CHAPTER 3
EXPERIMENTAL METHODOLOGY AND TECHNIQUES USED IN THIS RESEARCH WORK

3.1 INTRODUCTION

This chapter explains the experimental method that has been used for the preparation of alternate electrolyte, anode and cathode materials for SOFC application and also describes the instrumentation and working principle of various instruments that have been used for characterizing the prepared materials. Chemical precipitation method was used for the synthesis of nanocrystalline materials. In this research work cetyl trimethyl ammonium bromide (CTAB) was used as surfactant throughout the experiment to avoid agglomeration during the synthesis of nanomaterials. The thermal properties of the corresponding precursor samples were studied by thermo gravimetric analysis. Structural studies of the prepared nanocrystalline powders were done by using X-ray diffractometer. Morphological studies of the prepared samples were done by using SEM and Particle size analysis. The chemical structures of the materials were studied by FTIR spectroscopy. The elemental composition of the samples was detected by EDAX analysis. The high temperature electrical properties of the prepared samples were experimented by using AC impedance analyzer.

3.2 CO-PRECIPITATION PROCESS FOR THE PREPARATION OF ELECTROLYTE, ANODE AND CATHODE MATERIALS FOR SOFCs

Among the various techniques reported, co-precipitation technique is a simple and promising process to produce homogeneous and small-sized powders. It is a well known that soft chemical synthesis routes are economically so cheap. Surfactant addition play an important role in producing very fine nanomaterials with improved characteristics. In this work, a set of homogeneous alternate electrolyte, anode and cathode nano ceramic powders were synthesized by the co-
precipitation method with the addition of surfactant [cetyl tri methyl ammonium bromide (CTAB)]. CTAB is a cationic surfactant and also known as Cetrimonium bromide or hexa decyl trimethyl ammonium bromide. As any surfactant, it forms micelles in aqueous solutions. The schematic figure of the CTAB surfactant has shown below in the Figure 3.1. CTAB has used by many researchers for producing oxide materials with excellent particle characteristics.\(^{48}\)

\[
\text{Figure 3.1 The schematic structure of CTAB (C}_{19}\text{H}_{42}\text{BrN)}
\]

3.2.1 General Methodology of Co-precipitation Method

In the typical process, stoichiometric compositions of aqueous metal nitrate solutions [as basic materials] and sodium hydroxide solutions [as precipitator material] were prepared in distilled water. The surfactant was dissolved in the later solution. Initially, the aqueous metal nitrate solutions were added slowly drop-wise to the sodium hydroxide solution. They were mixed perfectly by a magnetic stirring apparatus at room temperature for an hour. Throughout the experiment, the pH was maintained above 9 by the addition of alkali in order to get precipitation.\(^{48}\) The resultant precipitate (Metal hydroxide) was filtered and dried. The resultant material was calcined to get a phase pure product. After calcination, the samples were well powdered by grinding process using a pestle and mortar. The general representation of co-precipitation method is given in Figure 3.2.
3.2.2 Details and different compositions of electrolyte, anode and cathode nanocrystalline materials

The elaborative preparative procedures and the reaction mechanisms improved in the preparation of electrolyte, anode and cathode materials were presented in the chapters 4, 5 and 6. The list of nanocrystalline materials studied in this research work is indicated below.

- For electrolyte application of SOFC
  - $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}/\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{2-\delta}$
  - $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}/\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{2-\delta}$
  - $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}/\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$

Figure 3.2 General representation of co-precipitation Method
• Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ - Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$
• Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$
• Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$

For anode application of SOFC

• NiO-Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$ - Ce$_{0.9}$Y$_{0.1}$O$_{2-\delta}$
• NiO-Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ - Ce$_{0.8}$Y$_{0.2}$O$_{2-\delta}$
• NiO-Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$ - Ce$_{0.9}$Sm$_{0.1}$O$_{2-\delta}$
• NiO-Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ - Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$
• NiO-Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$
• NiO-Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$

For cathode application of SOFC

• La$_{0.9}$Sr$_{0.1}$Co$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$
• La$_{0.8}$Sr$_{0.2}$Co$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$
• La$_{0.9}$Sr$_{0.1}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$
• La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$

All the above nanocrystalline materials were analysed by using appropriate characterization techniques.

