CHAPTER 2

MATERIALS AND EXPERIMENTAL METHODS

2.1 INTRODUCTION

In this chapter, materials used for the preparation of two different types of composites such as gadolinium doped barium cerate and samarium doped barium cerate is discussed completely and the various methods involved in the characterization of powder and pellets are elaborated. Both the composites $\text{Ba}_x\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ and $\text{Ba}_x\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ are prepared stoichiometrically with mole fraction of barium ($x = 0.1, 0.2, 0.3$ and $0.4$) through chemical co precipitation method. The composite electrolytes are then characterized through DSC-TG analysis to know their calcination temperature. Structural investigation is carried out using XRD analysis for the conformation of their phase purity and crystallinity. The average particle size distribution of as prepared powder is analyzed using HRTEM and the elemental compositions are qualitatively studied through EDS analysis. Morphology information and density of the composites are obtained using SEM and Archimedes principle. AC impedance analysis is carried out for both the composites to know their electrical response and their total ionic conductivity.
2.2 MATERIALS USED FOR POWDER SYNTHESIS

Cerium nitrate hexahydrate, Gadolinium oxide, Samarium nitrate and barium nitrate (99.5% pure) are used as the precursor powder for the preparation of GDC-BCG and SDC-BCS composites purchased from Sigma-Aldrich.

2.2.1 Co-precipitation method

Co-precipitation method is the promising technique used to prepare the homogeneous fine powder. The precursor powder is heated to obtain the desired oxides of the initial compound. The process of thermal decomposition of the precursor powder is termed as calcination. Distinct from solid state reaction method, co-precipitation method finds its own advantages in the synthesis of oxide powders and mixing them homogenously at the molecular level. Preferentially in chemical route, ammonium hydroxide is used as precipitation agent. NH₄OH is mixed uniformly with the solution of precursor metal salts such as barium nitrate, cerium nitrate and gadolinium. In order to maintain the homogeneity of the precursor solution, the pH value is limited to lesser than 10. Drying the precursor powder is also an important step to avoid the formation of aggregates in the powder samples to obtain the porous powder. Hence, this co precipitation method is highly advantageous to prepare the homogeneous nano powder.

2.2.2 Preparation of GDC-BCG powder

The gadolinium doped barium cerate powder is successfully synthesized through wet chemical, co-precipitation method. The precursors and its purity used for the preparation are shown in Table 2.1. The
composition fixed for the preparation of GDC-BCG powders is shown in Table 2.2. The powder with various Ba content are christened as P-Ba10CG, P-Ba20CG, P-Ba30CG and P-Ba40CG. The Stoichiometric mixture of cerium nitrate and barium nitrate powders is dissolved individually in a separate beaker with 50 ml of distilled water. Gadolinium oxide (99.9%, Sigma–Aldrich) is converted into gadolinium nitrate by dissolving in 5 ml of nitric acid. The mixture is continuously heated until the oxide dissolved completely into gadolinium nitrates. Gadolinium nitrate is dissolved in 50 ml of distilled water separately in a beaker.

Table 2.1 Precursors name, purity, and source of GDC-BCG powder

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Precursors</th>
<th>Purity (%)</th>
<th>Resource</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cerium nitrate hexahydrate</td>
<td>99.5</td>
<td>Sigma–Aldrich</td>
</tr>
<tr>
<td>2</td>
<td>Barium nitrate</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Gadolinium oxide</td>
<td>99.9</td>
<td></td>
</tr>
</tbody>
</table>

All the three solutions are taken in a separate burette and mixed together in a beaker by adding drop-by-drop. The mixture is stirred continuously at 500 rpm to obtain homogeneous solution.

