

NANOSCOPIC STUDY OF CORROSION
DYNAMICS AND PROPERTIES OF
ANTICORROSION COATINGS ON COPPER
AND ALUMINIUM ALLOYS

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Doctoral Dissertation
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NANOSKOPSKA ŠTUDIJA KOROZIJSKE DINAMIKE
IN LASTNOSTI PROTIKOROZIJSKIH PREVLEK NA
BAKRU IN ALUMINIJEVIH ZLITINAH

Doktorska disertacija

Supervisor: Prof. Dr. Igor Muševič

Ljubljana, Slovenia, June 2017

To My parents, Hanaa Qassem, and Samy Kreta.

Acknowledgments

I would first and foremost, like to express my sincere and deepest gratitude to my supervisor Prof. Igor Muševič for giving me motivation, guidance, and feedback. His vision, rich knowledge, and experience have guided and motivated me to finish this work.

I am also thankful to all the researchers in the Department of Materials Chemistry-National Institute of Chemistry, and to its head Prof. Miran Gaberšček for giving me the opportunity for discussions. Especially Dr. Angelja Kjara Surca for supplying aluminium samples and supporting with IRRAS measurements, and Dr. Mohor Mihelčič for helping with the preparation of gel coating, Dr. Ivan Jerman for giving me access to use the micro-Raman microscope, Dr. Marjan Bele for making his furnace available to use, Dr. Jože Moškon for his guidance to use the potentiostat, Ms. Ivana Maver, and Ms. Jerneja Pirnat for handling all the administrative issues.

I do really appreciate the work from all the skilled people from the mechanical workshop at Jožef Stefan Institute for fabricating the cell design quickly and precisely.

I would love to thank my parents and my siblings (Mohamed, Noha, and Nahla) for their continuous support. I would love to thank my mother for all the inspiring ideas and her endless care, and support. I must also thank my father who taught me a lot in this life, and I always wished he could witness this moment.

I am grateful to all of my friends who shared the times of happiness and sadness with me. At hard times they were by my side helping and encouraging me.

Finally, I would like to thank the Slovenian Research Agency for funding most of this work with a project number H017002.

Abstract

This thesis mainly concerns with developing a technique using AFM to enable the in-situ measurements of samples under different conditions in liquid. Not only the technique can be applied to corrosion investigation, but can in principle be used in any electrochemical study that requires real-time monitoring of the change of topography during exposure to selected electrochemical conditions.. Unlike conventional electrochemical methods, which give average information about surface properties the use of AFM, allows detection of surface changes on nanoscale.

In order to study the corrosion or electrochemical reactions, an electrochemical cell was designed. The new design enables easy access to the AFM scanner from the top. It also allows using a different sample size of the working electrode as well as the usage of the comparably large volume of liquid or electrolyte. Furthermore, the cell can be used as a fluid flow cell and most importantly, allows locating the same spot in the air and after injecting the liquid into the cell. Two designs having appropriate functionalities were fabricated. Based on a simulation using the finite element approach, which revealed the effect of electrode geometrical arrangement on the electric field distribution inside the cells, one of the two possible cells was selected for further studies. The designed cells were used to study the corrosion action of aluminium alloy AA2024 and copper, with different coatings under different conditions, in NaCl (0.5M) solution as a corrosive environment.

The corrosion of aluminium alloy was studied under different conditions. First, AA2024 was studied in NaCl (0.5M) without applying any electrical potential to find the spontaneous change of the surface. Then different chronoamperometric pulses were applied on a different sample to find how the surface changes. Afterwards, AA2024 was gel-coated by dip coating method such that different experiments were carried out while measuring electrochemical impedance and open circuit potential, chronoamperometric and chronopotentiometric tests were conducted.

Copper samples were tested in analogy to the aforementioned tests of aluminium. Bare copper samples were tested for a spontaneous corrosion and dissolution of grains was detected whereas electrochemical impedance and open circuit potential were measured at the same time of corrosion to understand the relation between the dissolution of the copper and the variation of electrochemical impedance.

A thin film of gel layer was used to coat copper samples by dip coating method. Different experiments were carried out to test the coating resistance to corrosion. The first experiment consisted of a long time immersion of sample without applying any external potential and the electrochemical impedance as well as open circuit potential were measured as a function of time. The next test involved application of a step potential from the cathodic to anodic direction to monitor the dissolution of the film. At last, cyclic voltammetry was carried out to check the possible destructive nature of this technique with respect to tested samples.

In the last set of experiments, a thin film of graphene oxide was applied to copper samples by drop casting and then partly reduced by annealing in argon atmosphere. The reduced graphene oxide coated samples underwent several tests. By analogy to previous

experiments, the first test comprised the immersion of coated sample for a long time in the electrolyte and monitoring the surface properties with time. Then the step potential excitation was carried out followed by extensive chronoamperometric testing in conjunction with AFM measurements.

Keywords: AFM, SEM, EDS, Micro-Raman, Graphene, Sol-Gel, thin-film, Anti-corrosion coating, EIS, cyclic voltammetry, chronoamperometry, chronopotentiometry, FEM-Simulation, Electrochemical cell, AA2024, Copper, Corrosion.

Povzetek

Doktorsko delo se osredotoča na razvoj AFM tehnike, ki omogoča in-situ meritve vzorcev v tekočini pri različnih pogojih. Tehnika je uporabna pri študiju korozije, pa tudi pri raziskovanju drugih elektrokemijskih sistemov, kjer je potrebno spremljanje topografskih sprememb v realnem času po izpostavitvi vzorca izbranim elektrokemijskim pogojem. V našem primeru smo zasledovali nanoskopske fizikalne spremembe na površini izbranih vzorcev po izpostavitvi v korozivnem elektrokemijskem mediju.

Izvedba in-situ AFM meritev v elektrokemijskem okolju zahteva uporabo primerne elektrokemijske celice. V ta namen smo v prvem delu doktorata razvili lastno celico, ki omogoča enostaven dostop AFM skenerja ter uporabo različnih dimenzij vzorca, ki ima praviloma funkcijo delovne elektrode. Izvedba celice omogoča meritve na istem mestu vzorca - tako v zraku kot kasneje ob dodatku elektrolita, ki je lahko v celici v običajnem mirujočem stanju, ali pa ga skozi celico pretakamo z različnimi hitrostmi. Na osnovi teoretičnih simulacij, kjer smo proučevali vpliv geometrične razporeditve elektrod na potek električnih silnic v celici, smo izbrali optimalno geometrijo za naš konkreten dizajn. Optimirane celice smo nato uporabili za študij korozijskih procesov najbolj znane aluminijeve zlitine (AA2024) ter nezaščitenega in površinsko obdelanega bakra. V vseh primerih smo kot korozivni medij uporabili 0.5 M raztopino NaCl. Korozijo AA2024 smo proučevali tako pri pogojih odprtih sponk, kjer reakcije na površini potekajo spontano, kot pri uporabi različnih kronoamperometričnih pulzov, ki korozijske reakcije bodisi pospešijo ali zavrejo. Proučili smo tudi vpliv izbrane površinske zaščite (nanašene s sol-gel metodo) na potek korozije. Informacijo o topoloških spremembah, ki smo jo pridobili z in-situ AFM, smo nadgradili z rezultati impedančnih, kronoamperometričnih in kronopotenciometričnih meritev.

Na podoben način kot AA2024 smo proučevali tudi izbrane bakrove sisteme. Spontane korozijske procese na površini nezaščitenega bakra smo najprej proučevali pri napetosti odprtih sponk, in sicer s kombinacijo in-situ AFM in impedančne metode. Enak pristop smo nato uporabili pri bakru, ki smo ga predhodno prekrili s sol-gel filmom oziroma s filmom na osnovi grafenskega oksida. Slednjega smo po nanosu reducirali s segrevanjem v argonu. Lastnosti obeh zaščitnih prevlek smo dodatno proučili z uporabo stopničastega potencialnega vzbujanja – tako v anodni kot v katodni smeri. Nazadnje smo izvedli še obsežnejše meritve obeh sistemov s ciklično voltametrij, katere namen je bil predvsem identificirati potencialno območje, znotraj katerega so uporabljene prevleke še stabilne.

Ključne besede: AFM, SEM, EDS, mikro-Raman, grafen, sol-ge, tanek film, protikorozijska prevleka, impedančna spektroskopija, ciklična voltametrij, kronoamperometrija, kronopotenciometrija, simulacija z uporabo končnih elementov, elektrokemična celica, AA2024, baker, korozija

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Abbreviations

AFM	...	Atomic force microscope
BSE	...	Backscattered electrons
CA	...	Chronoamperometry
CE	...	Counter electrode
CP	...	Chrono potentiometric
CV	...	Cyclic voltammetry
CVD	...	Chemical vapour deposition
EBSD	...	Electron backscattered diffraction
EDS	...	Electron dispersive spectroscopy
EDX	...	Energy dispersive X-rays spectroscopy
EFM	...	Electric force microscope
EIS	...	Electrochemical impedance spectroscopy
FEM	...	Finite element method
FESEM	...	Field emission scanning electron microscope
GO	...	Graphene oxide
IRRAS	...	Infrared reflection absorption
MFM	...	Magnetic force microscope
MPTMS	...	(3-Mercaptopropyl) trimethoxysilane
OCP	...	The open circuit potential
RE	...	Reference electrode
RGO	...	Reduced graphene oxide
SE	...	Secondary electrons
SECM	...	Scanning electrochemical microscope
SEM	...	Scanning electron microscope
SPM	...	Scanning probe microscopy
STM	...	Scanning tunnelling microscope
TEM	...	Transmission electron microscope
WE	...	Working electrode

Symbols

A_i	...	Instantaneous amplitude value of detected light signal from AFM tip.
A_{sp}	...	Set point of the deflection amplitude.
β	...	Half the tip's cone angle.
β_a	...	Anode symmetry factor.
β_c	...	Cathode symmetry factor.
C	...	The capacitance.
c	...	Localized concentration of the oxidized species (mol/m ³).
c_i	...	Ion's concentration (mol/m ³).
c_o	...	Reference or initial concentration (mol/m ³).
d	...	The tip-sample distance.
D_i	...	Ion's i diffusivity (m ² /s).
ΔG	...	The Gibbs free energy change.
ΔG°	...	The standard Gibbs free energy change.
E_p	...	The p component of electric field in perpendicular to both s and the direction of propagation.
ϵ_o	...	The vacuum permittivity.
E_s	...	The s component of electric field in a direction parallel to the surface and perpendicular to the direction of propagation.
η_{app}	...	Applied overpotential (V).
η_{true}	...	Theoretical overpotential value (V)
F	...	Faraday's constant (96485.3 C mol ⁻¹).
F_{cap}	...	The capillary force.
F_e	...	Electrostatic force.
F_{vdw}	...	van der Waals force.
γ	...	The surface tension of the liquid.
H	...	Hamaker constant.
J	...	Current density (A/m ²).
$\mathbf{J}$	...	Current density vector (A/m ²).
J_o	...	Exchange current density (A. m ⁻²).
J_{oa}	...	Anode exchange current density (A. m ⁻²).
J_{oc}	...	Cathode exchange current density (A. m ⁻²).
κ	...	Conductivity.
L	...	Cell's characteristic length (m).
μ	...	Ion's mobility (mol m ² / (V.s)).
n	...	The number of electrons transferred or exchanged in a redox reaction.

$\mathbf{N}_i$	... Flux (velocity x concentration) (mol/ (m ² .s)).
P	... The vapour pressure.
$\emptyset$	... The angle of the meniscus.
φ_l	... Ionic potential (V).
φ_s	... Initial solid potential (V).
P _o	... The saturated vapour pressure.
R	... The tip radius.
R_g	... The universal gas constant.
r_k	... The kelvin radius.
ρ_l	... Electrolyte resistivity (Ohm.m ²).
R_p	... Polarisation resistance.
S _a	... Roughness average.
S _{ku}	... Kurtosis.
σ_l	... Electrolyte conductivity.
S _q	... Root mean square.
S _{sk}	... Skewness.
T	... The temperature.
θ	... The contact angle, or angle of incidence of light beam.
ϑ	... The phase shift angle between applied potential and measured current.
u	... The equilibrium potential.
u _{app}	... Potential applied to the working electrode (V).
u _{corr}	... Corrosion potential (V).
u ^o	... The standard electrode potential.
$\mathbf{v}$	... Velocity vector (m/s).
V _c	... Contact potential between the tip and sample.
V_{el}	... Electrode potential.
$V_{eq}(anode)$	... Anode's Equilibrium potential.
$V_{eq}(cathode)$	... Cathode's Equilibrium potential.
V _m	... The molecular volume.
V_{Solid}	... Potential of solid electrode.
W	... Wagner ratio.
Z	... The vertical (tip-sample) distance.
Z'	... Real impedance.
Z''	... Imaginary impedance.
z _i	... Ion's valence.

Glossary

- Anode: the electrode where the oxidation takes place at higher electric potential.
- Auxiliary or Counter) Electrode (CE): the electrode that helps pass the current flowing through the cell, such that the current travels between the working and counter electrodes. It is usually an inert electrode (e.g. platinum).
- Cell Potential (E): the resultant of all electrical potentials within an electrochemical cell.
- Electrochemical Cell: the device in which faradaic currents are present because of redox chemical reactions; In the case of spontaneous reaction the cell is galvanic. While it is electrolytic if the reaction is not spontaneous.
- Electrolyte: an ionic substance (typically a salt) that is present in a solution to ensure its conductivity.
- Interface (Junction): a surface forming a common boundary between two adjacent phases. These phases could be solid/liquid or even two liquids of different concentration or composition.
- Oxidation: the process of giving up electrons.
- Overpotential: the potential difference between the experimentally observed electrode potential and the corresponding thermodynamically determined potential.
- Reduction: the process of gaining electrons, and it is the reverse of the oxidation.
- Reference Electrode (RE): the electrode that can maintain a constant potential under changing experimental conditions. It is used as a potential probe in the electrochemical cell.
- Working electrode (WE): the electrode where studies of interest are taking place, in this context it refers to the sample under study.

Chapter 1

Introduction

Corrosion is an irreversible deterioration in the material properties due to the interaction between the metal and its surrounding environment, which could be the atmosphere, aqueous media, soils, acids, bases, inorganic solvent, molten salts, liquid metals, bacteria, and even human body. The deterioration in metals is a loss of the material and can be either dissolution of the material or formation of non-metallic layer (oxide layer). From a thermodynamic perspective, metals and alloys are tending to corrode or form an oxide layer in numerous environments, as the free energy decreases from the metallic to oxidised state. Therefore, metals exist in compounds such as oxides, hydroxides, carbonates, silicates, sulphides, and sulphates, excluding some elements such as gold or platinum which are less active (or chemically inert).

The deterioration in the material's properties can influence its performance, such as the mechanical properties that can be seen in material's ductility and strength [1] or some physical properties (e.g. optical properties, thermal or electrical conductivity, etc.).

From the economical point of view, corrosion is a vital issue as it costs millions of dollars for the companies in order to repair, do maintenance, or even replace the corroded objects. It was reported that corrosion all over the world costs between 1.3 and 1.4 trillion euro annually of nation's gross domestic product (GDP). In addition to its economic impact, it influences many other important issues such as environment pollution and safety; all of those are reflected on the human's health and safety [2].

Since corrosion is an electrochemical phenomenon and initiates at the surface of the material, it is worth to study the surface change in a specified corrosion environment. Extensive studies including many techniques, especially electrochemical and surface science tools, have contributed to better understanding of corrosion mechanisms in different environments.

The problem is that not many experimental techniques have the ability to measure in a liquid environment, where the corrosion action is usually taking place. While the Atomic Force Microscope (AFM) has the ability to do that work in different environments, there are currently no published studies of corrosion in-situ and in real time using the electrochemical AFM. Therefore, atomic force microscope will be used in this thesis, to determine the change in the morphology, upon exposure to corrosive electrolyte under different electrochemical conditions.

1.1 Background

1.1.1 Forms of corrosion

Corrosion of metals has different forms that can be summarised as follows [3].

1.1.1.1 Uniform attack

It occurs with equivalent intensity over the entire exposed area, in such a way that oxidation and reduction take place randomly on the surface.

1.1.1.2 Galvanic corrosion

When two different metals are electrically coupled in an electrolyte, the one that has the lower standard potential (anode) will start to dissolve while the electrode that has a relatively higher (more positive) standard potential (cathode) will be protected. The rate of corrosion is related to the anode-cathode surface area ratio; the smaller anode corrodes more rapidly than the large one due to the increased current density.

Galvanic corrosion can be reduced by:

- 1- Choosing dissimilar metals that are close in galvanic series.
- 2- Using as large as possible anode surface area.
- 3- Insulating dissimilar metals.
- 4- Connecting a third anode metal to the metals (cathodic protection).

1.1.1.3 Crevice corrosion

This type of corrosion occurs when the concentration of ions varies in the electrolyte and the electrolyte has a limited access between two pieces of the same metal (similar as in a crack) where the solution is stationary. The crevice has to be wide to allow the solution to penetrate through it and narrow enough to be stationary.

Crevice corrosion can be prevented by

- 1- Using welded instead of riveted or bolted joints.
- 2- Using non-absorbing gaskets when possible.
- 3- Removing accumulated deposits frequently.
- 4- Designing containment vessels to avoid stagnant areas and ensure complete drainage.

1.1.1.4 Pitting corrosion

This form is a localised form of corrosion that initiates by a hole on the surface. The latter could be due to a difference in the surface composition or a defect (e.g. a scratch or even a slight difference in the concentration on the surface). The hole propagates downward in a direction perpendicular to the surface because of the gravity. Oxidation occurs inside the pit itself whereas the complementary reduction takes place on the surface. This can result in a change in the concentration of the solution, which tends to be higher at the pit's tip.

1.1.1.5 Intergranular corrosion

This form of corrosion occurs between the grains, which is at the grain boundaries. In some metal alloys, it occurs because of heat treatment that results in diffusion of metallic particles to the grain boundaries. Therefore, the grain boundaries become highly susceptible to corrosion.

1.1.1.6 Selective leaching corrosion (dealloying)

This form of corrosion is found in alloys. It occurs when one metal of the constituents is preferentially dissolved in the solution. The mechanical properties are degraded. An example is a dezincification in brass metals, in which zinc is dissolved from a copper-zinc alloy.

1.1.1.7 Erosion-corrosion

It is a combination of two processes: a chemical attack and a mechanical abrasion, which is a consequence of fluid flow. All metal alloys are vulnerable to erosion-corrosion. It is more harmful in the case when the alloy is passivated by a protective film, as the film will be eroded because of the flow of the fluid. Soft metals such as copper and lead are especially sensitive to that form of corrosion, which manifests itself in the form of grooves and waves in the direction of the flow.

The flow velocity of the solution affects the erosion - the higher the velocity, the more pronounced the erosion. Another factor that can increase the erosion has bubbles or suspended solid particles. The design of the flow path of the solution, in that case, is important to avoid the turbulence. Turbine blades, valves, and pumps are more prone to that form of corrosion.

1.1.1.8 Stress corrosion

Stress corrosion occurs under a combined effect of mechanical stress and chemical attack. Some inert materials are susceptible to this kind of corrosion. It starts with small cracks, which continue propagating in a direction perpendicular to the applied stress. Most alloys are subject to stress corrosion under certain environment, even at a moderate level of stress. The stress that leads to stress corrosion does not have to be an external stress; it could, for example, be due to an abrupt change in the temperature that results in uneven contraction, or in the formation of (many) phase alloys such that each phase has a different expansion coefficient. Internal stress can arise because of gaseous and solid corrosion products entrapped inside the material.

A famous example of stress corrosion is the hydrogen embrittlement, in which atomic hydrogen diffuses into the crystal lattice of a material. Even if the concentration of hydrogen is as low as several parts per millions, this phenomenon can lead to a crack in the material. Although in most cases hydrogen-induced cracking is trans-granular, some systems may exhibit intergranular cracks. In order to occur, some source of hydrogen must be present such as pickling of steel in hydrochloric or sulphuric acid to remove the oxide layer, electroplating, and high-temperature treatment in the presence of hydrogen or water vapour (e.g. welding or cutting). In addition, hydrogen embrittlement requires a presence-poisoning environment such as sulphur, arsenic compounds, or hydrogen sulphide (sulphur) which can be found in petroleum fluids, natural gas, oil well, and geothermal fluids.

1.1.2 Corrosion prevention

Enhancing the corrosion resistance is a very demanding field of study. Many techniques and approaches are used to increase the corrosion resistance. Depending on cost, applicability, and durability, the most suitable material treatment technique is chosen for effective improvement of its corrosion resistance. The most used approaches are the material selection, environmental adaptation, design, application of coatings, and cathodic or anodic protection, all of which are explained in more detail in continuation [3].

In fact, cost plays an important role when it comes to choosing the way of material protection against corrosion. Therefore, most often material selection is not an optimum solution for engineers. Alternatively, another alloy with somewhat less favourable characteristics is chosen.

1.1.2.1 Environment adaptation

The environment can have an important influence on the corrosion. Examples are decreasing the temperature of the fluid or lowering its velocity - depending on the corrosion form. Changing the concentration of the solution may also influence the rate of corrosion. For instance, by increasing or decreasing the concentration, the rate of corrosion can accordingly change, or the surface can be passivated.

1.1.2.2 Corrosion inhibitor

The inhibitor is a material which, when added to the environment, decreases the corrosion activity. The choice of an inhibitor material depends on the environment and the metal, indeed. Namely, both factors determine the corrosion mechanism and thus the choice of protection. For instance, some inhibitors may react with the dissolved active species; accordingly, the electrolyte becomes less active, which virtually stops the reaction. In another case, either the molecules of the inhibitor form a thin coating layer on the surface and protect it without interacting with the electrolyte, or it gets involved in the oxidation or reduction reaction on the surface thus eliminating them.

1.1.2.3 Material design

By design, we refer either to the engineering of the alloy itself in order to fit a specific environment under certain conditions (e.g. mechanical stress), or to designing the workpiece that enables easy access for cleaning, evacuation, and gas exclusion, if possible. In addition to considering the working conditions during the design process, in order to minimise the exposure to corrosion conditions. For example, in the designing of flow tubes the design has to consider the speed of the flow, therefore the erosion-corrosion can be minimised.

1.1.2.4 Anticorrosion coating

The coating is a physical layer that isolates the metal from the surrounding environment. In some cases, it is used decoratively, in other cases (and most often), it is functional and protective. A coating material can be a metal or non-metal (ceramic, polymer, composite material etc.). The criteria for the selection of coating are the quality of adhesion to the metal, reactivity, compatibility with the environment, and resistance to mechanical damage.

1.1.2.5 Cathodic protection

All of the eight forms of corrosion can be protected using this technique, which in some cases, is capable of completely stopping the corrosion. For example, cathodic protection is so far the optimum protection method in the field of infrastructure, reinforced concrete [4], and pipelines [5]. An external power supply is used to provide the metal with electrons thus making it more “cathodic”. In other words, this means that the spontaneous corrosion reaction in Eq.(1.1) is reversed to become a reduction reaction.



A sacrificial anode is often used. For example, an anode made of magnesium or zinc (both from the bottom of the galvanic series) is electrically connected to the metal that needs to be protected without using any external electrical power source.

Another way of implementing the cathodic protection is by connecting the negative terminal of a power supply to the metal that needs to be protected, whereas the positive terminal is connected to an inert anode (e.g. graphite). Galvanizing is a third way of using cathodic protection; in that case, steel is covered by a layer of zinc which works as a cathode to protect the steel from any corrosion attack.

1.1.2.6 Anodic protection

Another way to protect metals is by using the anodic protection, which is different in principle from cathodic protection. Anodic protection is achieved by applying an electrical current to the metal. The electrical current results in the formation of protective oxide layer on the surface, which passivates the surface. Anodic protection depends on the metal and the environment in which the oxidation takes place, which makes it limited to some metals such as aluminium [3].

1.1.3 Corrosion of aluminium alloy

Due to its abundance in the earth's crust [6] and convenient physical and chemical properties, aluminium (and its alloys) are used in a wide range of applications. In nature, aluminium is usually found in a mixture with other elements such as iron, silicon, and oxygen. Due to its highly negative standard electrode potential (-1600mV with respect to hydrogen electrode), aluminium is very unstable in moisture. Pure aluminium possesses a high corrosion resistance. Namely, owing to its high activity, a layer of protective oxide (native oxide) forms rapidly in different environments [7]. Corrosion of aluminium thus initiates in defects of the native oxide layer.

Aluminium strength can be enhanced by alloying it with other elements like copper (Cu), magnesium (Mg), manganese (Mn), silicon (Si), chromium (Cr), iron (Fe), and zinc (Zn). For the reason that aluminium has a low density, high thermal and electrical conductivity, as well as due to its strength, stiffness, high ductility, and non-toxicity, engineers are attracted to choose aluminium alloys in a variety of applications and products. Owing to the low density and high strength, aluminium is used extensively in aerospace and automotive industries - in order to reduce the weight and decrease the fuel consumption. Despite the fact that aluminium alloys have superior mechanical properties, they are more prone to corrosion.

Inclusions of the elements in alloys or their compounds constitute a second, so-called intermetallic phase, which is frequently considered a weak point of the aluminium alloy. Namely, this second phase is susceptible to electrochemical reaction leading to a micro-galvanic coupling, where intermetallic particles can behave either as anodic or cathodic sites with respect to the surrounding matrix [8,9]. Upon exposure to a corrosive medium, the anodic intermetallic particles are galvanically coupled to the surroundings and start to dissolve right away resulting in a pit [10–12]. The matrix itself, in turn, starts to dissolve around the particle making a trench in the case of the cathodic intermetallic particle [13].

Throughout the thesis, the primary focus is on the AA2024 alloy- a variant that is important for aerospace applications and still a subject of vigorous research. Copper is a

principle alloy element of AA2024, so both the corrosion mechanism and its prevention are of highest interest. Different phases have been identified in AA2024, such as S-Al₂CuMg (which is predominant), Θ -Al-Cu-Fe-Mn and (Al, Cu)_x(FeMn)_ySi. Depending on the preparation methods and the thermo-mechanical treatment, the alloying elements are distributed in the matrix that could lead to pit corrosion [17] if the second phase is distributed eventually over the surface or intergranular corrosion [15,16] in the case of diffusion of the second phase towards the grain boundaries. The latter form is more dangerous as it leads to failure in the mechanical properties because of cracking.

Although a myriad of works has been carried out in order to understand the corrosion mechanism of AA2024, the latter remains more or less unclear or at least ambiguous. The motivation of the present thesis is to study the complex dynamics of changes occurring in the AA2024 under corrosion environment. Therefore, the corrosion mechanism including the formation or failure of the passive film. The study of intermetallic particles in AA2024 is not the purpose of this thesis. However, the focus of this work is the change in the matrix itself.

1.1.4 Corrosion of copper

Copper is a widely used metal because of its special physical properties such as the very high thermal and electrical conductivities. Copper has a high corrosion resistance in water if oxygen is absent. Due to its higher corrosion resistance in comparison to other metals and alloys, copper is considered a comparatively noble metal. Furthermore, copper is used in many fields, owing to the aforementioned reasons. The most famous application of copper is in the field of electronics and communication, where it is used as a clad on epoxy sheets for printed circuit boards, as well as planar and microstrip antennas.

Like most metals, copper is commonly found in a polycrystalline form. When the polycrystalline copper is exposed to one of the aggressive environments (e.g. acids, salts, or even water that has an excess of oxygen) it starts to corrode. Extensive researches have been devoted to the development of inhibitors for copper, depending on the application and the environment where it is used [17–20].

Many researches have been carried out to study the effect of the crystallographic orientation of the metal on the corrosion properties [21–26]. For instance, Martinez-Lombardia found that the thickness of the naturally occurring oxide on the surface of copper is grain dependent [23]. Moreover, he could conclude that the anodic dissolution of each grain depends on its neighbouring one, and the faster grains to dissolve in 10 mM HCl are those having the orientation $\langle 111 \rangle // \text{ND}$, as well as grains between $\langle 111 \rangle // \text{ND}$ and $\langle 110 \rangle // \text{ND}$, whereas more inert grains were oriented closer to $\langle 001 \rangle // \text{ND}$.

1.1.5 Sol-gel anti-corrosion coatings

Chromate and chromium compounds are usually used as anticorrosion coatings for a wide range of metals and alloys. The high corrosion resistance of chromate-based chemicals is due to including the hexavalent chromium ions, which has a good corrosion resistance and improves the adhesion to the surfaces. Nevertheless, those chromium-based coatings are restricted because of their toxicity, in addition to their impact on human health and environments. Sol-gel coatings are environmentally friendly coatings and can replace the commonly used chromate coatings.

The sol-gel method is a chemical procedure that was originally used to synthesise inorganic materials such as ceramics and glass [27]. In this method, molecular precursors

in the liquid are condensed to form an alkoxide network [28–30]. There are some common terminologies associated with the sol-gel method, such as:

A colloid is a suspension of small dispersed particles (1-100 nm), in which the dominated forces are the short-range forces, while the gravitational force is negligible.

Sol is a colloid of solid particles in a liquid, which can be used to synthesise polymers or the particles that can be used to produce ceramics.

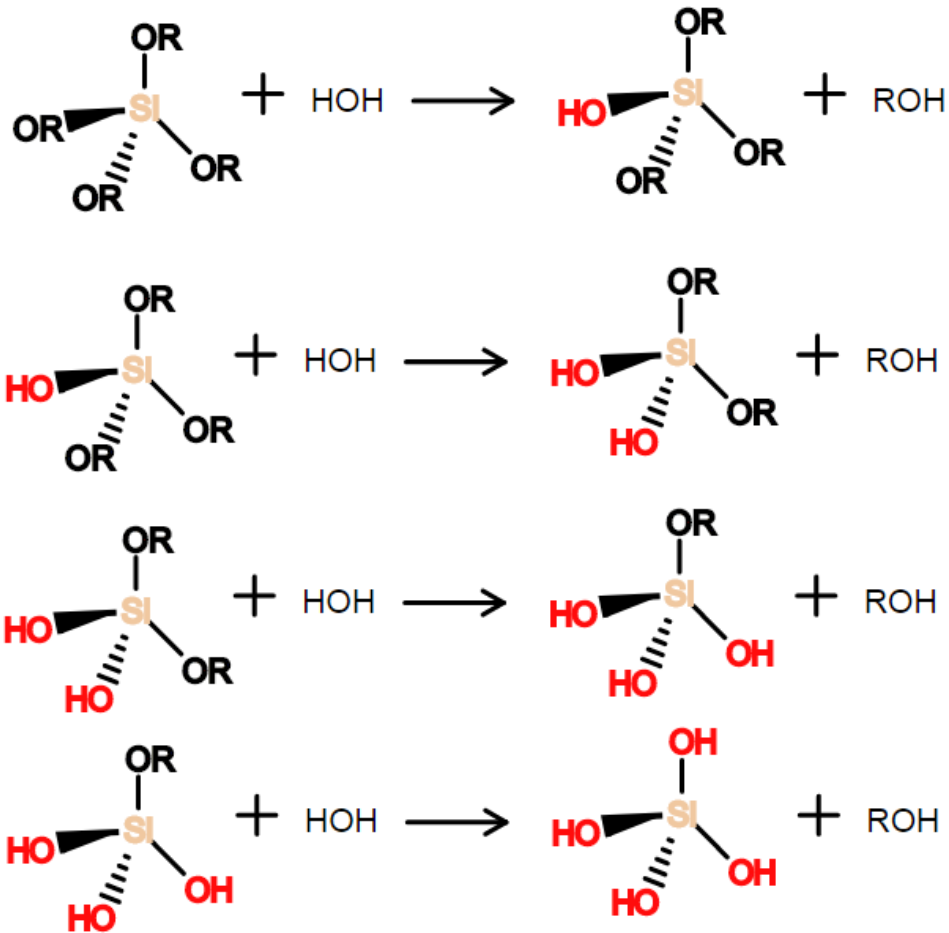
The precursor is the initial compound used to prepare sols, and is composed of a metal (in the case of inorganic sol) or a metal connected to organic chains (in the case of organic-inorganic hybrid sol).

The sol-gel can be either an inorganic or organic-inorganic hybrid. In the former case, the sol is used to form continuous inorganic networks, and the metal atoms are bridged through either oxide or hydroxide groups, which results in a generation of metal-oxide (M-O-M) or metal hydroxide (M-OH-M) polymers in liquid phase [28]. In the latter case, the precursor is usually a metal alkoxide $M(OR)_n$ and the sol is formed by dissolving it in an organic solvent. M represents the metal used to form the network (e.g. Si, Ti, Al, Fe ... etc.), and R is an alkyl group (C_xH_{2x+1}). The organic-inorganic hybrid method is preferred and commonly used because it is combining the advantages of inorganic compounds which represents the stiff backbone of the chain, and the polymeric behaviour of the organic compounds [31].

Commonly, the sol-gel occurs in four stages: (a) hydrolysis, (b) condensation and polymerization of monomers to form chains and particles, (c) growth of the particles, (d) agglomeration of the polymer structures followed by the formation of networks that extend throughout the liquid medium resulting in thickening, which forms a gel. In the hydrolysis, the alkoxide group (-OR) is replaced by a hydroxyl group (-OH) as given in Figure 1.1 – A. Hydrolysis and condensation occur at the same time, and produce low-molecular-weight products like water and alcohol as shown in Figure 1.1.

After drying the produced molecules and further condensation takes place, the network shrinks. However, the network is shrinking upon drying, the molecules built of the metal or silicon continue to grow, which is known as polymerization. These processes are dependent on the reaction conditions [31] such as temperature, pH, molar ratios of reactants, solvent composition, etc. References [27,28,32–34] have more details about the properties and processing of sol-gel coatings.

A)



B)

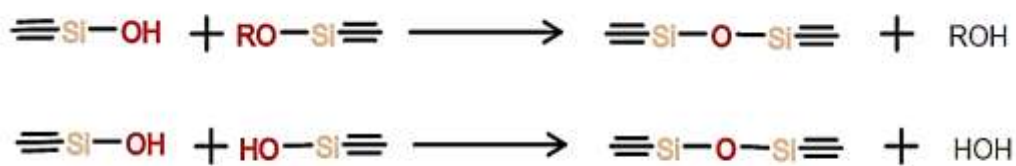


Figure 1.1: Hydrolysis (A) and condensation (B) involved in making silica sol-gel materials. Adapted with permission from [31].

Inorganic coatings have been studied, including the metal oxides prepared by sol-gel, such as alumina (Al_2O_3). The problem of inorganic coatings prepared by sol-gel is that they are porous and require to be annealed at relatively high temperatures. The high annealing temperature may result in a cracking depending on the substrate material and its thermal expansion coefficient. If there is a mismatch between the thermal expansion of the substrate and the coating, the coating will crack after annealing. In addition, the high-temperature

treatment limits the applicability of sol-gel to temperature-sensitive substrates. Alternatively, organic-inorganic hybrid sol-gel coatings are used.

The organic-inorganic sol-gel method gathers the advantages of using both the inorganic and organic compounds. Together, organic and inorganic components form a uniform thick coating [35,36]. The inorganic components improve the scratch resistance, the adhesion to the substrates and the durability, while the organic components enhance the flexibility, density. The advantages of the organic-inorganic hybrid method are:

- It is a low-temperature process, usually close to room temperature. Therefore, thermal evaporation and degradation of the species are lowered.
- Because the preparation of the sol-gel coatings is based on nontoxic compounds, they are prepared near the room temperature and do not consume lots of energy, as well as do not produce waste; it is environmentally friendly and a green method.
- It is prepared in the liquid phase, which makes it applicable to a wide spectrum of surfaces, such that it can be cast on any surface without the need of costly processes such as machining.

The sol-gel coating can be applied to substrates using different techniques such as the two most commonly used ones: dip coating and spin coating. Electrodepositing [37–39] and spraying [40,41] have been used recently. The sol-gel coatings have been widely used in different applications such as drug delivery [42–44], optical fibres and sensors [45,46], chemical and biochemical sensors [47,48], decorative and anti-corrosion coatings [49], anti-reflection coatings [50].

The sol-gel coatings were used as they are environmentally friendly for corrosion mitigation. Aside from the good adhesion to metallic substrates, sol-gel hybrid coatings have a low permeability to oxygen and water vapour and they are good insulators which makes them good for anti-corrosion [51–53].

In this thesis, organic-inorganic hybrid sol-gel coating is used for corrosion protection of copper and aluminium. The coating was applied to the substrates using the dip coating technique, then the films were characterised in the air before starting the in-situ AFM experiments. Afterwards, the film was tested in NaCl (0.5M) under different electrochemical conditions to find their resistance against breakdown under the applied conditions.

1.1.6 Graphene anti-corrosion coatings

Graphene is one of the carbon allotropes. It is a two-dimensional sheet of carbon atoms arranged in a hexagonal form. Owing to its two-dimensional atomically thin structure, graphene possesses an extraordinary combination of properties. Since it retains high electron mobility, it makes it a potential material to be used in transistor electronics as it has a superior mobility of $2.5 \times 10^5 \text{ cm}^2/\text{V.s}$ in comparison with $1500 \text{ cm}^2/\text{V.s}$ of silicon, and $8500 \text{ cm}^2/\text{V.s}$ of gallium arsenide (GaAs) [54]. In contrast with metals, graphene's electrical conductivity is not significantly influenced by the temperature change. So far, graphene is considered the strongest material, as it has a high mechanical strength of 1100 GPa which is 100 times larger than a sheet of steel of the same thickness [55]. It does not only possess the highest strength, it is also flexible. Moreover, it has a high thermal conductivity of $5000 \text{ W m}^{-1} \text{ K}^{-1}$, which is five times greater than that of a diamond [56]. Owing to its tiny thickness, graphene is optically transparent, as it has an opacity of 2.3% in the visible spectrum [57]. Furthermore, graphene has many of the distinguishable properties; such as chemical resistance [58], it is environmental friendly [59], and above all, it has a high specific surface area of $2630 \text{ m}^2/\text{g}$ [60].

The exceptional properties of graphene make it a potential candidate for a wide range of applications such as: electronics, micro and nano-mechanical systems (MEMS and NEMS), optoelectronics, batteries, solar cells, filters, actuators, sensors, and finally protective coatings. However, our interest in this work is to use graphene as anti-corrosion coating for metals.

Graphene can be synthesised in different ways depending on the anticipated size, purity, chemical and physical properties [61]. Graphene was first prepared in the form of flakes by mechanical exfoliation of graphite using scotch tape [62], and then different methods have been used to synthesise graphene. The most common methods for synthesising graphene are chemical vapour deposition (CVD) [63], chemical synthesis [64], chemical exfoliation. Some other methods were developed such as unzipping different carbon allotropes such as C60 [65], and carbon nanotubes [66–68]. In addition to other physical methods such as epitaxial growth [69–72], arc discharge [73,74], microwave plasma enhanced chemical vapour deposition [75], plasma exfoliation. Each method has its advantages and disadvantages. Mechanical exfoliation is capable of producing large area graphene flakes from a few layers down to the monolayer, its drawback is that it cannot reproduce the same flakes with the same structure, which influences the physical properties. For example, CVD is preferable in electronics application because it produces uniform layer(s) of a large area [76–80], and it is easy to transfer the graphene to another substrate by etching the initial substrate on which graphene was synthesised. However, preparation of large area pristine graphene layer(s) is best to be carried out by mechanical exfoliation.

Chemical exfoliation is a two-step process. First, chemicals are used to reduce the van der Waal forces between the graphite layers, resulting in an intercalated compound, and then the product is separated into single and multilayers by rapid heating or sonication. Brodie established the method for production of graphene oxide (GO) in 1859 [81], by adding potassium chlorate to a colloidal of graphite in fuming nitric acid. Then, Staudenmaier [82] modified the method by mixing concentric sulphuric acid and fuming nitric acid and gradually adding chlorate. Hummer developed the method of graphite chemical exfoliation by using KMnO_4 and NaNO_3 in concentrated H_2SO_4 [83]. The advantages of the Hummer method over the previous two methods are: first the reaction rate is faster as it takes a few hours to exfoliate/oxidise the graphite in comparison to four days for the other two methods, second the replacement of KClO_3 with KMnO_4 reduces the danger of the release of the explosive ClO_2 , and third the replacement of HNO_3 with KMnO_4 reduces the formation of a fog. The disadvantages of the Hummer method are: first the emission of toxic gases such as N_2O_4 , and NO_2 , second the residue of Na^+ , and NO_3^- are hard to be removed from the waste water after purification. Therefore, the Hummer method was improved by Tour and co-workers [84], by removing NaNO_3 from the reaction and increasing KMnO_4 and performing the reaction in a mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ with a volume ratio 9:1. This method is known as improved Hummer method, it has the advantage of reducing the emission of toxic gases. Like mechanical exfoliation method, chemical exfoliation also produces non-uniform and dispersed layers of graphene.

Graphene oxide is useful as it is hydrophilic, therefore the flakes in the solution do not agglomerate. In order to have a graphene-like product from GO, a reduction of GO is necessary. There are several ways to reduce GO that can be divided into chemical and thermal routes. Many chemicals have been used to reduce GO, such as sodium borohydride (NaBH_4) [85], hydrazine [86], and ascorbic acid [87]. A good and efficient chemical way is to use sodium borohydride (NaBH_4), but it reacts slowly in water. Hydrazine is mostly used for chemical reduction of GO, as it is the best to produce thin and fine reduced graphene oxide (RGO). Thermal reduction of GO uses heat to remove the oxide functional groups attached to GO [88,89]. Reduction at low temperature (150–300) °C detaches the water and oxides attached to GO, however, it is an incomplete reduction process.

Nevertheless, high-temperature reduction of GO yields a good reduction but introduces many defects in graphene. A solvothermal method was suggested by Dubin et al. [90], they could reduce GO in N-methyl-2- Pyrrolidinone (NMP) molecules at 200 °C. Plasma reduction of GO using methane/argon plasma was reported by Baraket et al. [91], and using hydrogen /argon by Lee and co-workers [92].

The excellent properties of GO and RGO make them a potential candidate for many applications, such as field effect transistor [58], sensors [93,94], batteries [95,96], anti-corrosion coatings [97], ion filters [98], and many other applications. Graphene can be defined as a nano-shield that can block the penetration of gas molecules. Scott et al. [99] used a monolayer of graphene to separate two regions after applying gas under pressure, and they found that graphene is the thinnest impermeable membrane. The impermeability of graphene [58] makes it an excellent candidate for many applications, such as anti-oxidation barriers, and anti-corrosion coating. Moreover, the graphene membrane can be used to selectively filter ions [98]. Graphene is used as an anti-oxidation and anti-corrosion barrier, as it isolates the surface underneath from any reaction. In other words, graphene passivates the surface owing to its impermeability. On the other side, the applied graphene barrier should be chemically inert to the environment in which the surface will be exposed, such as oxidants in case of using it as an anti-oxidant and corrosive environments if it will be used for anti-corrosion protection. Graphene was tested as an anti-oxidant of copper [100], graphene could protect the copper from oxidation by heating the sample up to 200 °C in air for 4 hours, as well as a good protection against hydrogen peroxide. Raman and x-ray photoelectron spectroscopy showed that the naked copper underwent a significant change while graphene preserved its initial structure even after the exposure to the oxidation conditions. In addition to the outstanding properties of graphene, it is also a biocompatible and environment-friendly material, which makes it a good material to be used with the biomedical stuff implanted in human or animal bodies [101–103].

Again, the impermeability of graphene makes it a good protective coating for different metals. For instance, Prasai et al. [97] used electrochemical methods to study the effectiveness of graphene as an anticorrosion coating for copper and compared the measurements of the bare copper in aerated Na₂SO₄, they found that graphene has a high corrosion resistance as it could keep its initial state, thus they suggested that the corrosion occurs on the edges of graphene flakes. Chen et al. showed that graphene is able to protect metals from oxidation [100], they could confirm that by using XPS, Raman, and SEM measurements after exposing the protected metal to oxidation conditions.

In this thesis, we used the chemical exfoliation method because of its easiness to produce graphene flakes and to apply them to any substrate in the liquid phase. Graphene dispersed in a liquid is more practical to apply to any surface at room temperature since it does not require high temperatures like CVD. Our motivation is to study the change in the topography of the graphene-coated metal(s), under some extreme corrosion conditions, tying the change of the topography to electrochemical characterization; we can get an insight into the defects that can lead to the breakdown in the coating.

1.1.7 Experimental techniques for studying localised corrosion

Most often, localised corrosion in alloys is initiated because of either intermetallic particles or non-metallic inclusions. The size range of these inclusions is from a few nanometers to a few microns. In pure crystalline metals, the size depends on the crystal orientation, while in polycrystalline alloys it depends on the crystallographic orientation, crystal size, as well as on the neighbouring crystal.

Many in-situ and ex-situ techniques have been used to monitor the evolution of the corrosion process. For instance, localised corrosion of metal was studied using transmission electron microscope (TEM) [104–106]. High-resolution transmission electron microscope (HR-TEM) is capable of imaging on the atomic scale. In combination with EDS, it can be used to find the elemental composition of the metal and map it. Atom probe tomography (APT) is a powerful tool for three-dimensional elemental mapping of the material with a very high spatial resolution. Electron Energy Loss Spectroscopy (EELS) can be used to find the bonding type between the corrosion species [107].

Stein demonstrated the effective use of ellipsometry in studying the formation of a passive film on lead metal when immersed in sulphuric acid (H_2SO_4) [108], and in passivation of copper in a sodium heptanoate solution (NaC_7) [109]. The advantage of this technique is that it can be used for in situ measurements, without introducing any mechanical damage. A drawback of this technique, however, is that it cannot be properly used for specimens sensitive to applied wavelength. A combination of confocal laser microscope and scanning electron microscope was used to study the corrosion in AA2024 [110].

Many of surface science tools have already been used to study the formation of oxide or passive layer on the Al alloy surface. As most of them work under vacuum, ex-situ measurements have to be applied. Examples are studies using X-ray photoelectron spectroscopy (XPS) [19], secondary ion mass spectroscopy (SIMS) [111], Infrared reflection absorption (IRRAS) [112].

Scanning probe microscopes are powerful tools for studying the corrosion under different conditions and environments. Moreover, they can be used to follow the change in topography on different ranges from micro- to sub-nanometre scale in the gaseous or liquid environment.

Scanning probe microscope is a large family of techniques, among which the scanning tunnelling microscopy (STM) and the atomic force microscopy (AFM) are most widely used and recognised.

The advantage of STM over AFM is that it can get higher resolution (atomic resolution) for a conductive surface. Nevertheless, AFM is superior to follow the changes of a surface under all the extreme conditions, without worries about any faradaic current. In contrast with STM, AFM can be used to study the change in an oxidised surface regardless of how thick the oxide layer, or even studying a soft material, in addition, it has the ability to follow dynamics of insulators. One drawback of the different SPM techniques is the limitation of the scanning area to be within $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$, in addition to its high sensitivity to the change in the surface morphology and chemistry, which can be considered as one advantage from another point of view.

In the field of corrosion, AFM and STM have been widely used [113–121] owing to their ability to resolve the change in topography under corrosion conditions. In order to carry out one in-situ measurement that requires having a fluid cell, a working electrode (the sample under study), a counter electrode, bi-potentiostat, and optionally a reference electrode, in that case alternatively, they are called electrochemical atomic force microscope (EC-AFM), or electrochemical scanning tunnelling microscopy (EC-STM). The fluid cell choice has always been very dependent on the experiment. Nonetheless, the criteria for choosing the cell is to have a large capacity for the liquid in order to avoid the evaporation of electrolyte.

Moreover, the electrochemical measurements can change due to the local change in the pH value, as well as increasing the solvation force that influences the topographic measurements (tip-sample interaction), a robust mechanical setup that can be stable not introducing any mechanical noise or vibrations that can affect the topographical, and electrochemical measurements, the possibility of using inlet and outlet ports for the fluid flow.

Cells of different capacities have been used for in-situ measurements, most of them are the commercial ones with the capacity of 0.1 ml [14,114,122], in some other studies, the capacity was even lower 50 μ l [18].

1.2 Thesis Motivation and Objectives

Corrosion is a complicated mechanism that is taking place in nature, where metals are exposed to an environment that could be humid air, liquids, some corrosive gases, and even bacteria. Watching and analysing the occurrence of the corrosion while it is taking place is not an easy task to be done. In this study, it is claimed that the dissolution of the metal submerged in a liquid can be revealed by measuring the change in the surface topography, and electrochemical parameters simultaneously. Correlating the physical change in corroded sample and the corresponding changes in the electrochemical properties is the main objective of this thesis, detailed analytical interpretation of electrochemical measurements is beyond the scope of the thesis.

With the intention of carrying out in-situ measurements, first a cell has to be designed to be compatible with the used microscope. Once the cell is designed and fabricated, EC-AFM will be used to do all the in-situ measurements in combination with electrochemical methods, so that the corrosion mechanism can be elucidated.

In this thesis, the localised corrosion of copper and aluminium is studied mainly using in-situ atomic force microscope (AFM). The goal is to follow the evolution of the corrosion by scanning the metal/electrolyte interface while it is immersed in a corrosive medium using AFM. This evolution will not only be observed as a function of time but also in dependence of the application of different electrochemical conditions. Combining the results with those obtained using conventional electrochemical techniques will allow reliable and accurate determination of different parameters (e.g. corrosion rate, open circuit potential, the formation of oxides, etc.). However, the main concern is to study the applicability of using different electrochemical methods to be combined with AFM. Scanning electron microscope (SEM) and energy dispersive X-rays spectroscopy (EDS) will be carried out ex-situ to find the change in the surface topography, as well as the elemental composition of the particles on the surface that can influence the corrosion behaviour, respectively. Subsequently, the effect of a protective coating using reduced graphene oxide will be presented. The graphene will be deposited on the metal's surface; afterwards, the coating will be characterised using SEM, and micro-Raman to find the coating quality. In-situ AFM will be carried out on the coated metals, to find their response to the environment and the weakness of such coating films.

1.3 Thesis Outline

In this thesis, Chapter 1 is an introduction to the thesis and it contains a brief overview of the different corrosion schemes, and techniques used to study the corrosion. It also sheds some light on the coatings of metals used in this work. Chapter 2 describes the techniques used in this thesis and the material used, such as the electrolyte, as well as the preparation of samples, and how the coatings are prepared. Chapter 3 shows the two different designs of electrochemical cells that were used in AFM measurements and it describes the physics used in the simulation and the selection of material. It also presents the test results of the cells before starting the in-situ experiments. Chapter 4 is concerned with the study of AA2024 corrosion using in-situ AFM and in both cases bare metal and gel-coated using different electrochemical methods. Chapter 5 is dedicated to the in-situ AFM study of copper and its anti-corrosion coatings. It first starts with studying the spontaneous corrosion of copper while measuring the electrochemical impedance, then continues with a study of corrosion under different electrochemical treatments of the covered samples. Finally, Chapter 6 shows the conclusions of the thesis work.

Chapter 2

Experimental Techniques and Materials

In this chapter, the experimental techniques used in this work will be briefly presented as well as the preparation of the samples.

2.1 Techniques

In this Section, the experimental techniques used to investigate the samples using different approaches will be presented. First, we will introduce the atomic force microscope (AFM) by giving a brief introduction about its working principle, and the setup of the experiment, which will be followed by the extraction of the different statistical parameters from the images. Second, scanning electron microscope (SEM) and electron dispersive X-Ray or electron diffraction spectroscopy (EDX/EDS) for microanalysis will be briefly described. Then, the micro-Raman will be presented as well as infrared spectroscopy and finally, the electrochemical methods used.

2.1.1 AFM

Atomic Force Microscope (AFM) is a member of Scanning Probe Microscopy (SPM) family. The scanning probe microscope is considered as one of the foremost advances in material science [123]. The large family of scanning probe microscopy has a common working principle. The principle of SPM is that the sample of interest is scanned laterally by using a probe while keeping the interaction parameter controlled between the sample surface and the probe using a feedback control and measuring the third dimension of length depending on that interaction. The SPM was developed in 1982, after the invention of the scanning tunnelling microscope (STM) by Gerd Binnig and Heinrich Rohrer [124,125].

The first AFM was working by controlling the tip-sample interaction by the virtue of maintaining the distance between the tip and sample constant, which is nowadays known as the contact mode. In contrast with the STM that is only capable of measuring conducting surfaces, AFM has the ability to scan any surface even though it is an insulator. AFM works in such a way that a sharp tip fixed at the end of a cantilever scans a sample. Because of the interaction between the atoms at the tip's apex and the atoms at the surface, the cantilever starts to deflect. In general, SPM can be used in different applications not only imaging, but in spectroscopy, and nano- or atomic-manipulation as well. According to the interaction between the tip and the sample, many techniques have been developed using the atomic force microscope. For example, by using a magnetic tip to study the magnetic structure of a surface, the deflection of the tip depends on the magnetic force and

in this case, it is called the magnetic force microscope (MFM). Analogously, if an electrically conducting tip is used to study the electrical properties of a surface, it is called the electric force microscope (EFM).

STM uses a sharp tip made of metal to scan a conducting surface at a distance less than 1 nm, by virtue of the tunnelling current. The distance between the tip and the surface is controlled by a feedback loop, which in turns measures the tunnelling current between the surface and the tip at a constant applied voltage. The tunnelling current flows from the tip's apex to the atoms on the surface of the sample. Since the tunnelling current is a quantum mechanical effect, it has two important properties: the first is that it can flow between two electrodes, despite a gap of insulator or vacuum, the second is that it decays with the increased distance exponentially. STM was used in this work to study the conductivity of graphene flakes prepared using Buckminsterfullerene (C_{60}) more details can be found in Ref [126].

On the one hand, the advantage of STM is that it can scan down to atomic resolution; on the other hand, STM is incapable of scanning surfaces of poor electrical conductivity such as an insulator, and biological samples. That was the motivation behind the invention of the atomic force microscope (AFM) in 1986 by Gerd Binnig, Calvin Quate, and Christoph Gerber [127].

The invention of the first AFM was based on measuring the static deflection of the probe, which is called the contact mode AFM. A year later Martin and co-authors presented a new technique for measuring the force between a tip and a material as a function of tip-sample distance, by making the tip oscillate at a close proximity of the material's surface [128]. At that time, the tip used was a bent tungsten wire, and the deflection detector was an interferometer. They were measuring the variation of the force when the distance is changing; they found out that the amplitude of the oscillation changes with the tip-surface distance, and that the change is related to the force gradient between the surface and the tip. They suggested using the amplitude in the feedback for imaging the surface. In 1987 in the IBM Thomas J. Watson Research Centre, an optical approach was developed to measure the lever deflection using a position sensitive detector by G. Meyer and N. Amer [129]. The AFM became more popular after they started making a micro-machined cantilevers made of SiO_2 or Si_3N_4 using different micro-fabrication processes [130]. Hansma et al. succeeded to image DNA in liquid using tapping mode (described in Section 2.1.1.2) in 1994 [131].

In this work, our concern is only using AFM owing to its ability to scan surface in different environments. Nevertheless, STM is capable of working in liquid but in that case, a faradic current is superimposed on the tunnelling current that limits its ability to work in some electrochemical tests.

2.1.1.1 Forces involved in AFM operation

The main interest of AFM are the forces of interaction between the tip and the sample; therefore, in this section, the forces involved in AFM measurements will be shortly discussed. The forces involved in AFM measurement have a different nature, some of them are attractive, while others are repulsive, and they have a different interaction range.

The main forces that exist in the air without applying any external field are the short-range, van der Waals, adhesion, and capillary forces. In a liquid, additional forces are present because of the field created at the solid/liquid interface that makes the rise of the electric double layer. The total force between tip and sample can be given by the Lennard-Jones [132] potential curve shown in Figure 2.1.

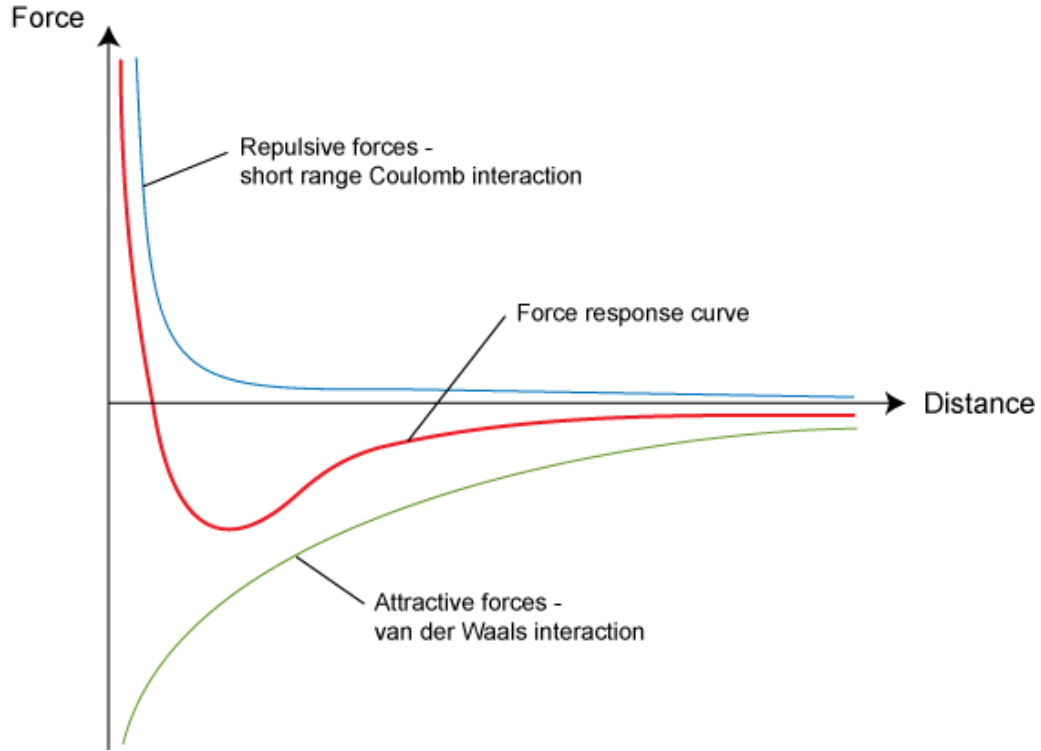


Figure 2.1: Lennard-Jones potential curve [132].

2.1.1.1.1 van der Waals forces

The origin of van der Waals forces is the electric dipole interaction between atoms or molecules. The dipoles could be either permanent or induced dipoles. The electrical dipole can be induced by another permanent dipole or dipoles that are created because of thermal fluctuation. The forces arise because of the dispersion forces that are formed owing to the interaction between the dipoles created because of fluctuations and the induced dipoles. The resultant van der Waals force is the sum of all the individual forces due to the dipoles interaction between the sample surface and the tip [132,133].

There are two famous models to describe the van der Waals forces in AFM operation in such a way that the tip is modelled as a sphere and a truncated cone with half a sphere at the end interacted with the infinite flat surface. In the two models, the bodies are treated as a continuous bulk material. In case of the first model where the tip is considered as a sphere, van der Waals force is given by

$$F_{vdw} = \frac{HR}{6d^2} \quad (2.1)$$

where H is the Hamaker constant and its value is different from one material to another, R is the tip radius, and d is the tip-sample distance [132].

In the second case [134] van der Waals force is given by

$$F_{vdw} = \frac{H}{6} \left(\frac{R}{d^2} + \frac{\tan^2 \beta}{d + R_\beta} - \frac{R_\beta}{d(d + R_\beta)} \right) \quad (2.2)$$

where β is half the cone angle, $R_\beta = R(1 - \sin \beta)$ for $d < R$ Eq. (2.2) reduces to Eq. (2.1).

For the positive value of the Hamaker constant, the van der Waals force is attractive while it is repulsive for the negative values. There are three cases for the van der Waals forces to identify whether it is attractive or repulsive. In the first case, the van der Waals forces are attractive when it is between two identical metals regardless of the medium between them. In the second case, it is also attractive between two different metals in air. In the last case, it could be attractive or repulsive between different materials in liquid depending on the value of the dielectric constants and refractive indices of the interfaces. van der Waals force can be manipulated to be repulsive or attractive by carefully selecting the medium properties at the interface between the tip and the sample [135,136].

2.1.1.1.2 Short-range forces

When two surfaces come into contact at a very close distance, they experience a quantum mechanic Pauli and electric repulsion. The two surfaces start to experience a deformation depending on their mechanical properties and the externally applied force between them. Many models describe the deformation of the surface when they get into contact. The first model was proposed by Hertz in which two elastic spheres were brought into contact without adhesion [137]. Two other models were developed to describe the deformation of objects with adhesion forces Johnson, Kendall, and Roberts (JKR) [138] and Derjaguin, Muller, and Toporov (DMT) [139]. JKR and DMT models are extensively used in AFM models since they describe the deformation using small tip radii. Short-range forces of the order of 0.5 nN were measured on Si(111) surface where atomic resolution could be obtained [140].

2.1.1.1.3 Capillary forces

Water condenses on hydrophilic surfaces under ambient conditions. Capillary condensation is a thermodynamic phenomenon [141] that relates the vapour pressure to the curvature of the liquid and it is given by Kelvin equation

$$R_g T \log\left(\frac{P}{P_o}\right) = \frac{\gamma V_m}{r_k} \quad (2.3)$$

Where r_k is the kelvin radius, which describes the size of meniscus and it is given by:

$$\frac{1}{r_k} = \frac{1}{r_1} + \frac{1}{r_2} \quad (2.4)$$

Here R_g is the universal gas constant, T is the temperature, P is the vapour pressure, P_o is the saturated vapour pressure, P/P_o is the relative humidity in case of water, γ is the surface tension of the liquid, and V_m is the molecular volume.

Kelvin equation implies that in the air the condensation depends on the relative humidity. The capillary force acts upon a tip if a meniscus is formed. This force [142] is given by;

$$F_{\text{cap}} = \frac{4\pi R \gamma \cos \theta}{1 + \frac{d}{R(1 - \cos \emptyset)}} \quad (2.5)$$

Where R is the tip radius, d is the distance between the tip and surface, θ is the contact angle, $\emptyset$ is the angle of the meniscus. The capillary force has its maximum value when the distance between the tip and sample is zero or the tip is in contact with the sample ($d=0$). For an AFM tip of radius 100 nm, the force can be of order 10^{-8} to 10^{-7} N, which is high in comparison to van der Waals force. Therefore, capillary force plays a big role in AFM

operation in ambient because of its adhesive nature. Consequently, the contact size is controlled by capillary forces when it is performed in air. Care has to be taken when the operation is performed in air, especially when working with hydrophilic surfaces. Nevertheless, capillary forces can be reduced or even eliminated by treating the surface of the sample using some molecules to render a hydrophobic surface, or by controlling the surrounding environment and temperature.

