Understanding of Aluminium Corrosion Phenomenon using Electrochemical Technique

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by

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Date: 10 May 2023

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DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "Understanding of Aluminium corrosion phenomenon using Electrochemical techniques" is based on the results of investigations carried out by Rahul Balkrishna Gawas in the Physics at the School of Physical And Applied Sciences, Goa University under the Supervision/Mentorship of Dr.Rajesh Kumar Shankar Hyam and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will not be responsible for the correctness of observations / experimental or other findings given the dissertation.

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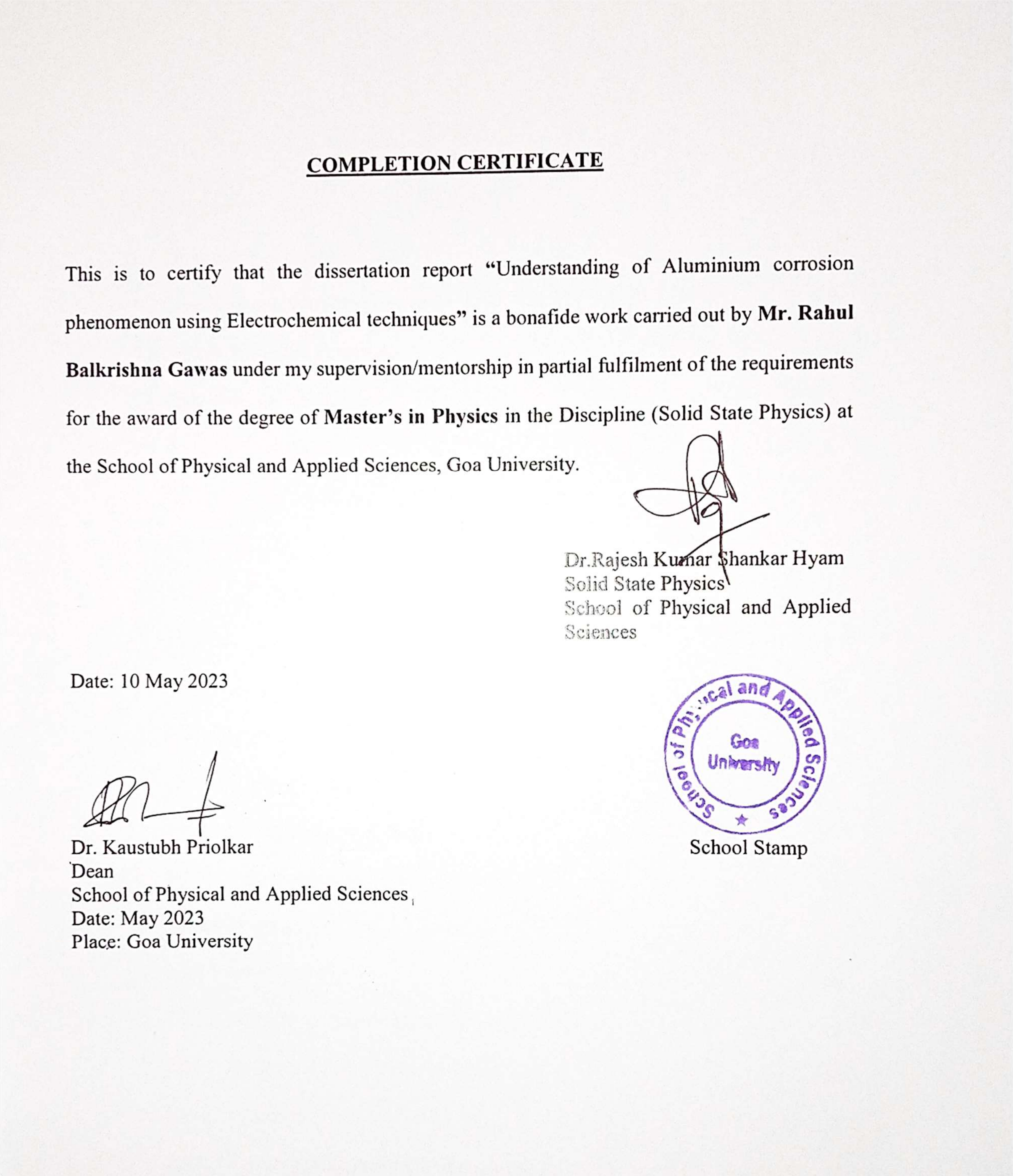

COMPLETION CERTIFICATE

This is to certify that the dissertation report **"**Understanding of Aluminium corrosion phenomenon using Electrochemical techniques**"** is a bonafide work carried out by **Mr. Rahul Balkrishna Gawas** under my supervision/mentorship in partial fulfilment of the requirements for the award of the degree of **Master's in Physics** in the Discipline (Solid State Physics) at the School of Physical and Applied Sciences, Goa University.

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CONTENT

1. Introduction

Corrosion may be defined as a destructive phenomenon, chemical or electrochemical, which can attack any metal or alloy and convert them into another insoluble and more chemically stable oxide or hydroxide. corrosion can also be defined as the deterioration of material by reaction to its environment.

1.1 Importance of corrosion studies.

The importance of corrosion studies is two folds. The first is economic, including the reduction of material losses resulting from the wasting away or sudden failure of piping, tanks, metal components of machines, ships, hulls, marine etc. Corroded electrical contacts can cause fires and other problems, corroded implants may lead to blood poisoning and air corrosion may cause damage to the art around the world. The second is conservation, the annual worldwide cost of corrosion is estimated to be over $2 trillion. Corrosion leads to waste of natural resources. Applied primarily to metal resources, the world's supply of which is limited, and the wastage of which includes corresponding losses of energy and water resources accompanying the production and fabrication of metal structures. [1]

1.2 Condition necessary for corrosion.

Electrochemical corrosion is the most important classification of corrosion. Four conditions must exist before electrochemical corrosion can proceed: [2]

- There must be something that corrodes, the metal anode.
- There must be a cathode.
- There must be continuous conductive liquid path (electrolyte).

- There must be a conductor to carry the flow of electrons from the anode to the cathode. This conductor is usually in the form of metal-to-metal contact such as in bolted or riveted joints.

1.3 Factors Influence Corrosion.

The nature and extent of corrosion depend on the metal and the environment. The important factors which may influence the corrosion process are:

1) Nature of the metal, nature of the environment and the corrosion products.
2) Temperature.
3) Concentration of electrolyte.
4) Electrode potential.
5) Aeration.
6) Agitation.
7) Hydrogen over voltage and pH of the electrolyte.

1.4 Classification of Corrosion.

All metallic materials consist of atoms having valence electrons which can be donated or shared. In a corrosive environment the components of the metallic material get ionized and the movement of the electrons sets up a galvanic or electrochemical cell which causes oxidation, reduction, dissolution or simple diffusion of elements.

Corrosion can be classified in many ways as low temperature and high temperature corrosion, direct oxidation and electrochemical corrosion, etc. The preferred classification is: Dry or chemical corrosion and wet or electrochemical corrosion. [3]

- **Chemical corrosion**: In which the metal is converted into its oxide when the metal is exposed to a reactive gas or non-conducting liquids.
- **Electrochemical corrosion:** The formation of hydrous oxide film occurs when the metal is immersed in a conducting liquid containing dissolved reactive

substance. The reaction is considered to take place at the metal solution interface, due to the heterogeneity on the metal surface, which creates local anodic and cathodic sites on the metal.

1.5 Types of Corrosion

1.5.1 General or uniform corrosion

Uniform corrosion is considered an even attack across the surface of a material and is the most common type of corrosion. This corrosion results from the continuous shifting of anode and cathode region of the surface of a metal in contact with the electrolyte and leads to nearly uniform corrosive attack on the entire surface. Differences in electrical potential occur on the surface of a piece of metal due to small differences in chemical composition, phase differences, amount of cold work, etc. These differences set up small corrosion cells each with an anode and cathode. Corrosion continues until the metal is consumed or the film of rust formed on the surface sets up a barrier to the electrolyte. [4]

1.5.2 Galvanic corrosion

When two different metals are exposed to a corrosive environment, an electrical potential difference will exist. If the two metals are connected, the more active metal will become the anode in the resulting galvanic cell and its corrosion will be increased. If to reduce corrosion it is good practice not to use dissimilar metal, but if it is, the following precautions be used.

- Attempt to electrically isolate the metal.
- Keep out moisture.
- Use metals that are close to one another in the galvanic series.
- Put corrosion inhibitor in the solution.
- Design so that the anode /cathode area ratio is high.

1.5.3 Localized corrosion

localized corrosion comes in many variation, such as pitting corrosion, crevice corrosion and filiform corrosion.

- **Pitting corrosion:** This type of corrosion happens when a small break in the metal form. The subsequent hole or cavity becomes anodic, while the surrounding metal become cathodic. This produces a localized galvanic reaction, leading to the structural failure of the metal. Pitting is difficult to locate and manage, as it is often masked by other materials produced during the formation of corrosion.
- **Crevice corrosion:** Crevice corrosion occurs when there is a difference in ion, or oxygen, concentration between the metal and its surroundings.