Table 2.2 Weight ratio for GDC-BCG compositions

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Barium Nitrate (mole fraction)</th>
<th>Cerium Nitrate (mole fraction)</th>
<th>Gadolinium Oxide (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Ba10CG</td>
<td>0.1</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>P-Ba20CG</td>
<td>0.2</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>P-Ba30CG</td>
<td>0.3</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>P-Ba40CG</td>
<td>0.4</td>
<td>0.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>
The pH value of the mixture is maintained at 10 by adding ammonium hydroxide. The mixtures get precipitated as hydroxides of Cerium, Barium and Gadolinium.

![Schematic flowchart of synthesis route and characterization methods to analyze GDC-BCG composite](image)

**Figure 2.1** Schematic flowchart of synthesis route and characterization methods to analyze GDC-BCG composite

The mixture is stirred continuously at 1000 rpm for 30 minutes to get homogeneous solution. Once the homogeneous solution is obtained, 10% of PEG (Poly Ethylene Glycol) is added as binder to the mixture and stirred continuously for 30 minutes to obtain the mixture in gel form. The obtained gel is dried in hot air oven at 95°C for 12 hours. The dried gel is heated in muffle furnace at 400°C for 2 hr to obtain the as prepared powder.
Figure 2.1 shows the experimental procedure for the preparation of GDC-BCG powder and the various characterization steps involved to study thermal, structural, morphology and electrical properties of composites.

### 2.2.3 Preparation of SDC-BCS powder

The samarium doped barium cerate electrolyte is systematically synthesized through chemical co precipitation method. The precursor and its purity used for the preparation are shown in Table 2.3. The composition fixed for the preparation of SDC-BCS powders is summarized and shown in Table 2.4. The powder with various Ba content are christened as P-Ba10CS, P-Ba20CS, P-Ba30CS, and P-Ba40CS. The three salts solutions are dissolved separately each in 50 ml of distilled water. All the three solutions are taken in a separate burette and mixed together in a beaker by adding drop-by-drop. The mixture is stirred continuously at 500 rpm to obtain homogeneous solution.

The pH value of the mixture is maintained at 10 by adding ammonium hydroxide. The mixtures get precipitated as hydroxides of Cerium, Barium and Gadolinium. The mixture is stirred continuously at 1000 rpm for 30 minutes to get homogeneous solution. Once the homogeneous solution is obtained, 10% of PEG (Poly Ethylene Glycol) is added as binder to the mixture and stirred continuously for 30 minutes to obtain the mixture in gel form. The obtained gel is dried in hot air oven at 95°C for 12 hours. The dried gel is heated in muffle furnace at 400°C for 2 hr to obtain the SDC-BCS powder.
Table 2.3  Precursors name, purity and source of SDC-BCS powder

<table>
<thead>
<tr>
<th>Serial No</th>
<th>Precursors</th>
<th>Purity (%)</th>
<th>Resource</th>
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<tr>
<td>1</td>
<td>Cerium nitrate hexahydrate</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Barium nitrate</td>
<td>99.5</td>
<td>Sigma–Aldrich</td>
</tr>
<tr>
<td>3</td>
<td>Samarium Nitrate</td>
<td>99.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4  Weight ratio for SDC-BCS compositions

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Barium Nitrate (mole fraction)</th>
<th>Cerium Nitrate (mole fraction)</th>
<th>Samarium Nitrate (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Ba10CS</td>
<td>0.1</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>P-Ba20CS</td>
<td>0.2</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>P-Ba30CS</td>
<td>0.3</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>P-Ba40CS</td>
<td>0.4</td>
<td>0.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 2.2 shows the experimental procedure for the preparation of SDC-BCS powder and the various characterization steps involved to study thermal, structural, morphology and electrical properties of composites.

