

Experimental Techniques and Methods

2.1 Introduction

The material synthesis, characterization, and device fabrication performed in the thesis are described in this chapter. The metal oxides and thiolates are characterized with various techniques to understand the morphology, structural purity, and composition. Various material characterization techniques such as XRD, Raman, SEM, TEM, EDS, XPS, DSC, TGA, BET, FTIR, and magnetic measurements were used to understand the nature of the materials synthesized. The methodology for the cleaning and fabrication of the electrodes is explained briefly. In the upcoming sections, each of the techniques used are discussed more in detail.

2.2 Material Characterization Techniques

2.2.1 X-ray Diffraction (XRD)

XRD provides information related to the crystal structure, structural purity, crystallinity, lattice stress, and strain. The x-rays are widely used because of the similar order of magnitude of the interatomic spacing in crystalline solids and wavelength of XRD. The XRD works on the basic principle of Bragg's law. Bragg's law can be given as

$$n\lambda = 2d\sin\theta \quad (1)$$

Where λ corresponds to the X-ray wavelength, d is the interplanar spacing, θ is the angle between the incident X-ray beam and scattering plane, and n is an integer. The structural information of the sample can be understood with the diffraction peaks obtained because of the interference. X-ray diffraction helps in understanding the crystallographic properties of the desired crystalline materials. From diffraction data, the crystallite size, strain, and stress of material can be determined.

2.2.2 Raman Spectroscopy

Inelastic scattering, as a result of the difference in the wavelengths, is observed due to Raman scattering. Several shifts are observed, as the scattering is associated with different rotational and vibrational modes. The Raman spectrum is a plot of intensity versus the frequency of the Raman shift. The sharp bands in the Raman spectrum are characteristic of the specific functional groups of materials and compounds. This information can act as a fingerprint technique for determining the chemical structure or to identify the compound. It is a complementary technique to FTIR. The intensities provide important information regarding specific vibrations that are used for the semi-quantitative and quantitative analysis. Raman spectroscopy is used mainly for the identification of the carbon structure. The specific characteristic bands in Raman provides information about the layers and defect present. In the case of doping in metal oxides, it gives information about the stain in the lattice due to the incorporation of metal ions. Raman spectroscopy also helps in understanding the structure of the metal oxides.

2.2.3 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) provides information related to the morphology of the sample. The FESEM has a higher resolution and greater energy compared to SEM, which provides high-resolution imaging in the range of ~10 nm. The data is most commonly in the form of an image obtained from the scanning of the secondary electrons. The SEM image is a map of secondary electrons emitted from the surface as a function of spatial position. It provides information related to the topography of the sample. The exact roughness of the samples from the plane image view cannot be determined, as the images obtained from the SEM are a function of the spatial position.

2.2.4 Transmission Electron Microscopy (TEM)

In TEM, a high-energy beam of electrons accelerated with 30 kV to 300 kV is used. The smaller wavelength of the electrons provides easy resolution at the angstrom level. TEM can be utilized to obtain the finest details of a crystal structure, and in some instances, it gives information about the arrangement of atoms. The interactions between the electrons and the atoms are used for obtaining the features such as the crystal structure, dislocations and grain boundaries, etc. TEM is also used for studying the growth of layers and defects in the crystal lattice of the material. In alliance with EDS, it can be used explicitly for determining the elemental composition in nm range areas. High-resolution transmission electron microscopy can help in analyzing the structure, shape and size, and growth of the nanomaterials in a particular direction.

2.2.5 Energy Dispersive Spectroscopy (EDS)

It is difficult to understand the material without knowing the composition. In such cases, electron dispersive spectroscopy can be an advantageous alliance with the image obtained using backscattered SEM. It is also valuable for determining the composition and distribution of materials in the samples. In addition to SEM and TEM imaging data with an electron beam, these techniques generate X-rays. These X-rays can be collected using a detector and characteristics of a particular element present in the sample. When the X-ray data obtained from the samples is mapped as a function of spatial position, we can see a map showing the distribution of the particular elements in the sample.

2.2.6 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermal technique that utilizes the in and outflow of heat as a function of temperature or time while the sample is provided with a known controlled temperature. It can be used to understand properties like glass transition temperature, crystallization, melting, specific heat capacity, oxidation behavior, purity, and thermal stability of the materials. DSC can analyze multiple materials, including plastics composites, pharmaceuticals, organic materials, petroleum, explosives, etc. In DSC, the heat flow rate is compared between the sample and the reference material to provide the difference. This difference provides us the information regarding the oxidation characteristics, crystallinity, and heat of fusion, etc. The heat flow profile obtained helps to understand the best processing temperatures and acts like a fingerprint to compare the thermal properties and their performances.

2.2.7 Thermogravimetric Analysis (TGA)

TGA is a thermal technique in which the weight changes in a material are noted as a function of temperature/time under a controlled gas (N_2/Ar) atmosphere. TGA is used for a wide variety

of analyses; for example, it can be used to study the thermal stability of the sample, the additives and filler content in polymers, different moisture, and solvent content. It gives an idea about the decomposition temperature and percent composition of components in a compound. The basic principle of TGA is weight change. In short, the temperature is increased gradually, and simultaneously the weight of the sample is measured using a weighing balance attached. If there is a loss in mass, it involves losing a volatile component, especially moisture, to 100 °C. The various chemical reactions which involve mass losses, combustion, oxidation, or decomposition can be known from a TGA temperature profile. TGA can also be used for studying the thermal transitions in the material.