2.1.1.1.4 Forces in liquids

When the tip and sample are immersed in a liquid, most of the forces such as capillary and van der Waals start to reduce or even disappear. However, other forces start to appear due to the interaction of the liquid with the solid such as the solvation or electric double layer surface.

Solvation forces are short-range forces, which are introduced by the solvent molecules-surface interaction. These forces can cause a spatial force oscillation due to the very thin layer of molecules formed on the surface [143]. The oscillation range extends over few molecular dimensions. The oscillations are more obvious if the organic solvent is used because of the large size of the organic molecules [144–146], but also it could be observed in water [147–149]. It was observed that the period of oscillation matches the water molecular size [149].

When a surface is immersed in a polar solution, water, in particular, the surface becomes charged. The charging of the surface is due to either the dissociation and/or ionisation of the surface atoms or ions adsorption from the solution. As the surface becomes charged, the electric field of the surface starts to attract oppositely charged ions from the solution within the vicinity of the surface. The thickness of the layer depends on the ions concentration and their valence. There are two layers, the first is very thin (Helmholtz layer) bounded to the surface, and a diffusive double layer extending farther from the surface. The molecular resolution could be achieved by screening the long-range electrostatic forces by changing the ion concentration of the buffer solution [150,151].

2.1.1.1.5 Electrostatic force

Electrostatic force arises due to the existence of the charges interaction. The charges could be an electronic charge trapped in an isolating tip and on the surface after contact, or due to the contact potential different between two different metals, which equals to the difference in the work function of the two metals. Some experiments use external electric potential applied to the tip (e.g. using conducting AFM to measure the conductivity of graphene flakes [126]) if the medium between the tip and the sample is dielectric, that could lead to trapped charges in the dielectric medium. Surface charge starts to decay and the resultant electrostatic force can be measured down to a single charge [152]. The electrostatic force between the tip and the sample obeys the coulomb's law. The electrostatic force is a long-range force, which means the interaction is not only with the tip's apex, but also with the whole tip body, and the cantilever as well. Neutral polar surfaces can also interact with a charged tip.

If a tip is biased to external potential V , and the contact potential between the tip and the sample is V_c , then the electrostatic can be given in terms of the capacitance C and the distance between the two surfaces z by

$$F_e = \frac{1}{2} \frac{dC}{dz} (V - V_c)^2 \quad (2.6)$$

It is quite sophisticated to find analytical solution of the electric force because it is necessary to find the gradient of the capacitance, which is very dependent on the geometry

of interface. Moreover, due to the irregularity of the tip geometry, it is hard to compensate the electrical electrostatic forces using external electrical bias [153]. In case of using a conical tip with half sphere of radius R at the end in air where the dielectric constant is ϵ_0 , the electrostatic force is given by the approximation [134]

$$F_e = \pi \epsilon_0 \frac{R}{z} (V - V_c)^2 \quad (2.7)$$

2.1.1.2 AFM operation modes

AFM can be operated in different ways. The way of controlling the feedback signal determines which operational mode is used. The operation modes shown in Figure 2.2 can be separated into two categories static modes and dynamic modes. Static and dynamic modes can be used by detecting the static and dynamic cantilever deflection properties, respectively. The most popular modes used in AFM operations are contact and tapping modes.

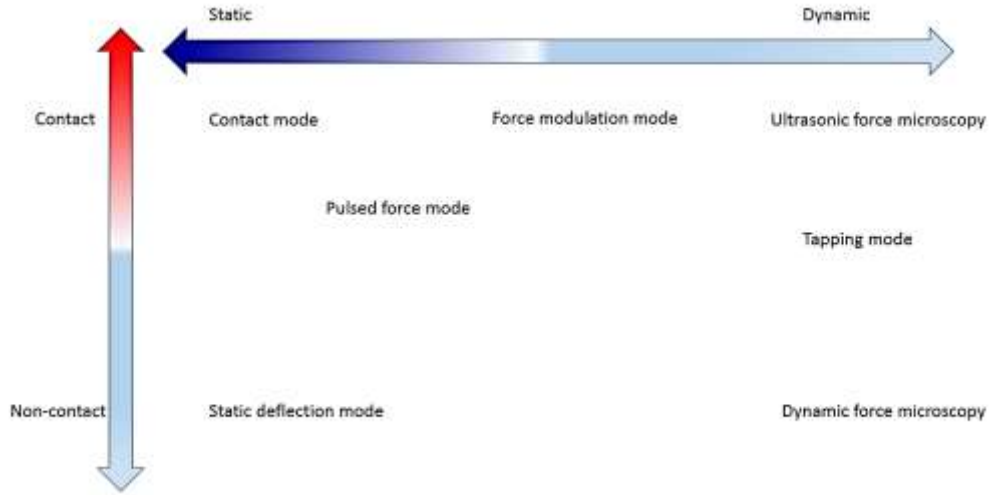


Figure 2.2: Different AFM operating modes. Readapted from Ref. [154].

In the case of static modes, the contact mode is the most used. There are two ways to use it, constant height, or constant force. For the constant force mode, the cantilever deflection is kept constant and the height is measured, while the constant height mode maps the variation of the force over the surface. Contact mode is running in the repulsive force regime by keeping the tip very close to the sample.

In the case of dynamic modes, the cantilever oscillates. According to the interaction of the tip with the sample's surface, the oscillation properties change. Depending on the feedback parameter, the mode is determined. These parameters could be the oscillation amplitude, Eigen frequency, or the phase difference between the excitation signal and the response of cantilever.

If the feedback parameter is frequency, this mode of operation is called non-contact or dynamic force microscopy mode. Non-contact mode proved its ability to scan the surface

with high resolution down to atomic resolution. The non-contact mode is usually running under ultra-high vacuum in order to pertain a high-quality factor of the cantilever oscillations.

Measuring the frequency response of the tip when it is in contact with the surface gives information about the mechanical properties of the sample, specifically when the tip is oscillated in the ultrasonic frequency range [155,156].

When the cantilever is oscillating near its Eigen frequency in an intermittent contact with the surface, and the feedback parameter is the amplitude, this mode is called tapping mode which was used in this thesis work.

In the tapping mode, the cantilever oscillates near its resonance frequency. The root means square value of the oscillation is measured using the photodetector value and is feedback to control the tip-sample distance. Due to intermittent contact, the amplitude is reduced as the tip approaches the sample. The oscillation of the tip reduces the horizontal forces, which enhance the resolution; it is still dependent on the tip geometry, though.

One more advantage of the tapping mode is that it enables phase imaging. When the tip oscillates at a frequency close to its Eigen frequency, there is a phase shift between the excitation and detected signal of the cantilever, which is recorded using a lock-in amplifier. Phase imaging gives information about the mechanical properties of the surface. Furthermore, it can be related to the energy dissipation of the tip-sample interaction. In general, phase imaging can resolve surface inhomogeneity on a nano-scale, and even has the ability to show higher contrast when it is compared to topographic images. Figure 2.3 depicts the difference between the phase and topographic imaging of a gel-coated aluminium alloy.

2.1.1.3 AFM instrument

The basic concept of AFM as mentioned above is that the force of interaction between the tip and the sample is measured. Thus, the sharp tip, which is working as a force sensor, is mounted at the end of a cantilever. Consequently, the cantilever deflects according to the interaction of the tip with the surface. By determining the deflection of the cantilever, the force can be determined accordingly. Therefore, the basic components to implement an AFM are: probe, mechanical oscillator (to oscillate the tip in tapping mode), deflection detector, scanner to move the tip over the sample, the controller to control the feedback signals and the scanning parameters, image processor and user interface.

2.1.1.3.1 Feedback control

The cantilever tip system oscillates at its resonance or excitation frequency. The photodiode measures the root mean square value of the oscillation amplitude. The amplitude and phase are extracted from the detected signal by correlating it to the input signal at the excitation frequency or its harmonics by using a lock-in detector. In order to maintain the tip oscillating at a constant amplitude while it is scanning the surface, a feedback loop is used to control the amplitude value (or the other parameters such as frequency, or the phase). The feedback loop compares between the instantaneous and reference values of the amplitude A_i and A_{sp} , respectively, and try to keep the instantaneous value (A_i) close to the set point (A_{sp}). In other words, the function of the feedback loop is to maintain the error signal ($A_{sp}-A_i$) as small as possible by the means of proportional integral differential system. The output of the feedback loop sends a voltage to the piezo scanner to change the Z position by approaching or withdrawing the tip in order to minimise the error. The scanning speed of the microscope is limited by the speed of the feedback loop circuit. Current scanner can scan up to 25 frame per second[157,158].

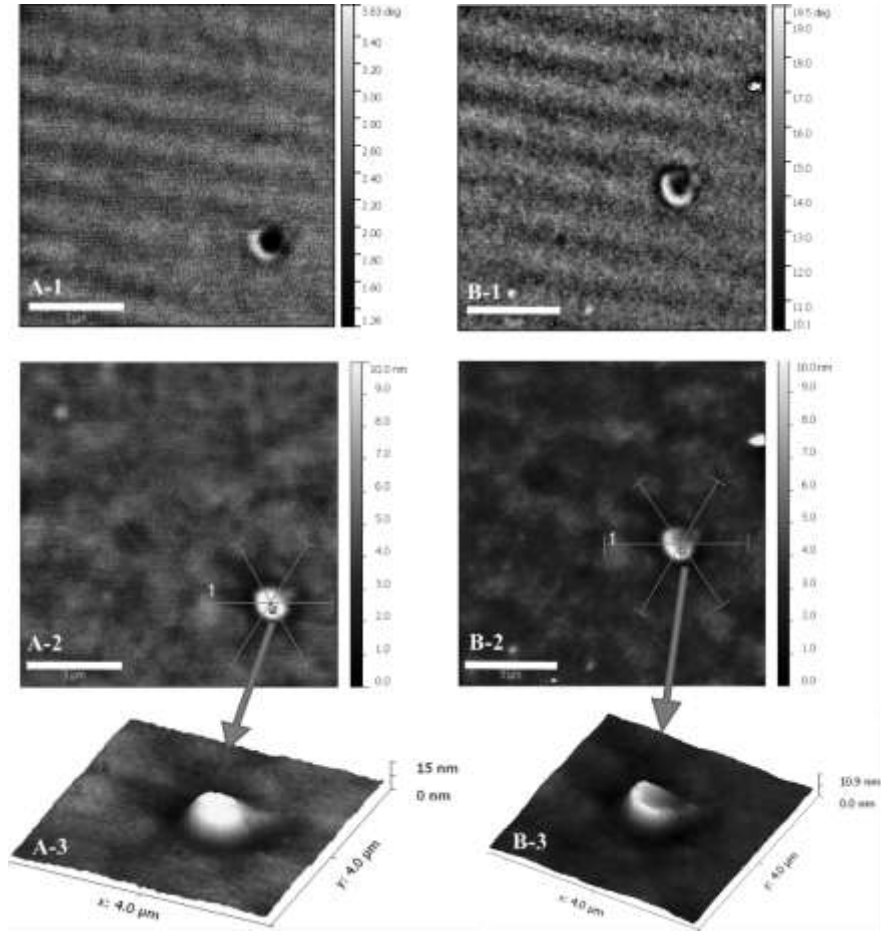


Figure 2.3: An example of different AFM image representation in tapping mode of gel-coated AA2024 in NaCl (0.5M). A) Represents the image before applying a potential pulse, and B) after applying an anodic pulse to the sample. A-1, and B-1 are phase images, A-2, and B-2 are 2D topography images with scale bars of 3 length, A-3, and B-3 are topography images [159].

2.1.1.3.2 Optical Beam Deflection

Methods of detecting the bending of the cantilever tip system produced by the tip surface forces are at the heart of force microscopy. The sensitivity and simplicity of the optical beam deflection method [129,160] are two of the factors that have contributed to the rapid success of the AFM. A light beam coming from a solid-state diode is reflected at the back of the cantilever and the deflection is monitored by position sensitive photodetectors consisting of several photodiodes. The photocurrents are fed into a differential amplifier that generates an output signal in volts. The use of four segmented photodiodes enables the detection of both normal and lateral forces [157].

The ultimate detection sensitivity of the optical beam deflection method is limited by the thermal noise. A properly tuned beam deflection system enables detection of cantilever deflections below 0.01 nm. The beam deflection method has a caveat for it does not directly measure the deflection of the cantilever z (vertical displacement) but its change in slope dz/dx . A force applied on the tip produces both a change in the cantilever deflection and a change in the slope. For a rectangular cantilever, the application of the Euler-Bernoulli theory and some geometrical considerations allow us to deduce a relationship between changes in slope and changes in deflection [157,161,162].

The deflection along the cantilever length L produced by a force F applied at the free end is

$$z(x) = \frac{F}{2k} \left[3 \left(\frac{x}{L} \right)^2 - \left(\frac{x}{L} \right)^3 \right] \quad (2.8)$$

Then,

$$z(L) = \frac{2L}{3} \frac{dz(L)}{dx} \quad (2.9)$$

The above equation is valid for a static force applied at the tip; nonetheless, it will also be used to describe the tapping mode AFM. It can also be deduced that the amplification of the deflection in the photodiode is proportional to the ratio between the cantilever photodiode distance D and the cantilever length,

$$\Delta A \approx \frac{2D}{L} \Delta z \quad (2.10)$$

2.1.1.3.3 Other detection methods

Several other methods have also been proposed and applied to detect the cantilever deflection [157,160–168]. Quate and co-workers introduced self-sensing methods to detect the cantilever bending [168]. A piezoresistive layer deposited on top of the silicon cantilever changes its resistance with changes in the cantilever geometry. In this way, the cantilever deflection can be measured. Self-sensing methods based on piezoelectric materials can be small size and compact; however, the signal-to-noise ratio is not as good as in optical beam deflection. Another type of self-sensing method uses quartz tuning forks [157,165].

2.1.1.3.4 Tip-sample motion system

Piezoelectric actuators provide positioning with high accuracy and sub-angstrom precision. Both the tip oscillation and the relative position of the tip, to the sample surface, are performed by means of piezoelectric actuators. Two different piezoelectric actuators are common in the tapping mode AFM. A dither piezo glued at the clamped end of the cantilever is used to excite the cantilever oscillation. The other piezo actuator is used to displace the tip with respect to the sample surface. This piezo scanner could be placed either underneath the sample surface or above it. Commonly, the piezo scanner is a hollow and segmented tube that enables motion in the x , y , and z directions. Tube scanners are preferred because they are compact, implying higher resonant frequencies. In addition, the same scanner could cover a wide range of scanning areas from nm^2 to μm^2 . The downside is the existence of some coupling between the lateral and the vertical displacements.

Piezoelectric scanners do not have a linear relationship with the voltage that produces the mechanical deformation. They suffer from a series of problems such as hysteresis, creep, ageing, or thermal drift. These factors might cause serious distortions in the imaging process. Hysteresis may be corrected by the use of algorithms implemented in the software that controls the tip displacement. Hysteresis and creep are more noticeable for large displacements while thermal drift is more visible for small tip displacements. The most effective way to minimise the difference between the real and the nominal tip displacements is by using the so-called of close loop systems. In a closed loop scanner, the actual displacement in x, y, or z direction is measured by a magnetic, capacitive, or optical system and is compared with its nominal value. An error signal is generated and a process to minimise this signal is implemented. The sensitivity of piezoelectric scanners (volts/nm) might change with use and time. For this reason, it is advisable to recalibrate the scanners once per year by using calibration gratings for the x, y, and z-axes. A different tip motion system called the force sensing integrated readout and the active tip has been proposed [163]. This method integrates the tip motion with force sensing by combining a micromachined electrostatic actuator to move the tip and an integrated optical interferometric displacement detector in a micro-scale volume [157].

2.1.1.3.5 Imaging acquisition and display

Imaging acquisition and display account for the processes performed on the signal coming out of the photodiodes to generate an image that conveys meaningful information on the topography and other properties of the surface. Many AFM manufacturers provide software for image processing and representation [157].

A key factor to bear in mind is the limit that the frequency bandwidth imposes on the imaging acquisition time t_a . The imaging acquisition time can be conveniently expressed in terms of f_x , the scanning frequency in the fast-moving direction, and the number of scan lines N in the tip's slow moving direction, $t_a = N/f_x$. The feedback bandwidth B should always be larger than $1/t_m$, where t_m is the time taken by the tip to travel between the closest features resolved by the instrument λ . Then

$$B \geq \frac{1}{t_m} = \frac{v_x}{\lambda} = \frac{2\Delta x f_x}{\lambda} = \frac{2\Delta x N}{\lambda t_a} \quad (2.11)$$

Where v_x is the tip speed in the fast-moving direction and D_x is the lateral image size. The feedback bandwidth is determined by several factors such as the mechanical resonances of the cantilever and tip-sample motion system, the quality factor, and the time response of the feedback controller [169–171].

2.1.1.3.6 Cantilever tip system

The cantilever tip system has two elements: the cantilever and the tip. The cantilever is the transducer that converts the force sensed by the tip into a deflection that can be recorded and measured. The use of microelectronic processes has made possible the integration of the cantilever and the tip into a single device, the cantilever tip system. However, it seems convenient to describe the properties of the tip independent of those of the cantilever. On the one hand, the cantilever body outweighs the tip by several orders of magnitude meaning that inertial effects depend mostly on the cantilever mass. On the other hand, the proximity of the tip to the surface makes it possible to confine the tip-surface interaction to the size of the apex of the tip. Tip's aspect ratio is important as it

controls the resolution of the imaging, thus sharpening the tip is important if an atomic resolution is required [157]. That could be implemented in different ways, either by etching the tip chemically or using focus ion beam to have a sharp tip (Figure 2.4-D) or by integrating nanotubes to the end of a tip (Figure 2.4-E).

Cantilevers are fabricated in microelectronic facilities with some of the technologies used to fabricate integrated circuits such as photolithography and etching procedures [130]. The majority of AFM cantilevers are made of either silicon or silicon nitride (Si_3N_4). Most commercial cantilevers are either (Figure 2.4) v-shaped (Figure 2.4-B) or rectangular beams (Figure 2.4-A). Rectangular cantilevers have a trapezoidal shape. Nonetheless, some applications might require the development of special geometries to enhance the response of higher cantilever modes [172].

The cantilever properties of interest in the tapping mode AFM are the force constant, the resonant frequency, and the quality factor. The force constant enables to transform intermolecular and nanoscale forces into force measurements. The resonant frequency is one of the factors that control the time response of the instrument and the quality factor is a measure of the hydrodynamic damping of the cantilever with the environment (liquid or gas). The quality factor Q also includes the cantilever internal energy losses, although these are usually negligible with respect to the hydrodynamic damping.

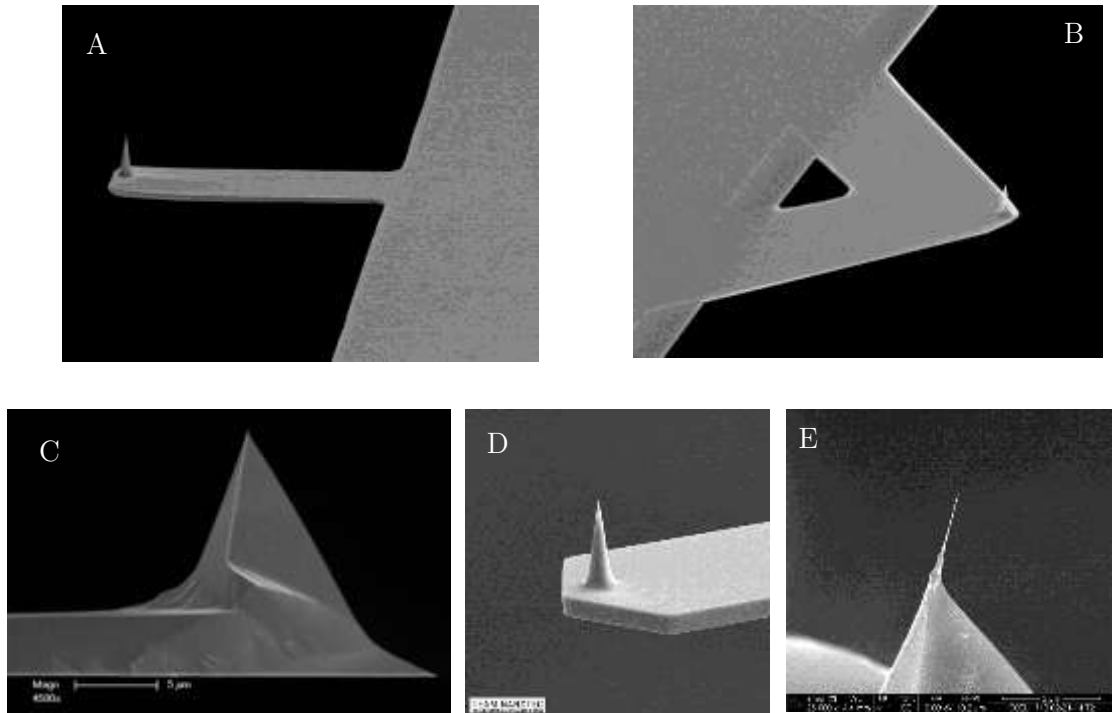


Figure 2.4: Different AFM commercial tips. A) and B) show rectangular and V shape cantilevers, respectively [173]. C) triangle base [174], D) conical tip [175], and E) Carbon nanotube integrated tip [176].

In this work, Agilent AFM 5500 shown in Figure 2.5 was used for all the in-situ measurements. For bare aluminium 4-sided silicon tips with the radius less than 50 nm (Nanosensors), gold coated on a detector and a tip side, with a nominal spring constant of 0.1 N/m, the resonance frequency of 75 kHz in the air and the cantilever length of 200 μm .

For the rest of experiments, uncoated 4-sided silicon tips were used with a nominal spring constant of 0.1 N/m, resonance frequency 90 kHz in the air, and cantilever length of 150 μm . All AFM experiments were carried out in tapping mode in order to avoid relocation of corrosion products, and decrease the influence of the tip-sample interaction.



Figure 2.5: Atomic Force Microscope Agilent 5500.

2.1.1.4 Surface parameter extraction

In order to have a deeper insight into the change of the surface topography, the central moments of each image were studied. The first central moment is the roughness average S_a in Eq. (2.12), it gives a general description of the surface, however, it is not a good parameter to describe the small changes in the amplitude if they are centred around a

value will give just an average without any information about the distribution of the features on the surface.. It does not give information about peaks and valleys as the root mean square Eq. (2.13) S_q does. For example if the surface exhibits an odd function the average can give information about the level of the surface but will not give information about the number of peaks and valleys, which represent the roughness of the surface. However, the root mean square S_q , gives information about the change in the roughness because of considering the second moment around the average of the height. The third central moment is the skewness Eq. (2.14) S_{sk} , which is a measure of surface asymmetry. It can take positive and negative values as it is an odd function (function of the third power of the difference between the local height and the average height) ; such that the positive skewness means empty surface (peaks), whereas the negative skewness means full surface (valleys), the Gaussian surface has a skewness value of zero. The fourth central moment is the kurtosis S_{ku} , Eq.(2.15) it describes the sharpness of the surface and it takes positive values because it is a function of the fourth power of the difference between the local height and the average height, it has a value 3 for a Gaussian surface, while the spiky surface has values greater than 3 and less than 3 for a bumpy surface. Low values are corresponding to sharp valleys, whereas high values are corresponding to sharp hills [177]. The images were first exported as JPEG files to a folder and then were converted to a matrix in MATLAB. The matrices of the images processed using MATLAB script to calculate the statistical parameters using the equations (2.1-2.4) [178].

Roughness average;

$$S_a = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} |Z(x_k, y_l) - \bar{Z}| \quad (2.12)$$

Roughness root mean square value,

$$S_q = \sqrt{\frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [Z(x_k, y_l) - \bar{Z}]^2} \quad (2.13)$$

Skewness,

$$S_{sk} = \frac{1}{MNS_q^3} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [Z(x_k, y_l) - \bar{Z}]^3 \quad (2.14)$$

Kurtosis,

$$S_{ku} = \frac{1}{MNS_q^4} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [Z(x_k, y_l) - \bar{Z}]^4 \quad (2.15)$$

Where, M and N are the number of pixels in the horizontal and vertical directions, respectively. $Z(x_k, y_l)$: is the height at x_k , and y_l . $\bar{Z}$ is the average height.

2.1.2 Scanning electron microscope and energy dispersive X-ray spectroscopy

Scanning electron microscope (SEM) is a member of the electron microscope family, which can produce an image of a sample by focusing a beam of electrons to raster a sample. Scanning electron microscope works like an optical microscope except that it uses a focused accelerated electron beam. SEM has the advantage of higher magnification and resolution over the optical microscope. The advantage of scanning electron microscope (SEM) over transmission electron microscope (TEM) is that the first has the ability to analyse and image bulk samples [179]. The purpose of using SEM in this study is to have a quick and powerful tool to scan a large area of samples, in comparison to AFM. Moreover, SEM has the ability to analyse a sample if it is supported with X-ray detector. The interaction of electrons with the atom of the sample results in a loss of electrons kinetic energy. Many signals are generated depending on the interaction nature owing to the dissipated energy. These signals carry a lot of information about the sample, such as the topography, the chemical composition, or even the crystal structure.

Namely, the sample-electron interaction results in emission of electrons and/or photons. The emitted electrons can be secondary electrons (SE), backscattered electrons (BSE), and electron back-scattered diffraction (EBSD), while the emitted photons can be X-ray photon, and visible photons in the case of cathodoluminescence. Figure 2.6 depicts the interaction volume of the different signals, and the electron interaction range, which is between 10 nm and 10 μ m. The interaction range depends mainly on the electron energy, and the sample density [180]. SE are generated due to the inelastic collision of electrons with the inner electron shell of atoms. When an inner shell is ionised, an electron from a higher level makes a transition downward to fill in the vacancy in the inner shell and releases quanta of energy and there are two possibilities. The first is that the quanta of energy are emitted in the form of a photon in X-ray range to characterise the atom, the second possibility is that the quanta of energy are given to another atomic electron to leave the atom with a characteristic kinetic energy. The resolution of the microscope depends on the nature of the interaction of the electron with the surface, in other words, the electrons energy and the detected signal identify the resolution. Secondary and Auger electrons can leave a very thin layer of the surface and have low interaction volume as depicted in Figure 2.6, as they are generated not only because of the incident beam of primary electrons, but also the back-scattered electrons from the bottom layer of the surface.

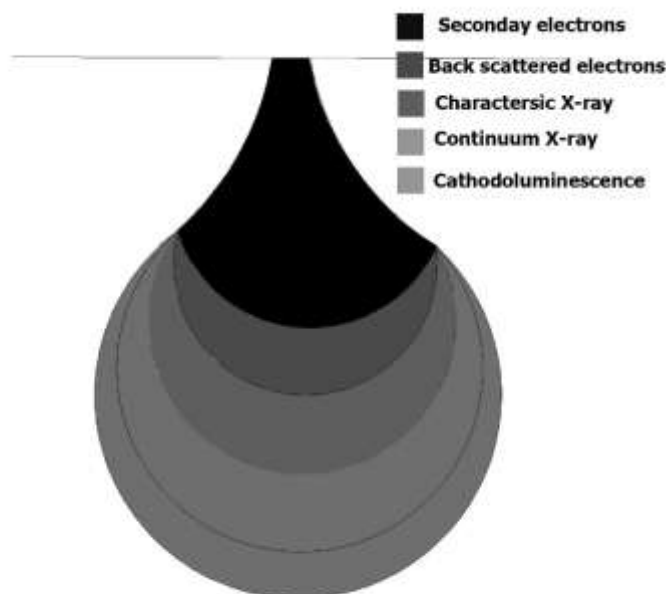


Figure 2.6: Electron-sample interaction volume.

The principle of SEM can be depicted from Figure 2.7. Electrons are generated using an electron gun that could be from thermionic, Schottky, or field emission cathode. The generated electrons are accelerated by passing them in an electric field between a cathode and anode of voltage between 100 V and 50 kV.

The accelerating voltage is divided into two ranges, low and high. The first range is at low accelerating voltages (within 0.1-5 kV), which is called the low voltage range that is usually preferable for sensitive samples such as biological samples. The second range is the normal range above 5 kV; this range is used for scanning insensitive samples, and necessary in the case of doing X-ray dispersive analysis.

Depending on the source of electrons and its current, the beam diameter is determined. In the case of using thermionic cathode, the diameter is of range 10-50 μm , while it is within the range of 10-100 nm if Schottky or field emission cathode is used. In order to narrow down the beam's diameter, electric or magnetic lenses are used to confine the beam and could reach 1-10 nm at the sample's surface with a current of electron in range of 10^{-9} – 10^{-12} A. Some other operating modes require a large beam diameter, in that case the current is increased to about 10^{-8} A, and the beam diameter could be around 0.1 μm . The beam then reaches the electrically conducting sample and starts to rasterize over the sample using a set of electric or magnetic lenses to deflect the beam [180]. The signals are collected using SE or BSE detectors and amplified, they are sent to the computer to be processed and saved. The current of electrons reaches the collecting plate and controls the brightness of the image. Consequently, an image is formed depending on the brightness that is due to the interaction of the electron beam with the surface. The sample starts to contaminate upon exposure to the beam for a long time, and carbon film starts to deposit on the surface [181,182]. Therefore, fast scan, ultra high vacuum, and low electrons energy are required to preserve the surface from contamination.

Energy dispersive X-ray spectroscopy (EDS) is a technique used to identify the chemical composition of a sample depending on the emitted X-ray photon. As mentioned above,

when an electron of high energy hits an atom, it ionises the inner shell of the atom and results in an excited electron, which could leave the atom or move to a higher unoccupied energy level. In the latter case, a characteristic X-ray photon is released after the decaying of an electron to a lower energy level. There are two different ways to measure the emitted X-ray photons; energy dispersive, and wavelength dispersive detector. In this study, the energy dispersive spectrometer was used. In this case, the detector measures the quanta of energy followed by the analysis of these quanta using a multichannel analyser, thereafter each x-ray photon of different energy can be counted and displayed. For quantitative analysis, the detector has to be calibrated against a standard sample.

In this study, the SEM micrographs were recorded on a field emission scanning electron microscope (FE-SEM) Supra 35 VP (Carl Zeiss) equipped with an energy-dispersive spectrometer (EDS) INCA 400 (Oxford Instruments). The sensor was of an emergency type and with 10-mm² area. The samples were mounted on aluminium stubs using carbon tape to avoid charging of the sample.

The imaging and EDS analysis were carried out using 20 kV accelerating potential, and at a working distance of 8.5 mm. For EDS analysis before acquiring a spectrum for each sample, the spectrometer was calibrated using a standard cobalt sample.

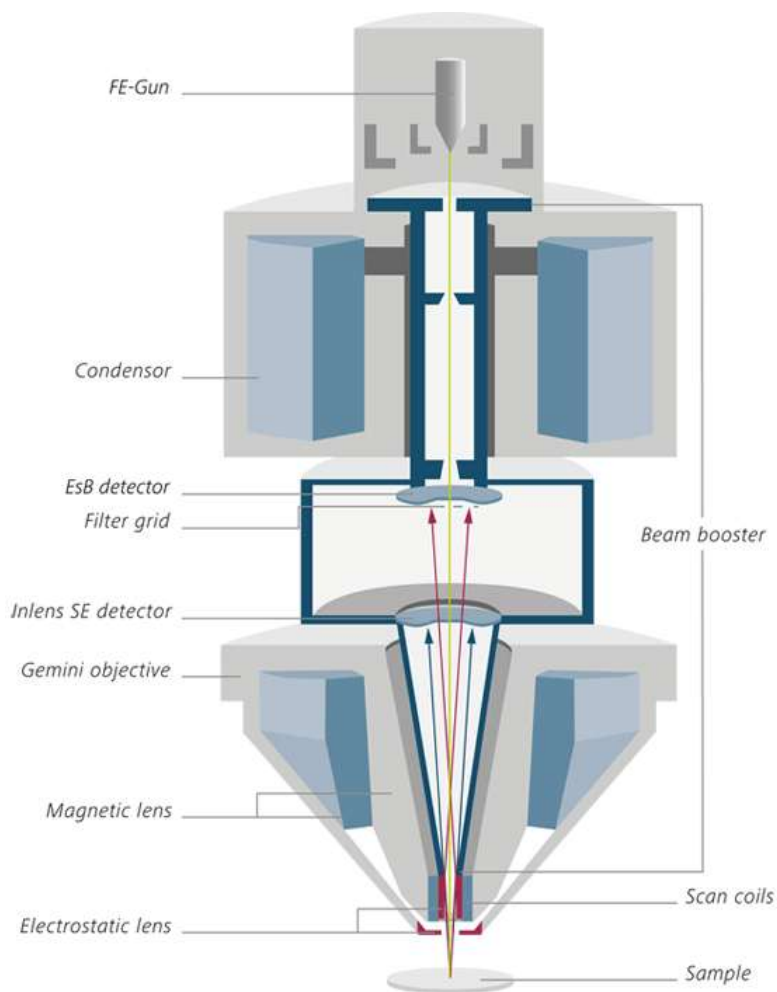


Figure 2.7: Schematic cross-Section of FE-SEM optical column [183].

2.1.3 Infrared reflection-absorption spectroscopy (IRRAS)

Infrared (IR) spectroscopy is one of the first techniques that was applied to the characterisation of adsorbates in the 1940s. IR radiation is an electromagnetic radiation with a wavelength range from 0.78 to 1000 μm . In the field of spectroscopy, the wavenumber is preferably used to represent the wavelength, and it is given by the reciprocal of the wavelength. IR is divided into three regions (Table 2.1) depending on the wavelength, and consequently the energy. Owing to its low energy, IR is incapable of making any electronic transitions. Nevertheless, IR energy has the ability to induce rotational and vibrational excitations in molecules. The middle region is where IR spectroscopy is performed, such that qualitative analysis is common [184–186]. This region is divided into two subregions: the first subregion is within the range 1200–3600 cm^{-1} and usually called group frequency region, and the second subregion is within the range 600–1200 cm^{-1} and called fingerprint region. The fingerprint region is characteristic for the whole molecule, while the group frequency region is used to identify the functional group(s) in the structure. The group frequencies differ from one structure to another, and they can be found within a range or a band of frequencies. Near-IR region is usually used in the quantitative analysis [187]. Far-IR region is used in studying hydrogen bonds, and rotations in gases [188].

Table 2.1 Infrared three regions

INFRARED REGION	WAVELENGTH (μm)	FREQUENCY (Hz)	WAVENUMBER (cm^{-1})
NEAR	0.78-2.5	3.8×10^{14} – 1.2×10^{14}	12800-4000
MIDDLE	2.5-50	1.2×10^{14} – 6×10^{12}	4000-200
FAR	50-1000	6×10^{12} – 3×10^{11}	200-10

The absorbed IR energy is converted into vibration energy of the molecules. The classical description of molecules is a point connected with springs. The atoms vibrate in different ways, called vibration modes. For a molecule with N atoms, the number of vibration modes is $3N-5$ if it is linear and $3N-6$ for a nonlinear molecule. These modes of vibrations are called normal vibration modes, during these vibration modes the angle and/or length of the bond change. The normal modes of vibration are coupled to each other. The coupling of the different vibrations results in a slight change in the absorption frequencies of a functional group. The condition of absorption of IR radiation is that the vibration has to change the dipole moment of the molecule. That composes the selection rule that can identify if the molecule is IR active or inactive.

In this study, IRRAS was used to study the change in aluminium alloy AA2024 after different treatment in mid-IR range. IRRAS is an optical technique usually used to study very thin layers on the surface of metals that are reflective. The principle of IRRAS is a polarised light incident on the surface with an angle θ . The electrical field of the incident beam has two polarisation components; $\mathbf{E}_s$ in a direction parallel to the surface and perpendicular to the direction of propagation, and $\mathbf{E}_p$ component perpendicular to both s and the direction of propagation as illustrated in Figure 2.8. The electrical field of the reflected beam its $\mathbf{E}_{s,r}$ component is in the opposite direction of the corresponding one of the incident beam with a little change in the magnitude. The two “s” components of the incident and reflected beam almost cancel each other. The p component of the reflected beam depends on the angle of incidence θ , however, when a glancing incidence of the beam

(θ is close to 90°), the fields give a large component perpendicular to the surface [189]. The absorption intensity is proportional to the square of the electric field magnitude, therefore the sensitivity is greatly enhanced when the beam hits the surface at an angle near to glancing on the one hand, and the beam covers a larger area of the adsorbed molecules on the other hand. Therefore, near grazing angle was used in this study. More details about the technique can be found in references ([184–186,189]).

IRRAS measurements were carried out using a Bruker spectrometer IFS 66/S using a monolayer grazing angle specular reflectance accessory (Specac) equipped with a standard polarizer for obtaining the P-polarised light and under the near-grazing incidence angle of 80° .

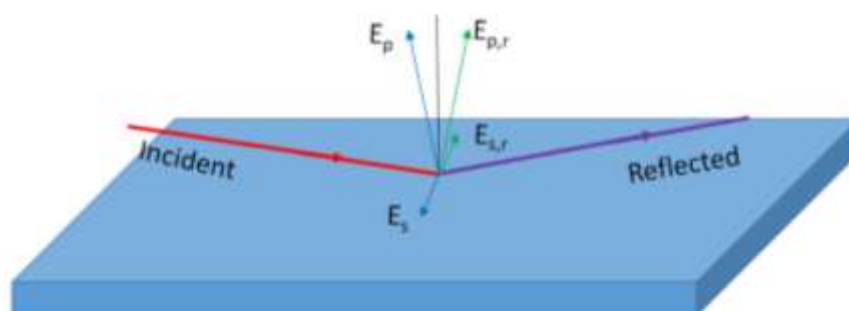


Figure 2.8: Electric vectors of s- and p-polarized radiation incident on a metal surface. The subscript r refers to the components of the reflected electrical field vector.

2.1.4 Raman microscopy

Raman scattering was discovered by C. V. Raman in 1928. When light is scattered by an object such as molecule or crystal, photons are elastically scattered. Such photons have the same energy (frequency) as the incident photons. Only a small fraction of the incident photons (about a photon per 10⁷ photons) scatter with a frequency different from the incident one. Raman scattering is the process that takes place due to an inelastic scattering. Different from IR spectroscopy, Raman scattering can take place with a change in not only vibrational and rotational, but also electronic transitions of molecules. One advantage of Raman spectroscopy over IR is that the presence of water is not hindering its applicability.

When a monochromatic light illuminates the sample of interest mostly using a laser source as a highly coherent monochromatic light source, the scattered spectrum consists of a strong line centred, and weaker lines on both sides of that line. The central line is due to the Rayleigh scattering (elastic scattering), while the weaker lines are because of the Raman scattering. The lines with an energy lower than the incident energy are called Stokes lines, whereas the lines with energy above the incident line are anti-Stokes lines. Figure 2.9 shows the different transitions, such that in the case of Rayleigh scattering the molecule is excited to a virtual state and decays back to the initial state. While in Stokes Raman transitions, the molecule is excited to a virtual energy state, and decays to an energy state higher than the initial one, generating photons with energy lower than the incident photons' energy. In the case of anti-Stokes Raman transitions, the transition of the molecule from an excited state above the ground state to a virtual state, and decay back to the ground state. Anti-

Stocke Raman transitions are less common at room temperature according to Boltzmann distribution [190].

As aforementioned, a laser source is used to excite the sample of interest to have a Raman scattered photon. It is necessary that the laser energy should be larger than the vibrational energy of the molecules and less than the energy that may induce electronic transition. The laser source could also introduce a damage of the sample under study or even burn it, if its energy is high.

Raman spectra are represented by the measured intensity vs. the Raman shift (cm^{-1}). Raman spectroscopy can be combined with a confocal microscope in order to enhance the resolution and to make lateral Raman mapping possible using either a scanning table or a scanning mirror. The scattered light goes through a pinhole that filters out the light out of focus. After the pinhole, the light is transmitted to a filter that has the ability to block out the excitation wavelength to eliminate Rayleigh scattered light. After the filter, the light is passed to a spectrometer by means of mirrors, or optical fibre.

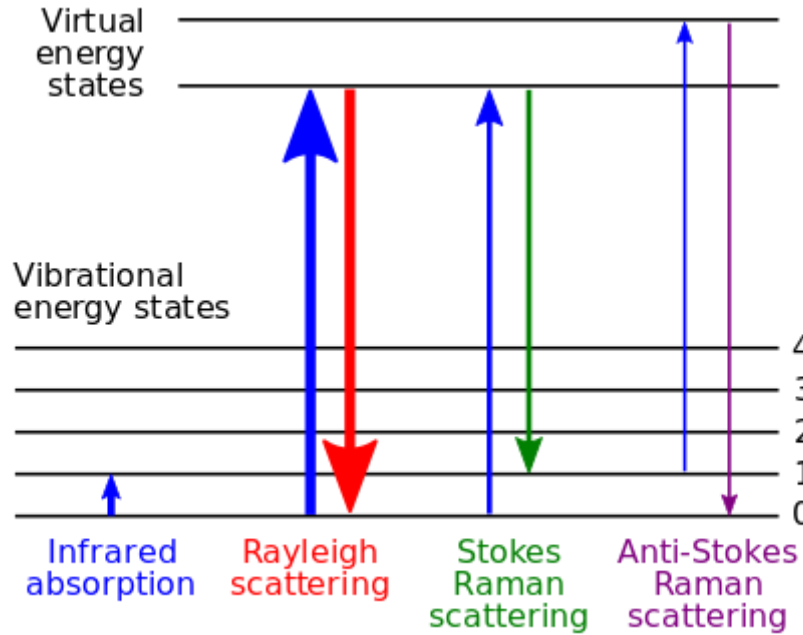


Figure 2.9: Energy diagram of different transitions.

In this thesis, Raman microscopy was used to study the properties of graphene oxide coating. Confocal Raman measurements were performed on a WITec alpha 300 spectrometer with a laser excitation wavelength of 532 nm. A schematic of confocal Raman is shown in Figure 2.10. The laser is coupled to the confocal microscope and hit the sample which is positioned on the scan table after being focused using a lens of magnification (20-100X). The photons are scattered back and passed through a filter, then coupled via an optical to the spectrometer to be analysed using diffraction gratings and displayed on a CCD. The lines displayed in CCD are then analysed using a data acquisition system, then displayed on a computer to be processed and saved.

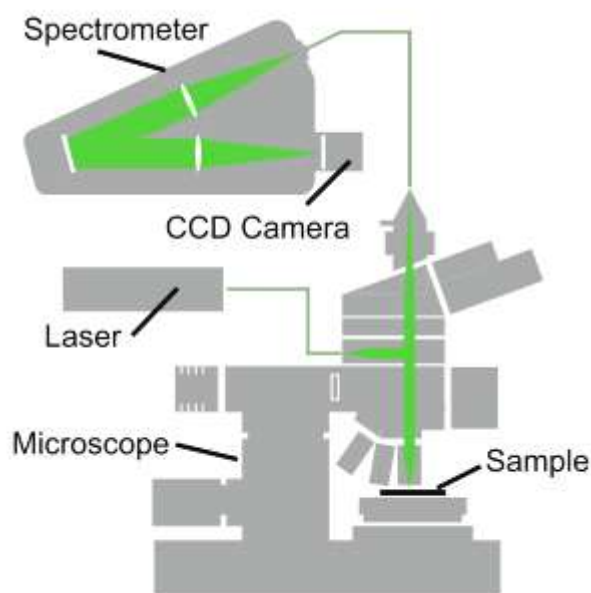


Figure 2.10: Schematic of WITec alpha 300 confocal microscope [191].

2.1.5 Electrochemical methods

Different electrochemical techniques were used in the thesis. All the electrochemical techniques used here are macroscopic, such that the technique was applied to the whole electrode.

The electrochemical techniques used are electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), chronoamperometry (CA), cyclic voltammetry (CV), staircase potential, and chronopotentiometry (CP).

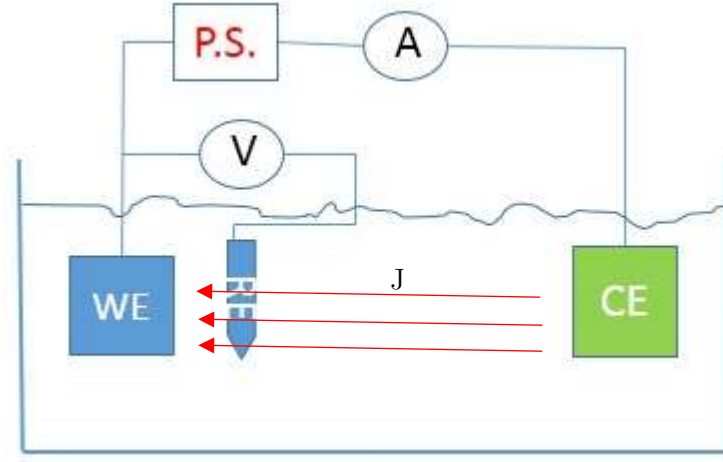


Figure 2.11: Schematic representation of a three-electrode electrochemical cell. WE is the working electrode, RE is the reference electrode, CE is the counter electrode, and P.S. is power source which could be A.C. or D.C. The arrows indicate the current lines in the electrolyte.

2.1.5.1 Open circuit potential

Open circuit potential is a thermodynamic parameter that can give an insight of the corrosion. In order to understand the concept behind open circuit potential, let us first consider the reduction reaction



Where O and R are the oxidised and reduced species and n is the number of electrons transferred or exchanged between O and R [192]. The change in free energy is controlled by concentration of both oxidised and reduced species and is related by the following equation

$$\Delta G = \Delta G^o + R_g T \ln \left(\frac{[R]}{[O]} \right) \quad (2.17)$$

Where [O], and [R] are the concentration of the oxidised and reduced species, respectively. R_g is the universal gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature. ΔG^o is the standard Gibbs free energy change, and ΔG is the Gibbs free energy change, which is related to the potential by the relation

$$\Delta G = -nFu \quad (2.18)$$

Where F is Faraday's constant (96485.3 C mol⁻¹), and u is the equilibrium potential between two electrodes when no current is flowing in the cell and is called the open circuit potential.

Furthermore, when the concentration of the oxidised and reduced species is equal, the second term in Eq. (2.17) vanishes and we have the relation

$$\Delta G^o = -nFu^o \quad (2.19)$$

u^o is known as the standard electrode potential. For spontaneous reactions, ΔG^o is negative and, in turn, their standard electrode potential is positive.

Moreover, the potential is related to the concentration of species, Nernst equation gives the relation by combining equations (2.17), (2.18), and (2.19).

$$u = u^o + R_g T \ln \left(\frac{[R]}{[O]} \right) \quad (2.20)$$

From the above equations, it can be concluded that OCP is a mixed potential such that when a reaction takes place there will be oxidation or reduction until they are equal and reach equilibrium. OCP is used in electrochemical measurements of corrosion, as it is a simple two-electrode technique such that in this technique the potential of the working electrode is measured against the reference electrode as shown in Figure 2.11 at zero current (without applying any external electrical signal) [193,194]. The change of OCP with time can give a qualitative insight of the change in the electrode, the shift to more negative direction is a sign of active corrosion [195], whereas a more positive direction indicates a passivation or corrosion inactive.

2.1.5.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a useful technique that has the ability to study many factors at the working electrode/electrolyte interface. Among others, these factors include double layer capacitance, kinetics, and stability of the working electrode [196–198]. EIS is quite an old technique [199] used extensively in the characterization of coatings as well as in studying the corrosion of metals [200]. An advantage of EIS is that it is a non-destructive technique, which makes it possible to use it simultaneously with measuring the topography to find the global change of the working electrode. Therefore, a real-time experiment of both EIS and AFM can give an insight of the dynamic change in the surface of the working electrode.

In EIS a small sinusoidal signal of a very small amplitude in the range of a few millivolts (1-10 mV) at a wide range of frequencies (1mHz-100kHz) is applied to the working electrode. The signal is either superimposed on applied potential to working electrode or applied at open circuit potential. The current response is phase shifted from the excitation voltage signal due to the characteristic of the electrochemical cell, giving rise to an impedance [201]. The impedance involves the contribution of each element in the electrochemical cell. The components of the cell that contribute to the impedance could be a passivated layer, a diffusion, solution resistance, or electron-transfer kinetics. The

contribution of each component is frequency dependent. For example, electron transfer dominates the high-frequency range while lower frequencies are dominated by diffusion [197,202].

EIS, as mentioned above, is measured by applying a sinusoidal potential $V(t)$ from the power source in Figure 2.11 to the working electrode at an angular frequency (ω), and measures the current $I(t)$ at the same frequency which is shifted by a phase angle (θ) from the potential. In that case, according to Ohm's law, the impedance is given by:

$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{V_o \sin(\omega t)}{I_o \sin(\omega t + \theta)} = Z'(\omega) + jZ''(\omega) \quad (2.21)$$

The impedance is a complex number, with real part Z' and imaginary part Z'' . Like any complex number, $Z(\omega)$ can be plotted in different ways. One representation of the impedance is by plotting the negative imaginary part against the real part, in this case, it is called a Nyquist plot (Figure 2.12-A). Another way of representing the impedance is to plot the logarithm of impedance magnitude given in Eq. (2.22), and phase against the logarithm of frequency given in Eq. (2.23) (Figure 2.12-B).

$$|Z| = \sqrt{Z'^2(\omega) + Z''^2(\omega)} \quad (2.22)$$

$$\theta = \tan^{-1} \frac{Z''(\omega)}{Z'(\omega)} \quad (2.23)$$

A spectrum of EIS can be modelled into an electric circuit composed of resistors, capacitors, inductors, and other electrochemical circuits so the characteristics of the surface can be identified. The most common and basic circuit used is Randle circuit, which is composed of a resistor and a capacitor connected in parallel, both in series with another resistor. The more sophisticated the physical properties of the working electrode, the more elements can be used to model the problem. Each element used in the circuit models a physical or electrochemical property of the working electrode. The basic elements that exist in Randle circuit are:

- 1- The resistance that represents the solution. The solution has an ionic resistance that depends on the concentration, temperature, and volume of solution in which the current flows in it.
- 2- Double layer capacitance. Upon immersing a metal in electrolyte, especially if it has high polarizability like as an aqueous solution, a separation of charges takes place such that a layer of ions adsorbs to the metal's surface and electrons on top of them forming a double layer of charges. The double layer acts like a capacitor of two plates with a separation in the order of angstroms. The value of the capacitance depends on many factors that control the formation of the double layer, including electrode potential, temperature, the concentration of the electrolyte, and polarizability of the solvent.
- 3- Polarisation resistance. When the electrode is polarised, the current starts to flow because of the electrochemical reactions at the surface of the electrode. The current

magnitude depends on two factors, the first is the kinetics of the reaction, and the second the diffusion of reactants. This is described by the Butler-Volmer equation, which at very small applied potential reduces to a relation between the polarisation resistance, and the corrosion current such that this resistance is the ratio between the change in the applied potential to the measured current.

- 4- Charge transfer resistance. When the system is at equilibrium without applying any external potential, there is a kinetic transfer of charges giving rise to a resistance.
- 5- Constant phase element (CPE). In case of a coating, the capacitance is not perfect, which means the phase shift is not 90° , therefore a CPE element is used to replace the imperfect capacitance.
- 6- Diffusion or Warburg impedance. Diffusion depends on the frequency applied, therefore it cannot be represented by a resistance, and instead, it is replaced by Warburg impedance. At high frequency, Warburg impedance is small, while it increases at low frequency. In the case of semi-infinite diffusion, the Warburg impedance is a special case of CPE, with a phase shift 45° . It can be seen on the Bode plot as a phase shift at 45° , and as a diagonal line on the Nyquist plot.

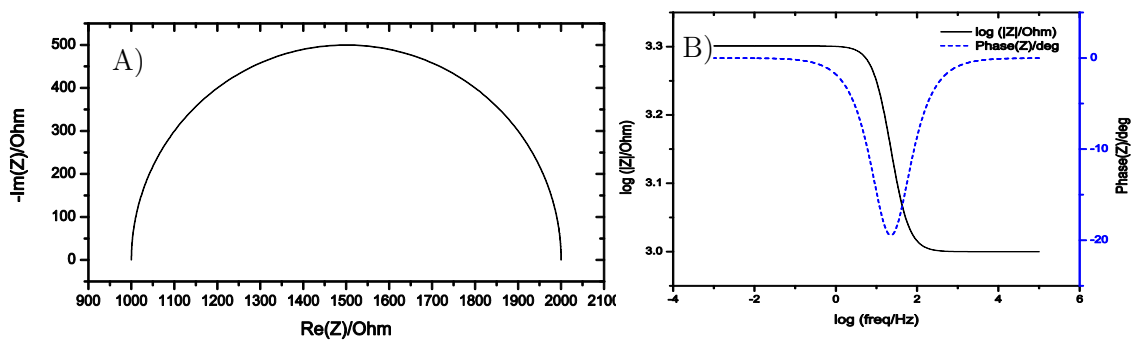


Figure 2.12: Representation of EIS. A) Nyquist plot, and B) Bode plot.

Many studies used EIS for the study of corrosion of metals and coatings. The degradation of the coating was studied and found that the real part of impedance decreases because of the destruction of the film and appearance of conductive paths that are penetrating the film towards the metal, in addition to water uptake [203–206]. Nevertheless, Walter and Deflorian found that the change in the coating resulted in a change in the capacitance [207–210].

In this thesis, electrochemical impedance was used to correlate the magnitude of the impedance as a convolved parameter to the physical change in topography. The use of the magnitude of impedance as a convolved parameter is a fast way to watch the overall change in the impedance, however, it may not be an indicator of which process is taking place. In this thesis, EIS was measured at OCP using a sinusoidal potential wave of 5 mV amplitude, and frequency range 7 MHz to 0.1 Hz, starting with the higher frequencies.

2.1.5.3 Cyclic voltammetry

Cyclic voltammetry is probably the most used approach among the voltammetry techniques. In this technique as shown in Figure 2.13, a potential sweep is carried out linearly from the initial potential to some vertex (E_1), next it is swept to a second vertex (E_2), and then ends up at the initial potential ($E_f = E_i$) while measuring the current. This procedure creates a cyclic effect. Cyclic voltammetry has different applications, as it is powerful in the determination of the reversibility of redox reaction [211]. It is often considered one of the basic experiments electrochemical study and most commonly used for acquiring qualitative information about electrochemical reactions [212,213]. It is widely used in corrosion science as a tool for testing the reversibility of the metals and their coatings. Plotting the current measured against the applied potential gives a voltammogram, which has oxidation and reduction current peaks at some potential. These peaks give an information about the potential at which a reduction or oxidation is taking place. The current peaks are influenced by many factors such as temperature, the electrolyte concentration, the sweeping rate, and the change of the oxidation or reduction state.

In this thesis, cyclic voltammetry was used to find the irreversibility of the coating and to correlate that to the change in topography. Multiple sweeps were carried out within a potential window from -500 to 500 mV around OCP with a sweeping rate 10 mV/s.

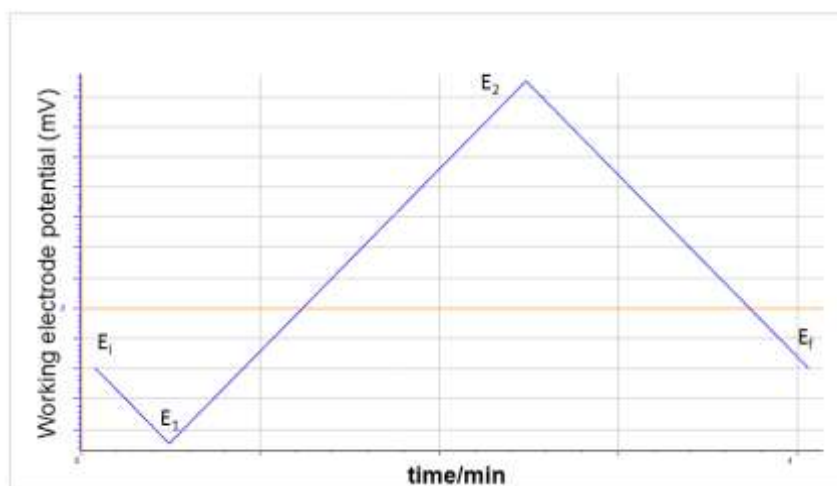


Figure 2.13: The potential waveform used in cyclic voltammetry.

2.1.5.4 Staircase voltammetry

The staircase voltammetry is another voltammetry technique. In this technique, the potential is increased in steps and dwelled for a period, then increased again while measuring the current. This technique is very close to linear sweep voltammetry, except that it is applied in digital steps rather than a constant sweeping rate. The scan rate can be approximated by the ratio of the step potential to the step period. Staircase voltammetry is supposed to reproduce the results of the linear sweep voltammetry. However, one advantage of staircase voltammetry over linear sweep voltammetry is that the former current is measured at constant potential and therefore it discriminates against charging currents. A detailed comparison between the linear sweep voltammetry and

staircase voltammetry can be found in Ref. [214,215]. More details about the theory can be found in Ref. [216].

Staircase voltammetry was used in this thesis to study the change of the coating when a different potential is applied while AFM is imaging the topography. Meanwhile, the current response of the applied potential was measured. The step period was chosen so that AFM could acquire an image within this period. Therefore, the applied potential and the current response could be correlated to the change in topography.

2.1.5.5 Chronoamperometric pulses

It is one of the voltammetry techniques, sometimes referred to as the potentiostatic pulse test (PPT). In this technique, a pulse of potential is applied to the working electrode and the current is measured. This technique is useful in case of high impedance coating, such that it can detect the degradation of the coating when EIS is unable to detect the degradation in its early stages for that high impedance coating. When comparing this technique to EIS, the latter has the advantage that it can find all the circuit elements for the equivalent circuit that models the system. However, PPT is capable of determining the simple equivalent circuit. Therefore, PPT is unable to determine some parameters such as coating capacitance. However, EIS yields a more accurate data in the case of coatings that do not have a very high impedance. Some studies used this technique to characterise the coating [217] and to examine the kinetics of oxide layer growth [218].

Pulses of different amplitude were applied to test the coating and induce it to degrade. The pulses were used in combination with other measurements such as EIS, and OCP, in addition to AFM.

2.1.5.6 Chronopotentiometric pulses

This technique is also referred to as galvanostatic pulse test. This technique is similar to chronoamperometric pulses, however, this is not a voltammetry technique [219,220]. In this technique, a pulse of constant current value is applied to the working electrode, and the corresponding change in the potential is measured [221]. The advantage of this technique is that it has control over the reduction and oxidation processes. In other words, the applied (oxidation or reduction) current results in a constant rate of oxidation or reduction of the electroactive species. Consequently, the electrode potential changes with time as the concentration ratio of reactant to product changes at the electrode surface [222].

In the present work, this technique was used to avoid the evolution of gas bubbles resulted from the chemical interaction of the electrolyte with the working electrode under the application of external potential, because of its ability to control the rate of reaction.

In this work, two different potentiostats were used. The first Potentiostat (Autolab PGSTAT 30 potentiostat-galvanostat) was used only in the polarisation experiments of aluminium in Section 4.2.1. The second potentiostat (Bio-Logic SP-200; Bio-Logic SAS, Claix, France) was used for the rest of the experiments.

2.2 Materials

In this section, the materials used in the thesis will be described. This section is starting with the preparation of the electrolyte solution as an important medium for the ionic transport in addition to its corrosive nature, and is followed by the mechanical polishing

of metal samples used for AFM measurements. Then the preparation of a gel, and reduced graphene oxide coatings, and initial tests of the samples before starting any electrochemical measurements is described.

2.2.1 Electrolyte

The electrolyte is the medium where electrochemical reactions take place, usually it is a solvent that has dissolved mobile ions to carry the current of charges. The importance of electrolyte is that those mobile ions in an electrochemical cell permit control and/or measurement of electrode potential in the cell with the help of a measuring device such as a potentiostat. The electrolyte selection criteria in our case were to have a medium of reasonable reactivity, in other words, it is not a very harsh medium for corrosion. In addition, it has a good conductivity, and finally it has to exhibit a low viscosity to allow ionic transport and should not represent an obstacle for the AFM Tip. Moreover, electrolytes can be divided into two categories, i.e., strong (e.g. sodium chloride in water) with high conductivity, and weak electrolytes (e.g. acetic acid in water) with low conductivity, depending on the degree of dissociation into ions. Throughout this work Sodium Chloride (NaCl) of a molar concentration 0.5M (29,220 ppm¹, or 2.922%²), was prepared as an electrolyte to be used for all the experiments as it mimics the concentration of sea water. To prepare the electrolyte of 0.5M concentration a mass of 29.22g of anhydrous NaCl was dissolved in one litre of Milli-Q water of resistivity 18.2 MΩ.cm at 25°C, then it was mixed overnight using a magnetic stirrer, and left for a few days to make sure that the solution was completely mixed to avoid the diffusion during the measurements. One important factor of the electrolyte is its electrical conductivity, which depends merely on the concentration and the temperature. In our case, we are interested in carrying out all the experiments at room temperature (25 °C), from the literature the conductivity was found to be around 4.67 S/m [223].

2.2.2 Samples polishing for AFM measurements

First coupons of aluminium AA2024-T3 (Goodfellow, UK) and pure copper (home produced, Slovenia) of dimensions 2 x 5 cm² were cut into discs of 7 mm diameter. The discs were embedded in a resin and left to dry to be prepared for processing. Then they were ground using SiC papers (Struers) of different grit sizes (800-4000) successively from the coarser to the finer, so as to remove the cutting debris, as well as to have a smoother surface. As shown in Figure 2.14-A the sample still looks rough, which is more clear from the AFM image in Figure 2.14-D. For a smoother surface, the ground samples were then polished using different mono-crystalline diamond pastes (Struers) with different particle sizes (9 µm, 3 µm). Figure 2.14-C shows that the surface looks smoother, with some defects, which are obvious in the corresponding AFM image (Figure 2.14-F), succeeded by finer particle size 0.25 µm, and as a final polishing step colloidal silica suspension of size 0.04 µm (OP-S, Struers). For minimising the corrosion damage, ethanol was used during all the grinding and polishing steps as a lubricant. After polishing, the samples were sonicated in ethanol for 15 minutes, and then they were dried using a gentle flow of high purity 99.99% nitrogen (Scientific Nitrogen, Messer, Slovenia). Then, samples were stored in a dry box for keeping them clean and away from humid air.

