Enhancing Aluminum's Anti-Corrosive and Electrical Properties by Graphene Coating and Comparing with Conventional Coating Methods

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Enhancing Aluminum's Anti-Corrosive and Electrical Properties by Graphene Coating and Comparing with Conventional Coating Methods

Abstract

After 2010, when graphene is discovered, there have been respectable attractions to the graphene by humankind because of its great electrical, mechanical, thermal, anti-corrosive capabilities. With its extraordinary properties which are superior to all available options, scientist tried to achieve its potential and make it an industry level option.

Aluminum is the second most widely used material as a busbar in the electrical energy distribution industry after copper. Unlike copper, it needs coating to prevent corrosion. Alternating current tends to intensify at the surfaces of conductors, therefore preventing the surface of conductors from corrosion is crucial. At the present time, there are several coating options for aluminum busbars including tin, nickel, silver, epoxy and polymer-based materials. Only silver tends to increase the busbars initial conductivity but it is only preferred when it is truly necessary, because of its cost.

In this study, it is aimed to reduce the resistance of aluminum material and protect it from corrosive environment by coating a single layer graphene over it. With this method, initial conductivity of aluminum busbar can be amplified and anti-corrosive property can be improved. Improved corrosion resistance means preserving aluminum busbar's electrical properties over long times.

Single layer graphene is synthesized over the copper film with chemical vapor deposition (CVD) method and transferred onto aluminum samples. After the coating process is finished, characterization is done with Raman spectroscopy, electrical resistance and wettability tests. Then, corrosive conditions were applied to the samples with NaCl solution to investigate long term reliability and performance.

The results show that, single layer graphene is synthesized successfully with CVD method. Surface resistance of aluminum samples decreased remarkably by achieving 33 times less resistance compared to bare aluminum and 10 times less resistance compared to tin coated aluminum. In wettability tests, about 17° higher contact angles than uncoated and tin coated aluminum samples were achieved. Even after the corrosion test, graphene coated samples succeeded to preserve their transcendencies. However, about half of the graphene coated samples couldn't preserve their properties because of the defects on graphene layers and performed worst among all samples.

Keywords: Graphene, graphene coating, aluminum, busbar, electrical conductivity, electrical resistance, corrosion, wettability, contact angle

Alüminyumun Elektriksel Özelliklerinin ve Korozyon Dayanımının Grafen Kaplama ile Artırılması ve Geleneksel Kaplama Yöntemleri ile Kıyaslanması

Öz

Grafen, 2010 yılında keşfedilmesinin ardından, üstün elektriksel, mekanik, termal ve paslanma önleyici özellikleri sayesinde insanlık tarafından büyük bir ilgi gördü. Mevcut tüm seçeneklerden daha üstün olan sıradışı özellikleri sayesinde, bilimadamları grafenin potansiyeline ulaşabilmek ve onu endüstri seviyesinde kullanılabilir bir seçenek haline getirebilmek için çalıştılar.

Alüminyum, elektrik enerjisi dağıtım sektöründe bakırdan sonra en çok kullanılan busbar malzemesidir. Bakırın aksine alüminyum, korozyon dayanımı için kaplanmaya ihtiyaç duyar. Alternatif akım, iletim esnasında, iletken malzemenin yüzeylerinde yoğunlaşır; bu nedenle, iletken yüzeylerinde oluşacak korozyonun engellenmesi çok mühimdir. Günümüzde, alüminyum busbar için kalay, nikel, gümüş, epoksi ve polimer bazlı kaplamalar gibi bir çok kaplama seçeneği bulunmaktadır. Sadece gümüş kaplama, alüminyum busbarın başlangıç iletkenlik değerini artırabilirken, maliyeti dolayısıyla sadece gerçekten ihtiyaç duyulduğunda uygulanması tercih edilmektedir.

Bu çalışmada, alüminyum malzemenin elektriksel direncini düşürmek ve onu aşındırıcı ortamlardan korumak için tek tabaka grafen kaplanması amaçlanmıştır. Bu yöntem ile, alüminyum busbarın başlangıç iletkenliği yükseltilebilir ve korozyona karşı dayanımı geliştirilebilir. Geliştirilmiş korozyon dayanımı, alüminyum busbarın elektriksel özelliklerinin uzun süre boyunca korunmasını sağlamak anlamına gelmektedir.

Tek tabaka grafen bakır film üzerinde kimyasal buhar biriktirme (CVD) metodu ile sentezlenmiş ve alüminyum numunelerin üzerine transfer edilmiştir. Kaplama işleminin bitmesinin ardından Raman spektrometresi, elektriksel iletkenlik testi ve ıslanabilirlik testi ile numune karakterizasyonu yapılmıştır. Daha sonra, numuneler NaCl çözeltisi ile aşındırıcı ortama tabii tutulmuştur. Bu sayede malzemenin uzun dönem performansı ve dayanıklılığı incelenmiştir.

Sonuçlar, tek tabaka grafenin CVD metodu kullanılarak başarı ile sentezlendiğini göstermektedir. Alüminyum numunenin yüzey direnci çıplak alüminyuma oranla 33 kat, kalay kaplı alüminyuma oranla ise 10 kat azalarak çarpıcı bir sonuç ortaya çıkarmıştır. Islanabilirlik testlerinde, çıplak ve kalay kaplı alüminyum numunelerden yaklaşık 17° daha yüksek yüzey temas açısı elde edilmiştir. Korozyon testinden sonra dahi, grafen kaplı numuneler bu üstünlüklerini korumayı sürdürmüştür. Ancak, grafen kaplı numunelerin yaklaşık yarısı, yüzeydeki grafen tabakasında oluşan bozulmalardan dolayı bahsedilen özelliklerini koruyamamıştır ve bütün numuneler arasında en kötü sonuçları göstermişlerdir.

Anahtar Kelimeler: Grafen, grafen kaplama, alüminyum, busbar, elektriksel iletkenlik, elektrik direnci, korozyon, ıslanabilirlik, temas açısı

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List of Abbreviations

AC	Alternating Current
Al	Aluminum
C	Carbon
CH_4	Methane
CVD	Chemical Vapor Deposition
$FeCl_3$	Iron Chloride
NaCl	Sodium Chloride
PMMA	Polymethylmethacrylate
PSX	Polysiloxane
PVA	Polyvinyl Alcohol
SiC	Silicon Carbide
Si/SiO_2	Silicon/Silicon Dioxide
δ	Skin depth [m]

Chapter 1

Introduction

1.1 Carbon

Carbon, symbolized with letter C and atomic number 6, is a nonmetallic element. Because it is a tetravalent element (has four electrons available on its outer orbit), it has the potential to form in several compounds.

Diamond, one of the most widely known Carbon compound, has a crystal structure of face centered cubic. It is known as one of the most famous material with high mechanical properties, and the highest hardness value. It has great thermal conductivity and electrical inductance. It has also transparent optical form that almost 100% of light can pass through diamond.

Graphite, another allotropic form of carbon, is also one of the most well-known compound made of Carbon. It has a three-dimensional crystal form and durable σ covalent bonds in the plane, but weak bonds in between the layers. Generally known as the main material for pencils, it has good electrical and thermal conductivity. Unlike diamond, it is a reflector for visible light.

1.2 Graphene

Discovered in 2004 and called as a "Miracle Material" by its founders Andre Geim and Kostya Novolesov [1], graphene is a two-dimensional sheet formed allotrope of graphite. Before the discovery of graphene, it is believed that two dimensional crystals were impossible to exist because they were not stable enough. Andre Geim and Kostya Novolesov disproved this belief with the discovery of graphene. They exfoliated bulk of graphite with tape and created graphene. This invention made them win the Nobel Prize. Nowadays, a lot of scientists are working on graphene because of its unique properties.

The carbon atoms are positioned into a honeycomb lattice structure. It has thickness of only one atom and bonds with adjacent carbon atoms in same plane.

1.2.1 Properties of Graphene

Scientists made several experiments to find out graphene's unmatched theoretical limits that are superior to other materials. It is found that graphene is stronger than diamond with a Young's modulus of 1 TPa and intrinsic strength of 130 GPa. Its electron mobility at room temperature is 2.5 x 10^5 $cm^2V^{-1}s^{-1}$ so it has the ability to carry extremely high densities of electric current than copper, such as a million times higher. It is flexible than rubber, and has thermal conductivity above 3000 WmK^{-1} [1-5].

1.2.2 Application Areas of Graphene

The invention of graphene and its extraordinary properties, attracted many scientists and engineers. Many of them started to find out a way to make graphene more applicable.

Existing and potential graphene application areas are; batteries, supercapacitors, sensors, transistors, touch panels, nano devices, electric carrying parts such as busbars, coating materials, solar cells, defence industry, gears that have resistance to impact, etc. [6-8].

1.2.3 Production Methods of Graphene

There are four reliable methods nowadays to obtain high quality graphene. Mechanical exfoliation method, which was the first method to produce graphene in history [9]; Graphitization of silicon carbide (SiC) substrate method which is also called epitaxial growth; Chemical exfoliation method which is also an old technique and similar to mechanical exfoliation, and Chemical Vapor Deposition (CVD) method which produces graphene on a metal substrate [10-14]. The properties of graphene depend on the method used in production.

1.2.3.1 Mechanical Exfoliation Method

This method is the primal and simplest method to produce a graphene layer. To produce graphene with mechanical exfoliation method, a bulk of graphite sample needs to be cut first. Then a small piece of cut graphite needs to be placed on an adhesive tape. After that, the tape is repeatedly folded and unfolded. Because the Van Der Waals forces between the layers are so weak, the graphite will gradually get more thinner by stripping the layers away. This step needs to be repeated until the remaining graphene has a thickness of one or few layers.

The efficiency of mechanical exfoliation method can be verified with Raman spectroscopy which is a non-harmful chemical analysis method done with an optical microscope and a laser light source. With this method, graphene can have mobility of 15,000 $cm^2V^{-1}s^{-1}$ [10,15-20].

1.2.3.2 Epitaxial Growth Method

Epitaxial growth method is a substrate based method where the isolated monolayer of graphene is grown on a single crystal SiC with vacuum graphitization. Graphenes produced with epitaxial growth method has an electron mobility value range of, lower than graphenes produced with exfoliated graphene methods, but higher than the ones produced with (CVD) method.

To produce graphene with epitaxial growth method, firstly the SiC needs to be thermally treated at ~1300°C under vacuum atmosphere. This results the sublimation of silicon atoms while carbon atoms remained on the surface, over entire SiC wafers. The sublimation process needs to be controlled carefully. The thickness of graphene can be controlled with time and temperature. This method can cause several structural defects because of high annealing temperature. In high temperature, the carbon atoms might get burnt. Therefore, the carbon atoms might be contaminated by oxygen and hydrogen atoms [19,21-25].

1.2.3.3 Chemical Exfoliation Method

Chemical exfoliation method is is similar to mechanical exfoliation method. It is one of the oldest technique to produce graphene. Chemical exfoliation method outclasses mechanical exfoliation method with its high efficiency and the ability of scalability.

To produce graphene with this method, firstly graphite intercalated compounds are need. The aim of this step is to enlarge the spacing between the graphene layers. With this, it is aimed to soak graphite to mixture of nitric acid and sulfuric acid. This causes graphite to form alternative layers of graphite and intercalant. As the graphite layers split in time, thickness of the layers decreases. This causes to get graphene sheet with few layers [26-29].

After that, it is aimed to exfoliate the graphite sheet by rapid evaporation of the intercalants between two layers. The efficiency of exfoliation can be enhanced with additional methods like ultrasonication or ball milling.

The main advantage of this method is that it is very simple. But the disadvantage of it is, the graphite nanoplatelets produced with this method has a thickness up to few hundred layers [.

1.2.3.4 Chemical Vapor Deposition (CVD)

CVD method is currently the best method to produce graphene. It is relatively cheap compared to other methods. It has the ability to produce high quality graphene. Metal substrates are needed for graphene synthesis. Copper is the most used one but there are also alternative substrates like nickel, palladium, ruthenium and iridium.

In low temperature, electron mobility up to 7350 $cm^2V^{-1}s^{-1}$ is reported in researches [33-35].

To produce high quality graphene with CVD method, five steps are required; heating, annealing, growing, cooling and backfilling the inert gases.

In the heating process, the copper or nickel substrate and gases are heated up to the designated temperature. Hydrogen and argon are used in this step.

In the annealing process, it is aimed to diminish the surface of the catalyst. To diminish the surface, the gas atmosphere and the temperature needs to be maintained. By maintaining these conditions, the catalyst surface gets cleaned and the surface morphology (crystalline orientation, grain size of the metal substrate and roughness) gets modified.

In the third step, the growing process, the graphene starts to grow on metal substrate. There are different methods for growing graphene. It can be one step or multiple steps. During these steps, the pressure of gases, the ingredient of gases, residence time, temperature of environment, flow velocity of gases can be modified. To grow graphene on substrate, gases including carbon are needed. Methane (CH_4) is the most commonly used gas for this purpose. It has strong C-H bonds, so its thermal decomposition occurs at a high temperature [36].

Cooling process is the fourth step. In this process, the reactor gets cooled in argon and hydrogen atmosphere. Because the temperature gets lowered, the C-H bonds are strong enough to stand still. However, the carbon sources are closed. The atmosphere is generally similar till 200°C, to that in the annealing process. The aim of this process is to prevent the metal surface which is not covered with graphene from oxidation and the graphene layer from oxygen containing groups. Because substrates with high solubilities are used, the cooling process is crucial for graphene growth due to the solubility dependence.

