CHAPTER II

MATERIALS AND METHODS

2.1 Materials

To synthesize cerium oxide based solid electrolytes, the following materials were used. Cerium (III) nitrate hexahydrate (99%) and niobium (V) oxide (99.5%) were purchased from SDFCL, India. Neodymium (III) chloride hexahydrate (99.9%) and dysprosium (III) chloride hexahydrate (99.9%) were purchased from Sigma Aldrich, India. Samarium (III) oxide (99.9%) and Praseodymium oxide (99.9%) were purchased from Himedia, India. Zirconium (IV) chloride (98%), Ammonium hydroxide (30%) and deionized water were obtained from MERCK, India. All reagents were of analytical grade and used without further purification. All the glassware used in this experimental work was acid washed.

2.2 Synthesis procedure of ceria based solid electrolytes

The 0.1 N solution of cerium nitrate (Ce(NO$_3$)$_3$.6H$_2$O) was prepared by using deionized water for 800 mL. Then the solution is subjected to forced hydrolysis and condensation for 60 hours. Ammonium hydroxide was added slowly (4 drops/min) in the solution to convert the sol into gel. Yellowish gelatinous precipitate was formed. The precipitation was washed thoroughly until the traces of NO$_3^-$ were removed by centrifugation and filtered using high quality Whatmann filter paper. The resultant powder was ground in agate mortar to get cerium oxide. To
convert the oxides from chlorides, the similar procedure has been followed for neodymium (III) chloride hexahydrate, dysprosium (III) chloride hexahydrate and zirconium (IV) chloride.

**Reaction Mechanism**

\[ \text{CeCl}_2 + \text{H}_2\text{O} + 2\text{NH}_4\text{OH} \rightarrow \text{CeO}_2 + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O} \]  

In order to obtain ceria based solid electrolytes, the synthesized cerium oxide was mixed with various synthesized and commercially available oxides (Sm\(^{3+}\), Pr\(^{3+}\), Nb\(^{5+}\), Zr\(^{4+}\), Nd\(^{3+}\) and Dy\(^{3+}\)) within the system of \(A_{1-x}B_xO_{2-x/2}\) and \(A_{1-x-y}B_xC_yO_{2-(x-y)/2+y}\). Further, it was ground for several hours to get a homogeneous mixture and annealed at 600 °C for 2 h under air atmosphere.

**2.3 Instrumentation techniques**

**2.3.1 X-ray diffraction**

In this work, the synthesized solid electrolytes were characterized by powder X-ray diffraction (XRD) using PANalytical X’pert pro powder diffractometer. This facility is available at Department of Physics, Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India. The CuK\(\alpha\) radiations (\(\lambda = 1.5406 \text{ Å}\)) from a copper target were used. X-ray diffraction pattern were recorded from 10° to 120° (2\(\theta\)) in steps of 0.02° with four decimal accuracy. Rietveld refinement was performed by using JANA2006 program and this program allowed to refining the lattice constants, atomic positions and occupancy factors. The fit quality was evaluated by the residual (R) – weighted pattern (R_{wp}) and goodness of fitting (\(\chi^2\)).

X-ray diffraction is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD is based on the elastic scattering that is the change of direction of the electromagnetic waves motion without any energy loss. Diffraction results from the
coherent sum of all the electromagnetic waves that are diffused from the atoms belonging to the same family of reticular planes [1-3]. Figure 2.1a and 2.1b indicates the block diagram of powder X-ray diffractometer and Bragg’s scattering from lattice planes with spacing “d” with the same angle of incidence and the angle of reflection.

Fig. 2.1 a) Block diagram of powder X-ray diffractometer b) Bragg’s scattering from lattice planes with spacing “d” with the same angle of incidence and the angle of reflection

2.3.1a Working principle

In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å is incident on a specimen and is diffracted by the atomic lattice of the sample which acts as a three dimensional grating causing the X-ray beam to be diffracted according Bragg’s law,

\[ 2d \sin \theta = n \lambda \]  

(2)

where d is the spacing between atomic planes, \( \lambda \) is the X-ray wavelength, \( \theta \) is the Bragg’s angle and n is an integer (order of diffraction).
The diffraction pattern, that includes position (angles) and intensities of the diffracted beam provides information about the sample and are discussed below:

- Angles are used to calculate the interplanar atomic spacing (d-spacing). Because every crystalline material will give a characteristic diffraction pattern and can act as a unique ‘fingerprint’, the position (d) and intensity (I) information are used to identify the type of material by comparing them with patterns for over 80,000 data entries in the International Powder Diffraction File (PDF) database, complied by the Joint Committee for Powder Diffraction Standards (JCPDS). By this method, identification of any crystalline compounds, even in a complex sample can be made.