The obtained compound powder is grounded using mortar and pestle for about 30 minutes before calcination. In order to determine the calcination temperature, the obtained dry powder is heated at 300°C, 600°C and 900°C.
2.3 DENSIFICATION PROCESS

The disc shaped GDC-BCG and SDC-BCS pellets are obtained from as prepared powder pressed at 15Mpa in a stainless steel die of 12 mm diameter. The thickness of all the pellet is fixed at 1mm. Before compaction, the powder is mixed with 1 % of Poly vinyl alcohol (PVA), which acts as a binder or fillers for granulation leads to density the pellet. The addition of PVA to the precursor powder will also provide good sintering environment and in turn increases the green strength to the pellet. The well-compacted disc-shaped composites are named as Ba10CG, Ba20CG, Ba30CG and Ba40CG for the GDC-BCG disc and Ba10CS, Ba20CS, Ba30CS and Ba40CS for SDC-BCS.

2.4 PELLET CHARACTERIZATION METHODS

The density measurement is carried out for all the composites and characterized though XRD, SEM and impedance analysis. The density of all the composites is measured by Archimedes principle. The phase purity of the composites is studied through structural analysis. Scanning Electron Microscopic analysis is performed on the surface of the pellets to study the microstructure composites. The ionic conductivity measurement of the GDC-BCG and SDC-BCS composites are obtained using impedance analyzer.

2.5 CONVENTIONAL SINTERING

Sintering becomes an essential parameter to densify an electrolyte and to use them as mixed ionic conductor in solid oxide fuel cells. In conventional sintering, the energy transferred from heating element to the sample surface (Thakur et al. 2002). The conventional sintering process leads to the reduction of free energy of the powder only at the molecular level and
creates some defects for the diffusion of ions or atoms within the solid ceramic. The sintering mechanism may also lead to several diffusion paths for the movement of oxide ions such as grain boundary diffusion, surface diffusion and surface lattice diffusion which results in the densification of the solid ceramics Rahaman et al. (1995). In conventional sintering, high dense ceramics are taken in an alumina crucible and undergone sintering in an electric furnace with the heating rate of 10°C /minutes for the dwell time of 6 hrs at 1200°C, 1300°C, 1400°C and controlled cooling rate of 20°C /minutes up to 600°C. The sintering temperature of all the samples is controlled using Eurotherm temperature controller.

2.6 MICROWAVE SINTERING

The electromagnetic waves with frequencies range from 0.3 GHz and 300 GHz and corresponding wavelengths ranging between 1mm – 1m are normally termed as Microwaves. In Microwave sintering the ceramic material absorbs the electromagnetic energy volumetrically and transforms this energy into heat. The microwave processing is relatively a new development for ceramics and composite materials and fundamentally different from the conventional heating process In particular, the frequency range of microwave always lies just above higher than radio waves and below than the visible light in electromagnetic spectrum (Katz 1992). Recently, researchers have devoted their special interest to increase the rate of reaction rapidly in solid electrolyte for SOFC applications through microwave sintering technique (Jiao et al. 2010). Over 50 years ago, (Von Hippel & Morgan 1955) have started to discuss the possibility of processing the solid ceramics using microwave heating and the experimental result obtained through microwave is merely studied in the mid-1960s by (Tinga & Voss, 1968). In fact the results of many investigations on sintering the ceramic materials with the help of microwave are widely employed and reported (Bykov et al. 2001, Huang et al. 2009).
The absorbed heat is transferred between objects by means of three mechanisms such as conduction, convection, and radiation. In microwave sintering (MS), the material is heated by means of energy conversion. The direct transformation of this heat energy to the materials takes place at molecular level is due to the interaction of electromagnetic wave and results in reducing the energy consumption drastically (Fu 2008). The rapid rate of heating occurred in materials will result in decrease the sintering temperatures of solid electrolyte. Rapid heating occurred in the material is mainly due to internal and volumetric heating mechanism which reduces thermal gradient and provides the uniform heating environment for solid electrolyte (Yang et al. 2005).