2.2.8 X-ray Photoelectron Spectroscopy (XPS)

XPS is an analytical technique that resembles the photoelectric effect. In this technique, the x-rays are bombarded on the specimen, and the energy of the electron of emitted electrons is quantified. The most common X-ray source is AlK α . The X-rays can only penetrate the few micrometers in-depth, but only very few electrons from the surface (~5 nm) surface are emitted without losing energy. This is due to the collisions of the electrons with other atoms while escaping out from the surface. In this process, the kinetic energy (KE) of the ejected electrons is measured using a detector, and the binding energy (BE) of the electrons is determined. A simple relationship between binding energy (BE) and kinetic energy (KE) is as follows:

$$E = BE + KE + \varphi \quad (2)$$

XPS technique is more sensitive for elements with higher atomic numbers. The significant advantage of this technique is it can provide sufficient differences in binding energy for different chemical bonds and states. For example, it is possible to separate various bonds like C-C from C-O and O-C=O in a given compound sample and used for compositional and surface analysis. The area under the peak gives an estimated percentage of the element present in the sample. XPS technique can be employed on a variety of materials for analyzing the surface states. The major disadvantage of this method is the requirement of the high vacuum conditions and sample handling since it a highly surface-sensitive technique.

XPS analysis needs a deep understanding of the position and intensity of peaks. It is also necessary to understand the high-resolution spectra data. In XPS, peak position plays an essential role by indicating the elemental and chemical composition of the sample. For example, in a given sample variant, it helps us to understand whether the surface has metal, oxides, or hydroxide formation on the surface, which helps further to interpret the results. Most of the high-resolution spectra have broad curves which need to be deconvoluted before interpretation. Various software can be used, and they have multiple functions necessary to be taken care of during deconvolution. In the case of spinels and mixed metal oxides, it provides us valuable information about the presence of the oxidation states. These oxidation states can be quantified using the ratios of the area under the curve from both the spin-orbit couplings. These ratios can provide us the information on the dominant species present on the surface of the catalyst. Furthermore, XPS can be used to quantify elemental composition by considering the area under the curve. While starting the spectrum analysis, the baseline correction and carbon shift correction play a significant role. Carbon shifts are usually corrected in the instrument software, but one can always crosscheck the Cls carbon position. XPS not only reveals the presence of the surface states but can also help us to understand doping. Doping can result in chemical shifts and hence is a powerful, sophisticated, and helpful technique in understanding the chemical states of the material.

2.2.9 Surface Area Analysis by BET (Brunauer-Emmett-Teller)

BET surface analysis works on the principle of adsorption. The adsorption is nothing but the adhesion of atoms or gas molecules on the surface. The adsorption of the gas molecules depends on the surface area and depends on various physical parameters like the pressure, temperature, the strength of interaction, etc., between the molecules and the substrate. In surface area analysis by BET, nitrogen is widely used because of its availability with high purity and its vital interaction with many solids. The surface is cooled using liquid nitrogen to obtain a detectable amount of adsorption of gas molecules since the interactions between the gas and solid phase are weak. In the sampling procedure, the nitrogen gas is stepwise released into the sample cell. A partial vacuum is created to obtain a lower atmospheric pressure. The adsorption stops after attaining the saturation pressure, even with a further increase in pressure. The pressure highly sensitive pressure transducers in the equipment note the slight changes in the pressure because of the adsorption process. The material is heated to remove the nitrogen and quantified. The data collected is then displayed as BET isotherm. The minimum sample requirement for a proper determination of surface area is 0.5 g of minimum sample is required for the BET to determine the surface area successfully. A lower temperature is maintained throughout the experiment to maintain a strong interaction between gas molecules and the sample. There are various types of adsorption isotherms possible based on the pore structures and pore sizes.

2.2.10 Fourier-transform Infrared Spectroscopy (FTIR)

The basic principle of the vibrational spectroscopy technique is the interaction of the infrared spectrum upon reaching a material. Characteristic vibration in the molecules is seen when there are inelastic collisions of infrared light with the molecules of the samples. The collisions produce characteristic vibrational frequencies depending upon the nature of the bonds. The vibrational modes can be either with Raman active (light scattering happens due to the various polarizability during vibrations) or IR active (light is absorbed due to the change in the dipoles during vibrations) or both. Hence, this technique is a complementary technique to confirm the chemical bonds present in the samples. The basic principle of operation of FTIR is Michelson's interferometer. The beam source of IR is split through the mirror, where the path difference of both the split beams creates constructive and destructive interference. To understand the convert the spectrum as a function of wavenumber, the Fourier transform is carried out. The Fourier transform reduces the signal-to-noise ratio of the output spectra.

