of each of the resistances. Based on theoretical energy input and cell voltage, the thermodynamic analysis defines various electrolysis efficiencies. These efficiencies are then used to compare different electrolysis cell designs and determine how to overcome key resistances to increase efficiency. The kinetic analysis reveals that reaction resistances are influenced by alkaline concentration, ion transfer, and reaction sites on the electrode surface, the latter of which is determined by electrode materials. A quantitative relationship is established between cell voltage components and current density, which links all resistances and demonstrates the importance of reaction and bubble resistances. The importance of gas bubbles forming on the electrode surface is highlighted, as is the need to reduce ion transport resistance.

2.2 NANOMETRIC Ni_5P_4 CLUSTERS NESTED ON NiCO_2O_4 FOR EFFICIENT HYDROGEN PRODUCTION VIA ALKALINE WATER ELECTROLYSIS

For hydrogen production via acidic water electrolysis, a number of non-noble catalysts are being developed. However, for more cost-effective alkaline hydrogen production, the limited kinetics of the water dissociation Volmer step and the

subsequent proton recombination Tafel step for these non-noble electrocatalysts generally result in a sluggish hydrogen-production process. By phosphating NiO clusters on NiCo₂O₄ as a simple method for nesting nanometric Ni₅P₄ clusters on NiCo₂O₄ (achieving Ni₅P₄@NiCo₂O₄) is developed. When used as a high-efficiency electrode for alkaline water electrolysis, the Ni₅P₄@NiCo₂O₄ can efficiently and preferentially convert H₂O to H₂ with a low overpotential of 27 mV at 10 mA cm⁻² and a Tafel slope of 27 mV dec⁻¹, which is comparable to platinum and superior to state-of-the-art platinum-free electrocatalysts. Calculations using the density functional theory show that NiCo₂O₄ species have a better ability to electrolyze water into the H* intermediate, and that Ni₅P₄ clusters help with the subsequent desorption of the H₂ products. The Ni₅P₄@NiCo₂O₄ electrocatalyst is promising for scalable alkaline hydrogen production because of the promoted kinetic steps.

2.3 ELECTROCHEMICALLY FABRICATED NiCu ALLOY CATALYSTS FOR HYDROGEN PRODUCTION IN ALKALINE WATER ELECTROLYSIS

An electrodeposition method was used to make NiCu alloy catalysts for alkaline water electrolysis with different alloy compositions. The bulk and surface Cu content in NiCu alloys, as well as the catalyst particle size, gradually increased as the deposition potential became more positive, as confirmed by various spectroscopic and electrochemical techniques. The deposition potential was also found to affect the surface coverage of the catalysts. The mass activities of NiCu alloys were correlated with bulk and surface Cu contents to investigate the Cu alloying effect, and the catalytic activities of the prepared NiCu alloys to hydrogen evolution reaction (HER) were investigated with cyclic voltammetry in a 6.0 M KOH electrolyte at 298 K.

2.4 CHARACTERIZATION OF THE Ni-Mo CATALYST FORMED *IN SITU* DURING HYDROGEN GENERATION FROM ALKALINE WATER ELECTROLYSIS

The goal of this study was to investigate the electrocatalytic efficiency of Ni-Mo catalysts obtained by *in situ* electrodeposition in a 6 M KOH electrolyser using quasi-potentiostatic, galvanostatic, and impedance spectroscopy techniques. According to our previous research, there is a synergetic effect, which is strongest under industrial conditions (high temperature and current density). Tafel slopes are around 120 mV, and exchange current densities are around 102 mA cm⁻² (three orders of magnitude

higher compared to the bulk Ni). Furthermore, the formed deposit is extremely stable during prolonged electrolysis. The Tafel slopes, exchange current densities, apparent activation energy, apparent electrochemical surface, and stability of the in situ formed Ni-Mo catalyst are all shown in the results. The findings point to significant catalytic activity.

2.5 FAST ELECTRODEPOSITED NICKLE-IRON HYDROXIDE NANOSHEETS ON SINTERED STAINLESS STEEL FELT AS BIFUNCTIONAL ELECTROCATALYSTS FOR OVERALL WATER SPLITTING

The use of hydrogen fuel produced by a water splitting reaction to store intermittent renewable energy is a hot topic, and electrocatalysis has been a hot topic in research. A simple electrodeposition method was used to create an efficient bifunctional electrocatalytic electrode of nanoporous nickel-iron hydroxides coupled with a small amount of metal Ni/Fe based on stainless steel fibre felt (SSF). The prepared catalysis electrode can improve overall water splitting performance significantly. Nickel-iron hydroxide composites are used to fill the gaps in SSF, and metal Ni/Fe is simultaneously generated through electrodeposition to improve conductivity. The synthesised electrode performs well in both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), requiring only overpotentials of 100 mV for the latter and 210 mV for the former. The obtained electrode also exhibits excellent activity when used as both an anode and cathode for full water splitting, achieving an overall cell voltage of 1.80 V to achieve 100 mA cm⁻². After a long-term durability test, there is almost no potential for a drop. The synergistic action between the NiFe (OH)_x nanosheets and SSF substrate, which benefits the chemisorption of oxygen and hydrogen-containing intermediates, maybe the cause of the increased water splitting activity, according to electrocatalysis studies. The prepared electrocatalyst's high activity and stability should allow it to overcome the major drawbacks of existing electrolysis technologies and pave the way for the development of next-generation water splitting technologies.

2.6 HETEROLAYERED NI-Fe HYDROXIDE/OXIDE NANOSTRUCTURES GENERATED ON A STAINLESS-STEEL SUBSTRATE FOR EFFICIENT ALKALINE WATER SPLITTING

Naoto Todoroki et al (2019) For large-scale hydrogen production using alkaline water electrolysis, highly active and inexpensive anode materials are required (AWE). Through constant current density electrolysis, heterolayered nanostructures of Ni-Fe hydroxides/oxides with high activity for the oxygen evolution reaction (OER) were synthesised on a 316 stainless steel (SS) substrate. The thicknesses, morphologies, and compositions of nanostructures created by dealloying and surface oxidation of SS elements with severe oxygen microbubble evolution were all affected by the electrolysis time. The heterolayered Ni-Fe hydroxide/oxide nanostructures were generated during the initial stage of electrolysis, growing nanofiberlike Ni-Fe hydroxide layers with increasing electrolysis time of up to 5 h, according to nanostructural analyses. The nanofiber structures were densified as a result of the prolonged electrolysis. At 10 mA/cm², the OER overpotential was estimated to be At 20 °C, the Ni-Fe layered double hydroxide achieved a voltage of 254 mV, outperforming a standard OER catalyst such as Ir oxide and yielding the value of the Ni-Fe layered double hydroxide (LDH). Furthermore, at current densities greater than 100 mA/cm², the OER property outperformed Ni-Fe LDH catalysts. Furthermore, stable electrolysis was achieved for 20 hours under conditions similar to the practical AWE of 400 mA/cm² in solutions at 20 and 75 degrees Celsius. As a result, highly active nanostructures for alkaline water splitting anodes could be produced using a simple surface modification method.

2.7 EMERGING NANOPOROUS ANODIZED STAINLESS STEEL FOR HYDROGEN PRODUCTION FROM SOLAR WATER SPLITTING

The use of a nanoporous anodized stainless steel 316L (NASS316L) as a photoanode for visible-light-induced photo electrocatalysis of hydrogen production from water splitting has been discovered. This research was unique in that it adapted the anodization conditions to convert stainless steel from an inert (water-resistant) state to a highly efficient "low-band gap" semiconductor. Several key anodization

parameters were investigated, as well as their impact on the morphology and water splitting activity of the NASS316L. Finally, the anodization was optimised at 40 V for 5 minutes at room temperature in an ethylene glycol electrolyte containing ammonium fluoride, methanol, water, and sulfuric acid. Surprisingly, the sulfuric acid content in the anodization recipe was critical in fine-tuning the morphology for improved photo electrocatalysis water splitting. Furthermore, the NASS316L photoanode had a narrow band gap (1.77 eV) with an indirect transition, allowing it to absorb solar radiation in the visible range. It also maintained a flat band potential of 0.78 V, which effectively maintained the separation of the generated charge carriers when illuminated.

2.8 TRANSFORMATION OF STAINLESS STEEL 316 INTO A BIFUNCTIONAL WATER SPLITTING ELECTROCATALYST TOLERANT TO POLARITY SWITCHING

The development of highly active bifunctional electrocatalysts that can operate in the harsh alkaline electrolyte used in commercial electrolyzers is a constant challenge. Furthermore, due to the rapid start-up and shut-down conditions, which rapidly deteriorate the anode and cathode materials, commercial units cannot be directly integrated with intermittent renewable energy sources. The transformation of stainless steel (AISI 316) into an electrocatalyst that facilitates overall water splitting while showing excellent tolerance to reverse polarity conditions is demonstrated here using a very simple electrochemical conditioning approach followed by galvanic replacement with gold nanoparticles at a level of 0.5 at. percent. With a low Tafel slope value of 29 mV dec⁻¹, the electrocatalyst is not only very active for the OER, but also shows excellent performance. High current densities of 100 mA cm⁻² can be achieved for the HER. At a cell voltage of only 2 V, current densities greater than 150 mA cm⁻² for overall water splitting in 6 M NaOH can be achieved in a two-cell configuration, indicating potential commercial applicability. Furthermore, the electrodes show a high tolerance for reversing the polarity of the cell for up to 216 hours while maintaining equal performance.

2.9 FACILE FABRICATION OF SUPER-HYDROPHOBIC FAS MODIFIED ELECTROLESS NI-P COATING MESHES FOR RAPID WATER-OIL SEPARATION

Due to the high separation efficiency and consistent recyclability, the development of a super-hydrophobic coating/film mesh for directly separating oil from water is highly desired. With the FAS modified electroless Ni-P composite coatings, we describe a simple and inexpensive method for fabricating super-hydrophobic/super-oleophilic stainless steel meshes. The Ni-P particles on the mesh are spherical with a uniform size diameter and form a nanoscale rough surface when they concatenate. The as-prepared meshes have static contact angles ranging from $124.4 \pm 1.5^\circ$ to $167.9 \pm 2.1^\circ$. These meshes have excellent water resistance, anti-fouling, and penetrating through oil properties. Without using any additional driving force or chemical agent, the prepared meshes can rapidly and continuously separate water-oil mixtures. The most effective separation efficiency is 96.8%. For long-term separation of water-oil mixtures, the super-hydrophobic mesh is stable and reliable. Finally, a separation mechanism for water-oil mixtures using super-hydrophobic meshes is proposed. The prepared meshes are expected to be a viable candidate for effective waste oil clean-up and other rapid water-oil separation processes.

2.10 EFFECTS OF SURFACE NANO CRYSTALLIZATION PRETREATMENT ON LOW-TEMPERATURE ION SULFURIZATION BEHAVIOR OF 1Cr18Ni9Ti STAINLESS STEEL

A 10 μ m thick nanocrystalline surface layer was fabricated on 1Cr18Ni9Ti stainless steel using supersonic fine particle bombardment (SFPB). The original and SFPB-treated (SFPB treated) surfaces were then subjected to low-temperature ion sulfurizing, which resulted in sulphide layers of varying thickness. The phase constituents and grain size of the nano-crystallized surface layer were studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM). SEM and energy dispersive spectroscopy were used to investigate the surface morphologies and compositions of the sulphide layers (EDS). The valence states of the sulphide layers were detected using an X-ray photoelectron spectroscope (XPS). The distribution of elements with depth was measured using Auger energy spectroscopy (AES). The results show that SFPB treatment refines the surface layer microstructure to nano-

grains with grain sizes of about 30 nm and random crystallographic orientations. The thickness, density, and FeS content ratio of the sulphide layers can all benefit from surface nano crystallization pretreatment. According to the findings, the high-density crystal defects and increased surface chemical activity are primarily responsible for the SFPB surface nano crystallization treatment's improved ion sulfurization treatment efficiency.

2.11 SELF-SUPPORTED STAINLESS STEEL NANOCONE ARRAY COATED WITH A LAYER OF NI-Fe OXIDES/(OXY)HYDROXIDES AS A HIGHLY ACTIVE AND ROBUST ELECTRODE FOR WATER OXIDATION

Water oxidation electrodes that are highly efficient, durable, and inexpensive are critical for large-scale hydrogen production via electrolysis of water. A self-supported stainless steel (SS) nanocone array coated with a layer of nanoparticulate Ni-Fe oxides/(oxy)hydroxides was fabricated using a two-step process that was simple, low-cost, and easily scalable. The formation of a layer of Ni-Fe oxides/(oxy)hydroxides featuring the NiFe_2O_4 spinel phase on the nanocone surface by electrodeposition of $[\text{Ni}(\text{bpy})_3]^{2+}$ on the surface of an AISI 304 SS plate by acid corrosion greatly increased the specific surface area of the substrate, and the subsequent formation of a layer of Ni-Fe oxides/(oxy)hydroxides featuring the NiFe_2O_4 spinel. The intrinsic activity and stability of the SS-based electrode were significantly improved. With 232 and 280 mV overpotentials, the as-prepared electrode demonstrated superior activity for the oxygen evolution reaction (OER) in 1M KOH, achieving 10 and 100 mA cm^{-2} current densities, respectively. The electrode maintained its high activity over 340 hours of chronopotentiometric testing at 20 mA cm^{-2} , and it also showed good stability over 100 hours of electrolysis at high current density (200 mA cm^{-2}). The used SS-based electrode can be easily regenerated with the original OER activity, which is especially important for practical application. The superior activity of this SS-based electrode is due to a synergistic combination of the SS substrate's high conductivity, the nanocone array's large electrochemically active surface area, and a uniformly coated nanoparticulate Ni-Fe oxide/(oxy)hydroxide layer with an electrochemically active surface area.

2.12 STAINLESS STEEL MADE TO RUST: A ROBUST WATER-SPLITTING CATALYST WITH BENCHMARK CHARACTERISTICS

Because of the large overpotentials commonly used materials on the anode side, the oxygen evolution reaction (OER) is known as the efficiency-limiting step for the electrochemical cleavage of water. Ni-Fe oxides are preferred anode materials for the electrocatalytically driven water-splitting reaction because they dramatically reduce OER overpotentials. We show that a simple surface modification with AISI 304, a general-purpose austenitic stainless steel, results in the formation of an ultra-thin layer consisting of Ni, Fe oxide with a purity >99 percent, most likely due to a dissolution mechanism. The unusually efficient anodic conversion of water into oxygen is due to tallow overpotentials of 212 mV at 12 mA cm² current density in 1M KOH and 269.2 mV at 10 mA cm² current density in 0.1 M KOH. The Ni, Fe-oxide layer formed on the steel forms a stable outer sphere, and the surface oxidised steel samples were found to be inert against longer operating times (>150 ks) in an alkaline medium. Furthermore, chronopotentiometry measurements of Faradaic efficiency revealed a charge to oxygen conversion close to 100%, supporting the conclusion that no "inner oxidation" based on further oxidation of the metal matrix below the oxide layer takes place. These key figures, obtained with a material that is almost unrivalled in terms of cost and accessibility, are among the best ever presented activity characteristics for the anodic water-splitting reaction at room temperature. Ni enriched thin layer firmly attached to the steel substrate, as demonstrated.

