

Summer Internship Project Report

Anti-Corrosive Coatings on copper substrates

Submitted by

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**School of Basic Sciences
INDIAN INSTITUTE OF TECHNOLOGY BHUBANESWAR**
Summer Internship 2022



भारतीय प्रौद्योगिकी संस्थान भुवनेश्वर

INDIAN INSTITUTE OF TECHNOLOGY BHUBANESWAR

Date- 29th August 2022

TO WHOM IT MAY CONCERN

This is to certify that **Mr. Kaling Vikram Singh**, Integrated M.Sc. student of National Institute of Science Education and Research Bhubaneswar (NISER) has been successfully completed his summer internship from 06th June to 15th August 2022 on the topic, “Anti-Corrosive Coatings on Copper Substrates”. During this period his character and conduct are good.

I wish him success in his future endeavours.

Prof. Saroj Kumar Nayak



Prof. Saroj Kumar Nayak
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Acknowledgment

The successful accomplishment of this report is the outcome of the contribution of a number of people to whom I am grateful and thank them from the very depth of my heart.

In the beginning I would like to convey my sincere gratitude to my honorable teacher and advisor Prof. Saroj Kumar Nayak, School of Basic Sciences, IIT Bhubaneswar. Without his guidance and assistance, this report would not have seen the light of day.

I would like to thank Balaram Polai, Soumyajeet Das who guided me throughout the tenure and helped me in conducting experiments and tests. I thank Dr. A. A.Srinivasan and Dr. Moloy Sarkar, Reader-F , NISER, Bhubaneswar who helped me to use Zeta-sizer at their laboratory. Without their support, this report would not have been complete.

I would also like to thank NISER and IIT for providing a platform for arranging internships to broaden the exposure to sciences and industries.

Abstract

The rusting phenomenon is as old as the planet itself. With the development of industry, corrosion costs have drastically increased and are now projected to be between \$300 billion and \$450 billion, or 3 to 5% of the GNP of wealthy countries. Corrosion management has been the focus of thousands of alloy developments, and it is a key factor in the creation of novel ferrous and non-ferrous alloys. To counteract corrosion, a number of corrosion control techniques have been created, including coatings, cathodic protection, alloying additives, and designing for corrosion protection. Recently, the electrophoretic deposition (EPD) technology has been used to successfully create graphene-based materials, and these materials have shown a variety of exceptional capabilities. We have used EPD as our mechanism to coat graphene oxide nano particles on copper substrates.

Surface characterizations were studied through SEM and the conditions for deposition were normalised through zeta potential tests. We have outlined the experimental deposition parameters as well as conducted Potentiodynamic polarization and Water contact angle tests to find corrosion rates and establish a correlation between hydrophobicity and corrosion rates. A voltage of 10 V for 5 seconds was found to give crack-free and high green dense deposit that prevents corrosion by upto 3 times better than bare copper. The potentiodynamic polarization curves showed that there was a reduction in corrosion rates as the hydrophobicity of substrates increased. This was achieved through coating with GO nanoparticles onto copper substrates. The method used is quite simple, affordable, and time-efficient.

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Chapter 1

Introduction

Human civilization has always struggled with corrosion and its affect on economy, whose accounts go back to times of Plato. Industries used various ways to protect metals. Some used to coat them with coal tar, some used less corrosive materials like lead, oakum or tarred rope. People in 19th century started experimenting with corrosion protection using modern techniques but reliable techniques were developed by 20th century. As industrialization took over, materials were subjected to harsh conditions, corrosion protection became integral part to proper operation of industries [1].

The estimated cost accounting to maintenance, repairs and replacement of existing structures is 4%-8% of the GDP of the nation of a developed country. Due to varied environmental conditions, it becomes difficult to predict metal service lifetime pertaining corrosion. With changing weather and harsh climates, the loss to economy is increasing every year and people are trying to find new methods/technologies to reduce damages due to corrosion [2].

Copper, owing to its high electrical, thermal conductivity, high ductility is used for various purposes in multiple industries. Copper is susceptible to corrode in non-inert atmosphere like sea water and oxygen rich atmosphere. Recent advances in Nano-technology has enabled us to prepare corrosion resistant coatings on substrates that help in longevity of metals. Researchers have tried ceramic coatings [3, 4], epoxy coatings [5] and polymer coatings [6] out of which, graphene coatings have showed extraordinary results [7].

graphene or graphene oxide is a highly ordered structure with graphene sheets stacked on top of each other through interlayer and intralayer cross-links. It is a material composed of hexagonally arranged carbon atoms. Due to sp^2 hybridization, these structures have a free electron that provides high

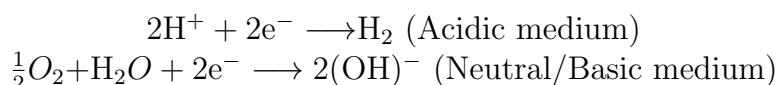
electrical and thermal conductivity. It has high electrical mobility, very high tensile and mechanical strength. Owing to these properties of Graphene, in this project, we have tried to develop anti-corrosive coatings to reduce corrosion rates in metals like copper. We have electrodeposited graphene oxide on copper substrates using electrophoretic deposition.

1.1 Corrosion

Corrosion is the conversion of metals into their stable oxides due to interaction with the environment. Corrosion mostly occurs in aqueous solutions and the process can be explained through anodic electrochemical reaction as:



This reaction is feasible if there is a cathodic reactant that accepts the electrons. Thus, we have:



The metals then further may stay dissolved in medium or precipitate as solids. The corrosion stops after a while as metals form a oxide layer film that prevents any direct contact of the environment to metals, reducing corrosion rates[8].

the corrosion depends on parameters such as diffusion, pH, Conductivity, Temperature, electrochemical Potential. Based on the corrosion rates, the corrosion types have been divided into various types.

Types of Corrosion

General Corrosion

General corrosion, sometime referred to as uniform corrosion, occurs when a corroded metal substrate is soluble and results in general thinning of the metal leading to decrease in strength. A very good example of the general corrosion is iron rusting in atmosphere. The rust in iron is a combination of iron oxides incorporating various contaminants from the atmosphere such as chlorides, sulphates, carbonates etc.

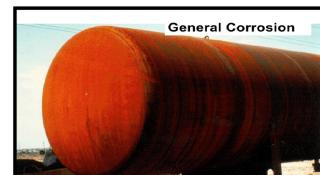


Fig1:General Corrosion[9]

Galvanic Corrosion

When two metals of different anodic potentials are kept in contact, the one with more oxidization potential protects the other metal at the expense of rapid corrosion. The larger the difference between the metals, the stronger is the corrosion protection. An example of galvanic corrosion is the statue of liberty. The gaskets separating the copper skin and metal support disintegrates over time causing corrosion in steel.



Fig.2:Galvanic Corrosion[10].

Pitting Corrosion

Pitting corrosion occurs when a passivated metal or alloy is exposed to harsh saline environments. The actual mechanism of pitting corrosion is still under study but the chloride ions cause local breakdown of protective films. The proposed theory includes[11] (1) penetration of chloride ions through the point defects in the passive films by chloride (2)competitive absorption of chloride and oxide ions and (3) dynamic depassivation-repassivation. The sites where the passive layer is locally destroyed, active corrosion starts and the sites become more anodic . The reaction is given as:

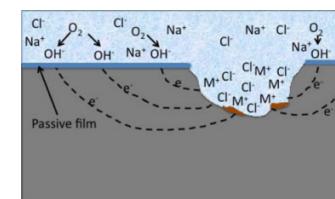
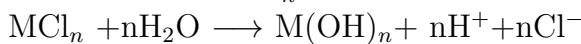
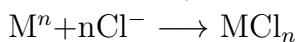


Fig3:Pitting Corrosion[11]

Crevice Corrosion

Often, due to stagnant environment,such a water taps, pipes, some sites of a material become anodic with respect to the other sites of metal, leading to corrosion.Stainless steels appear to be more vulnerable to crevice corrosion because the passive Cr₂O₃ film cannot be maintained when oxygen levels in the crevice fall. The addition of molybdenum to stainless steel improves the material's resistance to both pitting and crevice corrosion.