2.2.11 Magnetic Measurements

The magnetic measurements can be carried out using a vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID). In VSM, generally, the material is magnetized using an external magnetic field by converting the dipole field of the sample into ac electrical signal. In VSM, the magnetic sample to be analyzed is kept in the uniform magnetic field and then vibrated sinusoidally with a vibrator. The sample's magnetic moment is directly proportional to the induced voltage in the pickup coil and is independent of the applied magnetic field. The voltage generated is measured using piezoelectric signals generated, and the weak signals are amplified using a lock-in amplifier. The hysteresis of a magnetic material can be obtained by measuring the magnetic field of the external electromagnet. The overall magnetic field can be measured using a SQUID magnetometer. It is highly sensitive and can detect smaller magnetic fields. The SQUID geometry consists of two superconductors separated with thin insulations forming a Josephson junction. The alternating magnetic flux in the pickup coil is produced by the up-down movement of the sample. The SQUID antenna and the superconducting coil together measure the magnetic signal. This device acts as a flux to voltage convertor.

2.3 Electroanalytical Techniques

2.3.1 Voltammetric Techniques

a. Linear Sweep Voltammetry (LSV)

LSV comes under the category of voltammetric methods in which the potential between the working electrode and a reference electrode is swept linearly with time, and the current at a working electrode is measured simultaneously. The LSV plot is made up of current versus potential versus the reference electrode (Figure 2.1a and b). The changes in the peak curve with increasing and decreasing potential sweep is the symbol of oxidation or reduction of the species. The potential at which the peak is observed is the peak potential for oxidation or reduction corresponding to the different oxidation states of the electrochemically active samples. Simply it gives us an estimation of the peak potentials at which oxidation or reduction of species takes place. The peak in LSVs can serve as a signature for particular species in the solution, while the limiting current can determine the concentration of the solution.

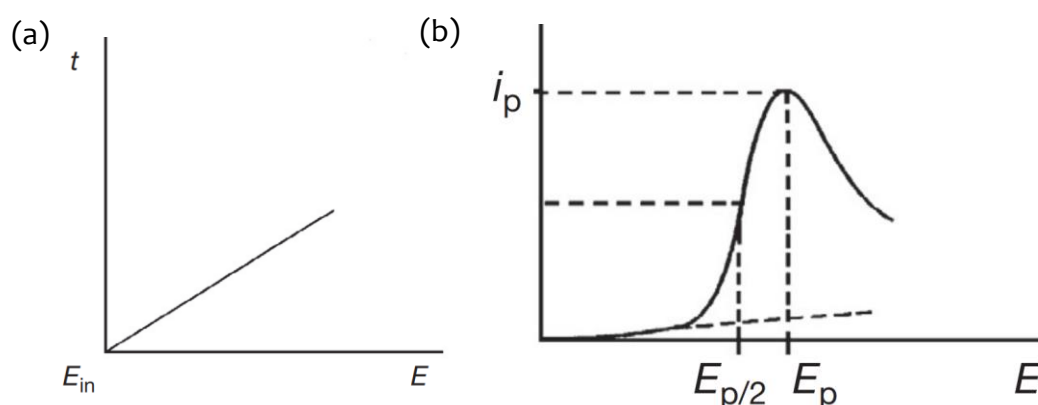


Figure 2.1: Potential waveforms for linear sweep (a) and (b) the corresponding voltammogram. Figure adapted from reference [Bontempelli et al., 2019]

b. Cyclic Voltammetry (CV)

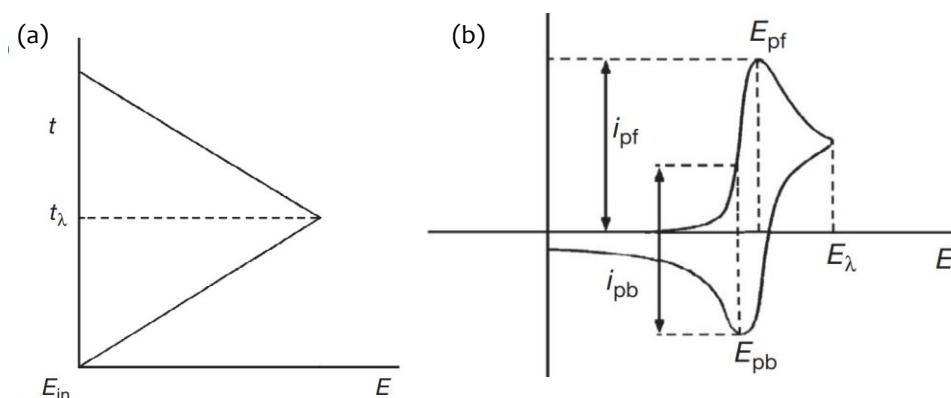


Figure 2.2: Potential waveforms for cyclic sweep (a) and (b) the corresponding voltammogram. Figure adapted from reference [Bontempelli et al., 2019]

In a cyclic voltammogram, a current is measured in both potential sweeps of reduction and oxidation cycles. The working is similar to LSV, but unlike LSV, it had both reduction and oxidation cycles combined (Figure 2.2). It is a useful technique that can help in understanding the thermodynamics involved in the redox processes. It is also widely studied to understand the kinetics of electron transfer in an electrochemical process. CV can be useful in determining the

diffusion coefficient and the surface area of the electrode. The Randel-Sevciks equation governs the peak current in CV. The Randel-Sevciks equation is given as

$$I_p = (2.69 \times 10^5) \times n^{3/2} \times A \times C \times D^{1/2} \times v^{1/2} \quad (3)$$

Where I_p is Peak current, n is the number of electrons, C is the concentration (mol/cm³), A the electrode area (cm²), D is the diffusion coefficient (cm²/s), and v is the scan rate (V/s).