2.13 SELF-GENERATED N-DOPED ANODIZED STAINLESS-STEEL MESH FOR AN EFFICIENT AND STABLE OVERALL WATER SPLITTING ELECTROCATALYST

The mesoporous structure of N-doped anodized stainless-steel mesh (NASSM) is demonstrated as a highly efficient, stable, and bifunctional electrocatalyst with tuned electronic structure and surface morphology in this study. Anodic oxidation with Cr as a non-catalytic substance was followed by nitrogenization and in situ removal of the SSM surface to regulate the morphology with a mesoporous structure. With a low Tafel slope of 49.7 mV dec⁻¹ and excellent stability for over 100 hours, NASSM showed an overpotential of 225 mV at 10 mA cm², which was higher than that of

commercial IrO₂/C catalyst. At 10 mA cm², NASSM had a 146 mV overpotential and a Tafel slope of 60.1 mV dec⁻¹. At 10 and 20 degrees Celsius, NASSM showed potentials of 1.61 and 1.76 V as a bifunctional electrocatalyst.

2.14 STAINLESS STEEL SCRUBBER: A COST-EFFICIENT CATALYTIC ELECTRODE FOR FULL WATER SPLITTING IN ALKALINE MEDIUM

Finding a cost-effective bifunctional catalytic material for water splitting can sometimes come from the most unexpected places. The use of a stainless steel (SS) scrubber directly as a catalytic electrode for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) of water electrolysis in 1 M KOH is described in this paper. In HER, the iR corrected overpotential for an SS scrubber calculated at a 10 mA cm⁻² areal current density is 315 mV, which is 273 mV higher than Pt/C. Similarly, at 10 mA cm⁻², the SS scrubber required 418 mV, which is only 37 and 98 mV higher than Ni(OH)₂ and RuO₂, respectively. The kinetic analysis revealed that the SS scrubber had simple kinetics for both processes. Their corresponding Tafel slope values are 121 and 63 mV dec⁻¹, respectively. Furthermore, the two-electrode cell, which was made with the same SS scrubber electrode, delivered 10 mA cm⁻² at 1.98 V. Above all, the SS scrubber had demonstrated ultrahigh stability for total water splitting in both half-cell and full-cell studies. Furthermore, in terms of electrode material cost per gramme, the SS scrubber outperforms all other water splitting electrocatalysts with a price of \$0.012 USD, which is \$2.228 USD less than pure Ni, \$59.658 USD less than RuO₂, and \$158.028 USD less than Pt/C 20 wt percent catalyst. The SS scrubber can be adapted for cost-effective large-scale water treatment, according to the overall study.

2.15 N AND P DOPED POLY(3,4-ETHYLENEDIOXYTHIOPHENE) ELECTRODE MATERIALS FOR SYMMETRIC REDOX SUPERCAPACITORS

A symmetric redox supercapacitor was created using stainless steel (SS) electrodes coated with n and p doped Poly(3,4-ethylenedioxythiophene) (PEDOT). FTIR, Cyclic Voltammetry, and AC Impedance spectroscopy were used to investigate the supercapacitor's characterization and performance. At a scan rate of 10 mV s⁻¹, the supercapacitor showed a maximum specific capacitance of 121 F g⁻¹. The active-reactive power behaviour measurement yielded a time constant of 12 milliseconds

for the supercapacitor, indicating that the system is suitable for use at low frequencies.

2.16 INTERFACE STUDY FOR STAINLESS STEEL FIBRE-REINFORCED ALUMINIUM MATRIX COMPOSITE

A vacuum high-pressure diffusion-bonding technique was used to create regular interface zones with uniform thickness in an AISI 304 stainless steel-reinforced aluminium-matrix composite. Extensive and intensive experiments were conducted to investigate the growth of interfacial compounds as hot-pressing time and temperature were varied. The overall growth rate of the interface was discovered to follow a parabolic law in the early stages. The interface growth rate fell behind that predicted by the parabolic law after a certain amount of diffusion time. To explain the deviation, a modified parabolic law was developed, which proved to be a better model for fitting the experimental data. The activation energy was found to be 152 kJ mol^{-1} , which was slightly lower than previous findings. The lower the activation value, the better.

CHAPTER 3

AIM AND SCOPE

3.1 AIM

Based on the literature overview on the requirement of cost-effective alternative energy resources and the current status of the electrode materials used for alkaline electrolyser, it is essential to develop a cost effective, efficient electrode materials which can increase the overall water splitting rate.

3.2 SCOPE:

Scope of the present study is set as

- Utilization of stainless-steel based substrates for further modification to improve the catalytic activity.
- Selection of suitable catalyst materials and deposition technique for surface modification
- Optimization of the process parameters such as time, potential, current.
- Testing the Electrocatalytic activity towards HER and OER reactions
- Long term stability of the electrode materials and post analysis of the electrode materials

CHAPTER 4

MATERIALS AND METHOD

4.1 CHEMICALS:

All the chemicals which are used for experiment are used without any further purification. The chemicals used are 0.05M of nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) from KAM-VIT Chemicals Private limited Chennai, 1M potassium hydroxide (KOH) from Antares Chem Private Limited Mumbai, Conc. Hydrochloric acid (HCl) Aarthi Chem Limited, ethanol ($\text{C}_2\text{H}_5\text{OH}$) from Bajaj Hindustan Limited Mumbai for cleaning the electrode. The Stainless steel -304 mesh and 316 coupons were used for catalyst loading and the resultant electrodes are used for alkaline water electrolysis.

4.2 ELECTROCHEMICAL DEPOSITION:

In the present study, chronoamperometric and chronopotentiometric method were employed to fabricate modified electrode. Prior to the deposition the SS electrodes (1 cm X 2.5 cm) was sonicated in 1 M HCl 5 minutes, followed by washing in copious amount of Millipore water and finally with ethanol to remove any organic contaminations. The samples were dried and used for electrodeposition and further electrochemical measurements.

4.2.1 CHRONOAMPEROMETRY:

Chronoamperometry is an electrochemical technique where the potential of the working electrode is stepped and the resulting current from faradaic processes occurring at the electrode is monitored as the function of time. By this method one can deposit a material of interest on to the electrode and the current generated is depended on the redox behaviors of the element to be deposited. Under this stepped potential, the system made a transition from no reaction to steady state reaction, which is controlled by the rate of mass transfer of ion toward electrode surface. This transition is always followed by current transient (Ahmed 2018)). In the present study, nickel is deposited by chronoamperometric method under different applied potential say 0.9V, 1V, 1.3V and 1.5 V and the deposition time was kept as 120 s. Stainless steel mesh was used as the working electrode, platinum electrode and silver-silver chloride electrode (Ag/AgCl) as the counter and reference electrode,

respectively. Various process parameters such as deposition potential and deposition time are employed for optimum catalytic activity. Fig 4.1 shows the schematic representation of the electrochemical set up used for the electrodeposition process and related measurements.

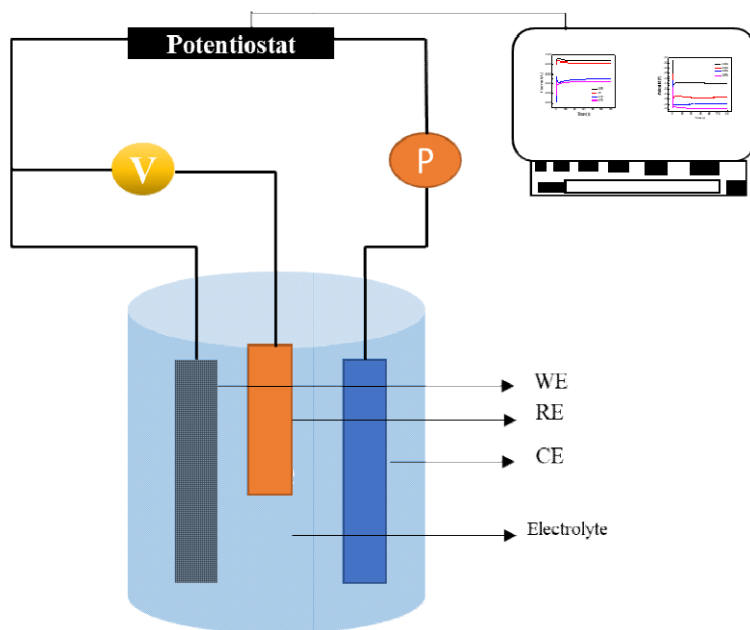


Fig 4.1: Schematic of electrochemical cell of three electrode system, WE – working electrode, CE-counter electrode and RE-reference electrode

4.2.2. CHRONOPOTENTIOMETRY:

Chronopotentiometry is another technique used commonly in electrodeposition process, where a constant current is allowed to flow between two electrodes. The potential of the working electrode is monitored as a function of time with respect to reference electrode. In the present study, nickel electrodeposition on SS mesh was carried out varying applied current 0.02A, 0.03A, 0.05A and 0.07A with a deposition time of 60s under three electrode configurations as shown in Fig 4.1.

4.2.3 POTENTIOSTAT:

All the deposition and electrochemical experiments in the present study was carried out using a potentiostat (Biologic VSP 300). A potentiostat is an analytical instrument designed to study the electrochemical processes by controlling the working electrode's potential in an electrochemical cell. The potentiostat contains internal circuits which are functioned to generate and measure the potential and current. Fig

4.2 shows the digital photograph of the potentiostat used in the present study and the circuit diagram of a potentiostat. All the experiments in the presented in this thesis are conducted in 3- electrode configuration. In the potential controlled method, the working electrode potential is measured with respect to that of reference electrode but there will be tiny current flow between working electrode and the counter electrode. A basic potentiostat can be modelled as an electronic circuit consisting of four components: the electrometer, the I/E converter, the counter amplifier, and the signal. ((Bard, Faulkner et al. 2001))

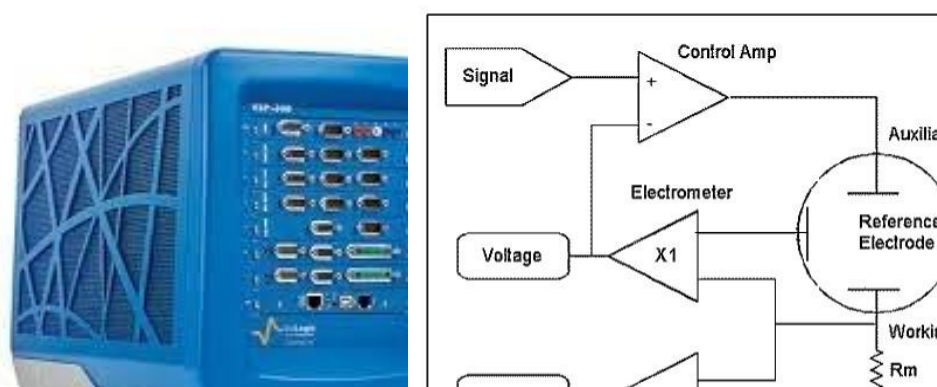


Fig 4.2: Digital photograph of Potentiostat (Biologic VSP 300) and Circuit diagram of a potentiostat.

4.2.4 THREE ELECTRODE SYSTEM:

4.2.4.1 Working electrode:

Producing reliable electrochemical data requires the working electrode to have the appropriate configuration be reasonably prepared and to be particularly clean. The working electrode used for electrochemical studies here is stainless steel mesh and stainless-steel coupons. The stainless steel was cut into pieces with area of $1 \times 1 \text{ cm}^2$. Then these cut stainless steel electrodes were cleaned with 0.1M HCL and then with ethanol and ultrapure water. The cleaning of electrode is done by sonication process and dried in oven for 5 hours at 125°C . Thereafter, the stainless- steel electrode is electrodeposited with nickel from nickel sulphate hexa hydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) by chronoamperometry and chronopotentiometry technique at different condition. And these modified Stainless-steel electrode act as working electrode for electrochemical studies pertaining to both OER and HER.

4.2.4.2 Counter electrode:

The counter electrode must rapidly supply or sink electron for the reaction at the working electrode without limiting it. Thus, the mostly recommended counterelectrode is Pt wire, foils with diameter 0.5*360 or meshes with diameter of 32mm because which has large current for both hydrogen evolution and oxygen evolution reaction and it also balance the charge at the working electrode. The counter electrode needs to produce homogeneous electric field between working and counter electrode. The counter electrode should not lead to the contamination of working electrode. Thus, the suitable counter electrode Pt electrode (Liang, Dong et al. 2018)

4.2.4.3 Reference electrode:

To accurately measure or control the potential applied to the working electrode is measured with respect to a reference electrode. Thus, reference electrode should have a stable and well-defined potential. The most widely used reference electrode are saturated calomel electrode with potential of 0.241V at saturated KCl and the silver chloride with potential of 0.280V at 1M KCl, For an alkaline electrolyte the reference electrode used is mercury oxide, mercury sulphate or silver sulphate is recommended because in Ag/AgCl reference electrode, alkaline condition may shift the reference potential due to the diffusion of OH⁻ into the chamber of reference electrode altering the pH of KCl filling the solution and which causes oxide formation (Schweitzer and Pesterfield 2010). Thus, the selection of reference electrodes must be carefully made according to the electrolyte. In the present study, for catalytic measurements, the reference electrode is used is mercury oxide (Hg/HgO) with potential of 0.098V, then all the measured potential should be converted to RHE scale.

4.3 MORPHOLOGICAL ANALYSIS:

This morphological analysis is used shape, size and type of deposition by various techniques such as scanning electrochemical microscopy (SEM) and Transmission electron microscopy (TEM). In the present study, field emission SEM (FESEM) was used as the major tool to evaluate the morphology of the modified SS electrodes.

4.3.1 Field Emission Scanning Electron Microscopy

Field emission scanning electron microscopy (FESEM) is used to study the microscopic structure of the compound which helps to distinguish the phases of the compound easily. The FESEM works on the principle of applying kinetic energy to produce signals on the interaction of electron. These signals provide a wide range of information on morphology, chemical composition and crystalline structure and this signal depend on the nature of the compound which is being probed and emerged from specific emission volume from within the compound. The FESEM consists of secondary electron signals, backscattered electrons, x-rays signals and some amount of heat and light. (Amelinckx, Van Dyck et al. 2008)

4.3.1.1 Working principle of FESEM:

The electrons are emitted from the field emission source which is accelerated by high electric field gradient and these primary electrons are focused and deflected by electrons lenses. This help to produce a narrow scan beam that will bombard the material/object. As a result of this, secondary electrons from each spot of the materials are emitted. The angle and velocity of secondary electron is related to the surface topology of the material. Then the detector catches these secondary electrons and produces an electrical signal. Finally, this electronic signal is amplified and transformed to video scan-image that can be monitored and proceed further analysis. A schematic showing the working principle of FESEM

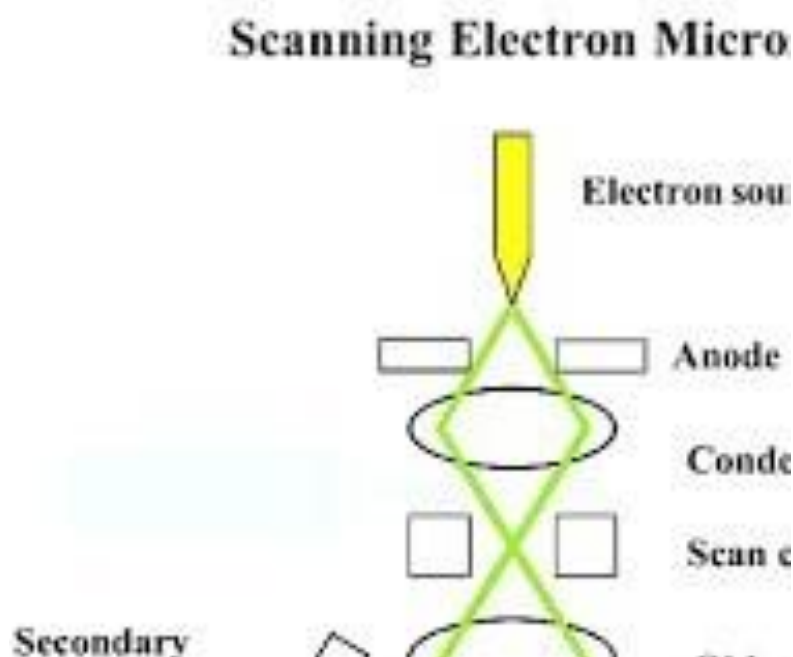


Fig4.3: Schematic of field emission scanning electron microscopy

4.4 STRUCTURAL ANALYSIS:

To know the structure and phases of the deposited Ni, It is essential to characterize the material for its composition and phase. In the present thesis, X-ray diffraction (XRD) and micro-Raman analysis are carried out for this. A brief idea about working principle of XRD and Raman spectra is given below.