The final step is the backfilling process. In this process, inert gases such as argon and nitrogen are backfilled to use future synthesises. Schematic of the process is shown in Figure 1.1.

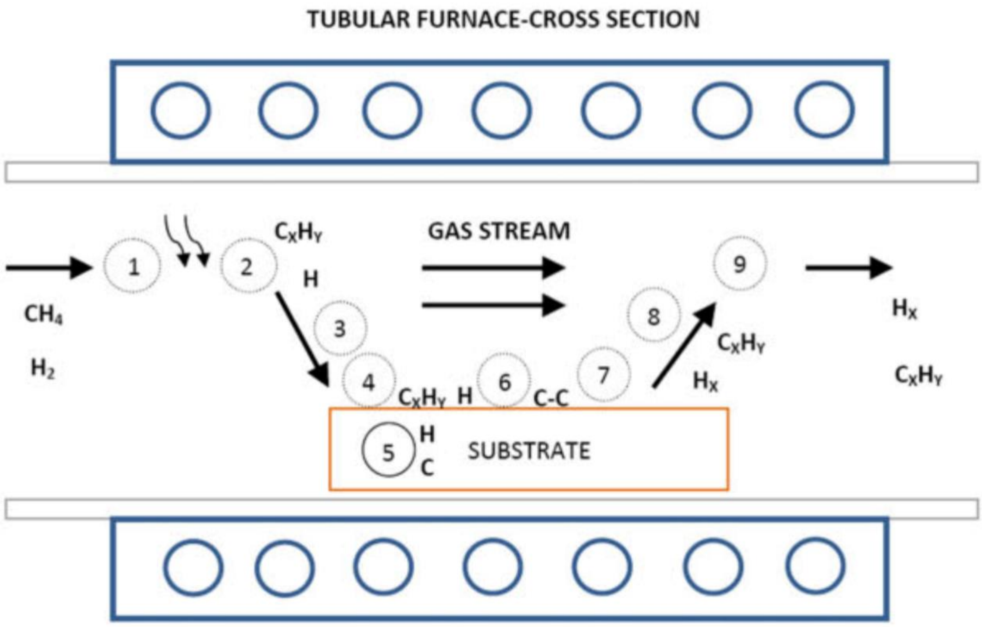

Figure 1.1: Schematic process of graphene synthesis with CVD method [37]

1.3 Busbar

Busbar is a material which is made from an electrically conductive metal. It is used in electrical power distribution industry to transfer high power electricity. The most widely used material to make busbars is copper. Aluminum (Al) is the second most widely used material after copper. Brass, nickel and silver are also used in types of different busbars.

Copper busbars are widely used as a busbar in power distribution industry. They are solid enough to stand still, soft enough to be drilled for joint connections and they have good electrical and thermal conductivity. They also have high melting point (1083°C) so they can be used in specific conditions without any problem. Copper also has a mediocre resistance against corrosion. Several types of usages can be seen in Figure 1.2.

Figure 1.2: Example of copper busbars

The main disadvantage of copper is that it is expensive. It also has high density so the solution with copper will be heavy. Moreover, production methods for copper busbars are limited so it can be mostly found in solid bar forms. The bar form has a weak bending strength compared to other forms. This results physical weakness for short circuit scenarios.

Aluminum busbars are widely used in trunking systems in the power distribution industry. They are also solid enough to stand still and soft enough to be drilled for joint connections. Aluminum has also high electrical conductivity, yet relatively low when compared to that of copper. It has electrical conductivity of approximately 61% of copper having the same cross-section. Because it is very lightweight, it can be 30% lighter compared to copper for the same current carrying capacity. It offers better heat dissipation than copper. It can be extruded easily so that, different shaped aluminum busbars can be easily produced and this results good physical strength against short circuit scenarios. Sub-connections can be made without drilling because of unique shapes. Aluminum is the most abundant solid material by mass on Earth so that, aluminum busbars are nearly 30% cheaper than copper ones. Moreover, because aluminum is not considered as a commodity, the price of aluminum does not fluctate as much as copper. Several types of aluminum busbars can be seen in Figure 1.3.

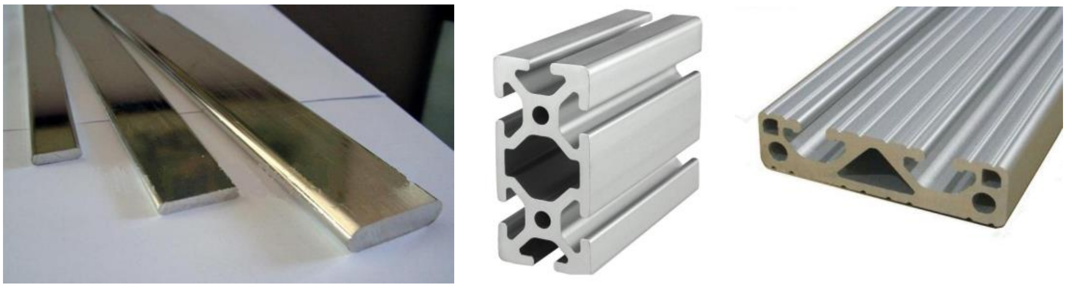

Figure 1.3: Example of various aluminum busbars

The main disadvantage of aluminum is that it is vulnerable against corrosion. It oxides so easily that it needs protection against corrosive environments.

Silver busbars are used only in special conditions because of their extremely high price compared to other material options. Silver is usually choosed against other materials when the other materials are unable to meet the requirements. It has the best electrical conductivity and the highest thermal conductivity among all materials. It is extremely resistant against corrosion. Even if it oxides, the oxide of silver has much higher electrical conductivity than any other material. This causes a natural coating for silver.

Brass and nickel are the other alternatives for copper, aluminum and silver. But they have significantly lower electrical conductivity so that they are mostly used in applications where the power need is low.

Aluminum, which has a constant rise day to day in market share, is the best potential alternative material against copper. Although it is vulnerable against corrosive environment, this gap can be closed with several coating options.

There are a variety of shapes of busbars, such as solid bars, flat strips, rods or even special shaped profiles. Special shaped profiles can be strong against forces and be reliable because of their unique forms. Several types of busbars are seen in Figure 1.4. The shape of busbar affects current carrying capacity critically because it allows high heat dissipation with its large surface area. The large surface area also provides high conductivity because of the skin effect [38-39].

Figure 1.4: Examples of busbars with a variety of shapes

In alternating current (AC), distribution of current flow decreases in core, while increasing exponentially towards the surface. This tendency is called the skin effect. Skin depth (δ) is a definition that describes the depth where the current density is equal to 1/e (roughly 37%) of the value at the surface (see Figure 1.5). It mostly depends on the conductive material and the frequency of current.

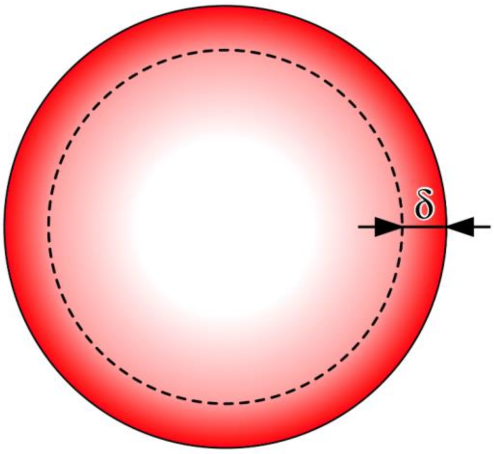

Figure 1.5: The projection of skin effect tendency [40]

For example, in copper at 60 Hz alternating current, the skin depth is approximately 8.5mm. This means that, any type of busbar made of copper with a wall thickness of more than 8.5mm can be considered as an inefficient busbar because of the low current density at its core.

1.3.1 Coating of Busbars

There are several reasons that busbars need coating. The reasons depend on the busbar material, the deficiency of the busbar or the environment which the busbar will work. Coatings are usually expensive to apply so they should only be applied when truly required [41].

1.3.1.1 Coatings to Provide Electrical Insulation

The main reason for this coating is to make a protective barrier against short circuit and electrical contact in the event of dielectric creepage or direct contact. The main problem for this coating is that the coating will reduce thermal conductivity of the main material; therefore, the selected busbar should have a large cross-section. This type of coating is only used when it is critically needed.

1.3.1.2 Coatings to Prevent Corrosion

Corrosion is the main reason why most of the busbars are coated. Oxide of busbar materials (except silver) has dramatically lower electrical conductivity. In environments containing ammonia, sulphur and chlorine compounds, especially where the humidity is high, the protective coating is a must to do. Anti-corrosive coatings can be made with metallic and non-metallic materials.

Tin, nickel and silver are the most used elements for metal coatings. The choice should be made regarding to the usage conditions of busbar.

Tin coatings must be made as tin alloys because pure tin tends to form whiskers and whiskering may occur serious problems. Tin alloy coating is the most popular aluminum busbar coating method nowadays. It is strong against corrosion; it has a mediocre cost compared to silver and nickel coating. But, because it is harmful for the environment, the usage ratio is decreasing over time.

Nickel coating is a good alternative against tin alloy. It is cheaper than aluminum. It is reliable in low humidity conditions. It provides harder surface than any other metal coating; for this reason, it requires high pressure when making joint connections. It is also a weak solution against environments that have high humidities. Moreover, because it has low electrical conductivity, it lowers the busbar’s overall electrical conductivity.

Silver coating is the best option over all other metal coating options. It is effective against almost all of the corrosive environment scenarios. Because it has the highest electrical conductivity over all metals, it raises the busbar’s overall electrical conductiviy. Beside all these advantages, it is very expensive. Because of that, it is only preferred when other coating options are ineffective.

Metal coatings can be ineffective against corrosion if there is any uncoated spots left on the surface. The coating must be continuous all over the busbar surface.

For very corrosive environment scenarios, non-metallic coatings are preferred. The coating material is usually the same with those used for electrical insulation. They usually are not preferred because they decrease the overall electrical and temperature conductivity of the busbar.

1.3.1.3 Coatings to Increase Current Carrying Capacity

Busbars are generally painted if there is need to increase its electrical conductivity. But in practice, the increment is generally not enough to be worth. In some situations, painting may even affect negatively. It reduces the effectiveness of the convection of heat, while increasing the radiation of heat. Therefore, it is a reasonable choice only when the busbar has wide edges.

1.3.1.4 Other Reasons for Coating

In some situations, busbars can be coated for cosmetic purposes. They can be painted or coated to hide fingerprints and other marks. In some other situations, busbars can be coated to prevent galvanic corrosion between joints. It is only necessary when different materials need to be joint together and these materials tend to create galvanic corrosion during contact. For example, aluminum and copper tend to create galvanic corrosion when they are in contact with each other. To prevent this, tin based coating must be applied between aluminum and copper. Tin coating will act as a buffer between these two materials and prevent galvanic corrosion.

1.3.2 Coating Graphene over Aluminum Busbar

With its unique properties, graphene has the potential to cover aluminum's deficiencies and create the ideal material solution for electrical power distribution industry. It has a better electrical conductivity than all the other busbar materials. Graphene is a water repellant material. Its anti-corrosive strength is higher than aluminum. It has a mechanical strength far higher than aluminum. Based on these properties, graphene-aluminum couple can be a good solution in industry.

1.4 Recent Studies about Coating Graphene

There are plenty of studies made to investigate the graphene's superior properties.

Vesna et al. investigated the corrosion behaviour and electrochemical characteristics of graphene coatings on both copper and aluminum [42]. They synthesized graphene with CVD method. Then they transferred graphene from copper to the aluminum surface mechanically. After that, they investigated the corrosive behaviour of graphene coated aluminum and copper in 0.1 M NaCl solution. They found that, while graphene coated copper surface has corrosion inhibitor properties, the graphene coated aluminum acts similar to aluminum oxide on a bare aluminum surface. They are estimated that, the reason of low anti-corrosive properties for graphene coated aluminum was the possibility of galvanic corrosion. They also stated that, the anti corrosive properties can be enhanced by purifying the deposition of graphene to achieve more homogeneous coating and thereby avoid the probable galvanic corrosion.

It is proven that aluminum is a good corrosion inhibitor even in environment with high humidity [43]. It is because the oxide film creates a natural protection against further corrosion. However, it is still weak in environments such as with chloride ions [44]. With the development of nanotechnology, lots of corrosion inhibitor nanocoatings made with nanomaterials started to be synthesized onto metals such as aluminum.

Ehsani et al. made a review about recent studies of graphene and graphene/polymer as a coating for metals like steel, aluminum and copper in corrosive environment [45]. Hikku et al. coated aluminum with a blended material which is a mix of graphene and polyvinyl alcohol (PVA) and investigated its corrosion resistant properties against bare aluminum and PVA coated aluminum [46]. This research is made in 3.5% NaCl solution. The results were very promising. While the bare aluminum has a corrosion rate of 45.25 mpy and PVA coated aluminum has corrosion rate of 2.576 mpy, the graphene-PVA coated aluminum has a corrosion rate as low as 3.853×10^{-4} mpy.

Graphene's chemical inertness makes it one of the best materials against corrosive chemicals, even comparable to one of the strongest chemicals, Hydrogen Fluoride [47-49].