¹ Concentration in part per million (PPM)=molarity x molar mass x 1000

² Concentration in percentage = solute's mass dissolved per 100mL of solvent

2.2.3 Preparation of bare metal samples for coating deposition or in-situ AFM measurement

Since the surface has to be flat and clean, it was necessary to investigate the surface cleanness before depositing the coating, or using the bare metal sample for in-situ AFM. Checking the samples topography showed that there are some giant particles, presumably left from the polishing particles as depicted from Figure 2.14-F. Therefore, samples were cleaned by sonicating them in Hexane, Acetone, and Methanol for 15 minutes each in the case of aluminium alloy, while in the case of copper they were sonicated in Acetone and Isopropanol twice for 30 minutes each, then dried using a gentle flow of high purity 99.99% nitrogen (Scientific Nitrogen, Messer, Slovenia).

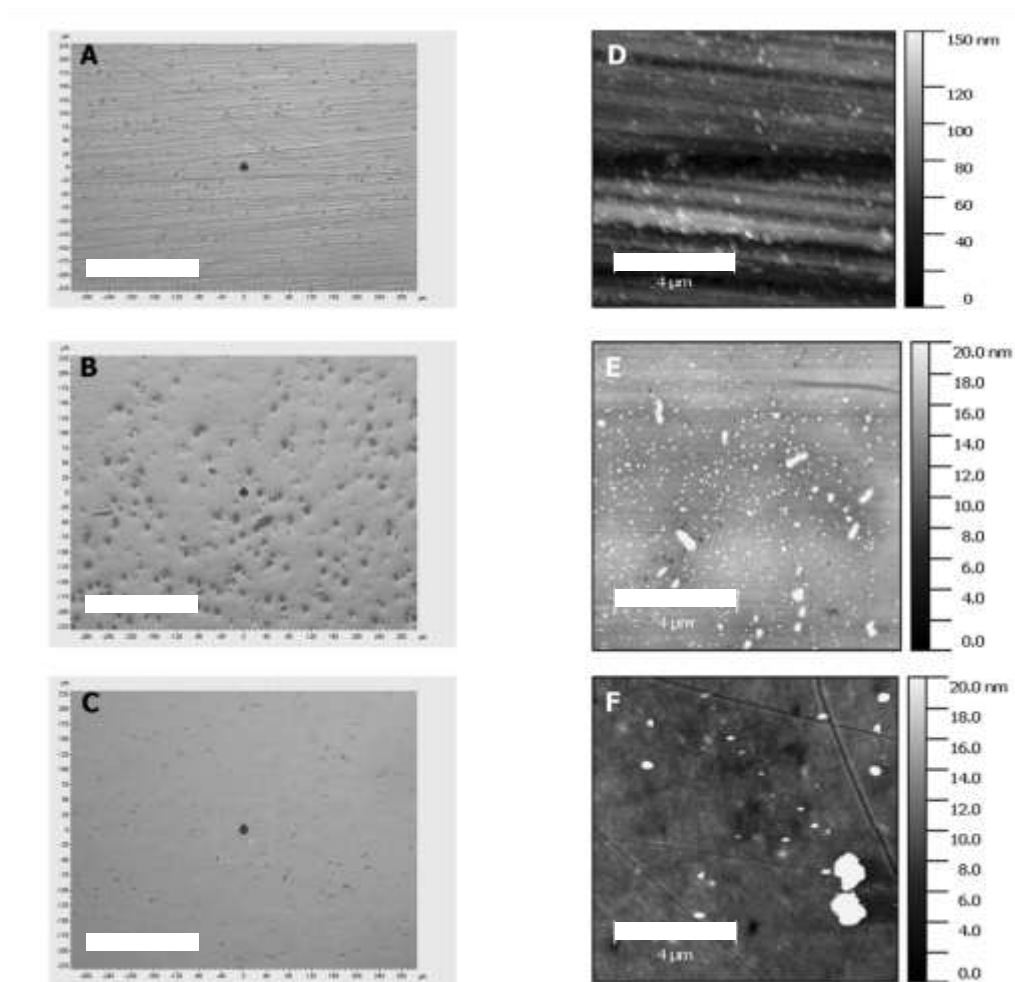


Figure 2.14: Different stages of the sample polishing. The images in the left column are optical images taken using the optical microscope with scale bars of 200 μm length. In the right column are the AFM topography images with scale bars of 4 μm length. A, and D after grinding using SiC paper, B, and E after polishing down using a particle of size 3 μm , C, and F after polishing using OP-S.

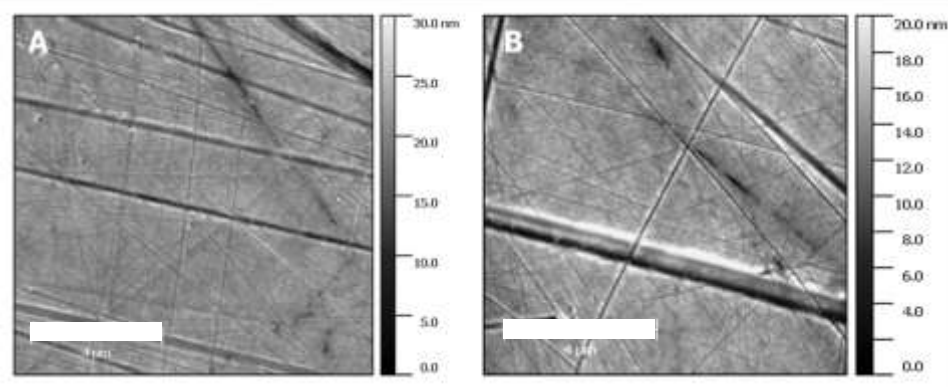


Figure 2.15: AFM topography of AA2024 samples after cleaning. The scale bars are of 4 μm length.

2.2.4 Preparation of gel coated samples

Coating was first prepared in a liquid phase by mixing 1 g of the precursor (3-Mercaptopropyl) trimethoxysilane 95% (Sigma Aldrich) in 10 g of isopropanol (Sigma Aldrich) while stirring for 30 minutes, then 0.275 g of nitric acid (Sigma Aldrich) was added and the solution was magnetically stirred for an hour. During the time of stirring the samples were cleaned, as mentioned in Section 2.2.3, and dried. Subsequently, the coating was applied to the metal surface using dip-coater, in such a way that the metal was dipped into the solution, and then pulled with a speed of 10 cm/minute. The coated samples were then thermally treated by taking them directly to a hot oven at 120 °C. After one hour of heating the samples were removed from the oven and left to cool down to ambient temperature, then they were stored in a dry box.

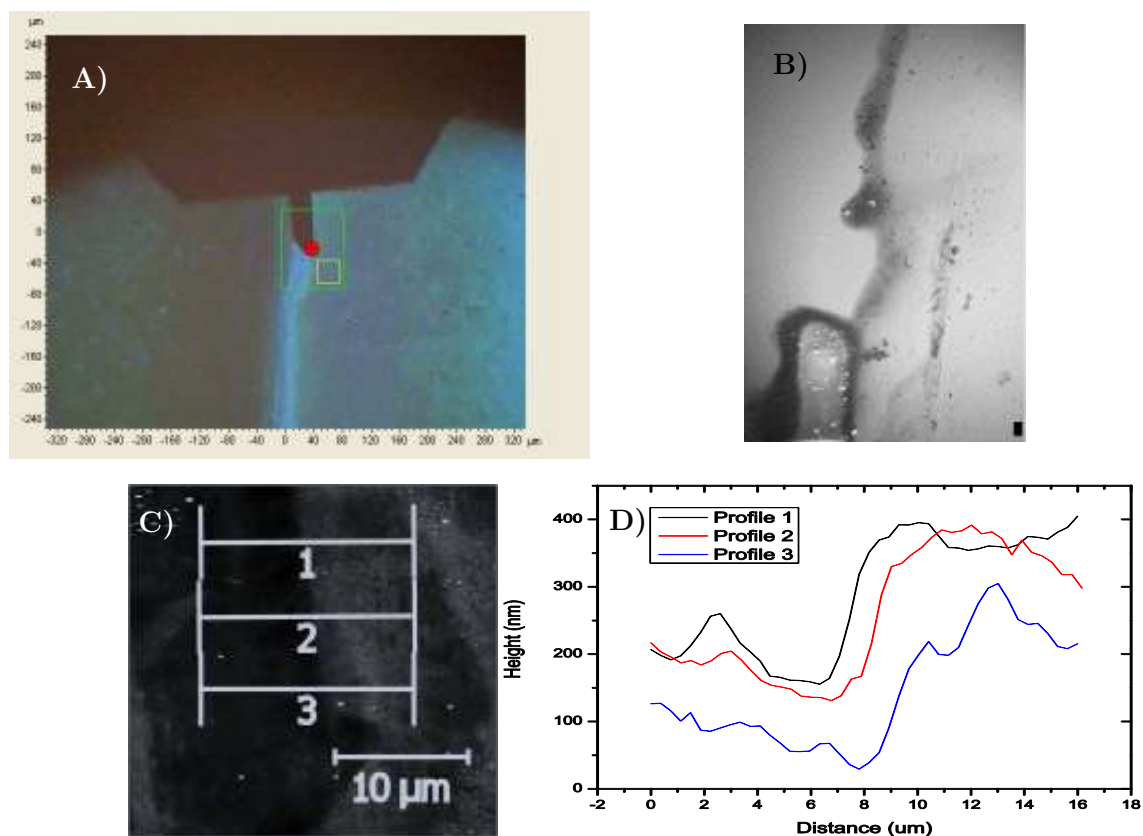
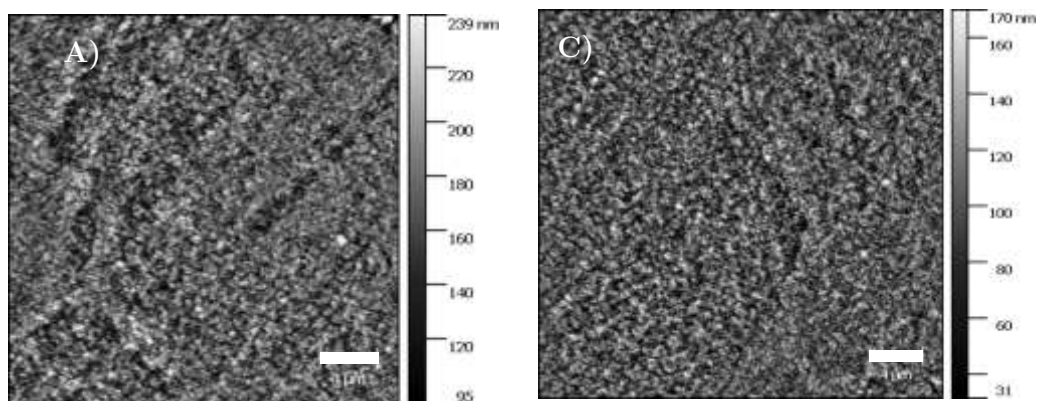


Figure 2.16: AFM topography of a copper gel-coated coupon. A) Optical image, B) SEM micrograph of the coating's edge, C) AFM topography with numbered profile lines across the edge of the coating plotted in D).



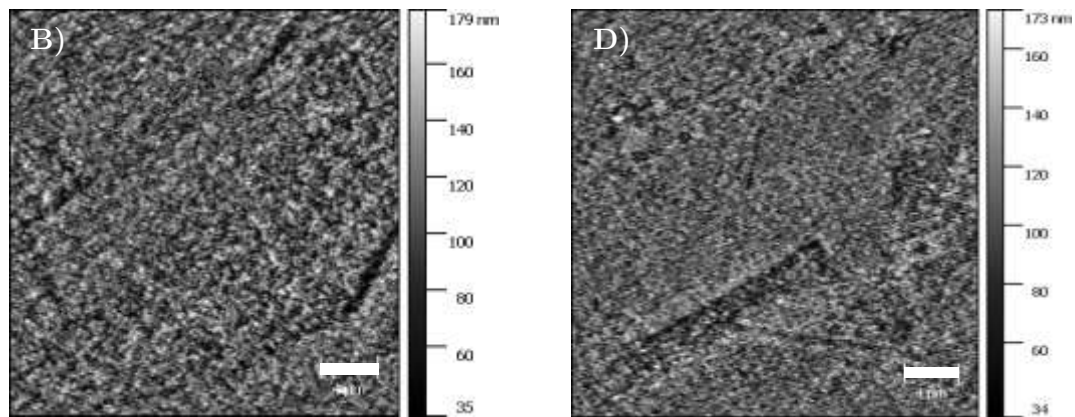


Figure 2.17: AFM topographic images of gel-coated samples: aluminium alloy (A, and B), and copper (C, and D). The scale bars are of 4 μm length.

The coating was applied to both coupons and disks. The coupons were prepared in order to study the thickness of the film using AFM, as well as its uniformity using both AFM and SEM.

In order to find the coating thickness, some coupons were only partly coated - but otherwise using the same conditions. Using the optical microscope attached to the atomic force microscope, the AFM tip was positioned at the edge of the coating as can be seen in Figure 2.16-A. The optical image shows the AFM tip at the edge of the coating with a coating on the right side. While Figure 2.16-C shows the AFM topographic image with line profiles across the coating, this still presents a difficulty in determination of thickness because of the residual of the coating film on the copper side. The height was extracted from the line profile and plotted in Figure 2.16-D, to give a conclusion about the film thickness average 110 nm.

The samples were scanned to check their quality and if coating was homogeneously deposited on the substrate surface. First, the AFM was used to scan the samples and find their roughness. Random locations were scanned on the surface of both copper and aluminium gel-coated samples. As can be depicted from Figure 2.17, each image is of a size of 20 μm x 20 μm . The coating looks evenly distributed on the surface of both aluminium and copper. Some depressions appear on the surface that could be due to the heat treatment after dipping. Since AFM is slow to scan large areas, SEM was used to study the coating's homogeneity. The samples were scanned at a low acceleration voltage (1 kV). Figure 2.18 shows the coating distribution on the copper and aluminium samples. The images exhibit a relatively low contrast, which in turns means that the surface of the coating is uniformly distributed that agrees with AFM results shown in Figure 2.17.

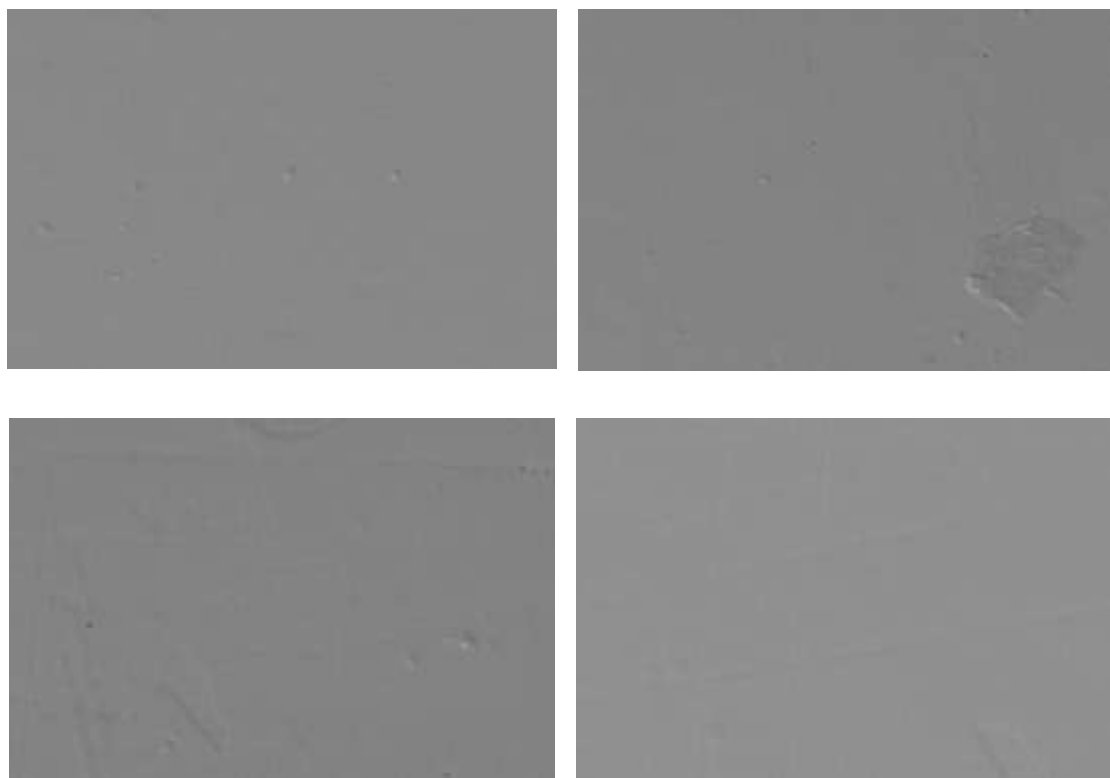


Figure 2.18: SEM micrographs of a gel-coated copper (the first row), and aluminium alloy (the second row). The size of the images is 90 μm x 60 μm .

2.2.5 Preparation of reduced graphene oxide

Reduced graphene oxide (RGO) was prepared by dispersing graphene oxide (yellowish brown paste) prepared using the modified Hummer method [224], in Milli-Q water 18.2 M Ω with concentration 1 mg/ml for 30 minutes. The solution was left in the refrigerator to cool down at 2 $^{\circ}\text{C}$ for two days and was not exposed to light. The samples were cleaned prior deposition as mentioned in Section 2.2.3. A 20 μl drop of the solution was evenly cast on the samples, then they were left to dry for a couple of hours under ambient conditions. For reducing the graphene oxide (GO) coating to graphene-like or reduced graphene oxide (RGO), the samples were then annealed in Argon 95%/H₂ 5% gas (Inoxline H5, Messer, Slovenia) with a flow rate 100 ml/minute at 150 $^{\circ}\text{C}$ for one hour. The annealing was carried out using a programmable oven. Figure 2.19 shows the temperature diagram of the programme used for annealing the RGO-coated sample. At the beginning, the samples were placed inside quartz tubes and sealed carefully using an O-ring, and the gas was purged into the tube with a constant rate of flow using a flow meter, at room temperature for an hour, to make sure that the tube was completely filled with argon/hydrogen gas. Then, the temperature was raised to 35 $^{\circ}\text{C}$ with a rate of 1 $^{\circ}\text{C}$ /minute and the temperature was kept fixed for an hour while purging the gas. At that moment, the temperature was increased again to reach the highest set temperature, which is the annealing temperature (in our case

150 °C with a dwelling time one hour). Lastly, the temperature was lowered at the same rate to the room temperature. Subsequently, the samples were taken out of the tube and stored in a dry box to avoid their exposure to air.

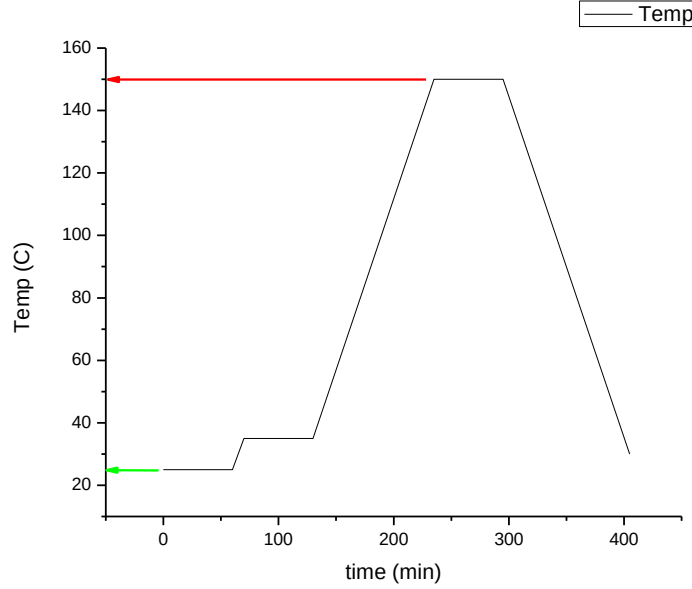


Figure 2.19: Annealing programme of GO-coated copper samples.

For checking the quality of the film, i.e., whether the total surface was completely covered, samples were studied using the scanning electron microscope (SEM), atomic force microscope (AFM), and Raman. SEM is useful in quickly studying a large area of the sample; consequently, the coating distribution on the sample can be studied. Figure 2.20 shows a different resolution of copper RGO-coated sample. As can be seen, the whole sample is covered with the film in Figure 2.20-A. By increasing the resolution (Figure 2.20-B), it can be seen that the reduced graphene oxide is covering the surface of the metal the contrast shows the flakes. Increasing the magnification (Figure 2.20-C) some wrinkles appear on the surface, which is common in the coating of graphene when in it is prepared in the liquid phase. In addition, the graphene flakes show a contrast, so it is obvious from Figure 2.20-D that the flakes have a relatively big size (with a maximum dimension on the order of few μm).

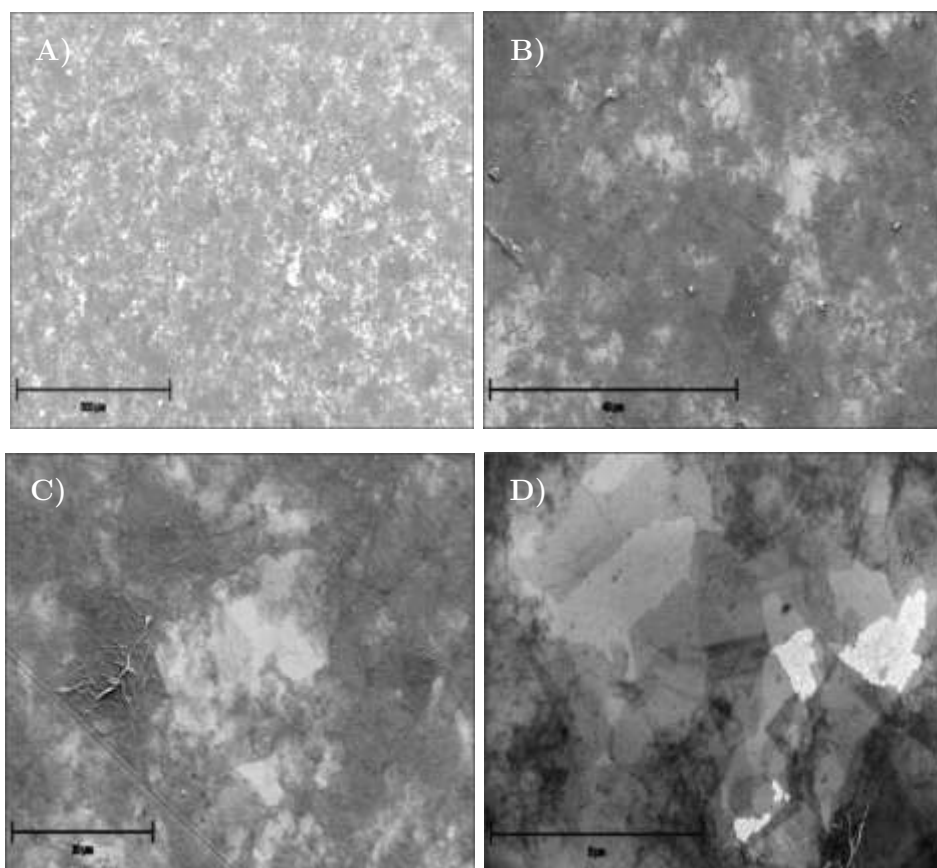


Figure 2.20: Scanning electron microscopy of an RGO-coated copper sample at different magnification. Scale bars are of length 300 μm , 40 μm , 20 μm , and 5 μm .

Micro-Raman was used to check the chemical composition of the coating, for example to check whether the film formed was graphene. This technique also gives information about the degree of reduction of graphene oxide. In order to study the chemistry of the surface before and after annealing, micro-Raman was used to scan a random area of a coated sample. The images on the left side in Figure 2.21 are a mapping of the G-band, and different spectra were selected and plotted on the graphs on the right side. The change in the spectra pattern before and after annealing confirms the partial reduction of graphene oxide, from the reduction of the G band with respect to the D band. A relatively high noise ratio in the spectra after annealing is noticed because a small light intensity was used to avoid the influence of laser on the coating as much as possible.

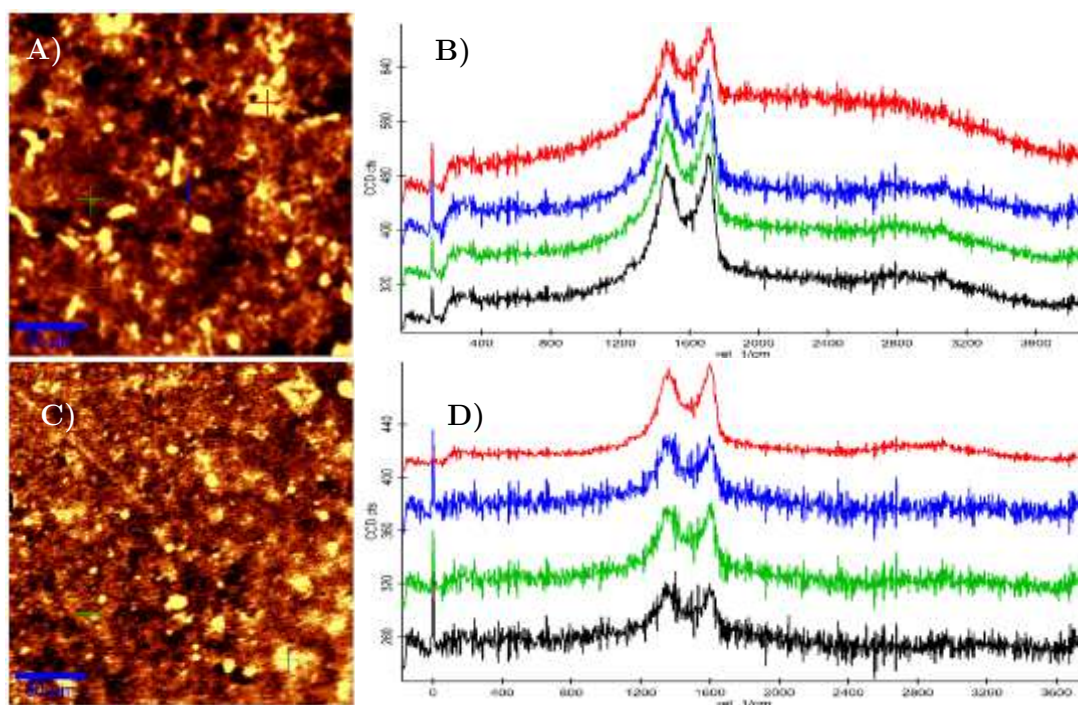


Figure 2.21: Micro-Raman of GO-coated copper. A and B before annealing, C and D after annealing. A and C are the mapping of G-band for areas of size 150 μm x 150 μm . B, and D are selected Raman spectra from the scanned area.

Finally, AFM was used to study the topography of the surface before and after annealing. It can be concluded from Figure 2.22 that no major change in the topography of the film after annealing occurred. In addition to that wrinkles are more dominant than flat flakes.

2.2.6 Preparing samples for in-situ AFM measurements in the cell

To start performing measurements using the electrochemical cell, first, the cell was cleaned by washing it using a detergent in tap water, and then it was rinsed carefully. Afterwards, it was sonicated twice in deionized water to clean it for 30 minutes with changing the water each time, and then it was sonicated in acetone for degreasing, followed by isopropanol 30 minutes each. At last, it was sonicated in Milli-Q water for 30 minutes. Next, the sample was then mounted in the centre of the cell. To make sure of good electrical contact with the conductor fixed at the bottom of the cell, a conducting silver paste was added below the sample (between the sample and the conductor at the bottom), which on the one hand ensures the electrical connectivity to the wire-connected potentiostat, and on the other hand it makes the sample mechanically fastened. The sample height was adjusted to make sure it is at the same level as the base of the cell. Thus, paraffin wax was applied to the circumference of the sample so that the edges of the sample will be covered and it helps in anchoring the sample.

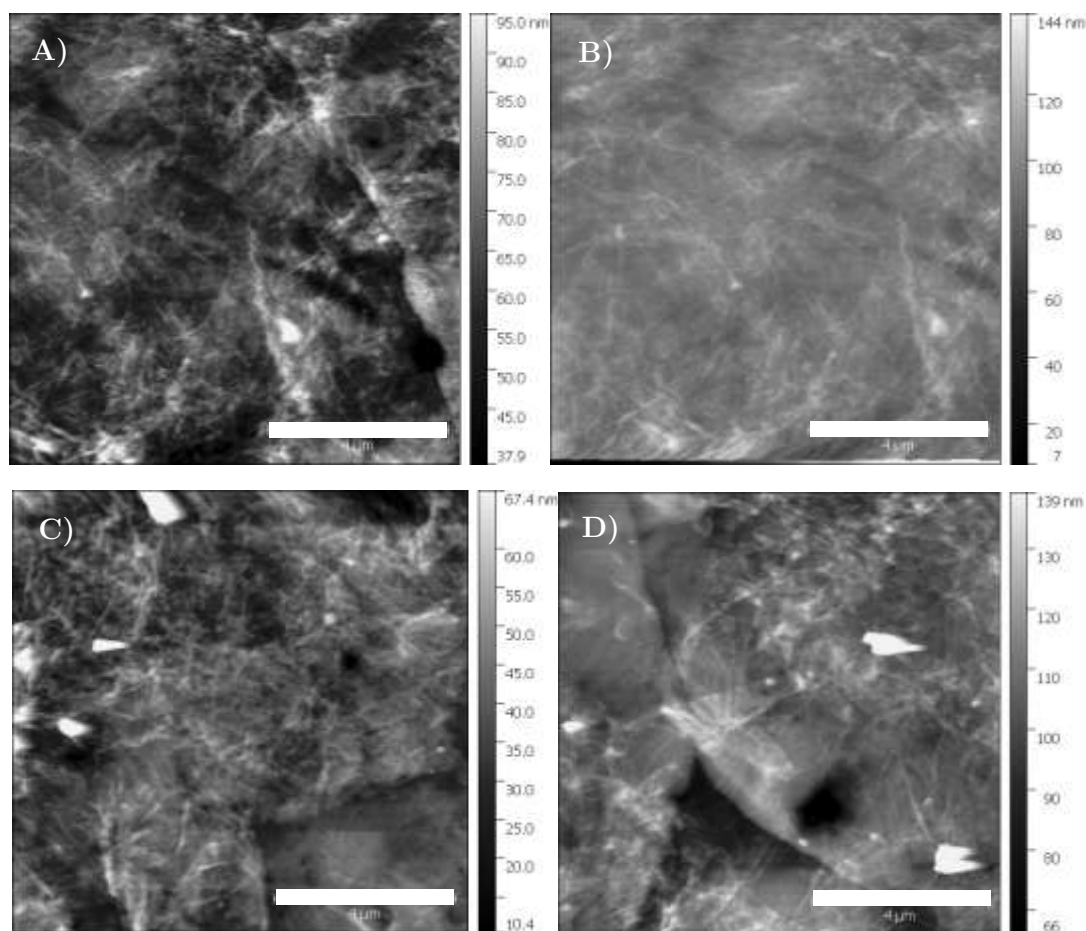


Figure 2.22: AFM topography of graphene coated copper. A, and B were taken before annealing, C and D were taken after the annealing. The length of scale bars is 4 μm .

Chapter 3

Electrochemical Cell Design and Simulation for In-Situ AFM

3.1 Introduction

In the field of corrosion, AFM and STM have been widely used [116,117,119–121,159,225] owing to their ability to resolve the change in topography under corrosion conditions. AFM is preferred over STM when it is working in liquid. Namely in the case of STM the current needs to tunnel from the tip to the surface; the tunnelling current is superimposed on the faradic current, which influences the measurements. On the other hand, in the case of AFM the surface topography is measured by deflection of a cantilever using optical detection method. In addition, when AFM is operated in liquid the capillary forces are eliminated. That makes AFM a powerful tool, as it does not only have the ability to investigate the electrode-electrolyte interface in different solutions but it is also capable of probing the change in topography during the application of different electrochemical measurements without introducing any perturbations to the electrochemical measurements.

Electrochemical techniques, such as electrochemical impedance spectroscopy, cyclic voltammetry, or other pulse techniques, have the ability to probe the changes in the surface that take place because of oxidation/reduction reactions.

Integrating both AFM and electrochemical techniques can yield a fruitful information about the local change of the surface in different fields, such as corrosion, surface catalysis, and metals deposition [226]. When AFM or STM are used for measuring the change of topography under electrochemical conditions, they are called electrochemical atomic force microscope (EC-AFM), or electrochemical scanning tunnelling microscopy (EC-STM). In order to carry out one in-situ measurement that requires having a fluid cell, a working electrode (the sample under study), a counter electrode, bi-potentiostat or potentiostat, and optionally a reference electrode.

In the case of using a cell for electrochemical measurement, it is preferable to use three electrodes cell as shown in Figure 2.11, in which a reference electrode is ideally used for independently measuring the potential of a point of the equipotential surface between the working electrode and the counter or auxiliary electrode. The counter electrode is used to close the circuit of the passed current. Three-electrode cell is preferably used in the case that electrochemical impedance spectroscopy is measured.

Most of the commercially available AFM liquid cells have a very small volume of 0.1 ml [14,114,122], in some other studies it was even less, 50 μ l [18]. Some commercial cells use O-ring to seal the sample and attach the cell's compartment on the top using springs and clips. This configuration requires a large sample area and makes the sample a subject to

crevice corrosion because the gas could be trapped between the surface and the O-ring or because of the concentration gradient nearby the ring. The small cell volume results in inaccurate electrochemical measurements since the small volume (within few hundred μl) affects the ionic transport and does not allow degassing of the cell. In the case of open cell designs, the small volume of electrolyte gives rise to an increased evaporation rate because of the relatively high surface to volume ratio, which consequently influences the electrochemical measurements. Moreover, the evaporation of liquid can result in a local change of viscosity, density, and pH value, and consequently, it makes the surface susceptible to local corrosion. Some configurations of commercially available electrochemical cells for AFM use the reference electrode (RE), and counter electrode (CE) located in the liquid ports and away from the working electrode. Not only has this configuration introduced electric field asymmetry, but also transport complications of ions.

In literature, a few alternative designs have been suggested [227–231]. Wanless et al. [227] introduced the first electrochemical cell for AFM that integrates all the electrodes in the cell instead of having them connected to the cell through liquid ports. They also considered the problem of field symmetry inside the cell, by using a ring of platinum ribbon, and quasi-reference electrode of platinum wire. The increased evaporation of the liquid for small cells was studied by Yaniv and Jung [229]. They used different cell sizes, and to compensate the evaporated liquid the cell was connected to an external reservoir of the liquid and reservoir compensates the evaporated liquid because of the difference in pressure. However, they found from the electrochemical measurements that the concentration is increasing and they deduced that it could be because of the evaporation of the solvent while the solute remains inside the cell. Valtiner developed an interesting design of electrochemical cell [231]. He also presented all the challenges in designing an electrochemical cell for AFM. In this design, the working and counter electrodes were made by physical vapour deposition of platinum on glass slides. The configuration of working and counter electrodes was coplanar. The diameter of the working electrode was 6 mm, enclosed inside the counter electrode, which has an inner diameter of 10 mm and the outer diameter of 30 mm. The reference electrode was inserted horizontally through a port. They used another setup of two separate compartments, which is relatively complicated to be used.

Yet, no cell could enable simultaneous AFM and EIS measurements. Thus, our goal is to design a cell that fulfils the following criteria. First, the cell needs to have a relatively large capacity (larger than 1 ml) for the liquid in order to avoid the effect of electrolyte evaporation. In addition, a robust mechanical setup is required; therefore, it does not introduce any mechanical noise or vibrations that can affect the topographical and electrochemical measurements, the possibility of using inlet and outlet ports for fluid flow. Moreover, the cell must have a uniform distribution of the field, so the error and/or distortions in measurement can be reduced. It is easy to be used, and cleaned. Finally, it allows using a standard reference electrode, which helps in reducing the error in the measured potential in an electrochemical cell.

In this chapter, first, two different designs of electrochemical cells will be presented followed by the fabrication and selection of the material. Then, the physics of charge transport in the electrolyte is introduced which represents the basics of simulation in the next section for the two different designs of an electrochemical cell for in-situ AFM measurements and electrochemical measurements, simultaneously. Finally, a test of the cell was carried out by measuring electrochemical impedance spectroscopy of aluminium alloy sample and scanned the surface before and after injecting the electrolyte into the cell.

3.2 Cell Design

For designing an electrochemical cell for SPM measurements, many factors have to be considered. The biggest problem, in this case, is the space constraint, which is shared between all the microscopes. Electrode arrangement is important since inappropriate arrangement can introduce error and/or distortion [232,233] in the electrochemical measurements.

The first cell was designed principally to study the spontaneous corrosion of samples by immersing them in the electrolyte. Therefore it was only one electrode in the preliminary design centred in the cell as shown in Figure 3.1-A. Then, the cell was modified to apply electrical pulses and measure selected electrochemical parameters, which is shown in Figure 3.1-B by using two additional electrodes; a platinum counter electrode in the form of rectangle, and standard Ag/AgCl/NaCl Satd reference electrode making an angle of 90° to the counter electrode. In order to be able to use this design, the AFM scanner head has to be removed every time to be able to inject the electrolyte into the cell, which consumes more time to re-install the scanner head. Here the biggest drawback is that it is hard to relocate the spot that was scanned before removing the scanner. This design drawback does not only cause difficulties in relocating the same spot in air and liquid but also the geometrical arrangement of the electrodes, which influences the electrochemical measurements that will be discussed later.

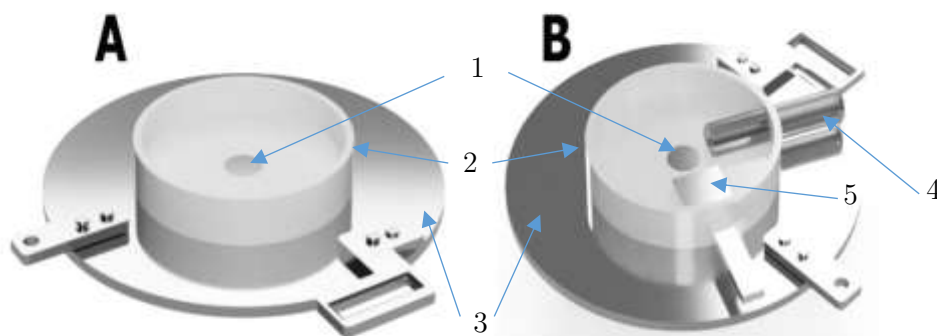


Figure 3.1: Schematic of the first electrochemical cell design. A) Preliminary design, B) three-electrode cell after upgrading the preliminary design (A) by embedding reference and counter electrodes. The working electrode (1) is centred in the cell body (2) that is made of Teflon, mounted on a stainless steel base (3) so it can be attached to the microscope. The standard Ag/AgCl reference electrode (4) is plugged in from the bottom, and the counter electrode (5) made of platinum sheet formed to make a cylindrical shell.

The second design shown in Figure 3.2 was constructed to make the measurements easier and more precise (i.e. decreasing the measurement error because of the geometrical

arrangement) by making all the electrodes with almost fixed positions for the purpose of repeatability of electrochemical measurements, and to be able to scan the very same spot area's topography in air and electrolyte. Moreover, the cell was also designed to be used as a flow cell for future applications such as in-situ AFM/STM electrochemical deposition. The design can be used also for optical measurements such as in-situ Raman by a slight modification to cover the top of the cell with a quartz glass. To be able to carry out such measurements, the geometrical arrangement of electrodes had to be considered. For designing the arrangement of the electrodes, one important criterion considered is to have a symmetric distribution of the electrical field inside the cell between the working electrode and counter electrode, which makes it a good cell for different applications such as measurements of electrochemical impedance, which is mostly used in this work and to be used for uniform in-situ AFM/STM electrochemical deposition, in future work. In this design, the working electrode was centred in the middle of the cell. A standard reference electrode Ag/AgCl/NaCl Satd was inserted from the bottom and made to be as close as possible to the working electrode maintaining that it will not disturb the tip from approaching the sample (working electrode). The counter electrode of the platinum sheet was made in the form of the cylindrical shell to surround the working electrode for maintaining the electrical field symmetry that will be shown in the simulation below.

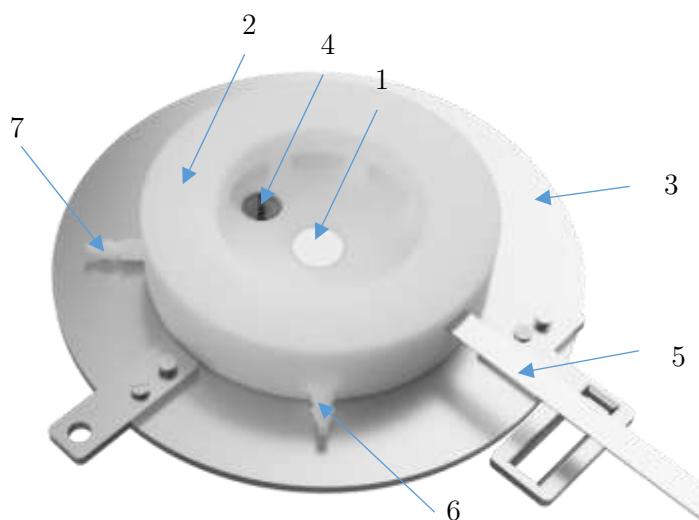


Figure 3.2: Schematic of the second cell design. The working electrode (1) is centred in the cell body (2) that is made of Teflon, mounted on a stainless steel base (3) so it can be attached to the microscope. The standard Ag/AgCl reference electrode (4) is plugged in from the bottom, and the counter electrode (5) made of platinum sheet formed to make a cylindrical shell. The cell has an inlet (6) and outlet (7) ports to enable injecting the liquid.

3.3 Background

Electrochemical cells are categorised into two different types of cells, either galvanic cell or electrolytic cell. A galvanic cell is a cell in which reactions are spontaneous, in other words, the change in Gibbs free energy is negative when the electrodes are connected. Galvanic cells are energy driving cells such as batteries where the chemical energy is converted to electrical energy. In contrast, the electrolytic cell is energy driven in which the change in Gibbs free energy is positive which means the reaction is not spontaneous, and it needs the energy to start. Electrolytic cells are energy driven, for example, the cells used for electroplating where the electrical energy is converted into chemical energy. Some cells can be galvanic and electrolytic, in that case they are called secondary galvanic cells, for example, the rechargeable batteries.

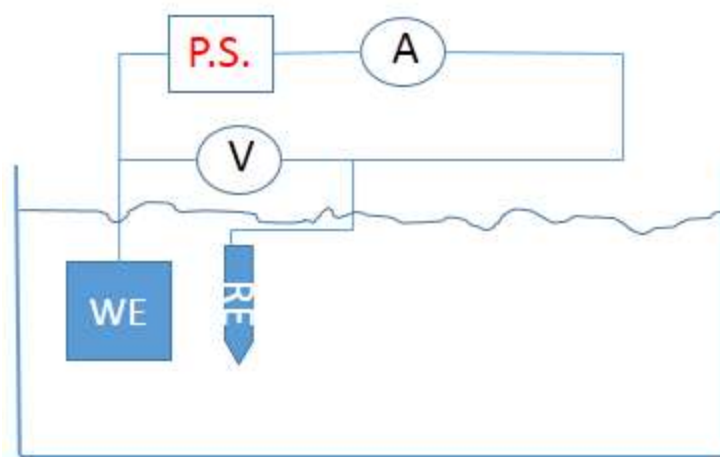


Figure 3.3: Schematic of two-electrode electrochemical cell. WE is the working electrode, RE is the reference electrode, and P.S. is power source which could be A.C., or D.C.

As mentioned above an electrochemical cell can be composed of either two or three electrodes. The two-electrode cell consists of a working electrode and a reference electrode. The current passes through both the working and reference electrode. In that case, to reduce the error and the potential drop between the electrodes, a large area, low resistance reference electrode is used. The problem with this cell is always the error in measuring the potential that requires the cell to have a low resistance. Therefore, the three-electrode cell is used to reduce the error in measuring the potential by incorporating an additional electrode to supply/sink the current called auxiliary or counter electrode. In the three-electrode cell, the current is applied between the working and counter electrode and potential is measured between the working and reference electrode [234]. The reference electrode should be reversible and has an unchangeable potential during the measurement [235]. The reference electrode consists of a salt bridge and is connected to the electrode through a lugging capillary, and to reduce the error the capillary is positioned in the vicinity of the working electrode. If the cell resistance is high, careful attention must be paid to the arrangement of the electrodes inside the cell as well as the electrodes geometry because of the ohmic drop.

The uniformity of current and potential distribution is of interest in the laboratory for minimising the error in the measurement of polarisation resistance, electrode kinetics, and most of the electrochemical measurements. Therefore, the motivation of this work is to study the effect of changing the cell and electrode geometries on the field distribution inside the cell, which consequently affects the electrochemical measurements because of the change in the local electrochemical potential distribution.

Current lines distribution is a critical issue in designing the electrochemical cell, since its non-uniformity is unfavourable in many cases because of its influence on the electrochemical processes in the cell. For instance, the area of the electrode that undergoes higher current density is more prone to degrade faster than its corresponding area with a lower current density. In many electrochemical systems, it is always desired to know the current density distribution to be optimised for the sake of first minimising the error in the measurements, and second minimising the unwanted effects (e.g. inhomogeneous deposition in the case of electrochemical deposition, and inhomogeneous degradation of electrodes).

The electrolyte has a finite ionic conductivity that consequently leads to an ohmic voltage drop between the electrodes across the electrolyte, which can be represented by a resistor as shown in Figure 3.4. This voltage drop reduces the potential applied to the electrode to change the overpotential at the electrode surface [236].

To elucidate the effect of the finite electrolyte conductivity, let us consider the three-electrode cell in Figure 3.4. If we need to apply a potential u_{app} to the working electrode (WE) to achieve an overpotential on the electrode with value η_{true} because of the solution finite conductivity a higher potential must be applied in order to compensate the potential drop across the electrolyte ($J\rho_l$) [236]. That can be given by the following equation:

$$u_{app} = \eta_{true} + J\rho_l + u_{corr} \quad (3.1)$$

where:

u_{app} : the applied potential to the working electrode (V).

η_{true} : the true value of the overpotential (V).

J : the current density (A/m²).

ρ_l : the electrolyte specific resistance (Ohm.m²).

u_{corr} : the corrosion potential (V).

It can be inferred from Eq. (3.1) that in order to reach a true overpotential value, a higher potential must be applied, which is obviously due to the term ($J\rho_l$). From Eq.(3.1), we can express the applied overpotential value as:

$$\eta_{app} = \eta_{true} + J\rho_l \quad (3.2)$$

Hence,

$$\eta_{app} = u_{app} - u_{corr} \quad (3.3)$$

Eq. (3.2) implies that if $(J\rho_l)$ is changing locally or is inhomogeneously distributed, then η_{app} has to be changed locally to maintain a fixed value of η_{true} , which means that u_{app} has to be changed locally to compensate the difference in $(J\rho_l)$.which is impractical.

Eq. (3.3) infers two possible cases:

- 1- If the electrode is polarizable ($\eta_{true} \gg (J\rho_l)$), ρ_l diminishes and becomes negligible.
- 2- If the electrode is non-polarizable ($\eta_{true} \rightarrow \text{zero}$), ρ_l comes into play and controls the current distribution.

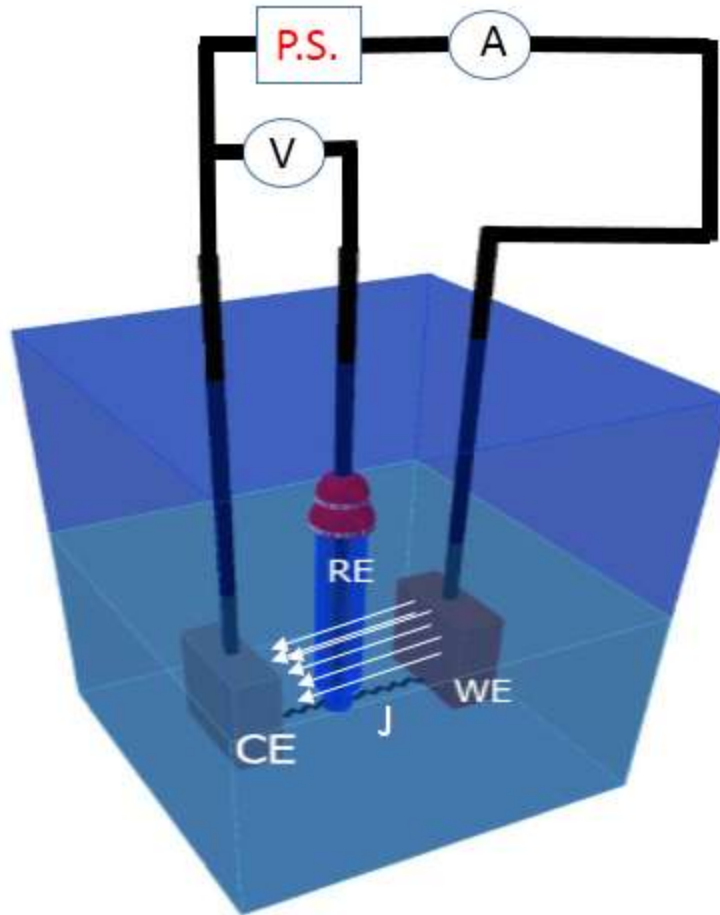


Figure 3.4: Schematic of a traditional three-electrode electrochemical cell. A larger u_{app} has to be applied to the cell to maintain the theoretical value of the overpotential that is because of the finite resistance of electrolyte between the counter electrode (CE), reference electrode (RE), the working electrode (WE), and PS is the power source. The arrows indicate the direction of the current vector ($\mathbf{J}$).

The rules for the current and potential distribution are as follows:

- 1- Current is described by current lines, and potential is described by isopotential (lines in 2D, or surfaces in 3D).
- 2- Current lines are perpendicular to isopotential (lines, or surfaces).
- 3- Current lines start and terminate at one of the electrodes.
- 4- In the case of primary current distribution (will be mentioned below), isopotential (lines, or surfaces) is parallel to the electrode's surfaces. In this case, the reaction is very fast at the electrode's surface and the cell is non-polarizable (interesting to be studied in the case of high current density cell).

- 5- In the case of secondary and tertiary current distribution, isopotential (lines or surfaces) may vary locally depending on the local value of the true overpotential. This variation of true overpotential is of great importance in different cases such as galvanic corrosion, cathodic protection, electrochemical deposition, etc. since the overpotential induces electrochemical reactions. The secondary and tertiary current distributions are described in sections 3.3.1.2 and 3.3.1.3, respectively.

To understand the current and potential distribution, we need to study the governing equations of the transport mechanism in the electrolyte. The current in the electrolyte is generated owing to the ionic movements, in other words, ions flow in electrolyte resulting in ionic flux N that can be given by Nernst-Planck Eq. (3.4) [235]. The three transport mechanisms are included in Eq. (3.4). The first term in Eq. (3.4) represents the diffusion mechanism in the electrolyte, which is due to the concentration gradient. The negative sign means that ions diffuse to the lower concentration region, while the second term represents the migration mechanism that takes place when charges (ions in this case) are influenced by an electric field. The negative sign means that positive ions move in the direction of the negative potential gradient, and the third term describes the convection transport mechanism because of the bulk fluid flow.

$$\mathbf{N}_i = -D_i \nabla c_i - z_i \mu_i F c_i \nabla \varphi_l + c_i \mathbf{v} \quad (3.4)$$

where

$\mathbf{N}_i$: Flux (velocity x concentration) (mol/ (m².s))

D_i : Diffusivity of ion i (m²/s).

c_i : Concentration of ion i (mol/m³).

z_i : Valence of ion i.

μ_i : Mobility of ion i, which describes its ease of motion (mol m²/ (V.s)).

F : Faraday constant 96485.33289 (A.s/mol).

φ_l : Ionic potential (V).

$\mathbf{v}$: Velocity vector (m/s).

The current density vector is given by

$$\mathbf{J} = F \sum z_i \mathbf{N}_i \quad (3.5)$$

Hence,

$$\mathbf{J} = F \left[- \sum D_i z_i \nabla c_i - \sum z_i^2 \mu_i F c_i \nabla \varphi_l + \sum z_i c_i \mathbf{v} \right] \quad (3.6)$$

Because of the electro-neutrality of electrolyte, the third term in Eq. (3.6) will vanish to have the current density described by

$$\mathbf{J} = F \left[- \sum D_i z_i \nabla c_i - \sum z_i^2 \mu_i F c_i \nabla \varphi_l \right] \quad (3.7)$$

With the intention of understanding Eq. (3.7), let us first begin with a simple cell arrangement with two parallel electrodes as shown in Figure 3.4. For the sake of simplicity, we can assume that the concentration gradient is negligible (i.e. $\nabla c_i = 0$), this assumption is true for the bulk of solution away from the electrode/electrolyte interface where an electrolyte double layer is formed. In this case, Eq. (3.7) reduces to Ohm's law given by Eq. (3.10).

$$\mathbf{J} = - \sum z_i^2 \mu_i F^2 c_i \nabla \varphi_l \quad (3.8)$$

By defining the conductivity

$$\kappa = \sum z_i^2 \mu_i F^2 c_i \quad (3.9)$$

Hence, the current density can be given by

$$\mathbf{J} = -\kappa \nabla \varphi_l \quad (3.10)$$

By having a look at Eq. (3.10), we can deduce that in the simple cell arrangement in Figure 3.4 the current density is constant everywhere in the cell between the electrodes because the potential gradient in the electrolyte is constant across the cell. It can be noticed also that the current density depends on the geometry of the electrodes due to the potential gradient term.

3.3.1 Current distribution

The current distribution in the electrolyte can be classified into three categories, depending on the reaction process.

3.3.1.1 Primary current distribution

In this case, the kinetics at the electrode/liquid interface are extremely fast which gives us the privilege to assume that the potential of the electrode is constant, which is given by the Nernst equilibrium potential. The only factor controlling the current distribution, in this case, is the potential distribution in the electrolyte, which in turn depends on the electrode geometry and the electrolyte conductivity. In this case, the resistors in Figure 3.4 have a finite value that represents only the solution resistance, therefore the current could be non-uniform in the case of the irregular geometry.

3.3.1.2 Secondary current distribution

In this case, the kinetics at the electrode/liquid interface are no longer fast like as in the primary current distribution, therefore they have to be taken into account during the calculations of the electrode current and the constant potential at the electrode is no longer a valid assumption. Moreover, the potential can vary locally on the electrode across the electrochemical interface, however, the domain equation in the electrolyte remains ohmic, which can be seen in Figure 3.4, with a larger resistor value to represent the slower reaction, which is due to the slower charge transfer.

3.3.1.3 Tertiary current distribution

In the case of the tertiary current distribution, mass and charge transport have to be considered since they both affect the electrode kinetics. Moreover, the concentration gradient can result, in this case, in concentration overpotential. Due to the big increase in the resistance value in Figure 3.4, current density distribution becomes more symmetric, as the current spreads because of the high interfacial resistance, which depends on the potential.

The non-uniformity of current can be described by the ratio of local current density divided by the average current density (the total current divided by the total area); hence, the variation of the current can be seen with the change in the position.

3.4 Simulation of the Electric Current and Potential Distribution in the Electrochemical Cells

The symmetry of the field distribution in the cell is an important factor in an electrochemical cell in order to reduce the error in measurement. The purpose of simulating the electric field in electrochemical cell is to find how the electrical currents and potentials are distributed inside the cells, and how they change with changing the electrode configuration. The simulation was carried out to find the current lines distribution in the cell as well as potential. Therefore, a comparison between the two different designs can be carried out.

To start the simulation of the current distribution in a cell, a set of differential equations is solved using the finite element method. Through defining the boundary conditions for each geometry, the solution can be determined. In this section, the simulation of the electrochemical cell will be discussed for calculating the current and potential distribution in two different cell geometries that were designed for in-situ AFM measurements.

3.4.1 Primary current distribution

First, I will start by studying the primary current distribution. As mentioned above the primary current density distribution is the case in which kinetics on the electrode surface are fast which gives the privilege for the assumption that the potential is constant on the surface with the application of potential to the cell (i.e. $V_{el} = \text{constant}$).

In order to find the field distribution, we assume that the working electrode is the anode and the counter electrode is the cathode.

Cathode potential was chosen to be zero ($V_C = 0$), since the potential of the electrode equals the potential difference between the electrode and the ionic potential of the adjacent liquid ($V_{el} = V_{Solid} - \phi_{liquid}$).

Since the kinetics are fast, that leads to the fact that the equilibrium potential equals the potential difference between the solid phase potential of the cathode and the adjacent electrolyte potential which implies that

$$V_{eq}(cathode) = V_C - \varphi_C = -\varphi_C \quad (3.11)$$

Since the cell potential is the potential difference between the anode and the cathode

$$u_{cell} = V_A - V_C = V_A \quad (3.12)$$

$$V_{eq}(anode) = V_A - \varphi_A = u_{cell} - \varphi_A \quad (3.13)$$

In addition, from the continuity equation, the current divergence is zero.

$$\nabla \cdot \mathbf{J} = 0 \quad (3.14)$$

3.4.2 Secondary current distribution

As mentioned above, the kinetics are not fast enough, therefore the constant potential at the electrode with the application of potential to the cell is no longer a valid assumption. Moreover, the electrochemical reactions taking place at the electrode interface have to be taken into account, which is given by the reaction driving force (overpotential).

The local current density is described by the Butler-Volmer equation

$$J_{local} = J_o \left[e^{\frac{\eta(1-\beta)F}{RT}} - e^{\frac{\eta\beta F}{RT}} \right] \quad (3.15)$$

Where

T: The temperature (K).

R: The gas constant (J/K.mol).

J_o : The exchange current density (A. m⁻²).

β : The symmetry factor, electrode dependent.

η : The overpotential that is the difference between the electrode potential and equilibrium potential.

$$\eta = V_{el} - V_{eq} \quad (3.16)$$

By substituting from Eqs. (3.11) and (3.13) into Eq. (3.16), the overpotential for the cathode and anode can be expressed by:

$$\eta_C = -\varphi_C - V_{eq}(cathode) \quad (3.17)$$

$$\eta_A = u_{cell} - \varphi_A - V_{eq}(anode) \quad (3.18)$$

3.4.3 Simulation setup

For simulation, the COMSOL Multiphysics commercial package was used. Before starting the simulation and solving the set of differential equations mentioned above in each case for the different current distributions, many steps have to be done. First, the geometry of each cell was plotted in 3D using AUTOCAD and imported into the COMSOL as illustrated in Figure 3.5. Such that the electrolyte was represented as a cylinder containing the electrodes. The working electrode only contacts the electrolyte on one surface, while the counter electrodes were simulated by two metals contained inside the electrolyte cylinder, of rectangular shape in the first design and cylindrical shell in the second design.

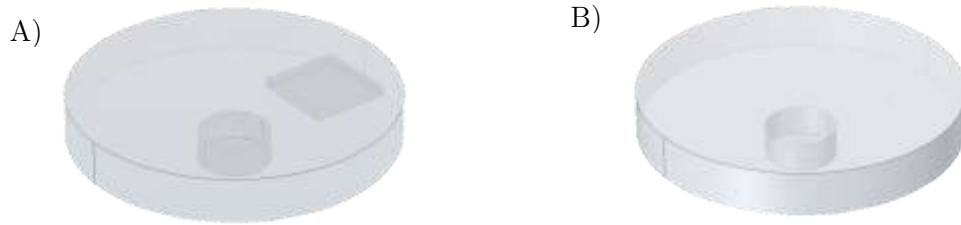


Figure 3.5: The two different cell geometries prepared for simulation. In both designs, the working electrode is centred in the cell (cylinder), while the counter electrode is rectangular in the first case (A) and a cylindrical shell in the second case (B).

Then, the meshing step is carried out, in which the domain of solving the governing equations is divided into meshes and COMSOL uses the finite element method to find the solution of the governing equations at each point of the vertex of the mesh with a giving

boundary conditions. The meshing procedure is critical as a bad meshing setting parameter leads to wrong results. The meshes were chosen in such a way that the boundaries between the electrodes and electrolyte interface meshed with a very fine thickness, namely 0.062 mm. 392000 elements were used in meshing each cell (Figure 3.6).

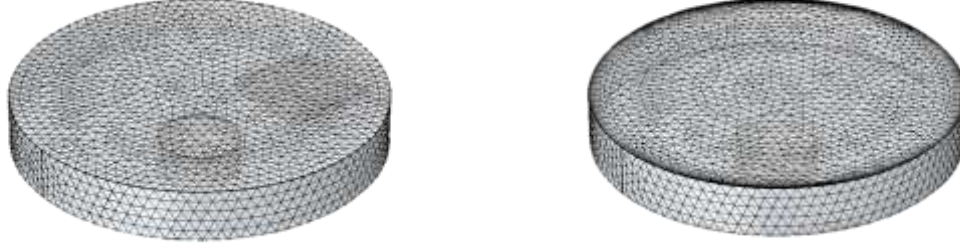


Figure 3.6: Meshing of the two different cell designs.

Trying to mimic the cell usage, the physical and chemical parameters of each material were defined (Table 3.1). Standard electrode potential was chosen for the platinum and the aluminium as a counter and working electrode, respectively. The conductivity of electrolyte was chosen to be that of NaCl (0.5M). An arbitrary value was chosen for the exchange current density. In this simulation, we assume that the electrolyte concentration is uniform, and homogeneous. Now, all the settings were ready to run the simulation.

Table 3.1: Parameters used in the simulation.