- The position (d) of diffracted peaks also provides information about how the atoms are arranged within the crystalline compound (unit cell size or lattice parameter). The intensity information is used to assess the type and nature of atoms. Determination of lattice parameter helps understand extent of solid solution (complete or partial substitution of one element for another, as in some alloys) in a sample.

- Width of the diffracted peaks is used to determine crystallite size and micro-strain in the sample.

- The ‘d’ and ‘I’ from a phase can also be used to quantitatively estimate the amount of that phase in a multi-component mixture [4].

2.3.1b Particle size determination

Diffraction peak positions are accurately measured with XRD, which makes it the best method for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the diffraction peak positions. Inhomogeneous strains vary from crystallite to
crystallite or within a single crystallite and this cause a broadening of the diffraction peaks that increase with sinθ. Peak broadening is also caused the finite size of crystallites, but here the broadening is independent of sinθ. This is because they have too small number of parallel diffraction planes and eventually they produce broadened diffraction peaks instead of sharp peak. When both crystallite size and inhomogeneous strain contribute to peak width, these can be separately determined by careful analysis of peak shapes [4].

If there is no inhomogeneous strain, the crystallite size D can be estimated from the peak width using Scherrer’s formula:

\[ D = \frac{(K\lambda)}{(\beta \cos \theta_B)} \]  

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width half maximum (FWHM) of a diffraction peak, \( \theta_B \) is the diffraction angle and \( K \) is the Scherrer’s constant of the order of units, usually \( \sim 0.9 \) [4-5].

2.3.2 Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) spectroscopy for the synthesized solid electrolytes were recorded using Perkin Elmer spectrum RX I with spectral range of 4000-400 cm\(^{-1}\) and this is available at The Standard Fireworks Rajarathnam Women’s College, Sivakasi, Tamilnadu, India.

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material [6]. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared
spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis [7].

2.3.2a Working principle

The key component in the FT-IR system in the Michelson interferometer is schematically illustrated in figure 2.2. The infrared radiation from a source enters the Michelson interferometer [7]. The interferometer is composed of one beam-splitter and two mirrors. The beam-splitter transmits half of the infrared (IR) beam from the source and reflects the other half. The two split beams strike a fixed mirror and a moving mirror, respectively. After reflecting from the mirrors, the two split beams combine at the beam-splitter again in order to radiate the sample before the beams are received by a detector [8-10].

![Fig. 2.2 Schematic representation of the Michelson interferometer](image)
2.3.3 Ultraviolet spectroscopy

Ultraviolet-Visible (UV-Vis) absorption spectra for the synthesized solid electrolytes were recorded in a Perkin Elmer Lambda 35 spectrophotometer. This facility is offered at The Standard Fireworks Rajarathnam Women’s College, Sivakasi, Tamilnadu, India.

UV spectroscopy is an important tool in analytical chemistry. The other name of UV (Ultra-Violet) spectroscopy is electronic spectroscopy as it involves the promotion of the electrons from the ground state to the higher energy or excited state [9]. The UV-Vis spectral region extends from 190 to 400 nm (UV range) and from 400 to 780 nm (Visible range). Generally, the most favoured transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) [11]. For most of the molecules, the lowest energy occupied molecular orbitals are s orbital, which correspond to sigma bonds. The p orbitals are at somewhat higher energy levels, the orbitals (nonbonding orbitals) with unshared paired of electrons lie at higher energy levels. The unoccupied or antibonding orbitals (\(\Pi^*\) and \(\sigma^*\)) are the highest energy occupied orbitals. In all the compounds (other than alkanes), the electrons undergo various transitions [12-13].

2.3.3a Working principle

UV spectroscopy obeys the Beer-Lambert law, which states that when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution. The expression of Beer-Lambert law is

\[
A = \log(I_0/I) = ECL \quad \text{---------------------- (4)}
\]
where \( A = \text{absorbance}, \ I_0 = \text{intensity of light incident upon sample cell}, \ I = \text{intensity of light leaving sample cell}, \ C = \text{molar concentration of solute}, \ L = \text{length of sample cell (cm)} \) and \( E = \text{molar absorptivity}. \)

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy [14-15]. Figure 2.3 shows the simplified schematic of double beam UV-visible spectrometer.

