Chapter 2

Synthesis and Characterization Techniques

This Chapter illustrates the synthetic protocols employed for various electrocatalyst and step by step fabrication procedure for working electrode. Lastly, various instrumentation techniques utilized for the characterization of the synthesized catalyst and the electrochemical characterization techniques are discussed in detail.

2.1 Introduction

This chapter provides a brief description of the various research techniques used for material synthesis, characterization, electrode fabrication and electrochemical measurements to develop active OER and HER electrocatalysts.

2.2 Material Synthesis Techniques

The synthesis of high-quality powder samples is crucial for creating superior electrodes. To achieve this, several factors need to be considered, which are as follows.

- **Selection of appropriate methodology:** The synthesis method chosen depends on the desired material and its properties. Common methods include solid-state reactions, solution combustion, sol-gel, co-precipitation, hydrothermal synthesis and more. Every method possesses distinct advantages and limitations, necessitating careful analysis.
- **Purity of starting precursors:** The precursor materials used should be of high purity to ensure the final product's purity.
- **Stoichiometric ratios:** To achieve the desired composition, it is crucial to maintain the precise stoichiometric ratios of the constituent components.
- **Reaction condition optimization:** The desired phase formation can only be attained by optimizing the reaction parameters, including temperature and reaction time.

In the following section different synthesis methods for transition metal oxides are described, which are as follows.

2.3 Synthetic Methods of Transition Metal Oxides

In general, transition metal oxides (TMOs) are synthesized through two most prominent methodology i.e. solid-state based method or solution-based methods.

Researchers have developed different synthetic approaches to prepare TMOs. Solution-based procedures, such as sol-gel, [1] coprecipitation, [2, 3] hydro/solvothermal, [4, 5] and solution combustion methods have been employed more often than solid-state methods due to their facile process and controllability. There is no shape and size control in solid-state methods as they form thermodynamic stable products. In contrast, we can control the shape and size of development in solution-based methods as it is a kinetically controlled reaction. Primarily sol-gel synthesis routes were followed in this thesis.

2.3.1 Solution-Based Methods

Synthesis techniques and procedures involving the chemical reactions or synthesis of materials in a liquid media, usually a solvent, are referred to as solution-based synthesis methods. These methods are often cost-effective, low-temperature, environmentally friendly and energy-efficient. [6] Some examples of methods used in solution-based synthesis are mentioned below:

2.3.1.1 Sol-gel Synthesis Method

The sol-gel method for synthesizing transition metal oxides (TMOs) offers several significant advantages, making it a popular choice in materials science. Sol-gel process is relatively economic, typically results in high-purity products with uniform composition, synthesis temperatures are generally lower than those required for solid-state methods. The solution-based nature of the sol-gel process facilitates the uniform incorporation of dopants or trace elements at the molecular level, enhancing the functional properties of TMOs. This method involves the hydrolysis of metal-organic precursors to form a gel-like network which upon drying and heating produces fine metal oxide particles.

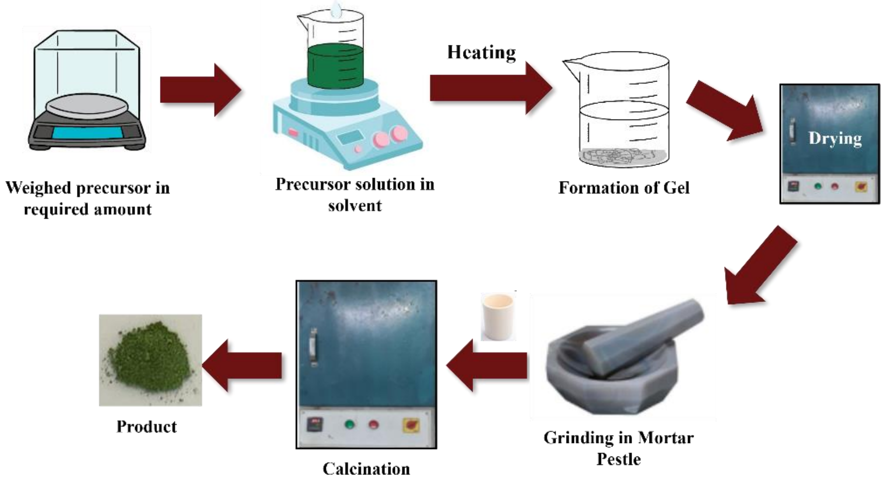

Figure 2.1 Schematic block diagram of sol-gel synthesis procedure.