Parameter	Description	Value
β_a	Anode symmetry factor.	0.5
β_c	Cathode symmetry factor.	0.5
u_{cell} (V)	Cell potential	1
$V_{eq}(anode)$ (V)	Equilibrium anode potential(Platinum)	1.188 [237]
$V_{eq}(cathode)$ (V)	Equilibrium cathode potential (aluminium)	-1.662 [238]
σ (S/m)	Electrolyte conductivity	4.6655 [223]
J_{oa} (A/m ²)	Anode exchange current density (Pt)	10^{-6}
J_{oc} (A/m ²)	Cathode exchange current density(AA2024)	10^{-6}
ϕ_{liquid} (V)	Initial liquid potential	$(u_{cell} - V_{eq}(anode) - V_{eq}(cathode))/2$
ϕ_s (V)	Initial solid potential	0
T (K)	Temperature	298

3.4.4 Simulation results

The purpose of running this simulation is to find the electrical current and potential distribution inside the electrode. The electrical potential distribution was extracted and plotted in Figure 3.7 whereas the current distribution shown in Figure 3.8.

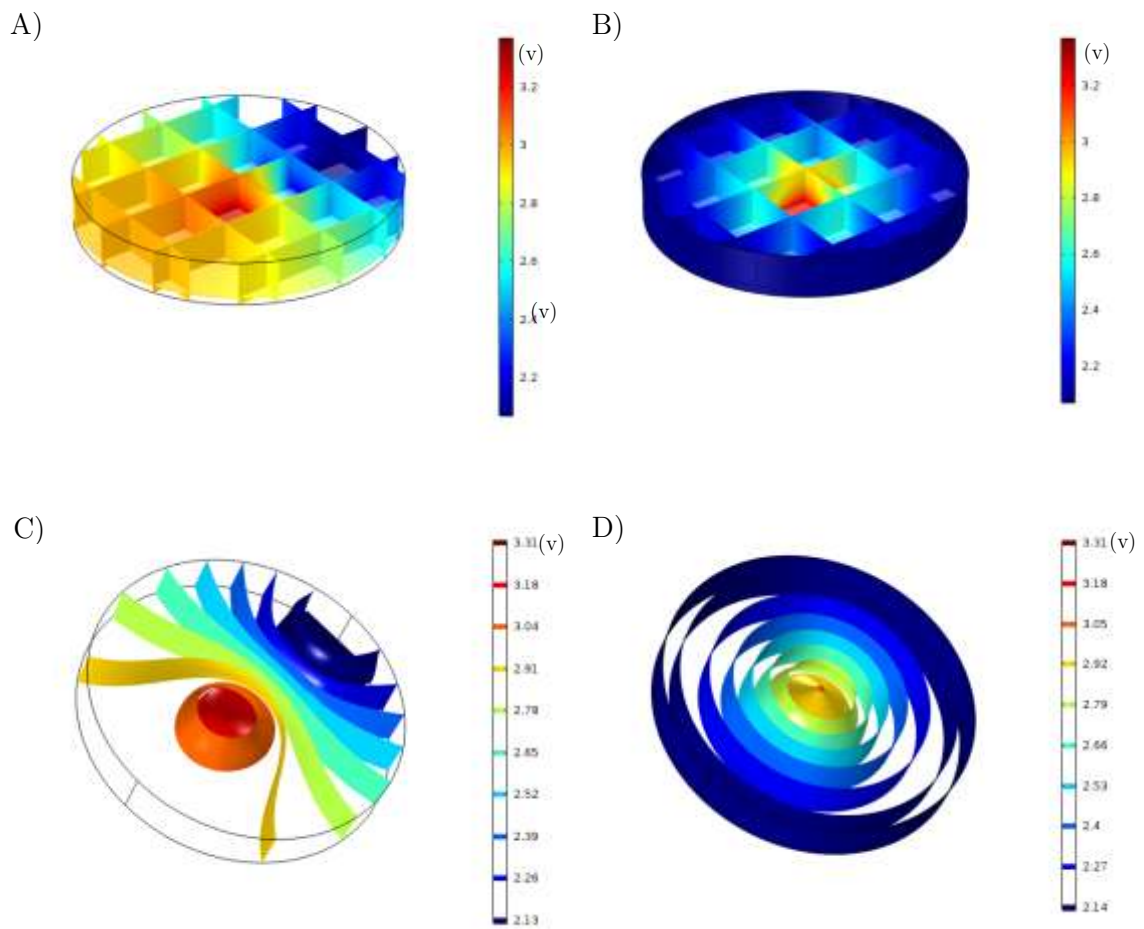


Figure 3.7: Electrolyte potential distribution of the first (A and C) and second (B and D) designs of the two electrochemical cells. A and B are grids of the electrolyte potential distribution. C and D the equipotential surfaces in the electrolyte for the two different electrochemical cell designs.

The electrical potential distribution is shown in Figure 3.7. It clearly illustrates how the electrical potential changes by changing the electrodes configuration. The electrical potential distribution in the first design is not uniform in either the horizontal plane nor the vertical as can be depicted from Figure 3.7-A, while the second design shows a

symmetric distribution of the electrolyte potential. To have a better visualisation of the potential distribution, equipotential surfaces were chosen in the two cells and plotted as shown in Figure 3.7-C and D. In the first design, the equipotential surfaces (Figure 3.7-C) have a semi-parabolic shape around the working electrode in the horizontal plane. In the second design, the equipotential surfaces are concentric cylindrical shells, the shape of cylinders starts to deform in the vicinity of the working electrode.

The electrical current distributing in the two designs is illustrated by plotting the current vector inside the electrolyte as shown in Figure 3.8. The distribution of the current inside the electrolyte in the case of the first design is so non-uniform (Figure 3.8-C) that the magnitude of the current nearby the working electrode (red) is high and starts to diminish as it goes closer to the counter electrode (blue) which is presented by the arrow size in Figure 3.8-A. In the case of the second design, the current lines look radial, and uniformly distributed on the working electrode (red), the current however has a higher magnitude at the edge of the working electrode.

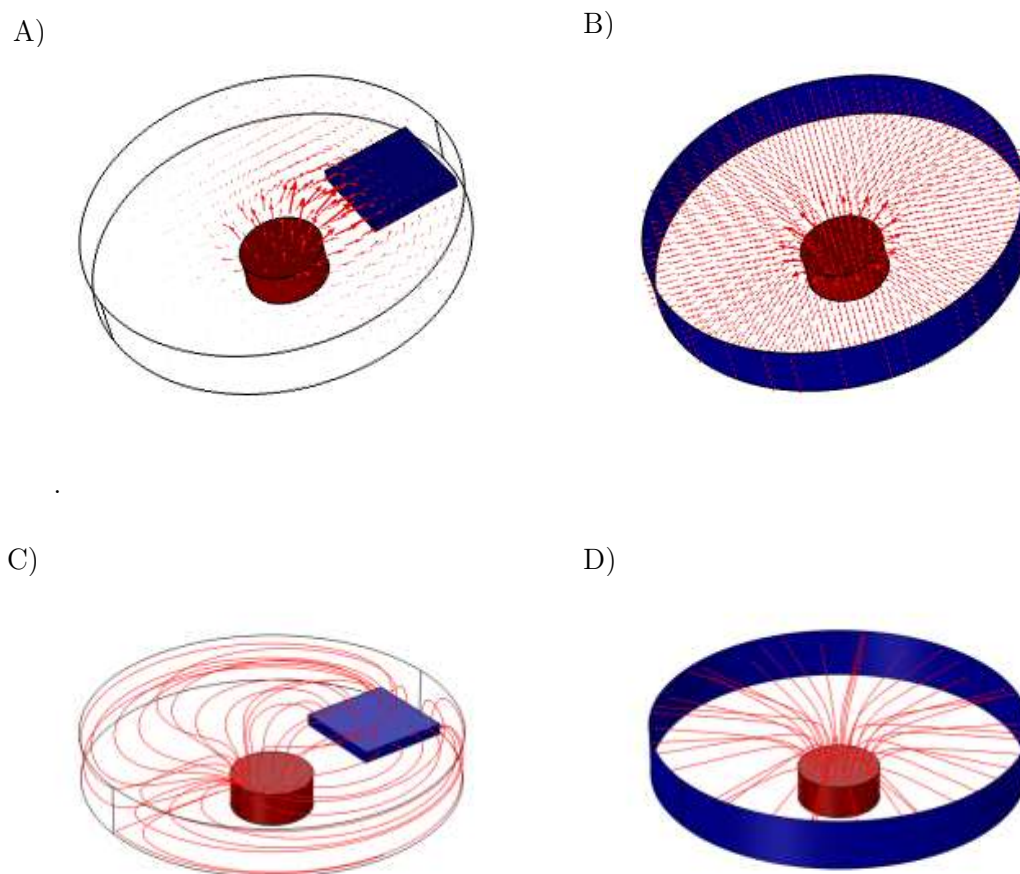


Figure 3.8: Current distribution. A) and B) electrical current potential vector represented by arrows in the two cells weighted by their magnitude. C) and D) Current lines distribution in the two different electrochemical cell designs.

The non-uniformity in the electrical and potential distribution leads to an error in the electrochemical measurements because of the polarisation resistance that arises due to the finite electrolyte conductivity. In this sense, the second design shows a better distribution and the field symmetry inside the cell which helps in reducing the measurement error.

3.5 Cell Fabrication

Before manufacturing the cell, the cell's material had to be selected carefully. Aside from the cost and ease of production, the main criteria for selecting a material for the electrochemical cell are the chemical and electrical resistivity. First, the cell material has to be inert when it is immersed in a corrosive solution (i.e. the electrolyte material), in other words, it must not dissolve when it is exposed to the electrolyte, which leads to a contamination of the electrodes that indeed influence the topographical measurements and could influence the electrochemical measurements as well. Second, the material used for the cell has to have a high electrical resistivity to the corrosive solutions; this way, a short circuit between the electrodes can be avoided. On top of that, the thermal stability of the material has to be considered to diminish the thermal drift during the experiment time.

The most common materials used in the production of electrochemical cells are glass, such as Pyrex [20] and quartz [228], or polymer, such as Kel-F [17] and Teflon [118,239,240]. Obviously, on the one hand, glasses have a high service temperature, in addition to the outstanding toughness value, they possess in comparison to polymers. On the other hand, polymers have superior electrical resistivity values and are resistive to most of the chemical compounds. In our case, Teflon was found the most appropriate material for cell construction based on the following advantages: ease of fabrication, low cost, high electrical resistivity, chemically inactivity towards mild and most harsher chemicals, easiness of cleaning.

The base of the cell was made of stainless steel, as it needs to be a magnetic material to be attached to the microscope, and quite resistive to corrosion in the case of any accidental leakage. The first cell was designed manually in the workshop, while the second was three-dimensionally designed using the CAD program and exported as a binary file to a computer numerical controlled (CNC) milling machine, where it was fabricated.

Table 3.2: Materials used in electrochemical cells.

<i>Material</i>	<i>Resistivity (MΩ-m)</i>	<i>Thermal expansion(°C- 1) X10-6</i>	<i>Density (kg.m-3) X103</i>	<i>Max Temp (°C)</i>	<i>Young's modules (GPa)</i>	<i>Chemical resistivity</i>
<i>Quartz</i> [365] <i>(Silica)</i>	0.7	0.55	2.2	1050	72.39	Reacts with Hydrofluoric acid, hot phosphoric acid and hot alkalies
<i>Pyrex</i> [366]	400	3.25	2.23	490	62.7	Reacts with Hydrofluoric acid, hot phosphoric acid, and hot alkalies.
<i>Kel-F</i> [367] <i>(PCTFE)</i>	108	70	2.10 - 2.14	120-149	1.5	Inert with the exception of some highly halogenated hydrocarbons and aromatic solvents
<i>Teflon</i> [368] <i>(PTFE)</i>	1010	124	2.7	260	0.3-0.8	Inert except with alkali metals, turbulent liquid, or gaseous fluorine; and a few fluorochemicals.

3.6 Electrochemical and AFM Results Using the Second Design

Prior to starting the in-situ experiment in real-time, the cells were tested for leakage for the purpose of safety. Then, they were moved to the microscope to check the mechanical dimensions before starting the experiment. As regards the first cell, it was mainly used in for the spontaneous corrosion study (see Section 4.1.1), and only partly using chronoamperometric studies. By contrast, the second cell, which was found more appropriate, was extensively used in many studies, from ex-situ measurements to various in-situ AFM studies coupled with electrochemistry.

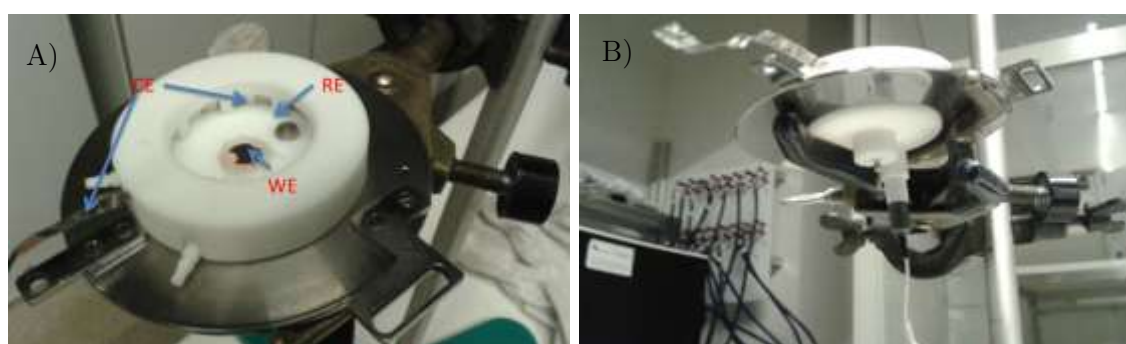


Figure 3.9: Photograph of the second designed electrochemical cell. A) Top view, and B) bottom/side view.

The second cell design shown in Figure 3.9 was tested first for leakage before starting the first in-situ experiment. The aluminium alloy sample was prepared for electrochemical impedance spectroscopy (EIS) measurement. The sample was first cleaned and prepared as described in Section 2.2.3. Then, it was placed in the cell after sealing it using paraffin wax as described in Section 2.2.6. Finally, the cell with its holder was attached to the microscope.

One of the purposes of designing the second cell was to relocate the same scanning spot after injecting the liquid into the cell, which enables us to find the change in the surface because of the immersion. The AA2024 sample was scanned in the air as shown in Figure 3.10-A, then the electrolyte NaCl (0.5M) was injected into the cell. The sample was scanned again as shown in Figure 3.10-B. Comparing the two images in Figure 3.10 we can find that the same area was scanned after injecting the electrolyte into the cell with a slight lateral shift.

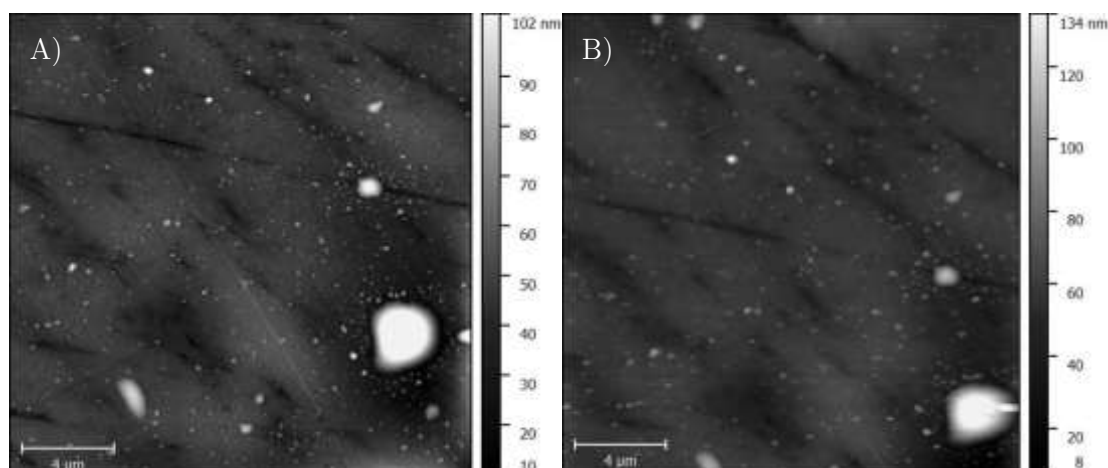


Figure 3.10: AFM topography images of the AA2024 sample. A) The sample scanned in the air, and B) the sample after injecting the electrolyte into the cell.

Electrochemical impedance spectroscopy was measured for aluminium alloy AA2024 using Ag/AgCl/NaCl (Satd) reference electrode in NaCl (0.5M) for the sake of testing the cell. In particular, we wanted to find out if the electrochemical impedance spectrum shows any noise or distortion. The test was carried out at OCP using a sinusoidal voltage signal of amplitude (5mV) with a logarithmically spaced frequency range from 50 kHz to 0.1 Hz. Nyquist plot of the spectrum is shown in Figure 3.11-A recorded after 60 minutes of immersion in NaCl (0.5M).

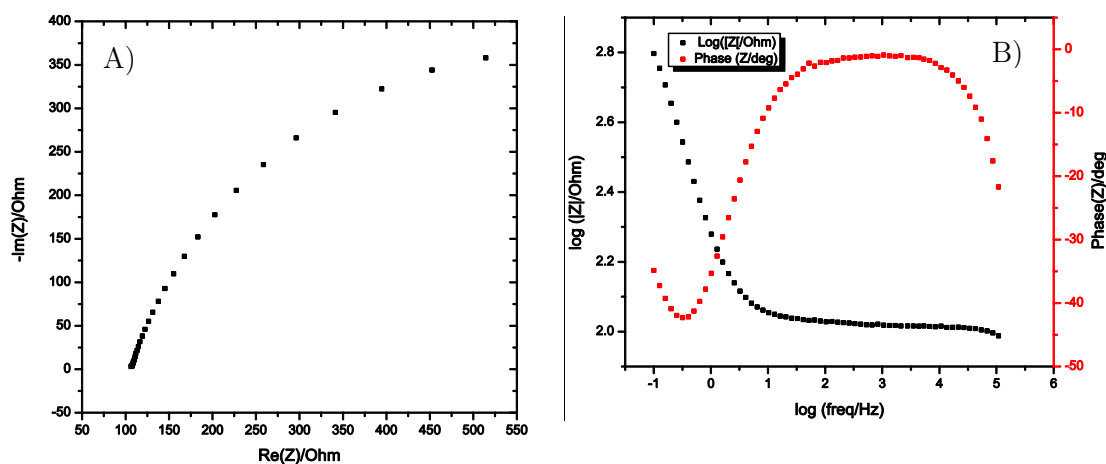


Figure 3.11: EIS measurements of AA2024 using the second cell design. A) The Nyquist plot of EIS, and B) The Bode plot of EIS.

3.7 Conclusions

Two different cell designs for in-situ AFM measurements were developed. They had a different electrode configuration but they both shared the advantage of having a large volume capacity for the electrolyte (5ml) in comparison to the commercially available cells. Further advantages of the developed cells are a relatively low cost, a high chemical and electrical resistivity due to use of Teflon components and the simplicity of use.

Simulations were carried out for the purpose of comparing the field distribution of the two cells. The results of simulations showed that one of the designs had a more uniform field distribution inside the cell, which is a very important factor when measuring the electrochemical impedance spectroscopy.

By adding an inlet and outlet ports to the liquid, it became possible to relocate the same scanning area measured in the air after the liquid was injected into the cell with a slight drift.

From the electrochemical impedance spectroscopy measurements, it was clear that the field was not distorted in the cell thanks to the uniform distribution of the potential and the current. Samples were imaged after the measurements using AFM and SEM. After being successfully tested, the cells were used for systematic in-situ AFM investigation of different systems of interest, as discussed in Chapters 4 and 5.

Chapter 4

In-Situ AFM of Aluminium Alloy and its Protection

4.1 Introduction

Aluminium is an abundant element in the earth's crust [6]. Additionally, it has convenient physical and chemical properties, which makes aluminium (and its alloys) a potential candidate for a wide range of applications. Like most of the metals, aluminium is usually found in a mixture with other elements such as iron, silicon, and oxygen. The most common source of aluminium in nature is called bauxite and it consists of different hydrated oxide phases of aluminium. Those phases are trihydrate gibbsite ($\text{Al}(\text{OH})_3$), monohydrate boehmite ($\gamma\text{-AlO}(\text{OH})$), and diasporite ($\alpha\text{-AlO}(\text{OH})$).

Due to its highly negative standard hydrogen electrode potential (-1.6 V with respect to hydrogen electrode), aluminium is very unstable in moisture. Pure aluminium possesses a high corrosion resistance that is due to its high activity, such that a layer of protective oxide (native oxide) forms rapidly in different environments [7].

For the reason that aluminium has a low density, high thermal and electrical conductivity, as well as due to its strength, stiffness, high ductility, and non-toxicity, engineers are attracted to choose aluminium alloys in a variety of applications and products. In order to enhance the mechanical properties of aluminium, it is usually alloyed by adding other elements like copper (Cu), magnesium (Mg), manganese (Mn), silicon (Si), chromium (Cr), iron (Fe), and zinc (Zn). Owing to the low density and high strength, aluminium is used extensively in aerospace and automotive industries - in order to reduce the aircraft's weight and decrease the fuel consumption. Despite the fact that aluminium alloys have superior mechanical properties, they are more prone to corrosion.

As mentioned in Chapter 1, the aluminium alloy is preferred nowadays because of its myriad advantages (e.g. its abundance, outstanding physical properties, and nontoxicity). Aluminium and its alloys are involved in many applications with different scales from the food cans to aircraft. In this work, AA2024 was chosen, as it is a good candidate for space applications. Corrosion is a crucial matter, as in this case may imply a risk of human life. Owing to their wide usage in the aerospace industry, the AA2xxx and AA7xxx series gained excessive attention from researchers who have carried out in-depth studies of their response and corrosion behaviour. The disadvantage of these alloys is their increased tendency for corrosion due to the significant content of copper. On the one hand, copper increases the alloy's strength and improves the mechanical properties; on the other hand, however, it increases the alloy's susceptibility to corrosion.

In this chapter, a short review about the corrosion of AA2024 will be presented and the anti-corrosion coating of AA2024. Then, the in-situ AFM study of aluminium alloy AA2024 and its coating will be presented. The experimental part of this chapter is divided into two sections. In the first experimental section, a study of the bare aluminium alloy is presented and the change of the surface while it is immersed in a corrosive medium to find the spontaneous change of the surface. Subsequently, the effect of applying chronoamperometric pulses will be shown. In the second experimental section, an in-situ study of gel-coated AA2024 is presented in three different ways; (i) first by studying the spontaneous change of the coating surface while immersed in the corrosive medium for a long time during which the electrochemical impedance, the surface parameters, and the open circuit potential are monitored. (ii) In the second part, a chronoamperometric pulses effect is studied by applying electrical pulses of different potential to the sample while measuring the electrochemical impedance and recording the change in the surface. In the end, studying the effect of chrono-potentiometric pulses is presented showing how the surface is changing by applying electrical pulses of different current values.

4.1.1 AA2024 corrosion

Aluminium alloys are classified into different categories according to the production process (cast and wrought alloys). We will focus primarily on wrought alloys, as they are used directly in the industry. The designation of aluminium wrought alloy families is always in the form AAxxxx, where x is an integer number (Table 4.1). The first letters (AA) stand for Aluminium Association, which is most often confused with aluminium alloy. The first digit identifies the principal alloying element and it is most often used to describe the aluminium alloy family. The second digit is used to identify the modification of the alloy, and the last two digits are used to identify a specific alloy in the series [241].

4.1.1.1 Microstructure of AA2024 alloy

The wrought aluminium alloy is divided into two groups according to the heat treatment. The first group is heat treated. Usually the alloy is solution heat treated, and then rapidly cooled or quenched to enhance its strength, or by cold working at room temperature. The group that is not treated by heat is strengthened by the alloying with selected elements. In the case of the heat-treated group for their production, the virgin metal is melted and cast and then an alloying element is added to produce the cast ingot. In this step, large intermetallic particles are formed, which are the second phase of aluminium. Then, the metal is treated to refine its mechanical properties by removing the elements that may cause cracking. Afterwards, many steps are applied, and each has its influence on one of the microstructures of the material such as the intermetallic particles, the grain size, the grain orientation, and the distribution of the intermetallic particles in the matrix. The intermetallic particles are formed during the alloy casting. There are two types of intermetallic particles - soluble, and insoluble. The soluble intermetallic particles are the compounds formed of the alloying elements. The insoluble intermetallic particles usually have an impurity element such as iron (Fe) or silicon (Si), for example $Al_6(Fe, Mn)$, Al_3Fe , and $\alpha-Al(Fe, Mn, Si)$. Approximately 60% of the intermetallic particles in AA2024-T3 are S-phase (Al_2CuMg) with dimension greater than 0.7 μm , with a very small fraction of the surface [242]. Another group of intermetallic phase possesses a noble potential in

comparison to S-phase and the aluminium matrix such as Al_7CuFe_2 , Al_6MnFe_2 , $(\text{Al}, \text{Cu})_6\text{Mn}$.

Table 4.1: Aluminium alloy families [243].

Aluminium Alloy Series	Principle alloying element	Corrosion resistance	Mechanical properties	Applications
AA1XXX	99% pure aluminium	Excellent	Poor	Chemical tanks, piping, and electrical bus bars
AA2XXX	Copper (Cu)	Low	Excellent	Aerospace and aircraft applications
AA3XXX	Silicon(Si)	Good	Moderate	Cookware, heat exchangers in vehicles, and power plants
AA4XXX	Manganese (Mn)	Good	Good	Filler for welding
AA5XXX	Magnesium (Mg)	Good	High	Shipbuilding, transportation, pressure vessels, bridges and buildings
AA6XXX	Mg and Si	Moderate	Good	Commercial road and railway vehicles, and in mechanical applications
AA7XXX	Zinc (Zn)	Satisfactory	High	Aircraft, aerospace, and competitive sporting equipment
AA8XXX	Other element			

An intensive study of the intermetallic particles was carried out by Hughes and co-workers [244–247] and they found nine different compositions after analysing about 18 thousand particles. In addition, they found that all the cathodic particles contain Si, except one intermetallic particle $\text{Al}_6(\text{CuMnFe})$. Smaller (sub-micron) particles, with sizes between 0.05 and 0.5 μm , usually referred to as dispersoids, exist in the alloy. Dispersoids usually have one or more transition metals. The main dispersoid in AA2024 is $\text{Al}_{20}\text{Mn}_3\text{Cu}_2$ and they are short rods [248]. The hardening precipitate is an additional group of particles exist in aluminium alloy, with a size less than 200 nm. These precipitates are clusters composed of Cu or Cu and Mg.

4.1.1.2 Corrosion of aluminium and its alloys

As aforementioned, aluminium is an active metal. Consequently, when aluminium is exposed to a medium containing oxygen, an oxide/oxyhydroxide layer is formed on its surface at room temperature [249]. At neutral pH, the film continues to grow and it passivates the surface [250]. The oxide layer protects the metal from corrosion. However, the pH value is altered from the neutral region, the passivation layer starts to dissolve. For instance when the surface is exposed to an acid that is not concentrated, the oxide layer starts to dissolve and produce a hydrogen gas. Depending on the concentration of the acid [251], the reactivity of the oxide is determined. The higher the concentration of the acid, the lower the reactivity of aluminium. For example, aluminium dissolves in diluted nitric acid while it is passivated if exposed to nitric acid in the concentration range (18%-22%). The thickness of the layer depends on the environment, temperature, and alloying element. For pure aluminium, the oxide layer formed in the air at room temperature around 2-3 nm, and can reach up to 20 nm if it is heated to 425 °C [252].

In corrosion studies, the films produced by the reaction of aluminium oxide with water are important [253]. Aluminium oxide reacts with water in different stages. First, the amorphous layer is formed by an electrochemical process, in which barrier film growth in the anodic half reaction while the cathodic reaction is the reduction of water [254]. Second, hydrolysis of the Al-O bonds on the surface takes place, which depends on the concentration of aluminium, temperature and pH value [254]. For example below 60 °C, the reaction mechanism between the aluminium oxide and water was suggested to be in three stages [254,255], first an amorphous layer ($\text{Al}(\text{OH})_3$) is formed, followed by boehmite layer formation ($\gamma\text{-AlO}(\text{OH})$), and finally, a layer of bayerite $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, resulting in a 3 layers film [256].

Under the application of electrical potential, an oxide layer is formed with different morphologies, either microporous or nanoporous, which again depends on the chemical nature of the solution [257,258]. The nano-porous oxide is formed if the electrolyte is neutral (has pH 5-7) [259], while the micro-porous oxide is formed if the electrolyte is acidic [258–262]. The nano-porous film is amorphous, compact, and has a uniform thickness. The anodization process in which a constant electrical potential is applied, i.e. it is considered a potentiostatic process. The current is measured, which in the case of nano-amorphous oxide film decays exponentially, whereas it behaves in four different stages for micro-porous oxide film. The first step is the formation of a thin oxide layer at which the current decreases indicating the growth of the oxide layer. The second step, the barrier (oxide) layer continues to grow up to a certain level [263–265], then fine pathways are formed in the oxide layer before the formation of pores [266], which can be seen as a small increase in the current. That was interpreted as a cracking in the oxide because of the non-uniform oxide thickness that makes the pores grow on the low thickness part of the barrier [265]. Thomson et al. suggested that a local cracking is formed in the oxide because of cumulative tensile stress and it results in the formation of pathways [259,261,267]. In the third step, the pathways continue to grow until stable pores are formed leading to a stabilisation of the porous film and no more pathways are formed. In the fourth step, the pathways and pores merge together to result in larger pores and the oxide layer reaches a dynamic equilibrium state resulting in an increase again in the current value [263,265,268]. Le Coz et al. revealed that the porous alumina consists of aluminium hydroxide $\text{Al}(\text{OH})_3$, aluminium oxyhydroxide $\text{AlO}(\text{OH})$ and hydrated alumina Al_2O_3 [269].

AA2024 is susceptible to different forms of corrosion depending on the service conditions, working temperature, and the acidity or alkalinity of the corrosive medium. A harsh corrosion attack was recognised in this type of aluminium alloys when exposed to halide media [270]. Although many studies assumed that corrosion in halides was enhanced due to the failure of the naturally occurring passive film, Bakos found that pitting of aluminium could also take place in the absence of chlorine [271].

Aluminium has a lower tendency for uniform corrosion with an exception if the surrounding medium is highly acidic or alkaline. In the case of the aluminium alloy, the surface is not uniform because of the intermetallic particle. This results in a formation of local electrochemical cells of anodes and cathodes due to the difference in chemical compositions, which can be considered a micro galvanic coupling. Corrosion initiates at those microcells and in that case three different possibilities exist. The first that a film is formed on the surface and protects the metal, the second that the intermetallic particle dissolves, and the third that the surrounding matrix dissolves. The second case results in a pitting corrosion, in which the corrosion initiates at the surface of the intermetallic particle and dissolves. This results in different electrochemical behaviours [272]. The alloying elements may affect the corrosion resistance. Silicon, zinc, and chromium do not have a major effect on the corrosion resistance. Magnesium additives increase the corrosion resistance of aluminium. Copper as a constituent of the second phase particles makes a galvanic coupling with the surrounding matrix [242], as described above. Therefore, copper reduces the corrosion resistance. The segregated compounds impose some flaws in the film on the surface [273]. The formed flaws act like a pathway through the native oxide layer. In other words, they represent weak points in which localised corrosion initiates [274]. Pitting depends again on the chemical environment such that some anions such as Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^- [275–279] are classified as aggressive anions to attack aluminium and its alloys. Aluminium alloy is susceptible to other forms of corrosion, such as intergranular [15]. Like any metal, aluminium alloy properties are influenced by the grain size [280]. Specifically, the larger the grain size, the lower the strength, the higher the corrosion resistance [281]. Because of the heat treatment in aluminium alloy, the dispersoids precipitate at the grain boundaries [8], therefore, corrosion can easily initiate at the grain boundaries in that case.

In this work, we are interested in studying the change in the matrix itself when it is immersed in NaCl (0.5M), and the formation of the films on the surface.

4.1.2 Aluminium alloy corrosion protection

As mentioned above, an oxide or oxyhydroxide layer is formed on the surface of aluminium when it is exposed to an oxidising or hydrating medium, respectively. However, the formed layer passivated the surface of the aluminium or its alloys deteriorates upon exposure to an aggressive medium such as chloride, which results in pitting [242,282–284]. Therefore, there is a need to protect the surface from corrosion when it is exposed to a corrosive medium by the means of a physical barrier between the surface and the attacking medium. Chromate conversion coatings have been used and proved their ability to protect the underlying metal from the aggressive media [285–287]. Because chromate coatings are toxic they are unfavourable and most of the governments are banning them. In an attempt to find an alternative to chromate conversion coatings with some environmentally friendly coating, the sol-gel coatings have been recently used widely as protective coatings.

Inorganic sol-gel coatings were used to protect aluminium substrates. The SiO_2 film was formed on aluminium by dipping aluminium in a silicic acid aqueous solution containing urea [288]. Tim found that the film adhesion was limited and heat treatment introduced

defects into the coating [288]. Yang et al. [289] studied the possibility of using a mixed inorganic coating with the composition $3.4\text{SiO}_2\text{-1ZrO}_2$ sol-gel coating on Al 2024-T3 substrate, the corrosion was tested in dilute Harrison's solution (3.5 g/L $(\text{NH}_4)_2\text{SO}_4$, 0.5 g/L NaCl). Yang found that the coating could resist the corrosion, then after two days of immersion, the impedance increased and pits started to develop in the coating. The increase in the impedance was due to the formation of aluminium and silicon oxides, which can inhibit the corrosion and prevent further pitting. The temperature treatment of inorganic sol-gel may introduce cracks and degrade the coatings.

In 1998, Chen et al. [290] developed inorganic-organic hybrid protective coatings on aluminium substrates by incorporating nanoparticles (Al_2O_3 , ZrO_2 , SiO_2). Parkhill and co-workers applied epoxy-silica sol-gel films to aluminium alloy [40]. The epoxy silica coating showed excellent barrier properties to corrosion. Several hybrid coatings were developed for corrosion protection of aluminium alloys, most of them are using organo-alkoxysilane precursor as the coating density can be increased because of the polymerization of the sol and enhance the coating properties [291], such as methacrylic [292,293], vinyl [294] epoxy [291,295,296]. Further enhancement of the hybrid coatings was developed by incorporating other functional groups, for instance to enhance the hydrophobicity of the coating phenyl group was used [38,297] and to improve the adhesion to the surface phosphonate was introduced [31,298,299]. Bis-sulfur silane was used to prepare protective coatings by adding silica nanoparticles to (bis-[3-(triethoxysilyl)-propyl]-tetrasulfide, BTSTS) [300,301]. It was found that the addition of silica nanoparticles to the film increases the thickness and the strength of the film. The silane enhances the adsorption to the metal surface by bonding the metal to Si through oxygen [300,301].

In this work, (3-Mercaptopropyl) trimethoxysilane (MPTMS) precursor is used to prepare hybrid sol-gel coating. MPTMS is one of the silane coupling agents which has two different reactive functional groups. The hydrolysis and condensation take place because of the methoxy groups, which is necessary for sol-gel approach. Bonding or adhesion to the surface is accounted to the thiol active group. Li et al. used the MPTMS coating to protect aluminium, by testing in NaCl (0.5M), it was found that MPTMS could reduce the corrosion current by an order of magnitude [302,303]. The sol-gel was applied to AA2024 to test its behaviour in NaCl (0.5M) and its ability to protect the used aluminium alloy from the corrosion under different electrochemical conditions. The power of combining AFM to find the topographical change simultaneously with measuring the electrochemical impedance spectroscopy either spontaneously (at OCP) or under potential/current control.

4.2 Experimental Results and Discussion

In this section, results carried out on bare and gel-coated AA2024 using in-situ AFM, and different electrochemical methods will be presented and discussed.

First spontaneous corrosion of bare aluminium immersed in NaCl (0.5M) electrolyte was studied to find the change in topography, and then the chronoamperometric test was carried out. The results were correlated with SEM/EDS and infrared spectroscopy.

Then, in-situ AFM was carried out on gel-coated aluminium immersed in NaCl (0.5M) under different electrochemical conditions. A sample was tested during a long immersion time of more than 11 hours. Afterwards, another sample was in-situ AFM tested under the application of chronoamperometric pulses while measuring the electrochemical impedance, and monitoring the change in topography. In the end, a chrono-potentiometric test was in-situ performed to find the change of morphology when this technique is used.

4.2.1 Bare AA2024 measurements (time, and chronoamperometric measurements)

In this study aluminium alloy samples were used to investigate their tendency to corrosion in NaCl (0.5 M) electrolyte. This study was carried out using the first cell design presented in Chapter 3. The purpose of these measurements was to study the surface morphology, first the spontaneous temporal change without applying any electrical signal and second by applying chronoamperometric pulses of different potential values. The purpose of the measurement of time dependence is to find the spontaneous change of the topography with time. However, in the second case, the system was stimulated using external chronoamperometric pulses.

4.2.1.1 AFM measurements

Polished AA2024 samples were prepared for AFM measurements using the procedures given in Section 2.2.2 and mounted into the cell as mentioned in Section 2.2.6. In this case, the cell setup in Figure 3.1A was used. Before starting in-situ AFM, each sample was scanned first in the air to check its quality, and whether it is good to start the experiment or not. Consequently, the AFM scanner head was removed, and NaCl (0.5M) was injected into the cell as a corrosive medium. The time was recorded at that moment of injecting the solution into the cell. Afterwards, the scanner was mounted again, and the tip was tuned. The surface of the sample was scanned for about 3 hours to find the change in morphology.

After the elapsed time for running the experiment, the files were collected and then processed. Surface parameters were extracted from the images as mentioned in Section 2.1.1 and plotted in Figure 4.2 – Figure 4.4.

The bare AA2024 sample exhibits a nearly Gaussian surface upon immersion as shown in Figure 4.1-A to have a roughness value of 2 nm after 14 minutes of immersion and skewness and kurtosis values of -0.34 and 4.6, respectively. The surface roughness started to increase gradually to be 5 nm in 72 minutes (Figure 4.2) with corresponding values of 2.38 for skewness (Figure 4.3), and 23.65 for kurtosis (Figure 4.4).

From the image in Figure 4.1-C, it can be seen that the surface started to be rougher and has some holes. Additionally, the shift in the image slightly to the right is due to the AFM scanner's thermal drift. The roughness started to decrease again after 72 minutes to have its lowest value during the course of the experiment, which was 3 nm after 106 minutes of immersion, while the skewness increased to be 1.95, which is because of the appearance of new features on the surface (Figure 4.1-D). The roughness kept increasing slowly to have a value of 4 nm with maximum values 6.0, and 109 of skewness and kurtosis, respectively after 124 minutes of immersion. The high values of skewness and kurtosis are expected because of the large variance in the height of the surface's features in addition to the shift of the image. Finally, the roughness started to decrease again to be 3 nm, along with a decrease in the values of kurtosis and skewness, as well.

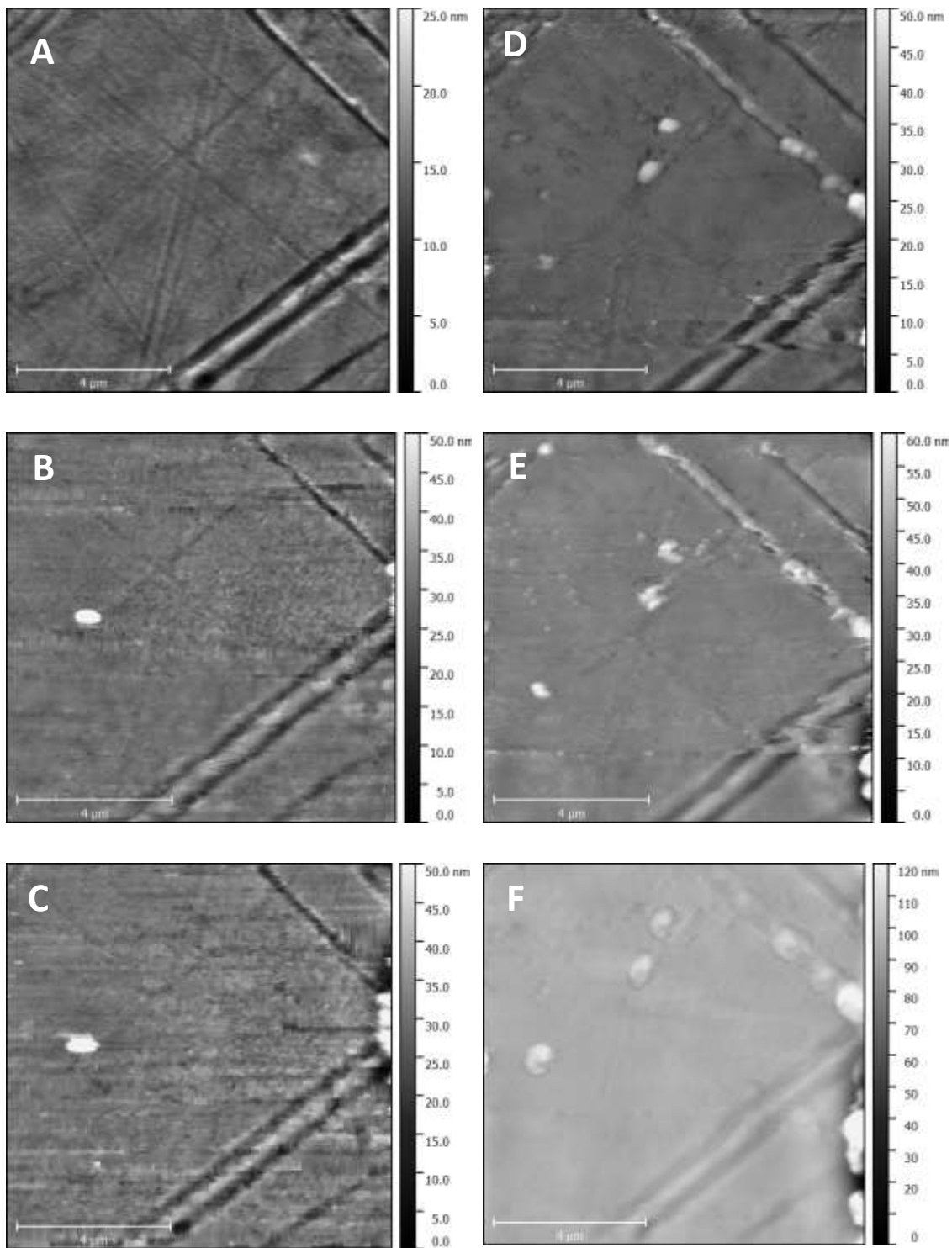


Figure 4.1: In-situ AFM topography measurement of spontaneously immersed AA2024 in NaCl (0.5M). The images were taken after immersion for A) 14 min, B) 67 min, C) 72 min, D) 106 min, E) 124 min, and F) 164 min. The time was recorded from the moment of injecting the liquid into the cell, and started to scan the sample after tuning the tip. The scale bars are of 4 μm length.

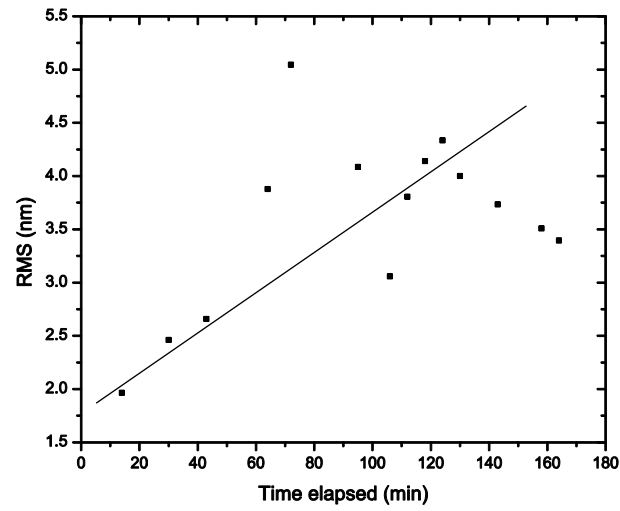


Figure 4.2: RMS temporal change of the value of spontaneously corroded AA2024 in NaCl (0.5M). The line represents a guide to the eye.

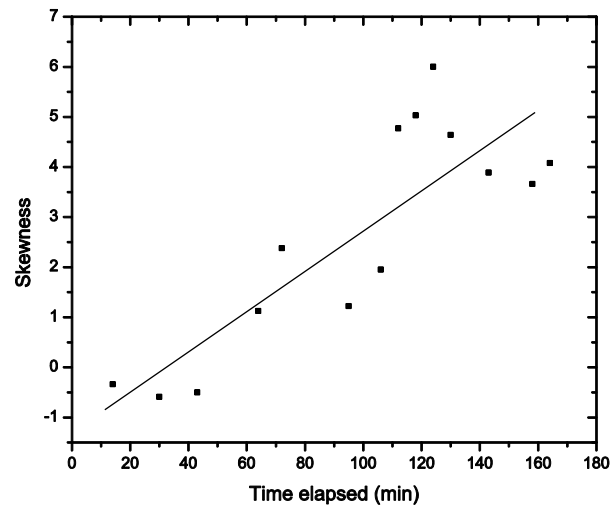


Figure 4.3: Skewness temporal change of the value of spontaneously corroded AA2024 in NaCl (0.5M). The line represents a guide to the eye.

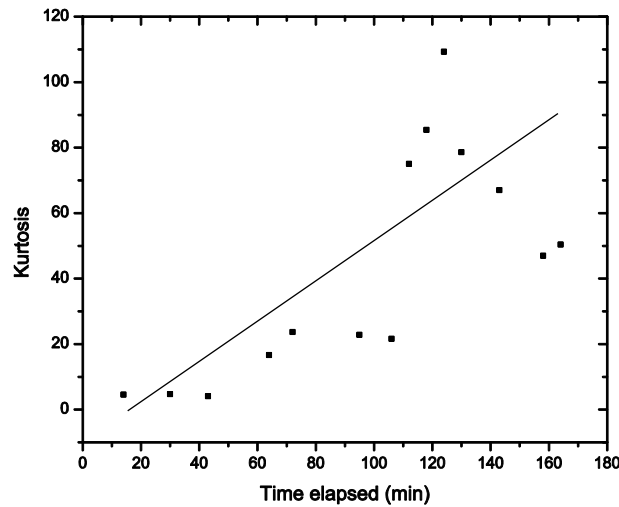


Figure 4.4: Kurtosis temporal change of the value of spontaneously corroded AA2024 in NaCl (0.5M). The line represents a guide to the eye.

Another bare AA2024 sample was measured, this time for using external electrical signals (chronoamperometric signals). The purpose was to in-situ study the change in morphology not only with time, but also with the application of different values of potential pulses from cathodic potential (-0.8 V/Ag/AgCl/NaCl Satd) to anodic potential (0.2 V/Ag/AgCl/NaCl Satd) each of 20 seconds duration to the working electrode. A three-electrode electrochemical cell was used in this measurement. This time the second designed cell in Figure 3.2 was used and connected externally to potentiostat Bio-Logic SP-200 (Bio-Logic SAS, Claix, France) so that the signals can be applied in a controlled manner.

The same procedure as mentioned in section 2.2.6 was followed to mount the sample into the cell. Afterwards, the solution was injected into the cell. The tip was re-tuned and approached the sample's surface. The sample was first scanned without applying any electrical signal under open circuit potential (OCP) (Figure 4.5-A). Afterwards, chronoamperometric pulses of different potential values, and 20 seconds duration were applied to the working electrode. AFM images were collected after the application of each chronoamperometric pulse, and some of them are presented in Figure 4.5. A dramatic change in the surface can be seen in Figure 4.5 in response to the electrical pulses. The measurements were carried out for about 3 hours, and then the sample was removed and files were collected and processed.

To understand better the observed changes, the surface parameters were calculated for each image, and plotted versus time and the applied potential pulse (Figure 4.6). First, the scanning was started after 4 minutes of immersion (Figure 4.5-A); it was found that the sample roughness was 4 nm and the corresponding values of skewness and kurtosis -1.84 and 12.71, respectively. A chronoamperometric pulse of amplitude -0.8 V/ Ag/AgCl/NaCl Satd and duration of 20 seconds was applied to the working electrode after 10 minutes of immersion. The effect was found quite negligible on the roughness while the skewness and

kurtosis increased which is an evidence of change in the surface topography. We found that the surface started to slightly shift and some features appeared to make the surface more asymmetric. Another pulse was applied to the working electrode after 20 minutes of immersion of amplitude -0.6 V / Ag/AgCl/NaCl Satd , and duration 20 seconds. The application of the last electrical pulse resulted in a change in the surface parameters. A small increase in the roughness, accompanied with a decrease in the skewness, and kurtosis. The change of the surface parameters is a consequence of the features that started to appear in the image. Specifically the surface started to be rougher and corroded in the bottom of the image. A more positive pulse of 20 seconds duration was applied of amplitude -0.4 V / Ag/AgCl/NaCl Satd caused a slight increase in roughness from 4 to 5 nm, with simultaneous increase in both the skewness (from -0.1 to 1.39), and kurtosis (from 20.63 to 23.50). After 52 minutes of immersion, a -0.3 V / Ag/AgCl/NaCl Satd pulse was applied to the working electrode with a duration of 20 seconds while imaging. It was found that the roughness started to increase rapidly although no potential was applied during the succeeding 30 minutes. The roughness reached a value of 9 nm, a noticed increase in the skewness was accompanied with the roughness increase, while the kurtosis started to decrease. The roughness attained its maximum value (18 nm) upon the application of -0.2 V / Ag/AgCl/NaCl Satd after 88 minutes of immersion. That increase of the roughness was due to the evolution of features on the surface. We were not sure if that they appeared because of the change in the surface itself or they were just corrosion products moved under the influences of liquid, therefore AFM image acquired at that moment was excluded. With the application of a -0.1 V / Ag/AgCl/NaCl Satd pulse at 95 minutes of immersion, the roughness value started to decrease. The roughness kept decreasing and the surface started to become smoother afterwards - when a pulse of amplitude, 0 V / Ag/AgCl/NaCl Satd was applied. Then, by applying more positive pulses, the surface roughness started to increase as well as kurtosis, and skewness, which can obviously be seen in the images because of the evolution of new features on the surface while the surface looked smoother than before but the features appeared to have a significant effect on the increasing roughness and the other parameters, the experiment was stopped after 180 minutes of immersion. The increase of the features' size on the surface could be either due to the change in the tip geometry, or a change in the feature surface. Since AFM tip could resolve some small particles on the surface in the last image, that means the AFM tip was relatively sharp. Therefore, that change of the surface topography was due to a growth of a layer on the surface.

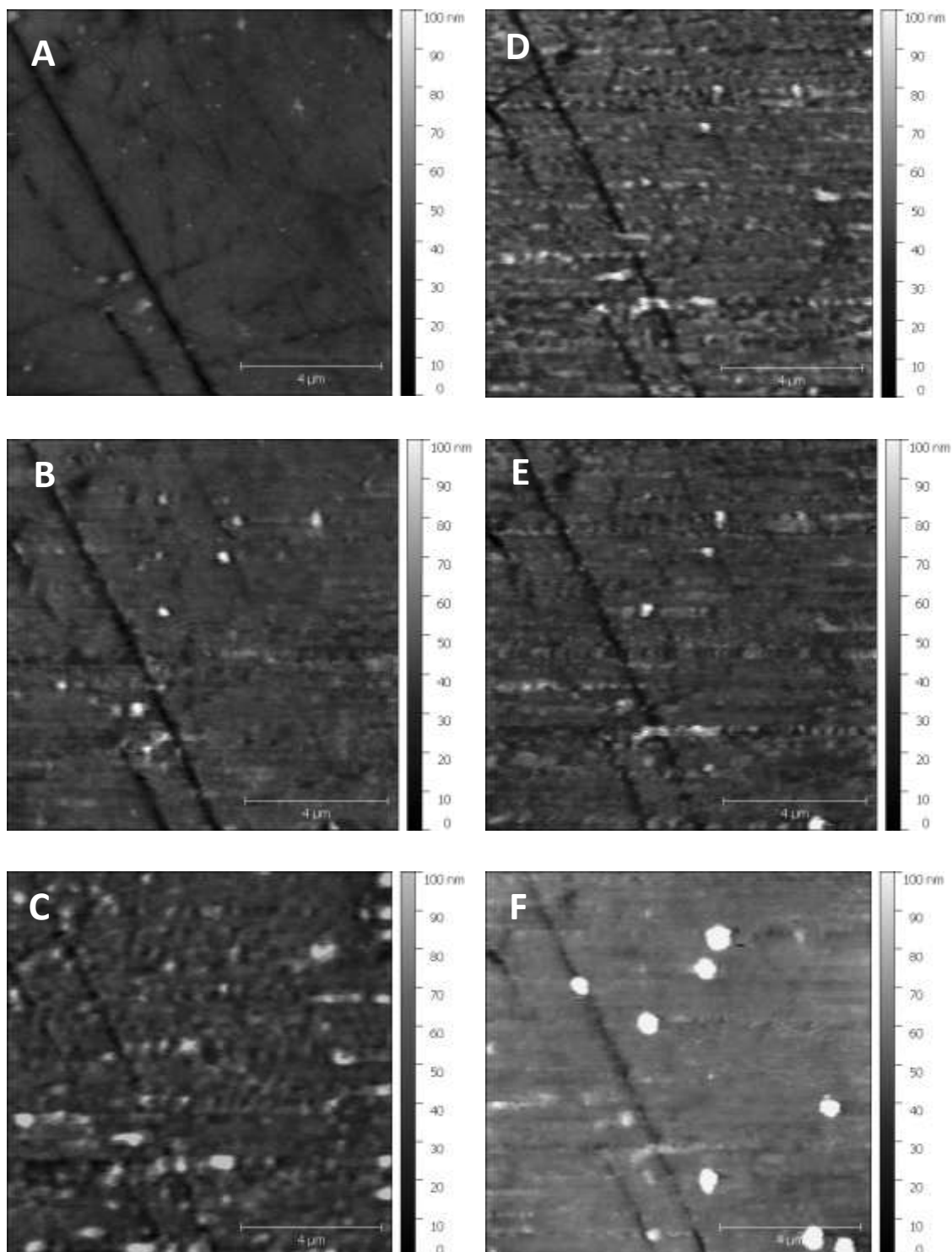


Figure 4.5: In-situ AFM topography measurement of immersed AA2024 with the application of chronoamperometric pulses: (A) 4 min; OCP, (B) 72 min; -0.3 V, (C) 95 min; -0.2 V, (D) 103 min; -0.1 V, (E) 110 min; -0.1 V, and (F) 175 min; 0.1 V. Time in min refers to the time elapsed after the introduction of 0.5 M NaCl electrolyte. The duration of each chronoamperometric pulse is 20 seconds. The images were collected after the application of chronoamperometric pulses. All the potential values are against Ag/AgCl/NaCl sat reference electrode. The scale bars are of $4\text{ }\mu\text{m}$ length.

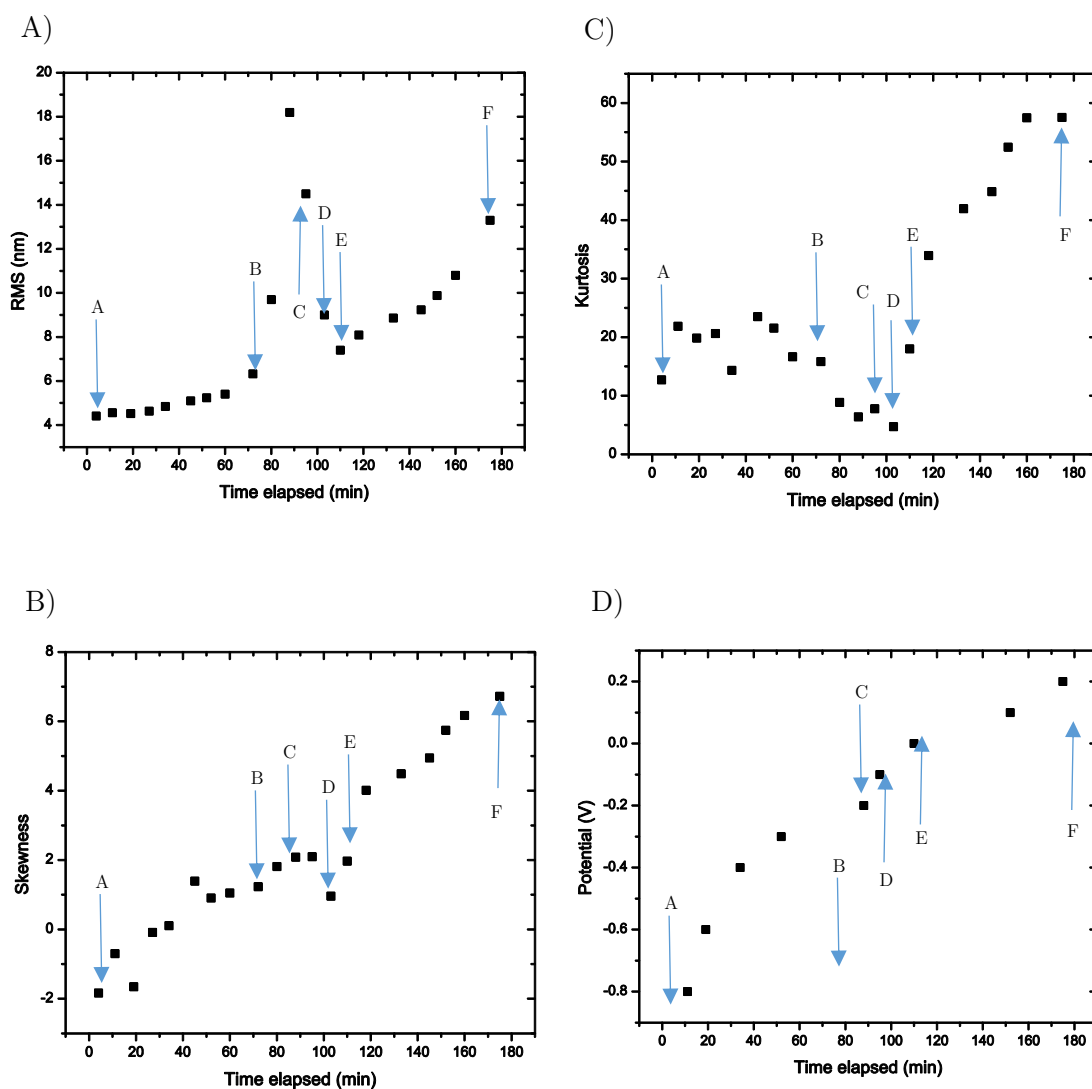


Figure 4.6: Surface parameters dependence of time and potential applied to AA2024 in NaCl (0.5M). A) The surface roughness RMS, B) the surface kurtosis, C) the surface skewness, and D) the applied potential pulse value with time (the duration of each pulse is 20 seconds). The arrows indicate the images selected in Figure 4.5.

To confirm the results of the samples measured under the influence of not only time but also electrical signals applied to the working electrode, an additional sample was measured. This sample was immersed in the electrolyte for more than 5 hours. . It can be noticed from the four images shown in Figure 4.7, that there was a shift in the scanning area. The marked area is a corrosion active area. It was first shown before the application of potential (Figure 4.7-A). Upon the application of potential -0.8 V/ Ag/AgCl/NaCl Satd

for 240 s the surface started to be more rough (Figure 4.7-B). By applying potential that is more anodic of value $-0.4\text{ V} / \text{Ag}/\text{AgCl}/\text{NaCl Satd}$ for 240s, the area started to be rougher (Figure 4.7-C). After more elapsed time of immersion (126 minutes), one more pulse was applied to yield even more rough surface, as well as some corrosion products, started to appear on the right side of the images (Figure 4.7-D). The problem we had with this sample is the evolution of gas bubbles upon application of anodic potential (Figure 4.8). After the application of the anodic potential, it was necessary to reposition the scanner, but it was quite hard to relocate the origin again because the gas was evolving vigorously. At that time, it was necessary to remove the scanner and replace the electrolyte in order to get rid of the gas bubbles. Because of the continuous shift, it is inconvenient to use the statistical parameters to compare between all the images, therefore some chosen images can be compared to find the change during the course of the experiment

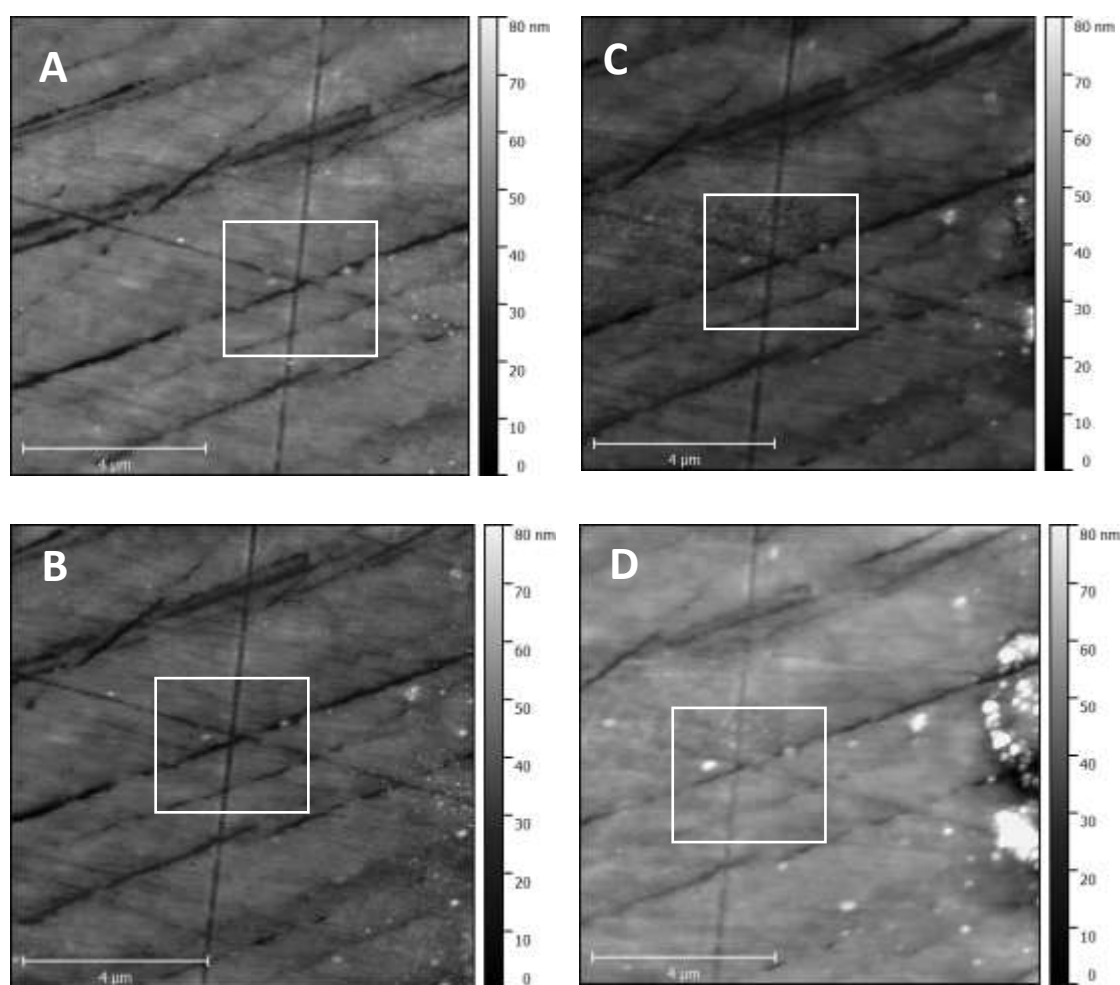


Figure 4.7: In-situ AFM topography measurement of immersed AA2024 with the application of chronoamperometric pulses. (A) 27 min, OCP (B) 32 min, $-0.8\text{ V}/\text{Ag}/\text{AgCl}/\text{NaCl Satd}$, 240s, (C) 101 Min, $-0.4\text{ V}/\text{Ag}/\text{AgCl}/\text{NaCl Satd}$, 10s, and (D) 126 Min, $-0.4\text{ V}/\text{Ag}/\text{AgCl}/\text{NaCl Satd}$, 10s [225]. The time in min refers to the time elapsed after the immersion, and the time in second refers to the duration of the applied pulse.