  This localized corrosion can often be found under gaskets, clamps, and other unmoving areas where low oxygen and acidic condition can lead to corrosion within crevices.
- **Filiform corrosion:** This corrosion occurs under surface that have been painted or coated. Defects in the paint or coating allows water to intrude, thereby causing corrosion below the protective layer, resulting in weakened surface.

1.5.4 Stress corrosion cracking

Failure is due to the simultaneous influence of static tensile stresses and a corrosive environment, often at elevated temperatures. Stress corrosion may result from external stress such as actual tensile loads on the metal or expansion/contraction due to rapid temperature changes. It may also result from residual stress imparted during the manufacturing process such as from cold forming, welding, machining, grinding, etc. [5]

In stress corrosion, the majority of the surface usually remains intact, however, fine cracks appear in the microstructure, making the corrosion hard to detect. The cracks typically have a brittle appearance and form and spread in a direction perpendicular to the location of the stress.

2. Characterization technique.

2.1 Scanning Electron Microscope

Scanning electron microscope (SEM) is a type of electron microscope that uses a beam of high-energy electrons to scan the surface of a sample to create a detailed image of its topography, morphology, and composition at a high resolution. SEM is widely used in various fields of science, including material science, nanotechnology, biology, and geology, to investigate the structure and properties of materials at a nanoscale level. Scanning Electron Microscope (SEM) was first conceptualized in 1927 by German physicist and inventor, H. Stintzing, who proposed a method of irradiating a sample with a collimated beam of light, X-rays, and corpuscles. However, this method was unable to produce a magnified image.

In 1935, a German electrical engineer named M. Knoll introduced a new paradigm of SEM where the sample was irradiated with an electron beam instead, and the image was obtained by scanning the surface of the sample with the beam. In 1938, Von Ardenne further developed the SEM by introducing DE magnifying lenses, called scanning transmission electron microscope, to scan thin samples. [1]

In 1942, Zworykin improved the SEM for scanning bulk samples with a few other alterations. Over the years, numerous advancements were made to the SEM technology, including improvements in resolution, sample preparation, and signal detection.

The first commercial SEM was introduced in 1965 by the Cambridge Scientific Instrument Company. Since then, SEM has become a widely used tool in various fields, including material science, nanotechnology, biology, and geology, for imaging and analysing materials at the nanoscale level. Today, SEMs are available with advanced capabilities such as environmental SEM, low-temperature SEM, and high-resolution SEM, among others.

The Scanning Electron Microscope (SEM) has a rich history that dates back to the early 20th century. One of the first proposed methods of SEM was offered by H. Stintzing in 1927 through a German patent application, but his proposed method was unable to produce a magnified image.

In 1935, M. Knoll, a German electrical engineer, introduced a new paradigm of SEM where the specimen was scanned with an electron beam to obtain an image. Then, in 1938, Von Ardenne developed SEM with slight modifications by introducing DE magnifying lenses called scanning transmission electron microscope to scan thin samples. In 1942, Zworykin improved the SEM for scanning bulk samples with a few other alterations.

Since then, SEM technology has advanced significantly, with improvements in resolution, signal detection, and sample preparation. The first commercial SEM was introduced in 1965 by the Cambridge Scientific Instrument Company, and SEM has become a widely used tool in various fields, including material science, nanotechnology, biology, and geology, for imaging and analysing materials at the nanoscale level. [2]

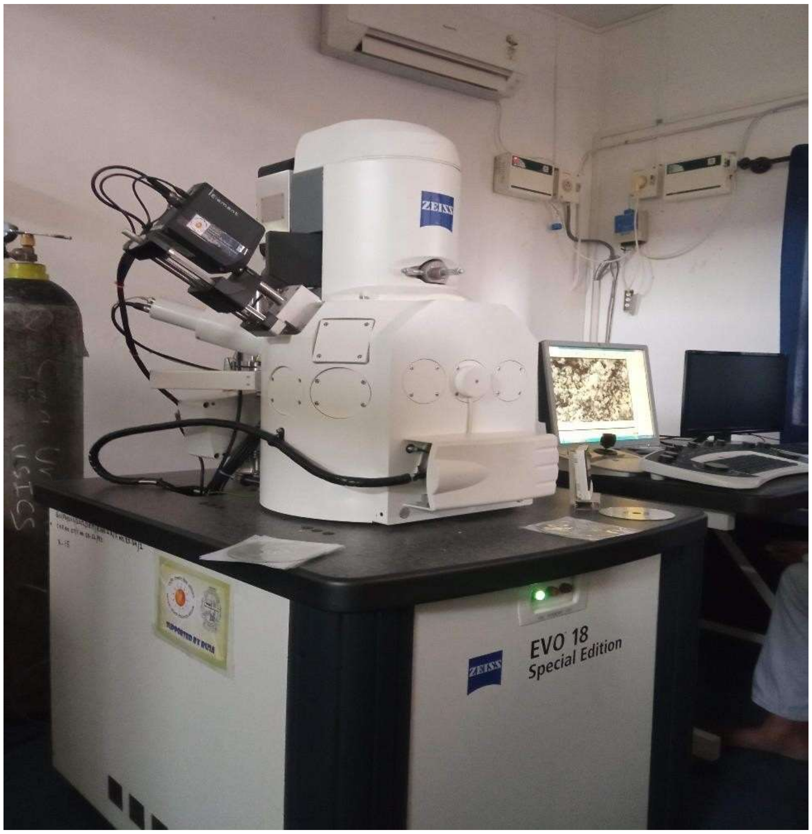

Figure 1: Scanning Electron Microscope (SEM)

2.1.1. Working Principal of SEM

SEM works on the principle of the interaction between high-energy electrons and a sample surface. The electron beam is generated by an electron gun and accelerated by a voltage to form a narrow beam. The beam is then focused by a set of electromagnetic lenses to a small spot on the sample surface. As the beam scans the surface, it interacts with the atoms and electrons of the sample, producing various signals, including secondary electrons, backscattered electrons, and X-rays. These signals are detected by the detectors and converted into an image by a computer.

2.1.2. Instrumentation of SEM

The basic components used in this system are: [3]

1) Electron gun.

The electron gun generates a beam of electron that is focused on the sample. There are three different types of electron gun they are:

Thermionic Emission: A thin tungsten wire filament act as cathode to generate thermos electrons by heating the filament. A positive voltage of about 1 to 50 KV is applied to the metal plate acting as anode to collect the electron. LaB_6 crystal is used as cathode, it is also used to reduce the sport size and required high vacuum due to its higher activity.

Field Emission: It works on field emission effect when high field is applied to the metal surface. There is an emitter which is made by a thin tungsten wire wielded to the tungsten single crystal whose tip is curved with the radius of about 100nm, which act as cathode. The electrons emit from emitter through tunnelling effect when positive voltage is applied. Hole is created in the extracting electrode to allow emitted electron to flow through it. Then electron beam containing some energy id obtained by applying voltage to the accelerating electrode present beneath the extracting electrode. The energy spread is less because no heating is required. Electron beam diameter is in rage 5-10nm and it required ultra-high vacuum of the order 10^{-8} Pa.

Schottky Emission Gun: It produces a stable and reliable electron beam with high brightness and small source size, resulting in improved spatial resolution and image. It has a tungsten single crystal coated with ZrO which act as cathode. ZrO reduces the work function to enhance the emission current at low cathode temperature. The electrons are shielded from emitter by Appling negative voltage to the suppressor electrode. Emitter is placed in ultra-high vacuum of the order 10-7 Pa.

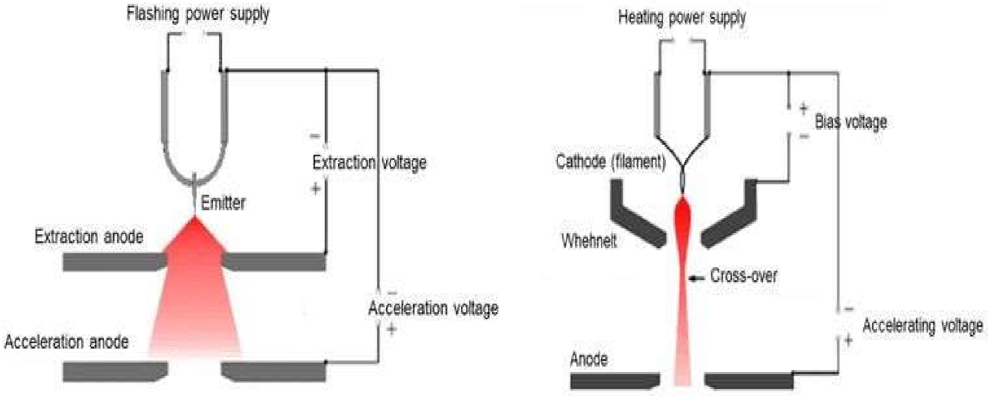

Figure 2: Thermionic Emission gun and Field Emission gum. [1]

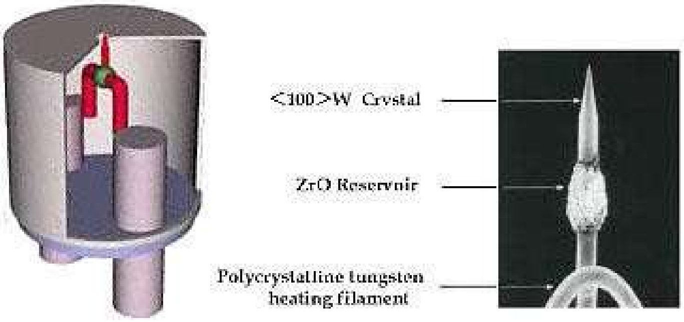

Figure 3: Schottky Emission Gun [2]

2) Lenses.