1.2 Corrosion Protection

Scientists have devised various methods to fight corrosion that include design modifications, protective coatings, Cathodic Protection and Environmental Control. In order to prevent corrosion, one can remove the medium for corrosion. Thus, environmental protection and design modifications such that metals susceptible to corrosion are not exposed to corrosive media such as salt water. Although, this is very expensive and required large modifications in the industries. Galvanic Protection includes a more reactive electrode that acts as sacrificial electrode to prevent corrosion in our targeted substrate. Cathodic protection works by forming a circuit with one or more anodes (external devices) in an electrolyte. From the anode, current travels through the electrolyte and out the structure's surface. Corrosion moves to the anode to stop further corrosion of the structure.

Coatings

A coating is a cover applied to a substrate. It is done for various purposes, primarily to prevent metal deterioration. Coatings can be classified by several different criteria, based on their functions, processing or properties. Thin films are used widely used in fields like optics, semiconductors, biomedical devices. These coatings have specialized functions. The real challenge lies in deposition of these coatings as their integrity is compromised owing to harsh climatic conditions [12]. On the other hand, industrial coatings are more robust and can withstand more mechanical aberrations. These coatings are composed of metals, ceramics and composites.

Coatings are widely used in industries such petroleum, aerospace and automotive. According to estimates, 75% of modern aircrafts have some kind of coatings to prevent damage with prolonged use. For resistance to wear, oxidation, and corrosion, high-temperature coatings have been used. Aluminum metal-matrix composites (MMCs), which provide strength while drastically lowering weight, are utilised to coat disc brakes in the automobile industry. Molybdenum coatings are frequently used in high-temperature engine components to increase wear resistance. [13].

There are various methods to apply thin film coatings onto substrate such as chemical vapour deposition, spin coating, etc with the most conventional one being electrochemical deposition. Electrochemical deposition is the process of depositing a material present in electrolyte onto electrode by applying an electric field. In this project, we used colloidal suspensions as electrolytes.

We deposited graphene oxide nano-particles onto metal substrates to obtain anti-corrosive coatings.

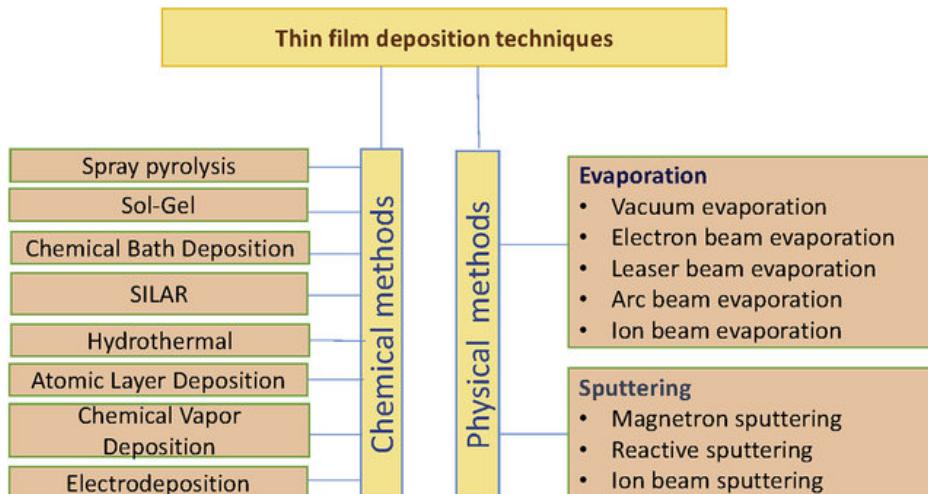


Fig.4.Film A:mean particle size: $3\mu\text{m}$; Film B-Mean particle size: $0.06\mu\text{m}$ [14]

Electrochemical deposition is affected by electrolyte based and experiment based parameters. The suspension related parameters include zeta potential, viscosity, particle size, concentration and conductivity. The process related parameters include voltage and deposition time.

1.2.1 Electrophoretic deposition

Suspension Related parameters

Particle Size

In order to get a smooth and homogeneous deposition, it is necessary for particles to be evenly dispersed. Large size particles , due to their inherent weight settle down and do not form a even distribution. Electrodeposition due to settling particles gives a gradient in the coatings, thicker towards bottom and thin towards the top of substrate. It is difficult to get uniform deposition from sedimenting suspension of large particles. The mobility due to electrophoresis must be higher than due to gravity to obtain good coatings. Additionally, a very high surface charge or an expansion of the electrical double layer area are required for electrophoretic deposition to happen with bigger particles.

Particle size has influence on cracking of deposits in thin films on drying. Sato et al.[15] reported the effects of reducing the size of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO)

particles on film cracking. They observed that by reducing particle size, the cracking reduced significantly. Hence, reduction in particle size improved the morphology of the YBCO superconducting film fabricated by electrophoretic deposition suggesting that it is a useful technique to minimize cracking of deposits.

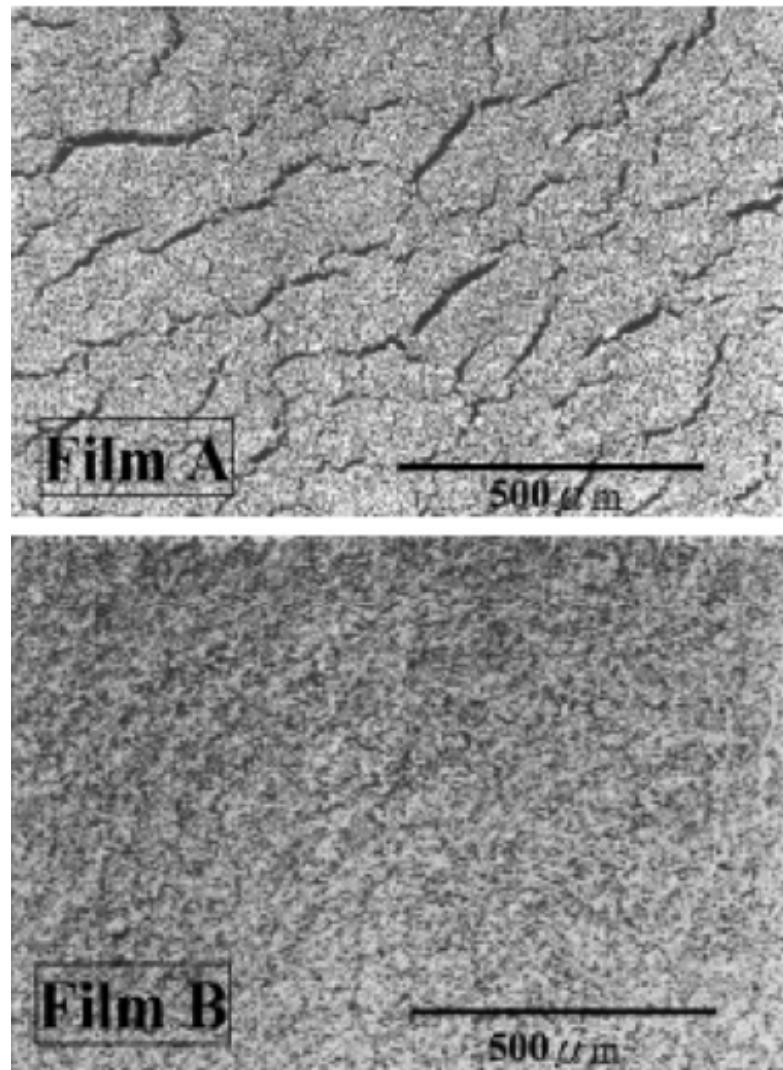


Fig.4.Film A:mean particle size: $3\mu\text{m}$; Film B-Mean particle size: $0.06\mu\text{m}$ [14]