After the last anodic pulse, gas bubbles were released and were very harsh, as can be clearly seen in Figure 4.8. The pictures were taken in the solution using the optical microscope-camera attached to AFM. Figure 4.8-A shows the sample before applying any electrical signal just after immersion in the solution. The bubbles started to release with the application of anodic pulses, with a long duration (Figure 4.8-B). Because of the gas evolution in the cell, it was necessary to remove the scanner head. Afterwards, de-gassing of the cell had to be done by slightly moving the liquid by suction and re-injecting it at a very slow rate of flow to avoid moving the species (corrosion products) near the working electrode. This time the tip was still thriving, so it enabled us to continue the measurements. The scanner was again repositioned and the tip re-tuned to approach the sample.

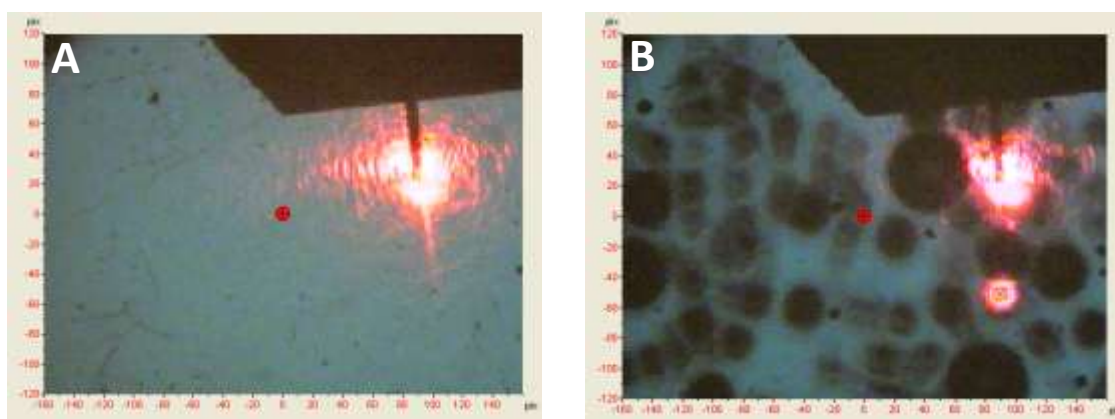


Figure 4.8: Optical images of the AA2024 in NaCl (0.5M) solution for the scanned area where the AFM cantilever is shined with the laser. Optical images were taken by the optical camera attached to the AFM: (A) optical image of the sample surface after immersion, and (B) optical image of the sample after applying anodic chronoamperometric pulse.

The surface was scanned again after locating an appropriate spot. Already before removing the scanner, time was elapsed and the surface started to get rough as shown in the last image (Figure 4.7-D) before having the harsh evolution of bubbles. Figure 4.9 shows the images were collected after removing the scanner and de-gassing the cell. Before removing the scanner, a pulse of $-0.4 \text{ V/Ag/AgCl/NaCl Satd}$ was applied, therefore the image shown in Figure 4.9-A was scanned after degassing and the last applied potential was $-0.4 \text{ V/Ag/AgCl/NaCl Satd}$. In Figure 4.9 the initial image of the new site seems to be rough with different features on the surface. After applying a more positive potential having a value of $0 \text{ V/Ag/AgCl/NaCl Satd}$, the surface started to be smoother. To have a clearer image, a 3D image was clipped from the pictures in Figure 4.7-A, and B with selecting the intermetallic particle in them, and profile lines were chosen as shown. From profile analysis of the particles (Figure 4.7-E), it is clear that the surface started to become smoother, in addition to trenching around the particle, which indicates that the particle could be a cathodic intermetallic particle.

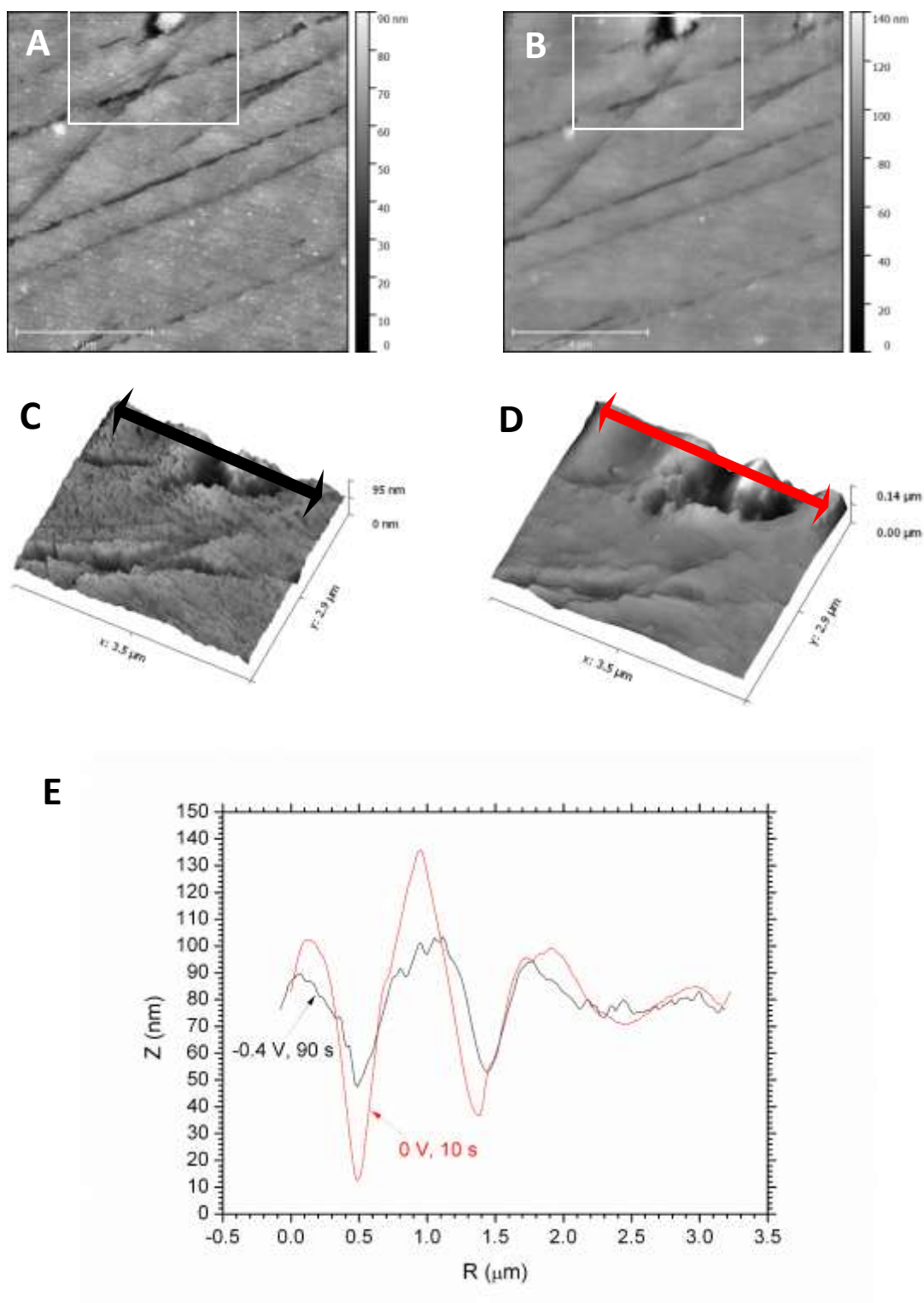


Figure 4.9: In-situ AFM topography of AA2024 immersed in NaCl (0.5M) after the application of different potential pulses. Topography after applying a chronoamperometric of (A) -0.4 V/Ag/AgCl/NaCl Satd for 90 seconds, and (B) 0 V/Ag/AgCl/NaCl Satd for 10 seconds,, (C), (D) corresponding 3D images of the marked areas in the two figures, respectively. (E) Profile line for the two linear sections in figures (C), and (D) [225].

4.2.1.2 SEM/EDS measurements

Samples were studied using SEM prior and after running electrochemical experiments. Before the experiments, the samples were studied to have an idea about the surface topography since SEM is a fast tool for scanning a large surface area of a sample. Moreover, EDS was used to study the different intermetallic particle inclusions. Samples were prepared as described in Section 2.2.2 and were mounted on stubs using a double-sided carbon tape. Many samples were studied and they all had similar characteristics. Intermetallic particles were present, low density of intermetallic particle (IMP) was found, though.

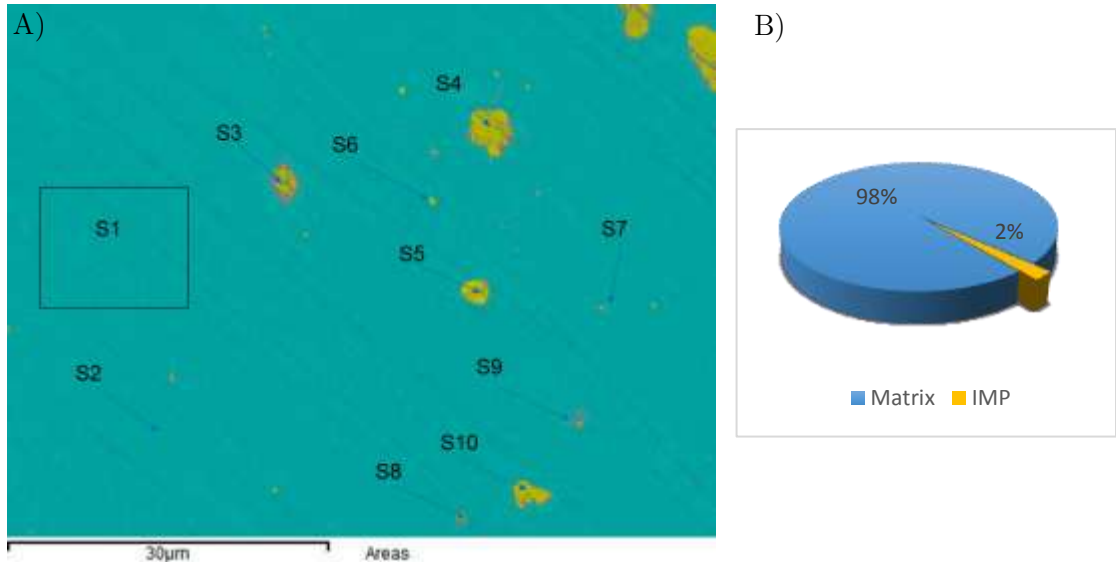


Figure 4.10: SEM image of a polished AA2024 sample. A) SEM image, B) the ratio of intermetallic particles (IMP) distributed all over the surface for the area presented in (A).

Therefore, an image is selected that can represent the different constituents of the sample. EDS spectra (Table 4.2) were collected for the different features seen in Figure 4.10. The features coloured in yellow represent intermetallic particles in the area presented in Figure 4.10.

From the EDS analysis in Table 4.2, the left column corresponds to the sites designated with arrows and S letter in Figure 4.10. The spectra denoted as 1 and 2 have the majority of aluminium (more than 90%) with a high percentage and some traces of Cu, Mg, and Si. While spectra 3 through 5 have a common feature that they have the ratio of Al: Cu: Mg ~ 2: 1: 1 that corresponds to the S-phase of AA2024 Al_2CuMg [14,110,244,247,300]. Spectra 6 and 7 have the ratio Al: Cu ~ 10: 1. Spectrum 8 has the ratio Al: Fe: Mn: Si ~ 13: 3: 3: 1 which is close to the θ -phase having a composition $\text{Al}_{12}(\text{Fe}, \text{Mn})_3\text{Si}$. Whereas, Spectra 9 and 10 represent the phase Al: Cu: Fe; Mn ~ 5: 1: 1: 1 [242,244]. It can be noticed that oxygen exists in all the spectra that could be due to the presence of the native oxide layer. The existence of different phases depends on the preparation method and treatment of the alloy. Carbon also exists which could be due to either the polishing process or the contamination because of the exposure to the electron beam. The traces in each spectrum is because of the penetration depth of X-ray, therefore some overlapped signals may come from the layer underneath the surface.

Table 4.2 EDS Spectra of AA2024 after polishing. Values are normalised in %at.

Spectrum	C	O	Al	Mg	Si	Mn	Fe	Cu
Spectrum 1	4.1	0.9	91.4	1.4	0.0	0.3	0.0	1.9
Spectrum 2	4.1	1.2	91.3	1.4	0.1	0.2	0.0	1.7
Spectrum 3	8.9	1.8	46.9	20.1	0.4	0.0	0.0	21.9
Spectrum 4	11.2	2.5	48.2	17.1	0.2	0.0	0.0	20.8
Spectrum 5	11.0	1.4	47.9	19.3	0.1	0.0	0.0	20.3
Spectrum 6	6.2	0.9	83.2	1.3	0.2	0.1	0.1	8.0
Spectrum 7	5.5	1.0	82.4	2.1	0.3	0.3	0.0	8.4
Spectrum 8	11.3	1.9	52.0	7.0	4.0	11.5	11.8	0.5
Spectrum 9	11.1	2.3	53.8	0.2	0.1	10.9	11.2	10.4
Spectrum 10	7.0	1.3	77.8	0.9	0.1	1.3	0.0	11.6

4.2.1.3 Infrared spectroscopy

To study the change of the surface chemistry, it was necessary to use one vibrational technique, therefore, the formation of a surface layer can be revealed. IRRAS was used to find the chemical change on the surface since EDS analysis proved the existence of oxygen. IRRAS in contrast to EDS is a global technique while the latter is a localised technique; consequently, it only gives the average of the exposed area.

Infrared spectroscopy is useful in finding the chemical change at the surface of reflective metals. Therefore, a polished coupon sample was prepared using the method in Section 2.2.2 to study the change of the surface using IRRAS. First, for studying the hydration, the AA2024 coupons were soaked in Milli-Q water for different times, and then IRRAS was measured for the surface.

Initially, the measured bands had a very low-intensity (Figure 4.11-A), which could be due to the low lateral coverage and/or the very thin thickness of the formed layer of the expected oxide/hydroxide. This layer could be formed initially after polishing and being exposed to air. Additional bands appeared in another initial sample exposed to air (Figure 4.11-B), which could be due to the inhomogeneous structure of the natural ores and/or the preparation and processing methods of aluminium.

It can be deduced from Figure 4.11-A that bands at 960 cm^{-1} start to disappear with the longer exposure time, which implies that Al-O-Al starts to shrink or transform. However, stretching bands between $550\text{--}700\text{ cm}^{-1}$ and 773 cm^{-1} start to improve [304] with longer exposure time. These bands correspond to tetrahedral and octahedral position of Al atoms, respectively. Tetrahedral and octahedral are different constituents of pseudo-boehmite.

Finally, samples were immersed in NaCl (0.5M) and different chronoamperometric pulses were applied (Figure 4.11-B). It can be ascertained from Figure 4.11-B that the more anodic the potential applied, the bigger the decrease of the band at 962 cm^{-1} , whereas the bands at $550\text{--}700\text{ cm}^{-1}$, 773 cm^{-1} , and 1090 cm^{-1} decrease.

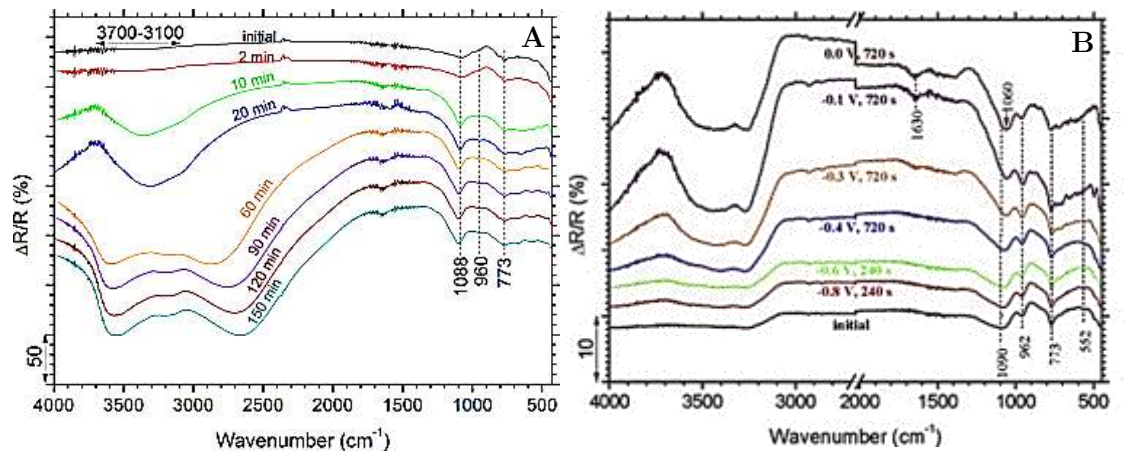


Figure 4.11: Ex-situ IRRAS of AA2024 immersed in NaCl (0.5M). A) Ex-situ IR measurements after immersion in Milli-Q water for different immersion times. B) Ex-situ IR measurements after application of different chronoamperometric pulses. The figures were adapted with permission from reference [225].

Table 4.3 IRRAS bands of immersed AA2024 in NaCl (0.5M).

<i>IR RA</i>	<i>Assignment</i>
<i>1157 shoulder</i>	-AlO(OH) [305–308], Al-OH [308]
<i>1118 shoulder</i>	
<i>1088 strong and broad</i>	Al-O stretching [305]
<i>960 medium</i>	Al-O-Al stretching [305]
<i>835 weak shoulder</i>	AlO ₄ stretching [309]
<i>773 strong</i>	Al=O angle bending [305]
<i>488 weak</i>	AlO ₆ stretching [309]
<i>467 weak</i>	AlO ₆ bending [309]

In-situ AFM study of bare AA2024 in NaCl (0.5M) was carried out at OCP and under potential control. The spontaneous change of AA2024 at OCP indicates the change of the surface which was clear from the statistical parameters as well as the AFM images. The chemical change of the surface revealed from IRRAS indicates the growth of a pseudo-boehmite layer after both hydration and anodic polarization in NaCl (0.5M).

4.2.2 Gel-coated AA2024

Different in-situ AFM – electrochemical measurements were carried out simultaneously. The samples were prepared first by polishing as explained in Sections 2.2.2 and 2.2.3, followed by coating preparation as described in Section 2.2.4 and mounted in the electrochemical cell for concurrent measurements as described in Section 2.2.6.

The coating was in-situ tested using three different electrochemical methods. The first sample was tested for a long immersion time while scanning in NaCl (0.5M) electrolyte, and measuring the open circuit potential and electrochemical impedance. The second sample was tested by applying chronoamperometric pulses of different potential excitation values. The third was tested by applying chrono-potentiometric pulses of different current values.

4.2.2.1 Spontaneous corrosion test

In this measurement, the sample was immersed while measuring the open circuit potential (OCP) and electrochemical impedance simultaneously with the topography. The purpose of this experiment was first to study the stability of the film under the influence of electrolyte immersion without applying any external electrical potential, and then to try to correlate the change in the topography to the change of electrochemical conditions.

The sample was checked first in the air, then electrolyte was injected into the cell, and the potentiostat was set to measure using the procedure in Appendix A.1. As regards OCP, however, it was monitored first for 50 minutes to capture the moment of injecting the liquid, as well as to follow the evolution of the potential during the early period of injecting the electrolyte into the cell.

4.2.2.1.1 In-situ AFM results

AFM started to scan the sample surface after tuning the tip and approaching the surface. Then, electrochemical impedance response was measured at OCP with an excitation amplitude of 5 mV. After each measurement, the cell was turned off and OCP was monitored for 3 minutes, and 7 seconds. The time elapsed from the moment of injecting the electrolyte and carrying out this experiment was more than 11 hours.

After the experiment, the files were collected for post-processing. First, they were exported to image format, then they were processed using MATLAB to extract the surface statistical parameters.

Figure 4.12 shows selected AFM images, to illustrate the change of topography during the course of the experiment. After injecting NaCl (0.5M) electrolyte into the cell, time was recorded. Started to record AFM images after 50 minutes of injecting the electrolyte. From the initial image of Figure 4.12-A, the surface looks to have some features dispersed over the surface of the sample. From the statistical analysis of the images, we can have an idea about the change in the surface during the immersion time. The temporal values of statistical parameters shown in Figure 4.13 and Figure 4.14 throughout the entire experiments summarise the change of the surface morphology. The initial image measured at 50 minutes after immersion has properties that resemble the Gaussian surface as it has a skewness value of 1.4 and roughness RMS in Figure 4.13 of 4 nm. Then, the roughness was increasing to reach a value of 8 nm after 138 minutes of immersion whereas the skewness reached a local maximum of 1.96 at 126 minutes. The increase of roughness is presumably due to the scanner drift, which is obviously due to the appearance of large particles on the upper right corner in Figure 4.12-B and these particles continued to move to the right side as shown in Figure 4.12-C. During the first 138 minutes of exposure, the roughness (Figure 4.13) was increasing rapidly in a rate of 4.83×10^{-11} m/min.

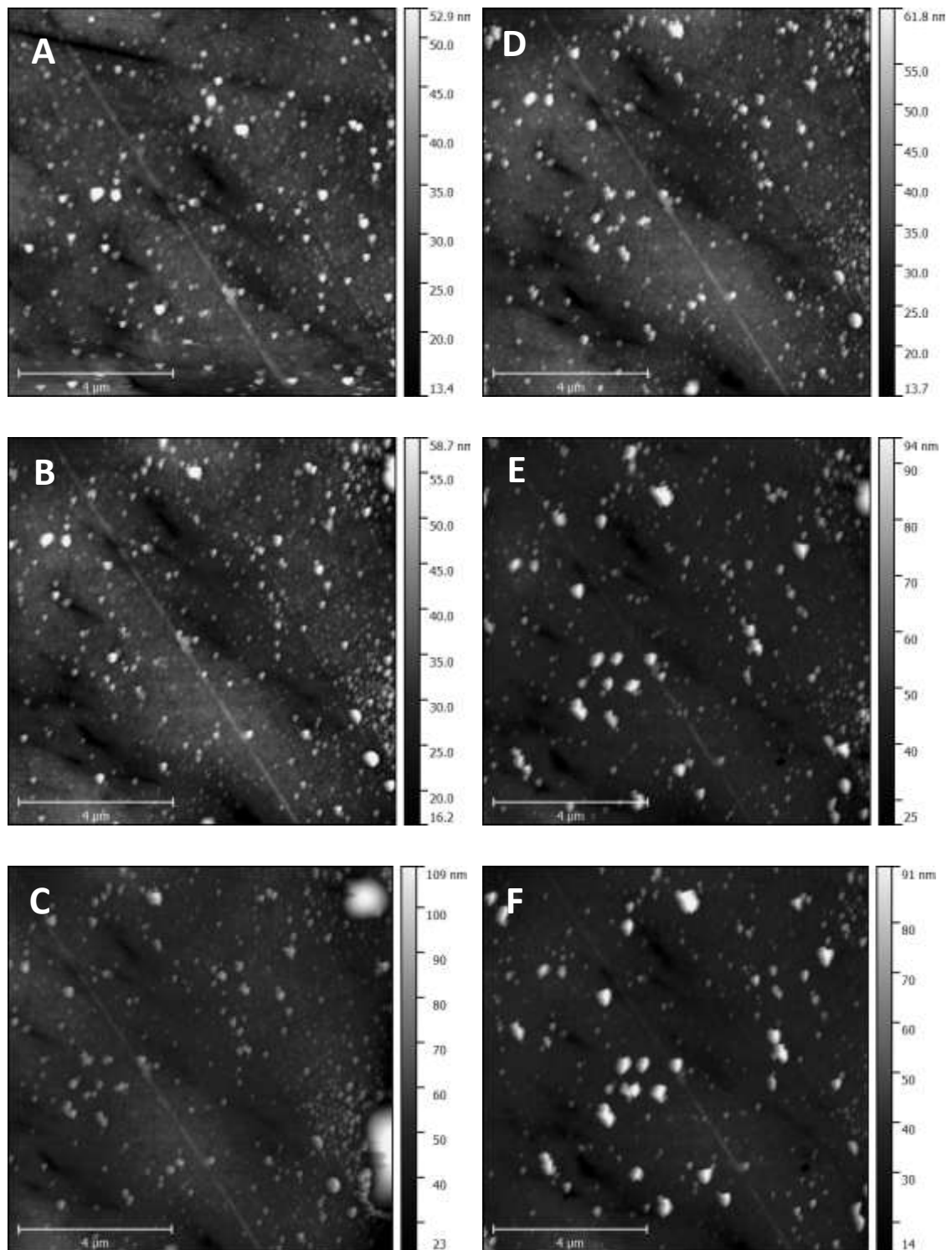


Figure 4.12: In-situ AFM topography of gel-coated AA2024 during the spontaneous corrosion test. (A) 50 min, (B) 69 min, (C) 138 min, (D) 145 min, (E) 422 min, and (F) 679 min. Time in min refers to the time elapsed after the introduction of NaCl (0.5M) electrolyte. The time was recorded from the moment of injecting the liquid into the cell, and started to scan the sample after tuning the tip. The scale bars are of 4 μm length.

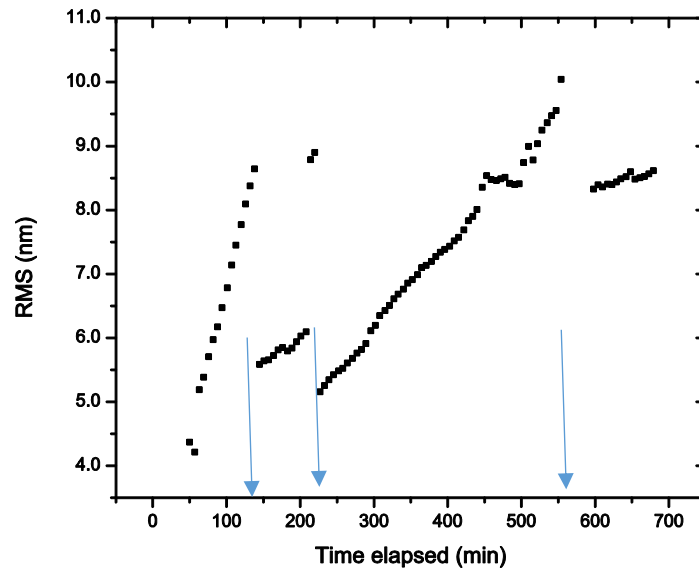


Figure 4.13: RMS temporal change of height of gel-coated AA2024 for long immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement. The arrows indicate the time of repositioning the sample.

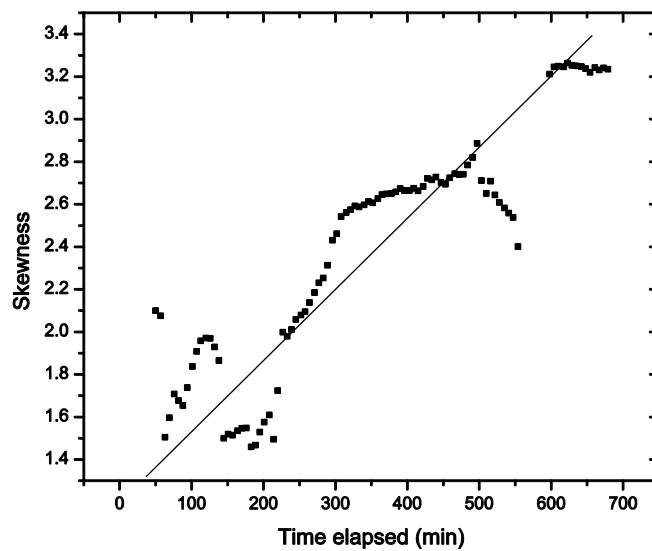


Figure 4.14: Skewness temporal change of gel-coated AA2024 for long time immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement. The line represents a guide to the eye.

After 138 minutes, it was tried to restore the image to its initial position to avoid the giant inclusions that appeared in Figure 4.12-C. The new position shown in Figure 4.12-D is close to the initial position, which has the RMS value of 6 nm and the corresponding skewness value of 1.5. The roughness RMS was increasing at a slow rate of 7.49×10^{-12} m/min to the minute 208. Then it was repositioned again at minute 227 to achieve a more stable setting without drifting to attain a roughness RMS value of 5 nm then the roughness RMS was increasing with an average rate of 1.33×10^{-11} m/min. A noticed jump in roughness was observed at 302 and 308 minutes, however, in this case it is not because of the drift. It was necessary to reposition the scanner again at the minute 453 which can be seen in Figure 4.13 to have a slightly decreasing roughness of an average rate 2.66×10^{-12} m/min. That change can be seen as a decrease in skewness in Figure 4.14. After 503 minutes of immersion, the roughness RMS started to grow again to reach a value of 10 nm with the average increasing rate of 1.64×10^{-11} m/min. After 598 minutes of immersion the tip was repositioned for the last time. The roughness RMS value was 8 nm at the minute 598 and increasing with an average rate of 3.06×10^{-12} m/min to have a final value 9 nm of RMS at the minute 679 while skewness has a negligible change.

The discontinuity in the RMS graph (Figure 4.13) is because of repositioning the scanner to the scanning area.

4.2.2.1.2 In-situ electrochemical results

As mentioned above, in the experiment the sample was immersed in NaCl (0.5M). The experiment was performed using a Bio-Logic SP-200 potentiostat (Bio-Logic SAS, Claix, France) at OCP. The measurements were started at the time of injecting the liquid into the cell. In this experiment, OCP was monitored in first 50 minutes after immersion, then alternating between measuring EIS and monitoring OCP during the course of the experiment. Experiment details are given in Appendix A.1. Figure 4.15-A shows the change of OCP value upon immersion in the electrolyte. It can be seen that OCP starts to stabilise after about 3 minutes of immersion to reach a value of -873.288 mV/Ag/AgCl/NaCl Satd, and was slightly decreasing to the value of -920 mV/Ag/AgCl/NaCl Satd after 30 minutes. Figure 4.15-B shows the evolution of OCP with time during the entire experiment. By inspecting the evolution of OCP in Figure 4.15-B, it can be deduced that OCP changes slightly during the experiment that reflects the stability of the film. A noticed change in the OCP value was observed after 92 minutes of immersion where it reached the value of - 897 mV/Ag/AgCl/NaCl Satd, then OCP was oscillating around -900 mV/Ag/AgCl/NaCl Satd. One more jump was observed in Figure 4.15-B at the minute 300 after immersion when OCP attained a value of -865 mV/Ag/AgCl/NaCl Satd. Then, OCP started to decrease gradually to become more cathodic.

EIS was measured at OCP with an amplitude of 5 mV/ Ag/AgCl/NaCl Satd. Figure 4.16 shows a Nyquist plot of EIS measured during the course of the experiment. there are different approaches towards interpretation of impedance spectra. One of them is to model the EIS data to fit a circuit. From this circuit different parameters can be extracted as each parameter represents a different mechanism in the system. Another approach, which is used here, is to monitor the variation of impedance as a function of given external variable (e.g. time, current, bias etc.) and try to use this information to elucidate the underlying processes. For example, the change of impedance spectra as a function of time is shown in Figure 4.16. The impedance is decreasing which is illustrated in the figure by

the different loops. The outer loop of impedance shown in Figure 4.16 corresponds to the initial impedance measured after 50 minutes of immersion .

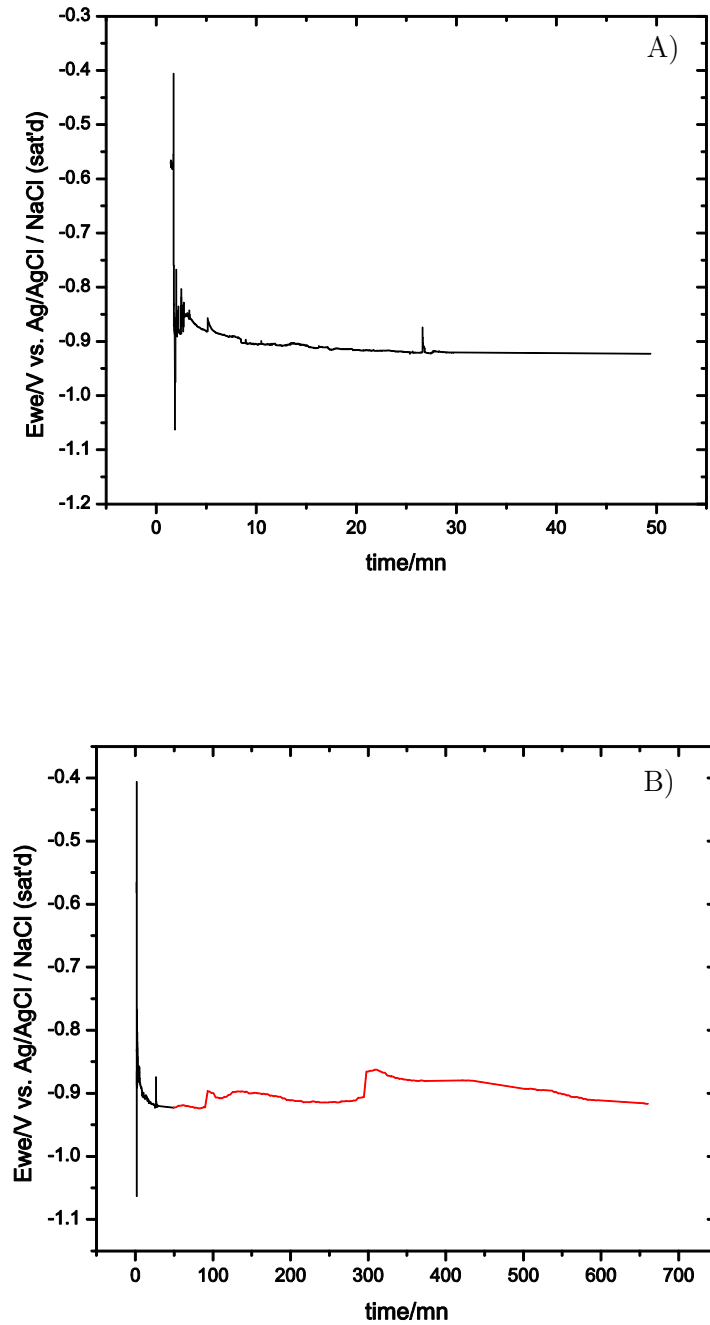


Figure 4.15: OCP evolution of immersed gel-coated AA2024 for the spontaneous immersion test in NaCl (0.5M). A) OCP evolution during the first 50 minutes of immersion, B) OCP evolution during the entire experiment.

To have a deeper view of the change in impedance, some frequencies were selected and the magnitude of impedance was calculated and displayed against time as presented in Figure 4.17. The high frequencies (7, 2, and 1 MHz) displayed in Figure 4.17 have a negligible change with time, those frequencies show the stability of the cell and connections. Lower frequencies shown in Figure 4.17 however indicate a significant change in impedance. Figure 4.17 reveals a smooth decrease of the impedance magnitude over time from 3 kOhm at the beginning to 1.5 kOhm for the frequency range 8 - 4 Hz. The different frequencies below 4 Hz have a common drop in the impedance magnitude at about 100 minutes after immersion. One more sudden drop of impedance magnitude was noticed in the frequency range 2.4 - 0.4 Hz around 300 minutes of immersion and showed an almost constant impedance afterwards. The impedance measured at frequency range 168 - 100 mHz started to increase after 300 minutes of immersion, though.

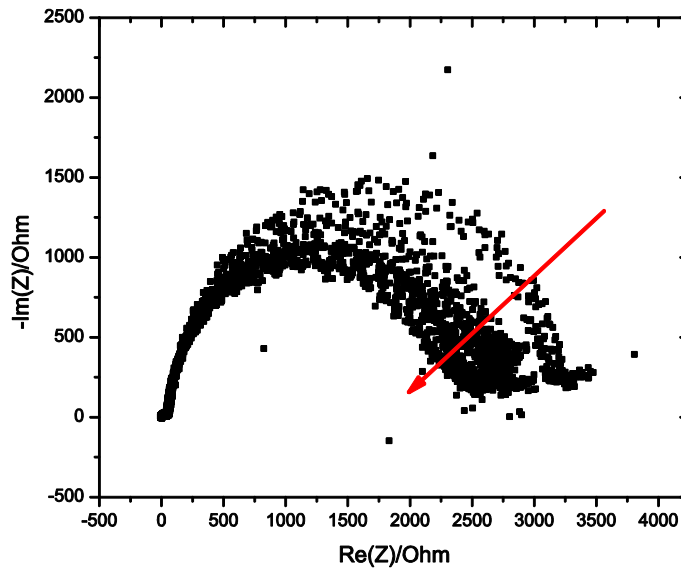


Figure 4.16: Nyquist plot of EIS measurements of gel-coated AA2024 for the spontaneous immersion test in NaCl (0.5M) during the 650 minutes of immersion. The arrow indicates the evolution of impedance with time.

The fast increase in roughness corresponds to a decrease in the impedance in the first 100 minutes that could be due to the increase of the surface effective area or the diffusion of the electrolyte through the coating. The discontinuity in roughness is due to the evolution of gas bubbles that shifted the tip from the scanning position after 100 minutes of immersion which could be seen in the drop of impedance magnitude at low frequencies and an increase of OCP. The increase of roughness accompanied by an increase in skewness means the surface becomes spikier which was presumably due to the growth of some species

adsorbed to the surface of the coating which can be seen in the AFM images. After 450 minutes of immersion, the increase of roughness goes along with a slow decrease of skewness that could be due to the fact that the amount of species adsorbed to the surface equals to the amount of holes or breakdowns of the coating that could show instability of impedance, as well.

After the elapsed time of immersion, it can be deduced that the film has a good stability in NaCl (0.5M) at room temperature. That could be seen in the slight change of roughness as the root mean square of the roughness during the course of the experiment. After immersion for more than 11 hours the overall change in roughness is only 5 nm accompanied by a positive increase in the skewness of less than 2. The low range of frequencies, which is more sensitive to the electrochemical change of the surface, varies slightly with time during the experiment time. The small change in the root mean square of the roughness during the long-time of immersion (11 hours) as well as the absence of gas bubbles indicate that the gel coating has a good corrosion resistance to NaCl (0.5M).

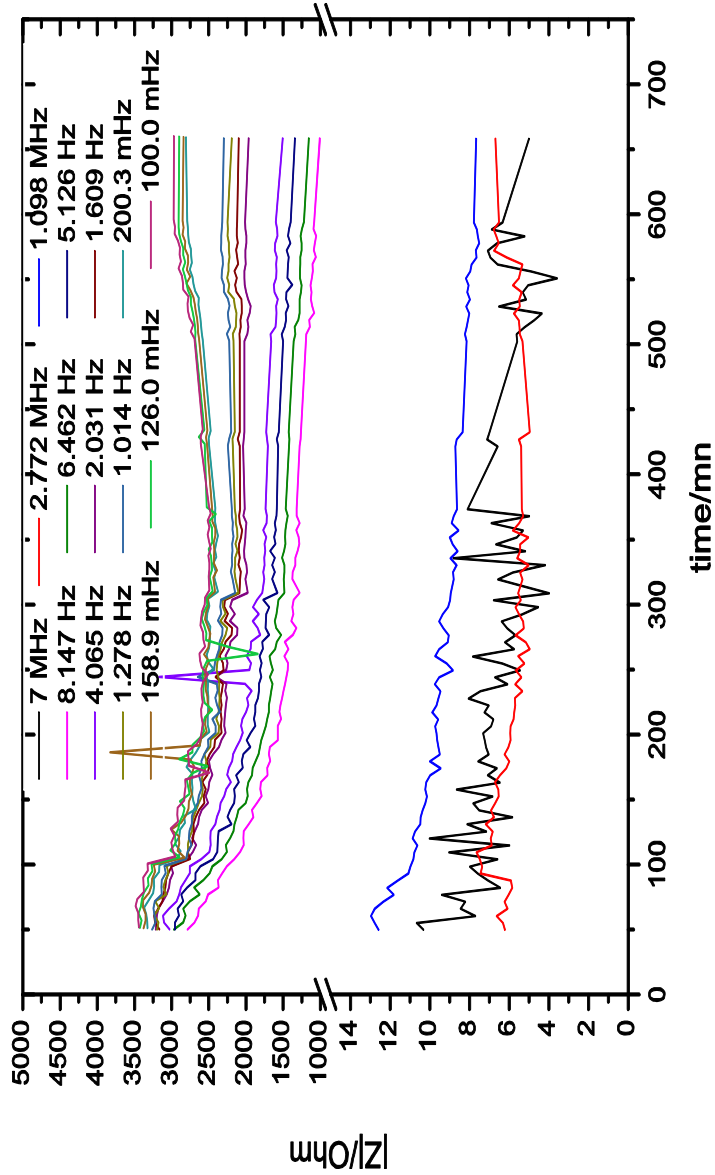


Figure 4.17: Temporal change of the EIS magnitude for selected frequencies of gel-coated AA2024 the spontaneous immersion test in NaCl (0.5M).

4.2.2.2 Chronoamperometric AFM

In this case, the gel-coated AA2024 sample was immersed in NaCl (0.5M) and electrical pulses of different potentials were applied to the electrode. After applying each pulse the cell was turned off, and open circuit potential was measured followed by measuring the electrochemical impedance. The change in the surface topography noticed upon the application of more anodic pulses, was an evidence of the coating dissolution.

4.2.2.2.1 In-situ AFM results

The sample was scanned in the air first, and then NaCl (0.5M) was injected into the cell. At the time of injecting the electrolyte, OCP was monitored, then the tip was tuned to approach the surface and scanning parameters were set. AFM started to scan the sample after 16 minutes of immersion. The images were collected, then processed as mentioned above to extract the statistical parameters: surface height RMS, and skewness.

The image shown in Figure 4.18-A is the initial image acquired at OCP after injecting the liquid into the cell and has a surface roughness RMS value of 9 nm and skewness 0.23 which is very close to the Gaussian surface. The sample showed a nearly linear increase in the roughness RMS value, as shown Figure 4.19, until the application of the first cathodic pulse -0.2 V Vs. OCP after 61 minutes of immersion. The evolution of gas bubbles leads to a shift of the scanning area, shown in Figure 4.18-B, to a new location that is obvious from the jump at RMS value at minute 61 in Figure 4.19. Interestingly, the roughness was increasing linearly with time and application of different chronoamperometric pulses with an average rate 0.14366 nm/minute. The skewness in Figure 4.20 was also increasing up to the turning point at 105 minutes of immersion to have the maximum value of 3.28.

Then, skewness started to decrease with the application of more anodic pulses, while roughness is increasing which is because of the coating dissolution, which is clear in the lower half of the image shown in Figure 4.18-C. The lower half of the image in Figure 4.18-C shows a continuing growth of the features on the surface. The coating was dissolving which is clear in the images shown in Figure 4.18 (C-F). Starting from Figure 4.18-D the surface started to show a real dissolution of the coating in the upper half of the images when compared with the image shown in Figure 4.18-B. The leftovers of the coating on the surface show a contrast, as their height is higher than the surface.

In this experiment, the last images acquired after 306 minutes of immersion show a deeper trench in the lower half of the image on one hand, and an increase of height of the features left over after the dissolution of the coating. That is the reason of decreasing in skewness in Figure 4.20 which became closer to a Gaussian. The skewness after 306 minutes of immersion is 0.625, which corresponds to a roughness RMS value of 51 nm. As aforementioned the total change of the roughness RMS value during more than 6 hours of the experiment is about 42 nm and have a linear increasing behaviour; however, skewness changes nonlinearly with time. The increase in the skewness value far away from the Gaussian surface is an evidence of the film break down while the decrease of its values at the end of the experiment is because of the semi-evenly distribution of the corrosion products.

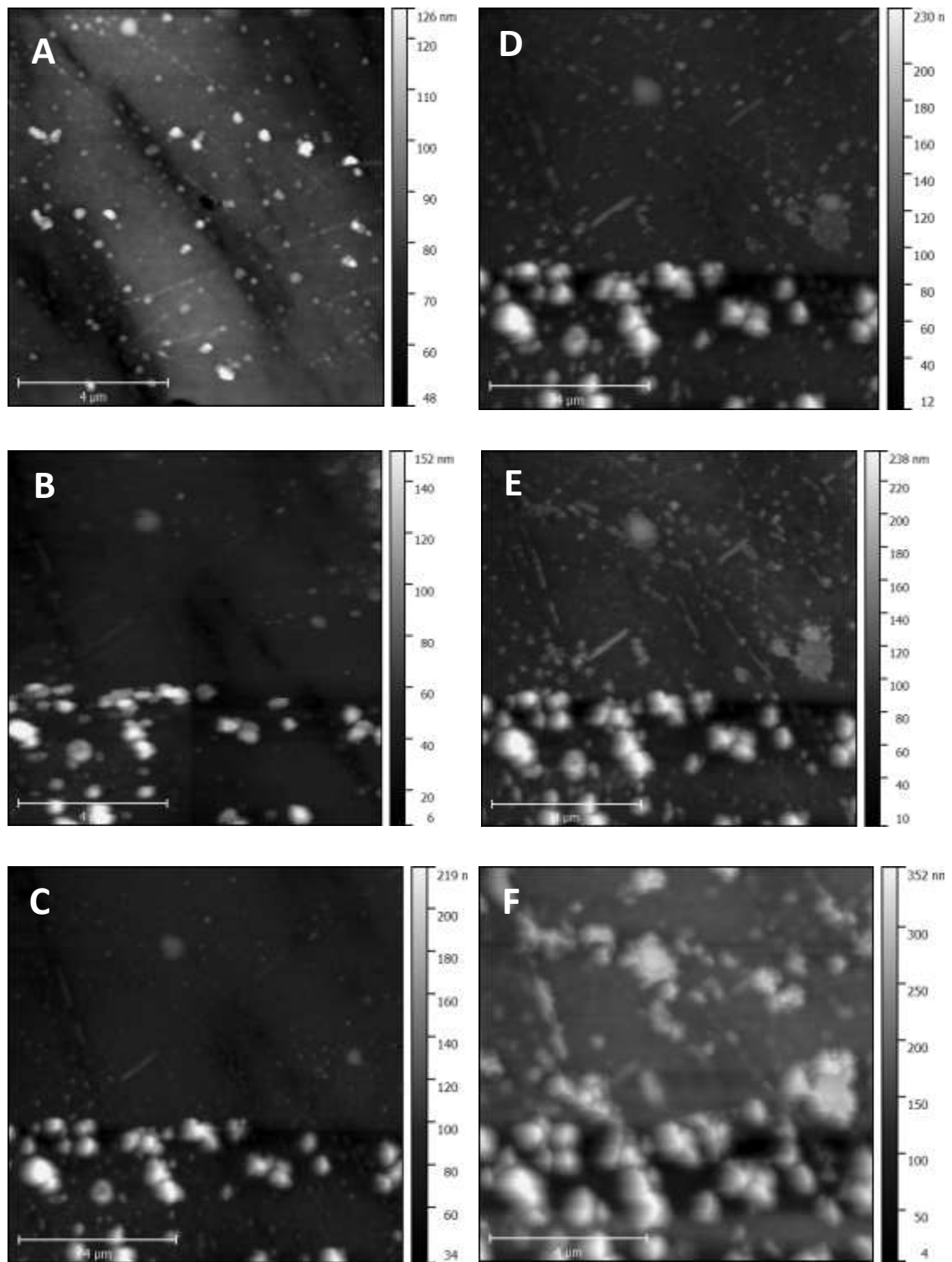


Figure 4.18: In-situ AFM topography measurement of gel-coated AA2024 immersed in NaCl (0.5M) for chronoamperometric test. (A) 27 min at OCP, (B) 67 min at -0.2 V vs. OCP, (C) 137 min at 0.05 V vs. OCP, (D) 155 min at 0.1 V vs. OCP, (E) 181 min at 0.15 V vs. OCP, and (F) 306 min at 0.2 V vs. OCP. Time in min refers to the time elapsed after the introduction of NaCl (0.5M) electrolyte. The length of scale bars is 4 μm.

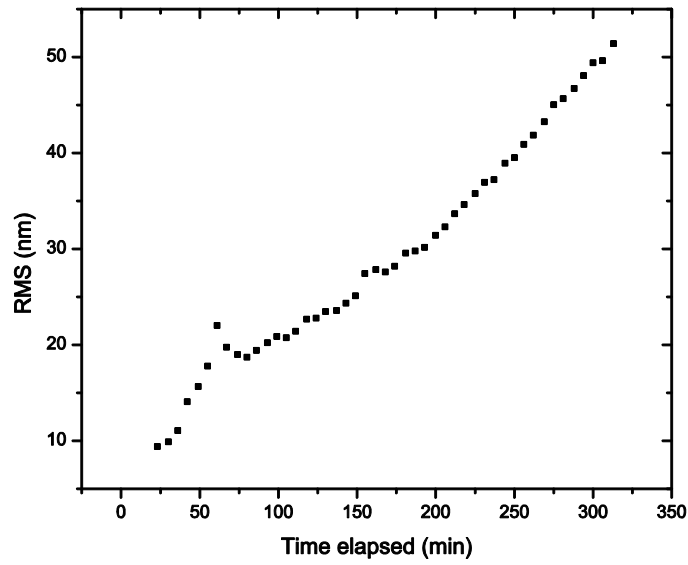


Figure 4.19: RMS temporal change of height of gel-coated AA2024 for the chronoamperometric test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

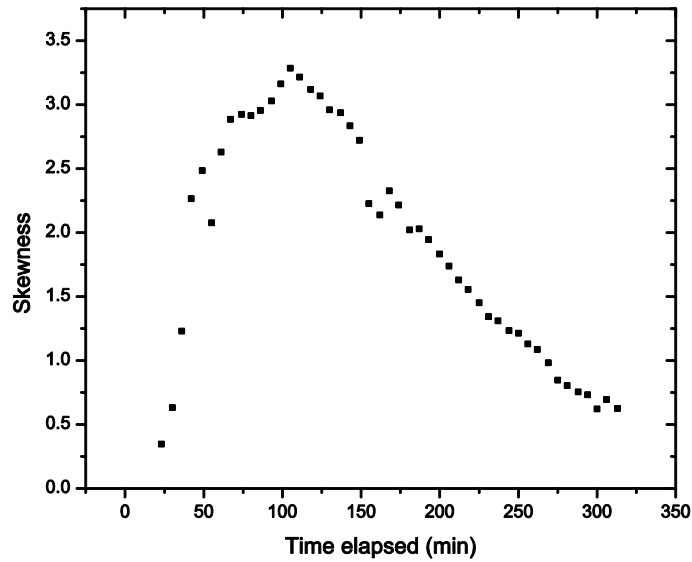


Figure 4.20: Skewness temporal change of height of gel-coated AA2024 for the chronoamperometric test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

4.2.2.2.2 In-situ electrochemical results

In this experiment, as mentioned above, the sample was immersed in NaCl (0.5M). The experiment was performed using Bio-Logic SP-200 (Bio-Logic SAS, Claix, France). The measurements were started at the time of injecting the liquid into the cell. In this experiment, OCP was measured in the first 30 minutes after immersion, then a loop of measuring EIS and OCP was repeated four times before polarising the sample. Subsequently, a sequence of steps consisting of pulses of different potential values were applied to the sample for a short duration of time, specifically 10 s, then the cell was turned off and OCP was measured followed by measuring EIS. Each sequence was repeated 4 times for each chronoamperometric pulse. Experiment details are given in Appendix A.2.

Figure 4.21 shows the change of OCP value upon immersion in the electrolyte. It can be seen that OCP is fluctuating in the first 30 minutes around a value of -600 mV/Ag/AgCl/NaCl Satd which could be because of surface contamination, or mechanical instability. Afterwards, EIS was measured at the corresponding OCP value which in turn was changing with time followed by monitoring OCP. As shown in Figure 4.22 OCP starts to stabilise around -585 mV/Ag/AgCl/NaCl Satd. A potential pulse with a value of -0.2 V vs. OCP and a duration of 10 s was applied four times. This resulted in a decrease in OCP value from -585 mV/Ag/AgCl/NaCl Satd towards more cathodic values, specifically to about -870 mV/Ag/AgCl/NaCl Satd in 16 minutes. Nevertheless, OCP started to be more stable with a slow increase upon application of CA pulses of -0.1 V vs. OCP, and in the course of the measurement of EIS during the relaxing time when the cell was turned off (i.e. no electrical pulses were applied). Furthermore, OCP was slightly increased during the time of applying CA anodic pulses of 0.05 V vs. OCP, as illustrated in Figure 4.22. In addition, OCP was decreasing to the cathodic direction when pulses that were more anodic were applied to the working electrode to have a final value of -850 mV/Ag/AgCl/NaCl Satd at the end of the experiment. The shift of OCP during the course of the experiment is about -250 mV/Ag/AgCl/NaCl Satd.

EIS was measured at OCP with an amplitude of 5 mV/ Ag/AgCl/NaCl Satd. **Error! Reference source not found.** shows a Nyquist plot of EIS measured during the course of the experiment. Before applying any CA pulses to the working electrode, EIS shows a high impedance value. With the application of more anodic pulses the impedance starts to decrease significantly which is clearly illustrated by the Nyquist plot of EIS measured after the application of each CA pulse. Moreover, the shape of the Nyquist plot starts to change after the application of CA pulses of amplitude -0.1 V vs. OCP, after about 100 minutes of immersion.

By joining AFM and electrochemical measurements, the mechanism of corrosion and dissolution of the film can be elucidated. First, upon immersion, the OCP was fluctuating, AFM measurements showed the Gaussian surface distribution, and the sample exhibited a relatively high impedance after 30 minutes of immersion. By applying the first CA pulses of amplitude -0.2 V vs. OCP, gas bubbles were evolved and AFM images were shifted to another location, whereas the impedance of the cell started to decrease accompanied by a large drop of OCP. All these phenomena may be seen as an evidence of coating dissolution. In addition, the OCP started to stabilise, then OCP started to slowly increase after the application of CA pulses of amplitude -0.1 V vs. OCP to be more positive. Despite the change of OCP to higher or lower values, the impedance showed a decreasing trend. Furthermore, the anodic CA pulses applied led to a noticeable dissolution of the coating,

which is clear in the AFM image shown in Figure 4.18-C. Besides the decrease in impedance, the spectra started to have a shape different from the initial loop. Applying more anodic pulses results in a decrease in impedance, along with a decrease in OCP, which is a sign of corrosion activity. The corrosion activity is clear in the dissolution of the coating, which is clear in all the different measurements AFM, OCP, and EIS. The problem of this technique is the evolution of gas bubbles in the case of using AA2024.

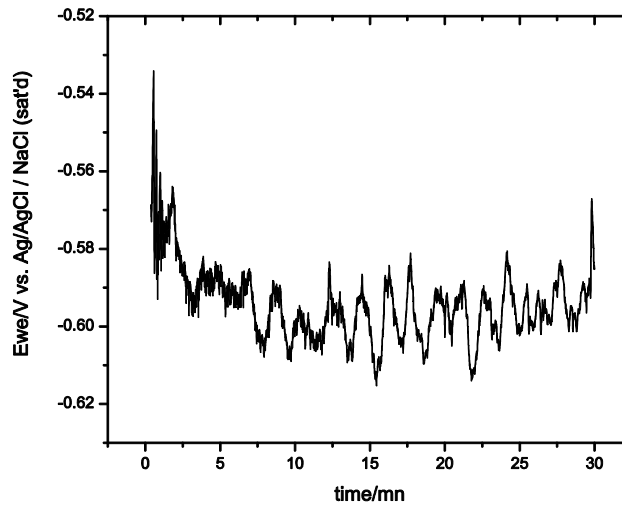


Figure 4.21: OCP measurements of immersed gel-coated AA2024 for the chronoamperometric test.

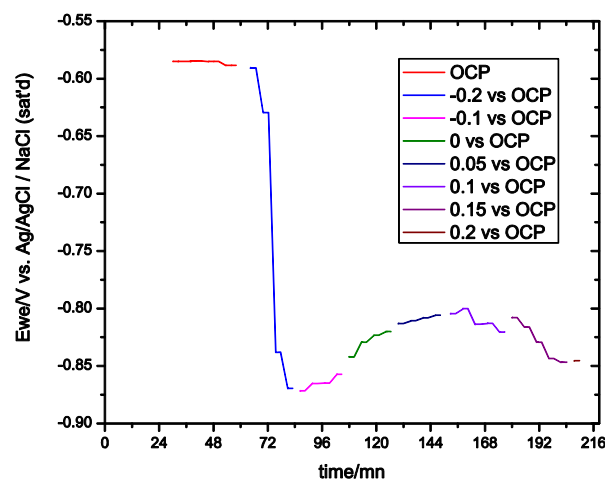


Figure 4.22: The temporal change of OCP of immersed gel-coated AA2024 in NaCl (0.5M) after the application of different chronoamperometric pulses.

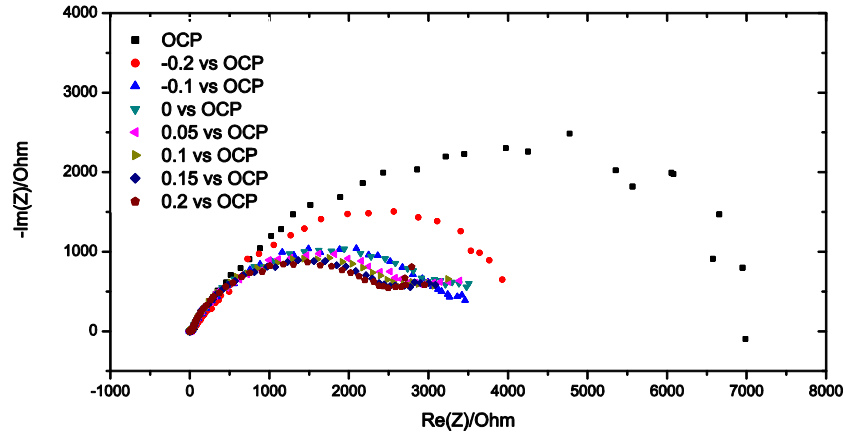


Figure 4.23: EIS measurements after applying chronoamperometric pulse each time.

4.2.2.3 Chronopotentiometric AFM

Because of the gas bubbles evolvement in the chronoamperometric technique, it was decided to use chronopotentiometry instead. In the in-situ chronopotentiometric experiment, electrical pulses of different current values were applied while imaging the topography. In analogy to the previous technique, after each pulse the cell was turned off, and open circuit potential was recorded followed by the electrochemical impedance measurement. From the knowledge of the previous experiment that corrosion is activated by applying a potential that is more anodic, in this experiment only anodic current of different values was applied to study the mechanism of dissolution of the film. The electrochemical measurements coincide with the previous ones as, that is the impedance is decreasing upon application of more anodic electrical pulses, which is an evidence of the dissolution of the film.

4.2.2.3.1 In-situ AFM results

The gel-coated AA2024 sample was scanned first in the air, afterwards, NaCl (0.5M) was injected into the cell. OCP was monitored immediately at the time of injecting the electrolyte, then the tip was tuned to approach the surface and scanning parameters were set. After 12 minutes of immersion, AFM started to scan the sample for more than 5 hours. The images were collected, then processed as mentioned above to extract the statistical parameters: surface height RMS, and skewness.

The image shown in Figure 4.24-A is the initial image acquired at OCP after injecting the liquid into the cell and has a surface roughness RMS value of 30 nm and skewness 6.13 which is far away from the Gaussian surface. This was due to the giant particle on the right side of the image and the other features. By applying chronopotentiometric (CP) pulses of a 0.1 mA amplitude, a slight change of the topography as shown in Figure 4.24-B was observed. An obvious change of the surface is noted in Figure 4.24-C after the application of different CP pulses described below (see Section 4.2.2.3.2). The dissolution of the coating became more clear after applying 0.6 mA CA pulses as can be observed in Figure 4.24-D. A significant change of the surface is presented in Figure 4.24-E after the

application of a 0.8 mA pulse, resulting in a big hole shown in the upper right corner of the scanned site. The surface lost its initial feature after applying a relatively high CA pulse of different amplitudes to end up with Figure 4.24-F at the end of the experiment.