![Fig. 2.3 Simplified schematic of double beam UV-Visible spectrophotometer](image)

### 2.3.3b Determination of band gap

The absorption of photons in a semiconductor with energy \( h\nu \) equal to or higher than that of the band gap \( E_g \) leads to the generation of excitons – optical transitions producing electrons in the conduction band and holes in the valence band. For such transitions to occur, the wave vector \( (k) \) must be conserved \( (k=0) \). In a direct band gap semiconductor where the wave vector
is conserved, the relationship between the adsorption coefficient ($\alpha$) near the absorption edge and
the optical band gap ($E_g$) obeys the following relation

$$(\alpha h\nu)^2 = A (h\nu - E_g) \quad \text{---------------------------------- (5)}$$

where ‘$\alpha$’ is the absorption co-efficient, $h\nu$ is the photon energy and ‘$E_g$’ is the Optical
band gap and ‘$A$’ is the proportionality constant. The optical band gap for the absorption edge
can therefore be obtained by extrapolating the linear portion of $(\alpha h\nu)^2 - h\nu$ to $\alpha = 0$ [16-17].

2.3.4 Photoluminescence spectroscopy

Photoluminescence spectra for the synthesized solid electrolytes were recorded from The
Standard Fireworks Rajarathnam Women’s College, Sivakasi, Tamilnadu, India using Perkin
Elmer Lambda 35 spectrophotometer.

Photoluminescence (PL) spectroscopy is a very efficient, contactless, nondestructive,
widely used technique for the analysis of the optoelectronic properties of semiconductors, which
requires very little sample manipulation. Photoluminescence is defined as the spontaneous
emission of light from a material under optical excitation and can be therefore used to provide
detailed information on discrete electronic states involving both intrinsic optical processes and
about the wide variety of defect which are endemic in practical semiconductor materials and
extrinsic optical processes (internal transitions involving defects and their energy levels) by
applying an external light with energy $h\nu \geq E_g$; where $E_g$ denotes the energy band gap and
observing the re-emitted photons [18-19].

2.3.4a Working Principle

Photoluminescence spectroscopy is an important technique of probing the electronic
structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess
energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence [15, 18]. Figure 2.4 exhibits the block diagram of the luminescence spectrometer.

**Fig. 2.4 Block diagram of the luminescence spectrophotometer**

Photo-excitation causes electrons within a material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a non-radiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radioactive process [20-22].
2.3.5 Scanning electron microscopy

In the present work, SEM images have been obtained from Gandhigram Rural University, Dindigul, Tamilnadu, India using TESCAN VEGA 3 LMU instrument.

SEM is a microscope that uses electrons instead of light to form an image. Since their development in the early 1950's, scanning electron microscopes have developed new areas of study in the medical and physical science communities. The SEM has allowed researchers to examine a much bigger variety of specimens. The scanning electron microscope has many advantages over traditional microscopes. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the degree of magnification [23-24]. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today.

2.3.5a Working principle

Figure 2.5 demonstrates the block diagram of a scanning electron microscope. A scanning electron microscope is in principle a microscope generating an electron beam scanning forth and back over a sample. Due to the interaction between the beam and the sample, several different signals are produced providing the user with detailed information about the surface structure, differences of atomic number within the sample or information about the elemental content [25-27].
Fig. 2.5 Block diagram of a scanning electron microscope

2.3.6 Transmission electron microscopy

In this research, surface morphological photographs were taken with JEOL 2100F transmission electron microscope available at University of Madras, Chennai, Tamilnadu, India. The synthesized solid electrolytes were dispersed in ethanol and it was ultrasonicated for 20 minutes. A drop of dispersion was coated onto the copper grid and TEM images were obtained.

The conventional electron microscopy is nowadays called TEM (transmission electron microscopy). The initial designs of the microscopes were able to magnify specimens up to seventeen times greater than that of a light microscope; modern designs have a resolution almost of 10,000 times greater. One of the major historical limitations of TEM was that electrons were largely unable to pass through thick specimens; until the diamond knife and ultra-microtome were designed in 1951; it was largely impossible to utilize this instrument to full capacity. While the theoretical upper limit of the transmission electron microscope is estimated to be as high as
10,000 times that of a light microscope, flaws in the equipment used lower the real limit. Combined with difficulty in preparing specimens, it is realistically only possible to resolve an object to about 0.025 nm whereas a light microscope can resolve an object to about 2 nm at maximum resolution [26, 28].