Figure 2.3 depicts the schematic diagram of microwave sintering unit and its main parts for operation. In microwave sintering, the pellet is taken in an alumina boat and is covered with alumina –zirconia insulator to minimize the heat loss during heating. Microwave provides volumetric heating for the intensification or development of unique micro structure in the solid electrolyte (Demirskyi et al. 2010).
The overall sintering procedure is carried out for 20 minutes with the heating rate of 45°C per minutes from room temperature to 1400°C using microwave furnace and the temperature is monitored through a cavity using an infrared Thermo sensor, Raytek (Ray XR G5SFA India) located at the top of the system.

2.7 METHODS OF CHARACTERIZATION FOR BOTH COMPOSITES

Gadolinium-doped barium cerate powders and Samarium doped barium cerate powder are experimentally prepared through wet chemical
method. The DSC/TGA thermogram is recorded for all the samples using (Netzsch, Germany, NETZSCH STA 449F/3) instrument under a nitrogen atmosphere at a constant heating rate of 10°C per minute from room temperature to 1100°C. X-ray diffractometric analysis is carried out for the as-prepared powder sample calcined at 300°C, 600°C and 900°C for the confirmation of phase purity and high crystallinity using CuKα radiation.

The structural analysis for both GDC-BCG and SDC-BCS powders, as well as the pellets are carried out by XRD analysis technique using a PANalytical X-ray diffractometer. HRTEM investigation is performed using JEOL JEM 2100 High-Resolution Transmission Electron Microscope (HRTEM) for all the as prepared powder samples. The distribution of average particle size with the increase in the concentration of barium in the precursor powder is observed. EDS spectrum results shows that the presence of all elements in the compound qualitatively. After compaction, the ceramic disc is undergone densification using the conventional and microwave furnace. The density of the pellets is measured by Archimedes principle using deionised water as the immersion medium.

The structural analysis for entire pellets is carried out using XRD analysis and SEM imaging is carried out with the help of FEI Quanta FEG 200- High-Resolution Scanning Electron Microscope. The sintered pellets are well cleaned in acetone, polished, coated with gold to prevent charge accumulation during SEM analysis. Scanning Electron Microscopic analysis has been taken on the surface of the pellets in order to study the development of microstructure in the solid electrolyte. The electrical conductivity measurement for all the samples is employed using NOVO control GmbH Alpha-A high-resolution analyzer and platinum electrodes were used with homemade sample holder for measuring the impedance as a function of frequency.
2.8 EXPERIMENTAL METHODS IN DETAILS

2.8.1 Thermal analysis methods

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) is carried out for the as-prepared powder samples using (Netzsch, Germany, NETZSCH STA 449F/3) instrument in nitrogen atmosphere. The calcination temperature of the as synthesized powder is identified based on the mass loss in the sample due to decomposition. The powder samples are grounded well and dried for about 3 hours before thermal analysis.

2.8.1.1 Differential Scanning Calorimetry

Differential Scanning Calorimetry is used to determine the calcination temperature of the as prepared powder. All the as prepared GDC-BCG and SDC-BCS powder samples are subjected to DSC analysis from 30°C to 1000°C in a controlled heating rate of 10°C per minutes.

2.8.1.2 Thermogravimetric Analysis

The TGA method is used to measure the amount and the percentage of weight loss occurred in the materials. The percentage of weight loss is recorded for different temperature range from 30°C to 1000°C in controlled heating rate of 10°C/min. In this thermal analysis, Alpha alumina pan is used as the reference material.
2.8.2 X-ray diffraction method

X-ray diffraction technique is a very effective tool to investigate the crystalline nature of the sample as well as to investigate the phase formation and qualitative compositional identification of the materials. The material to be investigated is belonged to crystalline one, will results in the existence of predominant peaks and for nanocrystalline or amorphous system those peaks will be observed as a shallow instead of identifying the well-defined peaks (Cullity BD 1978). In the present research work XRD pattern has been recorded using PANalytical X-ray diffractometer with Cu K\textsubscript{\alpha} alpha (λ=1.5406 Å) at 40kV and 20mA in the two-theta value range of 10° to 110°. Nickel is used as filter in the X-Ray diffractometer with the scanning rate of 0.01° step. The resultant diffraction pattern has been compared with the standard value from Joint Commission for powder diffraction standards (JCPDS). The formations of matrix phases are analyzed and indexed from standard patterns of PCPDFWIN-2013 database software provided by International Centre for Diffraction Data (ICDD).