Graphene's anti-corrosive strength also grounds on its resistance against oxygen diffusion [50-52]. With its high surface area and nonpolar construction, it is considered as a hydrophobic material [53,54].

It is also proved that graphene coatings on metal substrates do not affect the optical properties of the substrate metal underlying. It is reported that, even graphenes with 4 layers have transmittance higher than 90% [51,55].

Ertürk et al. tried to enhance the mechanical properties of aluminum with graphene coating [56]. They performed simulations of tensile experiments and it is claimed that the Young's modulus of aluminum can be increased by 88%. In the elastic region, graphene is not much able to perform its strength enough, while it shows its abilities in plastic region with an increase of 60% in the ultimate tensile strength.

Zheng et al. made a research about hydrophobic properties of graphene by fabricating biomimetic hydrophobic patterned graphene coated aluminum alloy [57]. They prepared graphene with CVD method and then transferred graphene to aluminum substrate surface. They investigated the surface structure, the wettability and anti-corrosive properties of graphene coated aluminum alloy. They found a result that the static water contact angle for the surface is 130.8±1°. Besides, the anti-corrosive properties of aluminum alloy were enhanced in accordance with the results of electrochemical experiments for corrosion.

Corrosion resistance properties of multi-layer graphene coated copper is investigated by Tiwari et al. [58]. They mentioned in their study that, there are many studies about corrosion resistant performance of graphene coating with diversed results. They asserted that the poor corrosion resistant performance results are caused by a defective layer of graphene and can be eliminated with multilayer graphene coating. With multilayer graphene coating using CVD method, they gained successful corrosion resistance results of approximately 400 hours in a chloride solution.

The superior anti-corrosive properties of graphene are also investigated by Liu et al. [59]. They studied the anti-corrosive properties of graphene coated aluminum by dip coating method. They validated the graphene coating performance with Raman sprectra analysis and made a uniform graphene coating on aluminum substrates. They investigated the anti-corrosion performance of graphene coating with potentiodynamic polarization test and electrochemical impedance sprectroscopy. They claimed to have reached corrosion resistance by three orders of magnitude higher than those without coating.

Kim et al. studied about nanocomposite film synthesis which contains graphene and polysiloxane (PSX) to create a material with high corrosion protection and electrical conductivity properties [60]. They claimed that, even the graphene has good corrosion preventing properties, it can be defected easily and loses its protective properties over time. To overcome this weakness, they studied to synthesize graphene/PSX based nanocomposite film and used it for coating metal substrates. They decreased the corrosion rate to 2.5% of the uncoated sample. They also succeeded to obtain electrical conductivity of 1700 Sm^{-1}.

This study differs from recents studies in literature by directly comparing market options of electrical power distribution industry with graphene coating. In the market, aluminum busbars are widely used to transfer low voltage electrical power. Most common types of aluminum busbars are bare aluminum and tin-coated aluminum.

This study is also carried out to mimic real-usage scenarios. Long-term behaviour of specimens were observed by exposing them to corrosive environment. Thanks to this approach, the graphene coated aluminum busbar’s electrical properties after years of usage can be estimated and compared with the market options.

1.5 Motivation and Scope of the Study

The motivation of this study is to create a new, more efficient and cost-efficient alternative graphene coating over aluminum busbars over conventional options in low voltage electrical power distribution market. Because graphene is composed of carbon atoms, the possibility of scarcity of raw materials or unexpected price fluctuations are not expected. With this raw material advantage and all the unique features, graphene has the potential to excel over current solutions in the market.

This study does not aim to find more efficient and low-cost way of producing single-layered graphene. Nowadays, it is known that producing single-layered high quality graphene is the bottle neck for making graphene one of the significant options in the market. But it is likely that this bottle neck problem will be overcome in near future. Therefore, this study skips producing graphene in an efficient way and focuses on the potential usage scenarios after production. The study scopes initial situation and properties of graphene coated aluminum with its primary options in the targeted market and long-term performance of these materials.

Chapter 2

Material and Methods

2.1 Properties of the Experiment Sample

The experiment samples are long but thin stick-like samples which are made from 2mm thick sheets of 6000 series aluminum. They have 5mm overall width and 67mm overall length; the width of the narrow section at the midpart is 4.2 mm (see Figure 2.1). Bare (uncoated), tin coated and graphene coated types of aluminum samples are used for comparison purposes in this study.

2.2 Graphene Synthesis

To synthesis high quality graphene, CVD method is selected because of its reliability. It is also the best mass production option to date. To produce graphene, the CVD furnace (PROTECH-PT-O1200-60IIIC-4C Model) in İzmir Katip Çelebi University is used (Figure 2.2). There are 6 steps to synthesize high quality graphene; these are

- Preliminary Preparation
- Heating
- Annealing
- Growing
- Cooling
- Final Step

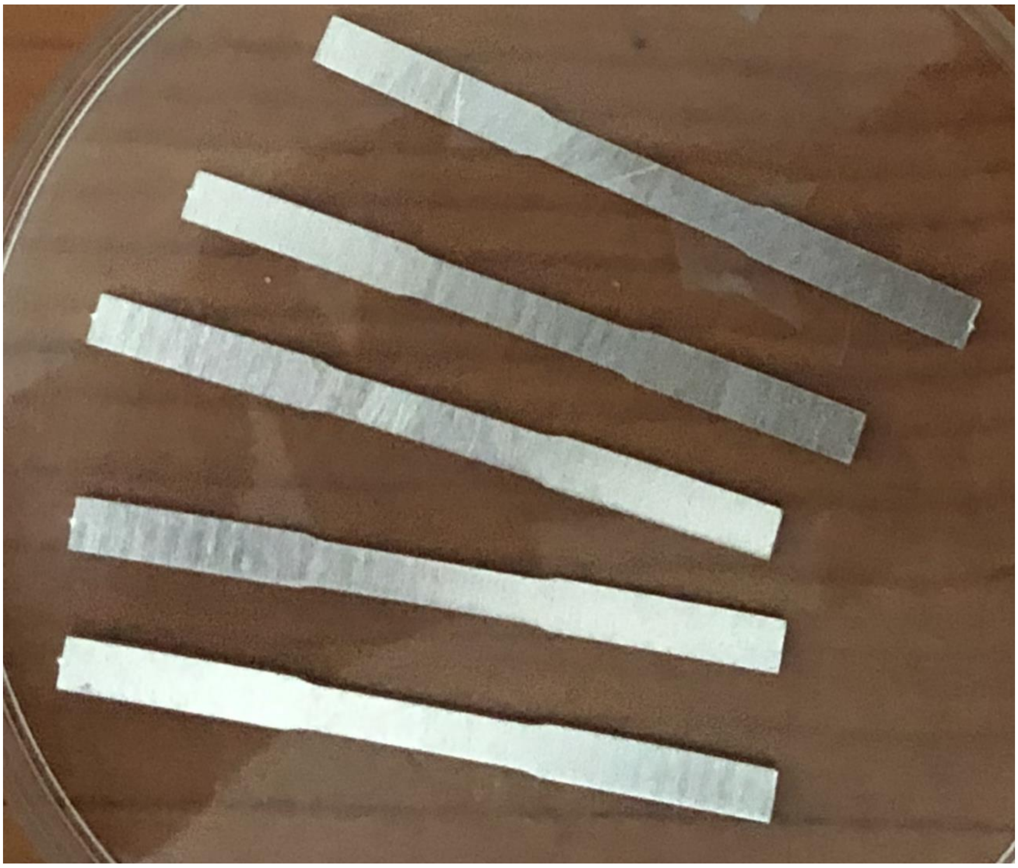

Figure 2.1: Aluminum samples used in this study

Figure 2.2: CVD Furnace used in this study

2.2.1 Preliminary Preparation

This step includes the preparation of metal substrate for the graphene synthesis. The metal substrate, which is 0.1mm copper sheet in this experiment, is cut into smaller pieces large enough to cover perfectly the aluminum sample's surface and also small enough to fit into the CVD oven. After that, the copper substrate's surface is cleaned with copper etchant to obtain better results (Figure 2.3). After chemical etching, the samples are cleaned with pure water.

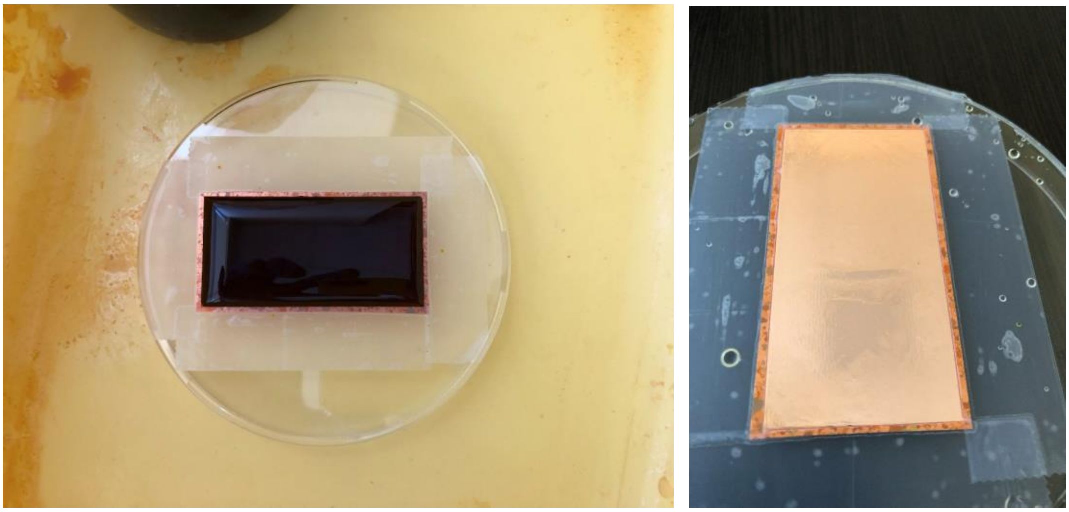

Figure 2.3: Copper substrate with copper etchant (left), copper substrate after cleaning with copper etchant (right)

2.2.2 Heating

The copper substrate is put into CVD furnace (Figure 2.4). Then hydrogen and argon gases are provided into furnace's controlled atmosphere. Then the furnace is heated up to 1070°C in 60 minutes. This temperature is close to the melting point of copper.

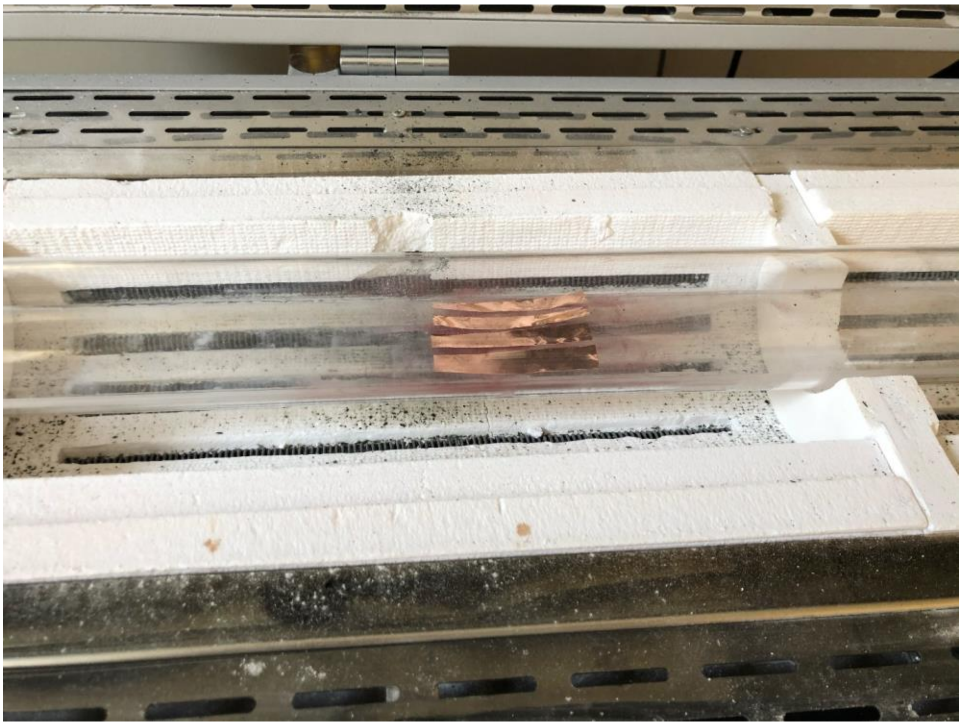

Figure 2.4: Copper substrates that are cut into proper dimensions and put into furnace

2.2.3 Annealing

In this step, the furnace temperature stays stable at 1070°C for 60 minutes. The aim of this step is to prepare the copper substrate and increase the ability to catch carbon atoms on the surface by modifying the surface of it. Copper evaporation must be avoided during this step. While annealing, the surface morphology changes, the surface roughness decreases (smoothens) and the grain size of the copper increases.

2.2.4 Growing

Growing step is where the graphene film starts to occur on copper substrate. Until this step, hydrogen and argon gases are flowed into the furnace. In this step, methane gas is flowed to start the growing process. The growing time changes with respect to the number of demanded graphene layers. In this experiment, the growing time was 2 minutes.

2.2.5 Cooling

Cooling step is where the controlled atmosphere's temperature starts to decrease to the room temperature. In this step, the methane gas flow stops and hydrogen gas flow increases.