2.3.6a Working principle

The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms [29-30]. Figure 2.6 represents the functional block diagram of transmission electron microscope.

![Functional block diagram of TEM](image)

**Fig. 2.6 Functional block diagram of TEM**
2.3.7 Electrochemical Investigations

Electrochemical measurements such as AC impedance spectroscopy, cyclic voltammetry and chronoamperometry were performed on a CHI608E electrochemical workstation available at Thiruvalluvar University, Vellore, Tamilnadu, India. It has conventional three electrode configuration with a Pt-wire as counter electrode, Ag/AgCl (in 1 M KCl) as a reference electrode and the synthesized solid electrolytes as working electrode. A 1 M H$_2$SO$_4$ aqueous solution was used as the electrolyte. The working electrode was prepared by doctor blade method using scotch tape as spacer. In the typical preparation, 5 mg of synthesized solid electrolytes were ground with 10 µL of Triton X-100 and 20 µL of deionized water to make a slurry. The slurry was spread on a 1.5 x 1.5 cm$^2$ fluorine-doped tin oxide (FTO) glass substrate with an active area of about 0.5 cm$^2$ and then dried in hot plate at 80 °C for 3 h.

Further to understand the oxide ion conductivity at intermediate temperature region (300 to 600 °C), the synthesized solid electrolytes were made in the form of pellets with the dimensions ~10 X 1.3 mm$^2$ (dia X thickness) and sintered around 1200 °C for 5 h under air atmosphere. Relative density of the pellets found approximately 95% of the theoretical density was obtained by Archimedes principle. AC impedance measurements were performed using CHI608E electrochemical workstation assisted with a muffle furnace in air atmosphere.

2.3.7.1 AC impedance spectroscopy

When used to study electrochemical systems, electrochemical impedance spectroscopy (EIS) can give you accurate, error-free kinetic and mechanistic information using a variety of techniques and output formats. For this reason, EIS is becoming a powerful tool in the study of corrosion, semiconductors, batteries, electroplating, and electro-organic synthesis [31].
The terms resistance and impedance both denote an opposition to the flow of electrons or current. In direct current (dc) circuits, only resistors produce this effect. However, in alternation current (ac) circuits, two other circuit elements, capacitors and inductors, impede the flow of electrons. Impedance can be expressed as a complex number, where the resistance is the real component and the combined capacitance and inductance is the imaginary component. The total impedance in a circuit is the combined opposition of all its resistors, capacitors, and inductors to the flow of electrons. The opposition of capacitors and inductors is given the same name reactance, symbolized by X and measured in ohms (Ω). Since the symbol for capacitance is C, capacitive reactance is symbolized by $X_C$. Similarly, since the symbol for inductance is L, inductive reactance is symbolized by $X_L$. Capacitors and inductors affect not only the magnitude of an alternating current but also its time-dependent characteristics – or phase. When most of the opposition to current flow comes from its capacitive reactance, a circuit is said to be largely capacitive and the current leads the applied voltage in phase angle. When most of the opposition to current flow comes from its inductive reactance, a circuit is said to be largely inductive and the current lags the applied voltage in phase angle. The more inductive a circuit is, the closer the difference in phase angle approaches 90 degrees. It’s sometimes easier to perform calculations using admittance, the reciprocal of impedance. Admittance is symbolized by Y and measured in siemens (S). Like impedance, admittance can be expressed as a complex number, where the conductance, the reciprocal of resistance, is the real component, and the susceptance, the reciprocal of reactance, is the imaginary component [31].
2.3.7.1a Working principle

A basic overview of the working principle of a potentiostat/galvanostat is shown in figure 2.7. Depending on the application, the connections of the instrument to the electrochemical cell can be (or must be) set up in different ways.