2.3.1.2 Co-Precipitation

One of the most used preparation techniques is precipitation, often utilized to make bulk materials with precise control over particle size and content. In this method, metal salts are precipitated from a solution by adding a precipitating agent. Filtration or centrifugation are two methods for separating the solid particles, sintering the solid particles at required temperature leads to final oxide-based compounds.

2.3.1.3 Hydrothermal/Solvothermal Synthesis

The hydro/solvothermal approach is one of the most extensive and adaptable methods for producing nanoparticles with desired morphology and controlled size. In a conventional procedure, reactants (metal salts) are dissolved in water, an organic solvent, or a combination of both. The solution is then placed in an autoclave made of teflon-coated stainless steel, heated to a specific temperature, and held for a predetermined time. By adjusting the reaction conditions, we can precisely regulate the resultant materials' size, shape and crystallinity.

2.4 Material Characterization Techniques

Various analytical techniques were used to characterize the synthesized materials, instrumental tools used in the present study are listed below:

2.4.1 Powder X-ray Diffraction (XRD)

The primary instrument for phase verification of polycrystalline materials is powder X-ray diffraction (PXRD), which generates a distinctive diffraction pattern utilized extensively for phase confirmation and/or identification.

This methodology is highly adaptable, applicable to both bulk materials (solid-solution) and thin films for the examination of crystal structure, phase and additional structural parameters, including average grain size, strain and crystallinity. [7]

In the present study, the X-ray patterns of all the samples were recorded on Rigaku Miniflex X-ray diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 1.54$ Å) and applied voltage of 40 kV.

2.4.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is typically utilized to determine the functional group attached to an atom or molecule. [8] The FTIR spectra of the materials examined in this thesis were acquired using a Perkin Elmer FTIR spectrometer in chapter 3 and 4 and Nicolet iS5 FT-IR spectrometer in chapter 5 with data captured in the range of 400-4000 cm^{-1} utilizing a KBr pellet.

2.4.3 Raman Spectroscopy

Raman and FTIR spectroscopy rely on the distinct vibrations of a molecule, allowing for material identification. However, Raman spectroscopy provides additional information about lower frequency vibrations, which can reveal valuable information about the crystal lattice. For the present study Renishaw inVia Raman microscope and Lab RAM HR evolution both Raman Spectrometers models were used for material identification.

2.4.4 UV-Visible Spectrophotometer

This instrument helps determine sample band gap and absorption characteristics in the visible and adjacent (near-ultraviolet and near-infrared) ranges. The UV-Visible spectra of the samples were recorded in the solid-state transmittance mode by a Shimadzu UV-2600 spectrophotometer in the 200–800 nm range.

2.4.5 Scanning Electron Microscopy (SEM)

Electron microscopy is an innovative imaging technology widely utilized in scientific and technical settings to examine the morphology and structure of nanomaterials. Scanning electron microscopy (SEM) can produce extremely high-resolution images of a sample's surface, revealing features within a size range of less than 1 to 5 nanometres. SEM micrographs feature a significant depth of field and a distinctive three-dimensional gaze that is helpful for analyzing the surface structure of a sample because of the extremely narrow electron beam. [9, 10] In the present study, Nova Nano SEM 450 scanning electron microscope (SEM) equipped with EDAX - Ametek detector was employed to understand the morphology and chemical composition of prepared samples.