4.4.1 X-ray diffraction (XRD):

X-Ray Diffraction technique is used to determine the crystallographic structure of the material. It also used to determine the crystal phase, composition and orientation of plane. The X-ray Diffraction is based on the principle of Bragg's law which state that the condition must be fulfilled to observe the constructive interference of radiation which is scattered by the atom in the crystalline sample. The XRD is the interaction between the incoming radiation and large number of crystal plane which leads to strong constructive interference and it is observed in an X-ray diffractogram. The condition which is explained by Bragg state that for given wavelength λ and interplanar distance d a constructive interference is possible at an angle θ is given by

$$n\lambda = 2d\sin\theta ; n= 1,2,3.... \quad \text{Equation 4.1}$$

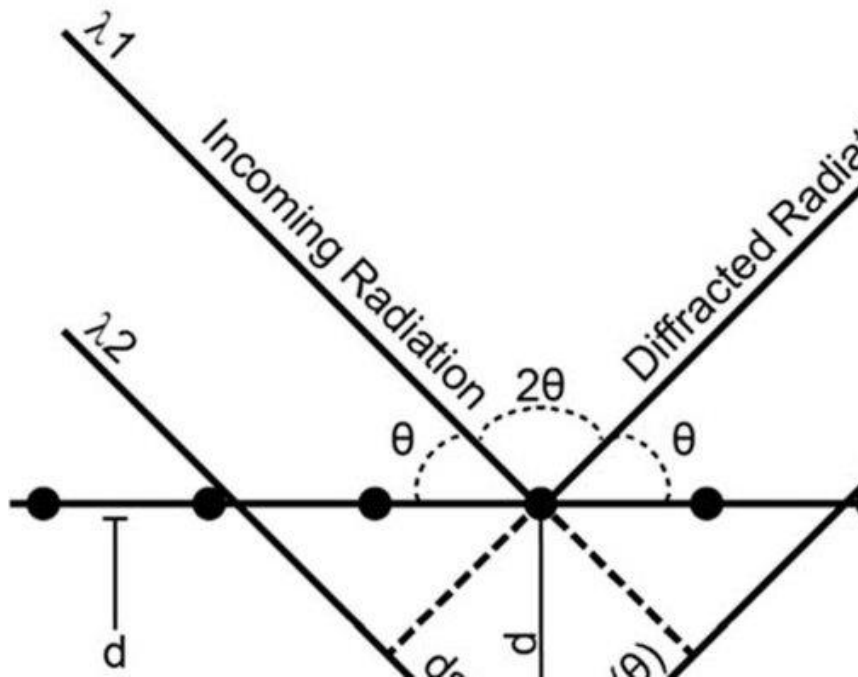


Fig 4.4: Schematic of Bragg's Diffraction (Stan, Beavers et al. 2018)

Fig 4.4 shows the schematic representation of Bragg's diffraction condition. X-Rays are first generated by directing highly accelerated electron against a metal target. When this monochromatic x-ray beam is incident on the crystalline sample, it interacts with the electron in the atom of the crystals. These electrons have the tendency to oscillate due to the incident x-rays radiation and emit electromagnetic radiation in all direction and interact with the crystal planes. These electromagnetic radiations may undergo either a constructive or destructive interference based on their amplitude and direction. For the constructive interference to occur the difference in path length of the incident and the diffracted beam must be an integral multiple of wavelength of the incident beam. The resultant XRD measurements are called diffractogram where the plot is between X-Ray intensity vs 2θ .

4.4.2 RAMAN SPECTROSCOPY:

Raman spectroscopy is a vibrational spectroscopic technique which is generally based on the inelastic scattering of monochromatic light which may usually be laser. Raman spectroscopy provides the information about the crystal structure and molecular vibration of the sample. The principle of Raman spectroscopy is

Raman Effect which state that the photon from monochromatic laser source is absorbed and then re-emitted by the Raman active sample. The frequency may be shifted upward or downward depending on the nature of the sample. This deviation of frequency from the frequency of incident photon is collected as Raman spectrum using CCD camera. Thus, the Raman spectrum gives information about vibrational and rotational transition in the sample. The Raman spectroscopy is a non-contact and non-destructive technique which has high spatial resolution that is down to sub microns. The Raman spectrum is plotted between intensity of scattered light versus wave number. Each peak seen in a Raman spectrum are originates from specific molecular or lattice vibration. The position of peak corresponds to mode of vibration of functional group present in the sample. Thus, Raman spectrum is used to obtain molecular fingerprint of the target material. Fig 4.5 shows the schematic of the Raman process

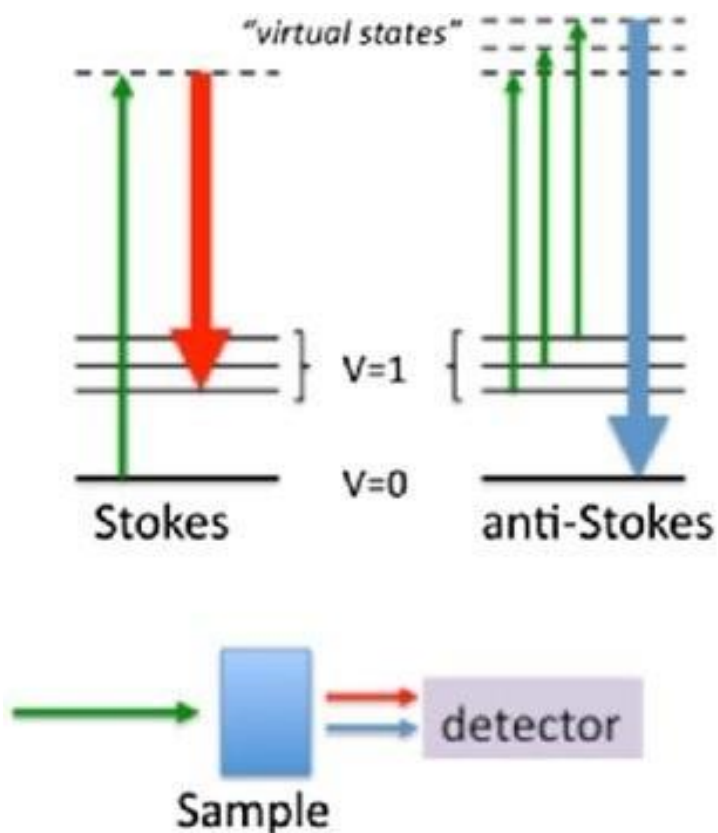


Fig 4.5: Schematic of Raman spectrum (Potcoava, Futia et al. 2014)

4.5. ESTIMATION OF ELECTRODEPOSITED ELEMENT:

The amount of electrodeposited nickel is estimated using inductively coupled atomic emission spectroscopy (ICPAES). For this Ni deposited SS is dipped in 5ml of 1M con. HNO_3 for 5 minutes and then the dissolved nickel diluted 10 times for ICPAES analysis.

4.5.1 Inductively Coupled Plasma- Atomic Emission Spectroscopy:

Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) is an analytical technique which is used for quantification of trace element present in the sample. It is emission spectroscopy which uses inductively coupled plasma as source for the excitation of atom present in the sample. The excited atom is de-excited into ground state by emitting electromagnetic radiation of particular wavelength characteristic to that element. The temperature of source ranges from 6000 to 10000 K. The intensity of emitted light will be proportional to the concentration of element present in the sample.

4.5.2 Working:

The inductively coupled plasma -Atomic Emission Spectroscopy consists of three systems which are sample introduction system, the plasma torch assembly and spectrometer. The sample is pumped into the nebulizer. The nebulizer generates an aerosol mist in spray chamber. The largest mist particles get settled down in the spray chamber whereas the finest particles will be swept vertically into plasma torch assembly along with argon gas. The sample which is mist is atomized and excited at the plasma. The excited atoms come to ground state with emission of light rays. The emitted light can be viewed horizontally by an optical channel and then it is passed into monochromator where the diffracting grating is present. The diffraction grating will split the light into its component color and then it is transmitted into detector. The generally used detector is photomultiplier tube which will convert the emitted light into electrical signal.

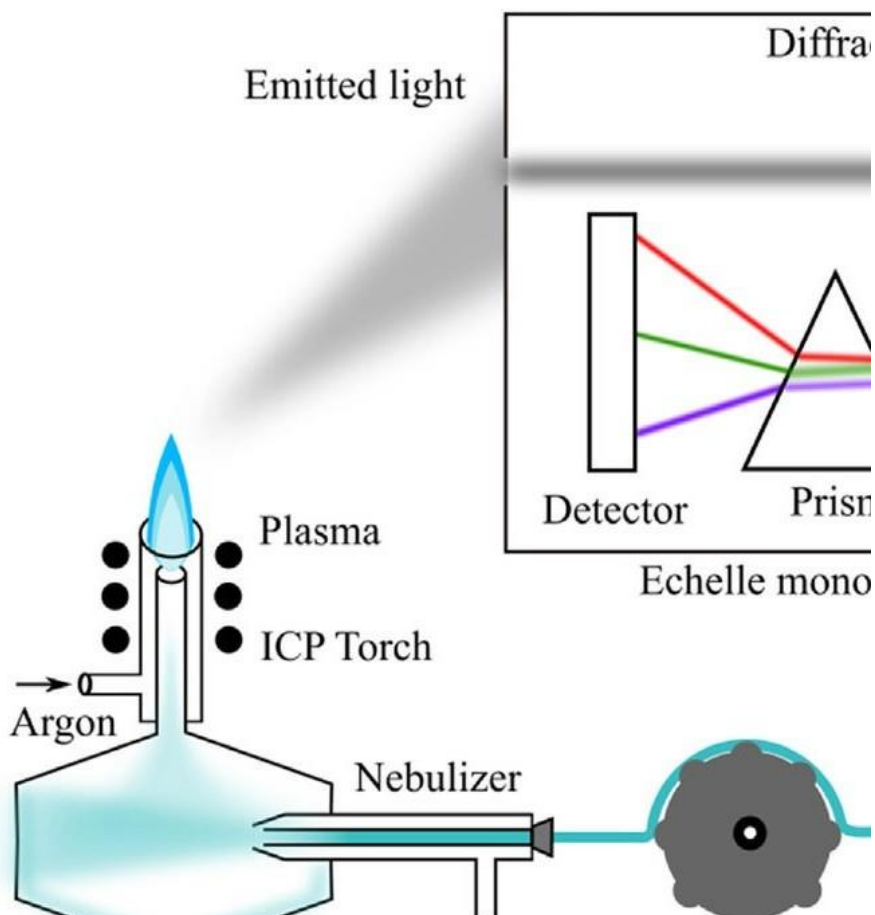


Fig 4.6: Schematic of Inductively Coupled Plasma -Atomic Emission spectroscopy. (Cherevko and Mayrhofer 2018)

4.6 ELECTROCHEMICAL MEASUREMENT:

Electrochemical measurements towards oxygen and hydrogen evolution were carried out using Biologic CSP 300 potentiostat. A three-electrode system was employed, in which coiled Pt electrode was used as the counter electrode, Hg/HgO (1M NaOH) as the reference electrode and stainless-steel mesh as with working electrode. Argon saturated 1 M KOH was used as the electrolyte. Electrochemical measurements were carried by conducting linear sweep voltammetry and cyclic voltammetry at a scan rate of 2 mVsec^{-1} in KOH (1 M). Before measurements the samples were cycled at a scan rate of 10 mV/sec for 50 times to refresh the catalytic surface. All the electrochemical measurements are reported against the potential vs RHE. For this, Hg/HgO reference electrode was calibrated in a three-electrode

configuration using cleaned Pt wires as working and counter electrode. 1 M KOH was used as the electrolyte which was purged using high purity H₂ gas before and during the measurements. LSV's were recorded at a scan rate of 1 mVs⁻¹ and the potential where the current was zero is taken as the potential of hydrogen electrode and was found to be 0.93 V from the LSV recorded (Figure S). The electrochemical data measured using Hg/HgO reference electrode were then converted to RHE using the equation (4.6.1)

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.93 \text{ V} - iR \quad (4.6.1)$$

All the measurements were iR compensated in the present study and the value of iR's were found by impedance measurement in KOH (1 M) and was in range of 5 to 10 Ω. The temperature during electrochemical measurements was 25±1°C. Argon saturated electrolyte was employed overpotential 'η' for oxygen evolution were calculated using the following formula:

$$\eta = E_{\text{RHE}} - 1.23 - iR. \quad (4.6.2)$$

The turn over frequency (TOF) for the oxygen evolution reaction at different η values were calculated using equation (4.6.3) (McCrory, Jung et al. 2013)

$$TOF = \frac{j_{\text{Sgeo}}}{4Fm} \quad (4.6.3)$$

Where j is the current density at η = 350 mV, S_{geo} is the geometrical surface area, the number 4 is the 4 electrons involved per mole of O₂, and 2 for 2 electrons involved per mole of H₂, F is the faradays constant of which value is 96483 C/mol) and 'm' is the number of moles of the metal ions involved in the catalytic reactions. Assuming all metal ions participate in the electrochemical reaction we calculated the number of moles of metal ions from the mass obtained from the ICPAES measurements and molecular weight of Ni and Co. Double layer capacitance were estimated by measuring the charging current at different scan rate (5- 60 mV/s) in a potential window of 1.13 to 1.23 V vs RHE and the current (both anodic and cathodic) at 0.98 V vs RHE were noted at each scan. The double layer capacitance, 'C_{dl}' were extracted from the slope of the current vs scan rate plot and the roughness values were calculated using the equation (4.6.4) (McCrory, Jung et al. 2013).

$$R_f = \frac{C_{dl}}{60} \quad (4.6.4)$$

Where, the value '60' represents the specific capacitance of a smooth oxide surface in $\mu\text{F}/\text{cm}^2$.

The electrochemical surface area (ECSA) in cm^2/mg was further calculated using equation (4.6.5), where m is the mass estimated in mg/cm^2 .

$$ECSA = \frac{R_f}{m} \quad (4.6.5)$$

The mass activities were calculated using mass loaded which was calculated from ICPAES measurements and the current density j , (mA/cm^2) at different $\square$ values using the equation (4.6.6). (Gao, Sheng et al. 2014)

$$\text{Mass Activity, MA} = \frac{j}{m} \quad (4.6.6)$$

The reproducibility of the electrochemical performance of the catalyst was ensured by repeating the measurements for 4 times. The stability of the electrocatalyst were confirmed by conducting chronoamperometric for 10 hours.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 DEVELOPMENT OF Ni MODIFIED STAINLESS STEEL ELECTRODE:

For the development SS based electrodes Ni was chosen as the catalytic surface on SS and the catalytic loading was done by electrodeposition process. The electrodeposition of nickel on stainless steel mesh from nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) electrolyte at pH 4 were carried out using constant potential (chronoamperometry (CA)) and constant current (chronopotentiometry (CP)) techniques. In the case of chronoamperometric deposition, a constant potential of -0.9, -1, -1.3 and -1.5 V vs Ag/AgCl was applied and deposition time was fixed as 120 s. Whereas, for chronopotentiometric deposition a current of -0.02, -0.03, -0.05 and -0.07 mA was applied for 60 s. Samples were labelled as Ni-SS-CA-0.9, Ni-SS-CA-1, Ni-SS-CA-1.3, Ni-SS-CA-1.5, Ni-SS-CP-0.02, Ni-SS-CP-0.03, Ni-SS-CP-0.05 and Ni-SS-CP-0.07. Figure 5.1 shows the current and potential transients recorded during the electrodeposition process. From the transients it is evident that Ni growth and nucleation is taking place on the SS surface resulting in uniform Ni deposition which will be further discussed in the subsequent sections. Figure 5.1 c and 5.1d are the digital photographs taken for electrodes developed under different conditions.