Dielectric Constant of electrolyte

The dielectric is a measure of energy a material can store when a voltage is applied across it. It is defined by the ratio of permittivity of the material with the permittivity of the free space. Powers[16] studied the variation of deposition over dielectric constant. He found a sharp increase in conductivity with dielectric constant was noted; which apparently refers to the liquid in

their pure state. Powers[16] obtained deposits only for electrolytes whose dielectric constants were between 12-25. With a low dielectric constant, there was no enough dissociative power leading to no deposition. Further, when he increased the dielectric constant, the conductivity increased leading to thinning of electric double layer, thus reducing electric mobility and hence no deposition.

Conductivity of electrolyte

Conductivity of electrolytes plays a crucial role in defining proper conditions for electrodeposition. If the conductivity is too high, the particle motion is low, leading to less electrodeposition and when it is too low, the suspended particles are charged and the suspension stability is lost. They found the existence of a narrow band of conductivity range at varying dispersant dosage and temperature, in which the deposit is formed[17]. The conductivities beyond these ranges were not suitable for deposition.

Viscosity of electrolyte

Viscosity is defined as the resistance of a fluid (liquid or gas) to a change in shape or movement of neighbouring portions relative to one another. Suspension having high viscosity lead to resistance in movement of nano-particles and obstruct the process of electrodeposition. In general, an ideal suspension shall have low viscosity, high dielectric constant and low conductivity [14].

Zeta Potential

The surface charge of nanoparticles is measured by their zeta potential. As the potential at the slipping plane, it is so named. This plane serves as the interface between fluid that is mobile and fluid that is still affixed to the surface. Zeta potential is significant because it affects the stability of the suspension by influencing the strength of repulsive interactions between particles, as well as the direction and speed of particle migration during electrophoretic deposition (EPD) and the green density of the deposit. [14]. The particle stability is determined by the interaction between the particles. A high electrostatic repulsion is required between high charge particles to prevent any agglomeration. Particle charge plays a crucial role in determine the green density. If the charge is too low, the particles would coagulate at the surface of the substrate and make the deposits porous sponge-like. On the other hand, if the charge is too high, the repulsive forces, make the nano-particles occupy positions, leading to high green density. Thus, it is important to control the particle charge and hence zeta potential.

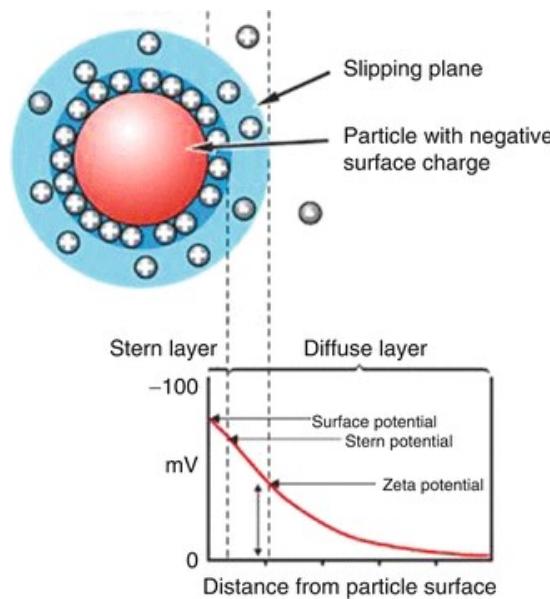
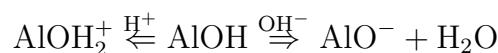


Fig.4.Film A:mean particle size: $3\mu\text{m}$; Film B-Mean particle size: $0.06\mu\text{m}$ [14]

There are several ways to vary Zeta potential using charging agents such as adding acids, bases, and specifically adsorbed ions or polyelectrolytes, to the suspension. Different agents vary the zeta potential through varied mechanism. The additives are chosen based on how they affect the polarity and depositions. In EPD, an suspension with high zeta potential is preferred as it enhances the stability, increases the green density and determines the migration velocity. The zeta potential is heavily dependent on the concentration of the constituents. Cheng et al.[18] reported variation in zeta potential by varying pH suspension of alumina and ethanol. He found the suspension to be most stable at ph 2.2 while stability was lost as pH reached 11. Wang et al.[19] proposed a charging mechanism for alumina.



Under higher pH, the AlOH forms AlO^- , but due to presence of water, it further forms AlOH^{2+} instead of AlO^- , leading to more absolute zeta potential at pH 2 than at pH 11. The effect of charging agents is also seen in conductivities and affect the electrodeposition.

Process Related

Effect of deposition Time

The deposition rate decreases over time. In a constant voltage EPD, it is expected as an insulating layer gets over the metal substrate, decreasing the

electric field over time but with constant voltage. Hence, over time, the deposition rates decrease. In early stages of EPD, the relation is mostly linear.

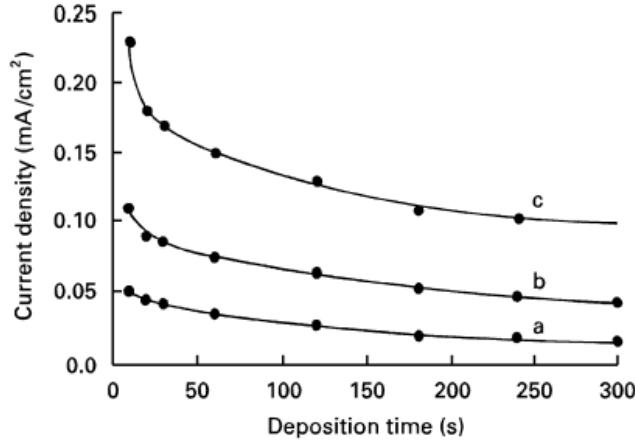


Fig.6. Current density versus deposition time for deposition of hydroxyapatite at different voltages: (a) 50 V; (b) 100 V; (c) 200 V [20].

Effect of Voltage

The amount of deposit increases with increase in the voltage, but the quality and green density of the coating is voltage dependent. Basu et al. [21] reported that more uniform films were achieved with moderate voltages(20-100 V/cm). The formation of coating on substrate is a kinetic phenomena and the accumulation rates influence the packing efficiency. More voltage leads to greater electric fields and hence turbulence in the suspension. This results in disturbance in flow and during deposition. Further, in very high fields, the particles might migrate with very high velocities and cannot find the best packing efficiency as lateral movement is restricted due to the force from the field.

Mechanism of Electrophoretic Deposition

There are various proposed mechanism of electrophoretic deposition. These include flocculation by accumulation, particle charge neutralization mechanism, electrochemical particle coagulation mechanism and Electrical double layer distortion and thinning mechanism.