After applying the first CP pulse with a current amplitude of 0.1 mA and 5s duration, a sudden drop of the skewness can be noticed (Figure 4.26) towards 4.77 which was because of image shift. The drop in the skewness goes along with an increase in the surface roughness RMS value, which was found to be 38 nm after 62 minutes of immersion as shown in Figure 4.25. The sample showed a nearly linear decrease in the roughness RMS value as shown in Figure 4.25 until 179 minutes of immersion to have a value of 36 nm with a 0.017 nm/minute rate of decrease in roughness RMS. Nonetheless, skewness shown in Figure 4.26 has a different behaviour as it was increasing until 156 minutes of immersion and had a value 4.97. Afterwards, it started to decrease, and a decrease is noted up to 179 minutes of immersion to a value of 4.48. After 191 minutes of immersion, a sudden drop is noticed in the skewness to have a value 0.05 rendering a Gaussian surface, in contrast to that an abrupt increase in roughness RMS was observed which had a value about 100 nm. The roughness RMS value kept increasing and the skewness kept decreasing until 216 minutes of immersion. Then it was difficult to scan the surface because it started to defect so it was hard to AFM to keep tracking of the surface changes with the same scanning parameters, therefore the latter were readjusted accordingly. After 254 minutes of immersion, the roughness RMS value started to decrease and the skewness started to increase to attain values of 185 nm, and -0.04, respectively. Skewness and roughness RMS started to grow again after 278 minutes of immersion to end up with the values of 5×10^{-4} and 228 nm, respectively.

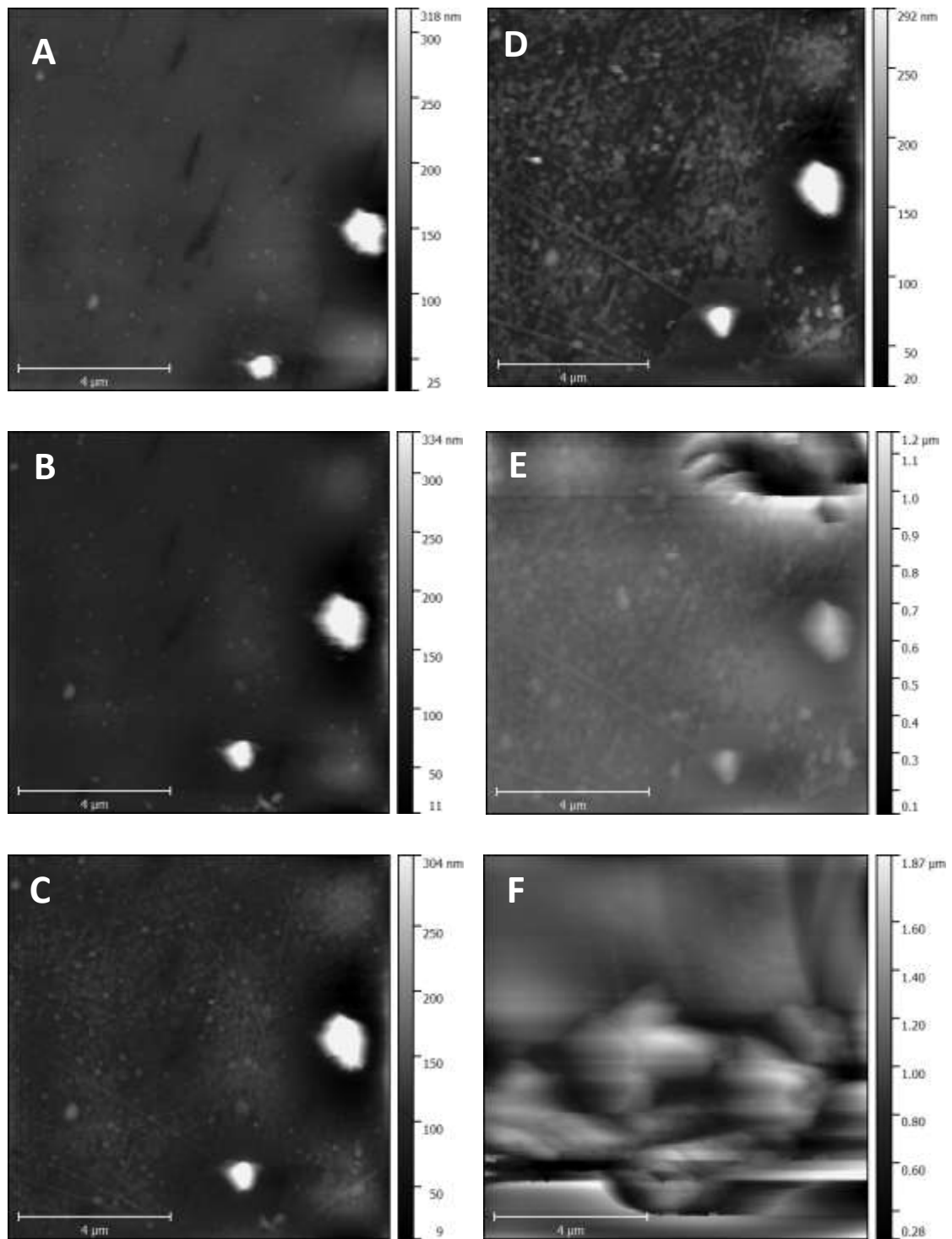


Figure 4.24: In-situ AFM topography measurement of gel-coated AA2024 immersed in NaCl for chronopotentiometry test. (A) 50 min at corrosion current, (B) 85 min after 0.2 mA, (C) 144 min after 0.6 mA, (D) 179 min after 0.6 mA, (E) 191 min after 0.8 mA, and (F) 313 min after 1.4 mA. Time in min refers to the time elapsed after the introduction of NaCl (0.5M) electrolyte. The current in mA is the value of the applied current pulse each of 5 seconds duration.

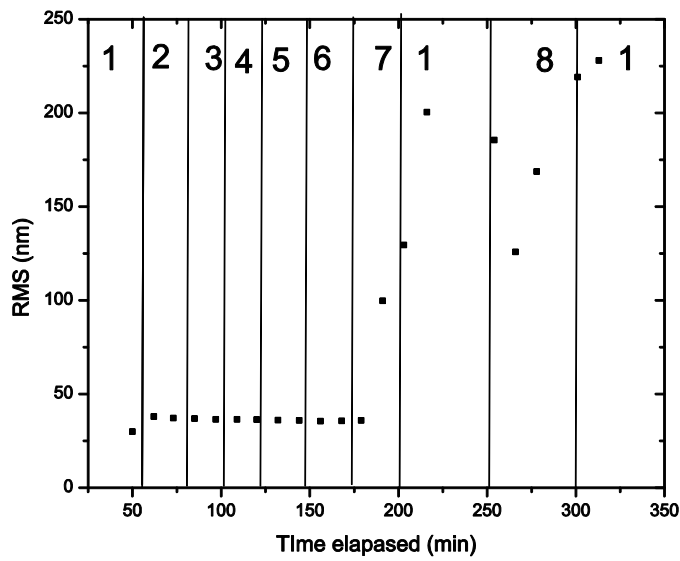


Figure 4.25: RMS temporal change of height of gel-coated AA2024 for the chronoamperometric test in NaCl (0.5M) extracted from the in-situ AFM topography measurement. The potential applied to each region indicated in the graph is as follows: 1) OCP, 2) -0.2 V, 3) -0.1 V, 4) OCP, 5) 0.05 V, 6) 0.1 V, 7) 0.15 V, and 8) 0.2 V. All the potential values are versus OCP measured at the start of the measurements.

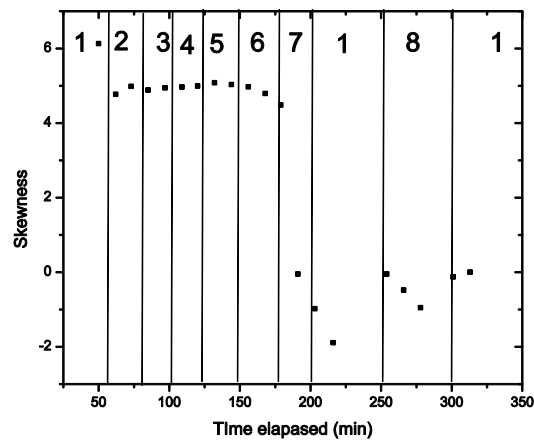


Figure 4.26: Skewness temporal change of height of gel-coated AA2024 for the chronoamperometric test in NaCl (0.5M) extracted from the in-situ AFM topography measurement. The potential applied to each region indicated in the graph is as follows: 1) OCP, 2) -0.2 V, 3) -0.1 V, 4) OCP, 5) 0.05 V, 6) 0.1 V, 7) 0.15 V, and 8) 0.2 V. All the potential values are versus OCP measured at the start of the measurements

4.2.2.3.2 In-situ electrochemical results

In this experiment, as mentioned above, the sample was immersed in NaCl (0.5M). The experiment was performed using Bio-Logic SP-200 (Bio-Logic SAS, Claix, France). The measurements were started at the time of injecting the liquid into the cell. In this experiment, OCP was measured in the first 30 minutes after immersion, then a loop of measuring EIS and OCP was repeated four times before polarising the sample. Subsequently, a sequence of steps consisting of pulses of different current values were applied to the sample for a short duration of time, 5s specifically. Then, the cell was turned off and OCP was measured followed by measuring EIS. Each sequence of steps was repeated five times for each chrono-potentiometric pulse. Experimental details are given in Appendix A.3.

Figure 4.27 shows the change of OCP value upon immersion in the electrolyte. It can be noticed that OCP starts to be steady after 10 minutes around a value of -600 mV/Ag/AgCl/NaCl Satd. Afterwards, EIS was measured at OCP followed by monitoring OCP, as shown in Figure 4.29 OCP is stable and not changing and has a value of -600 mV/Ag/AgCl/NaCl Satd. A current pulse of amplitude 0.1 mA with a duration of 5 s was applied five times. This resulted in a decrease in OCP value which became more cathodic with respect to the initial OCP and had a value -636 mV/Ag/AgCl/NaCl Satd. The decreasing trend of OCP towards the cathodic direction is sign of increasing corrosion activity. OCP continued to decrease and reached a value of -830 mV/Ag/AgCl/NaCl Satd. The shift of OCP during the course of the experiment is about -200 mV/Ag/AgCl/NaCl Satd.

EIS was measured at OCP with an amplitude of 5 mV/ Ag/AgCl/NaCl Satd. Figure 4.28 shows a Nyquist plot of EIS measured during the course of the experiment. Prior applying any CP pulses to the working electrode, EIS shows a high impedance value. By means of applying current pulses that are more anodic, the impedance starts to decrease, which is clearly illustrated by the Nyquist plot of EIS measured after the application of each CP pulse.

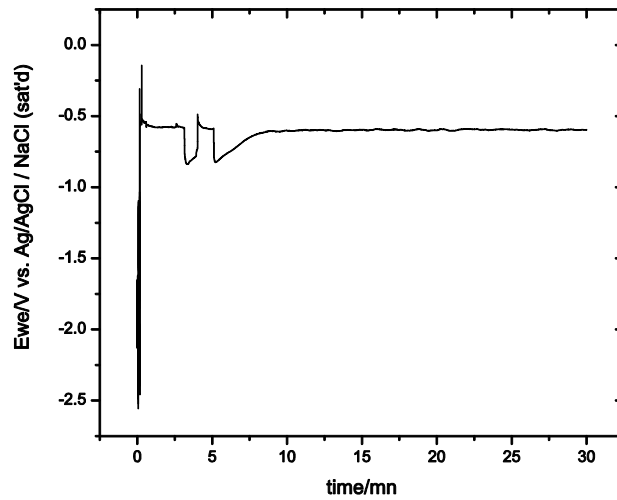


Figure 4.27: OCP measurements of immersed gel-coated AA2024 in NaCl (0.5M) for chrono-potentiometric test.

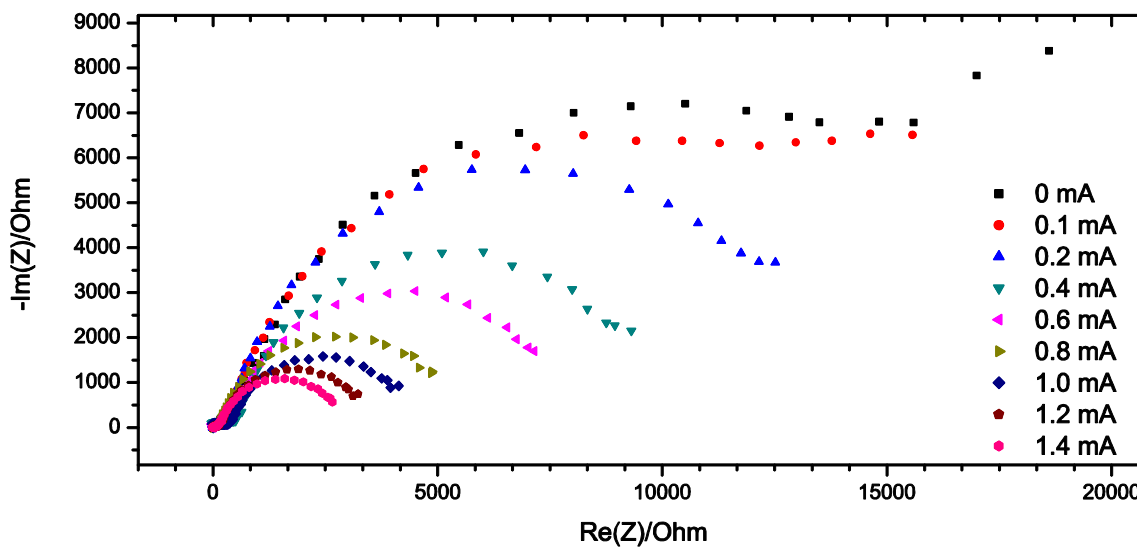


Figure 4.28: EIS measurements of immersed gel-coated AA2024 in NaCl (0.5M) after each application of the chronoamperometric pulse.

Combining AFM and electrochemical measurements, the mechanism of corrosion and dissolution of the film can be understood when applying a chrono-potentiometric pulse to a gel-coated sample. First, upon immersion, OCP started was stabilised after 10 minutes

of immersion, the initial AFM image showed that the surface was covered, and the sample exhibited a relatively high impedance after 30 minutes of immersion. Upon applying the first CP pulses of amplitude 0.1 mA, the impedance of the cell started to decrease simultaneously with a decrease of OCP. Despite the decrease of OCP, and impedance with the higher amplitude of current pulses applied, a negligible change could be noticed in the coating up to the application of CP pulses of amplitude 0.4 mA. The surface however started to change remarkably with the application of pulses that were more anodic. Furthermore, the application of anodic CP pulses of amplitude 0.8 mA led to a breakdown of the coating that appeared as a huge depression on the surface, which is clear in the AFM image shown in Figure 4.24-E. Applying more anodic pulses results in a decrease in impedance, along with a decrease in OCP, which is a sign of corrosion activity. The topography started to change entirely from the moment of applying CP pulse of amplitude 1mA. During the course of the experiment, no gas bubbles were evolved and AFM images did not show a significant shift to another location, which could help in monitoring the very same site from the beginning up until the end of the experiment.

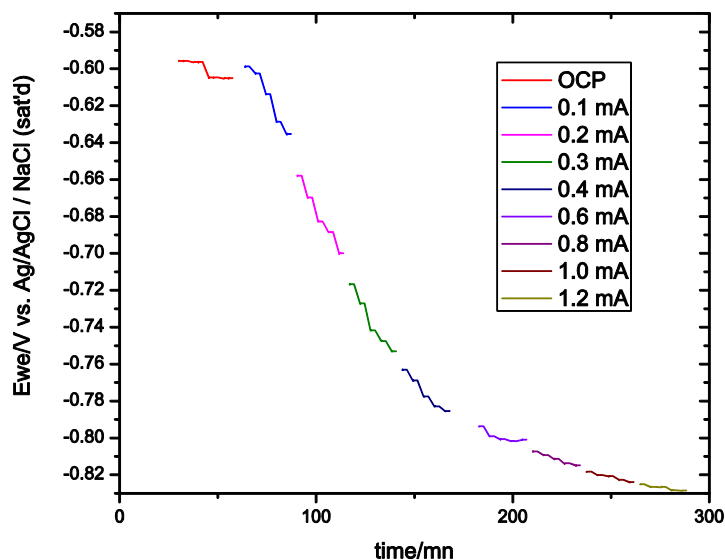


Figure 4.29: Evolution of OCP of gel-coated AA2024 in NaCl (0.5M) after the application of different CP pulses.

4.3 Conclusions

The study of bare aluminium immersion in NaCl (0.5M) revealed that the raw polished sample before any environmental or electrochemical treatment had a native oxide layer, which was confirmed by IRRAS measurements and EDS measurement. First, the experiments were carried out at OCP without applying any external potential to find how the surface spontaneously changes. It was found that the surface started to get rough, which can be seen in the change of kurtosis and skewness with time and after more than

an hour and a half it started to get smoother again. Interestingly, anodically polarised aluminium in NaCl (0.5M) showed the same behaviour.

IRRAS measurements implied the presence of initial native oxide layer. Hydration test indicated the growth of a pseudo-boehmite layer on the surface and disappearance of the oxide layer, which could be due to transformation, dissolution or over coverage of the native oxide. Likewise, testing of the samples by polarising them in a corrosive medium NaCl (0.5M) revealed the growth of pseudo-boehmite layer by applying anodic potentials.

By joining the different measurements of AFM and IRRAS it can be concluded that the pseudo-boehmite film starts to nucleate upon immersion in NaCl (0.5M), and it continues to grow with the time of immersion which makes the surface smoother. Alternatively, the process can be speeded up by anodically polarising the sample in an aqueous medium.

From the long-time immersion (about 11 hours) study of gel-coated AA2024 in NaCl (0.5M) we can conclude that the coating showed a good anti-corrosion resistance. The slight change in EIS of the spontaneously immersed sol-gel AA 2024 coated indicates a good corrosion resistance of the coating.

The application of chronoamperometric test was found to be efficient in testing the coating quality. In the present case, the coating could maintain its structure but started to break down on some locations which was presumably due to the weak adhesion at such locations. The application of more anodic pulses could break down the coating which was seen in the AFM images, the increase in the roughness and decrease of the electrochemical impedance. The problem of the chronoamperometric test is the evolution of gas bubbles in the case of AA2024 in NaCl solution, which disturbs the AFM tip and may introduce significant noise.

The application of chronopotentiometry appeared to be a good way to control the corrosion process so that it could be conveniently monitored with time. The application of anodic current values and measuring the impedance and topography in addition to OCP added important insight into the protection of the metal using the sol-gel coating. We observed noticeable changes in the surface with the application of different CP pulses and a gradual dissolution of the coating which was confirmed by the decrease in the electrochemical impedance value. The use of CP reduced the evolution of gas bubbles as its duration was not long. Interestingly OCP was decreasing in an exponential manner indicating a significantly increased corrosion activity of the surface. Although the studied sol-gel based films revealed some weaknesses, one needs to stress that the present films had a relatively low thickness (within about 120 nm).

Chapter 5

In-Situ AFM Study of Copper and Different Coatings

5.1 Introduction

Copper is the first metal used in mankind history. The pure form of copper has a reddish-brown colour. It exists in the Earth's crust in a ratio of about 50 parts per million (ppm) [310]. In nature, copper exists in the copper carbonates azurite and malachite, the copper sulphides chalcopyrite and chalcocite, and the copper(I) oxide mineral cuprite [311]. Copper exists in a polycrystalline form, with the largest single crystal reported of size $4.4 \times 3.2 \times 3.2$ cm [312].

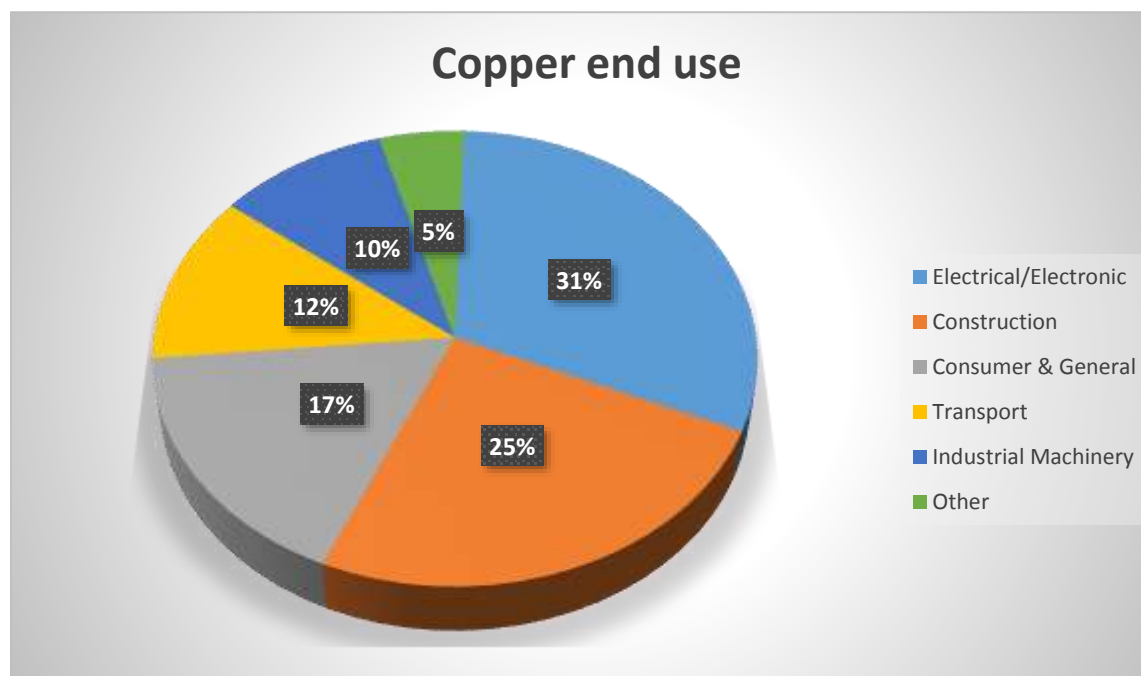


Figure 5.1: Copper industrial consumption in Europe [313].

Copper is widely used in different applications (electronics and telecommunications, offshore applications, building and construction, automotive, chemistry, medical purposes, marine engineering and many others). An overview of copper usage according to selected properties is given in Table 5.1. The chart shown in Figure 5.1 shows the end user applications. As can be depicted from Figure 5.1 the main copper is consumption (31%) is in the electrical and electronics fields because of its excellent electrical conductivity. The most widespread application of copper is in the field of electronics and telecommunication, where it is used as a clad on epoxy sheets for printed circuit boards, as well as planner and microstrip antennas. In addition, copper is also used in electrical wiring. The field of constructions comes into the second place of copper consumption owing to its appealing appearance. Copper is used in plumbing, roofing, and cladding which represents about 25% of copper consumption. The general consumption (17%) of copper includes copper alloys, antiques, and sculptures, different instruments, for example music, cookware, and coins. Transport is consuming about 17% of copper each year, for the components used in the vehicles. Industry machinery and other applications come at the end, such as motors, and all the other different applications.

5.1.1 Copper corrosion

In comparison to its alloys and other metals, copper is considered a noble metal in the absence of oxygen. The dissolution of copper depends on many factors, such as the medium, the pH value, the temperature, and the applied potential (anodic or cathodic). Copper is inert in water in the absence of oxygen and under cathodic potential at 25 °C [314]. In the presence of oxygen, copper is susceptible to corrosion.

The growth of Cu_2O and its structure depends on the pH of the surrounding medium. Feng et al. investigated the formation of cuprous oxide in aqueous solutions of different pH values [315]. It was found that the mechanism of corrosion is dependent on the pH of the solution and the corrosion products accordingly. At acidic pH values ($\text{pH} < 4$), the oxide film Cu_2O is porous, therefore it has a weak resistance to corrosion as copper dissolves mainly by diffusion in the solution. By contrast, the film has a crystalline form that acts as a diffusion barrier to anodic dissolution when pH value is in the range of (4-5), in this case, the anodic dissolution is controlled by a diffusion in both the oxide film and the solution. For pH values from 6 to 9, it was found that the oxide film gets thicker and has a higher corrosion resistance, and the anodic dissolution is merely controlled by the diffusion through the Cu_2O film. The film formed of Cu_2O is more dense and smooth in the case of immersion in a solution of pH 10, thus the surface was passivated. In the case of alkaline solutions of pH 10 and pH 13, the copper surface was covered by monoclinic CuO .

The formed oxide layer is influenced by the chloride ions such that the formed oxide layer passivates the surface, however, chloride ions start to interact with the oxide layer under some conditions including the long immersion time, high chloride concentration, or sample polarisation [316]. Thomas and Tiller found that in NaCl the oxide layer is protective and it breaks down on a rapid polarisation [316]. In addition, they found that the oxide film had a lower corrosion resistance to a higher concentration of chloride ions that was seen in the shift of the breakdown potential to be more negative and poorly defined. Furthermore, carbon contamination can influence the corrosion of copper [317]. Cornwell et al. [317] studied the corrosion of copper in different water supplies using carbon contaminated copper tubes with various degrees of contamination. They found that cuprous chloride was formed when a clean copper was immersed in water containing chloride due to the anodic dissolution of copper. The formed cuprous chloride transformed to cuprous oxide, which was precipitated on the surface. Moreover, the rate of copper's dissolution was increased for the carbon-contaminated surface in comparison to the alumina

abrasively cleaned surfaces, which is because of the formation of the contaminated oxide layer which is weakly adhesive to the copper surface.

Table 5.1 Applications of copper according to each physical property [318].

<i>Property</i>	<i>Industry/Type of Application</i>
<i>Aesthetics</i>	Architecture, sculpture, jewellery, clocks, cutlery.
<i>Bactericide</i>	Door hardware, marine internal combustion engines, and crop treatments.
<i>Biofouling Resistance</i>	General, hydraulic, and marine engineering, metalworking, aerospace, power generation, shipbuilding, offshore oil, and gas platforms.
<i>Corrosion resistance</i>	Plumbing tubes and fittings, roofing, general and marine engineering, shipbuilding, chemical engineering, industrial processes including pickling, etching and distilling, domestic plumbing, architecture, desalination, textiles, papermaking.
<i>Ease of fabrication</i>	Everything stated above plus printing.
<i>Electrical conductivity</i>	Electrical power generation, transmission and distribution, communications, resistance welding, electronics.
<i>Environmental friendliness</i>	Essential for the health of humans, animals and crops.
<i>Fungicide</i>	Agriculture, preservation of food and wood.
<i>Low temperature</i>	Cryogenics, liquid gas handling, superconductors.
<i>Mechanical</i>	General engineering, marine engineering, defence, aerospace.
<i>Non-magnetic</i>	Instrumentation, geological survey equipment, minesweepers, offshore drilling.
<i>Non-sparking</i>	Mining and other safety tools, oxygen distribution.
<i>Elasticity</i>	Electrical springs and contacts, safety pins, instrument bellows, electronic packaging.
<i>Thermal conductivity</i>	Heat exchangers and air-conditioning/refrigeration equipment, automotive radiators, internal combustion engines, mining.

Early studies of the corrosion of copper in seawater found that the surface of copper is covered largely by the corrosion products [319,320]. It was assumed that in neutral chloride solutions first a layer of cuprous chloride (CuCl) is formed. In the presence of sodium chloride solution cuprous chloride reacts and produces cuprous oxide (Cu_2O) which can be oxidised after time to form cupric hydroxide ($\text{Cu}(\text{OH})_2$), atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$), or malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) [319]. In the presence of a relatively higher concentration of chloride ion ($> 0.7 \text{ mol dm}^{-3}$), different complexes of cuprous chloride (CuCl_2^- , CuCl_3^{2-} , and CuCl_4^{3-}) are formed [321,322]. The formation of cuprous oxide in the presence of chloride ion is a precipitation reaction due to the reaction of the cuprous chloride complexes (the product of the dissolution of either the copper or CuCl) with the reduced oxygen [323,324]. The stability of Cu_2O decreases with the increase of the chloride ions concentration, and it is more stable than cuprous chloride at neutral and alkaline pH [324].

Despite the grain size influences the electrochemical behaviour of some metals such as magnesium [325,326] and titanium [327,328], the effect of grain size on the corrosion of copper is not clear. According to the electrochemical behaviour of copper and its alloys in the electrolyte, it was reported that the refinement of grain has a minor [329,330], increased susceptibility [331,332], and decreased susceptibility [333]. Thus, the nanocrystalline copper was found to be more electrochemically stable which could be due to the increased grain boundary density which in turn enhances the native oxide adhesion [333]. A study of copper corrosion in NaCl was carried out using EIS, FE-SEM, and field emission auger electron spectroscopy (FE-AES) by Van Ingelgem et al. [334]. Interestingly, they reported the corrosion of copper in NaCl takes place in different stages. First, they found a change in the surface due to the formation of an oxide layer that was uniformly formed on the surface, and they found the rate of growth of the oxide layer using FE-AES, and it continued to grow during the first 24 hours of immersion, then the formed oxide layer was attacked and a localised corrosion was noticed.

Copper corrosion has been studied using scanning probe microscope. Both AFM [17,18,114,121,240,335–339] and STM [23,340–342] have been used to study the corrosion of copper in different media. Zhang and Stimming used STM to study the dissolution of copper in aqueous perchloric acid (HClO_4) of different concentrations at OCP and they found that the rate of dissolution increases with the increase in the acid concentration. In literature, most of the copper corrosion studies were in sulphuric acid (H_2SO_4) and under anodic potential.

Pickering et al. [341] studied the anodic dissolution (in the Tafel region) of polycrystalline copper in a mixture of H_2SO_4 and Na_2SO_4 using STM. They noticed roughening of the surface due to the enhanced dissolution of low Miller index (hkl) planes. In addition, they reported smoothening of the plateau surfaces during the dissolution process. Cruickshank et al. [335] studied the dissolution of copper in H_2SO_4 using AFM and small anodic potentials (30 and 100 mV). It was found that a layer is formed on the surface due to the mechanical polishing of the surface with a thickness comparable to the size of the used polishing particles. Moreover, they found the layer started to dissolve under the application of 30 mV anodic potential, then a preferential dissolution of the grains began. The rate of dissolution was found to increase by increasing the applied anodic potential from 30 mV to 100 mV. Chan and co-workers [120] studied the dissolution of copper grains in H_2SO_4 again with the application of galvanostatic pulses, they could find a dramatic change in the surface in 20 minutes. It was found that the application of galvanostatic pulses develops the surface in such a way that the overlayer is removed followed by a growth of coarse features that were etched to form well-defined facets identified as $\{111\}$ closed packed planes. Afterwards, new facets started to develop, they were assigned to be $\{211\}$ and $\{221\}$ planes, which are less stable than $\{111\}$. Li and Lampner [240] studied the pitting of a thin film of copper deposited on a silicon wafer in 0.01M NaHCO_3 , they

found that the manner of applying a potential can control the shape and size of the formed pits. Bertrand and co-workers [17,18] studied the corrosion of copper in H_2SO_4 and Na_2SO_4 using AFM and the passivation of the surface using sodium heptanoate ($\text{CH}_3(\text{CH}_2)_5\text{COONa}$) and borate solution ($\text{Na}_2\text{B}_4\text{O}_7$).

In a series of publications, Martinez-Lombardia and co-workers used different combined techniques such as electron backscatter diffraction (EBSD) with ex-situ AFM [121], EBSD with STM [21,23], and EBSD with scanning electrochemical microscope (SECM) to study the corrosion of copper [24]. In their work, they found that the rate of dissolution of a grain is influenced by the neighbouring grain and their change in height is significant when the neighbouring grains are of near $\langle 100 \rangle // \text{ND}$ and near $\langle 111 \rangle // \text{ND}$ [121]. In addition, by employing SECM they found that the grains with orientation $\langle 001 \rangle // \text{ND}$ are more reactive than the grains with orientation near $\langle 111 \rangle // \text{ND}$ in the case of passivated copper while in contrary $\langle 111 \rangle // \text{ND}$ is more active than $\langle 001 \rangle // \text{ND}$ in the case of activated copper in chloride solution that could be due to the effect of the neighbouring grains [24]. Furthermore, STM studies confirmed that the coherent twin grain boundaries have a high resistance to corrosion [21], and by combining STM and SEM suggested that grains oriented closer to $\langle 111 \rangle // \text{ND}$ or in between $\langle 111 \rangle // \text{ND}$ and $\langle 110 \rangle // \text{ND}$ have a fast rate of dissolution with a neighbouring corrosion resistance grains oriented closer to $\langle 001 \rangle // \text{ND}$ [23]. Recently, Chen et al. [342] used STM to locally passivate the surface at the grain boundaries in NaOH by the anodic polarisation of the sample.

In this study, we are interested in finding the change of the surface topography and find its correlation to the change in the electrochemical impedance as well as the open circuit potential that are measured simultaneously, which can give a new insight into the interpretation of the corrosion mechanism.

5.1.2 Copper corrosion protection

As previously mentioned, copper has outstanding physical properties such as high mechanical strength, high-temperature resistance, high corrosion resistance. When copper is exposed to a wet environment, a hydroxide layer will be formed as well as other complexes. The formation of the layer changes its shiny colour or even influences its electrical and thermal conductivities. Therefore, some applications of copper required protecting the surface from corrosion. There are several ways to protect the copper from corrosion such as alloying or coating. Alloying affects the physical properties of copper such as the thermal and electrical conductivity, which is critical in some applications. Copper coatings have been used including polymers [343,344], sol-gel coatings, and graphene [97]. Here, we chose sol-gel and graphene as eco-friendly coatings to test their resistance to corrosion of copper in NaCl (0.5M).

Sol-gel coatings have already been used to protect the copper from corrosion. Boysen used inorganic sol-gel to protect the external surface of the copper kitchen, by coating it with $\text{SiO}_2\text{-ZrO}_2$ [345]. Incorporating ZrO_2 into the coating solved the problem of the thermal expansion mismatching between the copper and SiO_2 . Hybrid sol-gel coatings were used to promote the adhesion to the surface. Despite alkoxysilane having a good adhesion to most of the metals because it connects to the metal's surface through the silanol group, it was reported that silanol groups had a poor bonding to the copper surface, which is because of the formation of copper oxides (Cu_2O , and CuO) [346,347]. It is not easy to wet the oxide layer of copper by the sol solution [348].

Different precursors have been used to promote the adhesion to the copper surface. Li et al. [349] used to prepare the sol-gel coating for aluminium and copper. The precursor triacetoxysilane (TAVS) coating has a higher corrosion resistance than triethoxysilane

(TES), it was accounted for the hydrophobic nature of the vinyl group. Moreover, the 3-tri-methoxysilyl-1-propanethiol (TPS) has been used as it has a good adhesion to the copper surface. The TPS coating was studied as a protective coating for copper [350]. Mercapto group in the silane was used as it has a good adhesion to the copper surface [351,352]. Bescher et al. [353] used a mix of 3-glycidoxypropyltrimethoxysilane (GPTMS) and methyltrimethoxysilane (MTMS) and applied it to bronze and brass substrates. It was found that the mix had a good resistance to ultraviolet, and it enhanced the corrosion resistance. Tan et al. used epoxy and they found that the adhesion was promoted by incorporating 5 mol% of 3-mercaptopropyltrimethoxysilane (MPTMS) as well as enhancing the corrosion resistance [354]. Chen et al. studied the effect of the hydrolysis time on the corrosion resistance of (3-mercaptopropyl)triethoxysilane (MPTES) film on copper [355]. They used a different hydrolysis time and curing at 100 °C in air, and they found that the MPTES could reduce the corrosion current to about two orders of magnitude if the hydrolysis time was about 2 hours, and longer hydrolysis time reduces it to about three orders of magnitude and the best stable film was after 48 hours of hydrolysis. Zuchhi and co-workers, compared the protection of copper using different precursors [351], they found that silanol group did not interact directly with the copper surface. They concluded that the thiolate bond anchored the silane layer to the copper surface better than the oxane bond. Zuchhi had a further research to study the formation of the protective film on the copper surface [356], using different techniques including EIS, quartz crystal microbalance, Fourier transform infrared, and x-ray photoelectron spectroscopy. They found that MPTMS had a good adhesion to copper, and in the beginning was bonding weakly through H-bond, then after time it changed to strong bonding through thiolate group after the condensation of the film. In addition, they found that before the condensation of the film, the thick coating was weakly connected and then with ageing and curing it formed a strong siloxane bond. The formation of both siloxane and thiolate bonds led to a compact and adherent coating. Further curing of the coating showed less permeability and therefore enhanced corrosion resistance. In this study, we chose MPTMS to investigate its degradation under potential control.

In the case of the need to use a very thin layer of coating, coatings like polymers and sol-gel are not the best to use as in some cases to have a good corrosion resistance it is necessary to have a thick layer of coating, which increases the physical dimensions of the coated objects. Using a coating of a few nanometres thick is good for preserving the physical dimensions of the sample. Graphene is an atomic layer thick of carbon that makes it a good candidate to be used as a coating. Ideal graphene is more or less chemically inert [357]. Thanks for the sp^2 hexagonal lattice of graphene, carbon atoms provide a good impermeable physical layer that isolates the environment from interaction with the substrate. Graphene has proven its impermeability for oxidation, and therefore it can form a good protective layer against oxidation of metals [100,358]. Despite the outstanding ability of graphene to isolate a substrate from oxidation, the defects in graphene, such as dangling bonds, impurities, wrinkles, and grain boundaries, lead to an inhomogeneous degree of protection.

Parsai et al. used graphene as anticorrosion coating [97]. They mechanically transferred the chemical vapour deposited graphene layer(s) on copper and nickel substrates, and then they electrochemically tested it for corrosion resistance in Na_2SO_4 . They could realise that the graphene is a good anticorrosion coating and they found no oxidation takes place for the copper coating except for the uncovered area, which is at the graphene boundaries or its cracks. Minor defects in graphene were noticed in D bands by collecting Raman spectra after electrochemical treatment. They found that graphene coating prepared by CVD could decrease the rate of corrosion by about 7 times in comparison to the bare copper. Krikland et al. grew graphene coating on nickel and copper and tested the samples as prepared for

their corrosion resistance to NaCl (0.1 M) [359]. Kirkland found that graphene could protect the metals, however, the coating was of a different thickness. He also realised that it affected the metals in a different way, such that it slowed the anodic dissolution reaction of nickel, while it slowed the cathodic reduction reaction for copper. Singh Raman and co-workers found that the resistance of graphene coated copper was enhanced by one and a half order of magnitude when it was immersed in NaCl (0.1 M) [360]. It was found that long time immersion of graphene coated sample could even increase the rate of corrosion more than the bare metal [361], which was due to the inhomogeneity of the coating such that it occurred at the micro-sized domains. The induced corrosion of metal due to defects in graphene was accounted for the galvanic coupling between the graphene and the metal, and graphene has a cathodic character with respect to copper in the presence of corrosive medium [362]. Recently, Wlasny and co-workers studied the atmospheric corrosion for Cu(111) and polycrystalline copper coated with graphene using CVD by means of different surface science tools [363]. He could find that the surface of the single crystal graphene coated copper (111) was not affected by the atmosphere while in the case of the polycrystalline graphene coated copper was oxidised. He accounted it to the intercalation of the electrolyte between the graphene layer(s) and the surface of the copper.

In this work, we are trying to study the dynamic change of (3-mercaptop) trimethoxysilane (MPTMS) and reduced graphene oxide (RGO) under the application of cathodic and anodic potentials to find the change in the topography, and if the coating breaks down and corrosion starts to be active.

5.2 Experimental Results for Copper and Discussion

In this section, different bare and coated copper samples were used for various in-situ AFM electrochemical measurements.

First, bare copper was studied for spontaneous corrosion in NaCl (0.5M) electrolyte while measuring the electrochemical impedance and monitoring the open circuit potential for more than 15 hours.

Then, gel-coated copper was in-situ AFM studied under different electrochemical conditions when immersed in NaCl (0.5M). A sample was tested for long immersion time for more than 13 hours. The next sample was in-situ studied under the application of staircase potential to watch the dynamics of coating's breakdown. Finally, a cyclic voltammetry test was carried in-situ to find the change of morphology when this technique is used.

At the end, reduced graphene coating (RGO) was used as a coating of copper. First, in analogy to the test of gel coating, the sample was studied for long immersion time. Afterwards, another sample was AFM tested in-situ under the application of staircase potential. Finally, a sample was in-situ AFM tested by applying chronoamperometric pulses to find the coating resistivity to corrosion under electrical polarisation.

5.2.1 Bare copper study

The purpose of this experiment is to monitor the spontaneous change of bare copper when immersed in a corrosive environment such as NaCl (0.5M). Electrochemical impedance was measured as well as the open circuit potential simultaneously with monitoring the topography. The experiment was run for a long immersion time (more than 15 hours).

5.2.1.1 In-situ AFM results

The sample was prepared as described in Section 2.2.4 and mounted to the cell using the method in Section 2.2.6. The sample surface was checked first in the air, and then NaCl (0.5M) electrolyte was injected into the cell. After that AFM tip was tuned and started to scan the surface. Meanwhile, electrochemical measurements were carried out, simultaneously. AFM continued to scan the surface for more than 15 hours while it was immersed in NaCl (0.5M).

After the experiment, the files were collected for post processing. First they were exported to an image format as shown in Figure 5.2, then they were processed using MATLAB to extract the surface statistical parameters shown in Figure 5.3 and Figure 5.4.

A significant change in the topography is clearly displayed in Figure 5.2 during the course of the experiment. In order to elucidate the change of topography with time, it is necessary to find the change in height roughness RMS in Figure 5.3 and surface skewness. At the beginning of the experiment, specifically after 10 minutes of immersion Figure 5.2-A, the image has some artefacts in the fast scanning direction because of the rough surface, the surface exhibits a surface that is quite rough, as it possesses a roughness RMS of value 16 nm and skewness value 1.48. The surface roughness started to decrease after scanning for 30 minutes so its roughness RMS value is 11 nm while its skewness started to increase to have a value 2.55. The roughness RMS started to increase again after 40 minutes of immersion to have a roughness RMS value 12 nm, and a corresponding skewness value 1.87 near to the Gaussian surface. After 49 minutes of immersion, the surface is close to a Gaussian surface as it has a skewness value 0.58. The skewness kept decreasing quickly as shown in Figure 5.4 until it reached a maximum negative value of -7.43 after 106 minutes of immersion, and roughness of 33 nm. Then, the roughness was increasing linearly with time until 360 minutes of immersion to reach a value of 95 nm. However, skewness has a different behaviour in such a way that after 106 minutes of immersion, it started to decrease to reach a value of -5.93 after 219 minutes of immersion. Subsequently, skewness remained constant up to minute 257 with a very slight change to reach a value of -5.79. After that, it started to increase again and to reach a value of -4.65 at the minute 360 and corresponding roughness RMS value 95 nm.

An abrupt change in both the roughness RMS and skewness at minute 370 was observed to have values of 122 nm and -3.83, respectively. Roughness RMS and Skewness continued to increase to reach values of 128 nm, and -3.47 at 398 minutes. In addition, one more jump was noticed afterwards specifically at minute 417 to the values 162 nm and -2.40 of roughness RMS, and skewness, respectively. A negligible increase in the two parameters up to the minute 474.

One additional sudden change in the statistical parameters can be noticed in Figure 5.3 and Figure 5.4 at the minute 483 after immersion. The surface roughness continued to increase while skewness kept getting closer to a Gaussian surface to reach values of 210 nm, and 0.23, respectively.

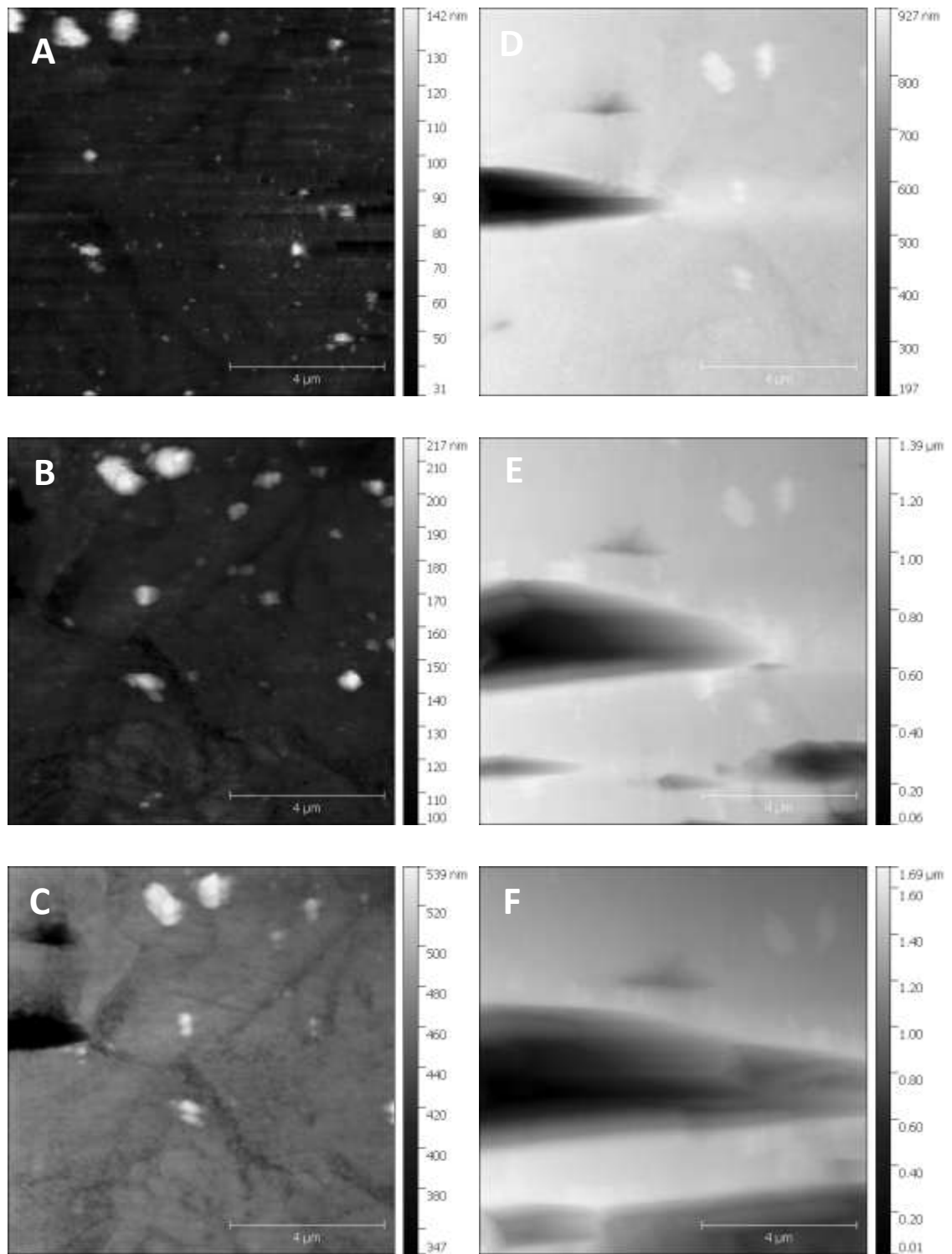


Figure 5.2: In-situ AFM topography measurement of bare copper immersed in NaCl (0.5M). (A) 10 min, (B) 40 min, (C) 106 min, (D) 360 min, (E) 483 min, and (F) 940 min, Time in min refers to the time elapsed after injecting the electrolyte into the cell.

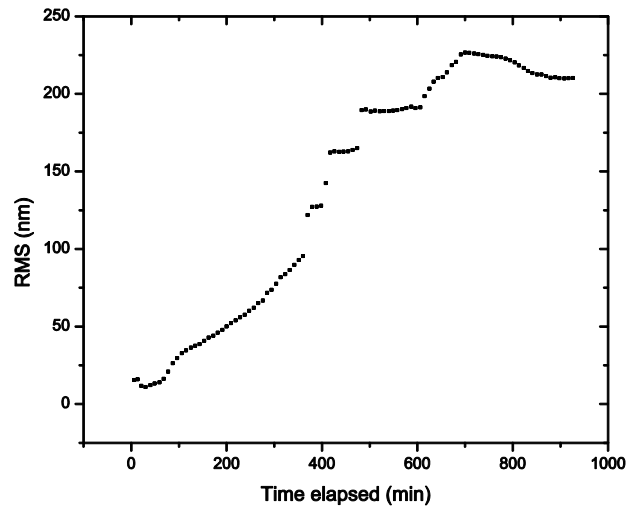


Figure 5.3: RMS temporal change of height of bare copper for long immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

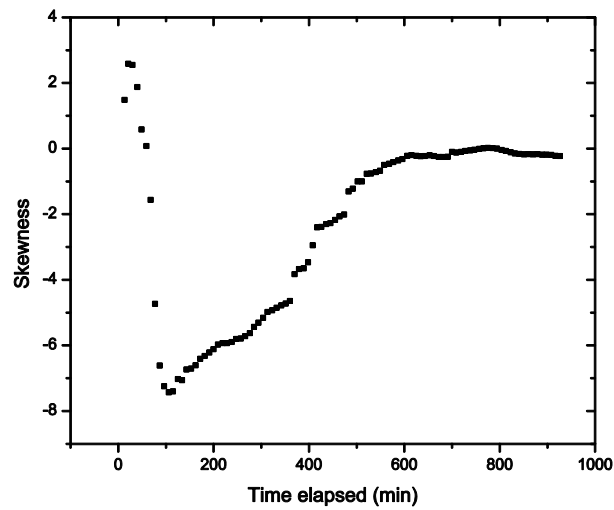
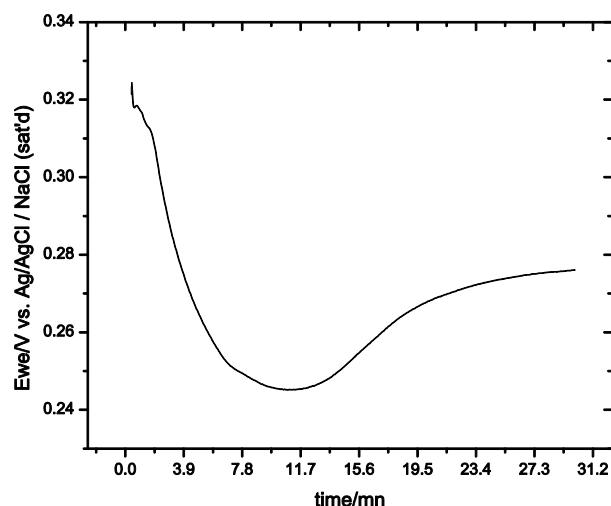


Figure 5.4: Skewness temporal change of height of bare copper for long immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

5.2.1.2 In-situ electrochemical results

A)



B)

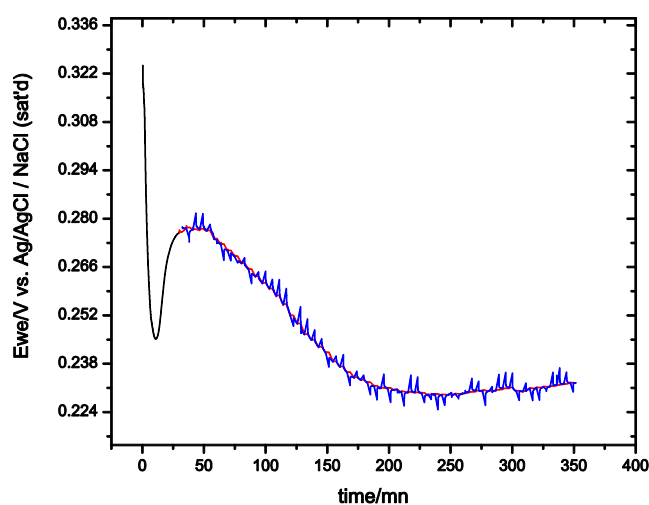


Figure 5.5: OCP measurements of immersed copper sample in NaCl (0.5M). A) OCP at the first 30 minutes, B) OCP during the entire experiment.

As stated above, in this experiment the sample was immersed in NaCl (0.5M). The experiment was performed using a Bio-Logic SP-200 potentiostat (Bio-Logic SAS, Claix, France) at OCP. The measurements were started at the time of injecting the liquid into the cell. In this experiment, OCP was monitored in first 30 minutes after immersion, then interchanging between measuring EIS and monitoring OCP during the course of the experiment. Experiment details are given in Appendix A.1. Figure 5.5-A shows the change of OCP value upon immersion in the electrolyte for the first 30 minutes. Figure 5.5-A depicts a change in the value of OCP upon injecting the electrolyte into the cell as it was

decreasing until it reached a minimum value of 245 mV/Ag/AgCl/NaCl Satd after 11 minutes of immersion.

Then, OCP started to increase again to have a value of 276 mV/Ag/AgCl/NaCl Satd at the minute 30. EIS measurements were started at that time. The Nyquist plot of the electrochemical impedance spectra measured during the 360 minutes of the experiment is shown in , whereas the temporal change of the magnitude of impedance at different frequencies is shown in Figure 5.7. We can find that the impedance started to increase a little up to 55 minutes of immersion to have its maximum value, and then it started to decrease. Figure 5.7 depicts a fast decrease of electrochemical impedance magnitude with time up to minute 133, simultaneously with a decrease of OCP in Figure 5.5-B. The magnitude of EIS started to decrease slowly from minute 133 to minute 173, then it was decreasing in a slower rate as shown in Figure 5.7. A negligible change in both electrochemical impedance magnitude and OCP from minute 173 onward till the end of the measurements at minute 360 was observed.

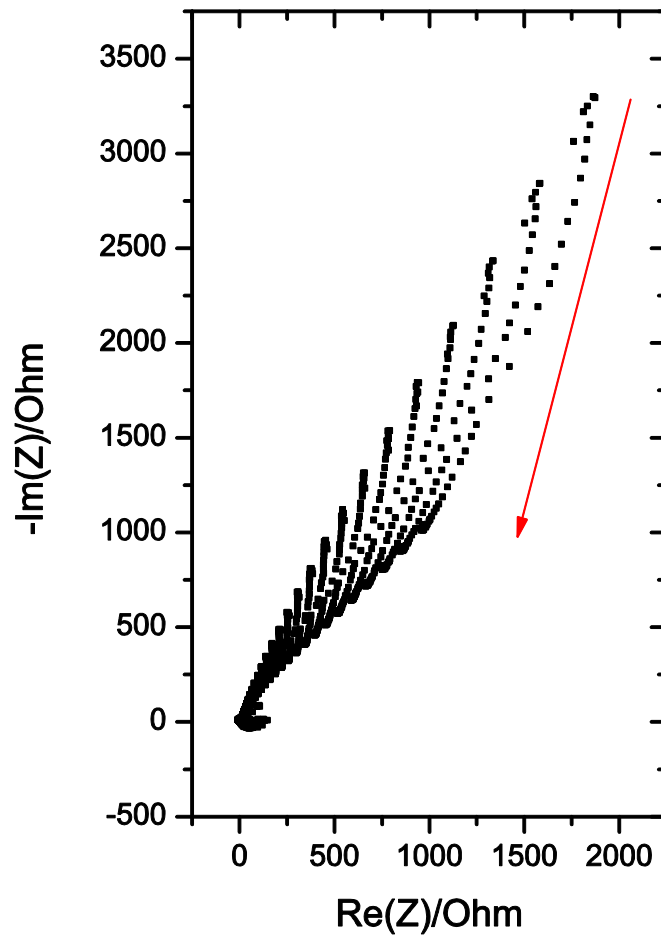


Figure 5.6: Nyquist plot of EIS measurements of immersed copper sample in NaCl (0.5M) for the spontaneous test during the 360 minutes of immersion. The arrow indicates the evolution of impedance with time. The arrow indicates the evolution of EIS with time.

Combining both AFM and electrochemical measurements, we can have a deeper insight into the dynamics of corrosion of copper in NaCl (0.5M). From the above results, a noticeable concurrent change in the topography, open circuit potential and electrochemical impedance during the course of the experiment. After the immersion, the open circuit potential was decreasing as a sign of the active corrosion that was monitored by AFM as obvious in the change of topography between Figure 5.2-A and Figure 5.2-B. The decrease of the impedance magnitude in Figure 5.7 is accompanied by an increase in roughness RMS and decrease in skewness, which is an evidence of the corrosion attack to the native oxide layer on the top of the copper surface. Then, the magnitude of impedance became constant as well as OCP, while the roughness RMS as well as the skewness were increasing to end up with a Gaussian surface. The latter occurred due to corrosion of copper itself and started to dissolve. In addition, the change in the surface measurements from AFM does not have a corresponding change in the electrochemical parameters, which could either be due to the insensitivity of the electrochemical measurements to the pitting and its development or because the electrochemical measurements are macro-scale measurements that are less sensitive to the minor changes in the surface topography especially in the early stages of corrosion as in our case. The second possibility is more expected.

Bare copper is susceptible to corrosion in NaCl (0.5M) after long immersion time. The change in the copper surface started to appear after about an hour, and NaCl (0.5M) started to attack the surface of copper more with time until the end of the experiment time after about 940 minutes of immersion.

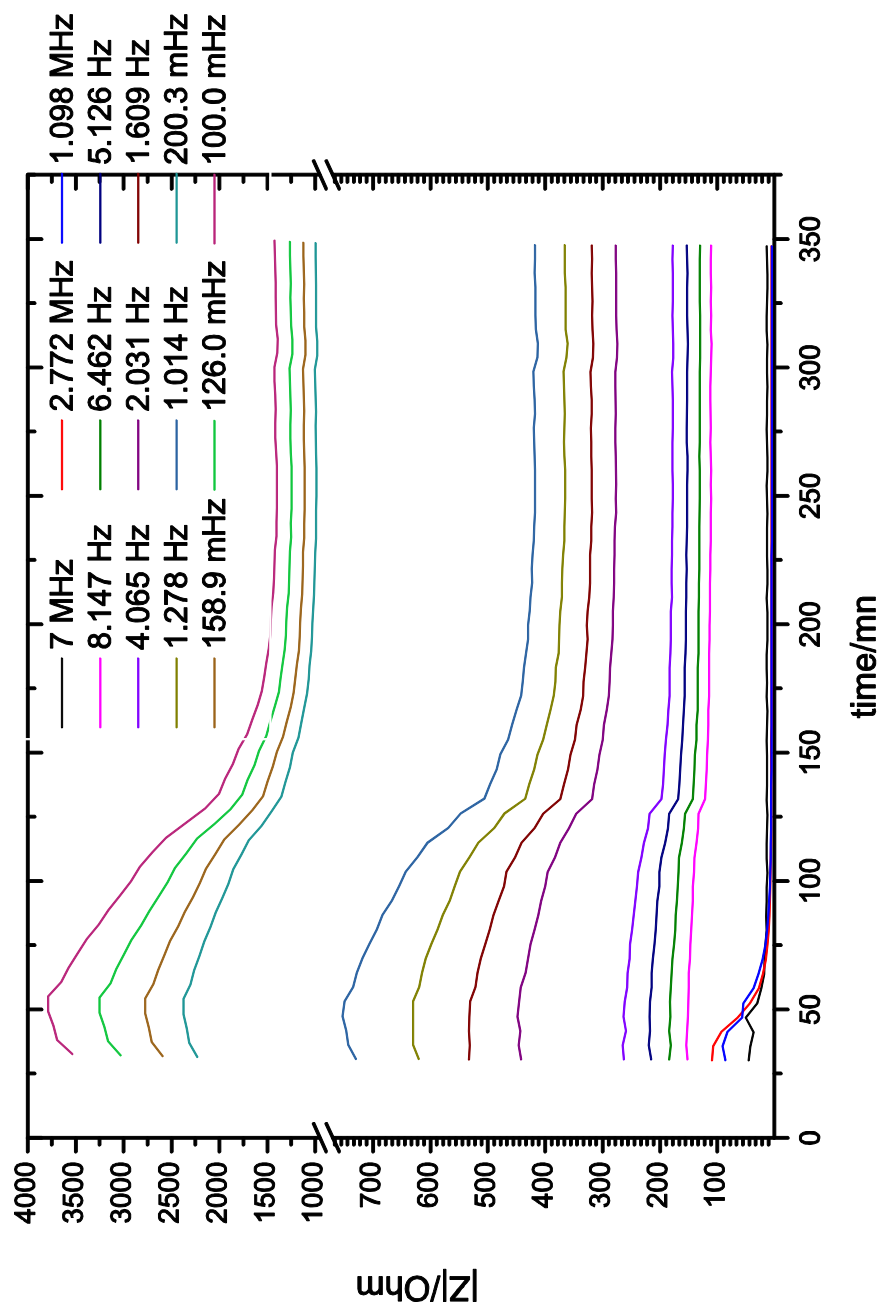


Figure 5.7: Temporal change of the EIS magnitude for selected frequencies.

5.2.2 Gel-coated copper

Different in-situ AFM - electrochemical measurements were carried out simultaneously. The samples were prepared first by polishing as given in Sections 2.2.2, and 2.2.3, followed by coating preparation as described in Section 2.2.4 and mounted in the electrochemical cell for simultaneous measurements as described in Section 2.2.6.

In-situ testing of the coating was carried out using three different electrochemical methods. The first sample was tested for long immersion time while scanning in NaCl (0.5M) electrolyte, and measuring the open circuit potential and electrochemical impedance. The second sample was tested by applying a step potential. The third was tested by running in-situ cyclic voltammetry to monitor the change of the topography upon applying this technique.

5.2.2.1 Spontaneous corrosion test

The purpose of this experiment was to study the spontaneous change of the coating while immersed in the electrolyte for a long time. Therefore, the film stability upon immersion in NaCl (0.5M) as a corrosive medium can be studied with time without applying any external electrical potential.

5.2.2.1.1 In-situ AFM results

In this experiment, the sample's surface was first scanned in the air. Then, NaCl (0.5M) electrolyte was injected into the cell. Immediately, OCP was monitored for 30. Meanwhile, the AFM tip was tuned, and then it approached the sample. Afterwards, the surface was scanned while measuring the electrochemical impedance, and open circuit potential, alternatively. The details of the electrochemical measurements used are given in Appendix A.1.

The experiment duration time was more than 11 hours of measuring topography, OCP, and electrochemical impedance, simultaneously. During the course of the experiment, there was some drift and was manually compensated by repositioning the tip. After the experiment, the AFM files were collected and converted to image files some selected images are displayed in Figure 5.8 at different times, and then they were processed using MATLAB code to extract the statistical parameters shown in Figure 5.9, and Figure 5.10.