In order to create a precise electron beam with the desired crossover diameter, a two-level lens system is used in SEM. This system consists of s condenser lens and an objective lens, both of which are made of metal cylinder with a cylindrical hole and operate in vacuum. These are positioned below the electron gun and create a magnetic field in their inner parts to either focus or defocus to beam.

- **Role of condenser lens**: The size of the electron probe in a scanning electron microscope is influenced by the strength of the condenser lens. Strengthening the lens results in a smaller probe size with a smaller b/a ratio, while weakening the lens leads to a broader probe size. The beam current is controlled by the C1 and C2 lenses, which adjust the size and intensity of the beam spot. An aperture is created by introducing a small hole in the metal between the two condenser lenses and the objective lens to allow the beam to pass through and reach the objective. The aperture plays a crucial role in determining the resolution of the microscope, as it controls the size of the spot

- **Role of objective lens**: it is used for focusing and determines the final diameter of probe.

3) Scanning coils.

This coil deflects the beam in X and Y direction in order to scan the sample surface in a raster pattern

4) Sample stage.

A motorized plate is utilized in scanning electron microscopes, which has three directional movements: X, Y, and Z, that can be controlled by inputting values in the software. Samples are placed on this plate and can move smoothly in the desired direction. The horizontal movements, X and Y, are used to modify the field of view, while the vertical movement, Z, is crucial for image resolution and depth of focus. In addition to these movements, the plate can also rotate and tilt. Furthermore, the stage movement can be manually controlled using the mouse in the software's user interface.

5) Detector.

Characteristics if sample are measured at different beam position to form image. Secondary electrons emitted from the sample are measured using secondary electron detector.

- **Secondary Electron Detector:** The detector used in SEM is called the E-T detector which has a scintillator coating at the tip and is charged with a high positive voltage of

10 KV. When secondary electrons emitted from the specimen come in contact with the detector, they are magnetically attracted towards the positive voltage. In addition to this, there is a collector electrode placed before the scintillator which helps in the collection of these secondary electrons by applying a few volts to it. The scintillator produces light when the electrons hit it, and this light is guided to the Photo Multiplier Tube (PMT) through a light guide. The light is converted to electrons and then amplified as an electric signal. The E-T detector was developed by Everhart and Thornley. Some SEMs use Through the Lens (TTL) detectors above the objective lens to achieve higher resolution.

6) **Display Unit and recording system**

The output in the form of amplified electronic signal is send to the display unit. To form SEM image, scanning is synchronized with electron beam scan and brightness on the display unit. Usually, very fast scan speed is used while focusing for observation, whereas slow speed is used for capturing or saving the image.

2.1.3. Infrastructure requirement for SEM

- Constant power supply.
- Vacuum system.
- Cooling system.
- Vibration free floor.
- Room free of ambient electric and magnetic fields.

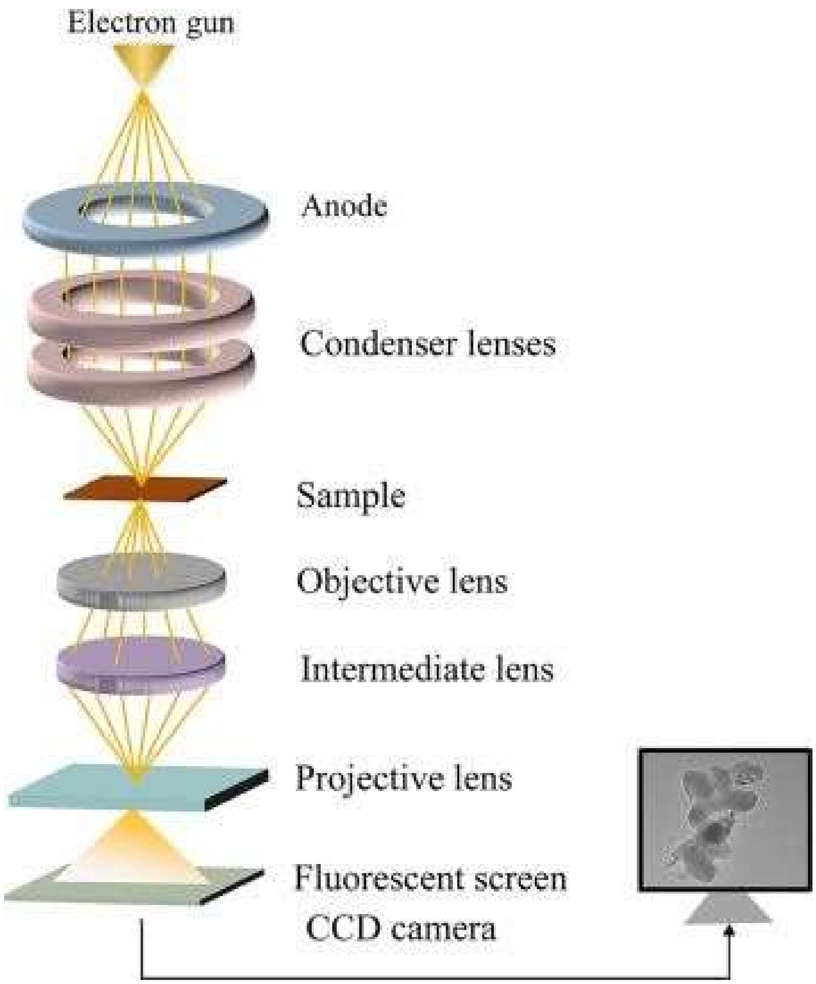

Figure 4: Instrumentation of Scanning Electron Microscope. [3]

2.2 Raman Spectroscopy

Raman spectroscopy is a powerful analytical technique that is used to investigate the vibrational properties of molecules. It is a non-destructive method that provides information about the chemical structure, functional groups, and crystalline properties of a material. [4]

2.2.1 History on Raman Spectroscopy

Raman spectroscopy was discovered in 1928 by Indian physicist C. V. Raman and his student K. S. Krishnan. Raman was studying the scattering of light in liquids and noticed that a small fraction of the scattered light had a different frequency than the incident light. He realized that this was due to the interaction of the incident light with the vibrational modes of the liquid molecules.

They published their paper titled "A New Type of Secondary Radiation" in the journal Nature in 1928. In this paper, they described the shift in frequency of the scattered light and showed that this shift was characteristic of the chemical composition of the sample. This discovery had a significant impact on the field of physics and chemistry and led to the development of Raman spectroscopy as an analytical technique.

On further studying about the scattered light they discovered a new phenomenon known as the Raman effect. They found that the Raman effect was not limited to liquids but could also be observed in solids and gases. They also showed that the Raman effect could be used to identify the vibrational modes of molecules and to determine their chemical composition. In the 1930s and 1940s, Raman spectroscopy was primarily used as a research tool in physics and chemistry. Raman spectroscopy is a well-established analytical technique which provide information about the vibrational modes and chemical composition of materials and this has made it a very good tool in many areas of research and development. [5]

2.2.2 working principal of Raman Spectroscopy

The basic principle of Raman spectroscopy is based on the Raman scattering effect, which occurs when a photon interacts with a molecule, leading to a shift in its energy and wavelength. [6]

When a photon from a monochromatic light source, such as a laser, interacts with a molecule, the majority of the scattered photons have the same energy and frequency as the incident photon. However, a small fraction of the scattered photons will have different frequencies due to their interaction with the vibrational modes of the molecule. This shift in frequency is known as the Raman shift and is characteristic of the molecule's chemical structure and environment.

The Raman shift is caused by the interaction of the incident photon with the vibrational modes of the molecule. When the photon interacts with the molecule, it induces a dipole moment in the molecule, which in turn causes the molecule to vibrate at a particular frequency. The scattered photon will then have a slightly different frequency from the incident photon, due to the interaction with the vibrating molecule. This shift in frequency provides information about the molecule's vibrational modes and chemical structure. Raman spectroscopy can be performed in two modes: Stokes and anti-Stokes scattering.

2.2.3 Stokes and Anti-Stokes Scattering

Stokes and anti-Stokes lines are two types of Raman scattering that can be observed in Raman spectroscopy. [7]

Stokes Raman scattering occurs when the scattered photon has a lower energy and frequency than the incident photon. This occurs because the scattered photon loses energy to the molecule during the scattering process. Stokes lines appear in the Raman spectrum at a frequency lower than the excitation laser frequency. The Stokes lines correspond to vibrational transitions from higher energy levels to lower energy levels.