Hamaker[22] studied and reported that due to pressure, incoming nanoparticles overcome the forces of repulsion and get accumulated at the substrate surface. Grillon[23] reported that particles get neutralised on contact with the substrate. Under the following conditions, this method is inappli-

cable, although it explains initial stage deposition from highly diluted suspensions: (a)EPD for extended periods of time (thick deposits), (b) when particle-electrode processes are stopped, such as when a semi-permeable membrane causes deposition between the electrodes, and (c) when reactions take place at the electrode that change the surrounding pH.[7]. koelmans[24] reported that due to accumulation of nano particles at the electrode, the ionic strength is close to flocculating strength. This leads to reduction of inter particle repulsion and hence forming a layer. Finally, Sarkar and Nicholson[25] explained the invalidation of the concentration approach. They reported that when nano-particles migrate, due to difference in pressure, there is distortion in lysosphere. This leads to thinning of the layer in the front while thickening of layer at behind. When the nano-particles strike these accumulated particles at the electrodes, the lysospheres mix and then coagulation occurs.

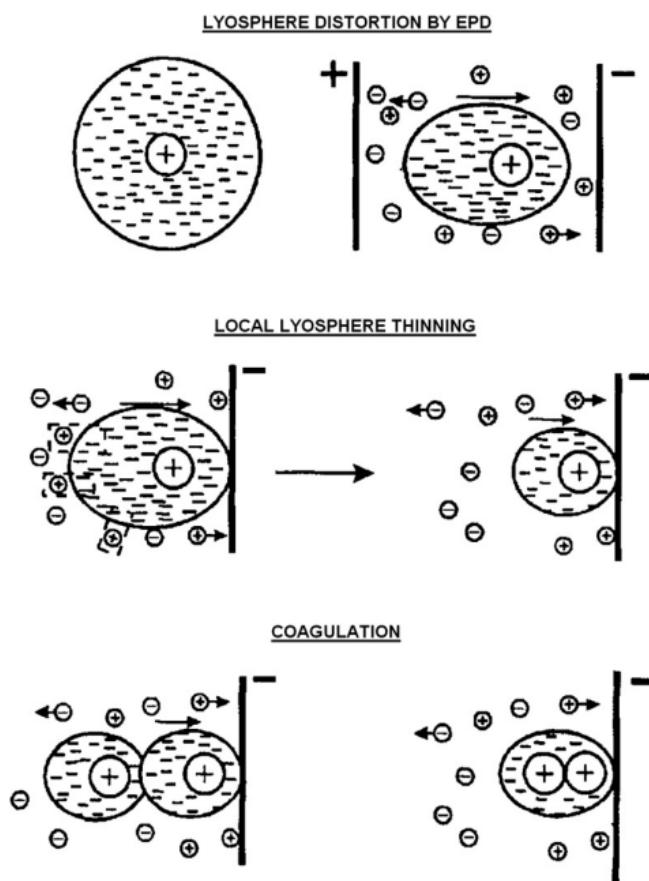


Fig.7.Electrical double layer distortion and thinning mechanism for electrophoretic deposition [14].

1.2.2 Hydrophobicity

A substrate is called hydrophobic if it repels water. Metals whose water contact angle is greater than 90° are said to be hydrophobic in nature. Hydrophobic compounds tend to have $-sp^2$ carbon chains and rings as chemical groups (hydrocarbons). These chemicals are incapable of forming hydrogen bonds, hence therefore have relatively low surface free energies. Hydrophobic surfaces don't typically become wetted by water; instead, the droplets stay beaded up with high contact angle values. Hydrophobic nature reduces the moisture exposure. This leads to less ions in contact with the metal, giving metal corrosion resistance. Scientists studying materials have been experimenting with different compounds to change the surface characteristics of surfaces to make them hydrophobic. In order to give glass a hydrophobic property, silanes are frequently utilised. Concepts related to hydrophobicity have been used in paints, coatings, and textiles.

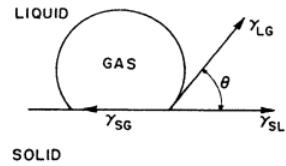


Fig.8:Water Contact Angle[26]

Chapter 2

Experimental Procedure

2.1 Raw Material

Copper sheets used in the study were 99% pure and purchased from the market. These sheets were 6mm thick. Graphene Oxide suspension (99%) was purchased form Graphenea with particle size: $< 10 \mu\text{m}$. The concentration and pH of the solution were 4 g/L and 2-2.4 respectively. Sand paper(SiC) of grit sizes varying from 320-1000 were purchased from the market. Steel electrodes were used counter electrodes. All aqueous solutions were prepared with ultrapure water ($> 18 \text{ M}\Omega$) from a Milli-Q plus system (Millipore).

2.2 Experiment

The samples were prepared according to the following table:

Experimental Details		
Concentration(g/L)	0.5	1
Time(s)	5	15
Voltage(V)	10	10

Fig.9.Experimental details of the samples.

Graphene Oxide suspension (4 g/L) was diluted using ultrapure water to obtain solutions of 1 g/L and 0.5 g/L concentration. These suspensions were then sonicated for 2 hours to obtain a uniform suspension. The pH of these solutions were varied from 4-10 using NaOH solution. Copper sheets obtained were polished using SiC papers from grit size 320 upto 1000. These copper strips were washed with acetone and sonicated in acetone to remove any contamination for 5 minutes. Steel counter electrodes (cathode) were due to better cathodic properties of steel.

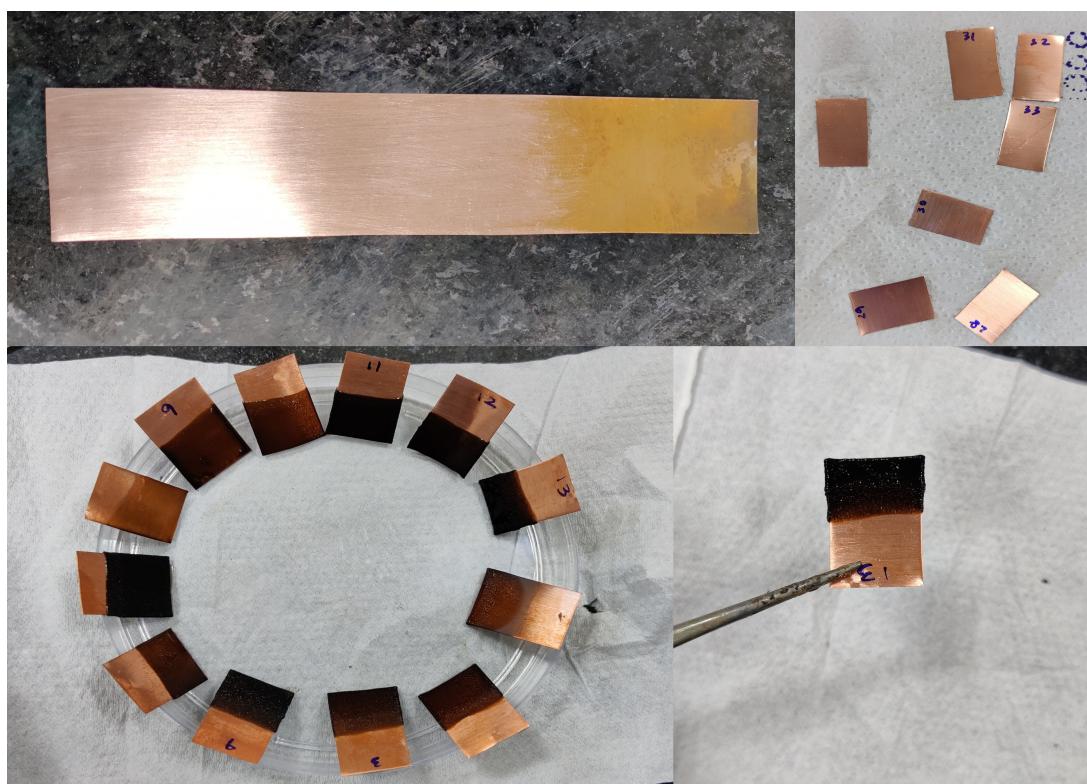


Fig.10.Samples prepared and coated samples. .