2.2.6 Final Step

This step is where the inert gases are backfilled and the furnace is opened. With this step, the graphene synthesis is completed (Figure 2.5).

Figure 2.5: Copper substrates with graphene layer after CVD

2.3 Coating Graphene over Aluminum Sample

2.3.1 PMMA Coating the Free Surface of Graphene

To transfer graphene over aluminum sample’s surface, the open (uncoated) side of graphene surface is used. First, the open surface is coated with polymethylmethacrylate (PMMA) by spin coating method as shown in Figure 2.6.

Figure 2.6: Copper substrates with graphene layer before PMMA coating (left), PMMA coating process with spin coating method (center), PMMA coated copper substrates with graphene layer (right)

2.3.2 Chemical Etching of Copper Substrate

After PMMA coating, the copper substrate must be erased from graphene film. Copper etchant is used for this purpose (Figure 2.7). Iron chloride ($FeCl_3$) is the common choice for etching copper because it etches copper effectively and slowly, so it can be controlled easily.

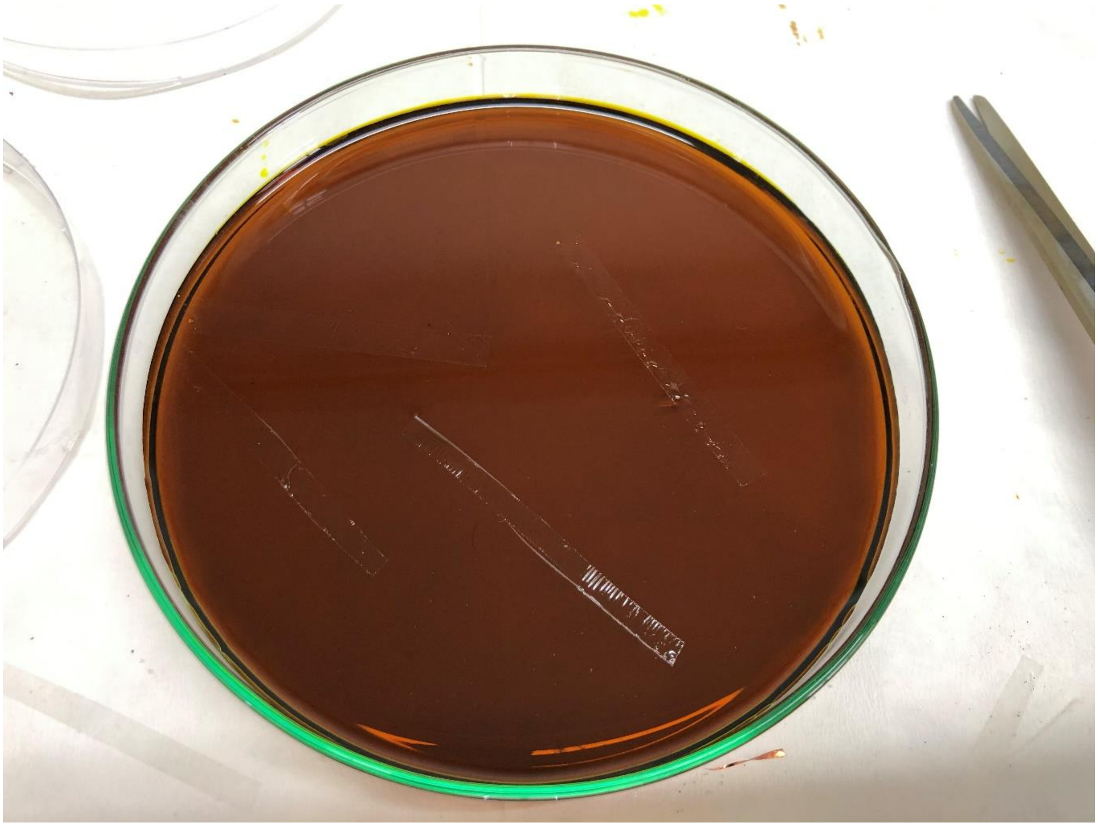

Figure 2.7: Graphene film with PMMA material

After chemical etching of copper, graphene is put into pure water for cleaning of copper-etchant residuals. Si/SiO_2 wafer is used in this transferring process (Figure 2.8).

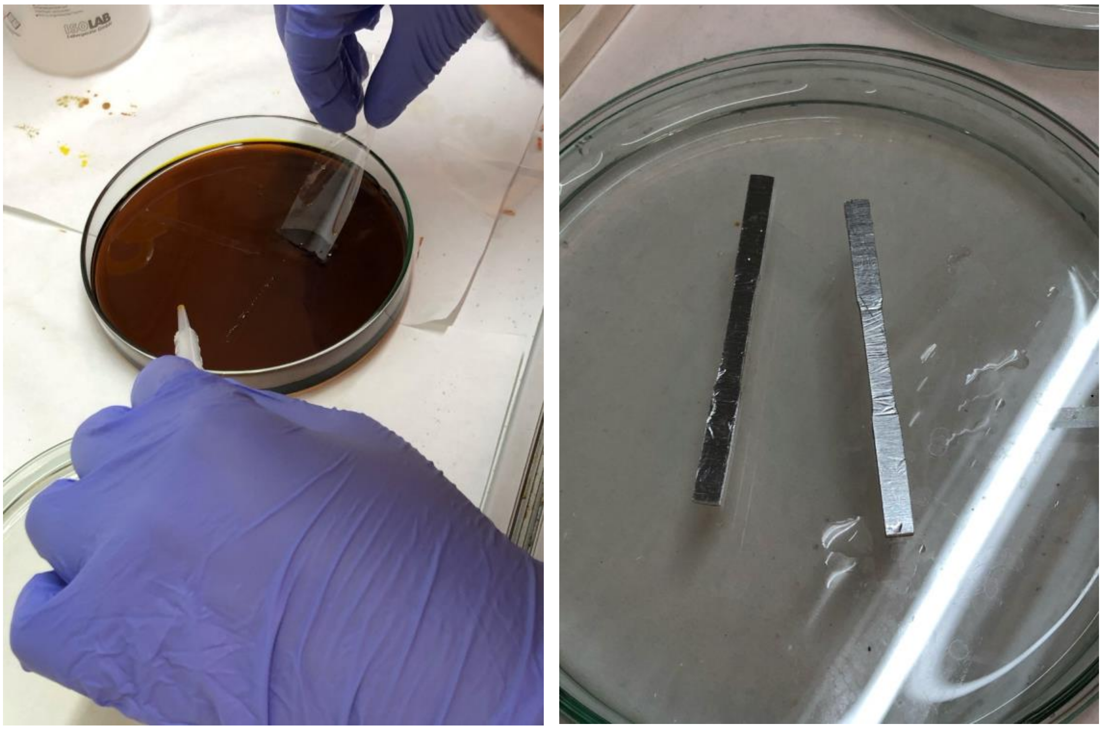

Figure 2.8: Graphene with PMMA taken into pure water with Si/SiO_2 wafer repeatedly for cleansing from copper etchant (left), graphene with PMMA transferred onto aluminum samples with Si/SiO_2 wafer (right)

2.3.3 Transferring Graphene over Aluminum Sample

After chemical etching, PMMA coated graphene film needs to be transferred over aluminum sample. To do this, the aluminum sample is put it the same pure water container with PMMA coated graphene film and meticulously aligned to bottom (uncoated) side of graphene film. After that, the sample is baked at 80°C in order to enhance the coating between graphene film and aluminum sample.

2.3.4 Chemical Etching of PMMA

The final step for transferring graphene film over aluminum sample is chemical etching of PMMA. For chemical etching of PMMA, acetone is chosen. The sample is taken into a container filled with acetone and the PMMA is removed from the surface of graphene film. Then it is put into pure water to clean from the etchant residuals. After that, the sample is baked at 80°C for 45 minutes in order to vaporize the residual water on the sample's surface.

Finally, the graphene is succesfully synthesized and coated onto aluminum sample.

2.4 Tin Coating of Aluminum Sample

In order to compare the graphene coating's efficiency and reliability, tin coated aluminum is used in the experiments.

Tin coating is the most common application for aluminum busbars in electrical distribution industry to protect aluminum busbar's conductivity by protecting it from corrosive environment.

9-13µm thickness of tin coating is applied to the aluminum sample (Figure 2.9).

Figure 2.9: Tin coated aluminum samples

2.5 Characterization of Samples

2.5.1 Raman Spectroscopy

Raman spectroscopy is used to define and measure the quality, efficiency and characteristics of the graphene film. It is also used for defining the amount of graphene layer.

The Raman spectroscopy is done only to graphene coated samples with Renishaw/In Via device in İzmir Katip Çelebi University Central Research Labs (Figure 2.10).

Figure 2.10: Raman spectroscopy device used in this study

2.5.2 Testing Electrical Resistance

Electrical resistance test is done to measure the conductivity. Since one of the main focus of this study is to enhance the conductivity of aluminum with graphene coating, this test is crucial for conclusion. Two tests are made for each sample; one before the corrosion test, one after the corrosion test.

In electrical resistance test, different currents are applied to the coated surface of aluminum samples, starting from -0.01mA and increasing to 0.011mA, with steps of 0.001mA. In each step, the corresponding voltage values are measured. After 22 different current pulses, the resistance values are calculated.

Keithley 2400 Sourcemeter device in İzmir Katip Çelebi University Central Research Labs is used to perform this test (Figure 2.11). This test is applied to all types of samples (uncoated bare aluminum, tin coated aluminum and graphene coated aluminum) twice. For each sample, first test is made before the corrosion resistance experiment, second test is made after the corrosion resistance experiment.

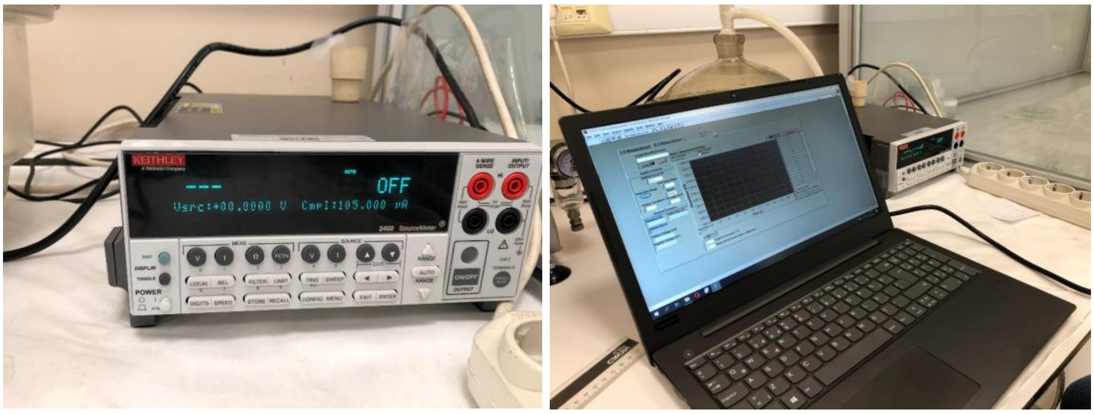

Figure 2.11: Electrical resistance measurement device and measuring software used in this study

2.5.3 Contact Angle (Wettability)

Contact angle test is done to measure the sample’s wettability performance. Wettability is the ability of a liquid to avoid contact with a solid surface. It can be measured with contact angle (Figure 2.12). Contact angle is the angle between liquid-vapor interface and solid-liquid interface.

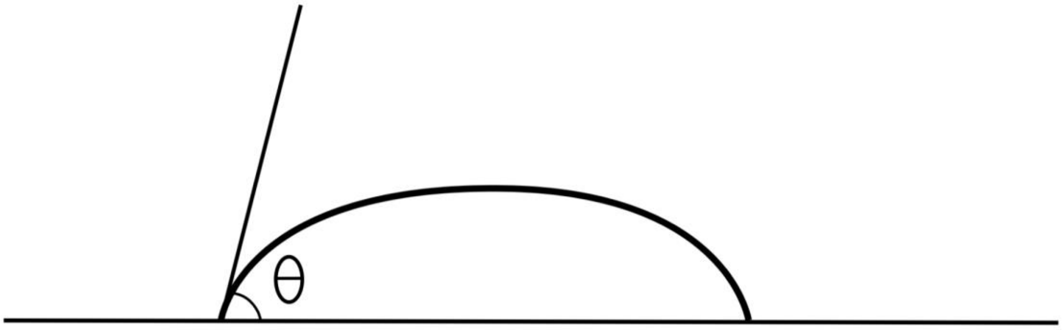

Figure 2.12: A liquid in contact with another material, presenting its contact angle [61]

Roughly, materials with a water contact angle smaller than 90° are accepted as hydrophilic material; those with a water contact angle larger than 90° as hydrophobic material; and those having a contact angle larger than 150° as super hydrophobic materials (Figure 2.13). Because hydrophobic materials repel water, they tend to have better anti-corrosive properties.