Further cyclic voltammogram (CV) was carried out to confirm the Ni deposition in 1 M KOH by correlating with the redox peaks appeared in CVs. In all the cases a distinct oxidation-reduction peaks are present and is positioned at ~ 1.4 and ~ 1.3 V vs RHE, vs RHE which is a characteristic redox peak positions for Nickel. (Crousier, Hanane et al. 1994) The amount of charge corresponding to each peak is a characteristic function of the electrode reaction taking place and hence gives an indication of the amount of nickel electrodeposited on the electrode surface. Figure 5.2(a) represent cyclic voltammogram of samples deposition by CA. The peak in the forward scan shows the oxidation of Ni^{2+} to Ni^{3+} and corresponding reverse peak is the reduction of Ni^{3+} to Ni^{2+} . From fig 5.2(a) we can say that, with increase in the applied potential, the peak intensity also increases and is higher for Ni-SS-CA-1.3 which becomes stable beyond this deposition potential (Ni-SS-CA-1.5) showing that further increasing the deposition potential does not create additional Ni active sites. Fig 5.2(b) represents the cyclic voltammogram of chronopotentiometry

techniques at Ni-SS-CP-0.02, Ni-SS-CP-0.03, Ni-SS-CP-0.05, Ni-SS-CP-0.07. Similar to the case of chronoamperometric deposition, in the case of chronopotentiometric deposition nickel deposition is evident by the presence of redox pairs corresponding to nickel as shown in Figure 5.2b. The current density values increase with increase in the applied current and are the highest for Ni-SS-CP-0.05 and thereafter it starts decreasing.

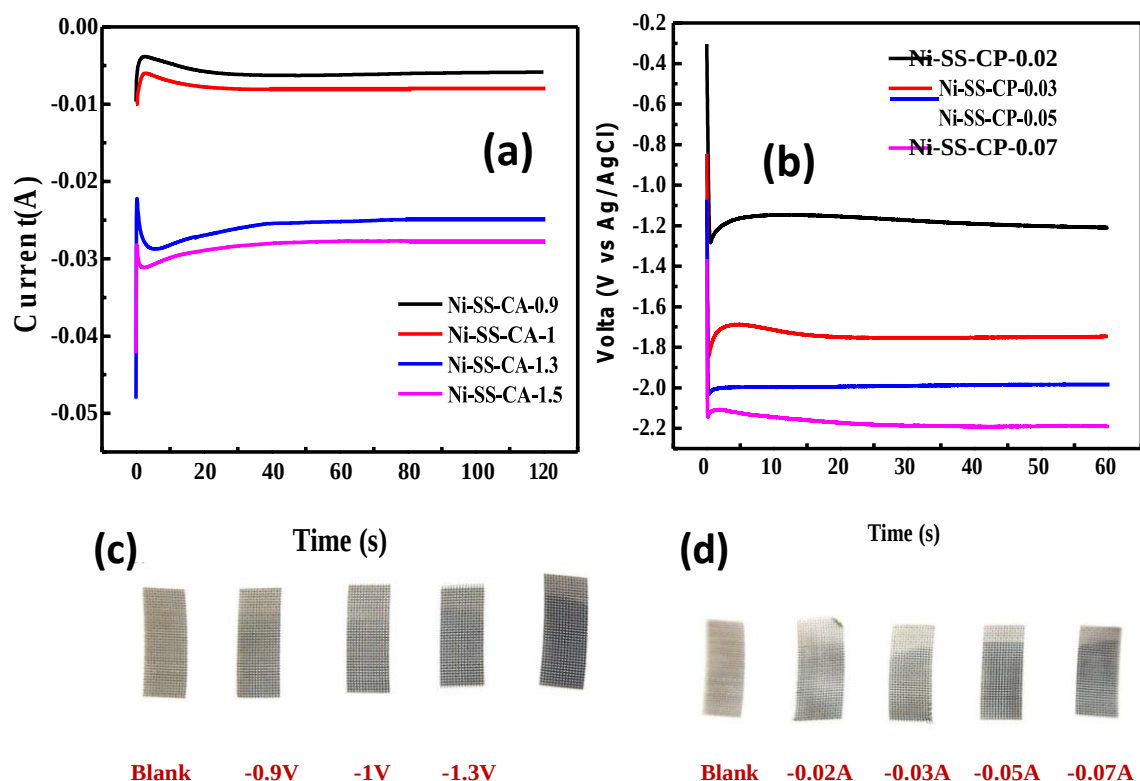


Fig 5.1: (a) Current and (b) potential transient recorded during electrodeposition. Digital images of Ni-SS electrodes fabricated by (c) CA and (d) CP deposition

5.1.1 Morphological evaluation

Further, morphological evaluation was carried out for representative nickel deposited electrodes using Field Emission Scanning Electron Microscopy (FESEM). Ni-SS-CA-1.3 and Ni-SS-CP-0.02 electrodes were chosen for this based on the best catalytic activity obtained which is discussed in the subsequent section. FESEM images of the blank SS Mesh (Figure 5.3a & b), Ni-SS-CA-1.3 (Figure 5.3c & d) and Ni-SS-CA-0.02 (Figure 5.3 e & 5.3 f) are shown below. A surface modification on SS surface is evident from the FESEM images (Figure 5.3 c-f). FESEM images show stress

induced cracks indicative of a fast nucleation and growth process both in CA and CP assisted deposition because of more nickel deposition it.

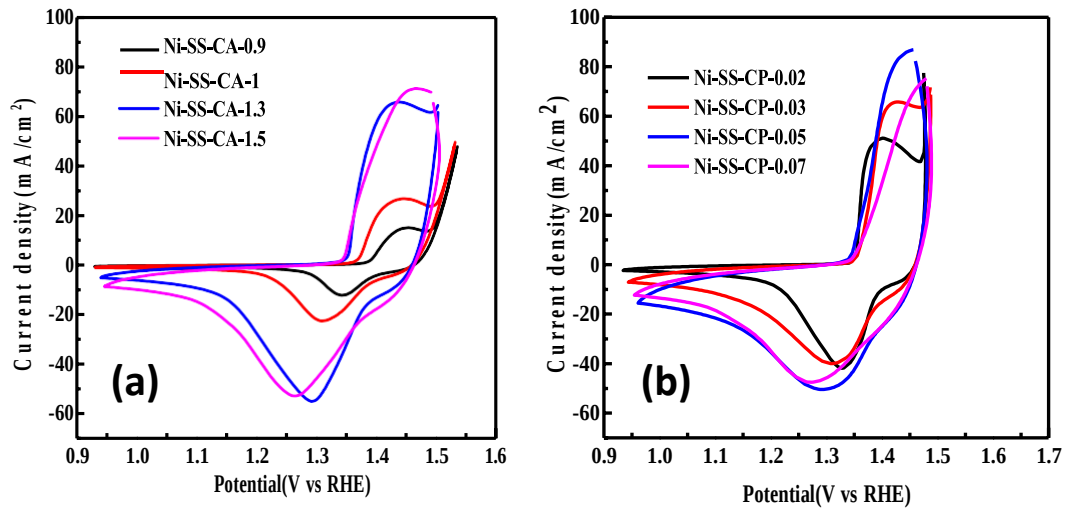


Fig 5. 2: Cyclic voltammetry recorded in Ni modified SS electrode performed in a potential window of 0.9 to 1.6 vs RHE in 1 M KOH solution at a scan rate of 50 mVs⁻¹

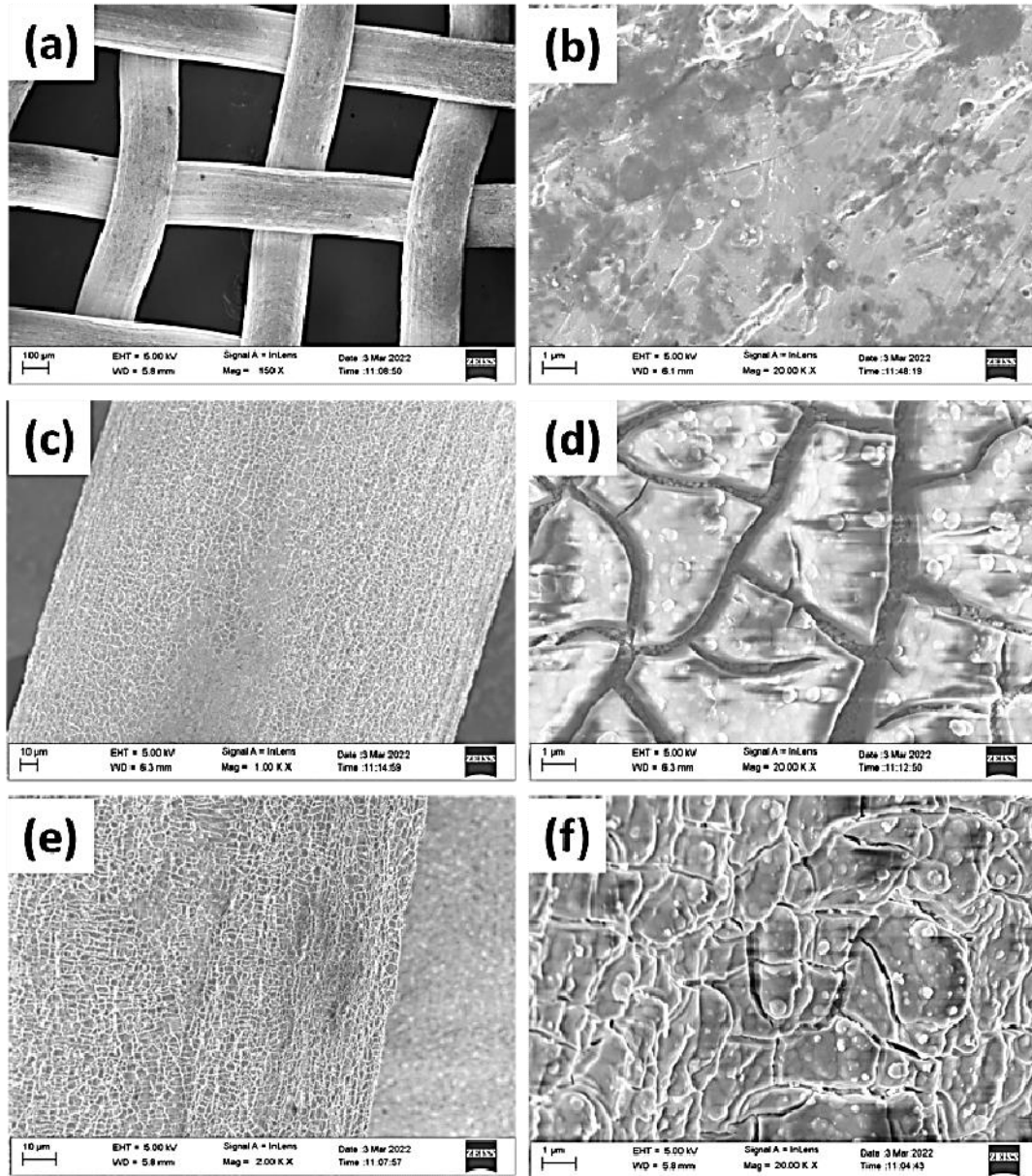


Fig 5.3: Field Emission Scanning Electron Microscopy images of Blank and Ni-SS electrodes. Low and high magnification images of (a) & (b) Blank SS, (c) & (d) Ni-SS-CA electrode and (e) & (f) Ni-SS-CP electrodes

5.1.2 Structural evaluation of the Ni-SS electrodes

Further the samples were taken for XRD analysis to evaluate the type of Ni deposition. Figure 5.4 shows the XRD pattern for blank, Ni-SS-CA-1.3 and Ni-SS-CP-0.02 electrodes. In addition to the characteristic peak corresponding to stainless steel (peaks at 51.07° , 59.73° , 89.57° and 111.39°) corresponding to (111), (200),

(220) and (311) planes respectively), weak peaks corresponding to α -Ni(OH)₂ phase (Song, Tang et al. 2002, Yang, Wang et al. 2005, Coudun, Grillon et al. 2006, Liu, Huang et al. 2010, Hall, Lockwood et al. 2015). was observed at 22.4° (001) and 42.60° (002) was observed in the case of Ni-SS-CA-1.3. Also, peaks related to (200) and (220) planes corresponding to metallic nickel is observed in the XRD pattern. This shows that CA assisted deposition resulted in a mixture of Ni (OH)₂ and Ni. For Ni-SS-CP-0.02 electrodes, signals corresponding to oxides, hydroxides and oxyhydroxide could not be detected. The deposition showed a contribution from metallic Ni ((200) planes) were discerned from the XRD pattern. Hence it is presumed that deposition by both CA and CP technique resulted in amorphous type of Nickel species with a minor contribution from metallic for Ni deposited on SS. Further micro-Raman analysis was conducted. The broad and weak features again confirm the formation of amorphous phase of Ni deposited. However, a weak peak at $\sim 520\text{ cm}^{-1}$ in both Ni-SS-CA-1.3 and Ni-SS-CP-0.02 shows the Ni-O stretching vibrational modes Ni-O-H bond (Hall, Lockwood et al. 2015). Intense Raman feature is observed at ~ 1384 and $\sim 1600\text{ cm}^{-1}$ shows the OH bending modes (E_g) and trapped OH bending modes, respectively in α -Ni (OH)₂. Whereas in the case of Ni-SS-CP-0.02 a broad feature at 820 cm^{-1} range shows the presence of α -Ni (OH)₂ (Hall, Lockwood et al. 2015). This peak was less intense in the case of Ni-SS-CA-1.3. Thus it can be concluded that galvanostatic deposition resulted in α phase of Ni(OH)₂, whereas potentiostatic deposition resulted in a mixture of α -Ni(OH)₂ and β -Ni(OH)₂ phases. It is reported that, when NiSO₄ precursor when used for electrodeposition, results in the formation of a mixture on α and β phases of Ni(OH)₂ with a dominant α -Ni(OH)₂ (Song, Tang et al. 2002, Yang, Wang et al. 2005, Coudun, Grillon et al. 2006, Liu, Huang et al. 2010, Hall, Lockwood et al. 2015). This further supports our observation.