2.4.6 Energy Dispersive X-ray Spectroscopy (EDS or EDX)

Energy dispersive X-ray analysis (EDAX), also referred to as energy dispersive X-ray spectroscopy (EDS or EDX), is an analytical technique employed in conjunction with transmission or scanning electron microscopy (SEM) to determine a sample's chemical composition, elemental distribution, and homogeneity analysis, among other applications. A non-destructive method known as EDX is employed to rapidly determine all constituent elements with atomic numbers $Z \geq 11$. [11]

2.4.7 Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) is a high-magnification, multifunctional instrument for analysing the structural and morphological characteristics of materials, such as shape, size and constituent distribution. Users can utilize TEM in numerous ways, depending upon their need. Examples include HRTEM (high-resolution transmission electron microscopy), selected electron diffraction and supplementary techniques like as elemental mapping and EDX (energy-dispersive X-ray spectroscopy). [12]

Present work utilized an FEI Tecnai G2 20 TWIN transmission electron microscope (USA) equipped with a LaB6 filament and an accelerating voltage of 200 kV to generate bright-field TEM micrographs and selected area electron diffraction patterns (SAED). Prior to depositing a drop onto a holey-carbon-coated copper grid (Pelco International, USA) for transmission electron microscopy (TEM) imaging, samples were diffused in 20 mL of anhydrous ethanol and subjected to sonication for 30 minutes. HRTEM micrographs were collected and analyzed using Gatan Microscopy Suite (Digital Micrograph) and ImageJ software.

2.4.8 X-ray Photoelectron Spectroscopy (XPS)

XPS is a non-destructive, surface-sensitive spectroscopic technique that assesses the chemical and electronic states of the constituent elements within a material.

The XPS of the samples in the present work was performed using Thermo Fisher Scientific's K-Alpha spectrometer, which was equipped with an aluminium (Al Kα radiation) monochromator source running at 15 kV and 20 mA.

2.4.9 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry (MS) that can detect metals and some nonmetals at concentrations as low as 1 part in 10^{15} (parts per quadrillion) on non-interfered low-background isotopes. This is accomplished by ionising the sample with ICP, then separating, and quantifying those ions with a mass spectrometer. [13]

In this thesis work, Agilent 7800 ICP-MS mainframe was used to determine the elements in the metal oxides.

2.4.10 BET (Brunner-Emmett-Teller) Surface Area Measurement

This technique illustrates the physical adsorption of gas molecules on solid surfaces and serves as an effective method for estimating the specific surface area of materials. Typically, the physical adsorption of non-corrosive gas molecules (N_2, Ar, CO_2, etc.) on the material's surface is utilized to determine the specific surface area, average pore volume and pore size distribution of the sample. [14]

In the present work, MicrotracBEL BET instrument operated under an N_2 adsorption−desorption medium at 77.3 K were used to analyze the specific surface of the sample.

2.5 Electrochemical Characterization

2.5.1 Catalyst Ink Preparation and Electrode Fabrication

The catalyst ink was formulated by dispersing 20 mg of catalyst material along with 5 mg of activated carbon in 1 ml of N-methyl pyrrolidone (NMP) solvent. Additionally, 5 µl of Nafion binder was incorporated into the mixture and subsequently subjected to ultrasonication for 30 minutes to achieve a uniform mixture. The catalyst ink was drop-casted to carbon paper (1 × 1 cm^2) with a loading amount of about 1 mg on the substrate. The electrode was subsequently dried at 80 °C for 12 hours in a vacuum oven and utilized as the working electrode.

2.5.2 Electrochemical Setup

Electrochemical measurements of the fabricated electrodes were carried out by using electrochemical workstation based on Pine research instrument (Wave driver 200) in a conventional three-electrode setup, using 1M KOH (chapter 3, 4) and 0.5 M H_2SO_4 (chapter 5) as electrolyte. Three-electrode setup which consists of catalyst-coated carbon paper of 1 cm^2 area (Chapter 3, 4) and catalyst-coated glassy carbon electrode (GCE) with a 5 mm diameter (0.196 cm^2 square area) for (chapter 5) as a working electrode. For the reference electrode Ag/AgCl/4M KCl (Chapter 3, 4, 5) while a platinum wire as a counter electrode (Chapter 3, 4, 5) were used. All the electrochemical analysis was done with the help of Aftermath software by performing cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) in N_2-saturated 1 M KOH (Chapter 3, 4) and 0.5 M H_2SO_4 (chapter 5) electrolyte. The electrolyte solutions were freshly prepared before each set of experiments. All potentials are reported versus the reversible hydrogen electrode (RHE), for the conversion of the obtained potential (vs Ag/AgCl) to the RHE in alkaline electrolyte Eq. 2.1 was used while in acidic electrolyte Eq. 2.2 was used.