Fig. 2.7 Basic diagram of a potentiostat/galvanostat

In potentiostatic mode, a potentiostat/galvanostat (PGSTAT) will accurately control the potential of the Counter Electrode (CE) against the Working Electrode (WE) so that the potential difference between the working electrode (WE) and the Reference Electrode (RE) is well defined, and correspond to the value specified by the user. In galvanostatic mode, the current flow between the WE and the CE is controlled. The potential difference between the RE and WE and the current flowing between the CE and WE are continuously monitored. By using a
PGSTAT, the value specified by the user (i.e. applied potential or current) is accurately controlled, anytime during the measurement by using a negative feedback mechanism.

As can be seen from the diagram, the CE is connected to the output of an electronic block which is called Control Amplifier (CA). The control amplifier forces current to flow through the cell. The value of the current is measured using a Current Follower (LowCF) or a Shunt (HighCR), for low and high currents, respectively. The potential difference is measured always between the RE and S with a Differential Amplifier (Diffamp). Depending on the mode the instrument is used (potentiostatic or galvanostatic) the PSTAT/GSTAT switch is set accordingly. The signal is then fed into the Summation Point (Σ) which, together with the waveform set by the digital-to-analog converter (E_{in}) will be used as an input for the control amplifier. The cell cables of the Autolab PGSTAT (figure 2.7) have a total of five connectors: WE, CE, RE, S and ground. The potential is always measured between the RE (blue) and the S (red) and the current is always measured between the WE (red) and CE (black). The ground connector (green) can be used to connect external devices to the same ground of the PGSTAT.

2.3.7.1b Instrumental process

The **counter electrode (also known as auxiliary electrode)**, is an electrode which is used to close the current circuit in the electrochemical cell. It is usually made of an inert material (e.g. Pt, Au, graphite, glassy carbon) and usually it does not participate in the electrochemical reaction. Because the current is flowing between the WE and the CE, the total surface area of the CE (source/sink of electrons) must be higher than the area of the WE so that it will not be a limiting factor in the kinetics of the electrochemical process under investigation.

The **reference electrode** is an electrode which has a stable and well-known electrode potential and it is used as a point of reference in the electrochemical cell for the potential control
and measurement. The high stability of the reference electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations of each participants of the redox reaction. Moreover, the current flow through the reference electrode is kept close to zero (ideally, zero) which is achieved by using the CE to close the current circuit in the cell together with a very high input impedance on the electrometer (> 100 GΩ).

The **working electrode** is the electrode in an electrochemical system on which the reaction of interest is occurring. Common working electrodes can be made of inert materials such as Au, Ag, Pt, glassy carbon (GC) and Hg drop and film electrodes etc. For corrosion applications, the material of the working electrode is the material under investigation (which is actually corroding). The size and shape of the working electrode also varies and it depends on the application.

**Two electrode setup**

In a two-electrode cell setup, CE and RE are shorted on one of the electrodes while the WE and S are shorted on the opposite electrode. The potential across the complete cell is measured. This includes contributions from the CE/electrolyte interface and the electrolyte itself. The two-electrode configuration can therefore be used whenever precise control of the interfacial potential across the WE electrochemical interface is not critical and the behavior of the whole cell is under investigation. This setup is typically used with energy storage or conversion devices like batteries, fuel cells, photovoltaic panels etc. It is also used in measurements of ultrafast dynamics of electrode processes or electrochemical impedance measurements at high frequencies (> 100 kHz).
**Three electrode setup**

The three-electrode cell setup is the most common electrochemical cell setup used in electrochemistry. In this case, the current flows between the CE and the WE. The potential difference is controlled between the WE and the CE and measured between the RE (kept at close proximity of the WE) and S. Because the WE is connected with S and WE is kept at pseudo-ground (fixed, stable potential), by controlling the polarization of the CE, the potential difference between RE and WE is controlled all the time. The potential between the WE and CE usually is not measured. This is the voltage applied by the control amplifier and it is limited by the compliance voltage of the instrument. It is adjusted so that the potential difference between the WE and RE will be equal to the potential difference specified by the user. This configuration allows the potential across the electrochemical interface at the WE to be controlled with respect to the RE.

**Four electrode setup**

The four-electrode cell setup is used for applications where the potential difference (between RE and S) which occurs as a result of a passage of a current across a well defined interface (between WE and CE) needs to be measured. This type of experimental setup is not very common in electrochemistry and usually it is used for measurements of junction potentials between two non miscible phases or across a membrane, giving the possibility to calculate the resistance of the interface or the membrane conductivity.