Anti-Stokes Raman scattering, occurs when the scattered photon has a higher energy and frequency than the incident photon. This occurs when the scattered photon gains energy from the molecule during the scattering process. Anti-Stokes lines appear in the Raman spectrum at a frequency higher than the excitation laser frequency. The anti-Stokes lines correspond to vibrational transitions from lower energy levels to higher energy levels.

The intensity of the Stokes and anti-Stokes lines is related to the temperature of the sample. The intensity of the Stokes line is much stronger than that of the anti-Stokes line because the population of the vibrational states is determined by the Boltzmann distribution, which favours the lower energy states at room temperature. As a result, the Stokes line is much more intense than the anti-Stokes line at room temperature. However, at higher temperatures, the intensity of the anti-Stokes line increases due to the increase in the population of higher energy states.

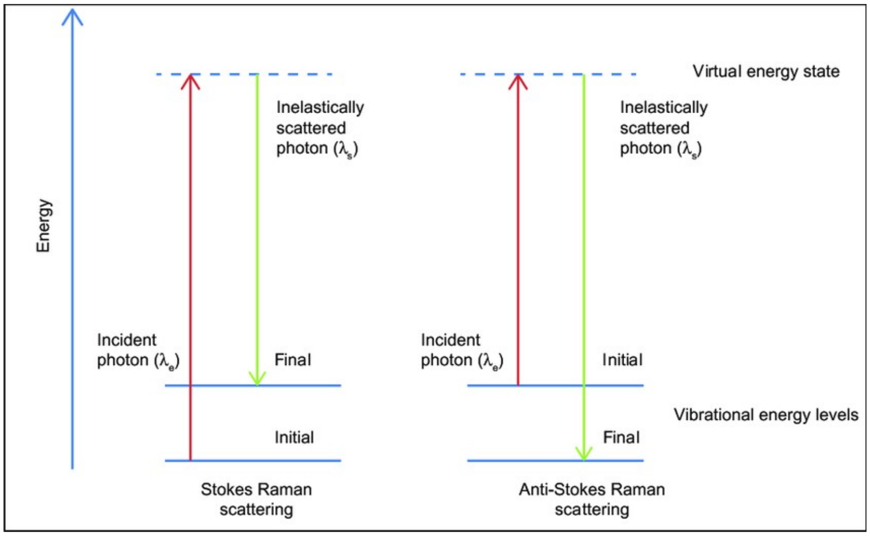

Figure 5: Stock and Anti-stock lines. [4]

2.3 UV Spectroscopy

UV spectroscopy, also known as ultraviolet-visible spectroscopy, is a technique that uses light in the ultraviolet and visible range of the electromagnetic spectrum to analyze samples. In UV spectroscopy, a beam of light with a specific wavelength is passed through a sample, and the amount of light absorbed by the sample is measured. This can provide information about the sample's electronic structure and the presence of functional groups. [8]

UV spectroscopy has a wide range of applications in chemistry, biochemistry, and materials science, such as determining the concentration of a substance in a solution, identifying unknown compounds, and studying the kinetics of chemical reactions.

2.3.1. Working principal of UV Spectroscopy

The working principle of UV spectroscopy involves the absorption of light by a sample in the UV and visible region of the electromagnetic spectrum. The absorption of light in this region is caused by the excitation of electrons from their ground state to higher energy states within the molecule. When a beam of light passes through a sample, the intensity of the light decreases due to the absorption of light by the sample. The amount of light absorbed is dependent on the concentration of the absorbing species and the path length of the light through the sample. [9]

The wavelength of light absorbed by a sample is determined by the electronic structure of the molecules in the sample. The absorption spectrum of a sample can be obtained by measuring the amount of light absorbed by the sample at different wavelengths.

UV spectroscopy is commonly used to analyze the electronic structure of molecules and the presence of functional groups. It is also used to determine the concentration of a substance in a solution and to study the kinetics of chemical reactions.

3. Synthesis and Corrosion studies of Aluminium

Aluminum is a chemical element with the atomic number 13 and symbol Al. It is a silvery-white, soft, non-magnetic, ductile metal in the boron group. It is the third most abundant element in the Earth's crust, after oxygen and silicon, and is widely used in various industries due to its low density, high strength, corrosion resistance, and good thermal and electrical conductivity. [1]

Aluminum is widely used in various industries, and it is exposed to different environments, such as air, water, and different chemicals. Corrosion studies of aluminum are important for improving the performance, durability, and safety of aluminum products in various industries, as well as minimizing the environmental impact of corrosion.

In this project we have learn the corrosion phenomena of Aluminium in different concentration of Sodium Hydroxide (NaOH). The study of aluminum corrosion in sodium hydroxide medium is important for several reasons. Sodium hydroxide is a commonly used chemical in various industrial processes, such as in the production of pulp and paper, textiles, and soap. It is also used as a cleaning agent and in the preparation of various chemicals.

3.1 Electrochemical cell

Electrochemical methods are widely used for studying the corrosion behaviour of metals and alloys. The setup for electrochemical corrosion studies typically involves an electrochemical cell, a potentiostat or galvanostat, and various electrodes and solutions. The electrochemical cell is the heart of the setup and consists of an anode, a cathode, and an electrolyte solution. The anode and cathode are connected by an external circuit, and a reference electrode is placed in the electrolyte to measure the potential of the anode relative to a known standard. A counter electrode completes the circuit and balances the current flow. [2]

It consists of two electrodes (an anode and a cathode) immersed in an electrolyte solution. Here are the basic components of an electrochemical cell for corrosion study.

- **Anode:** The anode is the electrode where corrosion occurs. In the case of metal corrosion, the anode is typically made of the metal (Aluminium) being studied.
- **Cathode:** The cathode is the electrode where reduction reactions occur. It can be made of a variety of materials, but in corrosion studies, it is typically made of an inert material such as platinum.
- **Electrolyte:** The electrolyte is the solution that surrounds the electrodes and allows the flow of ions between them. In my case, the electrolyte solution will be sodium hydroxide solution.
- **Reference electrode:** The reference electrode is used to measure the potential of the working electrode (anode) with respect to a known standard. A commonly used reference electrode is Ag/AgCl or calomel electrode.
- **Working electrode**: The working electrode is the electrode being studied (anode). In my case, it will be the aluminium specimen.
- **Counter electrode:** The counter electrode is used to complete the circuit and balance the current flow. It is typically made of an inert material such as platinum wire.
- **Potentiostat/galvanostat:** The potentiostat or galvanostat is used to control the potential or current applied to the anode and measure the resulting current or potential. This allows for precise control of the electrochemical conditions and the ability to study the corrosion behaviour under a wide range of conditions.

To set up the electrochemical cell for corrosion study, assemble the components described above in a suitable container and connect them to the potentiostat/galvanostat. Ensure that the electrodes are immersed in the electrolyte solution and that the working electrode is not in contact with the cathode or any other conductive material. The reference electrode should be placed close to the working electrode without touching it. Apply the desired potential or current to the working electrode using the potentiostat/galvanostat and monitor the resulting current or potential.

Corrosion study of Bare Aluminium in different concentration of Sodium Hydroxide (NaOH) with effect of temperature was studied using electrochemical setup (Electrochemical Cell).

Electrochemical cells are commonly used to study corrosion phenomena because they allow for controlled and precise measurements of the electrochemical reactions that occur during corrosion. By measuring the electrochemical properties of the corroding metal surface, we can get into the mechanisms and kinetics of corrosion, as well as the factors that influence the rate and severity of corrosion.

One common method for studying corrosion using electrochemical cells is to measure the corrosion potential (Ecorr) and the corrosion current density (icorr) of the metal surface. The corrosion potential is a measure of the thermodynamic tendency of the metal to corrode, while the corrosion current density is a measure of the rate at which corrosion is occurring. These measurements can be used to determine the rate of metal loss due to corrosion and to identify the factors that influence corrosion, such as temperature, pH, and the presence of corrosion inhibitors.

Another common method for studying corrosion using electrochemical cells is to perform polarization experiments, which involve measuring the current and potential of the corroding metal surface as a function of an applied voltage or current. Polarization experiments can be used to identify the different types of corrosion that occur, such as uniform corrosion, pitting corrosion, or crevice corrosion, and to determine the effects of various factors on corrosion, such as the concentration of corrosive species or the presence of corrosion inhibitors.

Figure 6: Electrochemical workstation

3.2 Preparation of Aluminium specimens

Bare Aluminium was cut into and electrode of dimension 5cm×1.5cm using a cutting machine, we have to make note that the edges should be sharp and fine. The specimen was clean using soap solution for 2 minutes and later clean with distilled water, so the oxide layer on the Aluminium specimen is removed. The specimen was dried and used for corrosion study.

3.3 Preparation of stock solution for corrosion study.

A stock solution of Sodium hydroxide was prepared by dissolving analytical grade sodium hydroxide pellets in distilled water. Solution of required strength 50mM, 250mM and 500mM was prepared by using dilution formula.