$$E_{RHE} = E_{Ag/AgCl} + 0.059\,pH + E^0_{Ag/AgCl} \tag{2.1}$$

where, $E^0_{Ag/AgCl}$ (in 4 M KCl) = + 0.199V; pH = 13.8 for 1 M KOH.

$$E_{RHE} = E_{Ag/AgCl} + 0.059p\mathrm{H} + E^{\mathrm{o}}_{Ag/AgCl} \tag{2.2}$$

where, $E^0_{Ag/AgCl}$ (in 4 M KCl) = + 0.199V; pH = 0.3 for 0.5 M H_2SO_4.

2.5.3 Electrochemical Characterization Techniques

Electrochemical characterization techniques are essential tools in studying and analyzing materials, reactions and systems in electrochemistry. These techniques provide insights into electron transfer, reaction kinetics and electrochemical stability. Below are some used techniques.

2.5.3.1 Cyclic Voltammetry (CV)

Cyclic voltammetry uses a three-electrode system which includes a working electrode, a reference electrode and a counter electrode. CV involves cycling the potential of a working electrode while measuring the resulting current. Cyclic voltammetry (CV) is frequently employed to explore the reduction and oxidation processes of molecular species, proving to be quite beneficial for examining electron transfer-initiated chemical reactions, such as catalysis. [15]

In the present study, before collecting the electrochemical data, the working electrode was activated by performing several scans of CV at a scan rate of 100 mV s^{-1} in the range of 0–0.8 V *vs*. Ag/AgCl (chapter 3, 4) and 0 – -0.8 (chapter 5) *vs*. Ag/AgCl. Cyclic voltammetry is also used to perform the durability test and measure the electrochemical double layer capacitance (C_{dl}) of synthesized catalyst for electrocatalytic OER and HER measurements. Catalyst durability was recorded by using cyclic voltammograms (CVs) at a scan rate of 50 mV s^{-1} for 1000 cycles. The electrochemical double layer capacitance (C_{dl}) was measured by performing CV at different scan rates in non-faradaic region. Current density differences ($\Delta J/2$) plotted versus scan rates where the slope represents C_{dl}.

2.5.3.2 Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry (LSV) is a simple electrochemical method that only requires a single linear sweep from the lower potential limit to the upper potential limit. Like cyclic voltammetry, LSV uses a three-electrode setup consisting of a working electrode, counter electrode and reference electrode. It measures the current flowing through a working electrode while the potential between the working electrode and a reference electrode is linearly sweeping over time.

In the present work, linear sweep voltammograms (LSVs) were performed at a scan rate of 5 mV s^{-1} from 0–0.8 V *vs*. Ag/AgCl (chapter 3, 4) and 0 – -0.8 *vs.* Ag/AgCl (chapter 5).

2.5.3.3 Electrochemical Impedance Spectroscopy (EIS)

Impedance is a measure of the ability of a circuit to resist the flow of electrical current. Electrochemical impedance spectroscopy (EIS) uses the application of a small sinusoidal potential to the working electrode in an electrochemical cell, while measuring the resulting current response. [16]

In the present work, electrochemical impedance spectroscopy (EIS) was performed to investigate the charge-transfer kinetics at the electrode/electrolyte interface, which was conducted with AC voltage with 10 mV amplitude at certain potential within the frequency range from 0.1 Hz to 100 kHz.

2.5.3.4 Chronoamperometry (CA)

Chronoamperometry is a time-dependent technique where a square-wave potential is applied to the working electrode. The current of the electrode, measured as a function of time, fluctuates according to the diffusion of an analyte from the bulk solution toward the sensor surface. [16] Long term stability test of materials synthesized in this thesis work was measured by chronoamperometric measurements which is conducted at a constant potential to maintain an initial current density of 10 mA cm^{-2}.