2.3.2 Galvanostatic Technique

a. Galvanostatic Charge-Discharge (GCD)

Galvanostatic charge-discharge is an analytical technique in electrochemistry that is useful for studying the device's charge-discharge and energy storage profile. One cycle consists of a charging and discharging profile, and the repetitive loop is used to study the stability of the device. In this method, a known constant current pulse is applied, and the potential is measured. This technique is popularly known as Chronopotentiometry. With the applied current, the potential changes unexpectedly because of the Internal Resistance (iR). An asymmetric triangular-shaped curve is observed in the case of ideal EDLC. Asymmetry is seen with the charge and discharge profile in ideal cases but deviates in practical cases because of the iR . In the case of faradic reactions, redox peaks are also observed in GCD like a CV. The specific capacitance is calculated using the discharge current and can be given as

$$C = I \times \Delta t / m \times \Delta V \quad (4)$$

where C is the capacitance, I is the applied current, m is the mass of graphitic carbon loaded, ΔV is the voltage window, and Δt is the discharge time.

b. Chronoamperometry and Chronopotentiometry

Chronoamperometry and Chronopotentiometry techniques are commonly employed for deposition, stripping, and studying the stability of the material. In Chronoamperometry, a constant voltage is provided with respect to the reference electrode for either oxidation or reduction, depending upon the requirement for a given specific period. It is commonly known as amperometry ($i-t$), and this technique is widely implemented for electrochemical sensing. It is also used for deposition and sometimes used to study the stability in a given specific period. Chronopotentiometry is a technique in which a constant current density is applied, and a change in the potential is noted. This technique is commonly used to study the stability in HER and OER and in a supercapacitor for studying the charge-discharge.

2.3.3 Pulse Techniques

a. Normal Pulse Voltammetry (NPV)

Normal pulse voltammetry (NPV) is a basic pulse technique and analogous to Normal pulse polarography, which involves the superposing of rectangular potential pulses with increasing amplitude (E_p) and constant pulse.

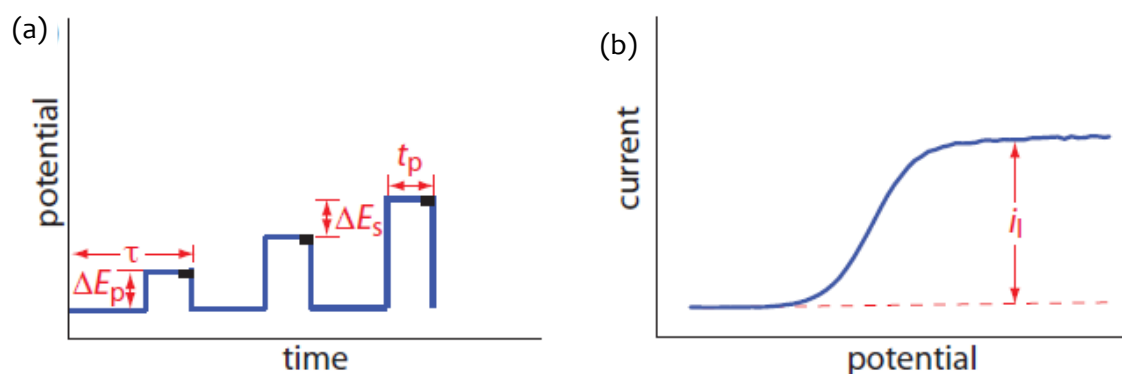


Figure 2.3: (a) Potential-excitation signals for NPV and its (b) corresponding voltammogram. Figure adapted from reference [Harvey, 2019].

In this technique, the current obtained with the applied pulse is measured and processed, which provides a smooth voltammogram with higher sensitivity (Figure 2.3a and b). It is widely used for studying the mechanism, quantitative chemical analysis, the kinetics of the reactions, and thermodynamics. The NPV provides better sensitivity than other non-pulse voltammetric techniques like LSV and CV. NPV is employed on solid electrodes, unlike polarography on a drop of mercury.

b. Differential Pulse Voltammetry (DPV)

In differential pulse voltammetry, the linear sweep voltammetry is superimposed with pulse voltammetry. In this method, the current is measured two times (Figure 2.4a and b). The current is noted before and after the pulse is applied. The difference between these two current values gives us the current values with the reduced capacitive current. DPV is used for quantitative chemical analysis and to study the mechanism, kinetics, and thermodynamics of chemical reactions. DPV as a pulse technique is used as an analytical tool that offers several advantages compared to NPV and other electrochemical techniques. DPV is a susceptible technique and allows directly to analyze the analytes at ppb (parts per billion) level. When used in combination with the i - t , it can be used in a stripping mode, and the measurements in the ppt (parts per trillion) of the analytes are possible. The sensitivity in DPV can be attributed to the short pulse time and the differential nature causing the reduced non-faradic contributions. The shorter pulse time provides a higher current density, and the differential measurement helps subtract the background processes.