**2.3.7.1c The Nyquist plot**

Figure 2.8.1 shows one popular format for evaluating electrochemical impedance data, the Nyquist plot. This format is also known as a Cole-Cole plot or a complex impedance plane
plot. In our study, we plotted the imaginary impedance component ($Z''$) against the real impedance component ($Z'$) at each excitation frequency [31].

![Nyquist plot](image)

**Fig. 2.8.1 Nyquist plot for a simple electrochemical system**

We saw that at high frequencies, the impedance of the Randles cell was almost entirely created by the ohmic resistance, $R_Ω$. The frequency reaches its high limit at the leftmost end of the semicircle, where the semicircle touches the x axis. At the low frequency limit, the Randles cell also approximates a pure resistance, but now the value is (% + $R_t$). The frequency reaches its low limit at the rightmost end of the semicircle. The Nyquist plot has several advantages. The primary one is that the plot format makes it easy to see the effects of the ohmic resistance. If you take data at sufficiently high frequencies, it is easy to extrapolate the semicircle toward the left, down to the x axis to read the ohmic resistance. The shape of the curve (often a semicircle) does not change when the ohmic resistance changes. Consequently, it is possible to compare the results of two separate experiments that differ only in the position of the reference electrode.
Another advantage of this plot format is that it emphasizes circuit components that are in series, such as $R_\Omega$. The Nyquist plot format also has some disadvantages. For example, frequency does not appear explicitly. Secondly, although the ohmic resistance and polarization resistance can be easily read directly from the Nyquist plot, the electrode capacitance can be calculated only after the frequency information is known. Although the Nyquist format emphasizes series circuit elements, if high and low impedance networks are in series, you will probably not see the low impedance circuit, since the larger impedance controls plot scaling [32-33].

2.3.7.2 Cyclic voltammetry

Cyclic voltammetry (CV) is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time. Unlike in linear sweep voltammetry, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as desired. The current at the working electrode is plotted versus the applied voltage (i.e., the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution [34-35].
2.3.7.2a Working principle

In cyclic voltammetry, the electrode potential ramps linearly versus time in cyclical phases shown in figure 2.8.2b. The rate of voltage change over time during each of these phases is known as the experiment's scan rate (V/s). The potential is applied between the working electrode and the reference electrode while the current is measured between the working electrode and the counter electrode. These data are plotted as current ($i$) vs. applied potential ($E$, often referred to as just 'potential'). In Figure 2.8.2b, during the initial forward scan (from $t_0$ to $t_1$) an increasingly reducing potential is applied; thus the cathodic current will, at least initially, increase over this time period assuming that there are reducible analytes in the system. At some point after the reduction potential of the analyte is reached, the cathodic current will decrease as the concentration of reducible analyte is depleted. If the redox couple is reversible then during the reverse scan (from $t_1$ to $t_2$) the reduced analyte will start to be re-oxidized, giving rise to a current of reverse polarity (anodic current) to before. The more reversible the redox couple is, the more similar the oxidation peak will be in shape to the reduction peak. Hence, CV data can provide information about redox potentials and electrochemical reaction rates [36].
For instance, if the electron transfer at the working electrode surface is fast and the current is limited by the diffusion of analyte species to the electrode surface, then the peak current will be proportional to the square root of the scan rate. This relationship is described by the Cottrell equation. In this situation, the CV experiment only samples a small portion of the solution, i.e., the diffusion layer at the electrode surface [37].

2.3.7.2b Instrumental process

CV experiments are conducted on a solution in a cell fitted with electrodes [36, 38]. The solution consists of the solvent, in which are dissolved electrolyte and the species to be studied.

The cell

A standard CV experiment employs a cell fitted with three electrodes: reference electrode, working electrode, and counter electrode. This combination is sometimes referred to as a three-electrode setup. Electrolyte is usually added to the sample solution to ensure sufficient conductivity. The solvent, electrolyte, and material composition of the working electrode will determine the potential range that can be accessed during the experiment.

The electrodes are immobile and sit in unstirred solutions during cyclic voltammetry. This "still" solution method gives rise to cyclic voltammetry's characteristic diffusion-controlled peaks. This method also allows a portion of the analyte to remain after reduction or oxidation so that it may display further redox activity. Stirring the solution between cyclic voltammetry traces is important in order to supply the electrode surface with fresh analyte for each new experiment. The solubility of an analyte can change drastically with its overall charge; as such it is common for reduced or oxidized analyte species to precipitate out onto the electrode. This layering of analyte can insulate the electrode surface, display its own redox activity in subsequent scans or
otherwise alter the electrode surface in a way that affects the CV measurements. For this reason it is often necessary to clean the electrodes between scans.