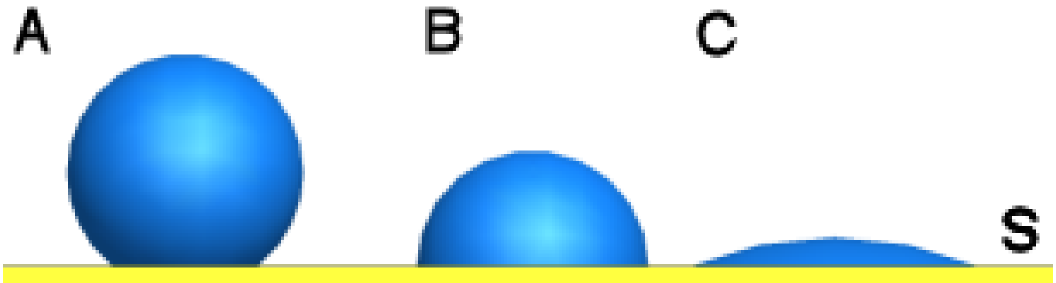

Figure 2.13: Liquid droplets with different contact angles [62]

Contact angle and surface tension measurement device in İzmir Katip Çelebi University Central Research Labs is used to perform this test (Figure 2.14). This test is applied to all types of samples (uncoated bare aluminum, tin coated aluminum and graphene coated aluminum) twice. For each sample, first test is made before the corrosion resistance experiment, second test is made after the corrosion resistance experiment.

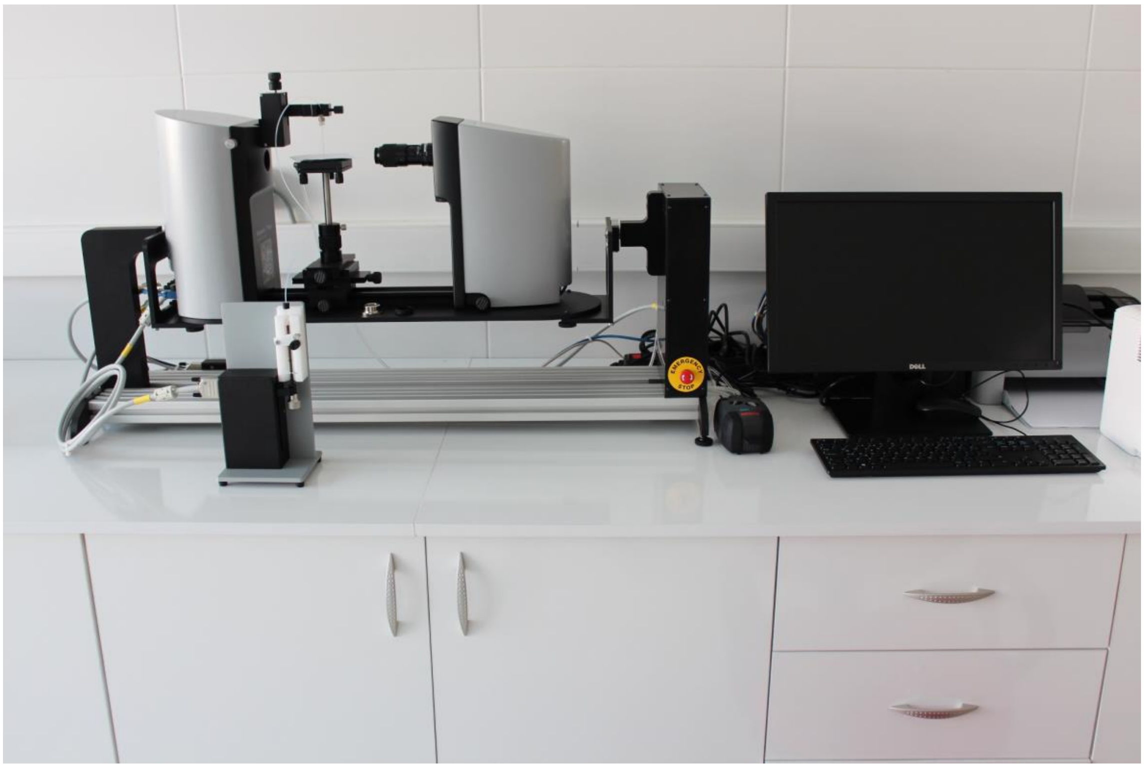

Figure 2.14: Contact angle measuring device used in this study

2.5.4 Exposing to Corrosion

Corrosion resistance experiment is made to compare the anti-corrosive properties of samples with different coating methods. A corrosive solution made of pure water and NaCl with 3.5%wt is prepared and applied to the related surfaces of samples for 220 hours (Figure 2.15). After 220 hours, all samples are cleaned from corrosive solution by repeatedly putting into pure water. After cleaning, samples are heated up to 80°C to clean residual water molecules. After the experiment, wettability and electrical resistance tests are done again to investigate the samples that are exposed to corrosive environment.

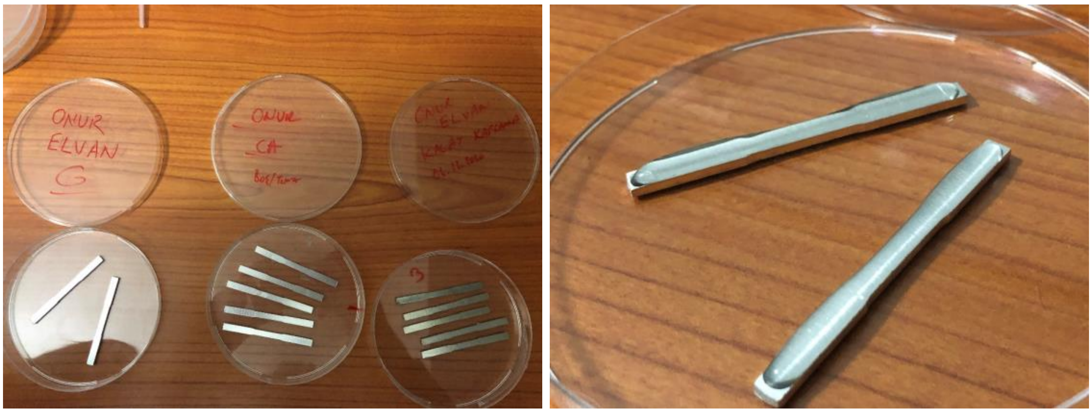

Figure 2.15: Samples exposed to corrosive conditions

Chapter 3

Results and Discussion

In this study, first, a graphene film is synthesized and coated over the aluminum samples successfully. Then, graphene coating on aluminum bar as a busbar protective coating material is compared with conventional coating method (tin coating) and uncoated bare aluminum bar. Electrical resistance and anti-corrosive properties are compared both before and after being exposed to corrosive environment.

3.1 Synthesized and Coated Graphene Film Results

The Raman spectroscopy results for the graphene film on aluminum sample showed similar results with the literature studies [63-65]. Background noise is seen in Raman spectroscopy because of the underlying aluminum. For this experiment, the G band is at 1587 cm^{-1} while the 2D band is at 2679 cm^{-1} (Figure 3.1).

Figure 3.2 shows the imaging from Raman spectroscopy of graphene coated aluminum sample. The image is magnified by 100 times.

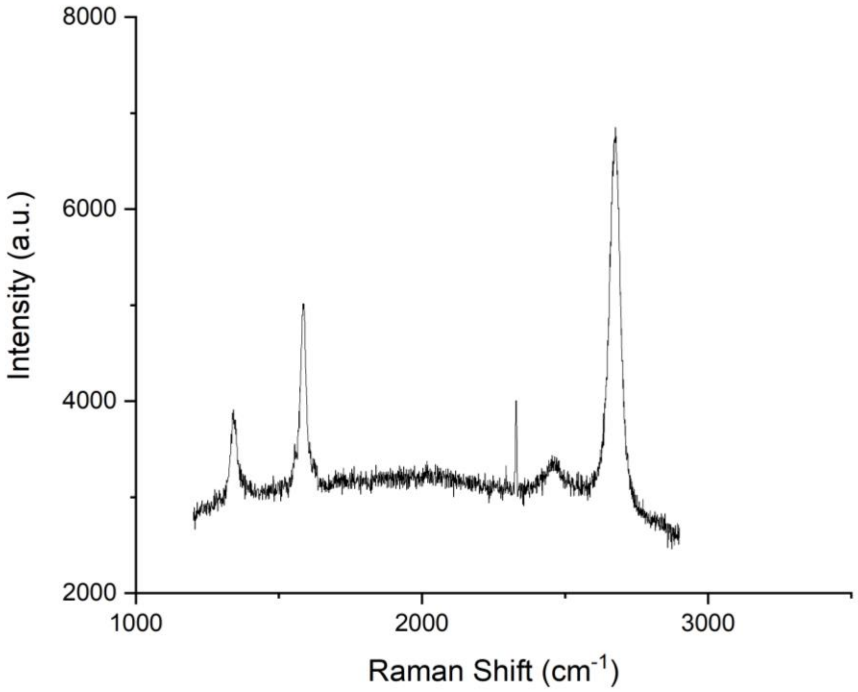

Figure 3.1: Raman spectroscopy result of graphene coated aluminum sample

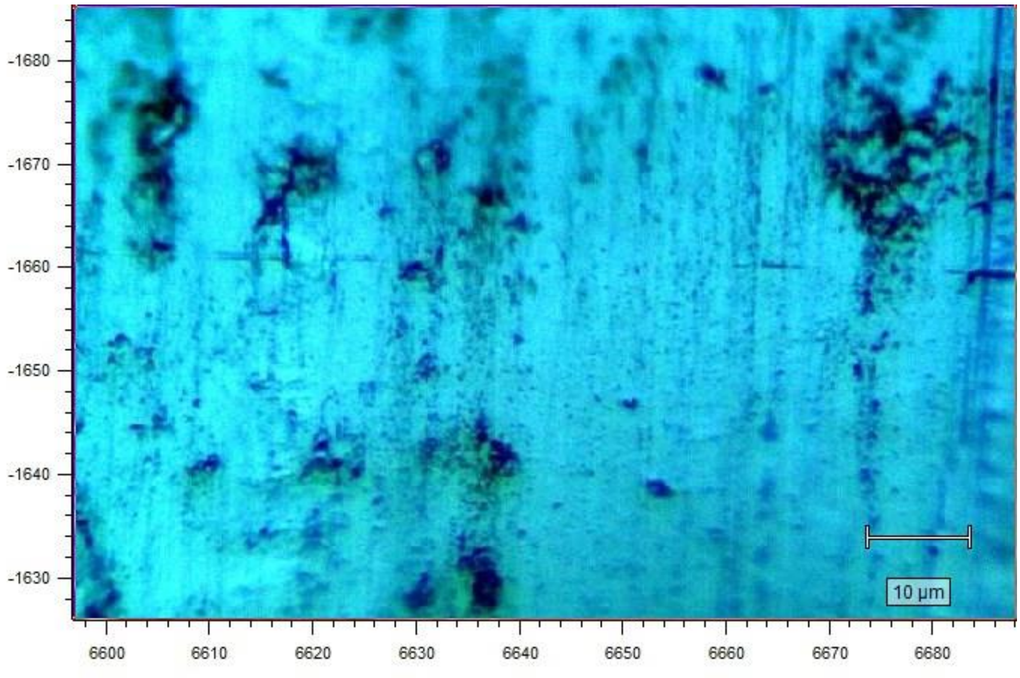

Figure 3.2: Raman image of graphene coated aluminum sample. Image magnification is 100X.

Thickness of the graphene layer can be determined by the ratio of G band and 2D band's intensity (Figure 3.3). According to Figure 3.3, it is observed that, single layer of graphene is successfully synthesized and coated over the aluminum samples.

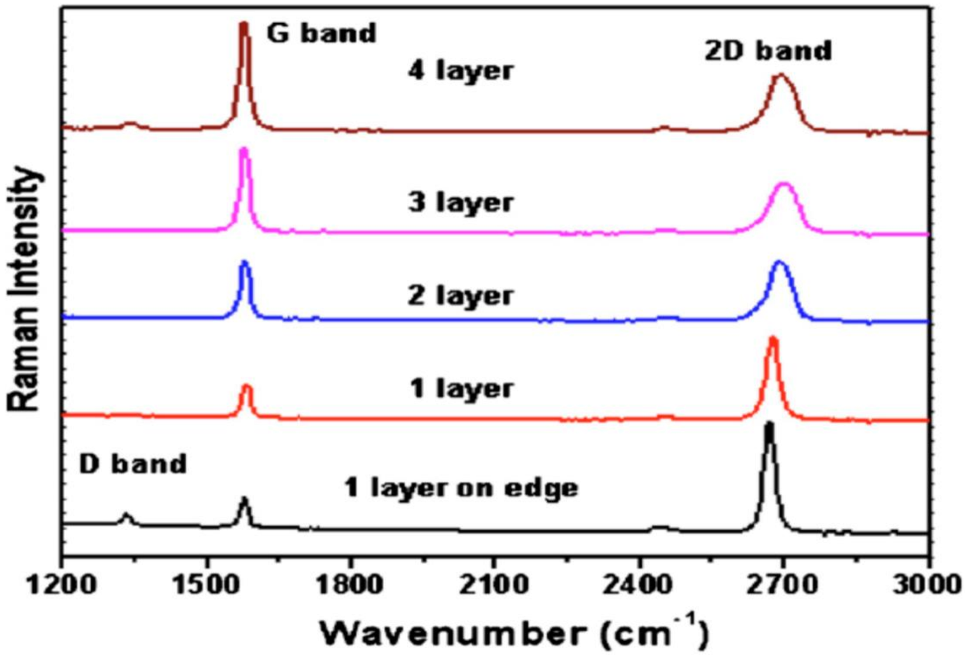

Figure 3.3: Raman spectra depending on thickness of graphene layers [66]

3.2 Electrical Resistance Test Results

The aim of this test is to find the superiority of graphene coated aluminum over bare aluminum and tin coated aluminum. The results reveal that this can be possible.