Weight of NaOH= (Molar mass* concentration*volume)/1000

To prepare 500mM Sodium hydroxide solution in 100ml distilled water, the amount of NaOH needed can be calculated as: (40.0*0*5*100)/1000 =2g.

2g of sodium hydroxide pellets was weight on weighing machine and was added to 100ml distilled water. sodium pellets were dissolved using glass rod. Similarly, the stock solution of strength 50mM and 250mM was prepared.

3.4 Procedure to perform corrosion study.

The steps to set up the electrochemical setup for the corrosion study of aluminium in sodium hydroxide:

1. Mount the aluminium specimen on the working electrode holder and connect it to the potentiostat/galvanostat.
2. Insert the reference electrode (e.g., Ag/AgCl electrode) and the counter electrode (e.g., platinum electrode) into the electrochemical cell.
3. Add the sodium hydroxide solution and the electrolyte solution to the electrochemical cell.
4. Stir the solution with a magnetic stirrer to ensure uniform mixing.
5. Keep the setup for 10 minutes, so the corrosion phenomena start.

6. Apply a potential or current to the aluminium specimen using the potentiostat/galvanostat.
7. Measure the corrosion potential and corrosion current of the aluminium specimen using the potentiostat/galvanostat.
8. Monitor the temperature of the solution during the experiment.
9. Record the experimental data and analyse the corrosion behaviour of aluminium in sodium hydroxide.

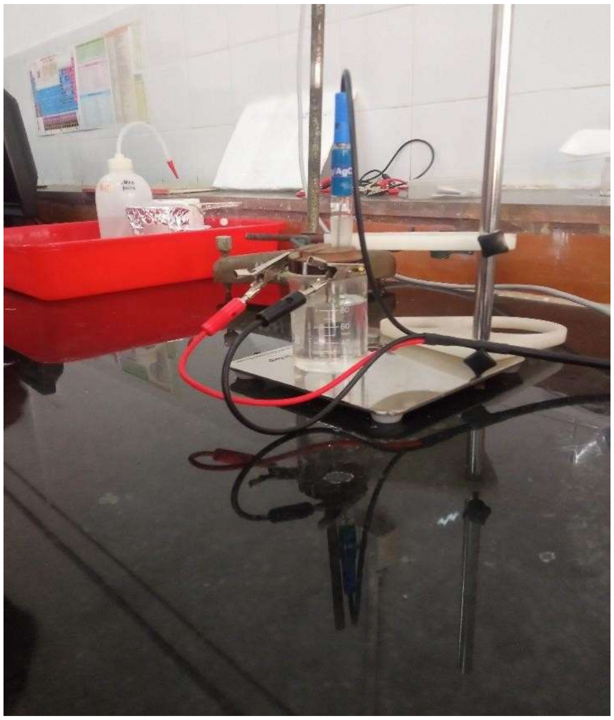

Figure 7: Electrochemical cell

3.5 Reaction of Aluminium in stock solution of Sodium Hydroxide

The corrosion of aluminium in sodium hydroxide solution occurs due to the formation of a highly alkaline environment at the surface of the metal, which leads to the dissolution of the aluminium oxide layer and subsequent exposure of the underlying metal to the corrosive medium. [3]

When aluminium is exposed to NaOH solution, hydroxide ions (OH^-) present in the solution react with the aluminium oxide layer on the surface of the metal to form soluble aluminate ions ($Al(OH)_4^-$):

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$

This reaction results in the dissolution of the aluminium hydroxide layer and the exposure of the underlying metal to the alkaline solution. The highly alkaline environment at the surface of the metal can also lead to the formation of hydrogen gas (H2) through the reduction of water molecules:

$2H_2O + 2e- \rightarrow H_2 + 2OH^-$

The formation of hydrogen gas can further increase the corrosion of aluminium and can embrittlement the metal. The rate and extent of corrosion of aluminium in NaOH solution depend on various factors, including the concentration and temperature of the solution, the presence of dissolved oxygen, and the surface characteristics and properties of the metal. Higher concentrations of NaOH and higher temperatures can accelerate the corrosion rate of aluminium. we will study how high concentration and high temperature increases the corrosion in aluminium.

4. Results and Discussion

A corrosion study of aluminium in sodium hydroxide solution at different concentrations and temperature variation was conducted to understand the effect of NaOH concentration on the corrosion behaviour of Al.

4.1 Tafel polarization measurements.

The effect of Sodium hydroxide medium on the corrosion rate of bare aluminum sample was studied using Tafel polarization technique. Corrosion parameters such as open circuit potential (OCP), corrosion potential (Ecorr), corrosion current density (Icorr), anodic slope (ba) and cathodic slope (bc) are obtained from the Tafel polarization curves. [1]

Open circuit potential: It is the potential difference between the metal surface and the surrounding electrolyte in the absence of any current flow. It can provide information on the corrosion potential of the metal, which is the potential at which the metal corrodes at a steady-state corrosion rate. The OCP can also provide information on the reactivity of the metal in different environments and can be used to predict the corrosion behaviour of the metal in a given environment. [2] In our study working electrode is aluminium surface, while the reference electrode is silver-silver chloride electrode (Ag/AgCl).

Corrosion potential (Ecorr): The corrosion potential is the intersection of the anodic and cathodic Tafel lines, which represents the equilibrium potential of the electrochemical reaction that governs metal corrosion.

Corrosion current density (Icorr): The corrosion current density is the current density at the corrosion potential, which represents the rate at which metal ions are dissolved from the metal surface due to electrochemical reactions. [3]

The Tafel plot is a graphical representation of the relationship between the logarithm of the current density and the applied potential in an electrochemical cell. The slope of the Tafel plot provides information about the rate-determining step of the electrochemical reaction

The Tafel slope is defined as the slope of the Tafel plot, which can be calculated using the following equation:

Tafel slope = (del(ln I) / del(E)) $^{-1}$

Where, I is the current density and E is the applied potential.

To calculate the Tafel slope, it is necessary to determine the values of ba and bc. These are constants that are related to the reaction mechanism and can be calculated using the following equations:

ba = (2.3RT)/ (αa * n' * P)

bc = (- 2.3RT)/ (αc* n' * F)

where,

R is the gas constant

T is the temperature in Kelvin

n' is the number of electrons transferred in the rate-determining step of the reaction

P is the partial pressure of the reactant gas

F is Faraday's constant

αa and αc are the transfer coefficients for the forward and backward reactions.

For anodic half reaction for potential Ecorr, current density is given by

Icorr= I_{0a} **exp[(2.3(Ecorr-Ea)/ba)]**

Where,

Ea equilibrium potential for anodic half reaction

Ioa anodic exchange current

For cathodic half reaction

Icorr= I_{0c} exp[(-2.3(Ecorr-Ec)/bc)]

Where,

Ec equilibrium potential for anodic half reaction

I_{oc} cathodic exchange current

For applied potential difference, change in the current is given by

del(I)=2.3Icorr(del(E)/ba +del(E)/bc)

Where **del(E)=(E-Ecorr)**

On rearranging,

Icorr=[(ba*bc*del(I)/(2.3ba +del(E)*bc)

The corrosion rate was calculated by using following equation.

Corrosion Rate = 3270 $* Icorr * M / A * n *$ 10

Where, Icorr = Corrosion current

A = Area of working electrode dipped inside the solution.

n = Valency of the Aluminium

M = Molecular weight of Aluminium

4.1.1 Corrosion study of Aluminium in different concentration of NaOH solution at room temperature.

The corrosion behavior of Aluminium in 50mM, 250mM and 500mM concentration of sodium hydroxide was studied using tafel curves. Figure 8 represent the Tafel polarization curve of aluminum in different concentration of sodium hydroxide medium at 303k temperature.

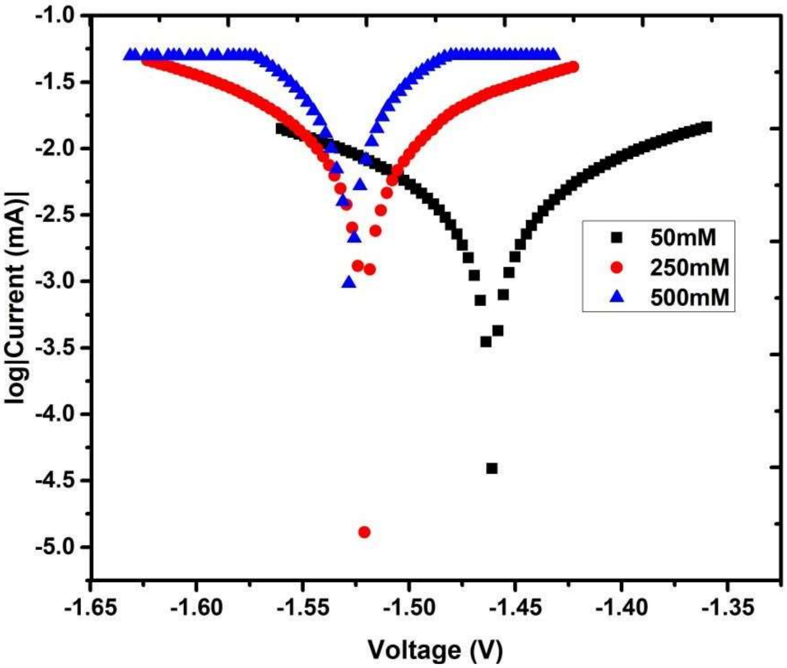

Figure 8: Tafel polarization curves for aluminum in different concentration of NaOH at 303k temperature.