The crystallite size for all the samples are calculated from equation (2.1) with 2θ value from XRD main reflection peak (111) plane for GDC phase and (113) plane for BCG phase using Scherer’s formula (Kumar et al. 1995).

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

(2.1)

where D is crystallite size in nm, \(\lambda\) is the radiation wavelength (for Cu K\textsubscript{\alpha} radiation, \(\lambda = 1.5406 \ \text{Å}\)), \(\theta\) is the diffraction peak angle and \(\beta\) is the broadening of the line (“half width”) measured at half of its maximum intensity (in radians) (Fu 2008). The corresponding lattice parameters, unit cell volume for orthorhombic perovskite structure belong to both BCG and BCS composite are
calculated using equation (2.2) and tabulated in Table: 3.4, 3.5, 4.4 and 4.5 respectively.

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]  

(2.2)

where hkl are the Miller indices, a b c are the lattice parameters and d is the spacing between the planes obtained from XRD results.

2.8.3 High resolution Transmission electron microscopy

High Resolution Transmission Electron Microscopic analysis is carried out for GDC-BCG and SDC-BCS samples to know the particle size distribution and morphology of the as prepared powder samples calcined at 900°C. A small amount of powder samples is taken and appropriately ultrasonicated using isopropanol as the solvent. Subsequently, a small drop of the ultrasonicated sample is dropped on a carbon coated copper grid (300 mesh size). The carbon coating provides physical support to hold the particles during analysis. The copper grid along with a drop of sample is then kept under IR lamp approximately for ~20 minutes to evaporate isopropanol. The samples are loaded one by one into the HRTEM analyzer and examined at an acceleration voltage of 200kV.

2.8.3.1 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDX) is an systematic method used for the elemental analysis of a powder sample along with HRTEM imaging. The spectrum analysis the presence of all the precursor elements in the compound (Dubal et al. 2014). In these EDS, a sample under investigation is being focused by a beam of electrons with high energy. Then
the incident beam stimulates an electron in an inner shell by producing an electron hole or electron vacancy. An electron from such an outer high energy shell fill up the vacancy and the difference in energy between the upper energy shell to that of the lower energy shell will results in the formation of an X-rays. The number and energy of X-rays emitted is a characteristic of atomic structure of the element from which it is emitted and the elemental composition present in sample is measured. EDS analysis is carried out to check qualitatively the presence of all elements like Gadolinium, Samarium, Cerium, barium, oxygen and the co existence of any other foreign materials in the compound.

2.8.4 Density Measurement

The density measurement for sintered pellet becomes very important aspects which greatly deals with microstructural and the electrical property of solid ceramics material used as electrolyte. Since, high dense composites with minimum porosity can exhibit high ionic conductivity when compared with the poorly densified ceramics. The presence of cracks and voids in poorly densified pellet will effectively block the conduction path of oxide ions and result in decreasing the conductivity of the solid ceramics. Hence, dense composites can give increased ionic conductivity.

The relative density of \((1-x)\text{Ce}_0.8\text{Gd}_{0.2}\text{O}_{3-\delta-x}\text{BaCe}_0.8\text{Gd}_{0.2}\text{O}_{3-\delta}\) and \((1-x)\text{Ce}_0.8\text{Sm}_{0.2}\text{O}_{3-\delta-x}\text{BaCe}_0.8\text{Sm}_{0.2}\text{O}_{3-\delta}\) system \((x=0.1,0.2,0.3,0.4)\) is measured by Archimedes principle (liquid displacement) method. In Archimedes principle, the pellet is immersed in a liquid called water with known density. The weight of the immersed sample in liquid \((W_i)\) and the weight of the sample measured in air \((W_a)\) are measured to calculate the experimental density \(\rho_{\text{exp}}\) using equation (2.3)
The theoretical density of each composition is measured from the average mass per unit cell divided by the unit cell volume as determined from X-ray powder diffraction method. The theoretical density ($\rho_{th}$) of the composite pellet is calculated from the following equation (2.4)

$$\rho_{th} = \frac{M}{VN_a}$$  \hspace{1cm} (2.4)