The graphene oxide suspension obtained was studied under DLS based zeta analyzer (Malvern zetasizer Nano ZS) to get zeta potentials by varying the pH. Based on observations, solution with pH 7 was used as the electrolyte. A constant voltage of 5-30 volts was applied employing a source meter (Model: 2410, Keithley Instruments, Inc., USA) for deposition time of 5-60 seconds with copper sheet at anode. The coated samples were carefully taken out of the solution and left to air dry over night. Tests for hydrophobic nature through measurements of Water contact angle (WCA) were done using ACAM-MSC by Apex instruments. Then the samples were studied under X-ray crystallography (Model: Bruker D7 ADVANCED).

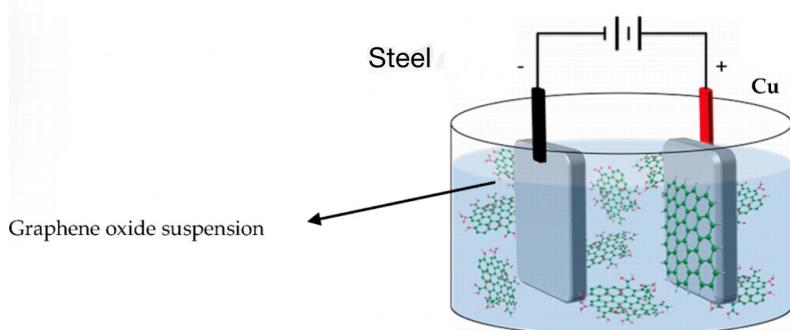


Fig.11. Setup for Electrophoretic deposition [14].

Potentiodynamic polarization were carried out in 3.5 wt% NaCl solution at ambient temperature with a three electrode electrochemical cell to evaluate the corrosion behavior of GO coatings. Electrolyte solutions were prepared with analytical grade NaCl and Milli-Q water. The reference electrode and counter electrode used were Ag/AgCl and Pt respectively. The area of the sample exposed to the electrolyte was 1 cm^2 . The tests were conducted using potentiostat/galvanostat (Model: Biologic SP-200).

2.3 Experimental Setup



Fig.12. Setup for Electrophoretic deposition.

The experimental setup consisted of a scissor jack with a retort stand. The retort stand was modified to fit electrodes for electrophoretic deposition. A source meter was connected with the electrodes using crocodile clips and connecting wires. Beakers were placed on the scissor jack to place the beaker at height suitable for deposition. Necessary connections were made to setup a two electrode electrodeposition system with steel as the counter electrode (cathode).

2.4 Characterization Techniques

Surface morphology

The surface topology of bare and Go coated copper were observed under scanning electron microscope(SEM). SEM is an electron microscope that uses focused beams of electrons to scan the surface. The electron interact with molecules on the surface and produce different signals such as reflected or back-scattered electrons, secondary electrons (SE) or characteristic X-rays and light. These signals are analysed in raster scan pattern and the position and intensity of signals are captured to produce an image. It is impossible to detect the roughness of a sample from a plane view image of the sample because images are in the form of the electron emission from a sample vs. spatial position. This is because the electron emission from the sample may not rely on the height. Roughness can only be assessed using a sample's cross section.

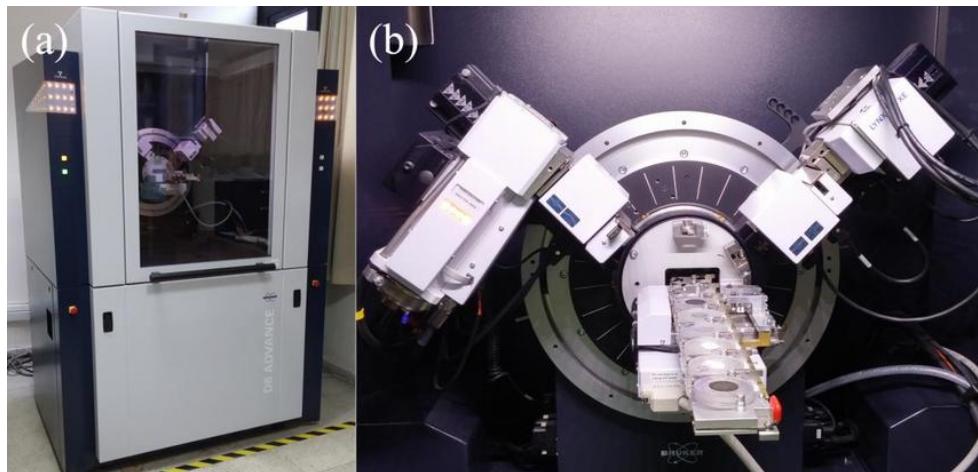


Fig.13. X-Ray Diffractometer[27].

X ray diffraction is an important tool used in material sciences to study the definitive structural properties of the substrate. Wavelength of $1 \times 10^{-10}\text{m}$

are used for the analysis of the substrate, which are of similar wavelengths as atomic spacings in crystalline solids. When a wave is incident, its diffraction can be understood based on Bragg's law. Bragg's law can be expressed as: $n\lambda=2ds\sin(\theta)$. The diffracted waves contain sharp maxima with the same symmetry as in the distribution of atoms if the atoms are arranged in a periodic fashion in crystals. The structure and composition is determined based on these maxima peaks. For testing copper strips, the 2θ angle was varied from 9° to 80° .

To prepare the sample for analysis, the DLS technique is utilised to assess the sample's size, zeta potential, surface charge, and other properties without agitating it. By measuring the speed at which particles and molecules are moving as a result of electrophoresis, the charge or zeta potential of these entities is ascertained. If a field is provided, zeta potential particles and molecules will move in the direction of the electrode. The zeta potential and field strength both affect how quickly they move. If the field strength is known, the speed of movement is measured using laser Doppler electrophoresis, and then proven zeta potential theories are applied.

Corrosion test and Hydrophobicity

The water contact angle is the measure of hydrophobicity of a substrate. Wetting, or the interaction of water with a surface, is essential to daily life as well as numerous biological and industrial processes. The contact angle measures how likely it is that the surface will become wet with water. It is the angle at the interface where water, air, and solids meet. High contact-angle values represent the surface's propensity to repel water, whilst low contact-angle values show the tendency of the water to spread and cling to the surface. Sessile-drop goniometry is the most popular technique for characterising surface-wetting because it is straightforward. The technique, which derives the contact angle from the droplet's shape, can be used with a wide range of substances, including biological surfaces, polymers, metals, ceramics, minerals, and more. The method's seeming simplicity is deceiving, though, as reducing random and systematic errors is necessary to get significant findings.



Fig.14:Sessile drop goniometer.