The result of Tafel polarization measurement are reported in table 1.

Concentration of NaOH solution mM	OCP V	Icorr 10^{-5} mA/cm^2	Ecorr V	Corrosion Intensity $g/cm^2/yr$	Corrosion Penetration rate mm/yr
50	-1.46	103.10	-1.461	0.404	1.497
250	-1.52	347.61	-1.51	1.703	6.310
500	-1.53	623.27	-1.528	3.054	11.314

Table 1: Result of Tafel polarization studies of bare Aluminium at Room temperature in different concentration of NaOH.

As we can see from the result that as concentration increases, corrosion rate also increases. The corrosion of Al in NaOH solution is controlled by the anodic dissolution of Al. The increase in

Icorr with increasing NaOH concentration is likely due to the increase in the concentration of hydroxide ions, which accelerate the anodic dissolution of Al. The value of Ecorr becomes more and more negative values with increasing NaOH concentration which indicates that the potential required to initiate the anodic reaction decreases as the concentration of NaOH increases. This is because the concentration of hydroxide ion in the solution has increased which enhances the corrosion rate.

4.1.2 Effect of temperature on corrosion rate.

The effect of temperature on the corrosion rate of the aluminium was studied by measuring the corrosion rate at different temperature range of 303K – 323K in the interval of 5 by keeping the concentration of NaOH constant. The figure 9,10 and 11 represents tafel polarization curve of aluminium in 50mM, 250mm and 500mM. The result is given in table 2,3and 5 respectively.

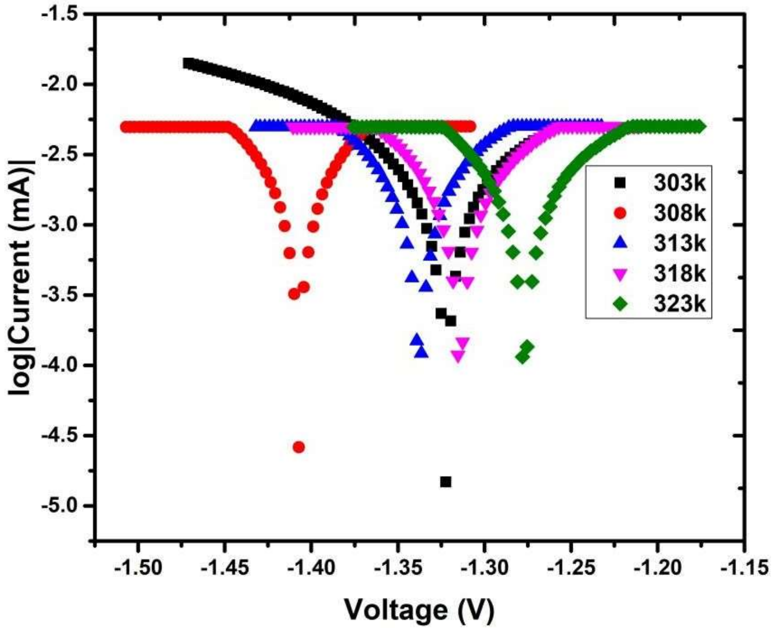

Figure 9: Temperature variation Tafel polarization curve for Aluminium in 50mM NaOH solution.

Temperature K	OCP V	Icorr 10^{-5} mA/cm^2	Ecorr V	Corrosion Intensity g/cm^2 /yr	Corrosion Penetration rate mm/yr
303	-1.43	31.7	-1.452	0.415	1.537
308	-1.45	38.7	-1.435	0.506	1.876
313	-1.429	38.7	-1.462	0.506	1.874
318	-1.456	46.1	-1.491	0.603	2.234
323	-1.465	71.9	-1.496	0.941	3.484

Table 2: Temperature variation result of Tafel polarization curve of bare Aluminium in 50mM NaOH Solution.

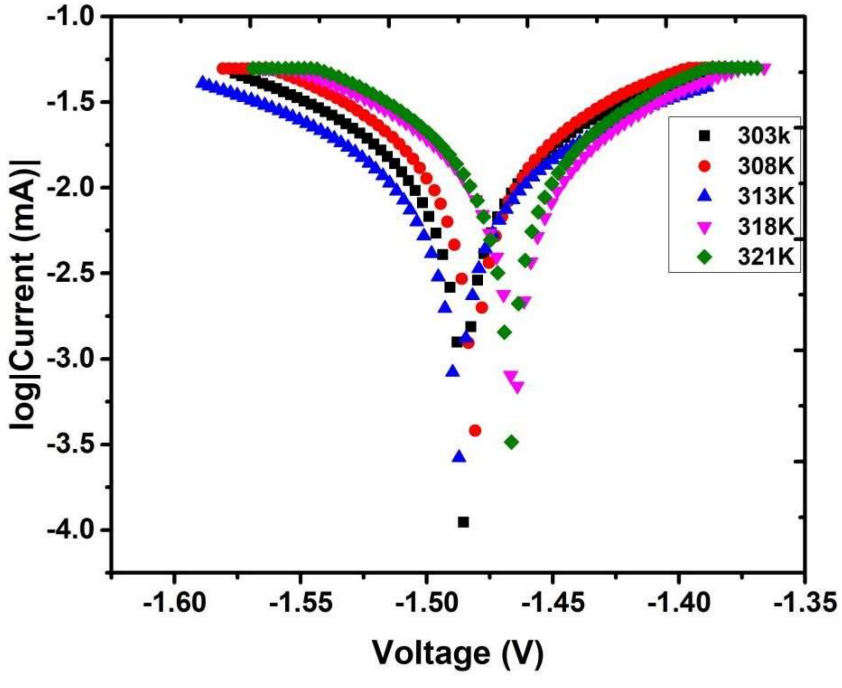

Figure 10: Temperature variation Tafel polarization curve for Aluminium in 250mM NaOH solution.

Temperature K	OCP V	Icorr 10^{-5} mA/cm^2	Ecorr V	Corrosion Intensity g/cm^2 /yr	Corrosion Penetration rate mm/yr
303	-1.473	456.2	-1.486	0.29	1.1
308	-1.484	603.1	-1.482	3.583	13.27
313	-1.512	377.62	-1.487	2.243	8.31
318	-1.467	545.6	-1.464	3.241	12.1
323	-1.503	597.8	-1.467	3.553	13.15

Table 3: Temperature variation result of Tafel polarization curve of Aluminium in 250mM NaOH Solution.

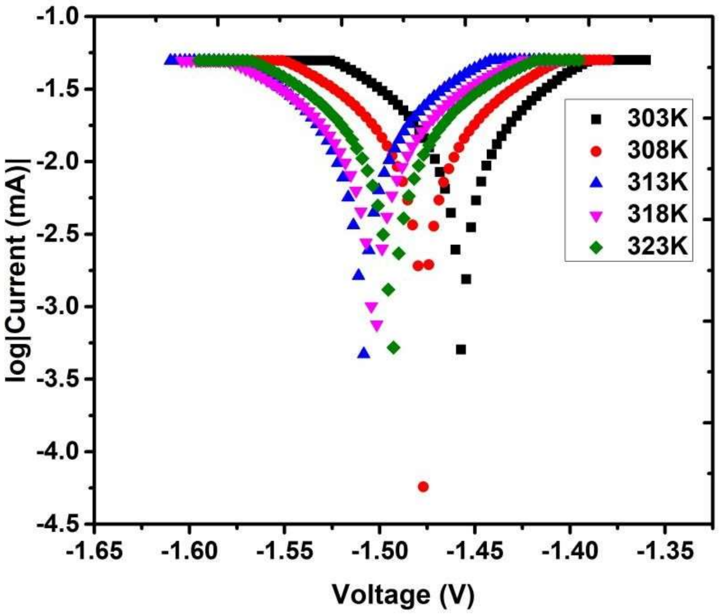

Figure 11: Temperature variation Tafel polarization curve for Aluminium in 500mM NaOH solution.

Temperature K	OCP V	Icorr 10^{-5} mA/cm^2	Ecorr V	Corrosion Intensity g/cm^2 /yr	Corrosion Penetration rate Mm/yr
303	-1.466	365.2	-1.45	4.77	17.67
308	-1.457	400.4	-1.46	5.23	19.38
313	-1.466	418.4	-1.47	5.47	20.26
318	-1.485	458.9	-1.49	5.99	22.21
323	-1.526	471.2	-1.52	6.16	22.81

Table 4: Temperature variation result of Tafel polarization curve of Aluminium in 500mM NaOH Solution.