Where $\rho_{th}$ is the theoretical density of pellet (\%), $M$ is the molecular mass (gmol$^{-1}$), $V$ is the unit cell volume (cm$^3$) and $N_a$ is the Avogadro number

Hence, from the experimental and theoretical density values, the relative density of the sintered pellets is calculated for all the samples using the following expression (2.5)

$$\rho = \frac{\rho_{exp}}{\rho_{th}}$$  \hspace{1cm} (2.5)

2.8.5 Scanning Electron Microscopy

Scanning electron microscope (SEM) analysis is considered as one of the precious technique widely used for the characterization of nanomaterials operated at intermediate temperature for solid oxide fuel cell application. The SEM is employed to inspect a much superior diversity of sample. As well as SEM analysis is used to obtain the morphological information on the surface of the sample. This method senses the X-rays produced as the result of an electron beam interactions with the specimens. In these present work, FEI Quanta FEG 200- High-Resolution Scanning Electron Microscope instrument is used to investigate the development of
microstructure with dual matrix in both \((1-x)\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}-x\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}\) (GDC-BCG) and \((1-x)\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}-x\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}\) (SDC-BCS) composite electrolyte.

### 2.8.6 Conductivity measurements

Conductivity measurement is carried out for all the composites using Novo control GmbH Alpha-A high-resolution electrochemical impedance analyzer. Platinum electrodes are used with homemade sample holder. The conductivity of the composites is obtained from the impedance spectra. Before electrical measurements, all the pellets are uniaxially pressed into a circular disc using hydraulic pellet maker with the dimensions of 12mm diameter and 1mm thick. The composites are sintered at 1400°C for 20min in microwave furnace.

Impedance measurement is carried out for both GDC-BCG and SDC-BCS composites from 300°C to 800°C in the frequency range from 1Hz to 1MHz. All the samples are placed in between two electrodes to carry out the electrical measurements. The real and imaginary part of impedances is plotted for the different barium contents to obtain the Nyquist plots. The real part \((Z')\) and imaginary part \((Z'')\) of cole-cole plot are referred as Nyquist plot.

The Nyquist plot exhibits the two semicircle regions, first one at lower frequency and second at high frequency regions for all the composites. The low frequency regions correspond to the capacitance nature of the materials and the high frequency semicircle represents the bulk properties of the composites. The high frequency intercepts is referred to the overall cell resistance which includes ionic resistance and the contact resistance coupled with the interface of the composites (Zhang et al. 2007). The Nyquist plots are
fitted using EClab software between the real and imaginary parts of the impedance. Constant phase elemental circuit is used to fit the Nyquist plot.

From electrochemical impedance data the specific type of electrical conductivity and resistance is calculated for all the samples at 700°C. The bulk conductivity and activation energy for all the composite is calculated using the following equation (2.6)

\[ \sigma = \frac{L}{SR} \]  

(2.6)

where \( \sigma \) is the conductivity, \( L \) is the thickness of the electrolyte, \( S \) is the electrolyte area tested, \( R \) is the corresponding resistance of the electrolyte.

The activation energy corresponds to the conductivity of the electrolyte is calculated from the linear fit of the Arrhenius curves using equation (2.7) as follows

\[ \sigma T = A \exp\left(\frac{-E_a}{kT}\right) \]  

(2.7)

\( T \) is the temperature (Kelvin), \( A \) is the pre-exponential factor, \( E_a \) is the activation energy and \( k \) is the Boltzmann constant.