### 3.3 CHARACTERIZATION TECHNIQUES

A brief discussion about the characterization techniques used in this research work is indicated in the following sections.

#### 3.3.1 Thermo Gravimetric Analysis (TGA)

In order to obtain the information about the exact temperature of the formation of phase pure compounds after completion of reaction, thermal analysis (TG) on the precursor materials was studied.

Thermo gravimetric analysis experiments were carried out with Perkin Elmer TGA 7 instrument (Figure 3.3.) under nitrogen atmosphere at a heating rate of 10 °C/minute between 25 °C and 700 °C. The dried precursor materials were finely ground and subjected to thermo gravimetric analysis.
3.3.2 X-Ray Diffraction (XRD)

X-ray powder diffraction is a rapid analytical technique primarily used for the phase identification of a crystalline material and can provide information on unit cell dimensions. The calcined material is finely ground, homogenized, and subjected to XRD analysis. The XRD reveals a detailed information about the chemical composition and crystallographic structure of materials.
XRD is one of the important characterization tools used in solid state chemistry and materials science. The schematic photograph of the XRD instrument used in this research work is given in Figure 3.4.

Powdered sample is placed on a sample holder and then illuminated with x-rays of a fixed wavelength and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the interatomic spacing (d value in Angstrom units) by using Bragg’s equation (Equation 3.1).

\[ n\lambda = 2d \sin\theta \]  \hspace{1cm} 3.1

Where, \( n \) is an integer (1, 2, 3, ......, n), \( l \) the wavelength, \( d \) the distance between atomic planes, and \( \theta \) the angle of incidence of the x-ray beam and the atomic planes.

XRD of metal nano particles give broad peaks. The broadening provides information about crystallite size by Debye- Scherrer equation. Crystallite size of the samples was calculated from XRD line broadening method using the following Scherrer relationship (Equation 3.2).

\[ D_p = \frac{k\lambda}{\beta \cos\theta} \]  \hspace{1cm} 3.2

Where ‘\( D_p \)’ is the crystallite size in nm, ‘k’ is a numerical constant (~0.9), ‘\( \lambda \)’ is the wavelength of X-rays (for Cu K\( \alpha \) radiation, \( \lambda = 1.5418 \) Å), ‘\( \beta \)’ is the effective broadening taken as a full width at half maximum (FWHM) (in radians), ‘\( \theta \)’ is the diffraction angle for the peak.

The lattice parameters are calculated from 2\( \theta \) values in the X-ray diffraction patterns by using DOS computer programming. The theoretical density (\( D_X \)) for the samples was calculated according to the formula (Equation 3.3).

\[ D_X = \frac{Z \times M}{N \times V} \text{ g.cm}^{-3} \]  \hspace{1cm} 3.3

Where, \( Z \) = number of chemical species in the unit cell, \( M \) = molecular mass of the sample (g/mol), \( N \) = Avogadro’s number (6.022 x 10\(^{23}\)) and \( V \) is the volume of the crystalline unit cell as determined by x-ray diffraction.
3.3.3 Fourier Transform Infrared (FTIR) spectroscopy

Identification of specific types of chemical bonds or functional groups based on their unique absorption signatures is possible by infrared spectroscopy. Chemical bond stretching and bending is possible by absorption of energy. This energy is in the IR range of electromagnetic spectrum. Fourier transform infrared spectroscopy (FTIR) offers several advantages than conventional IR spectroscopy and hence FTIR is widely adopted now-a-days. Functional groups attached to the metal nanoparticle surface show different FTIR pattern than those of free groups hence FTIR gives information about the surface chemistry of nanomaterials.117

Figure 3.5 FT/IR-4100 from JASCO, Japan

FTIR measurements were performed for the materials using a FTIR spectrophotometer, FT/IR-4100 from JASCO, Japan (Figure 3.5). The solid samples were thoroughly ground and mixed with KBr. The mixture was compressed to prepare disc for FTIR analysis by using KBr press as shown in Figure 3.6.