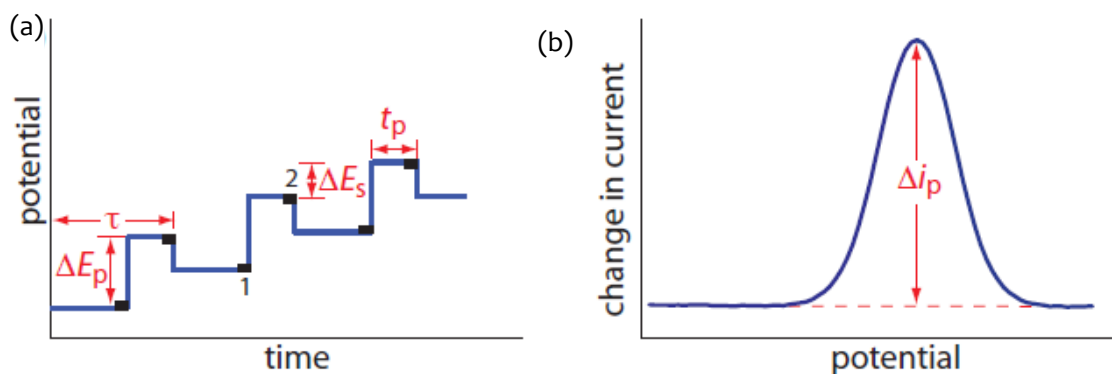


Figure 2.4: (a) Potential-excitation signals for DPV and its (b) corresponding voltammogram. Figure adapted from reference [Harvey, 2019].

c. Square Wave Voltammetry (SWV)

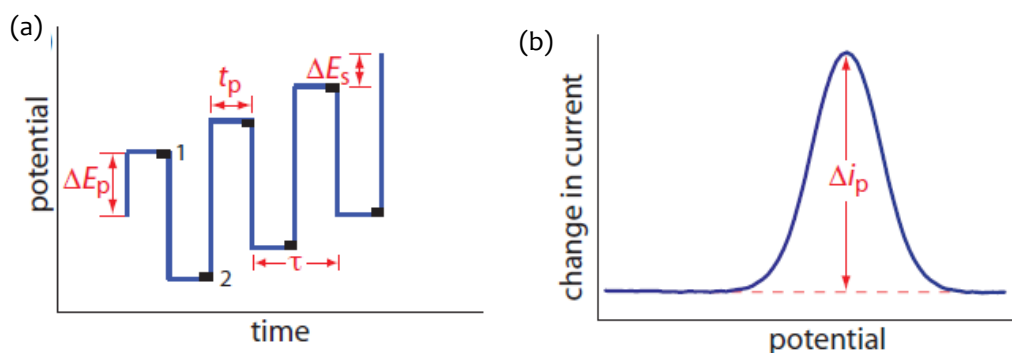


Figure 2.5: (a) Potential-excitation signals for SWV and its (b) corresponding voltammogram. Figure adapted from reference [Harvey, 2019].

The excitation signal in SWV consists of a symmetrical square-wave pulse of amplitude (E_p) superimposed on a staircase waveform of step height (E_s), where the forward pulse of the square wave coincides with the staircase step. The net current is obtained by taking the difference between the forward and reverse currents ($i_{for} - i_{rev}$) and centered on the redox potential (Figure 2.5a and b). The peak height is directly proportional to the concentration of the electroactive species, and detection limits as low as 10^{-8} M are possible. Square-wave voltammetry has several advantages. Among these are its excellent sensitivity and the rejection of background currents. Another is the speed (for example, its ability to scan the voltage range over one drop during polarography with the DME). This speed, coupled with computer control and signal averaging, allows experiments to be performed repetitively and increases the signal-to-noise ratio. Applications of square-wave voltammetry include the study of electrode kinetics regarding preceding, following, or catalytic homogeneous chemical reactions, determining some species at trace levels, and its use with electrochemical detection in HPLC.

2.3.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a highly sensitive and fundamental characterization technique while considering electrochemical measurements. In this technique time response of chemical systems is measured using smaller amplitude alternating current (AC) at a given voltage over a frequency range. It deals with the calculation of the impedance of the system. Impedance is the resistance for systems dealing with Alternating currents (AC).