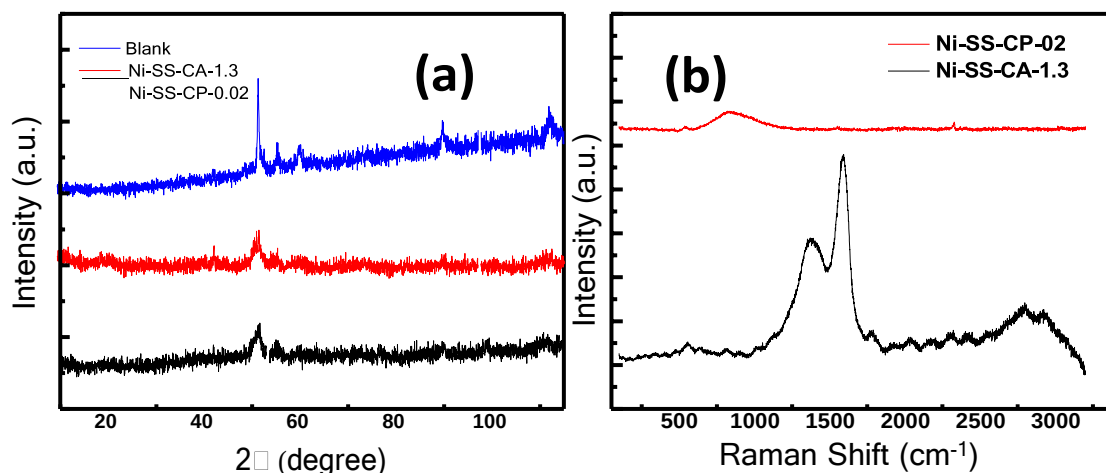


Fig 5.4: (a) X-Ray Diffraction pattern and (b) micro-Raman spectra of Ni-SS-CA-1.3 and Ni-SS-CP-0.02 electrodes

5.2 ELECTROCATALYTIC PROPERTIES OF Ni ELECTRODE:

Electrochemical studies are carried out for the Ni-SS electrodes to evaluate the oxygen evolution (OER) and hydrogen evolution (HER) activity. All the measurements were conducted in alkaline medium (1M KOH, pH13.5) and the potential all are reported with respect to Reversible Hydrogen Electrode (RHE). All the potential are corrected for iR , where I , catalytic current and R , solution resistance (~ 2 to 4 ohms).

Estimation of Electrochemical Surface area (ECSA) is an important step to identify number of active sites taking part in catalytic reaction and corresponding double layer capacitance (C_{dl}) is related to ECSA, Higher the C_{dl} higher is the ECSA. (Bard, Faulkner et al. 2001) For this, scan rate dependent CV was done in the potential ranges from 0.93 to 1.03 V vs RHE devoid of any faradaic contribution, and the double layer capacitance was measured. The double layer capacitance is directly proportional to the scan rate and the electrochemical surface area. Figure 5.5a shows a typical scan rate dependent CV recorded for Ni-SS-CA-1.3 sample and the current densities value are chosen at 0.98V both in anodic and cathodic region which corresponds to the absence of any other redox reaction. (Conway, Birss et al. 1997) From the plot of current density vs scan rate as shown in fig 5.5(b), the slope is extracted and is used to calculate C_{dl} . Fig 5.5 (c) and (d) shows the anodic current density vs scan rate plot for all the Ni-SS electrodes under investigation. From the

figure it is clear that the C_{dl} value for Ni-SS-CA-1.3 is higher than other samples. In a similar way, Ni-SS-CP-0.02 is higher than the other electrocatalyst as evident from fig 5.5(d). The estimated values for C_{dl} , roughness and ECSA tabulated and are shown in Table 5.1 and the R_f and ESCA values calculated to higher for Ni-SS-CA1.3.

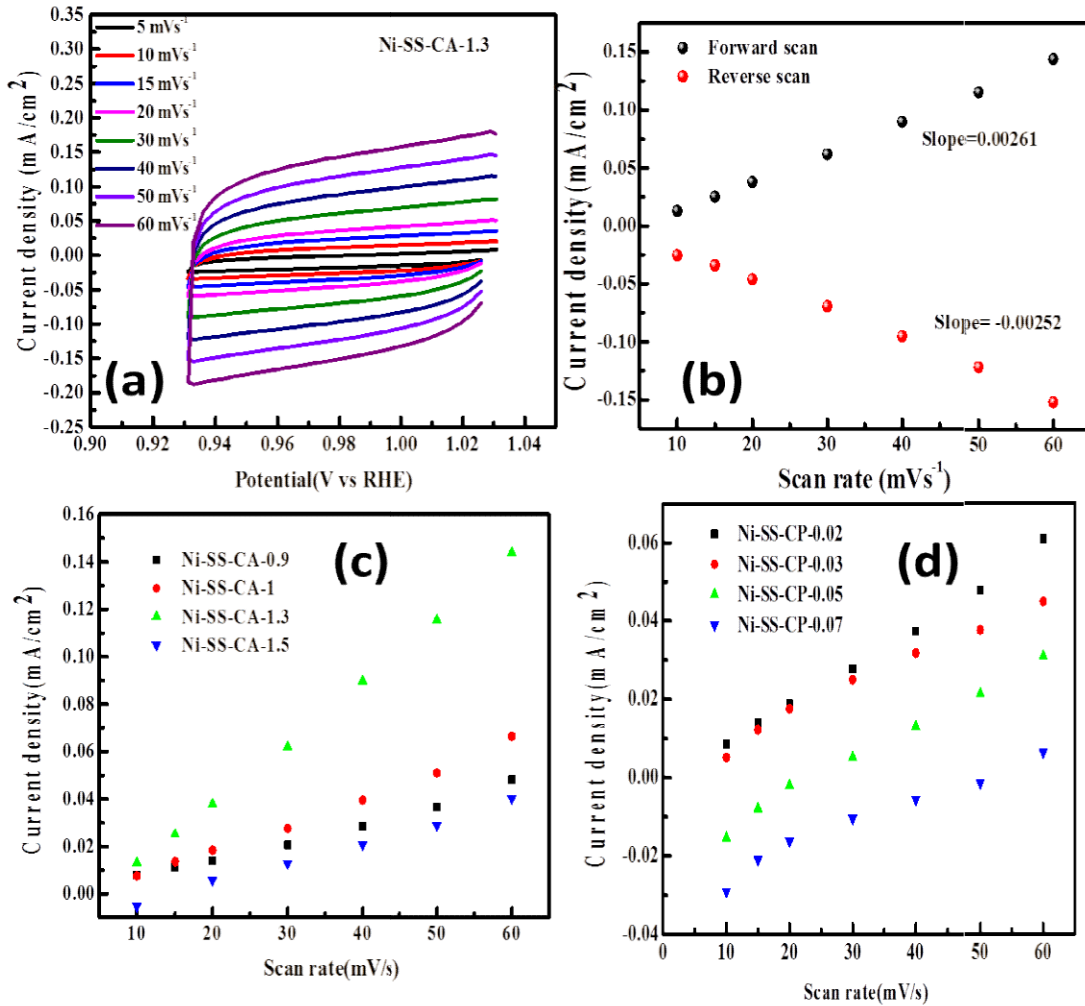


Fig 5.5: (a) CVs recorded at different scan rate in c_{dl} region for Ni-SS-CA-1.3 (b) current density at 0.98 V versus scan rate plot from which c_{dl} is extracted. (c) and (d) comparison of current densities variation with scan rate for different electrocatalyst sample.

Table 5.1: The ECSA and R_f estimated from C_{dl} and mass of nickel deposited on Ni-SS-electrodes.

Sample condition	Cdl Slope (mFcm ⁻²)	Roughness factor	Mass of Ni deposited (mgcm ⁻²)	ECSA (cm ² mg ⁻¹)
Ni-SS-CA-0.9	7.87X 10 ⁻⁴	0.0131	0.084	0.156
Ni-SS-CA-1	0.00114	0.0190	0.115	0.165
Ni-SS-CA-1.3	0.00261`	0.0435	0.239	0.182
Ni-SS-CA-1.5	8.697X 10 ⁻⁴	0.0144	0.340	0.042
Ni-SS-CP-0.02	0.00101	0.0168	0.203	0.083
Ni-SS-CP-0.03	7.53 X 10 ⁻⁴	0.0125	0.144	0.087
Ni-SS-CP-0.05	8.76 X 10 ⁻⁴	0.0146	0.236	0.062
Ni-SS-CP-0.07	6.33 X 10 ⁻⁴	0.0105	0.189	0.055

5.3. ELECTROCATALYTIC OER PERFORMANCE OF Ni-SS ELECTRODE:

Further, the electrocatalytic OER activity of the Ni-SS electrode developed under different conditions is studied. The electrode surface was refreshed for its electrochemical active sites by conducting 50 cyclic voltammogram cycles at a scan rate of 50 mVs⁻¹. Figure shows the linear sweep voltammogram (LSV) recorded at 2 mVs⁻¹ in 1 M KOH in a potential window of 1.2 to 1.6 V vs RHE. From the LSV plots it is observed that, the current density value was higher in the case of Ni-SS-CA-1.3 (Figure 5.6 a) and Ni-SS-CP-0.02 (Figure 5.6 b). The improvement in the activity for these electrodes is attributed to the higher ECSA obtained as evident from Figure 5.5 and Table 5.1. Further Tafel region is extracted from the LSV plot and the Tafel slopes values estimated from log(j) vs potential plots (Figure 5.6(c) and (d)). A lower Tafel slope value represents the faster kinetics for OER process. From fig 5.6(c) and

(d) we can easily say that Ni-SS-CA-1.3 and Ni-SS-CP-0.02 has lower tafel slope value (42.42 and 48.49 mVdec⁻¹, respectively) showing improved OER kinetics. The overpotential for the current densities of 10mAcm⁻², 25mAcm⁻², and 50mAcm⁻² are extracted for the electrocatalyst sample from LSV and is given in the fig 5.7 (a) and (b). From fig 5.7 it is clear that Ni-SS-CA-1.3 and Ni-SS-CP-0.02 has lower overpotential value at different current densities. Thus, the catalytic activity is improved when nickel is electrodeposited in the SS mesh which is attributed to the overall contribution from surface morphology, more number of electrochemical actives sites, highly active Ni(OH)₂ formation and conductivity. The electrochemical parameters such as Tafel slope, over potential and current density extracted from LSVs are tabulated in Table 5.2. Turn over frequency and mass activity calculated as given in Table 5.3 corroborates with the electrochemical measurements obtained. Based on the electrochemical parameters obtained, Ni-SS-CA-1.3 was the optimum electrodes for efficient OER with respect to OER kinetics, low overpotential and current density values.

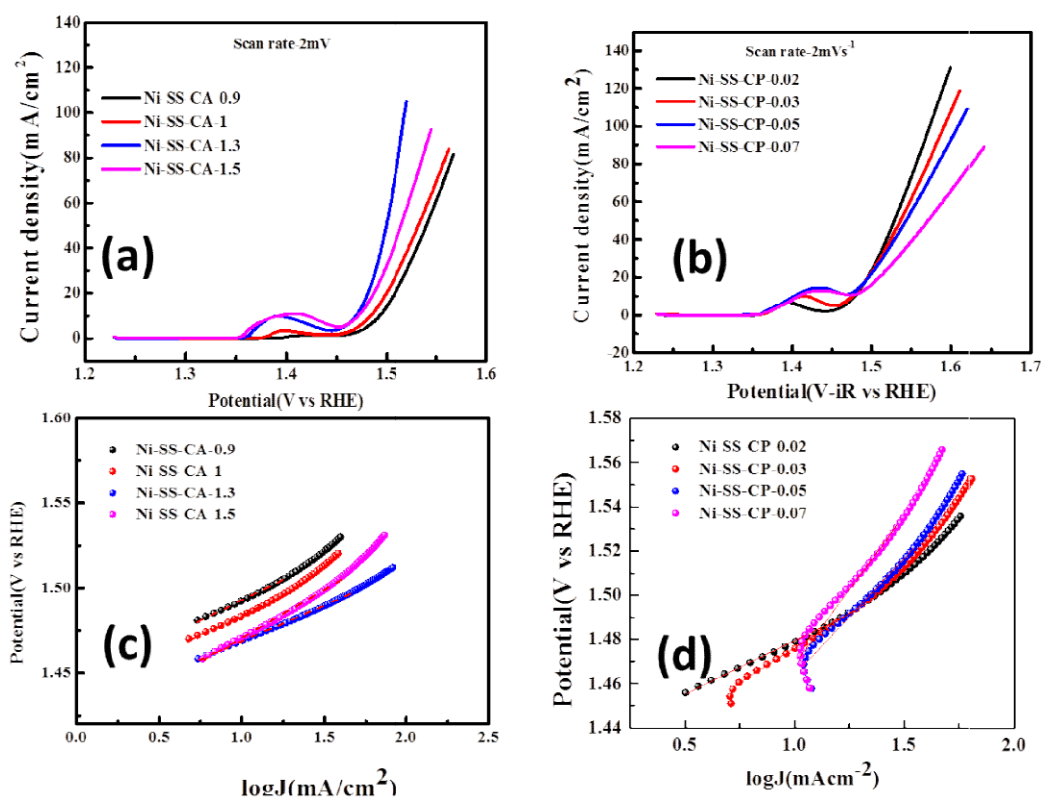


Fig 5.6: (a) and (b) LSVs recorded for the Ni-SS electrodes electrocatalyst at scan rate of 2mVs^{-1} (c) and (d) potential Vslog(J) plot from which tafel slope is extracted.

Table.5.2: The tafel slope value and current densities at different potential 250mV, 300mV, 350mV for Ni-SS electrodes

Samples condition	Tafel slope mVdec^{-1}	Current density at 250mV, (mAcm^{-2})	Current density at 300mV, (mAcm^{-2})	Current density 350 mV, (mAcm^{-2})
Ni-SS-CA-0.9	47.8	5.38	39.53	87.39
Ni-SS-CA-1	46.7	9.05	48.21	103.82
Ni-SS-CA-1.3	42.42	19.55	117.77	137.31
Ni-SS-CA-1.5	56.6	14.99	71.57	117.81
Ni-SS-CP-0.02	48.49	11.22	51.975	108.76
Ni-SS-CP-0.03	62.86	12.12	45.46	89.38
Ni-SS-CP-0.05	105.8	12.96	41.64	78.28
Ni-SS-CP-0.07	134.7	11.66	29.27	55.34

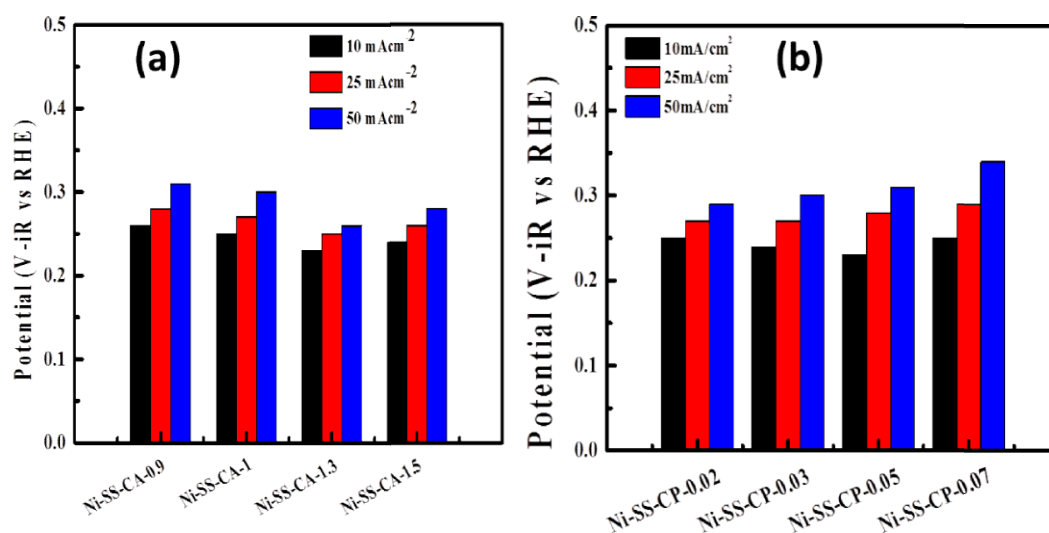


Fig 5.7: The overpotential (η) of Ni-SS electrodes for OER reaction at current density of 10mAcm^{-2} , 25mAcm^{-2} , 50mAcm^{-2} .