3.2.1 Results before Corrosion

The electrical resistance results before corrosion for samples are shown in Figure 3.4 below. Samples with the same coating methods have similar resistance values measured. Although they are similar, small differences of resistance values can be measured. Natural oxidation or even nano-scratches located on the surface might cause this.

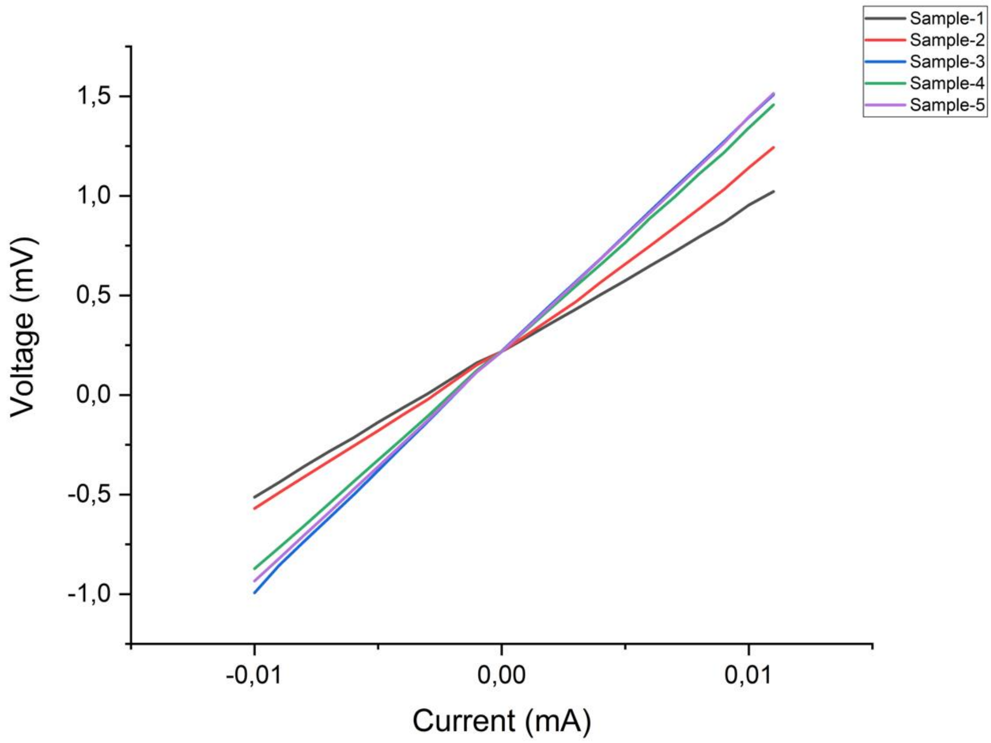

Figure 3.4a: Electrical resistance test results for uncoated aluminum samples before corrosion test

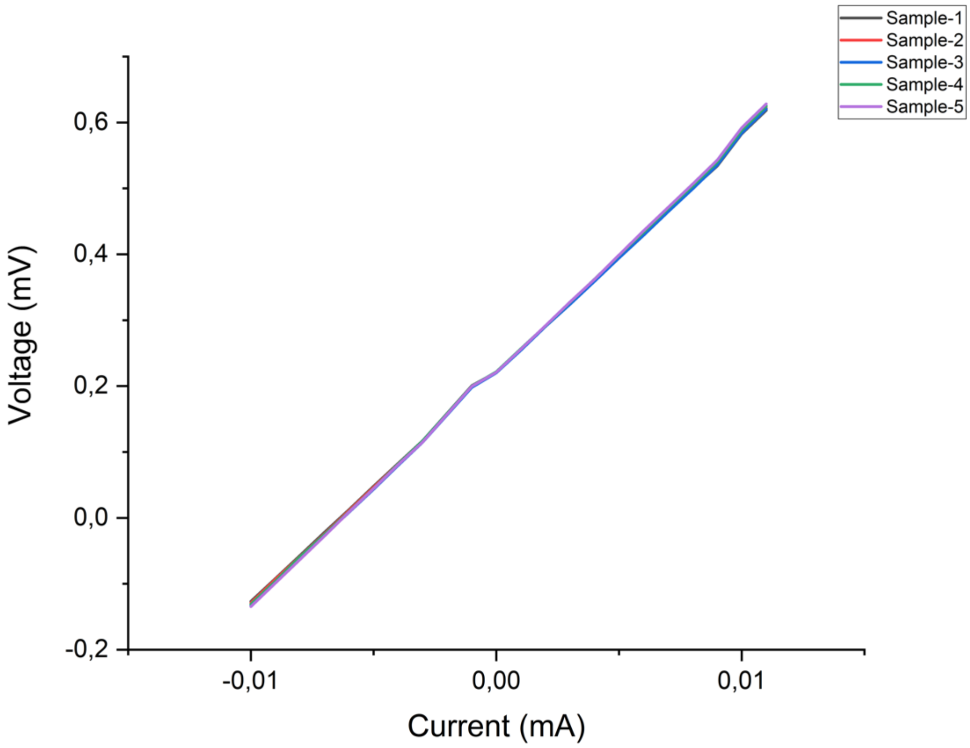

Figure 3.4b: Electrical resistance test results for tin coated aluminum samples before corrosion test

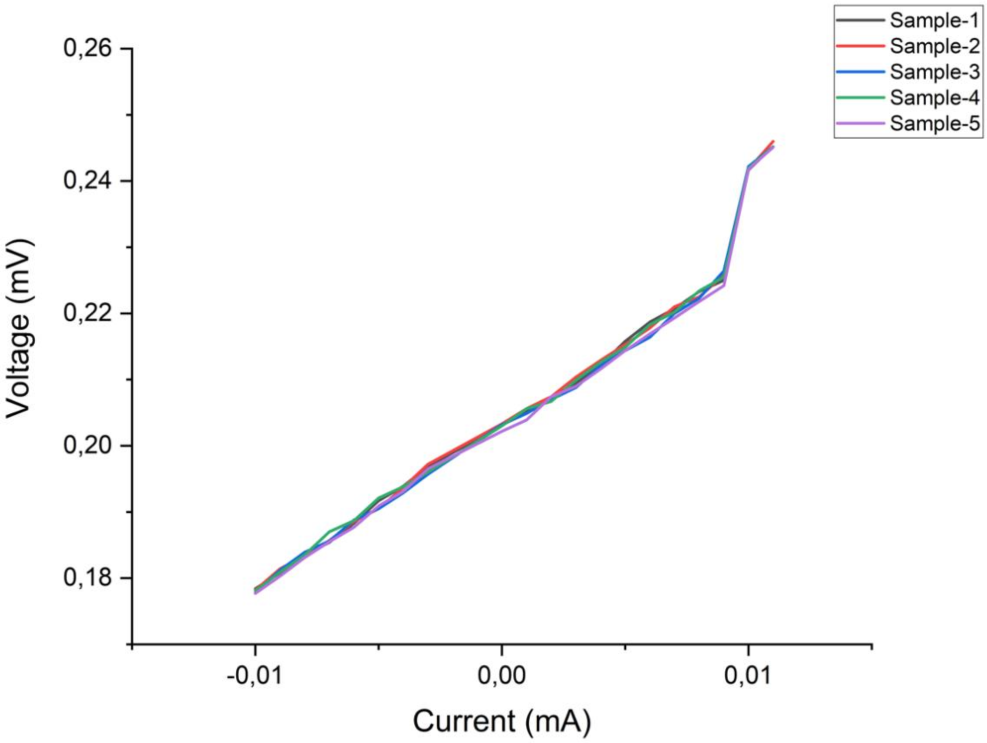

Figure 3.4c: Electrical resistance test results for graphene coated aluminum samples before corrosion test

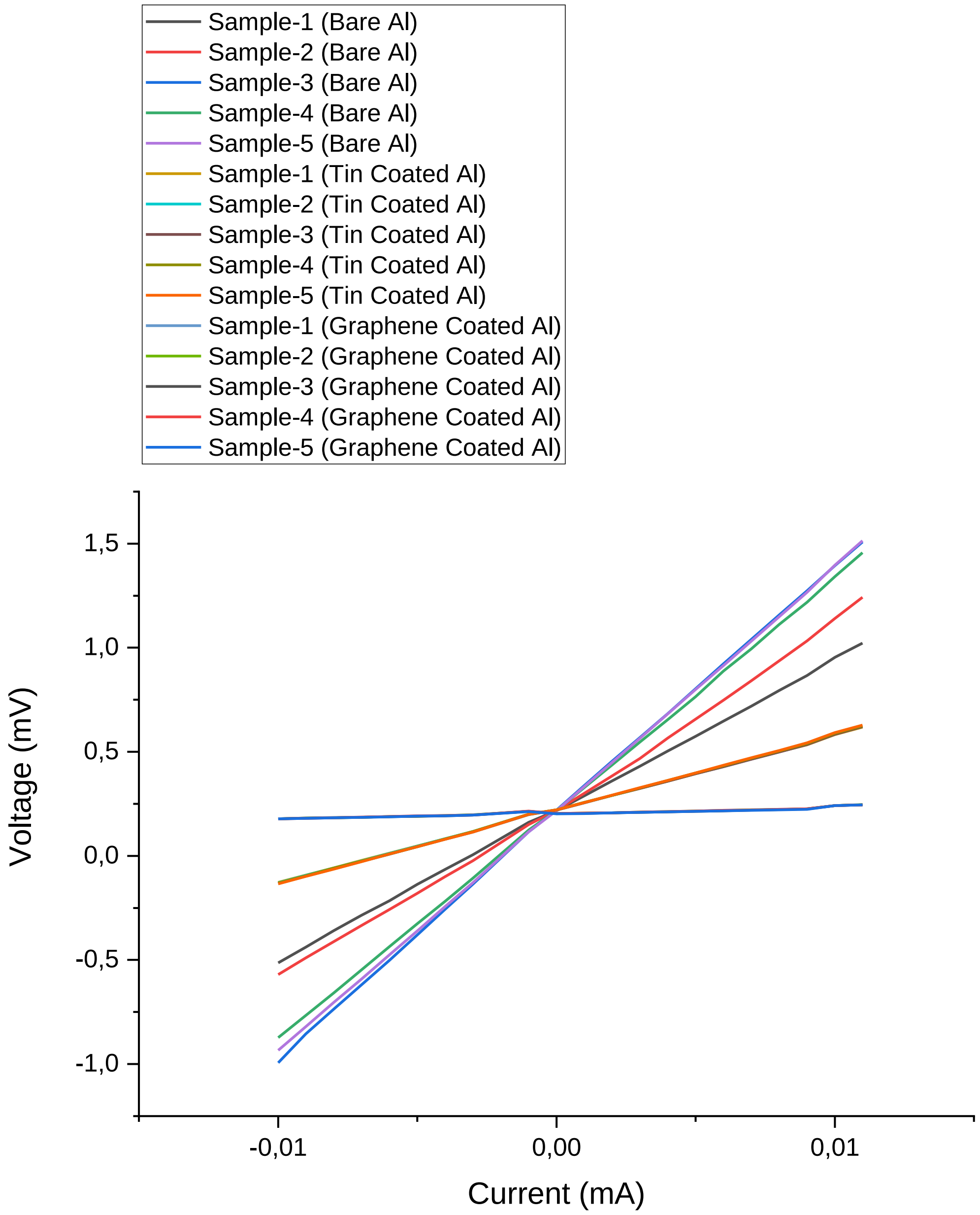

Figure 3.4d: Electrical resistance test results and comparison of all samples before corrosion test

The results show that, tin coated aluminum has less resistance than bare aluminum. While tin is less conductive than aluminum, it prevents aluminum from corrosion and keeps resistance low. Graphene coated aluminum has the best conductivity among all samples. This is because, it both prevents aluminum from corrosion and has much higher conductivity among them. With graphene coating, roughly 10 times better conductivity than tin coated samples and 33 times better conductivity than uncoated samples were achieved.

3.2.2 Results after Corrosion

The electrical resistance test results after corrosion are shown in Figure 3.5. The results show that, conductivities of all samples decreased in different rates. Graphene coated aluminum gives the best results with only 10.71% average increase in its resistance, while tin coated aluminum has 21.80% average increase and uncoated aluminum has 197.90% average increase in resistance. Details of the test results can be seen in Table 3.1.