Figure 3.6 KBr press for pellet preparation
The samples were air dried for water evaporation, the holder was mounted in the sample window of the spectrometer and the sampling window was scanned. FTIR spectra were recorded in the range from 400 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and averaged over 25 scans.

3.3.4 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX)

The SEM is a microscope that uses electrons instead of light to form an image. The SEM has allowed researchers to examine a much bigger variety of specimens. In the present work, JEOL Model JSM 6390 SEM instrument that is equipped with Oxford Instrument INCA energy EDX was used and it is shown in Figure 3.7. EDAX is a widely used technique to analyze the chemical compositions in a material under SEM. This method detects the X-rays produced as the result of the electron beam interactions with the sample. SEM-EDAX is many times routinely used to obtain morphological information of the surface of the sample and identification of chemical composition of the sample.

![SEM (JEOL model JSM 6390 instrument)](image)

Figure 3.7 SEM (JEOL model JSM 6390 instrument)

3.3.5 Particle Size Analysis

The particle size of the powder was measured with a Malvern particle size analyzer [(Malvern Instruments, Worcestershire, UK) Figure 3.8] using triple-distilled water as medium.
Before subjecting the sample for the particle size analysis, the sample was sonicated in triple distilled water with the ultrasonic processor (UP400S) as shown in Figure 3.9. After sonication, the samples were subjected to particle size analysis in this study.

**Figure 3.9 Hielscher ultrasonic laboratory device UP400S**

**3.3.6 Conductivity Studies**

Electrochemical impedance spectroscopy (EIS) has a very important role in the applied and fundamental electrochemistry. EIS is new and powerful technique for characterizing the electrochemical behavior of the materials.

The electrical characteristics of the prepared samples were determined by using Alternative current (AC) impedance analysis. The electrical conductivity of the material was calculated from the open circuit impedance spectra obtained for the samples.
The circular pellets were prepared from the nanomaterials by using the hydraulic pressure pelletizer (as indicated in Figure 3.10). Then, the prepared pellets were sintered at appropriate temperature (700 °C) for 3 hours and they were subjected for high temperature EIS analysis.

![Hydraulic pressure pelletizer](image1)

**Figure 3.10 Hydraulic pressure pelletizer**

Complex impedance spectroscopy measurements have carried out using a Solatron 1260 frequency response analyzer (FRA) combined with Solatron 1296 electrochemical interface (ECI). The electrochemical impedance spectroscopy setup (a common hardware configuration) for measuring the samples is shown in the Figure 3.11.

![Electrochemical impedance spectroscopy setup](image2)

**Figure 3.11 The electrochemical impedance spectroscopy setup**
Equivalent circuit modeling has been accepted as the means of interpreting electrochemical impedance results, as this offers a convenient way of analyzing and investigating changes in cell behavior. Results are plotted in the complex plane (Nyquist plot) or as magnitude and phase versus frequency (Bode plot).

The bulk resistance ($R_b$) can be determined from the intercept of the low-frequency part of the arc with real $Z'$-axis. As the temperature increases, the $R_b$ value shifts towards a lower impedance value.

The bulk conductivity can be obtained from the following equation. (Equation 3.4).

$$\sigma = \frac{t}{RA} \quad - - - - - - - - - - - - - - - - - - - - - 3.4$$

Where ‘$\sigma$’ is represented as total conductivity, ‘$t$’ and ‘$A$’ are the thickness and cross sectional area of the pellet and ‘$R$’ is a resistance.

Activation energies, correspond to the conductivity in high temperature range, were determined from the linear fit of the Arrhenius curves. Activation energy of all samples was calculated by using Arrhenius relationship equation.

Arrhenius equation, (Equation 3.5)

$$\sigma_{dc}(T) = \sigma_o \exp\left(-\frac{E_a}{K_BT}\right) \quad - - - - - - - - - - - - - - - - - - - - 3.5$$

‘$\sigma$’ is represented as direct current conductivity

$T$ = temperature

$\sigma_o$ = Pre-exponentional factor

$E_a$ = activation energy and

$K_B$= Boltzmann constant