Table 5.3: Showing the turnover frequency values and mass activity at different overpotential 200mV, 250mV and 300mV for Ni-SS electrodes

Condition	Mass (mgcm^{-2})	TOF at 200mV (10^{-2}s^{-1})	TOF at 250mV (10^{-2}s^{-1})	TOF at 300mV (10^{-2}s^{-1})	MA at 200mV (Ag^{-1})	MA at 250mV (Ag^{-1})	MA at 300mV (Ag^{-1})
Ni-SS-CA-0.9	0.084	0.0097	0.071	0.158	64.01	470.3	1039.7
Ni-SS-CA-1	0.115	0.012	0.064	0.137	78.58	418.6	901.4
Ni-SS-CA-1.3	0.239	0.012	0.075	0.088	81.81	492.8	574.6
Ni-SS-CA-1.5	0.34	0.0067	0.032	0.053	44.03	210.2	346.1
Ni-SS-CP-0.02	0.203	0.0084	0.039	0.081	55.19	255.7	535.1
Ni-SS-CP-0.03	0.144	0.0128	0.048	0.094	83.95	314.9	619.1
Ni-SS-CP-0.05	0.236	0.008	0.027	0.051	54.98	176.6	332.1
Ni-SS-CP-0.07	0.189	0.009	0.023	0.044	61.49	154.3	291.8

For an alkaline or AEM based electrolyser, an efficient HER generating electrode is necessary which should be active and stable in alkaline medium. With this intention to evaluate the bi-functional activity of the electrodes developed further HER activity of the electrodes were studied in 1 M KOH under argon gas purging and all potentials are reported with respect to RHE. LSVs are recorded at a scan rate of 2mVs^{-1} after 50 cycles of CV for refreshing the catalytic surface. Fig 5.8 (a) and (c) represent the LSVs of different electrodes developed. Among these electrocatalyst samples Ni-SS-CA-1 and Ni-SS-CP-0.02 has higher current density values and the HER kinetics were also higher because of higher surface area and conductivity of nickel deposited SS electrodes. Fig 5.8 (b) and (d) represent the potential versus $\log(J)$ plot from

which the Tafel slope is extracted. In the present study, Ni-SS-CA-1 and Ni-SS-CP-0.02 has lower Tafel slope value and hence higher kinetics for HER process. From the LSVs, we can calculate the overpotential at different current densities (fig 5.9 (a) & (b)). The overpotentials required generating different current densities of 10mAcm^{-2} , 25mAcm^{-2} , 50mAcm^{-2} was plotted as fig 5.9 (a) and (b) Ni-SS-CA-1 and Ni-SS-CP-0.02 has lower overpotential for all current density values indicating its high activity towards HER. Considering Ni-SS-CA-1.3 electrode, the activity towards HER is more or less similar to Ni-SS-CA-1 where the tafel slope value is $\sim 134\text{ mVdec}^{-1}$ and $\square$ to generate 10 mAcm^{-2} current is 200 mV . Hence, Ni-SS-CA-1.3 can be considered as a bi-functional electrode for overall water splitting process and is a suitable candidate to use as a cathode and anode materials in alkaline exchange membrane based electrolyser. All the electrochemical parameters extracted for HER process are tabulated and given as Table 5.4. Turn over frequency and mass activity calculated as given in Table 5.5 also confirms that Ni-SS-CA-1 and Ni-SS-CP-0.02 have better access of catalytic sites for HER reaction.

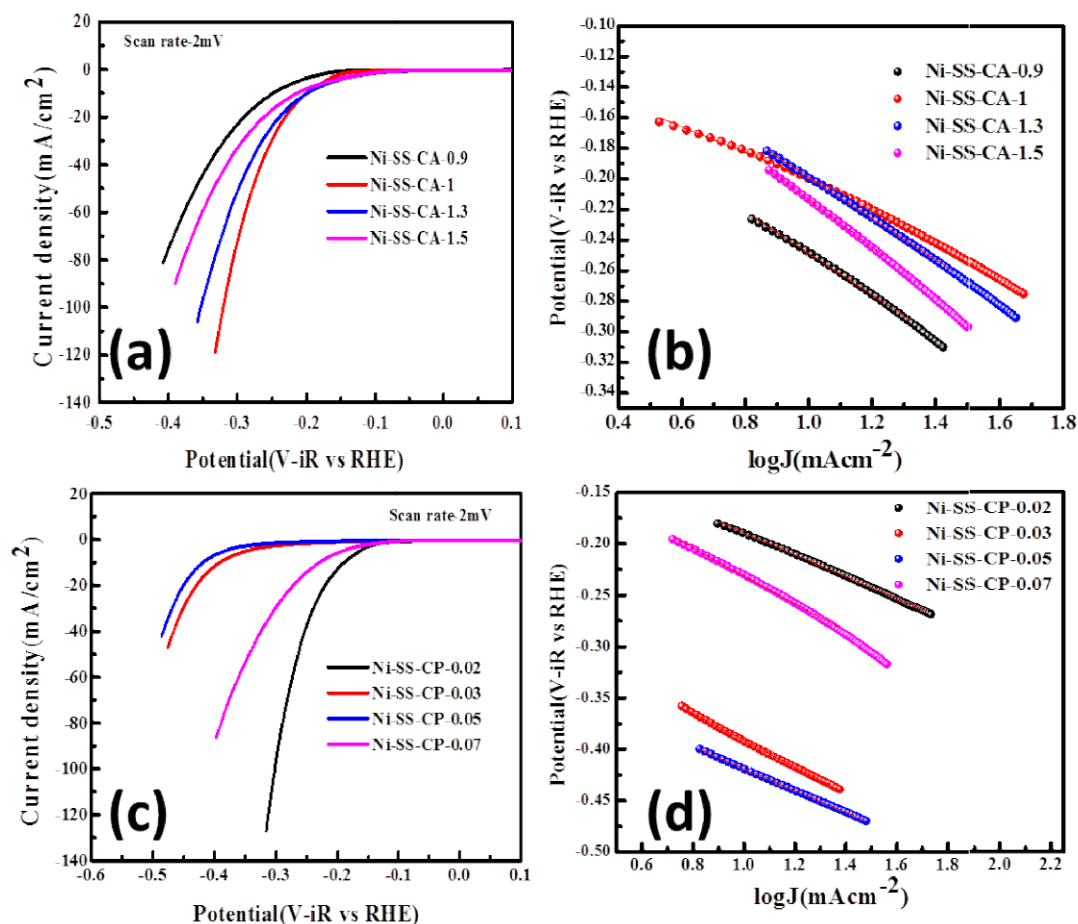


Fig 5.8: (a) and (c) LSVs of Ni-SS electrodes at scan rate of 2mVs^{-1} (b) and (d) Tafel slope plot.

Table 5.4: Electrochemical parameters such as tafel slope value and current densities at different potential 200mV, 250mV, 300mV for Ni-SS electrodes

Samples	Tafel slope, mVdec^{-1}	Current density at 200mV, (mAcm^{-2})	Current density at 250 mV, (mAcm^{-2})	Current density at 300mV, (mAcm^{-2})
Ni-SS-CA-0.9	134.9	-3.95	-10.66	-23.09
Ni-SS-CA-1	84.8	-8.48	-17.41	-33.05
Ni-SS-CA-1.3	134.9	-10.58	-24.41	-51.45
Ni-SS-CA-1.5	156.11	-10.48	-29.72	-72.89
Ni-SS-CP-0.02	106.9	-12.84	-37.69	-96.82
Ni-SS-CP-0.03	129.4	-0.98	-1.59	-2.63
Ni-SS-CP-0.05	106.2	-0.65	-0.89	-1.41
Ni-SS-CP-0.07	135.27	-5.84	-14.28	-29.55

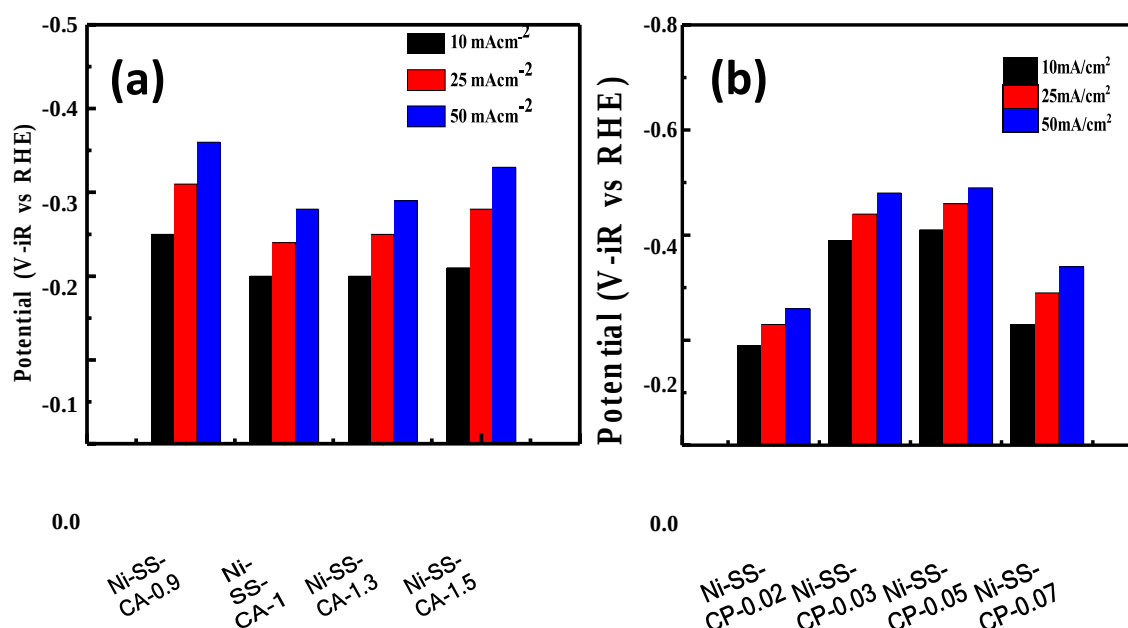


Fig 5.9: Over-potential at different current densities 10mAcm^{-2} , 25mAcm^{-2} and 50mAcm^{-2} for Ni-SS electrodes

Table 5.5: The turnover frequency value and mass activity at different overpotential 200mV, 250mV and 300mV for Ni-SS electrodes

Condition	Mass (mgcm ⁻²)	No.of .moles	TOF at 200mV (10 ⁻² s ⁻¹)	TOF at 250mV (10 ⁻² s ⁻¹)	TOF at 300mV (10 ⁻² s ⁻¹)	MA at 200mV (Ag ⁻¹)	MA at 250mV (Ag ⁻¹)	MA at 300mV (Ag ⁻¹)
Ni-SS-CA-0.9	0.084	1.432 X 10 ⁻⁰⁶	-0.0143	-0.038	-0.084	-46.99	-126.83	-274.72
Ni-SS-CA-1	0.115	1.96 X 10 ⁻⁰⁶	-0.022	-0.046	-0.087	-73.63	-151.17	-286.97
Ni-SS-CA-1.3	0.239	4.07 X 10 ⁻⁰⁶	-0.013	-0.031	-0.065	-44.27	-102.15	-215.30
Ni-SS-CA-1.5	0.340	5.79 X 10 ⁻⁰⁶	-0.009	-0.026	-0.065	-30.78	-87.29	-214.1
Ni-SS-CP-0.02	0.203	3.46 X 10 ⁻⁰⁶	-0.019	-0.056	-0.145	-63.17	-185.42	-476.31
Ni-SS-CP-0.03	0.144	2.46 X 10 ⁻⁰⁶	-0.002	-0.003	-0.005	-6.79	-11.014	-18.22
Ni-SS-CP-0.05	0.236	4.01 X 10 ⁻⁰⁶	-0.0001	-0.001	-0.002	-2.76	-3.775	-5.98
Ni-SS-CP-0.07	0.189	3.23 X 10 ⁻⁰⁶	-0.023	-0.023	-0.047	-75.31	-75.31	-155.8

5.4 EFFECT OF DEPOSITION TIME IN OER AND HER ACTIVITY OF Ni-SS ELECTRODE:

Further to optimize the deposition time, electrodes were fabricated as a function of deposition time and the CA assisted deposition was chosen with an applied potential of -1.3 V. After running CV for 50 cycles for catalytic surface activation OER studies were performed. Typical CVs for electrodes fabricated under different time of deposition is shown in Figure 5.10. The current density values were increasing with increase in deposition time and there after the values were more or less constant representing those maximum available surface-active sites are saturated at a deposition time of 120 s. (Tian, Zhou et al. 2007) Thereafter, from the scan rate dependent CV, Cdl are calculated by plotting current density at 0.98V against scan rate and the slope is extracted from the linear plot as shown in Figure 5.10. From the plots it is seen that for both anodic and cathodic current densities, the slope values are higher for 120s at all scan rate values. From the mass deposited on the

electrode surface (estimated by ICP AES), roughness factor and ECSA was estimated as a function of deposition time and is tabulated as Table 5.6.

Thereafter, Linear Sweep Voltammetry (LSV) is recorded for both OER and HER which was shown in the fig 5.11 (a) and (c). A higher current density is observed for Ni-SS-CAS-1.3 electrode with a deposition time of 120 s both in OER and HER curve. The Tafel slopes calculated for OER was lower indicating higher kinetics towards and the corresponding Tafel slopes as shown in fig 5.11 (b). Whereas for HER a higher Tafel slope is observed for electrodes fabricated with a deposition time of 120 s. the change in η required to generate desired current density, current density at different η values are tabulated in Table 5.7 and 5.8. The overpotential η required for generating current densities are plotted both for HER and OER process as a function of deposition time is calculated and is given in the fig 5.12 (a) and (b). From the fig 5.12 it is shown that 120s has lower overpotential value in both OER and HER. Table 5.9 and 5.10 shows the tabulated Turn over frequency and mass activity calculated and shows that samples deposited at 120 s have optimum number of catalytic sites for OER and HER reaction.