Common materials for the working electrode include glassy carbon, platinum, and gold. These electrodes are generally encased in a rod of inert insulator with a disk exposed at one end. A regular working electrode has a radius within an order of magnitude of 1 mm. Having a controlled surface area with a well-defined shape is necessary for being able to interpret cyclic voltammetry results [36].

To run cyclic voltammetry experiments at very high scan rates a regular working electrode is insufficient. High scan rates create peaks with large currents and increased resistances, which result in distortions. Ultra microelectrodes can be used to minimize the current and resistance.

The counter electrode, also known as the auxiliary or second electrode, can be any material that conducts current easily and will not react with the bulk solution. Reactions occurring at the counter electrode surface are unimportant as long as it continues to conduct current well. To maintain the observed current the counter electrode will often oxidize or reduce the solvent or bulk electrolyte [36].

**Solvents**

CV can be conducted using a variety of solutions. Using typical electrodes, solvents dissolve not only the analyte, often at mM levels, but also electrolyte, generally at much higher concentrations. For aqueous solutions, these requirements are trivial, but for nonaqueous solutions, the choices of suitable solvents are fewer.
Electrolyte

The electrolyte ensures good electrical conductivity and minimizes internal resistance such that the recorded potentials correspond to actual potentials. For aqueous solutions, many electrolytes are available, but typical ones are alkali metal salts of perchlorate and nitrate. In nonaqueous solvents, the range of electrolytes is more limited, and a popular choice is tetrabutylammonium hexafluorophosphate [39].

2.3.7.3 Chronoamperometry

Chronoamperometry is an electrochemical technique in which the potential of the working electrode is stepped and the resulting current from faradaic processes occurring at the electrode (caused by the potential step) is monitored as a function of time. However, as with all pulsed techniques, chronoamperometry generates high charging currents, which decay exponentially with time as any RC circuit [40-41]. The Faradaic current, which is due to electron transfer events and is most often the current component of interest decays as described in the Cottrell equation. In most electrochemical cells this decay is much slower than the charging decay-cells with no supporting electrolyte are notable exceptions. Most commonly investigated with a three electrode system. Since the current is integrated over relatively longer time intervals, chronoamperometry gives a better signal to noise ratio in comparison to other amperometric technique [36, 42].
2.3.7.3a Working principle

At the beginning of the transient experiment the potential of the working electrode is held at $E_i$ (Fig. 2.8.4 a). At $t = 0$ the potential is instantaneously changed to a new value $E_1$, and corresponding current time response is recorded as shown in figure 2.8.4b.

Figure 2.8.4 The chronoamperometric experiment a) The potential-time profile applied during experiment, $E_i$ is initial value and $E_1$ is the potential where no reduction occurs or some other potential of interest b) The corresponding response of the current due to changes of the potential
It is important that such an analysis has to be applied over a broad time interval in order to ensure the reliability of results. At short times the current consists of a large non-faradaic component due to charging of the double-layer capacitance. At long time, however, the natural convection (may be caused by temperature and concentration gradients) comes into effect and diffusion in that case is not the only mode of the mass transport. Hence, the typical time range of chronoamperometric measurements lies normally in the range from 0.001 to 10 s. However, there are a number of additional instrumental and experimental limitations [36]. For example, current and voltage characteristics of a potentiostat can limit the current maximum and time resolution. Even though the chronoamperometry is relatively simple technique, there are a number of difficulties, which are related to the interpretation of the current-transient curve. Hence, it is very important to find the possibility of comparative analysis of the chronoamperometric results with the results of cyclic voltammetry and other techniques. This type of comparison will also help to understand the studied system more completely and with better precision [36, 43].

2.3.7.3b Instrumental process

Chronoamperometry experiments are conducted on a solution in a cell fitted with electrodes. This instrumental technique is similar as cyclic voltammetry technique as discussed earlier in the cyclic voltammetry section. The potential was stepped up from an initial potential to a final potential and the step time was optimized. The initial potential was chosen, where no redox reaction occurred and the final potential was chosen where the reaction of interest was over. Current – time relation is monitored [5, 44-45].
References