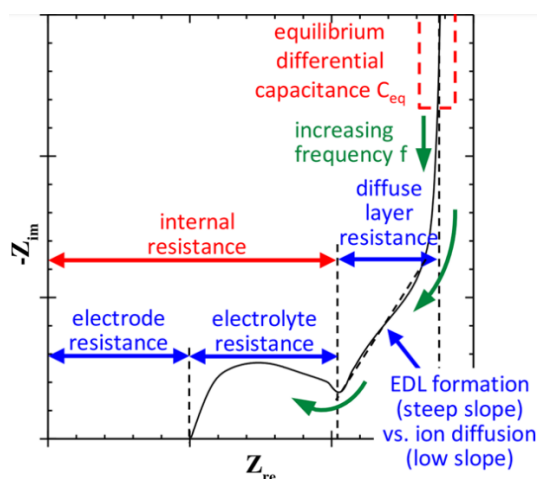


Figure 2.6: A typical Nyquist plot (Z' versus Z'') from EIS spectroscopy. Figure adapted from [Mei et al., 2018]

As alternating currents have a wave nature, two quantities are needed to define impedance, i.e., Magnitude of Impedance (Z) and phase shift (ϕ). As the impedance of a system is a complex number, it can also be broken into real (Z') and imaginary (Z'') parts. These four values are recorded while making an EIS measurement. The data is presented in two graphical forms known as the Nyquist plot (Figure 2.6). The plots have a logarithm scale, which is beneficial for representing data in a polar coordinates system and equal distribution between any two points. Based on the recorded data, models can be prepared, which are then used to explain various types of resistive components present in the system. EIS is useful in determining a wide range of dielectric and electrical properties and components in research fields studying batteries, corrosion, sensing, water splitting, etc.

2.3.5 Key Parameters Involved in OER, Supercapacitors, and Biosensing

Key Parameters Involved in OER

a. Current density (J)

The current normalization plays an important role in the comparison of the electrodes for performance. Major four methods have been widely used in the literature for the normalization of the current. These include:

1. Geometrical surface area
2. Electrochemically active surface area
3. BET surface area
4. Catalyst loading

There are merits and demerits of the method used, and they have been widely debated in the literature. However, all of the above methods are accepted by the research community for the fair comparison of the reports published research works.

b. Overpotential (η)

While evaluating the performance of an electrocatalyst, one of the most important indicators is the overpotential (η). The overpotential is defined at a specific current density. In theoretical terms, the water-splitting should happen at the thermodynamic potential; however, when dealing with the real systems, some extra potential is needed for the reaction to proceed because of the energy barrier. This difference in the actual potential and the theoretical potential is defined as the overpotential. The overpotential consists of three major components like activation overpotential, overpotential due to concentration, and overpotential because of the system's total resistance. The activation overpotential is the intrinsic property of the catalyst, and tuning the catalyst suitably can reduce the overpotential contributed by the activation overpotential. The sudden concentration drop near the interface of the electrode by depletion of the ions after reaction leads to the concentration overpotential. This overpotential can be minimized by using a highly concentrated electrolyte or by stirring the electrolyte. The resistance overpotential in the system can be reduced by compensating for the iR drop in the workstation.

c. Stability

Stability is one of the most important and essential parameters that determine the practical applicability of the electrocatalyst. In the stability test, the electrode is either subjected to chronoamperometry that is a constant potential is applied to obtain 10 mA/cm² of current and change in potential is noted, or chronopotentiometry in which the electrode is subjected to 10 mA/cm² and the change in the potential is observed with respect to time for longer durations. In these methods, various complexities can arrive because of the material thickness, changes in the current densities, and electrochemically active surface area of the electrode available for

electrode-electrolyte interaction. Short-time measurements and electrodes subjected to lower current densities will not provide any significant information about the degradation of the material if the material is too thick since the degradation is prolonged.

d. Tafel Slope and Exchange Current Density (J_0)

Tafel slope is one of the essential figures of merit that gives an idea about the kinetics of the reactions. Tafel plot is plotted with overpotential versus \ln of current density. It is one of the fundamental parameters used to compare the catalytic activity of the electrocatalyst. The electrocatalyst with lower charge transfer resistance tends to show lower Tafel slopes, signified by the fast reaction kinetics.

The electrochemical kinetics can be described using the Butler-Volmer equation, which can be given as

$$J = J_0 [\exp(\alpha_a \times F \times n \times \eta_a / RT) - \exp(\alpha_c \times F \times n \times \eta_c / RT)] \quad (5)$$

where J_0 is the exchange current density, α is the transfer coefficient of the anode or the cathode, F is faradays constant, T is absolute temperature, R is the universal gas constant, and n is the number of transferred electrons (OER involves four electrons) η is the overpotential (cathodic and anodic), and α is charge transfer coefficient (cathodic and anodic). The Tafel slope is an important parameter that gives a quantitative characterization to reveal different electrocatalytic kinetics and mechanisms of electrocatalytic activity. It depends on the assumption that a series of factors are constant as the value of a symmetry factor, surface coverage, etc.

Tafel slope can be obtained by simplifying the Butler-Volmer equation. The simplified equation can be given as follows:

$$\log(J) = \log(J_0) + \eta / b \quad (6)$$

Where J is anodic current and J_0 is exchange current, representing the rate of the reverse reaction and forward reaction at the equilibrium potential, η is the overpotential, and b is Tafel slope.

e. Turnover Frequency

Turnover frequency (TOF) is one of the other intrinsic parameters, which define the electrocatalyst activity. It is the rate of electrons delivery on the surface of the electrocatalyst in a given timeframe. In simple terms, the oxygen molecules are evolved from the surface of the electrocatalyst per electrochemically active surface area in the case of OER at the rate. TOF can be derived from that current density obtained at a fixed potential.