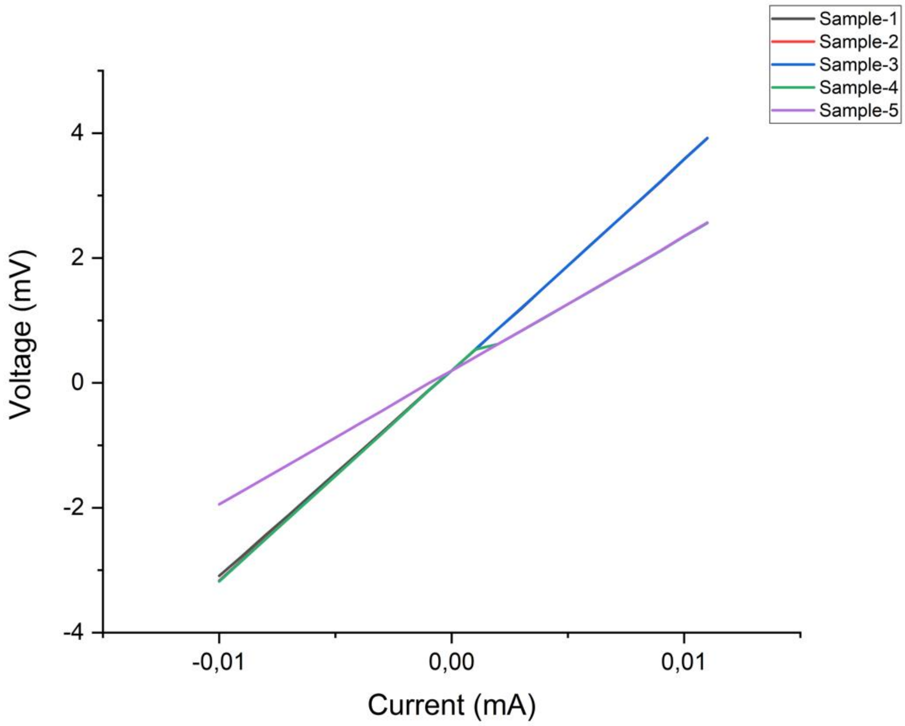

Figure 3.5a: Electrical resistance test results for uncoated aluminum samples after corrosion test

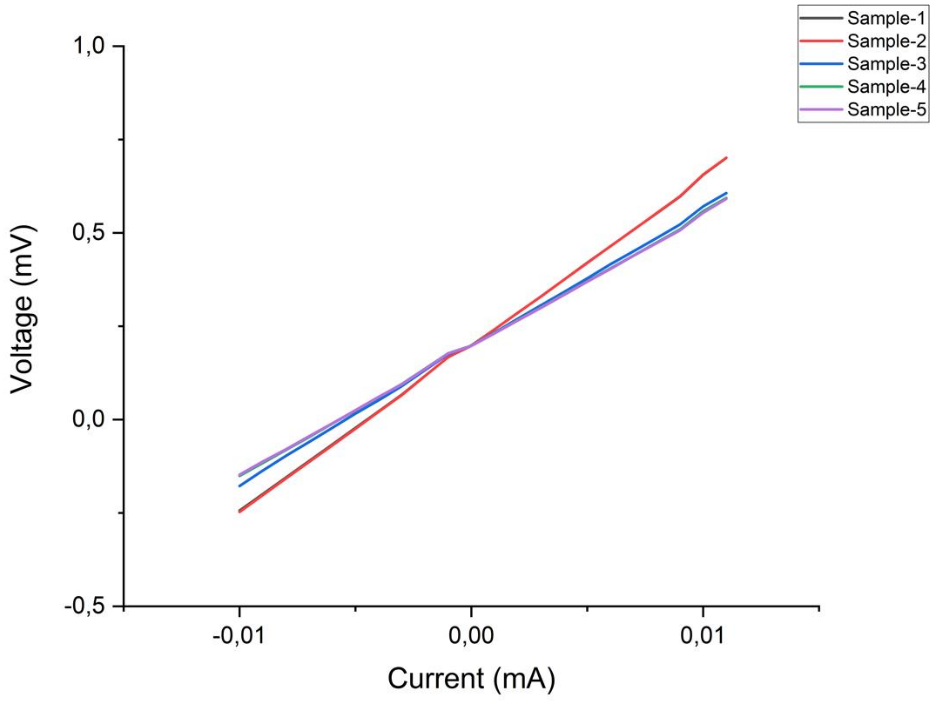

Figure 3.5b: Electrical resistance test results for tin coated aluminum samples after corrosion test

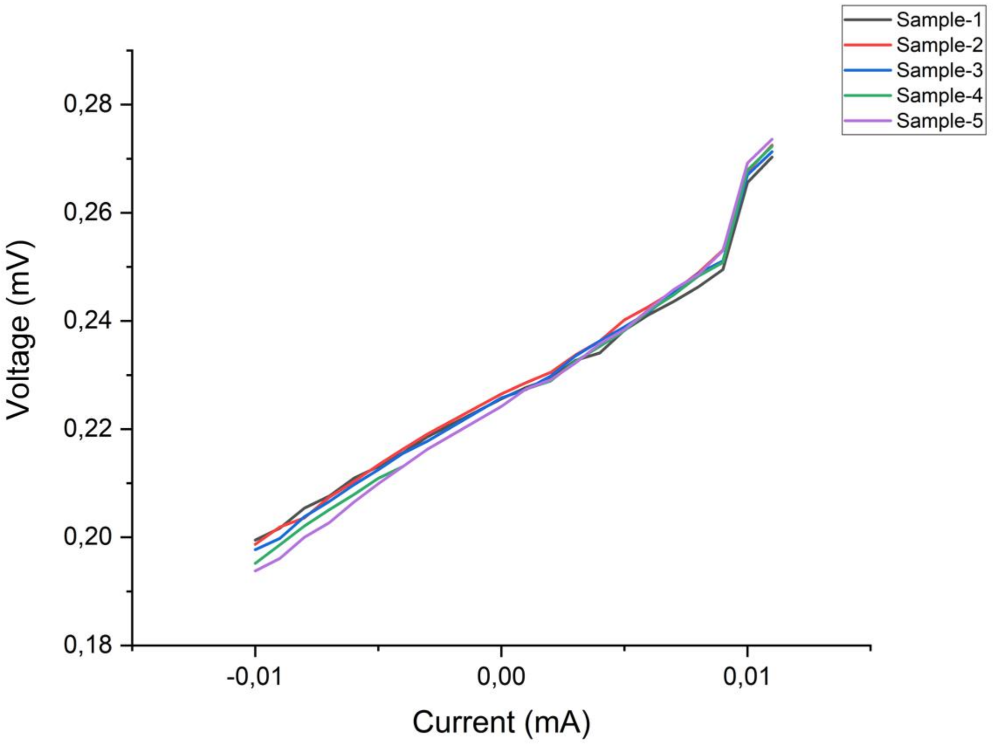

Figure 3.5c: Electrical resistance test results for graphene coated aluminum samples after corrosion test

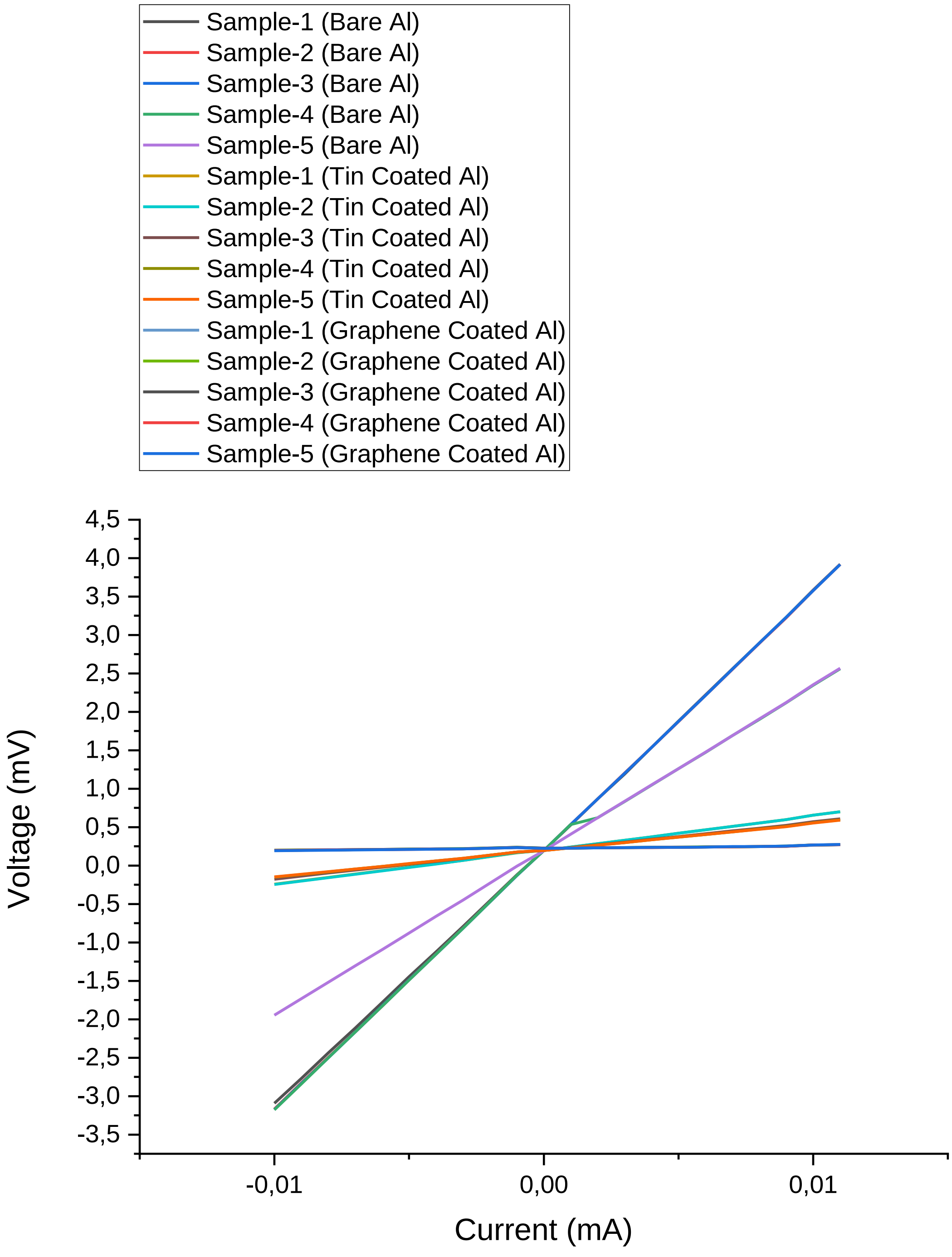

Figure 3.5d: Electrical resistance test results and comparison of all samples after corrosion test

Table 3.1a: Electrical resistance test results of all samples before and after corrosion test

Material	Electrical resistance (Ω) of 5 samples **before** corrosion test					Average
Bare Al	72.28	85.22	118.27	110.28	116.02	100.41
Tin Coated Al	31.32	32.22	32.29	32.42	32.24	32.10
Graphene Coated Al	3.01	3.02	3.01	2.99	3.00	3.01

Material	Electrical resistance (Ω) of 5 samples **after** corrosion test					Average
Bare Al	333.16	336.30	336.64	275.45	214.11	299.13
Tin Coated Al	44.47	44.66	36.72	34.94	34.68	39.09
Graphene Coated Al	3.14	3.28	3.27	3.40	3.55	3.33

Table 3.1b: Change of resistance after corrosion

Material	Change of Resistance (%)
Bare Al	197.90
Tin Coated Al	21.80
Graphene Coated Al	10.71

Vesna et al. [42] performed a similar study and found that graphene coated aluminum can have resistance values 12.34% of bare aluminum after 35 days of exposion to 0.1M NaCl solution. Liu et al. coated graphene over aluminum by dip coating and reached three orders magnitude higher corrosion resistance performance than the bare one [59]. These results are different compared to the results in this study. There might be several reasons for this diferrence. The first reason is, corrosive NaCl solution used by Liu et al. is 0.5M instead of 0.1M which is a much more harsh condition. Also the duration of the test is not given in the paper; it is most likely different than that of this study. As the second reason; measuring techniques and experiment type are different so it is presumable to obtain different results.

Graphene proved itself as an effective coating option for aluminum materials. But it must also be noted that, only 40% of the samples coated with graphene showed this performance while the rest of them has resistance values as high as uncoated aluminum because of the defects on their surfaces.

3.3 Contact Angle (Wettability) Results

3.3.1 Results before Corrosion

The wettability test results are seen in Table 3.2. According to the results, it can be said that while tin coating has no effect on repelling water molecules from the surface, graphene coating grants an increase of contact angle by an average of 17.47° (23,86%). While graphene has positive effect on wettability, it is observed that single layer graphene coating cannot make aluminum sample hydrophobic. Maximum contact angle that can be achieved with graphene coating is 96.18° (Figure 3.6), and minimum contact angle is 84.23° (Figure 3.7). Figure 3.8 shows contact angle images for uncoated and tin coated aluminum samples.