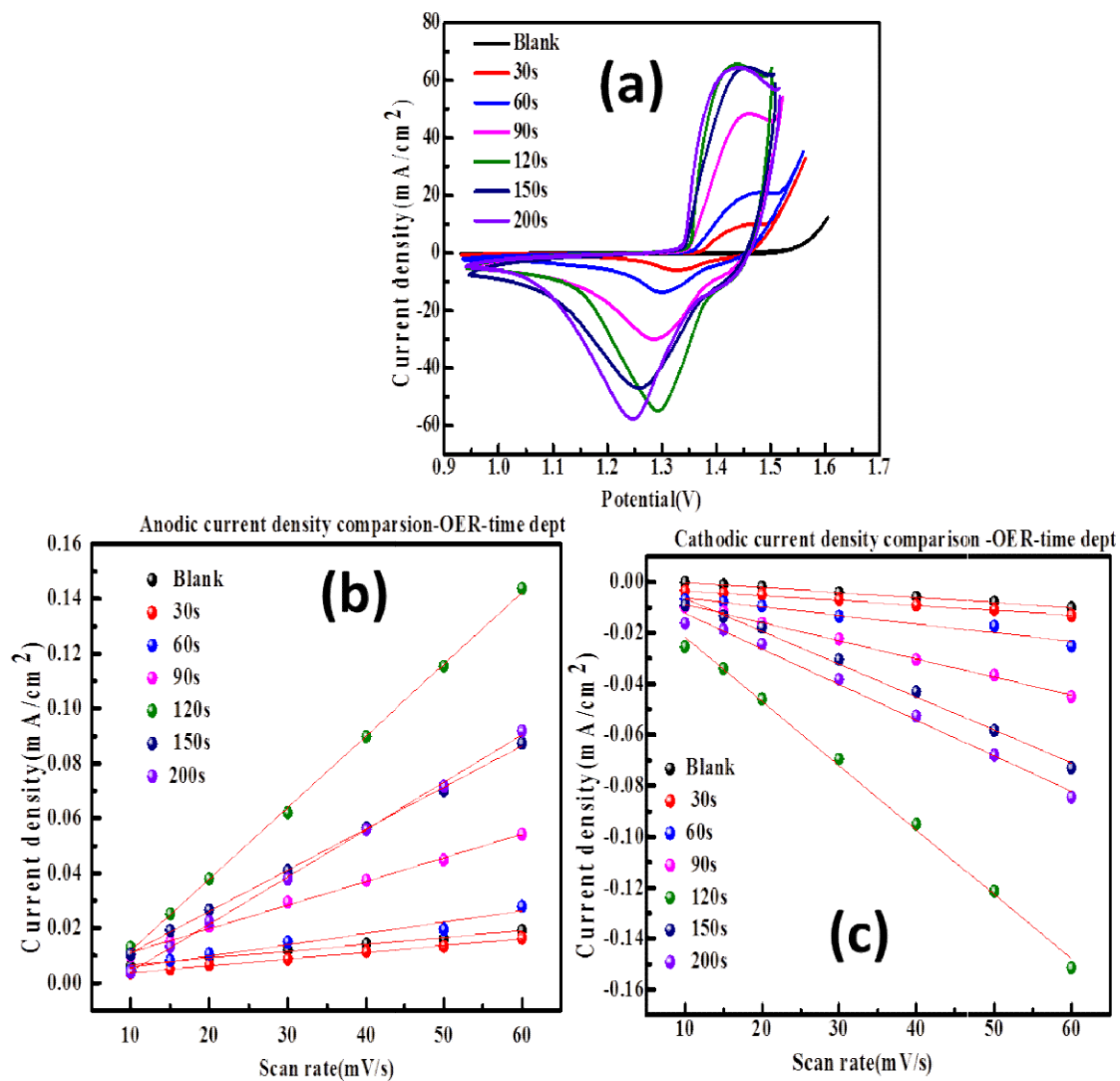


Fig 5.10: (a) Cyclic voltammetry recorded at different time with potential from 0.9 to 1.6 V. (b) Comparison of variation in different current densities at 0.98 V with scan rate.

Table 5.6: The ECSA and Roughness factor value estimated from c_{dl} slope and mass of Ni deposited on Ni-SS electrode.

Condition	Cdl slope (mFcm ⁻²)	roughness factor	Mass deposited (mgcm ⁻²)	ECSA (cm ² mg ⁻¹)
Blank	2.49 X10 ⁻⁰⁴	4.15 X10 ⁻⁰³	0	
30s	2.47 X10 ⁻⁰⁴	4.12 X10 ⁻⁰³	0.041	9.95 X10 ⁻⁰²
60s	4.14 X10 ⁻⁰⁴	6.90 X10 ⁻⁰³	0.085	8.06 X10 ⁻⁰²
90s	8.63 X10 ⁻⁰⁴	1.44 X10 ⁻⁰²	0.072	2.00 X10 ⁻⁰¹
120s	2.61 X10 ⁻⁰³	4.35 X10 ⁻⁰²	0.123	3.54 X10 ⁻⁰¹
150s	1.51 X10 ⁻⁰³	2.52 X10 ⁻⁰²	0.19	1.33 X10 ⁻⁰¹
200s	1.73 X10 ⁻⁰³	2.88 X10 ⁻⁰²	0.23	1.28 X10 ⁻⁰¹

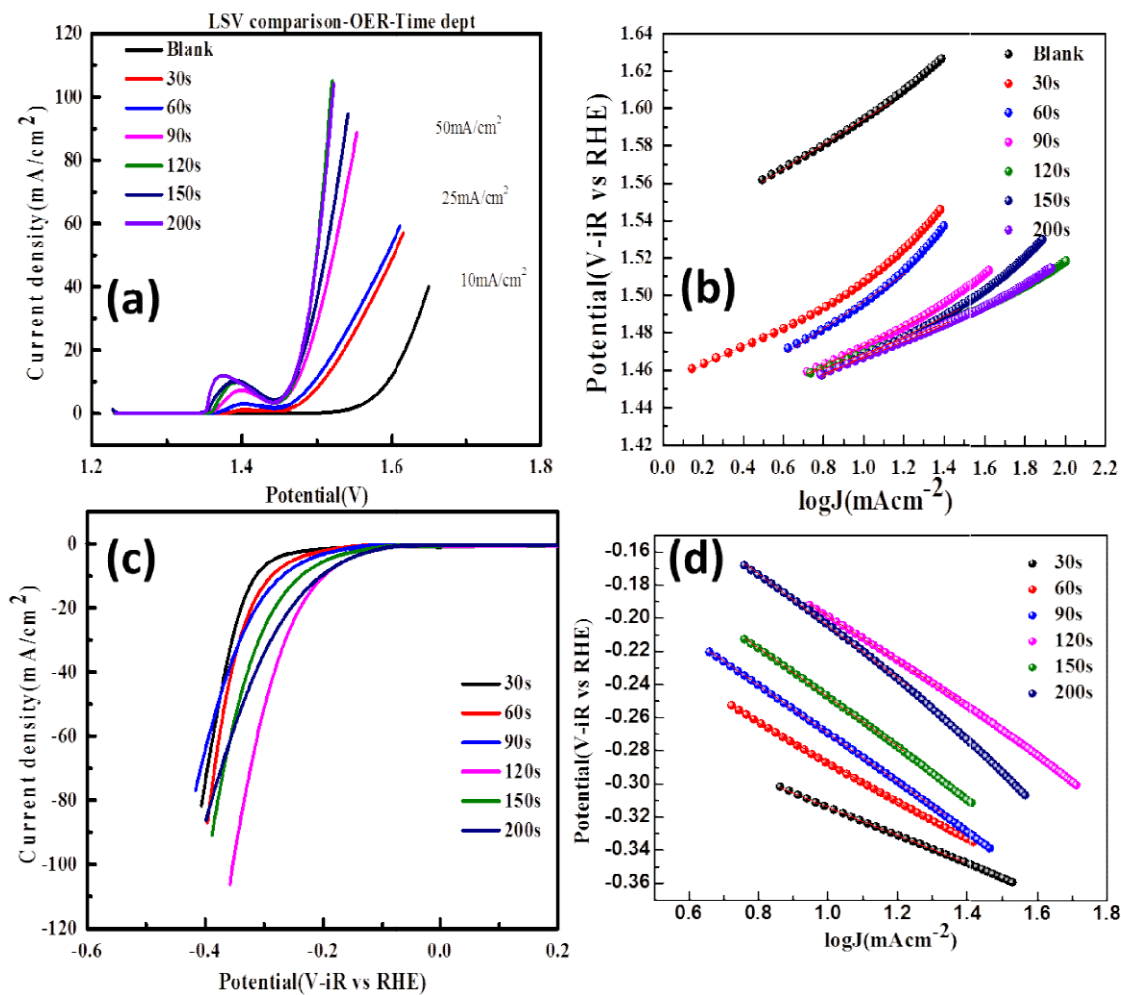


Fig 5.11: LSV of different time of Ni-SS-CA-1.3 with scan rate of 2mVs^{-1} (b) and (d) tafel slope plot.

Table 5.7:The tafel slope value and current density at different overpotential 250mV, 300mV and 350mV for various condition of time.

Condition	Tafel slope (mVdec^{-1})	Current density at 250mV, (mAcm^{-2})	Current density at 300mV, (mAcm^{-2})	Current density at 350mV, (mAcm^{-2})
Blank	66.4	0.11	1.16	6.60
30s	50.16	4.00	18.18	39.80
60s	72.48	6.14	22.84	44.63
90s	52.58	14.49	59.97	91.69
120s	39.8	23.06	123.14	139.39
150s	52.7	18.14	76.85	115.14
200s	42.76	21.36	109.15	138.37

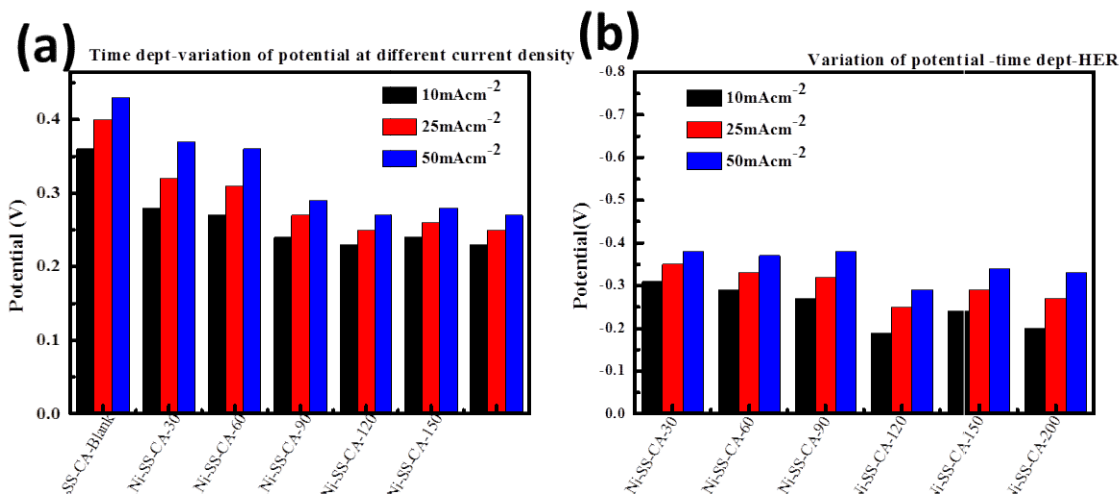


Fig 5.12: Overpotential of different current densities 10mAcm^{-2} , 25mAcm^{-2} and 50mAcm^{-2} for Ni SS-CA electrode deposited at different time duration

Table 5.8: The tafel slope value and current density at different overpotential 200mV, 250mV and 300mV for various condition of time.

Condition	Tafel slope (mVdec^{-1})	Current density at 200mV, (mAcm^{-2})	Current density at 250 mV, (mAcm^{-2})	Current density at 300mV, (mAcm^{-2})
30s	84.6	-2.01	-2.78	-7.27
60s	118	-2.27	-5.28	-12.99
90s	145.7	-3.37	-7.49	-16.33
120s	147.9	-10.58	-24.41	-51.45
150s	156	-5.69	-12.46	-26.37
200s	134	-10.27	-19.25	-34.52

Table 5.9: The turnover frequency value and mass activity values at different overpotential 250 mV, 300 mV and 350 mV for different deposition time.

Condition	Mass (mgcm^{-2})	TOF at 250mV (10^{-2}s^{-1})	TOF at 300mV(10^{-2}s^{-1})	TOF at 350mV(10^{-2}s^{-1})	MA at 250mV(Ag^{-1})	MA at 300mV(Ag^{-1})	MA at 350mV(Ag^{-1})
30s	0.041	0.0147	0.067	0.146	96.64	439.25	961.61
60s	0.085	0.011	0.041	0.079	71.80	267.09	521.92
90s	0.072	0.031	0.127	0.194	201.62	834.44	1275.79
120s	0.123	0.028	0.153	0.173	187.90	1003.40	1135.82
150s	0.189	0.015	0.062	0.092	95.64	405.19	607.07
200s	0.22	0.014	0.074	0.094	94.87	484.82	614.61

Table 5.10: The turnover frequency value and mass activity values at different overpotential 200 mV, 250 mV and 300 mV for various condition of time.

Condition	Mass (mgcm ⁻²)	TOF at 200mV (10 ⁻² s ⁻¹)	TOF at 250mV (10 ⁻² s ⁻¹)	TOF at 300mV (10 ⁻² s ⁻¹)	MA at 200mV (Ag ⁻¹)	MA at 250mV (Ag ⁻¹)	MA at 300mV (Ag ⁻¹)
30s	0.042	-0.0148	-0.021	-0.053	-48.564	-67.168	-175.651
60s	0.086	-0.008	-0.019	-0.046	-26.546	-61.746	-151.909
90s	0.072	-0.0143	-0.032	-0.069	-46.891	-104.218	-227.219
120s	0.123	-0.026	-0.061	-0.127	-86.211	-198.905	-419.24
150s	0.189	-0.009	-0.02	-0.0423	-30	-65.694	-139.033
200s	0.225	-0.014	-0.026	-0.046	-45.617	-85.504	-153.33

Further to see the effect of Ni deposition on polished surface, electrodeposition of nickel was carried out on polished stainless-steel coupon (1200 grit) with a geometrical surface dimension of $1 \times 1 \text{ cm}^2$. Once the electrodeposition is done, electrochemical studies towards OER and HER activities are carried out in 1M KOH (pH-13.5) and the potential are measured with respect to RHE. To start with, the double layer capacitance is calculated from non-faradic capacitive current region and from the current density values at 0.98 V as a function of scan rate and corresponding plot is shown in fig 5.13 (b). The slope value obtained are more or less similar to the one deposited on Ni mesh (0.002 mF), hence it concluded that the type SS surface does not have significant influence in generating number of electrochemically active sites using current approach (chronoamperometric electrodeposition).

Further, LSV is carried out towards OER reaction for Ni-SS coupons both for HER and OER (Fig 5.13 c). To generate a current density of 10 mAcm^{-2} , η required is 300 mV and the Tafel slope calculated is 79.5 mVdec^{-1} (Figure 5.13 d). Similarly for HER process, for 10 mAcm^{-2} current density, η required is 300 mV as observed from LSV (Figure 5.13 e). The Tafel slope value is $\sim 129 \text{ mVdec}^{-1}$ for HER reaction (Figure 5.13f). From the studies it is evident that SS surface when modified with Ni, irrespective

of the surface texture, a stable coating can be introduced for efficient OER and HER activity.

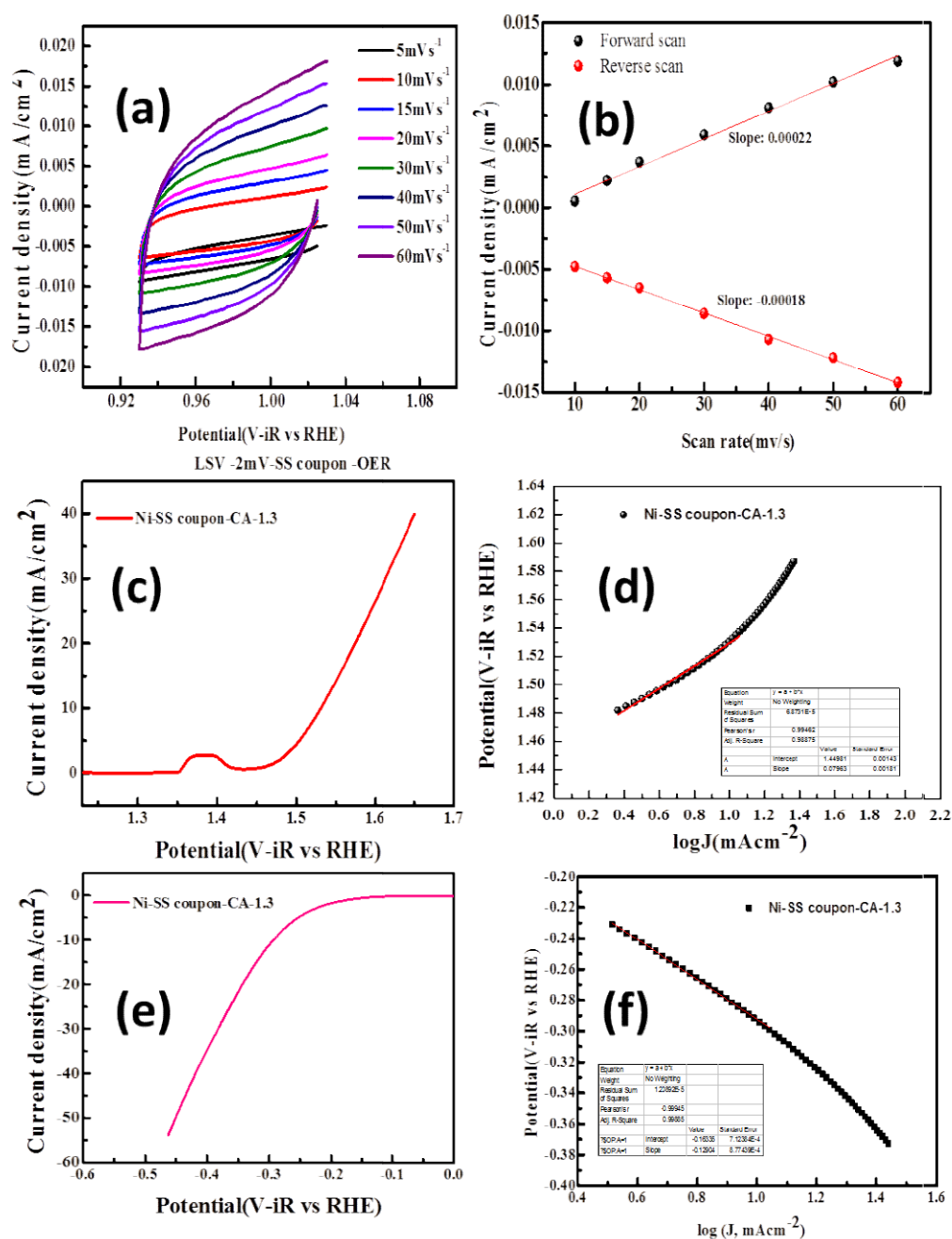


Fig 5.13: (a) CVs recorded at 6 different scan rate in the cdl region. (b) C_{dl} slope, (c) and (e) LSV of Ni-SS-CA-1.3 for OER and HER., (d) and (f) tafel plot for OER and HER.