TOF is calculated using the equation:

$$\text{TOF (s}^{-1}\text{)} = J \times S / 4 \times F \times n \quad (7)$$

Where J is current density (A/cm^2), S is the geometrical surface area of the electrode (cm^2), F is Faraday constant ($96485.33 \text{ C}/\text{mol}$), and n is the number of moles.

Key Parameters Involved in Supercapacitors

a. Specific Capacitance

The supercapacitor differs from a regular capacitor in terms of its very high capacitance. A supercapacitor stores energy using a static charge in which the potential difference is applied on the plates to form positive and negative charges similar to that of a capacitor. There are two storage principles, which contribute to the total capacitance of a supercapacitor

1. Double-layer capacitance is the capacitance in which the electrostatic storage of charges is achieved by the separation of charge in a Helmholtz double layer.
2. Pseudocapacitance is the capacitance in which the electrochemical storage of capacitor takes by faradaic redox reactions with charge transfer.

The capacitance of a supercapacitor is a function of the amount of the active material on the surface, electrode size, geometry, etc.

The specific capacitance in the case of CV (three electrode geometry) can be calculated using the following equation

$$C = \int I dV / (2m \times v \times \Delta V) \quad (8)$$

where $\int I dV$ is the area under the I-V curve, m is the mass of graphitic carbon loaded, v is the scan rate, and ΔV is the voltage window.

The specific capacitance in the case of GCD curves (two-electrode geometry) can be calculated using the following equation

$$C = I \times \Delta t / \Delta V \quad (9)$$

where I is applied current density, m is the mass of graphitic carbon loaded, and ΔV is the voltage window, and Δt is the discharge time.

b. Operating Voltage

Operating voltage is one of the critical parameters in supercapacitors as their voltage range decides the application. The safety of the device depends on the voltage operation range of the supercapacitor. The standard aqueous electrolyte-based supercapacitors have a voltage operation range of ~1 V while non-aqueous solvents range within 2.5 to 2.7 V. For a higher range of operating voltage, supercapacitors with ionic electrolytes can give an operating voltage range up to 3.5 V. The lower voltage operation range in case of aqueous electrolyte is due to the electrolyte breakdown (electrolyte decomposition). If the aqueous device is operated above the thermodynamic water-splitting voltage of ~1.23 V, it results in water splitting. High hydrogen generation may lead to a short circuit.

c. Energy Density

The energy stored in a capacitor per unit volume is its specific energy. Supercapacitors can store 10 to 100 times more energy than regular capacitors and are almost one-tenth of batteries. In a commercial supercapacitor, the energy density (volumetric specific energy) varies mainly in the range of 5 to 8 Wh/l. The specific power can be 10 to 100 times greater than that of batteries, which is nearly ~15 kW/kg for commercially available supercapacitors.

Energy density can be calculated using the following equations:

$$E = 0.125 \times C \times \Delta V^2 \quad (10)$$

Where C is the specific capacitance and ΔV is the voltage window.

d. Power Density

Power density can be defined as the rate at which energy can be delivered to or absorbed from the load. The supercapacitor must have a high specific power density to deliver instant high power in applications like regenerative braking, short-term energy storage, and small power backup for static random-access memory.

Power density can be calculated using the following equation

$$P = E / \Delta t \quad (11)$$

Where E is the energy density, P is the power density, and Δt is the discharge time.

Ag/AgCl to RHE conversion: All potentials were calculated with respect to a reversible hydrogen electrode (RHE) using the following equation:

$$E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059 \text{ pH} + 0.197 \text{ V} \quad (12)$$

Where $E(\text{RHE})$ is the potential with respect to reversible hydrogen electrode and $E(\text{Ag/AgCl})$ is potential with respect to Ag/AgCl electrode, and pH is for 1 M KOH electrolyte.

Key Parameters Involved in Biosensing

a. Sensitivity

Sensitivity is absolute quantity. It can be defined as the smallest amount or quantity of change that a measurement can detect. One can increase the sensitivity to get higher measurement accuracy. However, higher the sensitivity, narrower the measurement range, and less accurate are the results. The sensitivity is the slope of the calibration curve by plotting current density versus concentration.

b. Limit of Detection

The limit of detection is an essential parameter in biosensing. It gives a brief idea of whether the sensor will be helpful or not. The LOD of any fabricated sensor should be as low as possible to generate a response in the slightest presence of the analyte molecule. The limit of detection is calculated using various methods. The most common method is by using the standard deviation and slope of the calibration curve. The LOD can be calculated using the following equation

$$\text{LOD} = 3\sigma/s \quad (13)$$

Where σ is the standard deviation and s is the slope of the calibration curve.

b. Limit of Quantification

The limit of quantification gives a brief idea of the lower detection limit of the sensor. The LOQ of any fabricated sensor should be equal to or less than the minimum desired range of the analyte. The limit of quantification is calculated using the following equation

1. Direct detection through visible response in the current density
2. By using the standard deviation and slope of the calibration curve

The LOQ can be calculated using the following equation

$$\text{LOQ} = 10\sigma/s \quad (14)$$

Where σ is the standard deviation and s is the slope of the calibration curve.