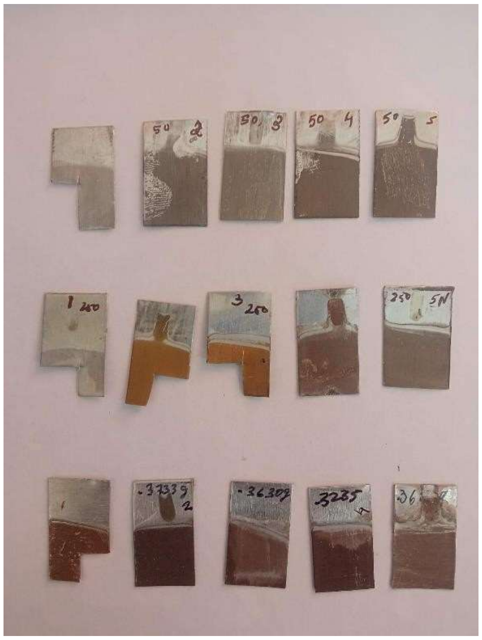

Image of Aluminium electrodes corrosion study for temperature variation at constant concentration NaOH medium, top row in 500mM, middle row in 250mM and bottom row in 50mM

We can see from the above result that, the corrosion rate of aluminium in NaOH is increases with increase in temperature due to the thermodynamic and kinetic factors affecting the corrosion process. In the corrosion process, the chemical reaction involves the dissolution of aluminium metal into the aqueous solution with the release of hydrogen gas, which is an exothermic reaction. The increase in temperature of the solution leads to increase in the rate of the reaction and consequently an increase in the corrosion rate. Also, the tafel plot, which is the measure of the rate of anodic and cathodic reaction can change with temperature due to the activation energy of the reaction. At higher temperature, the activation energy for the anodic and cathodic reactions may decrease, leading to lowering the tafel slope and higher corrosion rate.

4.2 Scanning electron microscopic study

The surface morphology for aluminium sample was examined by SEM images after corrosion test in 50mM, 250mM and 500mM sodium hydroxide medium. Before taking the SEM images the samples were heated at 350K for 1hr in heat furnace. SEM image of corroded sample along with average particle size is given below.

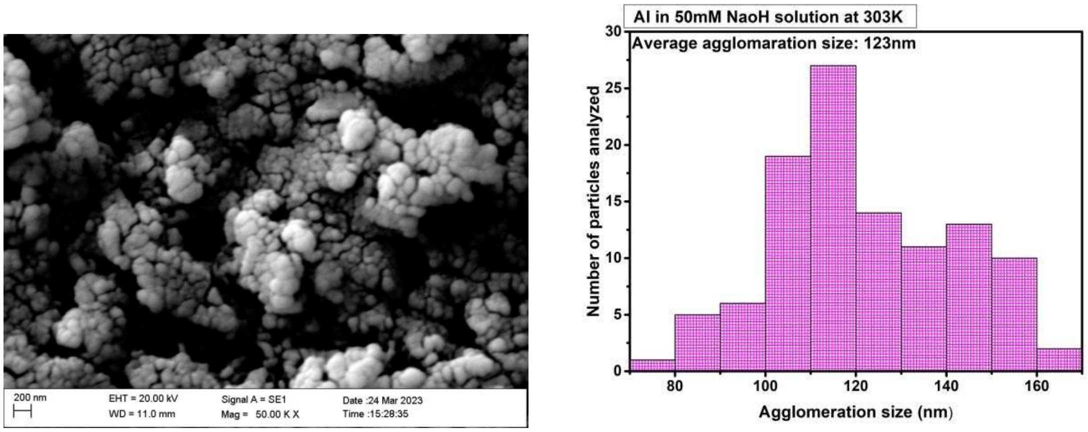

Figure 12: SEM imge of aluminium after immersion in 50mM NaOH medium at 303K and histrogram showing average agglomeration size.

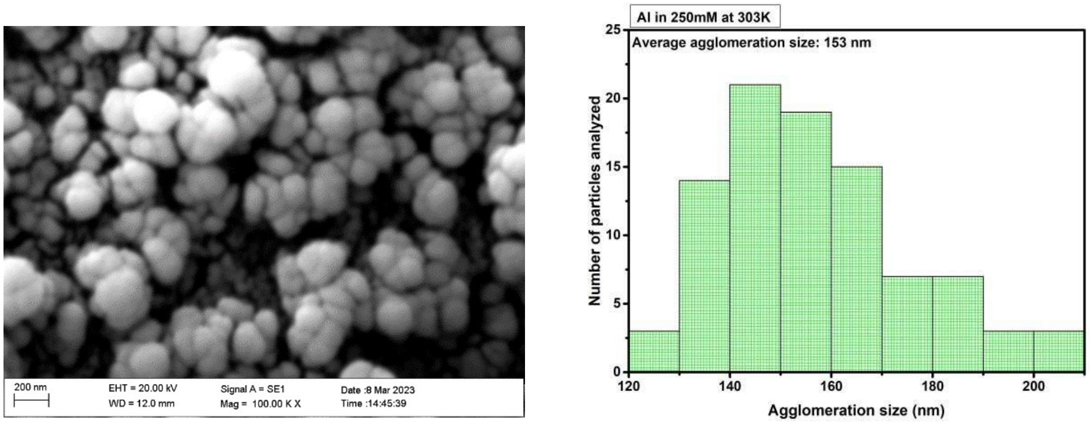

Figure 13:SEM imge of aluminium after immersion in 250mM NaOH medium at 303K and histrogram showing average agglomeration size.

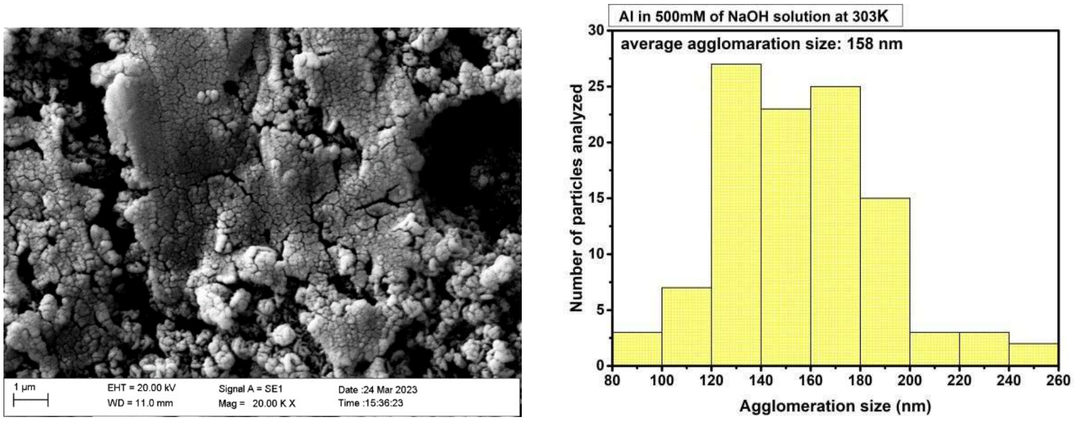

Figure 14:SEM imge of aluminium after immersion in 500mM NaOH medium at 303K and histrogram showing average agglomeration size.

Concentration of NaOH at 3003K	Average agglomeration size
50mM	123 nm
250mM	153 nm
500mM	158 nm

Table 5: Average agglomeration size of Al_2O_3 with increase in concentration of NaOH medium.

As the concentration of NaOH medium increases, we observe that the average agglomeration particle size increases, this is due to faster precipitation rate resulting from the more aggressive corrosion reaction. [4]

The following SEM images are obtained for Al in content NaOH medium at 250mM and varying the temperature.

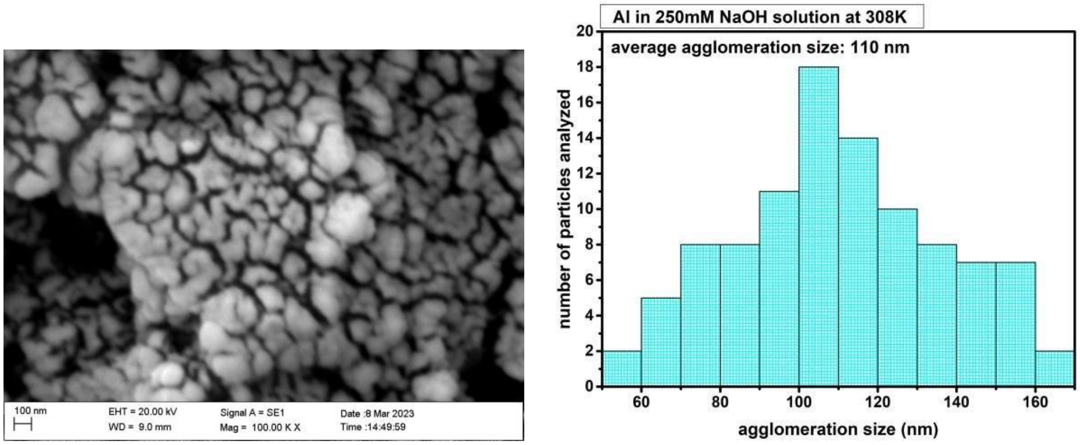

Figure 15 SEM imge of aluminium after immersion in 250mM NaOH medium at 308K and histogram showing average agglomeration size.