2.6 References

1. Stankic, S.; Suman, S.; Haque, F.; Vidic, J. Pure and multi metal oxide nanoparticles: synthesis, antibacterial and cytotoxic properties. *J. Nanobiotechnology*, **2016**, *14*, 1-20.
2. Ma, T.; Chen, J.; Chen, M.; Liu, S.; Luo, J.; Zou, H.; Yang, W.; Chen, S.; Nickel-cobalt-molybdenum sulfides with adjustable morphology via coprecipitation and hydrothermal conversion as high-performance electrodes for asymmetric supercapacitors. *J. Alloys Compd*. **2020**, *838*, 155631.
3. Nwodo, I.C.; Nkele, A.C.; Obodo, R.M.; Udeh, J.N.; Ani, P.C.; Chime, C.P.; Maaza, M. Ezema, F.I. Synthesis and characterization of co-precipitated nickel phosphate [$Ni_3(PO_4)_2$] nanoparticles prepared at varying precursor concentrations. *J. Indian Chem. Soc.* **2023**, *100,* 101026.
4. Pore, O.C.; Fulari, A.V.; Shejwal, R.V.; Fulari, V.J.; Lohar, G.M. Review on recent progress in hydrothermally synthesized MCo_2O_4/rGO composite for energy storage devices. *Chem. Eng. J.* **2021**, *426*, 131544.
5. Jin, J.; Dai, Y.; Lu, J.; Dai, X.; Tie, N.; Ma, F.; Wang, W.; Pu, L.; Zhang, H. Hydrothermal synthesis of NiO/$NiCo_2O_4$ nanomaterials for applications in electrochemical energy storage. *J. Mater. Sci.: Mater. Electron*, **2022**, 1-13.
6. Wu, H.J.; Fan, Y.J.; Wang, S.S.; Sakthinathan, S.; Chiu, T.W.; Li, S.S.; Park, J.H. Preparation of $CuCrO_2$ hollow nanotubes from an electrospun Al_2O_3 template. *Nanomaterials*, **2019**, *9*, 1252.
7. Drits, V.; Środoń, J.; Eberl, D.D.; XRD measurement of mean crystallite thickness of illite and illite/smectite: Reappraisal of the Kubler index and the Scherrer equation. Clays and Clay Minerals, **1997**, *45*, 461-475.
8. De Haseth, J.A. Fourier transform infrared spectrometry. In Fourier, Hadamard, and Hilbert Transforms in Chemistry. Boston, MA: Springer US. **1982**, 387-420
9. Chaudhari, S. Electron microscopy: an essential tool for the synthesis of thin film for practical applications. In Proceeding of national conference on electron microscopy at DMSRDE **1999**, December, 1-3.
10. Pennycook, S.J.; Nellist, P.D. eds. Scanning transmission electron microscopy: imaging and analysis. Springer Science & Business Media. **2011**.
11. Scimeca, M.; Bischetti, S.; Lamsira, H.K.; Bonfiglio, R.; Bonanno, E. Energy Dispersive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis. European journal of histochemistry: EJH, **2018**, 62.

12. Carter, C.B.; Williams, D.B. eds. Transmission electron microscopy: Diffraction, imaging, and spectrometry. Springer. **2016**
13. Nageswaran, G.; Choudhary, Y.S.; Jagannathan, S. Inductively coupled plasma mass spectrometry. In Spectroscopic methods for nanomaterials characterization **2017**, 163-194.
14. Naderi, M.; Surface area: Brunauer–Emmett–Teller (BET). In Progress in filtration and separation **2015**, 585-608.
15. Elgrishi, N.; Rountree, K.J.; McCarthy, B.D.; Rountree, E.S.; Eisenhart, T.T.; Dempsey, J.L. A practical beginner's guide to cyclic voltammetry. Journal of chemical education, **2018**, 95, 97-206.
16. Guy, O.J.; Walker, K.A.D. Graphene functionalization for biosensor applications. Silicon Carbide Biotechnology **2016**, 85-141.