5.5 Long Term Stability Evaluation of Optimized Ni-SS Electrode:

It is important to evaluate the long-term stability of the developed electrode to ensure the commercial utility. In this study, stability tests for the electrode were tested for oxidation reaction (OER), both under three electrodes and two electrode mode for a time period of 10 hours. A constant potential of 1.6 V vs RHE in 3 electrode mode and a current density of 66 mAcm^{-2} was generated initially and over a period of 10 hours the current density increased slightly (70 mAcm^{-2}) and the current density – time transient is given in Figure 5.14b. This is attributed to the favourable surface restructuring of Nickel coating. (Li, Wang et al. 2011) CV recorded before and after long term stability as given in Figure 5.14c showed no significant change in Ni redox sites (post CV was carried out in fresh KOH electrolyte Figure 5.14c. This was further confirmed by the LSV plots recorded both in used electrolyte (Fig 5.14d) and fresh electrolyte (Fig 5.14e). A long-term stability was also carried out under in 2 electrodes by applying a potential of 1.6 V and the current generated was constant for a period of 10 hours. Thus, the present study shows that the developed electrodes are stable and suitable for long time operation of electrolyzers with no change in catalytic activity. Post analysis showed no change in morphology and structural changes confirm the integrity of the electrodes. A typical drainage method was used to quantify the H_2 production over a specific time. It shows that approximately 12ml of H_2 was generated in 100s which is equal to the theoretical value (12.67ml) and the oxygen generated is approximately 6ml. Therefore, the faradaic efficiency is 94.7%.

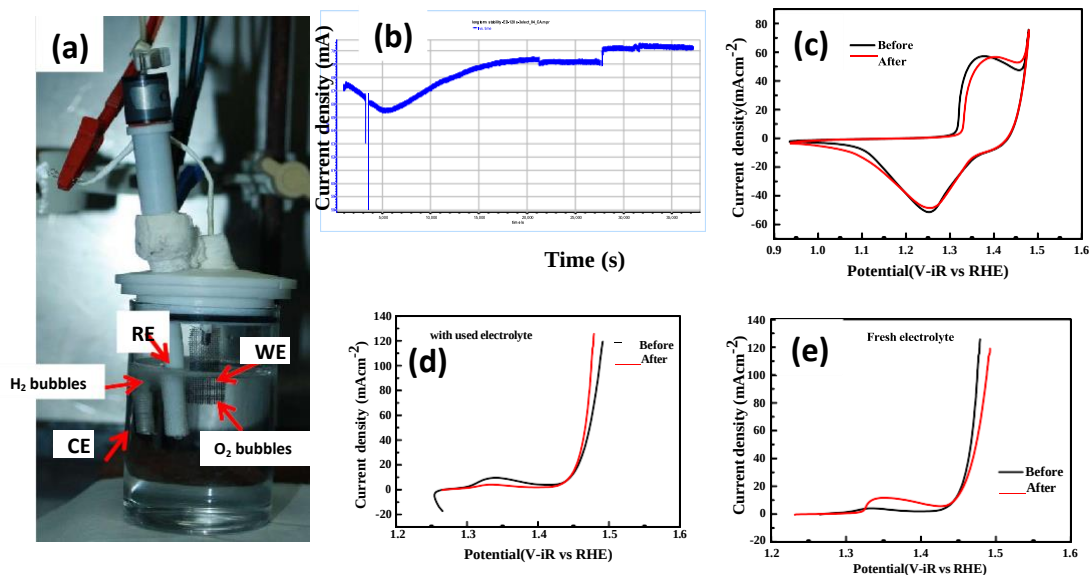


Fig 5.14: (a) image of electrochemical cell (b) Current-time transient plot for long term stability (c) CV recorded for before and after long term stability (d)and (e) LSV recorded for both used and fresh electrolyte

Table 5.11: Comparison of tafel slope and overpotential values for both OER and HER of present studies and reported literatures.

Sample	Method of deposition	Electrolyte	η (mV) for 10mAcm ⁻²		Tafel slope (mVdec ⁻¹)		Reference
			OER	HER	OER	HER	
Present study	Electrodeposition (Constant potential)	1 M KOH	260	290	42.2	84.8	
Nickel-Iron hydroxide on sintered stainless steel felt(SSF)	Electrodeposition	1 M KOH	210	100	42	120	(Zhu, Duan et al. 2020)
Ni-Fe hydroxide/oxide on 316 stainless steel	Electrodeposition	1 M KOH	254	-	-	-	(Todoroki, Wadayama et al. 2019)
Ni-Fe oxides species316 stainless steel	Electrochemical approach followed by galvanic replacement	6 M NaOH	-	-	29	101	(Sultana, Fernando et al. 2020)
Ni plated SS mesh	Electroplating	0.87M sodium sulfate, 0.21M nickel chloride and boric acid	800 m V vs Ag/AgCl				
Mild steel	Electrodeposition	1 M KOH	267	-	66	-	
Sulfurized stainless steel	Sulfurization	1 M KOH	136	262	42	147	(Liu, You et al. 2017)
Ni-Fe oxide on stainless steel mesh	Electrodeposition	1 M KOH	277	217	51	130	

Ni-Fe oxides on stainless steel	Electro- oxidation	0.1 M KOH	269.2	-	66	-	(Schäfer, Sadaf et al. 2015).
N-doped anodised stainless steel	Anodisation		225	-	49.7	-	(Yao, Sun et al. 2019)
Stainless steel scrubber	-	1 M KOH	418	315	63	121	(Anantharaj, Chatterjee et al. 2018)
N, P-doped on the stainless steel	Solid diffusion & phosphorisation process	-	231	172	88	125	(Li, He et al. 2021)
Ni and P on Stainless steel fibre	Chemical bath deposition and phosphorisation	-	223	149	-	-	(Gao, Xiong et al. 2019)
S- doped bimetallic Fe/Ni oxy(hydroxide) on carbon cloth & stainless steel mesh	Electroplating	-	248	-	77	-	(Kahnamouei and Shahrokhian 2021)
Ni-Fe oxy hydroxide on stainless steel	Two step fabrication procedure	1 M KOH	280	-	-	-	(Shen, Wang et al. 2018)

CHAPTER 6

SUMMARY AND CONCLUSION

Major findings and highlights of the present thesis is given below

1. Development of efficient SS based electrodes bearing Ni based catalyst was done by a scalable and cost-effective electrochemical deposition route. Both chronopotentiometric and chronoamperometric electrodeposition were explored for achieving the desirable phase for catalytic reaction.
2. Morphological and structural analysis showed a uniform deposition of Ni both in chronoamperometric and chronopotentiometric deposition. Preferential growth of $\square$ -Ni(OH)₂ was revealed from micro-Raman analysis which can actively participate in Ni²⁺ to Ni³⁺ reaction favoring the Electrocatalytic process of interest.
3. Electrochemically active surface area was calculated to evaluate the active sites available for catalytic reaction. Process parameters, applied potential, current and time of deposition were optimized to see the best catalytic activity towards OER reaction.
4. Ni-SS-CA-1.3 electrode, prepared by chronoamperometric technique at a constant potential of -1.3 V vs Ag/AgCl for deposition duration of 120 s, was found to be the best for OER reaction corroborating the ECSA values.
5. Further, to assess the Bi-functional activity of the electrodes HER activity was tested and process parameters were optimized. The Tafel slopes for OER and HER reaction were found to be 42.4 and 84.8 mVdec⁻¹, respectively, indicating the utility of the developed electrodes for future electrolyzers. Also, the overpotential obtained for generating a current density of 50 mAcm⁻² was lower ($\square$ =260 mV and 290 mV respectively for HER and OER reactions) when compared to the values reported in literature. A comparison of Tafel slope and over potential values obtained in the present study and reported literature are given as Table 6.1.
6. Electrocatalytic activity of Ni coated on Polished SS surface (SS-316, 1200 grit) was also evaluated to check the substrate effect. The Tafel slope of 79.5 mVdec⁻¹

¹and $\sim 129 \text{ mVdec}^{-1}$ was obtained for HER and OER reaction showing that surface texturing plays a role in altering the kinetics of the reaction.

7. Long term stability of the catalyst at high current densities is a challenge. Present studies showed that the catalyst modified electrodes are stable and undergo no phase change after 20 hours of operation. The post electrochemical analysis confirmed no significant change in electrochemical activity reflecting its long-term integrity.
8. The hydrogen generated is approximately 12ml for 100s and oxygen generated is approximately 6ml for 100s. Thus, the faradaic efficiency is 94.7%

REFERENCE

1. Ahmed, Z. "Electrodeposited copper on indium tin oxide. Reaction and nucleation mechanisms." *Academic Perspective Procedia* 1(1),2018, 565-571.
2. Anantharaj, S., Chatterjee, S., Swaathini, K. C., Amarnath, T. S., Subhashini, E., Pattanayak, D. K., & Kundu, S. "Stainless steel scrubber: a cost-efficient catalytic electrode for full water splitting in alkaline medium". *ACS Sustainable Chemistry & Engineering*, 6(2), 2018, 2498-2509.
3. Balogun, M. S., Qiu, W., Huang, Y., Yang, H., Xu, R., Zhao, W., ... & Tong, Y. "Cost-Effective Alkaline Water Electrolysis Based on Nitrogen-and Phosphorus-Doped Self-Supportive Electrocatalysts". *Advanced Materials*, 29(34),2017 1702095.
4. Bandarenka, A. S., Ventosa, E., Maljusch, A., Masa, J., & Schuhmann, W. Techniques and methodologies in modern electrocatalysis: evaluation of activity, selectivity and stability of catalytic materials. *Analyst*, 139(6), 2014 1274-1291.
5. Bard, A. J., & Faulkner, L. R. "Electroactive layers and modified electrodes". *Electrochemical methods: Fundamentals and applications*, 2,2001, 580-631.
6. Bertuccioli, L., Chan, A., Hart, D., Lehner, F., Madden, B., & Standen, E. Study on development of water electrolysis in the EU. *Fuel cells and hydrogen joint undertaking*,2014, 1-160.
7. Cherevko, S., Geiger, S., Kasian, O., Kulyk, N., Grote, J. P., Savan, A., ... & Mayrhofer, K. J "Oxygen and hydrogen evolution reactions on Ru, RuO₂, Ir, and IrO₂ thin film electrodes in acidic and alkaline electrolytes: A comparative study on activity and stability". *Catalysis Today*,2016, 262, 170-180.
8. Cherevko, S., & Mayrhofer, K. J. J. On-Line Inductively Coupled Plasma Spectrometry in Electrochemistry: Basic Principles and Applications. 2018, 326-335
9. Cipriani, G., Di Dio, V., Genduso, F., La Cascia, D., Liga, R., Miceli, R., & Galluzzo, G. R. "Perspective on hydrogen energy carrier and its automotive applications". *International Journal of Hydrogen Energy*, 39(16),2014, 8482-8494.

10. Conway, B. E., Birss, V., & Wojtowicz, J. "The role and utilization of pseudocapacitance for energy storage by supercapacitors." *Journal of power sources*, 66(1-2), 1997, 1-14.
11. Coudun, C., Grillon, F., & Hocheplied, J. F. Surfactant effects on pH-controlled synthesis of nickel hydroxides. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 280(1-3), 2006 23-31.
12. Crousier, J., Hanane, Z., & Crousier, J. P. Electrodeposition of NiP amorphous alloys. A multilayer structure. *Thin Solid Films*, 248(1), 1994, 51-56.
13. David, M., Ocampo-Martínez, C., & Sánchez-Peña, R. Advances in alkaline water electrolyzers: A review. *Journal of Energy Storage*, 23, 2019, 392-403.
14. Ekspong, J., & Wågberg, T. Stainless steel as a bi-functional electrocatalyst—A top-down approach. *Materials*, 12(13), 2019, 2128.
15. Gao, M., Sheng, W., Zhuang, Z., Fang, Q., Gu, S., Jiang, J., & Yan, Y. Efficient water oxidation using nanostructured α -nickel-hydroxide as an electrocatalyst. *Journal of the American Chemical Society*, 136(19), 2014, 7077-7084.
16. Hall, D. S., Lockwood, D. J., Bock, C., & MacDougall, B. R. Nickel hydroxides and related materials: a review of their structures, synthesis and properties. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 471(2174), 2015, 20140792.
17. Jaramillo-Gutiérrez, M. I., Sierra-González, S. M., Ramírez-González, C. A., Pedraza-Rosas, J. E., & Pedraza-Avella, J. A. Effect of electrodeposition parameters and surface pretreatment on the electrochemical hydrogen production using nickel-plated stainless steel electrodes. *International Journal of Hydrogen Energy*, 46(11), 2021, 7667-7675.
18. Kahnamouei, M. H., & Shahrokhian, S. Ultrafast Two-Step Synthesis of S-Doped Fe/Ni (Oxy) Hydroxide/Ni Nanocone Arrays on Carbon Cloth and Stainless-Steel Substrates for Water-Splitting Applications. *ACS Applied Energy Materials*, 4(10), 2021, 10627-10638.
19. Landon, J., Demeter, E., Inoglu, N., Keturakis, C., Wachs, I. E., Vasic, R., ... & Kitchin, J. R. Spectroscopic characterization of mixed Fe-Ni oxide electrocatalysts for the oxygen evolution reaction in alkaline electrolytes. *Acs Catalysis*, 2(8), 2012, 1793-1801.

20. Reier, T., Oezaslan, M., & Strasser, P. Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: a comparative study of nanoparticles and bulk materials. *Acs Catalysis*, 2(8),2012, 1765-1772.
21. Smith, A. M., Trotochaud, L., Burke, M. S., & Boettcher, S. W. Contributions to activity enhancement via Fe incorporation in Ni-(oxy) hydroxide/borate catalysts for near-neutral pH oxygen evolution. *Chemical Communications*, 51(25),2015, 5261-5263.