One of the key methods in traditional Tafel analysis is graphic extrapolation. Two divergent logarithmic plot lines that represent the anodic and cathodic currents are typical components of a Tafel plot, which is a graphical representation of the relationship between the current produced in an electrochemical cell and the electrode potential. The linear sections of the anodic and cathodic plots are extended back to their intersection to perform extrapolation. The corrosion current, I_{corr} , is obtained at the point where these two lines finally converge. The value of I_{corr} can then be used to calculate parameters like corrosion rate using certain mathematical calculations. The samples were studied between $E=-0.6$ V to 0.2 V with a scan rate of 1 mV/s.

2.5 Result and Discussions

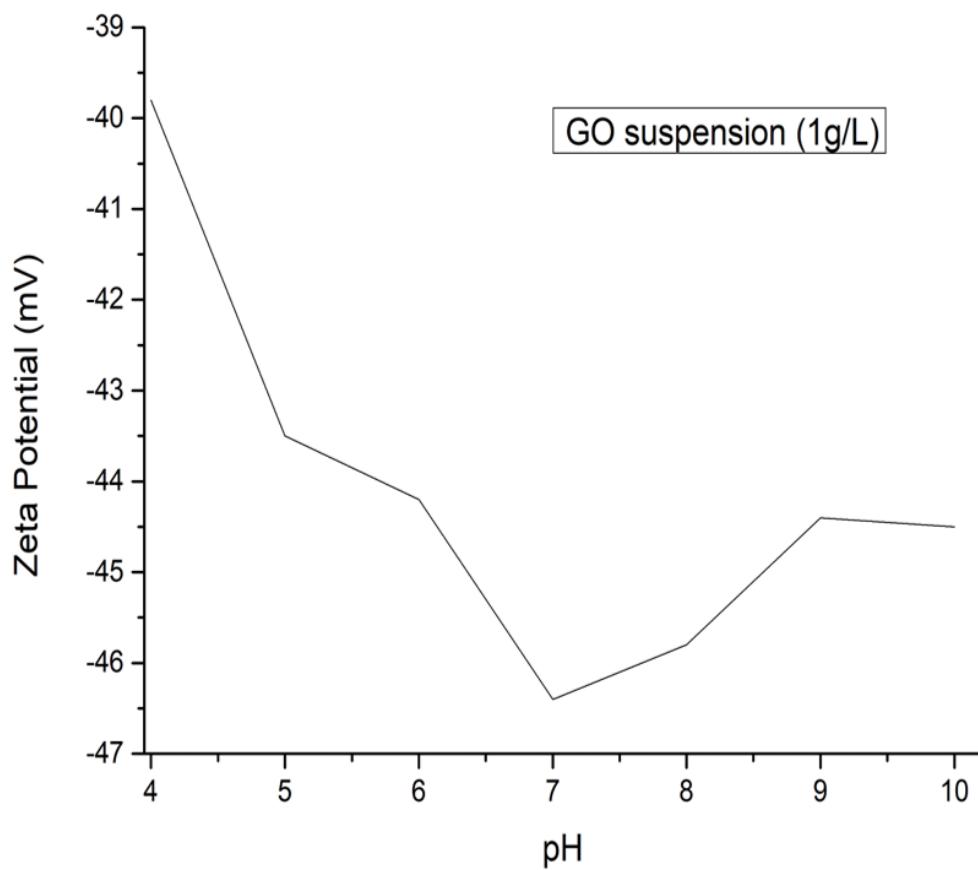


Fig.15.Graph of zeta potential vs pH .

The GO suspension obtained after tests in Zetanalyser depicted that the suspension attained maximum stability at pH~7. At pH~4, the zeta potential

was -39.8 mV and decreased to -46.4 mV at pH~7. Greater magnitude of zeta potential denotes greater charge density on the particle surfaces and in turn, more repulsion among the particles, leading to a stabler suspension. Further, an increase in the zeta potential was seen as the pH was increased. This is attributed to the inter particular repusions leading to thinning of the electric double layer and hence reducing the stability of the suspension. Hence, Graphene oxide nanoparticles were deposited at pH~7. The zeta potential justifies the process of electrodeposition as pH~ 7.

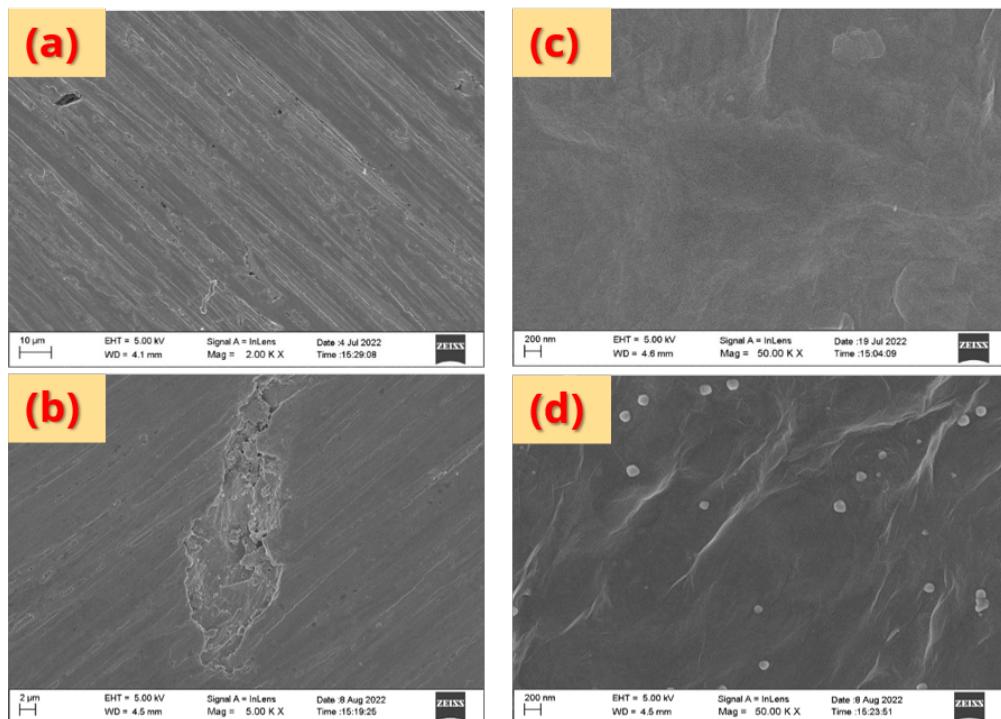


Fig.16.SEM images of sample:(a)Cu_Bare (b)Cu_101005
 (c)Cu_bare_aftercorrosion and (d) Cu_101005_aftercorrosion..

The SEM images of bare copper at $10\mu\text{m}$ show ridges formed due to polishing with sandpapers. The images of bare copper before (a) and after corrosion (c) show that there was destruction of metal when the substrate was exposed to corrosive media. Further, the SEM images in (b) show that graphene oxide nano particles were deposited over the copper substrate. These GO coatings were transparent due to transparent layer of Graphene oxide nanoparticles. The SEM images of GO coated copper(Cu_101005)(d)after corrosion test shows small crystals of NaCl deposited due to corrosion test although no destruction of the metal was visible. This shows that the coated GO

nano particles made a good passivation layer that protected the metal from action of the corrosive environment. These coatings were hence, able to provide protection from the environment by making a thin film that restricts the action of the environment.