After 17 minutes of injecting the electrolyte into the cell, the surface possesses a nearly Gaussian distribution as it has a skewness value of 0.39, and a roughness RMS value of 11 nm as shown in Figure 5.8-A. The roughness RMS started to decrease as shown in Figure 5.9 accompanied by an increase in skewness as the latter reached a value of 0.47 after 48 minutes of immersion, then skewness started to decrease again, presumably because of the number of depressions on the surface started to increase a little. Roughness RMS continued to decrease until it reached its minimum during the course of the experiment to have a value of 12 nm after 80 minutes of immersion. Both the roughness RMS and skewness continued to increase because of the features appearing on the surface as shown in Figure 5.8 such that these bright features represent some adsorbed particles on the surface of the coating.

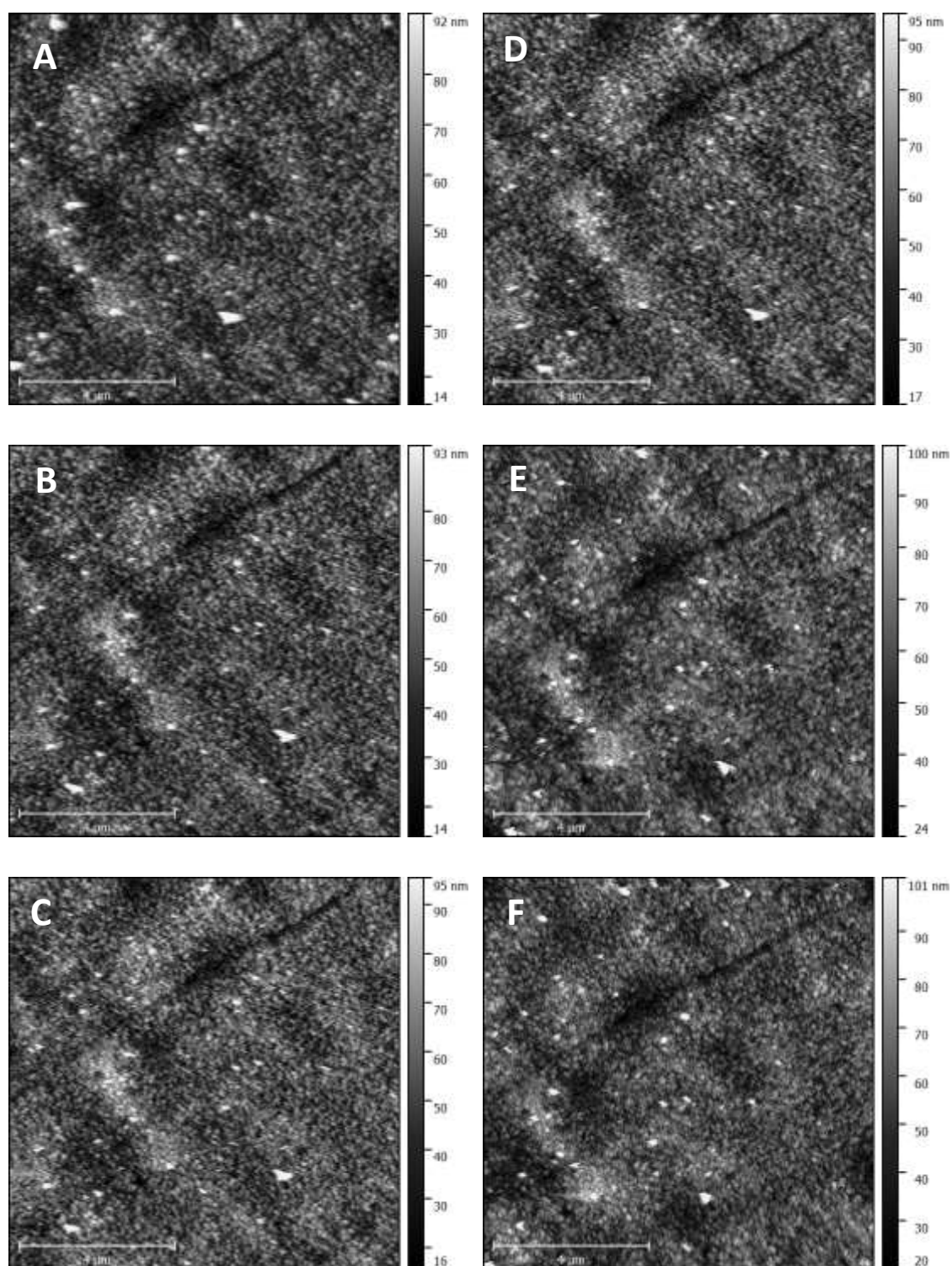


Figure 5.8: In-situ AFM topography measurement of immersed gel-coated copper. (A) 17 min, (B) 80 min, (C) 124 min, (D) 426 min, (E) 586 min, and (F) 699 min. Time in min refers to the time elapsed after the introduction of NaCl (0.5M) electrolyte.

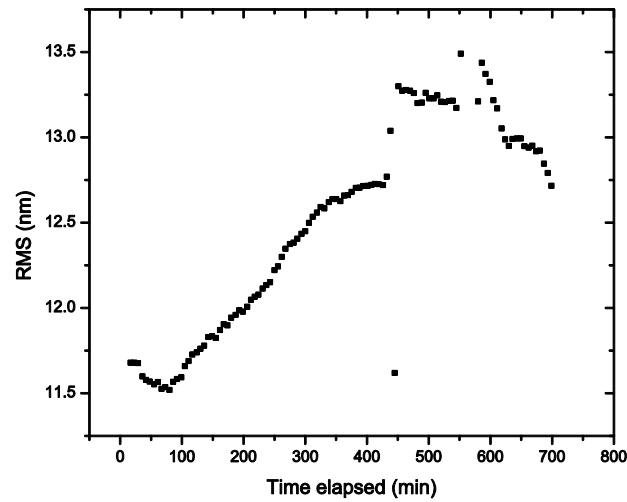


Figure 5.9: RMS temporal change of height of gel-coated copper for long immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

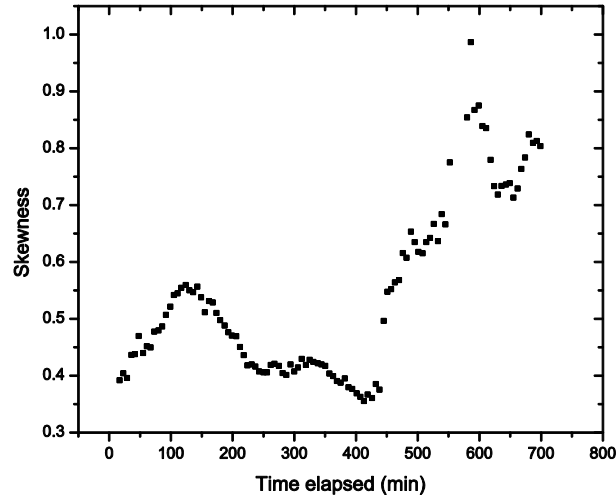


Figure 5.10: Skewness temporal change of height of gel-coated copper for long immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

The more the time elapsed the higher the increase in roughness RMS, and skewness. Up to the minute 130, the skewness started to decrease going towards a Gaussian surface, however, the roughness was increasing to be 11 nm while the skewness had a value of 0.55. The latter continued to decrease until it reached its minimum value after 419 minutes of immersion to reach a value of 0.37 and a corresponding roughness RMS value of 12 nm. After this moment, the roughness showed an abrupt change, as well as the skewness, which

started to increase as shown in Figure 5.9, and Figure 5.10. The abrupt change was taken place because of the sudden drift. The scanner was restored again to a position close to the initial position as presented in Figure 5.8. During the entire experiment no remarkable difference can be noticed, which is clear by comparing the initial image after immersion (Figure 5.8-A), and the image acquired after 699 minutes of immersion (Figure 5.8-F).

5.2.2.1.2 In-situ electrochemical results

As stated above, in this experiment the sample was immersed in NaCl (0.5M). The electrochemical measurements were carried out using Bio-Logic SP-200 (Bio-Logic SAS, Claix, France) at OCP.

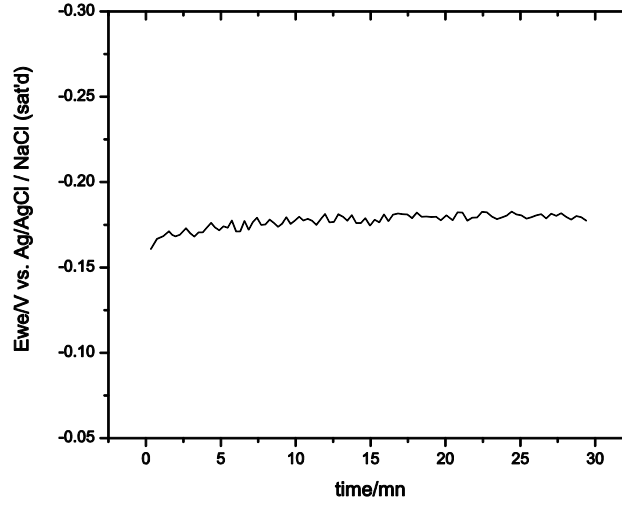
The measurements were started at the time of injecting the liquid into the cell. In this experiment, OCP was monitored in the first 30 minutes after immersion, then switching between measuring EIS and monitoring OCP during the course of the experiment. Experimental details are given in Appendix A.1. Furthermore, Figure 5.11-A shows the evolution of OCP value upon immersion in the electrolyte for the first 30 minutes. It can be seen that OCP starts to stabilise after about 2 minutes of immersion to have a value of -170 mV/Ag/AgCl/NaCl Satd, and it was slightly decreasing to be -179.5 mV/Ag/AgCl/NaCl Satd after 17 minutes. After 30 minutes of immersion, OCP reached a value of -181 mV/Ag/AgCl/NaCl Satd and started to alternate between measuring EIS and OCP. The evolution of OCP with time during the entire experiment is shown in Figure 5.11-B. By examining the evolution of OCP in Figure 5.11-B, it can be deduced that OCP changes slightly during the experiment that reveals the stability of the coating. A noticed change in the OCP value occurred after 70 minutes of immersion to reach a value of -180 mV/Ag/AgCl/NaCl Satd. Then OCP showed a sudden increase to the value of -159 mV/Ag/AgCl/NaCl Satd, after 126 minutes of immersion. Later, a decrease of OCP value after 162 minutes was observed, followed by increase again after 191 minutes of immersion. The change of OCP during the entire time of the experiment was 30 mV/Ag/AgCl/NaCl Satd.

Electrochemical impedance was measured at OCP with an amplitude of 5 mV/Ag/AgCl/NaCl Satd. Figure 5.12 shows a Nyquist plot of EIS measured during the course of the experiment. The impedance was decreasing which is illustrated in Figure 5.12 by the different loops. The outer loop of impedance corresponds to the initial impedance measured after 30 minutes of immersion, and its impedance continued to decrease as shown in Figure 5.12.

The change of the impedance magnitude during the time of the experiment can give a hint about the change of the coating during immersion. Therefore, the magnitude of selected frequencies was calculated and plotted in Figure 5.13. From the magnitude change of the extracted frequencies, the change of the magnitude over the time of the experiment is not remarkable; however, these changes are correlated with the change in OCP values as well as the change in topography parameters.

The magnitude of the impedance at the lowest frequency used, 100 mHz, can be examined to illustrate the temporal change of the impedance magnitude. After 48 minutes of immersion, the impedance magnitude started to decrease followed by increase after 70 minutes and a remarkable drop after 126 minutes. The magnitude of impedance started to increase again followed by a smooth decrease until the end of the experiment.

A)



B)

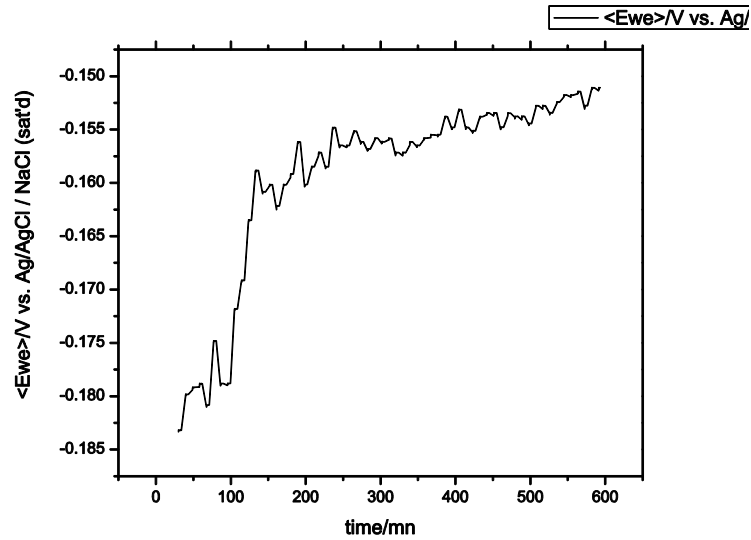


Figure 5.11: OCP evolution of immersed gel-coated copper for the spontaneous immersion test in NaCl (0.5M). A) OCP evolution during the first 30 minutes of immersion, B) OCP evolution during the entire experiment.

Joining the temporal change of statistical parameters extracted from AFM measurements, open circuit potential, and electrochemical impedance, a relation can be established. The roughness RMS value started to decrease while the skewness was increasing after 17 minutes of immersion that was accompanied by a slight decrease in OCP. The sudden decrease in impedance magnitude at the 48th minute goes along with an increase in the skewness. The abrupt fast drop of the impedance magnitude after 96 minutes of immersion goes together with an increase in the skewness. The change of the roughness during the experiment time is not large only within the range of 2.0 nm. The

change of skewness is also negligible (less than 0.6) during the course of the experiment. The change of OCP is also negligible during the experiment time (less than 30 mV), however, it became more positive which is a sign of the stability of the coating. The drop of the impedance magnitude value is either because of the drop of solution resistance or because of the change in the coating as it could be damaged, therefore the coating resistance drops. From the aforementioned changes in the topography statistical parameters, as well as the change in open circuit potential values, it can be concluded that the coating film has a good stability during the course of the experiment. Nevertheless, the drop in the electrochemical impedance can be clarified by modelling the impedance spectra in order to find out the change in the values of circuit components all over the time of the experiment. Accordingly, it can be identified whether that change in impedance values is because of the drop in electrolyte resistance, or a change in the coating resistance [203,364].

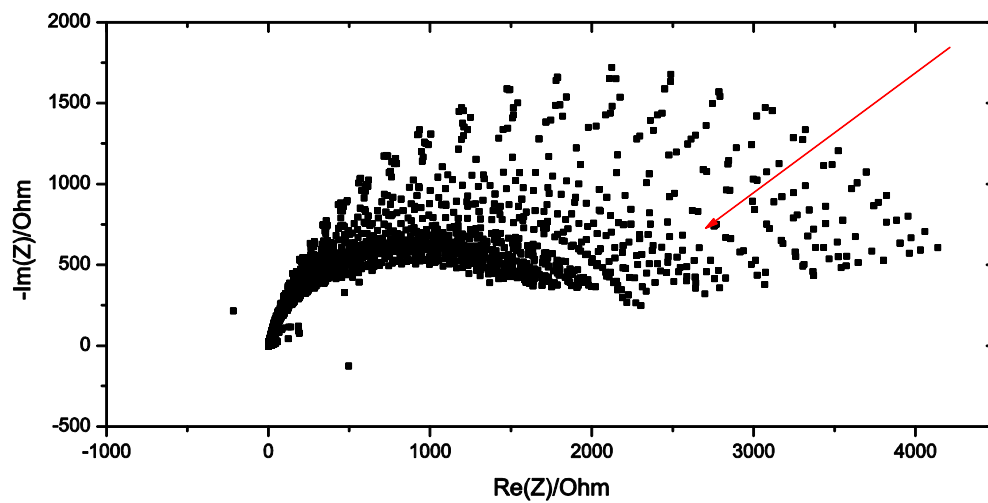


Figure 5.12: Nyquist plot of EIS measurements of immersed gel-coated copper in NaCl (0.5M) for the spontaneous test during the 800 minutes of immersion. The arrow indicates the evolution of impedance with time.

The gel coated copper has good corrosion resistance, which could be seen in both AFM the topography and the electrochemical measurements. The change in the statistical parameters was majorly due to the thermal drift of the scanner. The surface of copper was not corroded in comparison to the bare copper, which is a good sign of protection.

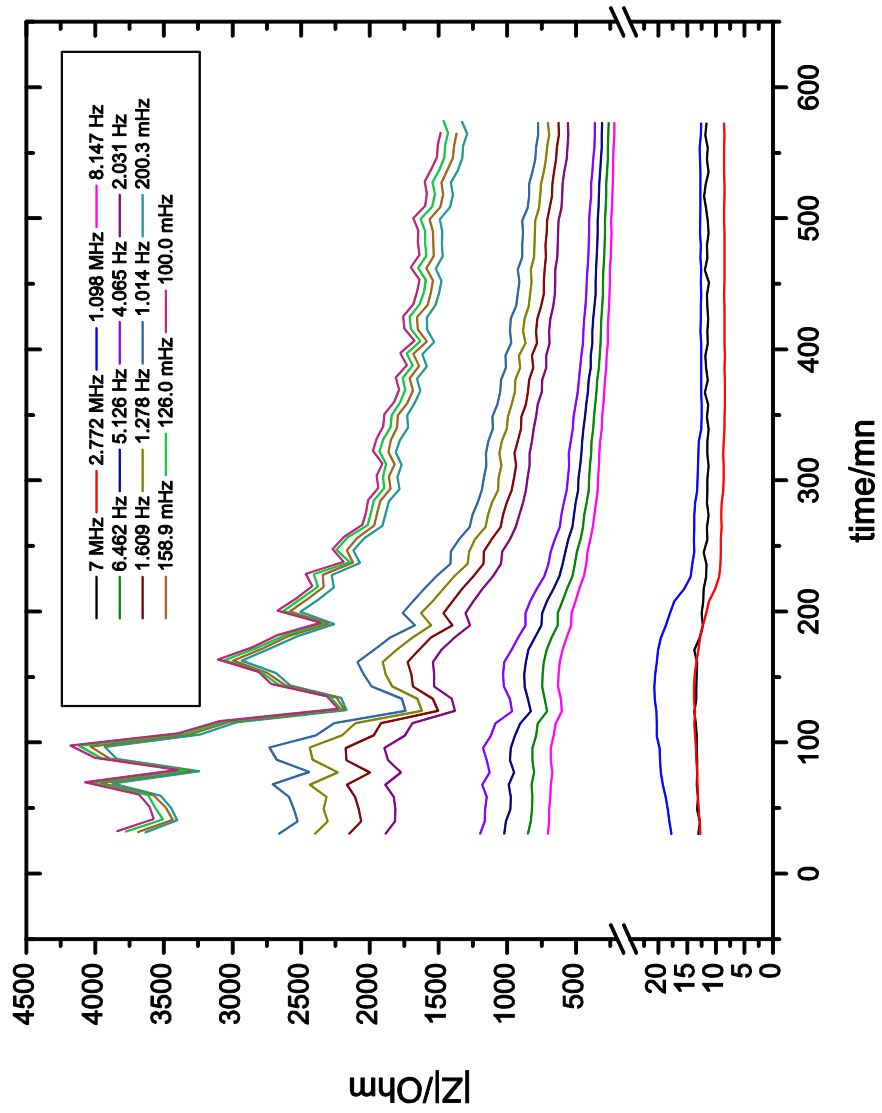


Figure 5.13: Temporal change of the EIS magnitude for selected frequencies.

5.2.2.2 Staircase voltammetry AFM

In this experiment, the sample was immersed in NaCl (0.5M) and staircase potential was applied while using AFM for scanning the surface. The purpose of this test is to study the dynamic of coating swelling.

5.2.2.2.1 In-situ AFM results

After checking the sample surface in air, NaCl (0.5M) was injected into the cell. Immediately, OCP was monitored upon injecting the electrolyte into the cell. Subsequently, the AFM tip was tuned, and then it approached the sample surface and started to scan the surface. The experiment lasted for about 7 hours, during this time the surface was continuously scanned while electrochemical measurement was carried out.

After the elapsed time of the experiment, AFM files were collected and then processed to extract the statistical parameters: surface height RMS (Figure 5.15), and skewness (Figure 5.16).

The first image of the coating was scanned after 15 minutes of immersion in the electrolyte, and before applying any potential, as shown in Figure 5.14-A. The initial image exhibits a quite rough surface since it has a roughness value of 9 nm and skewness value of 0.15. Roughness and skewness increased after 23 minutes of immersion to have a value of 10 nm for roughness RMS, and 0.2 for skewness. After 42 minutes of immersion, skewness and roughness RMS started to decrease upon the application of potential so their values are 0.19, and 9 nm, respectively. Up to minute 157 after immersion, roughness was decreasing and skewness did likewise, to reach values of 8 nm, and 0.11, respectively. Subsequently, the skewness started to increase to reach its maximum value of 0.33 within after 186 minutes of immersion, while the roughness RMS reached 7 nm. The change in the roughness is obvious in Figure 5.14-B, such that the surface looks smoother than the initial image and bumpier, therefore, the skewness increased. The skewness started to decrease again while the roughness continued to decrease; a sudden drop in skewness was noticed at the minute 249 since its value became 0.12 approaching again the Gaussian surface, as it can be seen in Figure 5.14-C. The skewness started to increase again after 280 minutes of immersion to reach a value of 0.25, which is due to the dissolution of the coating, as shown in Figure 5.14-D. The roughness RMS value showed an increase too as its value became 7 nm. A sudden decrease in skewness to have negative values accompanied by an increase in roughness RMS value after 299 minutes of immersion was observed towards respective values of -0.25 and 8 nm. The decrease in skewness was due to the appearance of depressions and the decrease of the peaks is indicated in Figure 5.14-E. While the roughness RMS was decreasing, the skewness was increasing up to the minute 349 after immersion to reach the corresponding values 6 nm, and -0.15. Subsequently, roughness RMS, and skewness continued to decrease up to minute 374, followed by increasing of skewness to have a final value of -0.25. At the same time, the roughness RMS value was changing slightly and ended up with a value of 6 nm after 406 minutes of immersion. The decrease of the roughness can be clearly seen in Figure 5.14-F, such that the surface looks smoother and has more troughs when compared with the initial image shown in Figure 5.14-A which is the reason for the decrease in skewness.

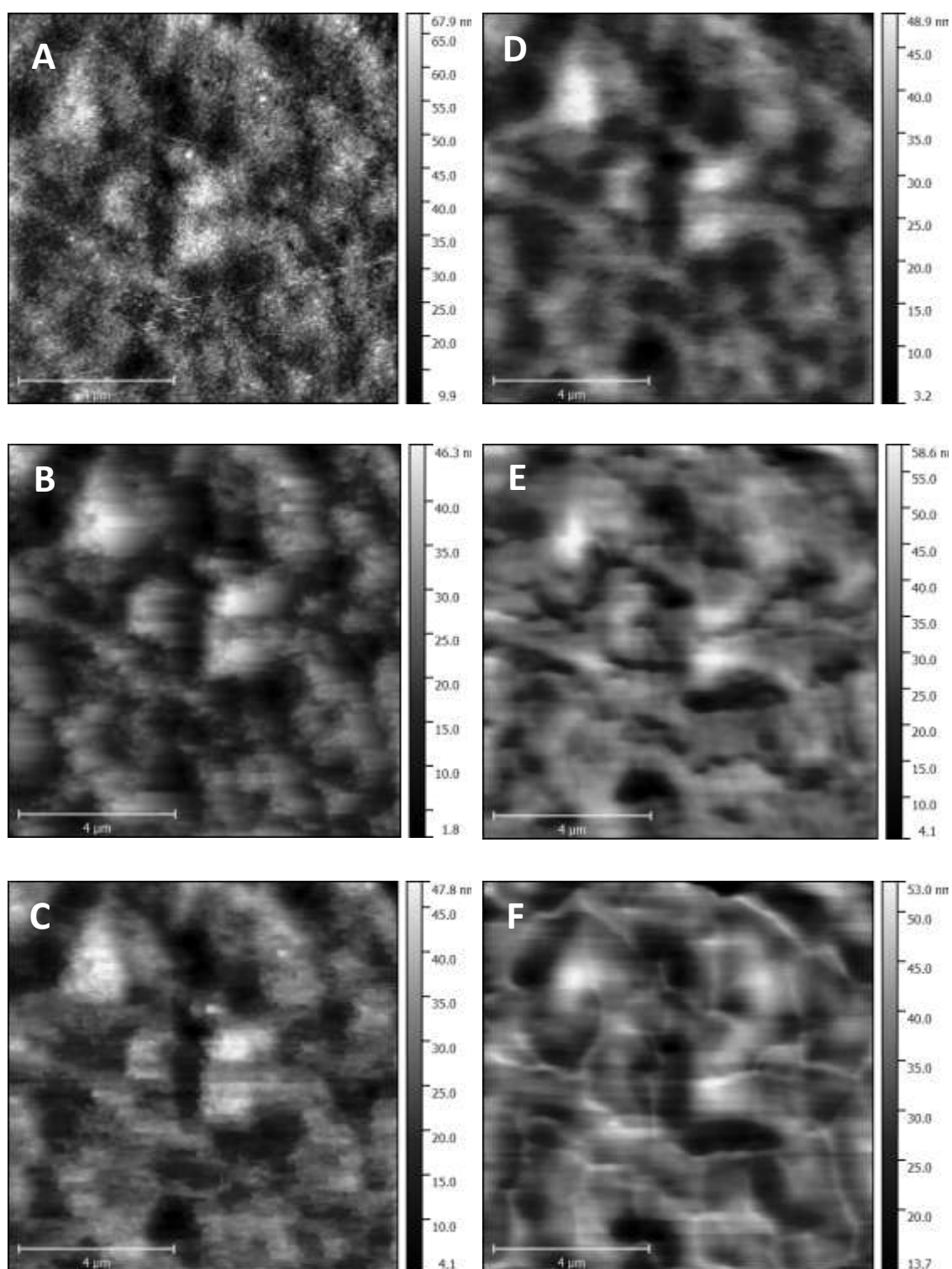


Figure 5.14: In-situ AFM topography measurement of immersed gel-coated copper for the step potential test. (A) 15 min at OCP, (B) 186 min at -330 mV/Ag/AgCl/NaCl Satd, (C) 249 min at -150 mV/Ag/AgCl/NaCl Satd, (D) 280 min at -73 mV/Ag/AgCl/NaCl Satd, (E) 299 min at -14 mV/Ag/AgCl/NaCl Satd, and (F) 406 min at 260 mV/Ag/AgCl/NaCl Satd. Time in min refers to the time elapsed after the introduction of NaCl (0.5M) electrolyte.

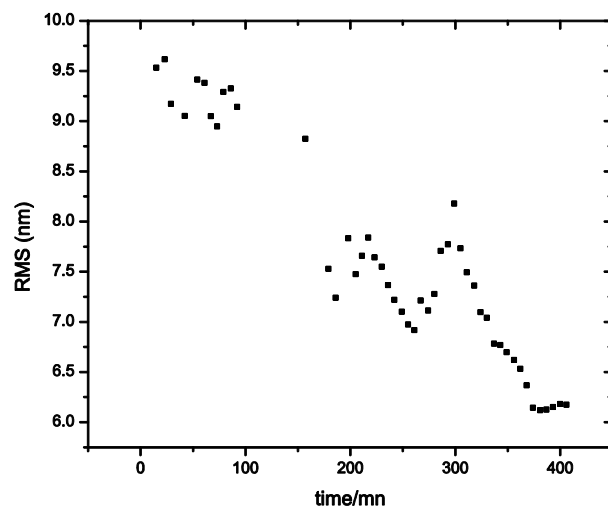


Figure 5.15: RMS temporal change of height of gel-coated copper for step potential test in NaCl (0.5M) extracted from the in-situ AFM topography measurement. AFM was continuously scanning the surface while the potential was simultaneously increasing in steps.

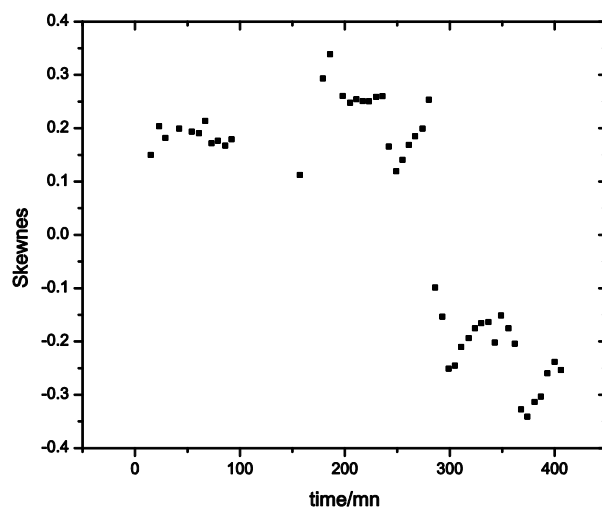


Figure 5.16: Skewness temporal change of height of gel-coated copper for step potential test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

5.2.2.2.2 In-situ electrochemical results

In this experiment, as indicated above, the sample was immersed in NaCl (0.5M). The experiment was done using Bio-Logic SP-200 (Bio-Logic SAS, Claix, France). The liquid was injected into the cell, at that moment the experiment started. At the beginning, OCP was monitored in the first 30 minutes after immersion, followed by application of potential steps (staircase), and measuring the current, simultaneously. The potential was started from -500 mV below the OCP, and it was incremented with 20 mV steps, up to the last potential step at 500 mV above the OCP. Experiment details are given in Appendix A.5.

The measurement of OCP upon injection of the liquid into the cell is shown in Figure 5.17. The applied potential step waveform and the current response are plotted in Figure 5.18.

From Figure 5.17, it can be depicted that the OCP value reached -187 mV/Ag/AgCl/NaCl Satd after a minute of immersion, then it was decreasing slowly to reach a value of -210 mV/Ag/AgCl/NaCl Satd after 10 minutes of immersion. OCP continued to decrease to reach a value of -240 mV/Ag/AgCl/NaCl Satd after 30 minutes of immersion.

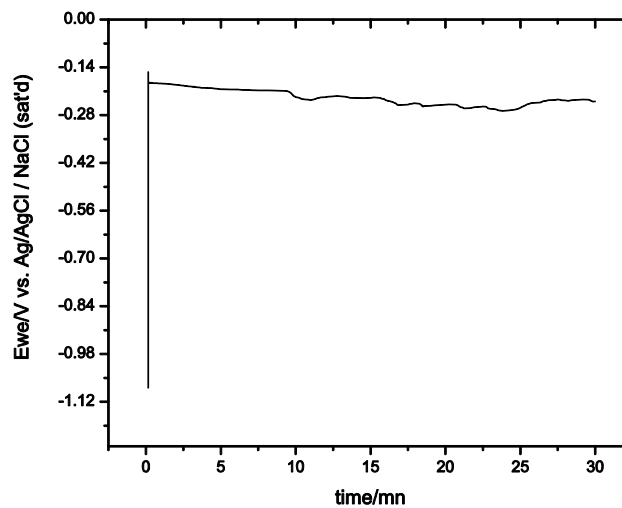


Figure 5.17: OCP measurements of immersed gel-coated copper sample in NaCl (0.5 M).

After 30 minutes of immersion and monitoring OCP, potential steps were applied to the working electrode starting from the cathodic direction as mentioned above from -500 mV below OCP to 500 mV above OCP. Initially, the potential value was -740 mV/Ag/AgCl/NaCl Satd with a corresponding current value -0.73 mA. The current magnitude started to increase by applying a potential that was more anodic until it reached -540 mA at the potential step -680 mV/Ag/AgCl/NaCl Satd. Afterwards, the current was only slightly changing around the value of -0.98 mA at the potential step -410 mV/Ag/AgCl/NaCl Satd. Subsequently, the magnitude of current started to decrease rapidly after the potential step -250 mV/Ag/AgCl/NaCl Satd to reach a current value of -0.81 mA. The current continued to decrease and reached -0.32 mA at the potential step -171 mV/Ag/AgCl/NaCl Satd. After 246 minutes of immersion, the current value was -0.13

mA when the applied potential was $-73 \text{ mV/Ag/AgCl/NaCl Satd}$. The current continued to decrease with decreasing the applied potential to have the last cathodic current -0.02 mA with a corresponding potential $-14 \text{ mV/Ag/AgCl/NaCl Satd}$ after 297 minutes of immersion. Then, potential steps that are more anodic were applied and the current response was anodic. The experiment was accomplished by applying the potential of value $260 \text{ mV/Ag/AgCl/NaCl Satd}$ after 297 minutes of immersion and the corresponding current value was 0.22 mA .

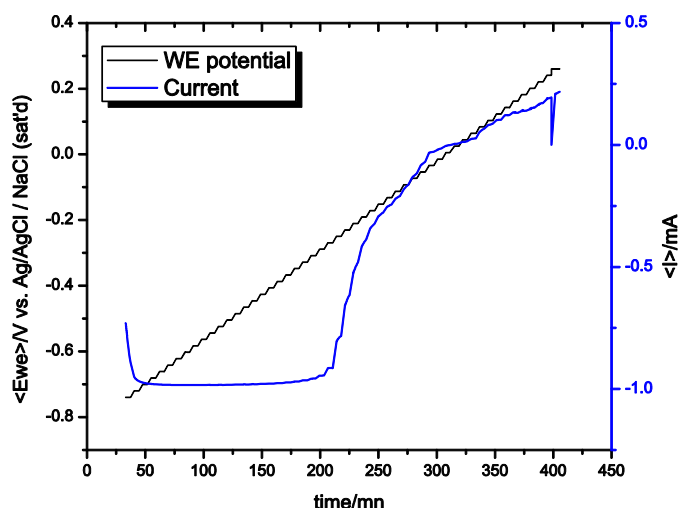


Figure 5.18: The waveform of the applied potential and its current response of immersed gel-coated copper sample in NaCl (0.5M).

The electrochemical and AFM measurements can be combined together in order to elucidate the dissolution mechanism of the coating. The coating topography before the application of any electrical potential was quite rough. Upon the application of the first step of potential, the current started to rise up. The rise of the current upon the application of the first two steps could be due to the reduction of the oxide between the coating and the metal surface. The increase in the current was accompanied by an increase in the roughness after 42 minutes of immersion. During the application of different potential steps until the minute 157, the current was almost constant around -0.98 mA and both the roughness RMS and the skewness were decreasing because of the smoothing in the surface and the surface was approaching Gaussian surface because of the dissolution of the coating. After 157 minutes of corrosion the current started to change slightly which was accompanied by a fast change in both the roughness RMS, and skewness in such a way that the roughness RMS dropped about 2 nm while skewness increased for about 1.5 . Furthermore, steps that are more anodic were applied and the current started to decrease which resulted in a decrease in the roughness RMS as well as the skewness, until the minute 280 the skewness dropped significantly and was closer to the corrosion potential at $-73 \text{ mV/Ag/AgCl/NaCl Satd}$, that is obvious in Figure 5.14-D. By means of applying anodic potential, the coating continued to swell, which is clear from Figure 5.14-E, and continued to swell which is possibly the reason for the small current values in the anodic direction.

5.2.2.3 Cyclic voltammetry AFM

The purpose of this measurement was first to find the effect of the cyclic voltammetry on the change of the surface, and second to find the irreversibility of the coating after multiple cycles. Cyclic voltammetry test (described in section 5.2.2.3.2) was carried on while the surface topography was measured. It was found that the film started to break down after the second cycle that was seen in the electrochemical impedance measurement before and after as well as the topographical change.

5.2.2.3.1 In-situ AFM results

The gel-coated copper sample was first scanned in the air to check the surface quality. Afterwards, the NaCl (0.5M) electrolyte was injected into the cell. At the instance of injecting OCP was monitored for 30 minutes, thus the injection time can be precisely identified. In the meantime, the AFM tip was tuned, and it approached the sample, then the surface was scanned. After 30 minutes of immersion of monitoring OCP, EIS was measured, and then cyclic voltammetry was carried out simultaneously with scanning the surface.

AFM could scan the sample for 270 minutes, after that it was hard to continue scanning. The surface became too rough to enable the AFM tip to scan it due to the coating breakdown. After carrying out the experiment, AFM files were converted to image files, some selected images are presented in Figure 5.19. After carrying out a number of cycles and processing of the images using a MATLAB the appropriate statistical parameters were obtained as shown in Figure 5.20 and Figure 5.21.

After 17 minutes of immersion the surface exhibits a Gaussian distribution as it has a skewness value -0.04 and roughness RMS value 12 nm as shown in Figure 5.19-A. The surface roughness was showing a slight change and reached a value of 12 nm after 29 minutes of immersion while the skewness was increasing to reach a value of 0.31 after the same time. Then the skewness continued to increase to have values of 0.67 after 36 minutes and 1.54 after 61 minutes while roughness RMS was 11 nm.

The skewness started to drop quickly to mimic a Gaussian surface as its value was 0.09 after 86 minutes of immersion with a corresponding value of 12 nm for roughness RMS. After 155 minutes of immersion, the roughness RMS was slightly changing and reached a value of 11 nm, the skewness was increasing to have a value of 0.25, though. That can be depicted from Figure 5.19-B, as the surface started to be bumpier when compared within Figure 5.19-A. Subsequently, the skewness continued to increase and roughness RMS started to increase as well as to have the values 0.31 and 15 nm after 199 minutes of immersion, respectively. The increase in roughness RMS and skewness is due to the change in the topography in the lower right corner of Figure 5.19-C, which is an evidence of the change in topography. After 20 minutes, specifically after 219 minutes of immersion, the roughness RMS increased abruptly to 37 nm and a corresponding skewness was 0.48. The abrupt change in the roughness is clearly due to the change in topography and the start of the breakdown of the film as can be seen in Figure 5.19-D. The roughness RMS continued to increase as its value raised to 170 nm after 238 minutes of immersion with a corresponding skewness value 0.6. By continuing the scanning, the roughness RMS was increasing to reach its maximum value of 221 nm after 245 minutes of immersion. The huge increase in the roughness RMS is clear in Figure 5.19-E. The coating is almost peeled out of the surface which can be depicted from the total height as it reached a value greater than 2 μm . The experiment was ended after 270 minutes (Figure 5.19-E) of immersion, as the surface was so tough. Moreover, the corrosion products were attached to the AFM tip and were impossible to continue the scan.

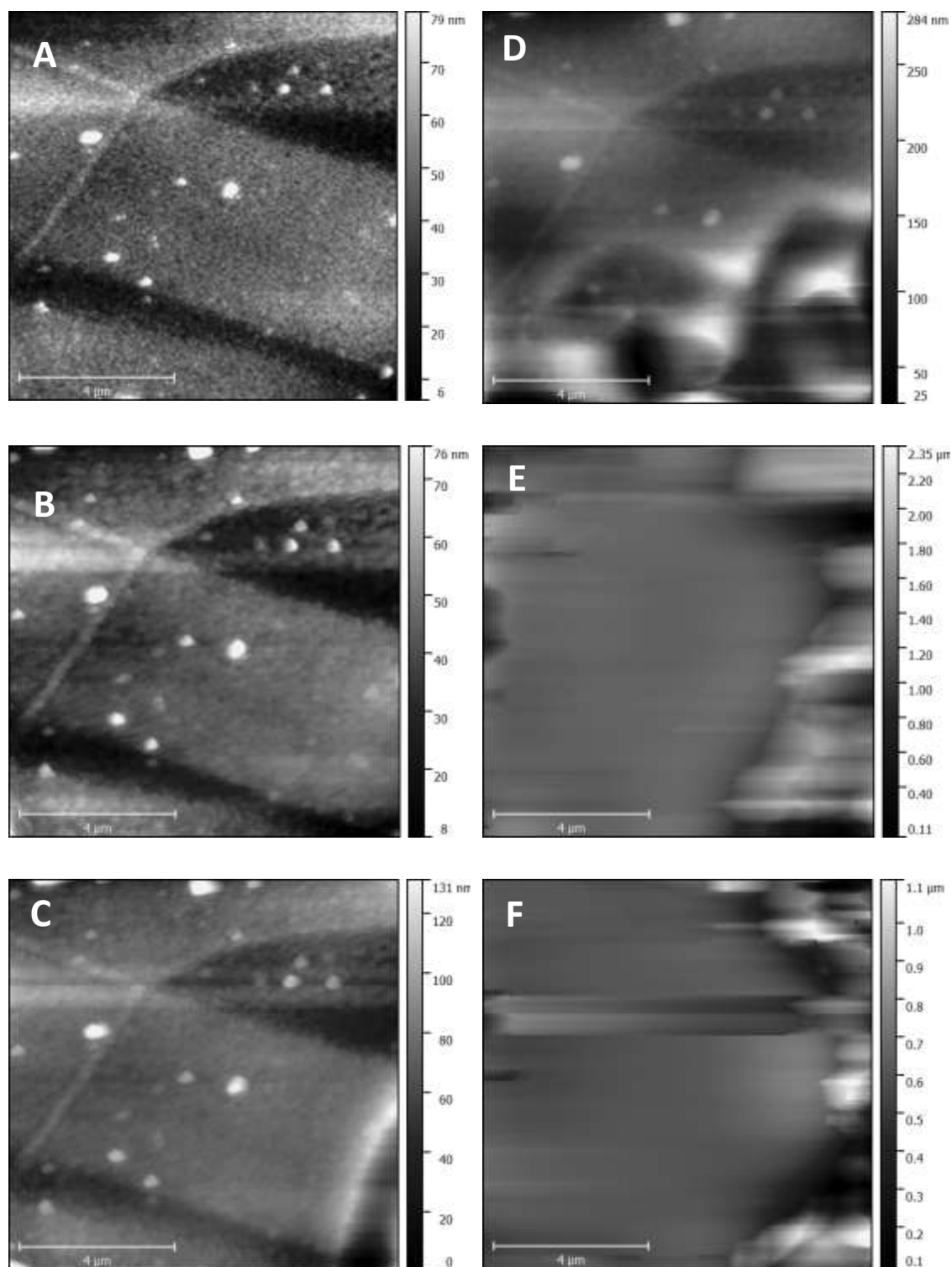


Figure 5.19: In-situ AFM topography measurement of immersed gel-coated copper. (A) 17 min, (B) 155 min after 8 cycles, (C) 199 min after 12 cycles, (D) 219 min after 15 cycles, (E) 245 min after 17 cycles, and (F) 270 min after 19 cycles. Time in min refers to the time elapsed after the introduction of NaCl (0.5M) electrolyte.

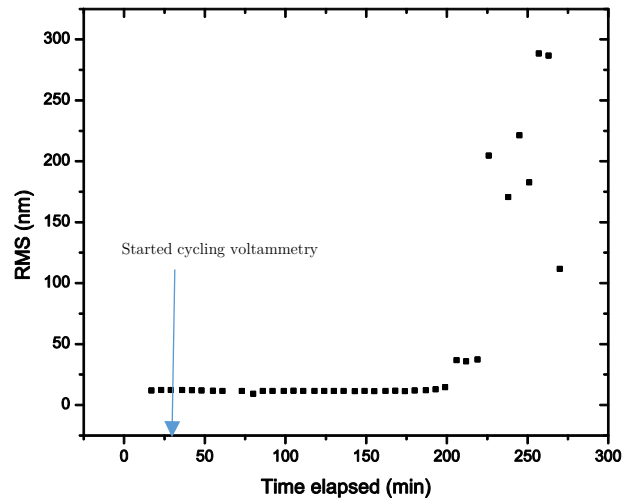


Figure 5.20: RMS temporal change of height of gel-coated copper cyclic voltammetry test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

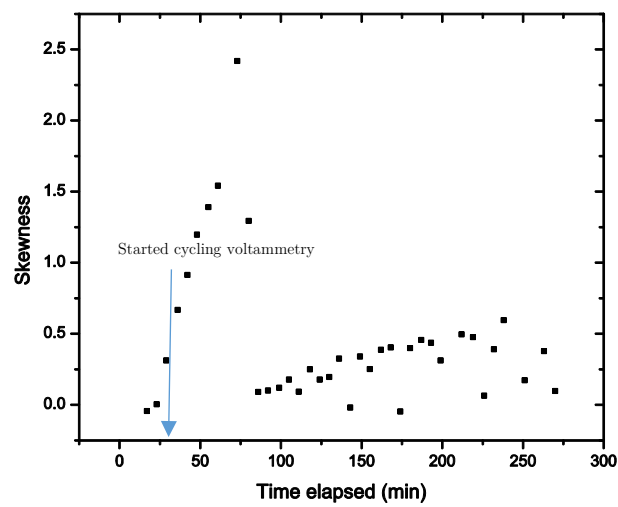


Figure 5.21: Skewness temporal change of height of gel-coated copper cyclic voltammetry test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

5.2.2.3.2 In-situ electrochemical results

In this experiment, as mentioned before, the sample was immersed in NaCl (0.5M). The experiment was done using a Bio-Logic SP-200 potentiostat (Bio-Logic SAS, Claix, France). The liquid was injected into the cell, at that moment the experiment started. At the beginning, OCP was monitored in the first 30 minutes after immersion, followed by relaxation for more than 30 minutes. Then, a cyclic voltammetry (CV) test was run for 30 cycles. After measuring each cycle, the system was set to relax for 6 minutes approximately. In each cycle, the potential was swept starting from OCP to -500mV in the cathodic direction, then to 1000 mV above this value, and back again to the initially measured OCP. Experiment details are given in Appendix A.4.

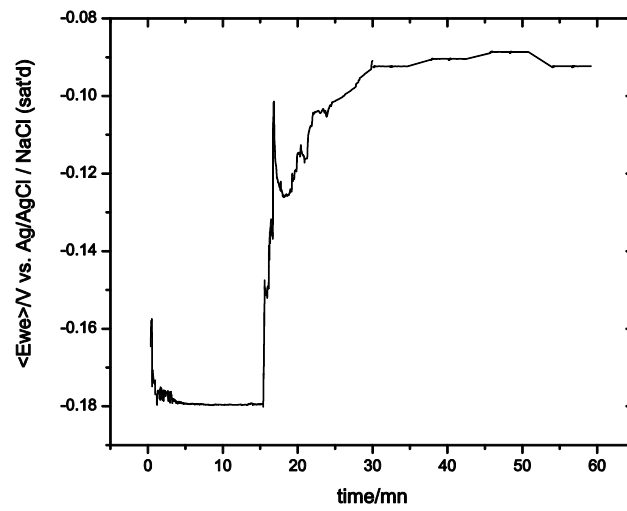
The measurement of OCP upon injection of the liquid into the cell is shown in Figure 5.22-A, whereas the potential waveform during the entire experiment is shown in Figure 5.22-B: OCP during the first 60 minutes, then OCP that was measured during the relaxation time between each cycle. Figure 5.22-A shows OCP starts to stabilise after 5 minutes of immersion to be -178 mV/Ag/AgCl/NaCl Satd. Then OCP increased to -102 mV/Ag/AgCl/NaCl Satd after 16 minutes followed by a decrease. Subsequently, OCP started to increase again until it reached a value of -92 mV/Ag/AgCl/NaCl Satd. After 30 minutes of immersion, OCP was quite stable and preserved the same value until 60 minutes. Then the first voltammetry cycle was run, after applying it the OCP dropped down to -133 mV/Ag/AgCl/NaCl Satd at the minute 87, after applying the second cycle it dropped more to -156 mV/Ag/AgCl/NaCl Satd which was at the 97th minute. After the third cycle, OCP became more anodic again to have a value of -46 mV/Ag/AgCl/NaCl Satd at the minute 108, and then started to decrease gradually to reach a value of -65 mV/Ag/AgCl/NaCl Satd after 130 minutes. OCP started to be more anodic again to reach a value of -62 mV/Ag/AgCl/NaCl Satd after 150 minutes of immersion. OCP continued to increase slowly towards the anodic direction and reached -60 mV/Ag/AgCl/NaCl Satd at the minute 219 and -6 mV/Ag/AgCl/NaCl Satd after 241 minutes of immersion.

The temporal change of the current by repeating the aforementioned cycles is plotted in Figure 5.23. At the beginning, the current is quite low. After the fourth cycle, the current started to increase and continued to rise with time.

Some cycles are selected and presented in Figure 5.24. The first cycle does not look regular and has a very low current response. After the application of many cycles, the current started to improve. The eighth cycle has pronounced broad peaks. The more the time elapsed with the application of further voltammetry cycles, the more current peaks increased. That shows the irreversibility of the system as well as the decreasing in the resistance of the coating by applying more cycles.

Joining the electrochemical and AFM measurements, we can understand how the film is changing with the application of more cycles. The increase of the peaks which correspond to the copper oxidation and reduction in NaCl means that the film became less protective. The destruction of the film is also clear in the AFM measurements as the roughness started to increase. It can be seen in the images that the film was broken down and even the surface of the copper started to appear at the end of the experiment.

A)



B)

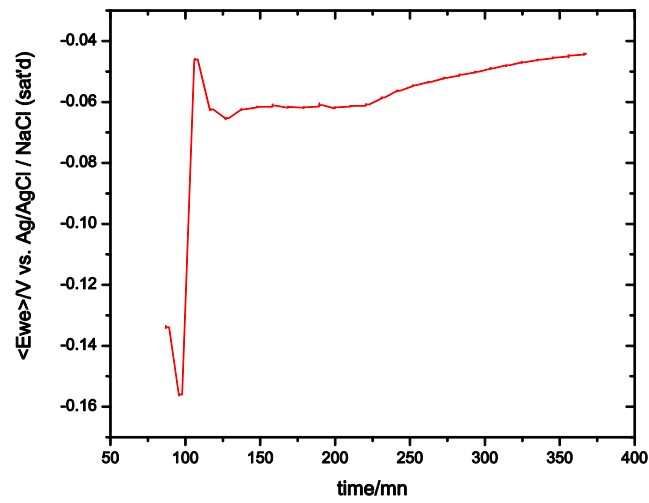


Figure 5.22: OCP measurements of immersed gel-coated copper sample in NaCl (0.5M). A) OCP in the first 60 minutes after immersion. B) OCP during the relaxation after applying voltammetry cycles.

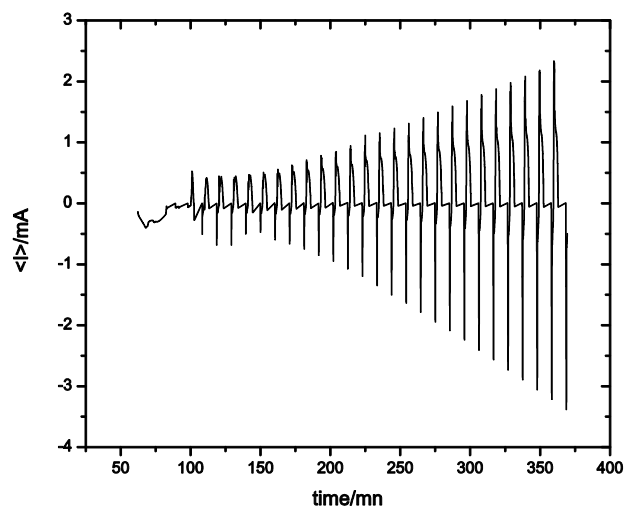


Figure 5.23: Temporal current response of immersed gel-coated copper sample in NaCl (0.5M) upon the application of voltammetry cycles.

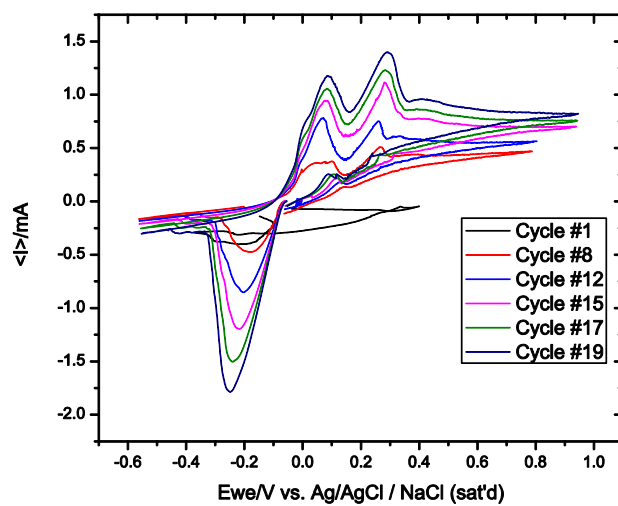


Figure 5.24: Cyclic voltammograms of gel-coated copper sample in NaCl (0.5M) upon the application of voltammetry cycles.

5.2.3 RGO-coated copper

Three in-situ AFM - electrochemical measurements were carried out. First, the RGO-coated copper samples were prepared by polishing as described in Sections 2.2.2, and 2.2.3, followed by coating preparation as described in Section 2.2.5 and mounted in the electrochemical cell for simultaneous measurements as described in Section 2.2.6.

In-situ testing of the coating was carried out in three different electrochemical methods. The first sample was studied for spontaneous immersion through scanning in NaCl (0.5M) electrolyte, and measuring the open circuit potential and electrochemical impedance. The second sample was studied under the application of potential steps. The third was tested by applying different chronoamperometric pulses while monitoring the change in topography and electrochemical impedance.

5.2.3.1 Spontaneous corrosion test

The purpose of this experiment is to study the spontaneous change of the coating while it is immersed in electrolyte without the application of any external electric signals. Consequently, the film stability upon immersion in a corrosive medium such as NaCl (0.5M) can be studied without applying any external electrical potential. Therefore, the sample was immersed in NaCl (0.5M), while the open circuit potential and electrochemical impedance were measured simultaneously with scanning the surface topography.

5.2.3.1.1 In-situ AFM results

In this experiment, the sample's surface was first scanned in the air. Then, NaCl (0.5M) electrolyte was injected into the cell. Immediately, OCP was monitored for 30 minutes. Meanwhile, the AFM tip was tuned, and then it approached the sample. Afterwards, the surface was scanned while measuring the electrochemical impedance, and open circuit potential, repetitively. The details of the electrochemical measurements used are given in Appendix A.1.

The experiment was run for about 7 hours of continuous scan of the surface in NaCl (0.5M) electrolyte. During the experiment time, there was some drift. After the experiment, the AFM files were converted to image files, some of them are displayed in Figure 5.25, and then they were processed using MATLAB code to extract the statistical parameters shown in Figure 5.26 and Figure 5.27.

The first image was scanned after 20 minutes of injecting the electrolyte into the cell. The surface looks quite rough and has a roughness RMS value of 60 nm that is presumably due to the wrinkles of RGO flakes as shown in Figure 5.25-A; however, the surface is close to the Gaussian distribution as it has a skewness value of -0.22. The roughness RMS continued to increase and it had a value of 69 nm while skewness was decreasing and its value was -0.29 after 77 minutes of immersion. The slight increase in the roughness RMS is because of the change in the topography at the top of the image in Figure 5.25-B. The roughness RMS continued to increase to reach a value of 70 nm and skewness continued to decrease to reach -0.3 after 108 minutes of immersion. Afterwards, skewness started to increase and to move towards the Gaussian surface, as its value was -0.27 after 177 minutes of immersion, whereas roughness reached its maximum value 71 nm. Subsequently, the roughness RMS started to decrease and reached a value of 66 nm, and corresponding skewness value -0.16 after 240 minutes of immersion. Some changes took place in the lower third of the image shown in Figure 5.25-C, which is the reason for the decrease

in roughness, and became closer to the initial surface shown in Figure 5.25-A. The surface roughness RMS continued to decrease until it came closer to the Gaussian surface after 316 minutes (Figure 5.25-D) and since the skewness value was -0.07 and the roughness RMS was 64 nm. Roughness RMS kept decreasing and skewness was getting close to zero as they have the values 62 nm and -0.05, respectively, after 360 minutes of immersion.

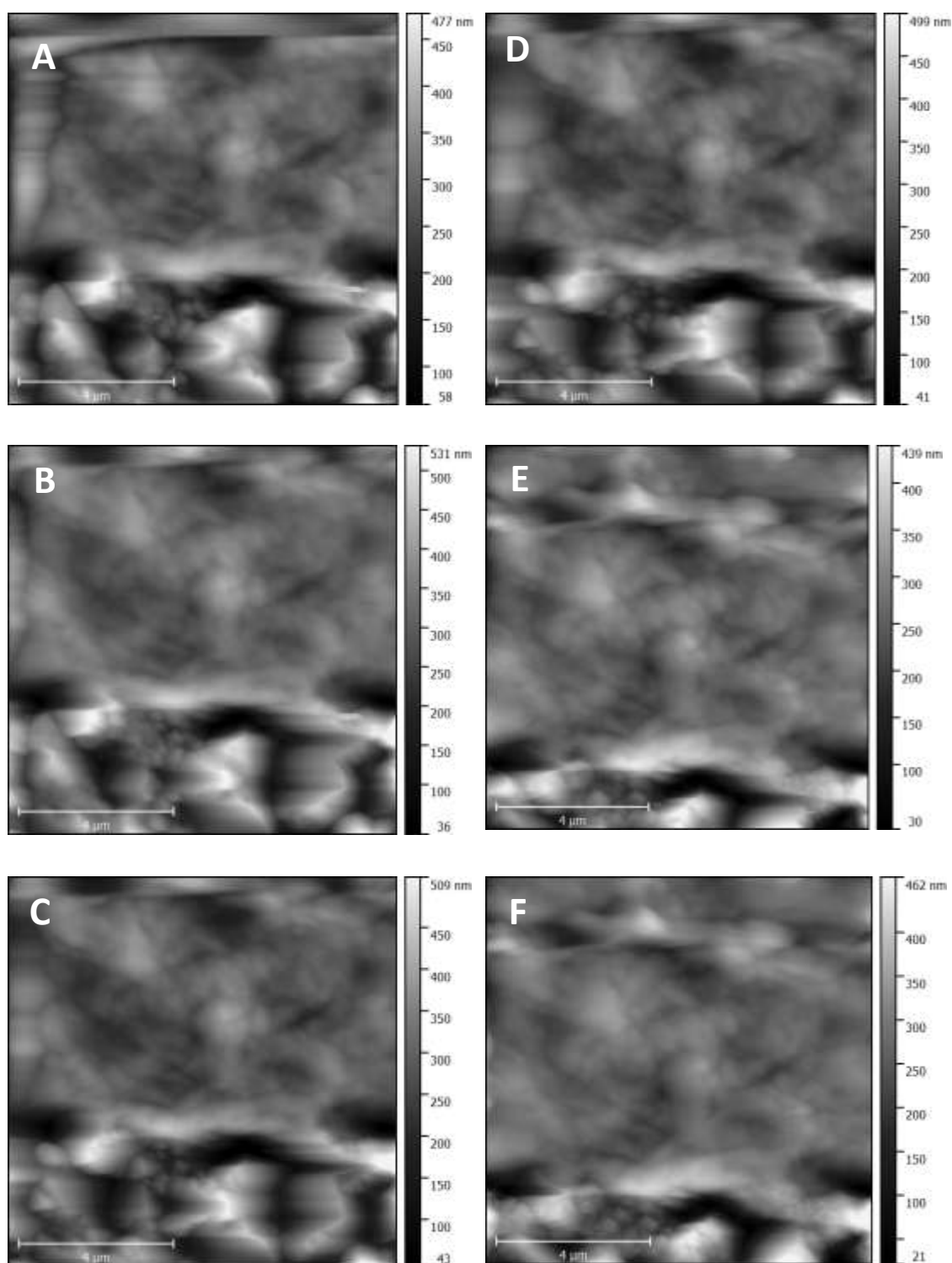


Figure 5.25: In-situ AFM topography measurement of immersed RGO-coated copper. (A) 20 min, (B) 77 min, (C) 240 min, (D) 316 min, (E) 390 min, and (F) 414 min, Time in min refers to the time elapsed after the introduction of NaCl (0.5M) electrolyte.

The noticed drop in skewness in Figure 5.27 after 390 minutes is due to the drift which is shown in Figure 5.25-E. The last image was acquired after 414 minutes of immersion Figure 5.25-F such that the roughness RMS and skewness values were 57 nm, and -0.37, respectively.

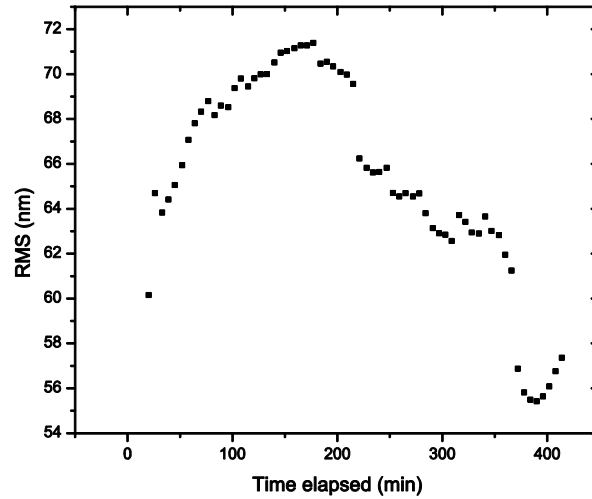


Figure 5.26: RMS temporal change of height of RGO-coated copper spontaneous immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

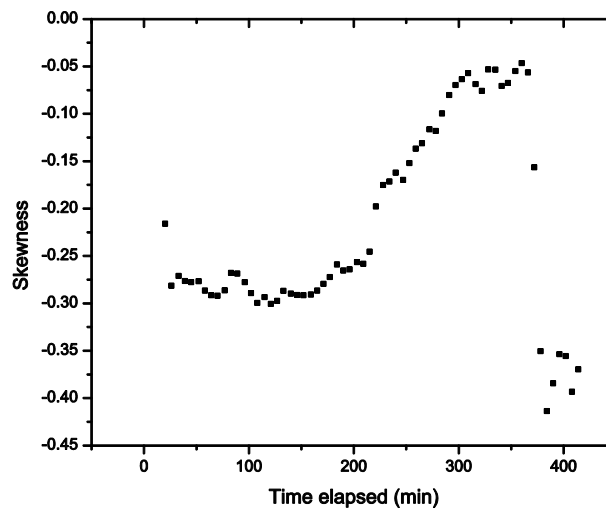


Figure 5.27: Skewness temporal change of height of RGO-coated copper spontaneous immersion test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

5.2.3.1.2 In-situ electrochemical results

As indicated above, in this experiment the RGO-coated copper sample was immersed in NaCl (0.5M). The electrochemical measurements were carried out using a Bio-Logic SP-200 potentiostat (Bio-Logic SAS, Claix, France) at OCP.