2.4 Fabrication of Electrodes

2.4.1 Fabrication of Au Mesh Electrodes

The Au mesh electrodes were fabricated by a combination of toner transfer patterning and crackle lithography (Figure 2.7). The crackle precursor spontaneously cracks, resulting in an interconnected network of space filled with Au metal by physical vapor deposition in a masked region. The physical masking is done by transferring laser-jet printed toner on a PET sheet to a glass substrate by hot pressing. The resulting Au network possesses a sheet resistance of Au mesh is $\sim 4 \Omega/\text{sq}$, which is slightly higher than the Au film $\sim 2 \Omega/\text{sq}$; however, it appears to be

significantly transparent. The transmittance of Au mesh coated with Ni-BT was measured to be ~ 60 % which is slightly lower than Ni-BT/FTO; however, sufficient for clear visibility. FTO electrodes of the same dimensions are patterned using an etching technique with Zn dust and HCl.

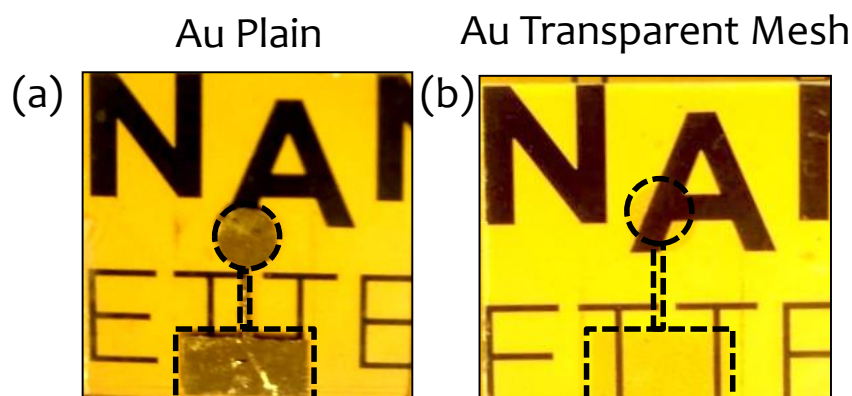


Figure 2.7: Photograph of (a) Au plain and (unpatterned) (b) patterned Au mesh electrode used as working electrodes.

2.4.2 Synthesis of Co Hexadecanethiolate and Ni Butanethiolate Precursors

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (CAS Number 10026-22-9) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (CAS Number 7718-54-9) were used as metal precursors for Co and Ni, respectively. Co Hexadecanethiolate and Ni butanethiolate precursors were synthesized by a general two-step method reported previously.[Gupta et al., 2017a; John et al., 2007b; Urgunde et al., 2018] Metal triethylamine complex (1 mM) was prepared by taking triethylamine (CAS Number 121-44-8) and metal precursor (2:1 molar ratio) in ethanol. Butane thiol (2 mM) (CAS Number 109-79-5) was added to Ni-amine complex while hexadecane thiol (2 mM) in the Co-amine complex, respectively, under continuous stirring. The Co Hexadecanethiolate (Co-HDT) and Ni butanethiolate (Ni-BT) precipitate formed were separated as a powder and repeatedly washed with acetonitrile and methanol. The solid powder was dried in a vacuum furnace for further usage. Powders of Co and Ni precursors were solubilized in toluene (5 mg/mL) in different molar ratios Co: Ni of 1:0, 0:1, 1:1, and 4:1. The solutions were drop-coated on a glass substrate and heated to the decomposition temperature in a closed furnace to convert them into hybrid Ni and Co oxides for further structural characterization.

2.4.3 Fabrication of Carbon Cloth Coated Electrodes

a. Pre-treatment of Carbon Cloth

The as-obtained carbon cloth was cut into the required size using a paper cutter. Unwanted extra threads were removed to obtain a uniform surface area. The carbon cloth was sonicated in dilute HCl for 10 mins and rinsed with deionized water 3 times. The cloth was further sonicated in IPA for 5 mins and rinsed with deionized water to remove any organic contaminants. The carbon cloth was dried for 2 h at 100 °C in a furnace. The carbon cloth obtained was cut into the required electrode areas to maintain the uniform surface area.

b. Electrode Fabrication

The pretreated and cleaned carbon cloth as described above were used as substrates for the fabrication of electrodes. The electrodes were dip-coated using the metal alkanethiolate ink solutions as per requirements. The layers were built up with multiple dip coatings and drying processes as per requirements. The obtained electrodes were completely dried and placed in the

tubular furnace for annealing at 350 °C in a nitrogen environment. The electrodes were cooled to room temperature for further contact making. The contacts were made using silver paint and copper foil. The black wax was used to cover the silver and the copper foil. The black wax provides multiple advantages, such as

1. It can be used to define the required surface area to be exposed
2. It prevents the silver paint and the copper foil from participating in the reaction
3. It provides additional strength to make the firm contact

2.5 Conclusions

In this chapter, experimental methods and techniques are discussed briefly. The different physical characterization techniques their basic principles have been discussed. The electroanalytical techniques such as LSV, CV, chronoamperometry, and pulse techniques like NPV, DPV, and SWV with impedance spectroscopy (EIS) are also explained in brief. The synthesis of Ni-BT and Co-HDT, along with the fabrication of the working electrodes, has also been discussed in this chapter.