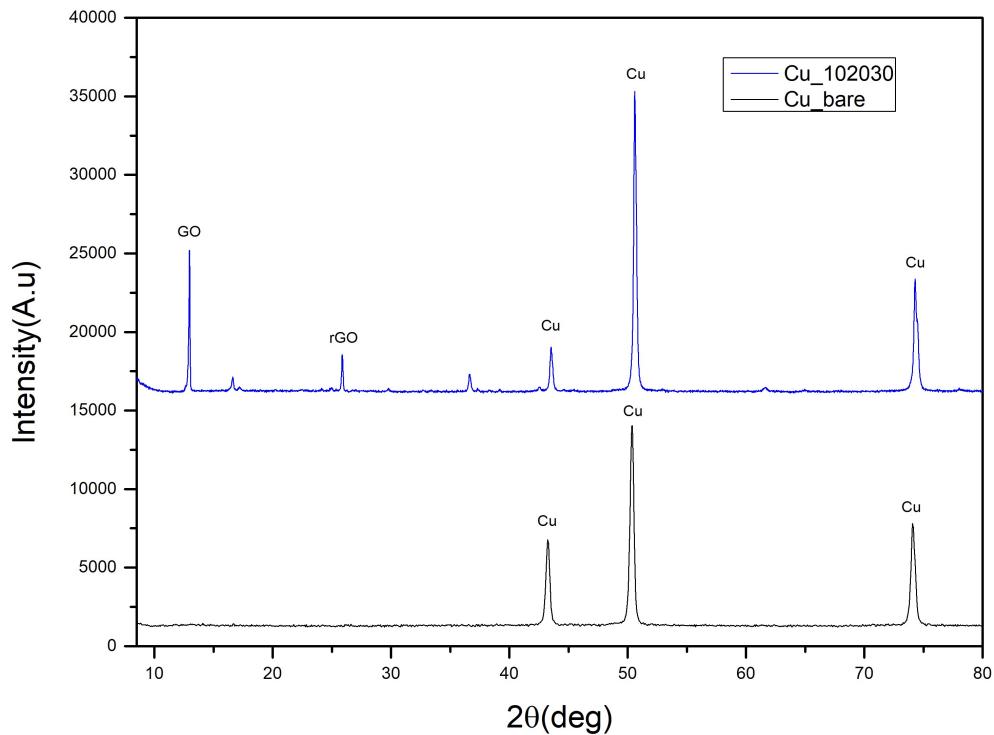
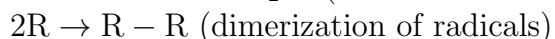


Fig.17.X-ray diffraction of Cu_bare and Cu_101005.

The XRD was done on bare and GO coated copper strips. For bare copper, the XRD data showed 3 peaks at $2\theta=43.4^\circ$, 50.5° , and 74.2° . The XRD plots of coated copper show peaks at $2\theta=11.7^\circ$ due to graphene oxide and $2\theta=25.8^\circ$ due to reduced graphene oxide (rGO) along with the copper peaks. The smaller peaks are due to NaOH used for diluting the solution. rGO is made during the process of EPD due to local heating and presence of high potentials due to voltage provided. The mechanism is given as:



The peaks show that a graphene oxide layer was deposited on copper substrates leading to respective XRD peaks confirming the presence of GO

nano particle layer on the substrate.

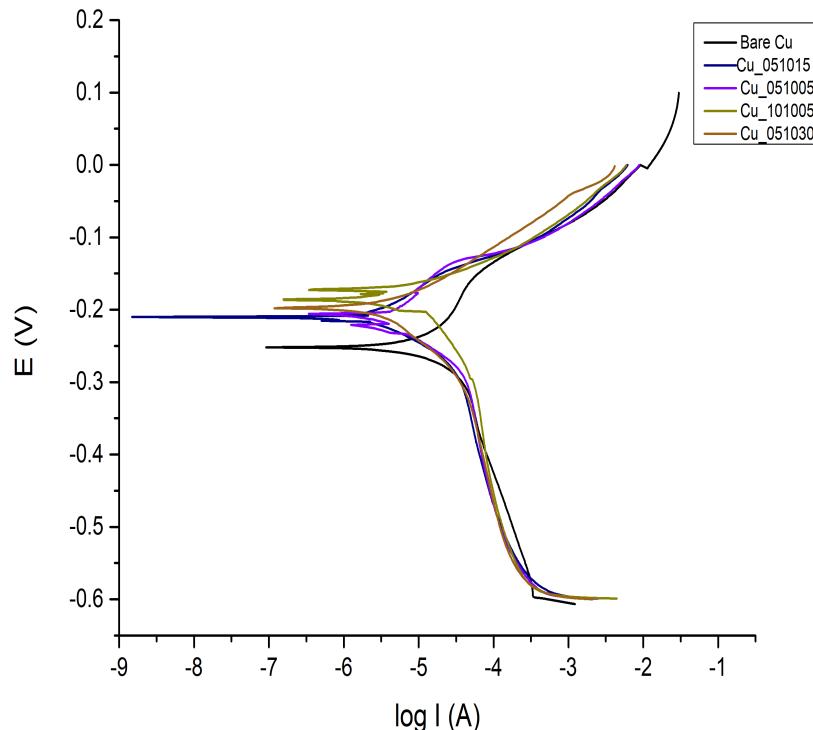


Fig.18.Tafel extrapolation curve.

Tafel extrapolation was done on bare and GO coated samples and the corrosion rate of Cu.bare was found to be 0.18558 mm per year (mmpY). It showed a corrosion potential of -251.617 mV with corrosion current 15.96312 μ A. The samples were studied between the range of -0.6V-0.2V. The study showed that there was a positive shift in the corrosion potential and a reduction in the corrosion currents in the coated samples. The sample Cu_101005 showed the best corrosion resistance with corrosion rate of 0.06118 mmpy. There was significant reduction in corrosion rates due to GO coatings. The sample Cu_051005 showed a corrosion rate of 0.09567mmpy and corrosion potential of -205.584 mV, more positive than of bare copper. The tafel plot shows that the coated samples, in general, showed better corrosion protection and were more corrosion resistant than bare copper.