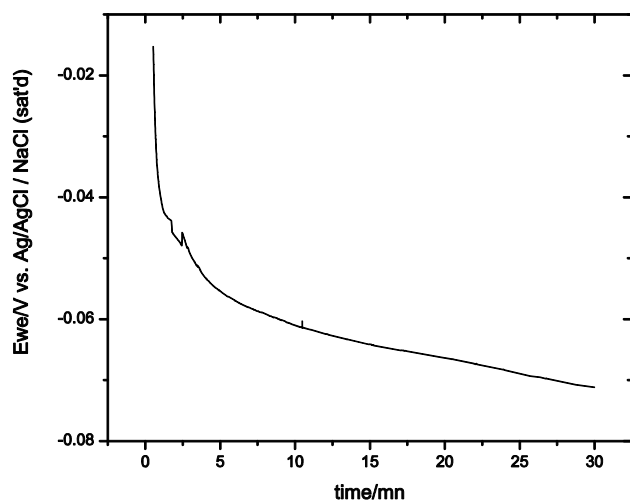
At the time of injecting the liquid into the cell, the measurements were started. In this experiment, in the first 30 minutes after immersion OCP was monitored, then, during the course of the experiment, we were switching between measuring EIS and monitoring OCP. Experimental details are given in Appendix A.1. Moreover, Figure 5.28-A shows the evolution of OCP value upon immersion in the electrolyte for the first 30 minutes. It can be seen that OCP decreases quickly in the first 30 minutes. After 5 minutes of immersion, OCP had a value of -55 mV/Ag/AgCl/NaCl Satd, and it was quickly decreasing to be -66.6 mV/Ag/AgCl/NaCl Satd after 20 minutes. After 30 minutes of immersion, OCP reached a value of -71 mV/Ag/AgCl/NaCl Satd and then started to switch between measuring EIS and OCP. The evolution of OCP with time during the entire experiment is shown in Figure 5.28-B. By examining the evolution of OCP in Figure 5.28-B, it can be deduced that the change of OCP starts to decrease at a slower rate as it reached -85 mV/Ag/AgCl/NaCl Satd after 77 minutes of immersion. OCP continued to decrease and reached its minimum value -95 mV/Ag/AgCl/NaCl Satd after 240 minutes. Then it started to increase again to -93 mV/Ag/AgCl/NaCl Satd after 77 minutes and to -92 mV/Ag/AgCl/NaCl Satd after 360 minutes of immersion. Eventually, OCP remained constant without changing until the end of the experiment.

Electrochemical impedance was measured at OCP with an amplitude of 5 mV/Ag/AgCl/NaCl Satd. Figure 5.29 shows some selected Nyquist plot of EIS measured during the course of the experiment. The impedance was slightly changing which is illustrated in Figure 5.29. The outer loop of impedance corresponds to the initial impedance measured after 32 minutes of immersion, and the impedance continued to decrease, as shown in Figure 5.29.

The change of the impedance magnitude during the time of the experiment can give a hint about the change of the coating during immersion. Therefore, the magnitude of selected frequencies was calculated and plotted in Figure 5.30. From the magnitude change of the extracted frequencies, the change of the magnitude all over the time of the experiment is not significant; however, these changes are correlated with the change in OCP values as well as the change in topography parameters.

The magnitude of the impedance at the lowest frequency used 100 mHz can be examined to illustrate the temporal change of the impedance magnitude. After 32 minutes of immersion, the impedance magnitude started to decrease with a slow rate followed by a slower decreasing rate after 108 minutes and a slight decreasing after 240 minutes. Impedance magnitude started to be constant after 360 minutes.

A)



B)

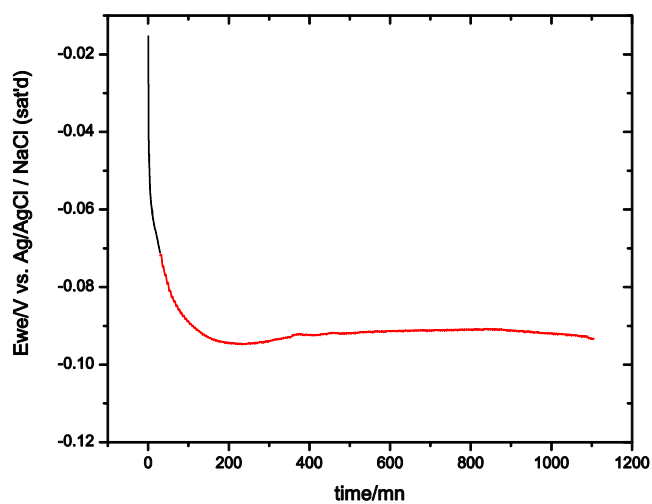


Figure 5.28: OCP measurements of immersed RGO-coated copper in (0.5M) NaCl for the spontaneous test). A) OCP evolution during the first 30 minutes of immersion, B) OCP evolution during the entire experiment.

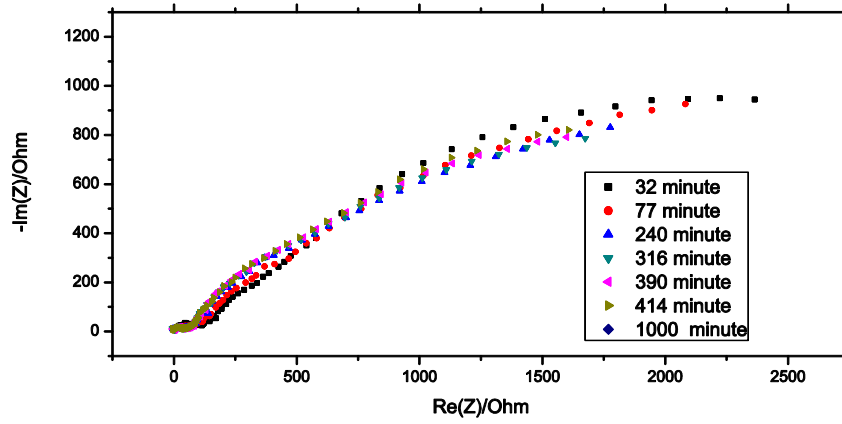


Figure 5.29: Nyquist plot of selected EIS measurements of immersed RGO-coated copper in (0.5M) NaCl for the spontaneous corrosion test.

Throughout this experiment, the total change of the roughness RMS during the immersion time is less than 10 nm if we neglect the drifting that took place at the end of the experiment. However, from AFM images shown in Figure 5.25 it is clear that no remarkable changes of the surface are noticed within 7 hours of immersion. Joining the temporal change of statistical parameters extracted from AFM measurements, open circuit potential, and electrochemical impedance, a relation can be established. The rate of decrease in the open circuit potential can be connected to a decreased rate of the electrochemical impedance magnitude. During the period of the fast decrease in the open circuit potential, namely from minute 30 to minute 108, a drop of about 20 mV, the impedance magnitude was decreasing at a fast rate which can be also seen in the decrease of skewness because of minor changes in the surface. After 108 minutes of immersion, OCP was decreasing slowly to reach a total drop of 5 mV up to minute 240 that was accompanied by a slower rate of decrease in the electrochemical impedance magnitude, as well as a slight change in the roughness. After 240 minutes of immersion, the open circuit potential started to increase again to reach a stable potential after 360 minutes of immersion. The roughness started to decrease slowly and the surface exhibited a Gaussian distribution. Eventually, OCP and the magnitude of electrochemical impedance remained almost constant without change. The change of OCP during the experiment is a sign of change in the surface, which is due to the reaction of the electrolyte with the coating. However, that change is very small, and OCP started to track back to the initial values giving a sign that it reached an equilibrium state which can be seen in the stability of the electrochemical impedance magnitude.

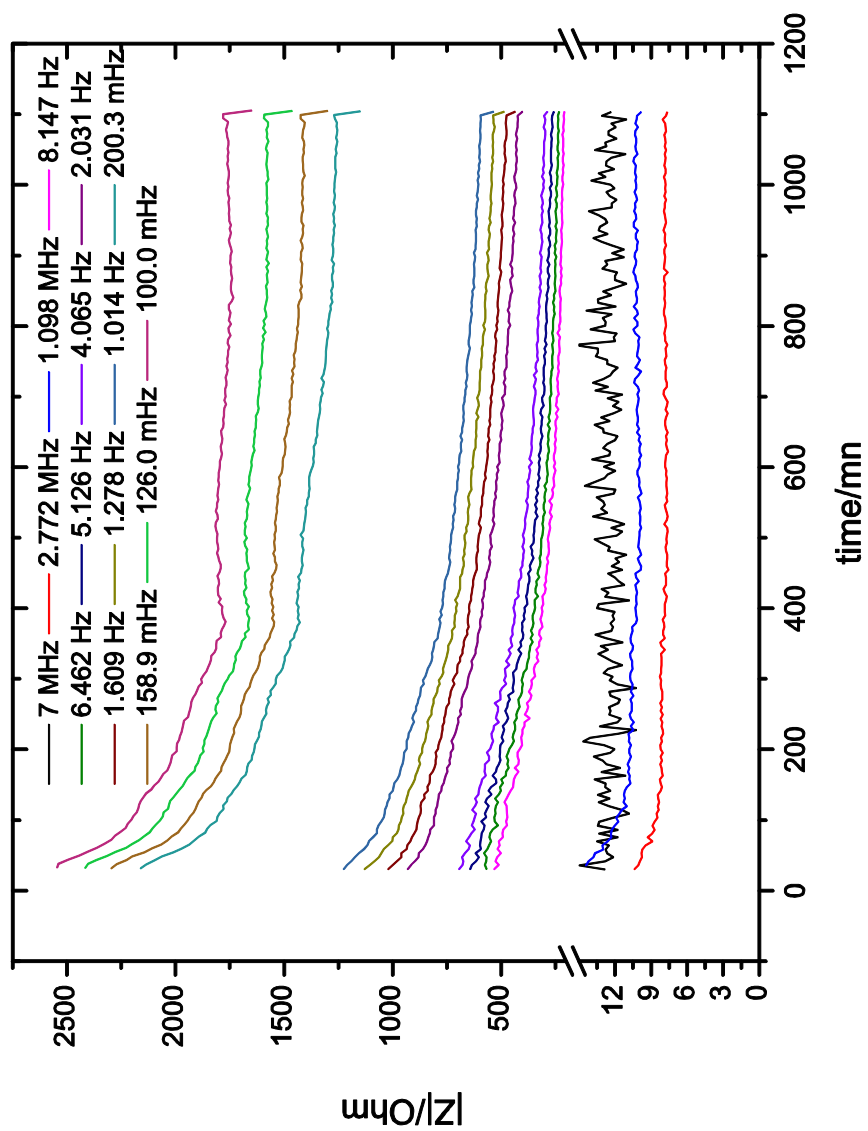


Figure 5.30: Temporal change of the EIS magnitude for selected frequencies.

5.2.3.2 Staircase Voltammetry AFM

In this experiment, the sample was immersed in NaCl (0.5M) and a staircase potential was applied while using AFM for scanning the surface. The purpose of this test is to study the dynamic of the change in the coating and to find its resistivity to the application of the potential.

5.2.3.2.1 In-situ AFM results

After checking the sample surface in air, NaCl (0.5M) was injected into the cell. Immediately, OCP was monitored upon injecting the electrolyte into the cell. Subsequently, the AFM tip was tuned, and then it approached the sample surface and started to scan the surface. The experiment lasted for about 7 hours. During this time the surface was continuously scanned while electrochemical measurement was carried out in such a way that OCP was measured in the the first 75 minutes of immersion, then the staircase potential was applied.

After the elapsed time of the experiment, AFM files were collected and then processed to extract the statistical parameters: surface height RMS Figure 5.32, and skewness Figure 5.33.

The first image of the sample was scanned after 22 minutes of immersion in the electrolyte at OCP, as shown in Figure 5.31-A. The initial image exhibits a quite rough surface and has a roughness value of 23 nm and a skewness value of 0.64. The roughness RMS value was slightly changing in a sub-nanometre range during this time up to 80 minutes after immersion to reach a roughness RMS value of 25 nm with a corresponding skewness value of 0.75 at minute 84.

Skewness and roughness continued to increase until minute 97 after immersion, when skewness was 0.95 and roughness RMS value was 24 nm. Skewness remained constant up to minute 122. The increase in roughness RMS is clear in Figure 5.31-B, the surface became rougher in comparison to Figure 5.31-A. Then, skewness started to decrease as it reached a value 0.52 after 172 minutes and a corresponding roughness RMS value of 30 nm. The increase in roughness is clear in Figure 5.31-C. However, the decrease in skewness is because of the appearance of new features. Afterwards, the skewness started to increase while roughness RMS was decreasing. After 210 minutes (Figure 5.31-D) they reached values of 0.65 and 28 nm, respectively. Subsequently, roughness RMS was increasing and skewness was decreasing, up to minute 260 such that roughness reached its maximum value 33 nm while the surface was getting closer to a Gaussian distribution as shown in Figure 5.31-E with skewness value 0.22. Roughness RMS, and skewness both continued to decrease up to minute 292, then they both started to increase to reach values 24 nm and 0.28, respectively. Next, a fast decrease in both of skewness and roughness RMS was observed as their values dropped down to -0.24 and 21 nm, respectively. Finally, both roughness RMS and skewness remained almost constant at the end of the measurements after 398 minutes of immersion (Figure 5.31-F) with values 21 nm and -0.26, respectively. The negative skewness is due to the drift of the scanning area, and the shifted area has characteristics different from the initial surface such that it is a full surface with holes in contrast to the initial surface it has an empty surface with peaks.

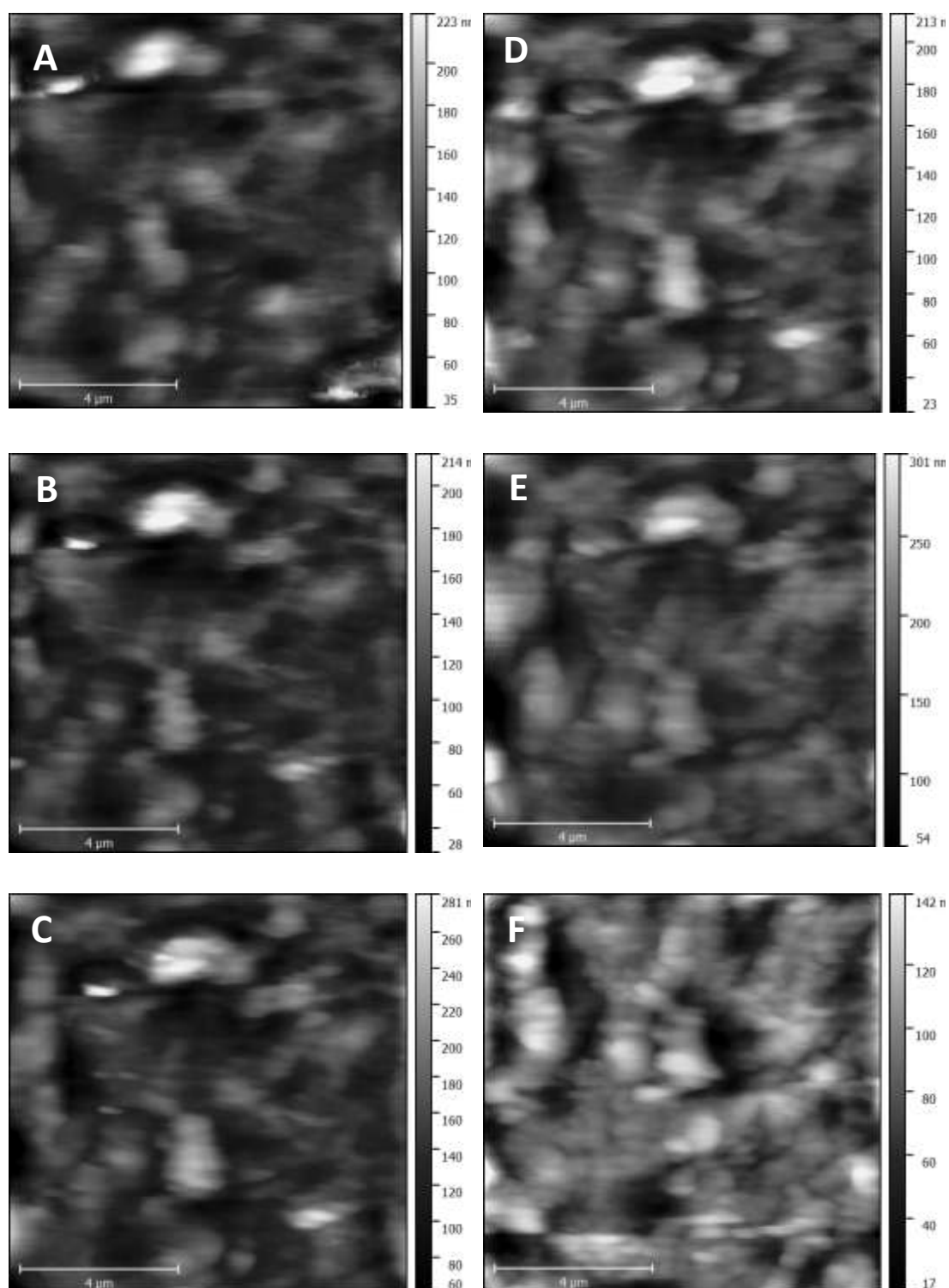


Figure 5.31: In-situ AFM topography measurement of immersed RGO-coated copper. (A) 22 min at OCP, (B) 122 min after -480 mV/Ag/AgCl/NaCl Satd, (C) 172 min after -305 mV/Ag/AgCl/NaCl Satd, (D) 203 min after -190 mV/Ag/AgCl/NaCl Satd, (E) 260 min after 10 mV/Ag/AgCl/NaCl Satd, and (F) 398 min after 362 mV/Ag/AgCl/NaCl Satd. Time in min refers to the time elapsed after the

introduction of 0.5 M NaCl electrolyte. The potential in mV is the value of the potential step applied at which the image was recorded.

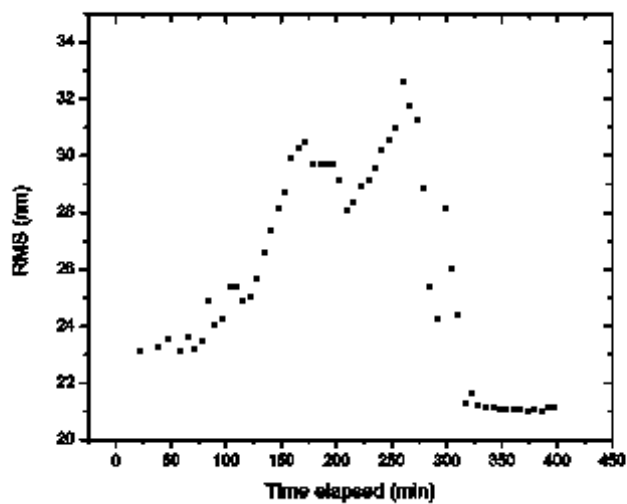


Figure 5.32: RMS temporal change of height of RGO-coated copper step potential test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

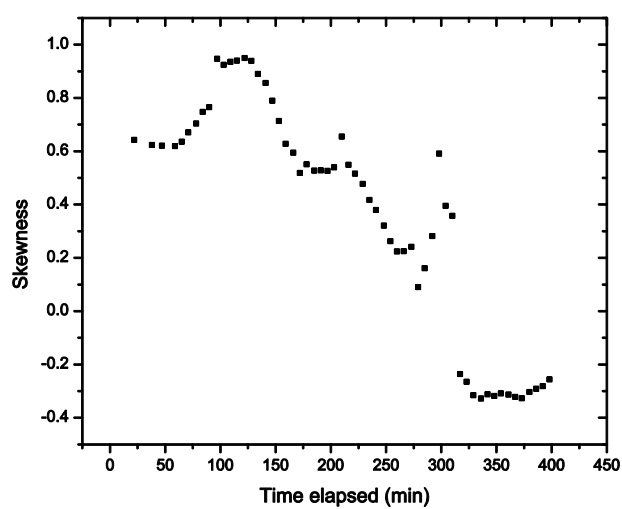


Figure 5.33: Skewness temporal change of height of RGO-coated copper step potential test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

5.2.3.2.2 In-situ electrochemical results

In this experiment, as indicated above, the sample was immersed in NaCl (0.5M). The experiment was done using Bio-Logic SP-200 (Bio-Logic SAS, Claix, France). The liquid was injected into the cell and at that moment the experiment started. At the beginning, OCP was monitored in the first 80 minutes after immersion, followed by application of potential steps (staircase), and measuring the current, simultaneously. The potential was started from -500 mV below the OCP, and it was incremented with 20 mV steps, up to the last potential step at 500 mV above the OCP. Experimental details are given in Appendix A.5.

The measurement of OCP upon injection of the liquid into the cell is shown in Figure 5.34, whereas the applied potential step waveform and the current response are plotted in Figure 5.35.

From Figure 5.34, it can be depicted that the OCP value reached -88 mV/Ag/AgCl/NaCl Satd after 2 minutes of immersion, then it was decreasing slowly to reach a value of -113 mV/Ag/AgCl/NaCl Satd after 10 minutes of immersion. OCP continued to decrease to reach a value of -133 mV/Ag/AgCl/NaCl Satd after 22 minutes of immersion. After 30 minutes OCP had a value of -133 mV/Ag/AgCl/NaCl Satd, then reached a stable value of -140 mV/Ag/AgCl/NaCl Satd after 71 minutes and remained almost constant.

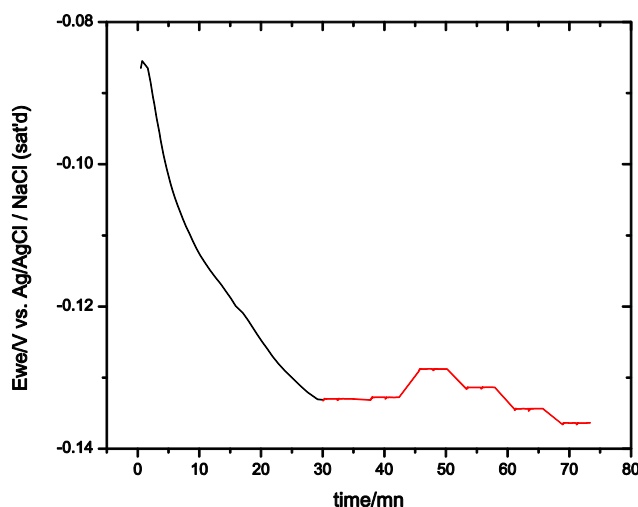


Figure 5.34: OCP measurements of immersed gel-coated copper sample in NaCl (0.5M).

After 80 minutes of immersion and monitoring OCP, potential steps were applied to the working electrode starting from the cathodic direction from -500 mV below OCP to 500 mV above OCP. The initial potential was -640 mV/Ag/AgCl/NaCl Satd has a corresponding current -0.108 mA. By applying a potential that is more anodic, the current response moves in the anodic direction as illustrated in Figure 5.35. A drop of the current with increasing the applied potential was noticed at minute 96 when the potential was -580 mV/Ag/AgCl/NaCl Satd. Then the current was increasing with the increase in the

applied potential and at minute 144 the current reached the corrosion current which then became anodic. Three jumps/peaks were noticed in the anodic direction. The first jump/peak in the current was noted after 248 minutes of immersion when the potential applied was -30 mV/Ag/AgCl/NaCl Satd, then the current was increasing at a faster rate. At minute 317 a second jump in the current was noticed, as the current reached a value of 0.771 mA when the applied potential was 225 mV/Ag/AgCl/NaCl Satd. The last jump was noticed after 323 minutes of immersion, such that the current was 0.80 mA when the potential applied was 244 mV/Ag/AgCl/NaCl Satd. Eventually the current decreased and the experiment ended after 398 minutes of immersion with a current 0.68 mA when the potential applied was 360 mV/Ag/AgCl/NaCl Satd.

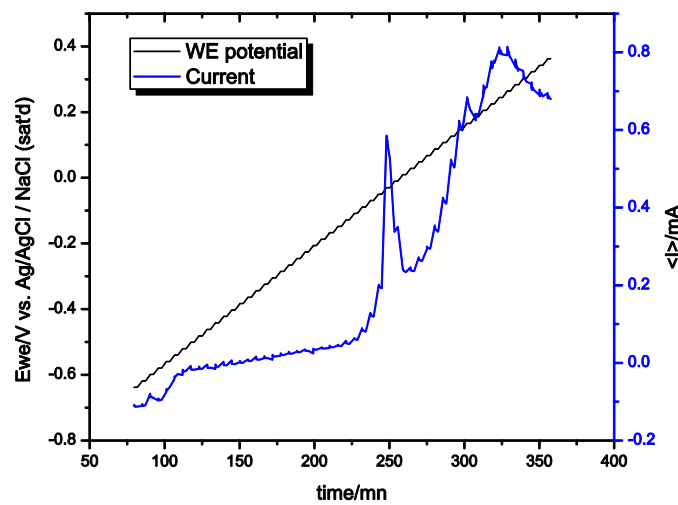


Figure 5.35: The waveform of the applied potential and its current response of immersed RGO-coated copper sample in NaCl (0.5M).

The change in morphology can be correlated to the applied potential as well as the current response. The first drop in the current after 96 minutes of immersion corresponds to a reduction that could be seen as an increase in the surface skewness and small increase in the roughness RMS value. Applying more anodic potential results in an increase in the roughness and decrease in skewness which is due to the formation of some species on the surface. This can be seen in Figure 5.31-B, as the depth of depression on the surface was decreasing which changes the surface towards a Gaussian surface. The change in the depressions height started to become more homogenous which could be due either to the reduction of the graphene flakes or the reduction of the native oxide underneath the graphene coating. The increase in the roughness by applying anodic current is because of the formation of some species on the surface, as seen in Figure 5.31-C. The jumps in the current represent oxidation peaks. After the first peak, the roughness started to drop, which is a sign of changes in the topography because of oxidation of graphene surface, and turn back to oxide. The jump of skewness and roughness after 290 minutes is because of the drift, and they both dropped quickly with the second and third oxidation peaks. The surface became smoother than the initial surface which is due to the formation of some thin layer

on top of the graphene coating, however, after the end of the experiment the surface does not look damaged.

5.2.3.3 Chronoamperometric AFM

In this experiment, electrical pulses of different potentials were applied to the sample immersed in NaCl (0.5M). After applying each pulse, the cell was turned off, and OCP was monitored followed by measuring the electrochemical impedance. The change in the surface topography was noticed upon the application of different chronoamperometric pulses, as well as a change in the electrochemical impedance was recorded.

5.2.3.3.1 In-situ AFM results

The sample was scanned in the air first, and then NaCl (0.5M) was injected into the cell. At the time of injecting the electrolyte, OCP was monitored, then the tip was tuned to approach the surface and scanning parameters were set. AFM started to scan the sample after 48 minutes of immersion. The images were collected, then processed as mentioned above to extract the statistical parameters: surface height RMS and skewness plotted in Figure 5.37 and Figure 5.38, respectively.

The image shown in Figure 5.36-A is the initial image acquired at OCP after injecting the liquid into the cell and has a surface roughness RMS value of 29 nm and skewness 0.25 which is very close to the Gaussian surface. However, the high roughness value is because of the features on the surface on the left side of the image. The roughness RMS continued to increase as well as the skewness so they reached values 33 nm, and 0.31, respectively, after 61 minutes of immersion.

Afterwards, the roughness RMS continued to increase, while the skewness started to decrease. The roughness RMS reached its maximum value 44 nm with a corresponding skewness value 0.15 after 80 minutes of immersion. The increase of roughness is due to the growth of the features on the surface as it is clear from Figure 5.36-B. Then skewness increased to reach a value of 0.22 after 99 minutes of immersion when the roughness RMS was 38 nm. Despite the fact that Figure 5.36-C looks rougher than Figure 5.36-B, the increase in skewness accompanied by a decrease in roughness RMS is because of the disappearance of the feature that was adsorbed on the surface on the upper right corner. Roughness RMS and skewness dropped quickly after 99 minutes of immersion to exhibit a nearly Gaussian surface of skewness -0.03 and roughness RMS 29 nm after 118 minutes. The drop in skewness is due to the detaching of the giant adsorbed features present in the prior time in the lower left corner of Figure 5.36-C resulting in a symmetry of the surface in Figure 5.36-D. Skewness and roughness RMS continued to decrease until minute 130, they had values -0.04 and 28 nm, respectively. Subsequently, skewness started to increase, while roughness was slightly decreasing up to minute 174; they have corresponding values of -0.17, and 27 nm. Figure 5.36-E shows the change in topography, the surface is getting smoother while some peaks started to appear in the upper right corner. Both roughness RMS and skewness were changing to have values 28 nm and 0.15 at minute 225 and dropped to 25 nm and 0.06 after 237 minutes of immersion, respectively. Finally, the values of roughness increased back again to 27 nm, and skewness to 0.31. The increase in skewness is because of the appearance of some new features on the surface as shown in the lower right corner of Figure 5.36-F.

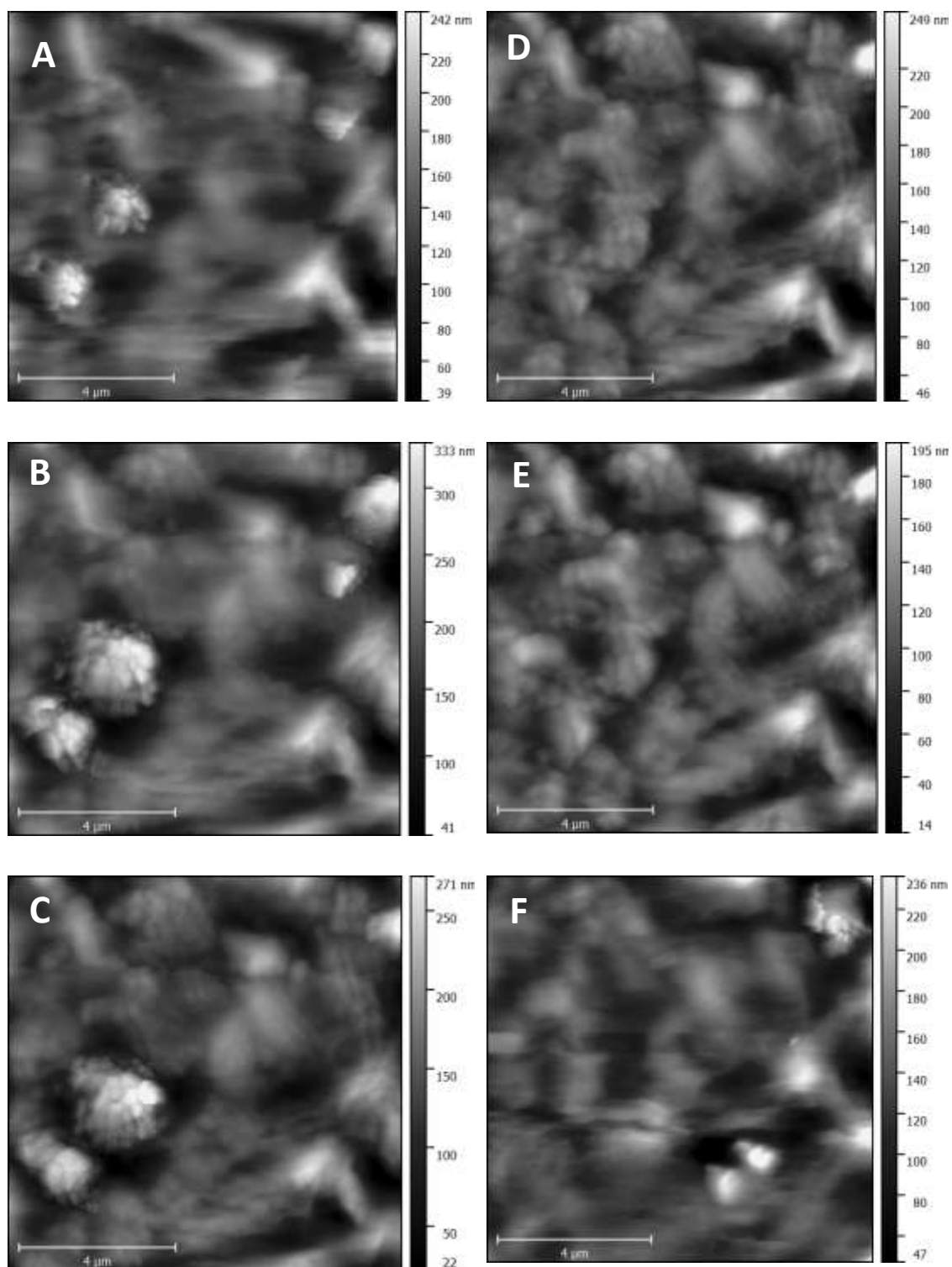


Figure 5.36: In-situ AFM topography measurement of immersed RGO-coated copper. (A) 48 min at OCP, (B) 80 min at -0.2 vs. OCP, (C) 99 min at -0.1 vs. OCP, (D) 118 min at 0.05 vs. OCP, (E) 174 min at 0.1 vs. OCP, and (F) 243 min at 0.2 vs. OCP, time in min refers to the time elapsed after the introduction of 0.5 M NaCl electrolyte.

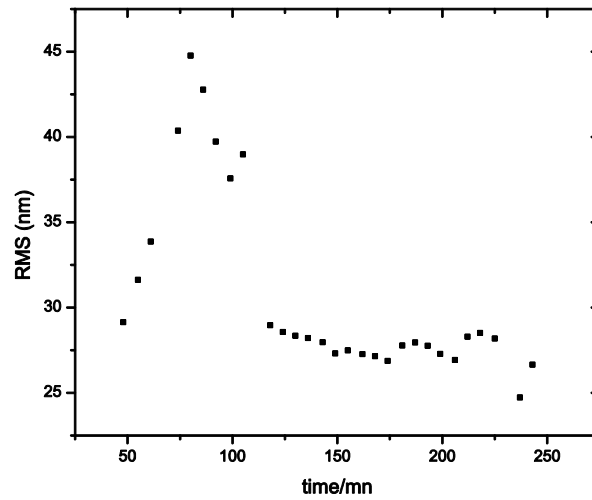


Figure 5.37: RMS temporal change of height of RGO-coated copper for the chronoamperometric test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

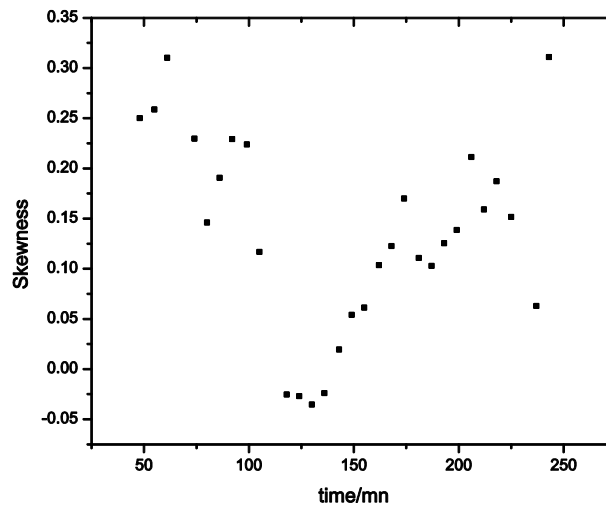


Figure 5.38: Skewness temporal change of height of RGO-coated copper for the chronoamperometric test in NaCl (0.5M) extracted from the in-situ AFM topography measurement.

5.2.3.3.2 In-situ electrochemical results

In this experiment, the sample was immersed in NaCl (0.5M). The experiment was performed using Bio-Logic SP-200 (Bio-Logic SAS, Claix, France). The measurements were started at the time of injecting the liquid into the cell. In this experiment, OCP was measured in the first 30 minutes after immersion, then a loop of measuring EIS and OCP was repeated four times before polarising the sample. Subsequently, a sequence of steps consisting of pulses of different potential values were applied to the sample for a short duration of time, 10 s specifically, then the cell was turned off and OCP was measured followed by measuring EIS. Each sequence was repeated 4 times for each chronoamperometric pulse. Experimental details are given in Appendix A.2.

Figure 5.39 shows the change of OCP value during the first 30 minutes after injecting the electrolyte. OCP started to drop quickly and became more or less stable after 3 minutes of injecting the electrolyte. OCP value after 3 minutes of immersion was -107 mV/Ag/AgCl/NaCl Satd. Then, OCP started to decrease slowly at a rate 0.56 mV/minute to reach -127 mV/Ag/AgCl/NaCl Satd after 30 minutes of immersion.

Afterwards, EIS was measured at OCP followed by monitoring OCP, as shown in Figure 5.40 OCP continued to decrease to attain a value of -133 mV/Ag/AgCl/NaCl Satd after 60 minutes of immersion. A potential pulse of value -0.2 V vs. OCP with a duration of 10s was applied five times. In the first two applied pulses, OCP was decreasing as depicted in Figure 5.40 (curve number 4), so it reached a value of -136 after 72 minutes. Then, by applying the third CA pulse, OCP started to be more anodic and reached its maximum anodic value of -111 mV/Ag/AgCl/NaCl Satd after 80 minutes of immersion, and then it started to decrease again towards the cathodic potential direction. Applying CA pulses that are more anodic resulted in a decrease of the OCP value until it reached a value of -230 mV/Ag/AgCl/NaCl Satd after 197 minutes of immersion. Afterwards, by applying the first CA pulse of 0.15 V vs. OCP, an increase in OCP was observed to reach a value of -221 mV/Ag/AgCl/NaCl Satd after 212 minutes, and then OCP started to decrease again to reach its minimum value -232 mV/Ag/AgCl/NaCl Satd during the course of the experiment after 225 minutes of immersion. Upon the application of CA pulse of 0.2 vs. OCP CA, OCP started to rise to reach a value of -213 mV/Ag/AgCl/NaCl Satd at the end of the experiment.

EIS was measured at OCP with an amplitude of 5 mV/ Ag/AgCl/NaCl Satd. Figure 5.41 shows a Nyquist plot of EIS measured during the course of the experiment. Before applying any CA pulses to the working electrode, EIS shows a relatively high impedance value. Applying the first CA pulse -0.2 vs. OCP resulted in a significant decrease in the impedance as shown in Figure 5.41. The electrochemical impedance continued to increase slightly until the application of the first anodic pulse 0.05 V vs. OCP, a jump in the impedance was noticed. However, the applied anodic potential was increased; a negligible change was noticed in the electrochemical impedance clearly illustrated by the Nyquist plot of EIS measured after the application of each CA pulse. Moreover, the shape of the Nyquist plot starts to change after the application of CA pulses of amplitude 0.05 V vs. OCP, after 142 minutes of immersion.

By comparing AFM and electrochemical measurements, the dynamics of change in the coating can be elucidated. First, upon immersion, the OCP was quite stable and slowly decreasing, whereas AFM measurements showed a quite rough surface, consistent with the nature of the graphene coating because of the wrinkles. In addition, the sample exhibited a relatively high impedance after 30 minutes of immersion. By applying the first CA pulses of amplitude -0.2 V vs. OCP, the roughness continued to increase while skewness decreased. That was due to the formation of some adsorbents on the surface. On the other side OCP

became nobler, giving rise that the reduction CA pulse passivated the surface to be more corrosion inactive. The drop in electrochemical impedance is due to either the dissolution or breakdown of the coating or change in the surface of the coating. Since the topography does not show a real breakdown of the coating, it means that there is a change on the surface of the reduced graphene. The increase in electrochemical impedance upon application of anodic CA pulses is presumably due to the oxidation of the surface of the coating, which was seen as a smoothness of the surface (decrease of roughness RMS) and a reduction in OCP value, which means the surface is more active for oxidation. The last AFM image shows a smooth surface, which agrees with the increased electrochemical impedance. Despite the harsh conditions applied throughout the experiment, the total change of the roughness RMS was less than 20 nm, which can give the impression that RGO is a good coating of copper under the aforementioned conditions.

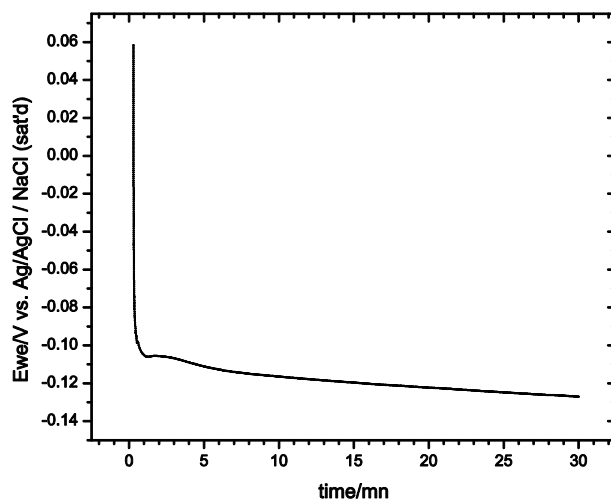


Figure 5.39: OCP measurements of immersed RGO-coated copper sample in NaCl (0.5M).

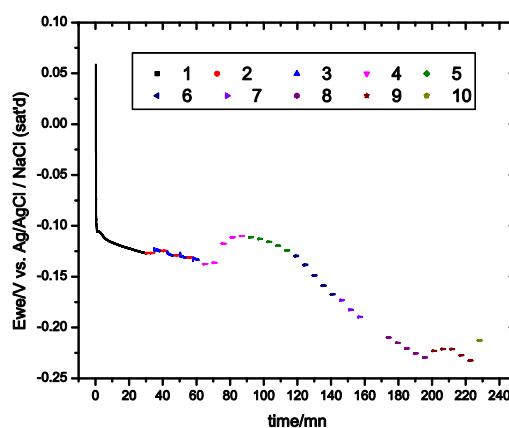


Figure 5.40: Evolution of OCP during the application of different CA pulses to the immersed RGO-coated copper in (0.5M) NaCl. The curves were collected during the relaxation time after the application of different CA pulses:

- 1) The first 30 minutes of immersion.
- 2) Measuring EIS before the application of any CA pulses.
- 3) Relaxation after EIS in (2).
- 4) After the application of -0.2 vs OCP pulses.
- 5) After the application of -0.1 vs OCP pulses.
- 6) After the application of 0 vs OCP pulses.
- 7) After the application of 0.05 vs OCP pulses.
- 8) After the application of 0.1 vs OCP pulses.
- 9) After the application of 0.15 vs OCP pulses.
- 10) After the application of 0.2 vs OCP pulses.

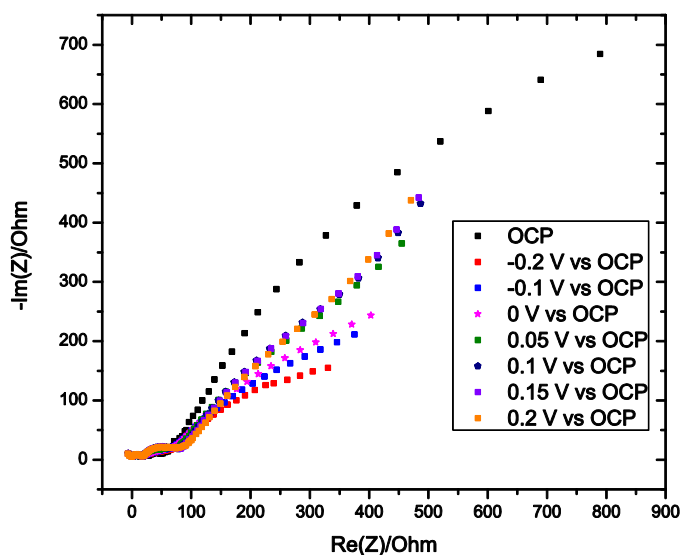


Figure 5.41: EIS of RGO coated copper immersed in (0.5M) NaCl before and after applying chronoamperometric pulses.

5.3 Conclusions

In the case of bare copper, in-situ AFM provides data about the change of surface properties even in cases when the global electrochemical response remains rather constant. By contrast, the latter becomes sensitive upon major surface changes such as during the breakdown of the protective oxide layer.

Using a sol-gel coating under the different electrochemical testing conditions we could find the following:

- During the testing of gel-coated copper upon immersion in NaCl solution for a long time, AFM showed a negligible change in the roughness as well as the skewness during the course of the experiment. The change of EIS during the early stages after immersion could be due to the diffusion of electrolyte into the film or the pressure of the liquid acting on the film to enhance its adhesion to the metal oxide which is likely to happen. During the immersion time, the coating showed a good corrosion resistance at open circuit potential.
- The change of topography observed during application of staircase potential to the gel-coated copper indicated that the film was swollen. The bare surface of copper did not appear even with the application of a wide range of potentials at a slow rate. The current values measured during the experiment indicated that the film had a reasonably high resistance to corrosion.
- It was proved that cyclic voltammetry is a destructive testing technique. The destruction of the surface was revealed upon the application of different cycling regimes. The appearance of characteristic peaks for copper during cycling coincided with corresponding changes in the topography indicating the peeling of the coating.

Using reduced graphene coating for copper samples under the different electrochemical testing conditions we observed the following:

- A minor change was noticed in AFM which indicates the stability of the coating at OCP. The change in OCP and EIS however was noticeable. The decrease of the magnitude of EIS and value of OCP could be due to the interaction of electrolyte either with the graphene defects or with attached groups remaining after the oxidation.
- Despite the conditions applied to the coating, the coating remained unchanged with slight modification of the surface's topography which gives a good indication of the passivity of the copper surface when it is coated with RGO.
- The impedance of RGO coated surface started to increase with the application of more anodic potential which is an indication of the enhancement of the corrosion resistance of the coating; a simultaneous change in the topography was noticed. Adsorbed species were recorded and disappeared with the application of the anodic potential.

RGO-based coating has a better corrosion resistance probably due to its low impermeability to water and gases.

Chapter 6

Conclusions

In this thesis, the main aim was to use AFM in combination with other electrochemical techniques in order to study the change of the surface in real time after exposure to electrochemical environment. First, it was necessary to design an electrochemical cell that can be integrated with the atomic force microscope.

A preliminary design that allows accommodation of a larger reservoir for liquid electrolyte (i.e. 4 ml) compared to commercially available cells was developed. The cell was tested for in-situ AFM measurements by immersing AA2024 and finding the change in the topography at OCP, without the application of any electrical pulses. Then the cell was modified by adding a counter electrode consisting of a platinum plate, and a standard reference electrode Ag/AgCl. Aside from the advantage of the large volume of the cell (4 ml), the design itself has some problems. The first drawback of this design is that it was necessary to remove the cell or the scanner in order to inject the electrolyte into the cell. The second drawback is the asymmetry in the electrodes configuration, which is a problem in the case of using the cell for electrochemical impedance measurements, owing to the lack of symmetry in the field distribution inside the cell, and upon the change of the position of both counter and reference electrode from one measurement to another. Therefore, it was necessary to propose a new design of the cell to consider the different aforementioned issues.

The new cell design solved the problem of the field symmetry inside the cell, the geometrical factors for the electrodes, and the flexibility of using the cell, the easiness of injecting the electrolyte into the cell without removing it, the robust mechanical design, and the fixed position of the electrodes. The new cell was designed and fabricated after running appropriate simulations using finite element method, so the difference between the two cells in the current and potential distribution inside the cell could be considered. The new cell design showed a symmetric current and potential distribution, which is an important factor to reduce the error in the measurement of electrochemical impedance spectroscopy as well as when using any other electrochemical technique. Moreover, the cell can preserve the same configuration each time when replacing the sample, which can help in having reproducible electrochemical measurements. Additionally, it increases the interval of confidence when comparing different measurements. In addition, the cell helped to locate the same scanning spot when changing the conditions from initial air to later electrolyte environment after injecting the liquid into the cell. The safety factor was considered in the design to avoid the leakage of the liquid and the short circuit between any electrodes, and consequently, avoid any fire risk.

Aluminium alloy was in-situ studied. First, the bare aluminium alloy was studied in NaCl (0.5M) at OCP (without the application of any electrical pulses) to find the characteristics of spontaneous corrosion of AA2024 in NaCl (0.5M) at room temperature.

Then, the corrosion was stimulated by applying chronoamperometric pulses. AFM measurements found that the surface roughness started to increase upon immersion in NaCl (0.5M), and spikes started to appear. However, after a long immersion time (3 hours) the surface became smoother (the roughness decreases). The change in the surface roughness indicates the nucleation of a layer on the top of the metal, and it continued to grow until the surface became smooth again. To find the chemical change of the surface, IRRAS was used first with the hydration test after soaking the sample in water for different durations, and then by polarising the AA2024 sample immersed in NaCl (0.5M). It was found that the AA2024 had a native oxide layer before the hydration test. After carrying out the hydration test at different temperatures, it was found that a layer of pseudo-boehmite was formed on the surface and the oxide layer disappeared, either because it was transformed, dissolved, or covered with the pseudo-boehmite.

In situ test of the sol-gel coating as a protective coating for aluminium alloy can be summarised as follows:

- The change of the sol-gel film topography during the spontaneous test was negligible. The noticed increase in the roughness during the first 100 minutes corresponds to a smooth decrease in the electrochemical impedance which could be due to minor breakdowns in the coating and was seen as features on the surface in AFM images. However, no major changes were noticed neither in AFM nor in electrochemical measurements.
- The application of chronoamperometric pulses introduced evolution of gas bubbles, and the coating started to break down upon the application of more anodic pulses. The combination of the different techniques showed the change in the coating from both topographic and electrochemical perspectives.
- The application of chronopotentiometry test showed a good control over the process. The application of anodic current values and measuring the impedance and topography in addition to OCP added insight into the protection of the metal using the sol-gel coating. A change was noticed in the surface with the application of different CP pulses and the gradual dissolution of the coating that was confirmed by the decrease in the electrochemical impedance value. The use of CP reduced the evolution of gas bubbles as the duration was short and CP pulses have a higher control of the redox processes over CA pulses. Interestingly OCP was decreasing in an exponential manner indicating the corrosion activity of the surface. The applied conditions indicate the weakness of the protective coating under such conditions keeping in mind that the coating was quite thin i.e. within 120 nm.

In situ electrochemical test of copper corrosion revealed the following:

- The study of bare copper at OCP by measuring AFM simultaneously with two different electrochemical techniques (EIS and OCP) gave an insight about the corrosion of copper. AFM could monitor the local change of the topography while electrochemical measurements gave an indication of the change on the macro-scale. The early stages of corrosion were monitored from EIS and OCP both indicated a significant corrosion, a dissolution of the native oxide layer, as well as the removal of the adsorbate on the surface that could be directly seen in the topography. AFM was capable of following the change for a long time of immersion while the changes of the surface were not accompanied by a change in the electrochemical measurements which could be due to the insensitivity of the electrochemical

measurements to the early stages of pitting; namely, the electrochemical methods measure the changes globally all over the surface in contrast to the AFM.

Using in-situ test of the sol-gel coating as a protective coating for pure copper under the different electrochemical treatments we found the following:

- The electrochemical measurements showed a gradual decrease of the EIS magnitude up to a certain time. The impedance values started to saturate after about 90 minutes of immersion. This was accompanied by a slight change in the OCP and it became nobler. On the other hand, AFM showed a slight change in the topography which can be negligible. The decrease in EIS impedance could be due to the diffusion of electrolyte to the defects of the coating until it saturated. The results show that the film had a good spontaneous anticorrosion resistance as it could preserve its structure during the course of the experiment.
- Under the application of staircase potential, the film could preserve its structure despite the harsh conditions. AFM showed a smoothing of the surface with the longer immersion time and the application of the more anodic potential. In addition, the surface of the coating started to swell with the application of more positive potential. It remained unclear whether this was because of the application of a more anodic potential or because of the water uptake. However, the film did not peel off the surface and showed a good adhesion to the copper surface. From the electrochemical measurements, the current in the cathodic side remained constant for different values of applied potential and started to increase when it was closer to the corrosion potential. The overall change of the current indicates the good passivation of the surface.
- The change in the topography was noticed after a few cycles, which agrees with the electrochemical measurements as the peaks of copper started to be more pronounced with the increased number of cycles. This measurement showed the power of combining AFM and electrochemical measurements. Whereas AFM has the ability to find the changes in topography, cyclic voltammetry can measure not only the corrosion properties of the coating but also can give an indication of the chemical change on the surface by via appearance of characteristics peaks of the species under test. This method can be used as a test for the destruction of coatings under cycling.

In situ test of RGO coating as a protective coating for pure copper by using simultaneous AFM and different electrochemical testing methods we found the following:

- Both AFM and electrochemical measurements showed that the change in the surface of the coating is negligible. AFM showed almost no change during the time of immersion of RGO-coated copper. A slight decrease was noticed in the EIS which could be due to the reactivity of the electrolyte with the different active groups that were not completely reduced during the reduction process. In addition, a decrease of the OCP was also noticed. This decrease agreed with the EIS measurements and could be mainly due to the interaction of the electrolyte with the attached groups' residue after the oxidation or due to the interaction of the electrolyte with the graphene defects.
- By applying a staircase potential to the RGO-coated copper, different features were noticed. A change in the topography was noticed such that with the application of more anodic potential flattened the surface of the coating. In addition, the

electrochemical measurements showed one small cathodic peak and two anodic peaks. They are not attributed to copper, therefore they are due to the interaction of the electrolyte with the coating itself.

- With the application of chronoamperometric pulses, the surface features started to change significantly. The newly grown features however were removed upon the application of anodic pulses. The electrochemical measurements showed a decrease in OCP which means an increase in reactivity of the graphene surface with the application of different chronoamperometric pulses. The EIS magnitude showed first a decrease upon the application of a relatively high cathodic pulse, then continued to increase with the application of more positive pulses. The increase of the EIS indicated the enhancement of the passivity of the coating which is presumably due to the oxidation of the surface due to the interaction of RGO with the electrolyte.

Combining the results of different tests performed on RGO-coated copper, one may conclude that RGO has a good corrosion resistance in NaCl. The application of different harsh conditions did not change the surface topography. However, at the same time changes in chemical activity of the surface were clearly detected. Those changes were attributed to localized processes on RGO and did not affect the corrosion protection of copper. This result represent a crucial difference between the RGO and sol-gel based protective films. Gel coated copper has a good corrosion resistance under open circuit potential as well as RGO coated copper. However, under harsh electrochemical treatments in case of the gel coated copper, the topography of the coating starts to change thus affecting the electrochemistry; under certain conditions the film was even destroyed.

The designed cell gave us the privilege to carry out many types of in-situ measurements. The cell has a good stability under different conditions. The development of the different electrochemical techniques by combining different electrochemical methods gives an insight into the mechanism of corrosion on the nanometer scale. Combining the results with a change in the topography adds more to the insight. The developed cell and techniques pave the way to similar testings of other coatings of interest and, finally, extending the approach to other electrochemical problems involving topological changes of surface with time.

Appendix A

Electrochemical Methods Setup

A.1 Spontaneous Immersion

In this technique, no electrical signals are applied to the working electrode, except a small signal for measuring the electrochemical impedance spectroscopy. First, the Open Circuit Potential is measured for 30 minutes (in some cases it was 50 minutes), followed by a loop of switching between measuring EIS, and OCP. The time of full scan of either EIS or OCP is 3 minutes and 7 seconds. EIS is measured at OCP using a sinusoidal potential signal of 5 mV amplitude. EIS was measured in the logarithmically spaced frequency range from 7 MHz to 0.1 Hz. In order to decrease the error of the potential drift through the measurement, a drift correction was used to lock the potential to the initial potential at which each measurement starts. The detailed steps are shown in Table 6.1.

Table 6.1: Spontaneous immersion test.

1. Measure OCP for (30-50) minutes upon the immersion
2. Loop (for N number of cycles)
 - 2.1. Measure EIS at OCP
 1. Frequency range 7 MHz – 0.1 Hz, Logarithmic spaced
 2. Amplitude: 5 mV (RMS 3.54 mV)
 3. Waiting period before each frequency (0.2 % of the period)
 4. Drift correction ON
 5. Time of the full scan is 3' 7"
 - 2.2. Measure OCP for 3' 7"

A.2 Chronoamperometric Test

In this technique, potential pulses are applied to a working electrode, each with a duration of 10 seconds. The potential pulses were of different amplitude values and polarities. First, OCP is measured for 30 minutes. Then, OCP and EIS were measured four times each. Afterwards, a loop of applying a potential pulse of 10 seconds duration, then the cell was turned off for 2 minutes and 57 seconds and EIS was measured. Each loop was repeated four times. The details of the technique are shown in Table 6.2.

Table 6.2: Chronoamperometric Test.

1. Measure OCP for 30 min upon immersion
 - 1.1. Loop to measure EIS and OCP for 4 times
 - 1.1.1. EIS
 - 1.1.2. OCP 3' 7"
2. Loop to apply chronoamperometric pulses (with potential values -0.2, -0.1, 0, 0.05, 0.1, 0.15, 0.2 V vs. OCP), OCP, and EIS.
 - 2.1. Loop (4 times)
 - 2.1.1. Apply chronoamperometric signal for 10"
 - 2.1.2. Turn off the cell and measure OCP for 2' 57"
 - 2.1.3. Measure EIS at OCP

A.3 Chronopotentiometric Test

In this technique, current pulses are applied to a working electrode, each with a duration of 10 seconds. The anodic current pulses were of different amplitude values. First, OCP is measured for 30 minutes. Then, OCP and EIS were measured four times each. Afterwards, a loop was applied with a current pulse of 5 seconds, then the cell was turned off for 2 minutes and 57 seconds and EIS was measured. Each loop was repeated four times. The details of the technique are shown in Table 6.3.

Table 6.3: Chronopotentiometric Test.

1. Measure OCP for 30 min upon immersion
 - 1.1. Loop to measure EIS and OCP for 4 times
 - 1.1.1. EIS
 - 1.1.2. OCP 3' 7"
2. Chronopotentiometry increment loop ($I = 0.1, 0.2, 0.4, 0.6, 0.8, 1.4$ mA)
 - 2.1. Loop (5 times for each current)
 - 2.1.1. Apply Chronopotentiometry signal for 5"
 - 2.1.2. Turn off the cell and measure OCP for 2' 57"
 - 2.1.3. Measure EIS at OCP

A.4 Cyclic Voltammetry Test

The cyclic voltammetry test was carried out on the working electrode. Starting from OCP to the first vertex in the cathodic direction at -0.5 V below OCP, then incremented in the anodic direction to 0.5 V above OCP with sweeping rate 10 mV/s. Before starting the cycling of the potential, OCP was recorded for 60 minutes.

A.5 Staircase Voltammetry Test

This test OCP is measured in the first (30 or 80) minutes after immersion, followed by stepping the potential from the cathodic to the anodic direction to test the corrosion. The initial cathodic potential was 0.5 V below OCP, then the potential was incremented in 51 steps to have a scanning range of 1 V. The duration of each step was 3 minutes and 7 seconds.

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Publications Related to the Thesis

Journal Articles

1. Kreta, A., Rodošek, M., Slemenik, P. L., Orel, B., Gaberšček, M., & Šurca, V. A. (2016). In situ electrochemical AFM, ex situ IR reflection-absorption and confocal Raman studies of corrosion processes of AA 2024-T3. *Corrosion Science*, 104, 290-309.
2. Rodošek, M., Kreta, A., Gaberšček, M., & Šurca, V. A. (2016). Ex situ IR reflection-absorption and in situ AFM electrochemical characterisation of the 1,2-bis(trimethoxysilyl)ethane-based protective coating on AA 2024 alloy. *Corrosion Science*, 102, 2016, 186-199
3. Talyzin, A. V., Luzan, S., Anoshkin, I. V., Nasibulin, A. G., Kauppinnen, E. I., Dzwilewski, A., Kreta, A., ... Grennberg, H. (2014). Hydrogen-driven cage unzipping of C [sub] 60 into nano-graphenes. *The Journal of Physical Chemistry. C, Nanomaterials and Interfaces*, 118, 6504-6513.

Conference Participations

1. Šurca, V. A., Kreta, A., & Rodošek, M. (2015). Combined approach: In situ coupling of electrochemical measurements of sol-gel materials with vibrational and AFM techniques. XVIII International Sol-Gel Conference, September 6-11, 2015, Kyoto, Japan.
2. Rodošek, M., Šurca, V. A., & Kreta, A. (2015). Coupling of electrochemical measurements with vibrational and AFM techniques. *Zbornik Referatov in Povzetkov*.
3. Rodošek, M., Kreta, A., & Šurca, V. A. (2015). AA 2024 and protective coating characterized with in situ AFM electrochemical measurements. "bottom-up Approaches of Hybrid Materials.
4. Rodošek, M., Kreta, A., & Šurca, V. A. (2015). In situ AFM elektrokemijske meritve aluminijeve zlitine in zaščitne prevleke. *Kemijske Znanosti* 2015, 1-2.
5. Kreta, A., Jamnik, J., & Hassanien, A. (2013). Hydrogenation of C60 into nanographenes. *Book of Abstracts*.

Other Publications

1. Kreta, A., Kaskela, A., Laiho, P., Mustonen, K., Žnidaršič, A., Jiang, H., Muševič, I., ... Kauppinen, E. I. (2015). Effect of structural parameters on transport properties of carbon nanotube networks. The Sixteenth International Conference on the Science and Applications of Nanotubes, June 28 - July 3 2015, Nagoya, Japan.
2. Kreta, A., Kaskela, A., Laiho, P., Mustonen, K., Jiang, H., Zupanič, E., Muševič, I., ... Kauppinen, E. I. (2015). Local transport properties in carbon nanotube networks. The Sixteenth International Conference on the Science and Applications of Nanotubes, June 28 - July 3 2015, Nagoya, Japan.

Biography

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- Graduated in June 2006 from Faculty of Science, Ain Shams University, Cairo, Egypt.
- Employed from May 2006 – May 2007 as a technical support engineer and trainer in Penta Experts Ltd for consulting services, in Cairo, Egypt.
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- Masters courses in September 2008 at the Faculty of Science, Ain Shams University, Cairo, Egypt.
- Dec 2008 – Sept 2009 joined the ultra-fast laser group in the Department of Physics, National Research Centre, Cairo, Egypt to work as a research assistant.
- Sept 2009 - Jan 2013 worked as a teaching assistant in the Faculty of Engineering, The British University in Egypt.
- Jan 2013 - Dec 2016 worked as a young researcher in the National Institute of Chemistry, Ljubljana, Slovenia.