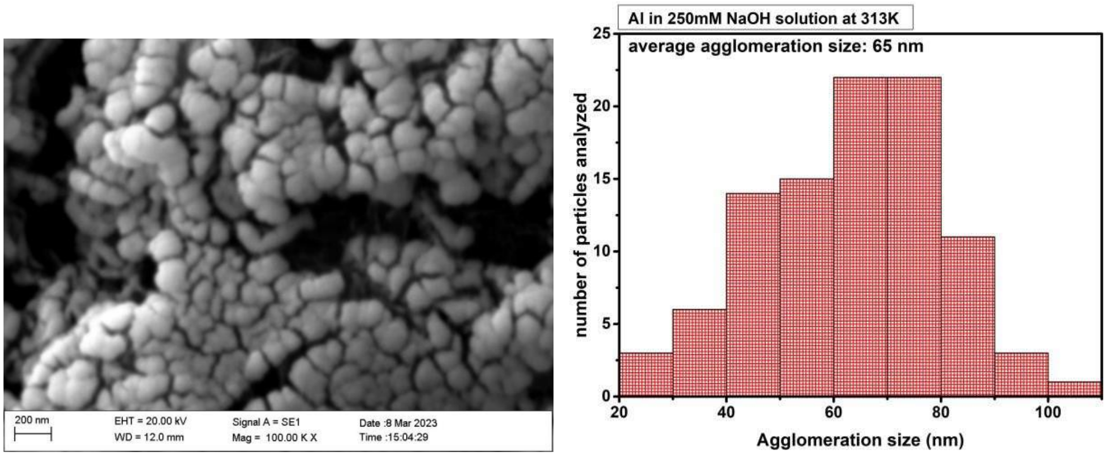

Figure 16 SEM imge of aluminium after immersion in 250mM NaOH medium at 313K and histogram showing average agglomeration size.

Temperature	Average agglomeration size
303K	153 nm
308K	110 nm
313K	65 nm

Table 5: Average agglomeration size of Al_2O_3 form on Al surface in 250mM NaOH at different temperature.

4.3 UV-Visible Diffusive Reflectance Spectroscopy Analysis

The band gap of Al_2O_3 which is form on the surface of Aluminium can be determined through UV spectroscopy, which measures the absorption of light in the UV visible region. The band gap energy (Eg) of a material is related to the energy of the photons that can be absorbed by the material. The band gap was calculated by using the Tauc's Plot and it was found to be 3.83 eV. For UV- Visible Spectroscopy we replace the absorption coefficient (α) in the Tauc's Equation (equation 1) with the Kubelka-Munk Function i.e., F(R ∞), which is the ratio of the absorption coefficient(k) to the scattering coefficient(s) in m-1.

$$(\alpha h\nu)^{\gamma}=A(h\nu-E_g) \qquad \text{Equation 1}$$

Where,

α is the absorption coefficient

h is the Planck's constant

ν is the photon's frequency

A is a proportionality constant

Eg is the band gap energy

γ denotes the nature of electronic transition

$(F(R\infty)h\nu)^{\gamma}=A(h\nu-Eg)$ Equation 2

Where,

$F(R\infty)=k/s=(1-R\infty)2/2R\infty$

R ∞ is the % reflectance obtained in the DRS data. The subscript ∞ denotes sufficient

Thickness of the sample layer that is thick enough to completely hide the support.

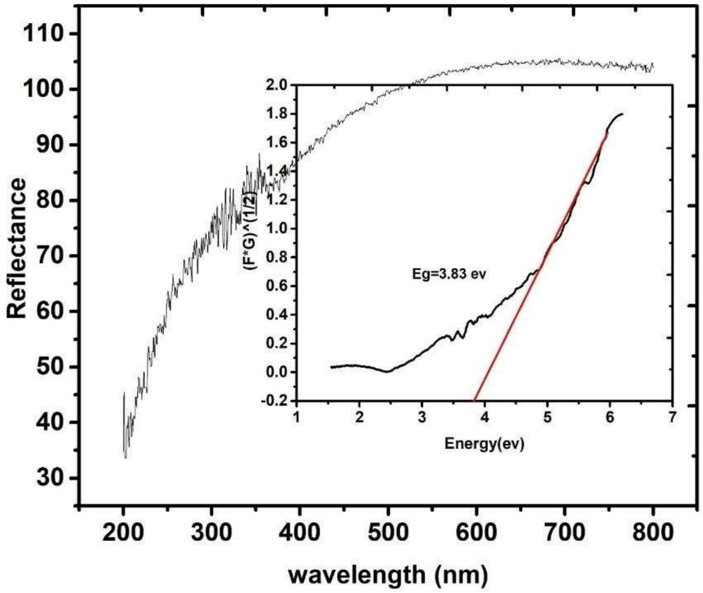

Figure 17: Band Gap of Al_2O_3

4.4 Raman Spectroscopy Analysis

The Raman Spectra of the as prepared samples were acquired using the LabRAM HR Evolution Raman Microscope. Raman spectroscopy of Al_2O_3 was done for 784 nm wevelength and it shows peaks at 410 cm^{-1}, 445 cm^{-1} and 643 cm^{-1} as shown in figure 18. The Raman spectrum of Al2O3 formed by corrosion of Al in NaOH will exhibit several prominent peaks at around 416, 496, and 698 cm^{-1}, which correspond to the E_g, F2g, and A1g modes, respectively. [5] The

E_g and A_1g modes correspond to symmetric stretching vibrations of the oxygen atoms in the Al2O3 lattice, while the F_2g mode corresponds to a symmetric bending vibration of the O-Al-O bonds. [6]

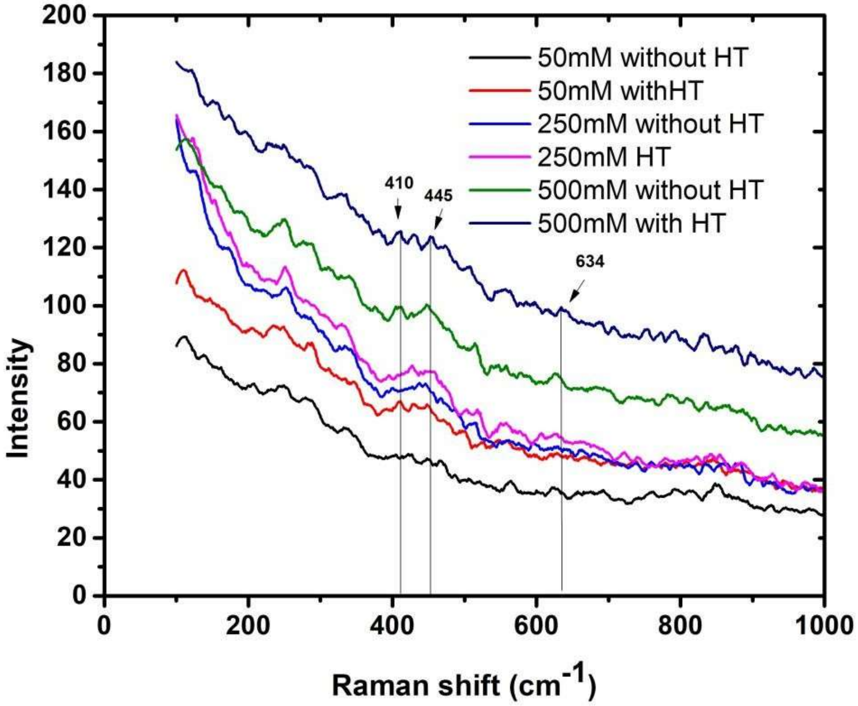

Figure 18: Raman peaks of Al_2O_3, which form on the surface of Al in different concemtration of NaOH with and whithout hear treatment.

5 Summary and conclusion

- Corrosion of Aluminium in sodium hydroxide solution was studied using electrochemical technique (Tafel plot , polarization curve) and found that the corrosion rate of aluminium in sodium hydroxide increases with increase in concentration and also with the increase in temperature.
- By kepping the bath temperature constant at room temperature (303K), we observer that the corrosion rate increases from 1.491, 6.310 and 11.314 for 50 mM, 250mM and 500mM.

- By keeping concentration of electrolyte constant and varying the temperature from 303K to 323K . We observer that the corrosion rate increases as temperature increases.
- Scanning electron microscopy study of sample shows that the average agglomeration particle size increases as the concentration of the medium in which corrosion study was carried out, increases. We also observed from SEM that by keeping concentration of medium same and increasing the temperature of bath during corrosion studies, average agglomeration size decreases.
- UV spectrum of Al_2O_3, the band gap was found to be at 3.83eV.
- Raman spectroscopy of Al_2O_3 shows three peaks at 410 and 445 cm^{-1} which corresponds to the symmetric stretching mode of the Al-O bond and peak 634 cm^{-1} which corresponds to the symmetric stretching mode of the O-O bond.

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References for figures:

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