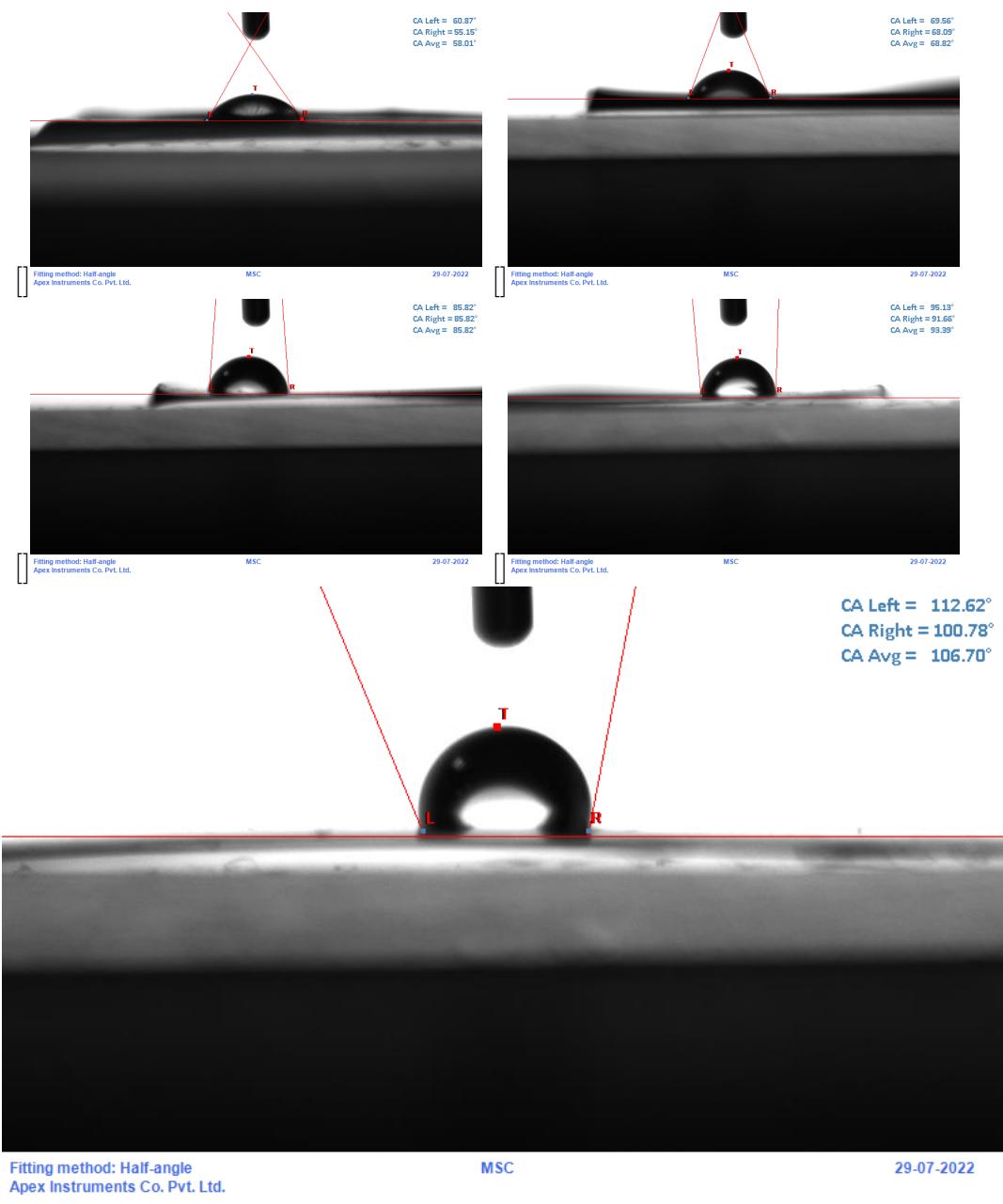


Fig.19.Water contact angles of samples: (a) Cu_bare (b)Cu_101015 (c) Cu_051030 (d) Cu_051005 (e) Cu_101005

Hydrophobicity tests were done and found that the static water contact angle (WCA of bare copper was 58.01° . This showed bare copper was hydrophilic and that it did not repel water. Samples made were then tested in the same conditions. Copper sample Cu_101005 showed exceptional hydrophobicity of 106.70° , giving it a hydrophobic nature. This can be attributed due to passivation layer of GO and rGO and rGO being hydrophobic makes the copper layer hydrophobic. Other samples coated with GO showed similar increase in the hydrophobicity. The sample Cu_051005 also showed increased hydrophobicity with an WCA of 93.39° . This suggested that best hydrophobicity was achieved with samples with a deposition time of 5 seconds. Other coatings showed increased hydrophobic nature than bare copper showing that GO acts as a passivation layer to prevent contact between substrate and moisture.

Sample Number	Water Contact Angle (deg)	Ecorr (mV)	Icorr (μA)	Corrosion Rate (mmpY)
Cu_bare	58.01	-251.617	15.96312	0.18558
Cu_101015	68.82	-245.884	13.56832	0.15775
Cu_051030	85.82	-210.149	11.10856	0.12914
Cu_051005	93.39	-205.584	8.22951	0.09567
Cu_101005	106.7	-173.401	5.26356	0.06118

Fig.20.Correlation between WCA and corrosion rates.

A direct correlation was seen between the hydrophobicity and corrosion resistance was observed in the substrates analyzed. The samples with best hydrophobic nature showed best corrosion resistance. It was observed that as the water contact angles increased, the corrosion potential of the substrate increased (become more positive) along with decrease in corrosion current and corrosion rates.

There was a strong correlation between water contact angle, and hence hydrophobicity, and corrosion rates. This can be attributed to the passivation

layer and hydrophobic properties of rGO and GO. The corrosion needs three things,(a) moisture (b) electron acceptor and (c) substrate for corrosion. Through the coatings, the moisture contact was reduced and the oxidation reaction was slowed. The rGO and GO layer also reduced contact of electron acceptors and hence reduced corrosion rates in general. Thus, we have established an strong correlation between hydrophobicity and corrosion.

2.5.1 Summary

1. The zeta potential reaches minima at pH~7.
2. Bare copper had a WCA of 58.01° and $E_{corr} = 251.617$ mV while Cu_101005 had a WCA of 106.7° and $E_{corr} = -173.401$ mV .
3. Other samples had similar trends in WCA and E_{corr}/I_{corr} .

These results show that:

- (i). pH~7 is the optimal pH for electrodeposition of GO nanoparticles onto substrate.
- (ii). There is a direct correlation between water contact angle and corrosion resistance.
- (iii). Coatings with deposition time 5 seconds give better corrosion resistance than others.
- (iv). 1 g/L suspension gives "good" coatings for corrosion resistance under suitable conditions.

Chapter 3

Future Work

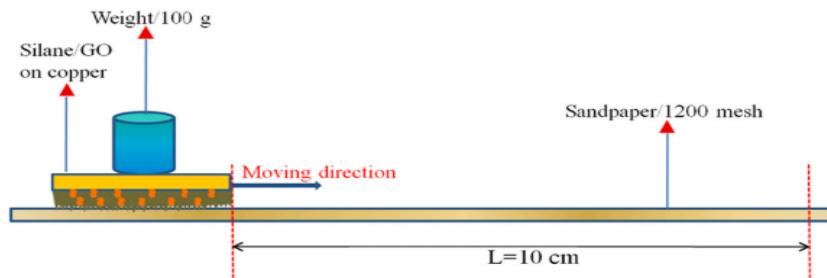


Fig.8. Setup for Abrasion test [27].

The study is based on the correlation between hydrophobicity and corrosion rates. There are multiple parameters that can affect coatings. The roughness of samples, the surface topology/morphology and concentration can be varied to understand the effects of each of these components in the coating quality. The method shown in Fig. can be used to study the abrasion stability of electrodeposited coatings. The hydrophobic surface of the electrodeposited samples must be placed down on 1200 grit sandpaper before being dragged forward along a straight line for 10 cm under the application of pressure equal to 100 g of weight, then backward another 10 cm to the starting position, which will be considered one cycle. The CA and SA of the abraded coating surface must be monitored after every 10 abrasion cycles. The surface robustness can be calculated using the data..

A GO composite can be used for coating on substrates. The technique we use is based on anodic electrodeposition as the zeta potential of the GO nanoparticles is negative. With use of suitable composites, zeta potential can be made overall positive and cathodic deposition can be achieved.

Chapter 4

Conclusion

We have shown how graphene oxide nanoparticles may be electrochemically deposited onto copper surfaces. The coating is highly dense, consistent in thickness, and free of any fractures. It has good oxidation and corrosion resistance properties in a hostile chlorine ion environment because of this, which may lead to new uses for materials used in maritime engineering that require extremely high salt resistance. The EPD process is advantageous over dip or spray coating in a range of industries because it prevents the production of coating pinholes or imperfections commonly seen in associated with dip or spray coating.

The correlation between hydrophobicity and corrosion was studied and can be applied in the industries for industrial equipment. The proposed EPD process is innovative in that it is aqueous based, easily scaleable, environmentally friendly, economical, and capable of being produced over a vast surface area. These findings imply that GO coatings that are hydrophobic and resistant to oxidation and corrosion have a lot of promise as high-performance protective shields for active metals that are susceptible to oxidation.

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