Table 3.2: Wettability test results, measured contact angles and comparison of all samples before corrosion test

Material	Initial Contact angle results (°)					Average (°)
Bare Al	66.41	76.91	73.81	73.83	73.26	72.84
Tin Coated Al	58.94	79.55	74.88	66.11	84.28	72.75
Graphene Coated Al	91.38	84.23	96.18	84.62	94.69	90.22

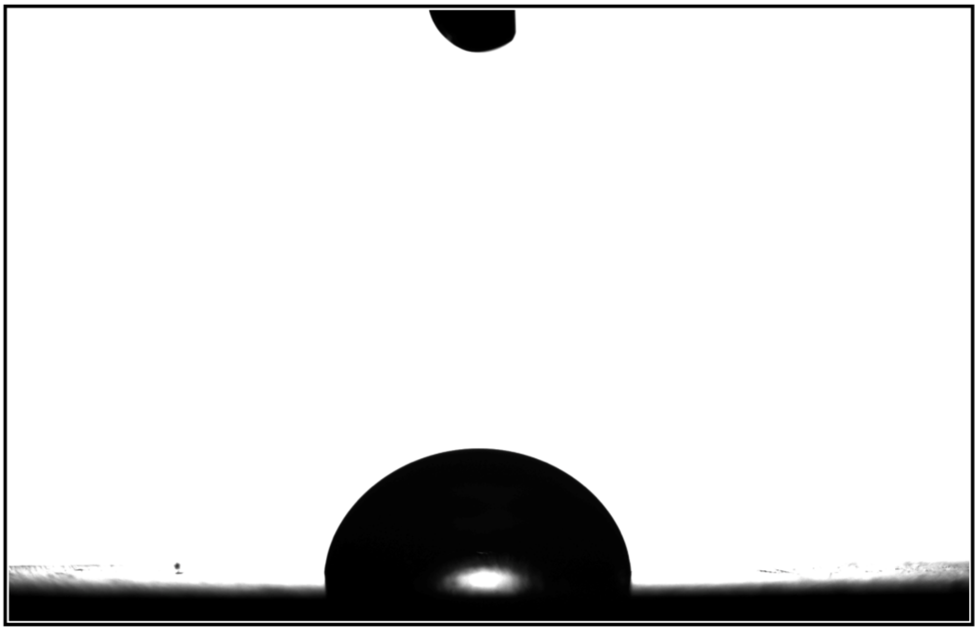

Figure 3.6: An image of liquid droplet on the surface of graphene coated aluminum sample before the corrosion test. Contact angle in this image is 96.18°.

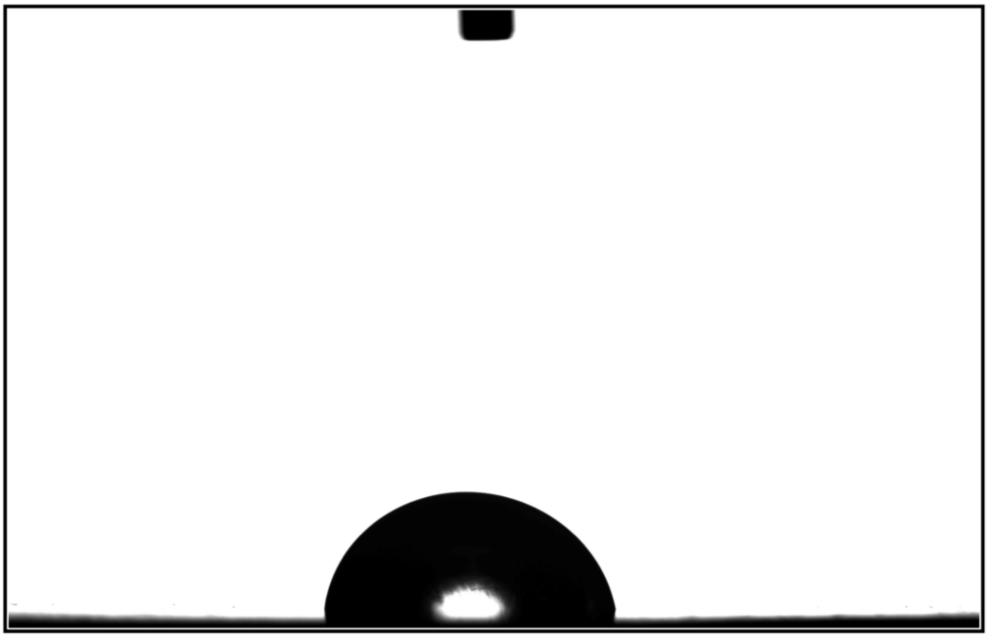

Figure 3.7: An image of liquid droplet on the surface of graphene coated aluminum sample before the corrosion test. Contact angle in this image is 84.23°.

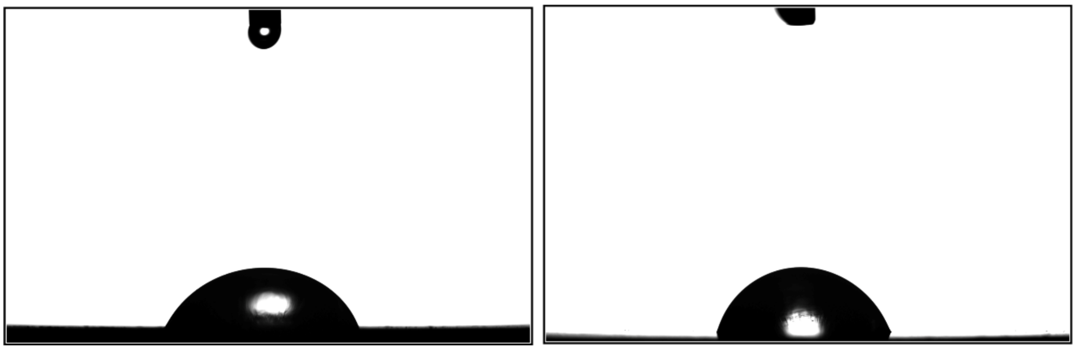

Figure 3.8: An image of liquid droplet on the surface of uncoated aluminum sample before the corrosion test (left), An image of liquid droplet on the surface of tin coated aluminum sample before the corrosion test (right)

Zheng et al. coated biomimetic hydrophobic patterned graphene over aluminum and reached 130.8° of water contact angle [57]. They have better results compared to this study. There might be several reasons for that. First of all, Zheng et al. used biomimetic microstructure processing (BMP) on substrate. Moreover, they used aluminum with a surface treatment. They measured 67.1° water contact angle on bare aluminum surface before the surface treatment which is almost similar to the measurements obtained in this study. After surface treatment over aluminum, they reached 78.5° of water contact angle. In addition to that, these results were achieved without any corrosive environment effect.

3.3.2 Results after Corrosion

The test results and the effect of corrosion to contact angles can be seen in Table 3.3. The average contact angle achieved with graphene coating after corrosion is 19.23° while samples with tin coating performed average of 16.38° and uncoated aluminum have 10.64° (Figure 3.9). After the corrosion test, contact angle for graphene coated aluminum sample decreased by an average of 71°. From results, it can be interpreted that graphene coating has almost no effect at preventing decrease of contact angle. Even the contact angle of graphene coated samples are higher than the other samples, all of them are accepted as hydrophilic materials.

Table 3.3: Wettability test results, average of measured contact angles and comparison of all samples before and after the corrosion test

	Average Contact Angle (°)	
Material	Before corrosion	After corrosion
Bare Al	72.84	10.64
Tin Coated Al	72.75	16.38
Graphene Coated Al	90.22	19.22

It must also be noted that, one of the graphene coated aluminum samples failed in contact angle test because of the defects on the graphene layer.

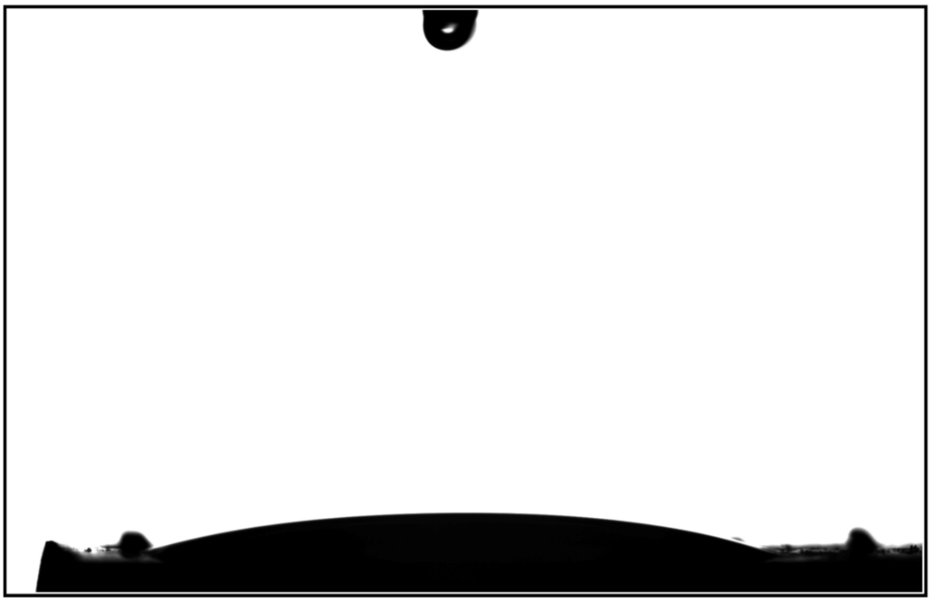

Figure 3.9a: An image of liquid droplet on the surface of graphene coated aluminum sample after the corrosion test

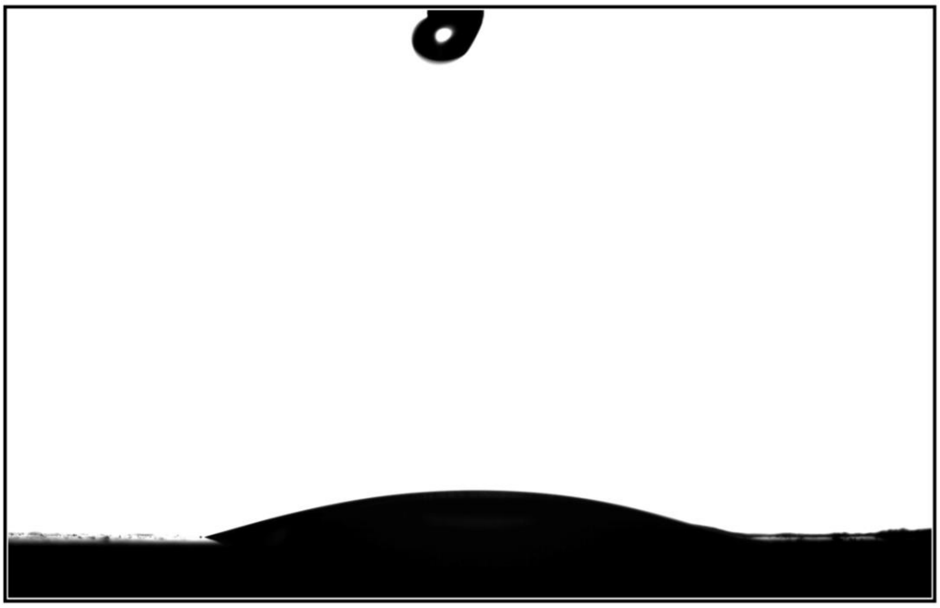

Figure 3.9b: An image of liquid droplet on the surface of tin coated aluminum sample after the corrosion test

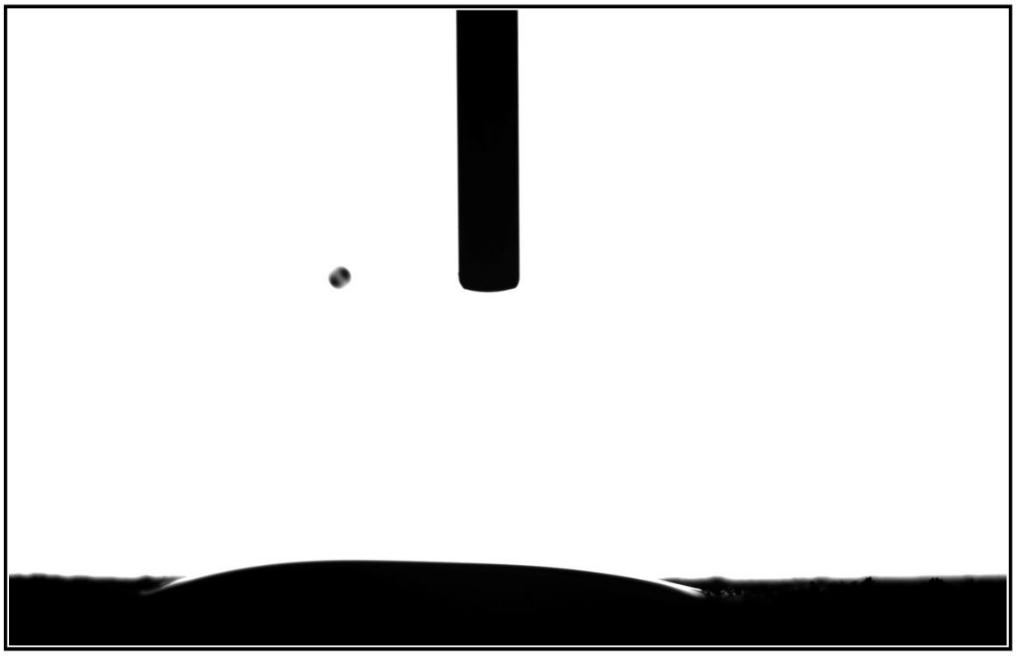

Figure 3.9c: An image of liquid droplet on the surface of uncoated aluminum sample after the corrosion test

Chapter 4

Conclusion

Single layered graphene is successfully synthesized and coated over aluminum samples. Due to this graphene coating, surface resistance dropped significantly compared to bare aluminum and tin coated aluminum. 11.74 times better compared to tin coated sample and 89.82 times better conductivity results were measured for graphene coated aluminum sample on its surface. Contact angle increased by about 17.5° compared to bare aluminum and tin coated aluminum which is a remarkable result.

All samples were exposed to corrosive environment of 3.5%wt NaCl solution for 220 hours. As a result of the corrosive environment, the electrical resistance of all samples increased in different rates. While the average increase in electrical resistance of graphene coated samples were 10.71% and the tin coated samples were 21.80%, uncoated aluminum's resistance increased dramatically by 197.90%. After corrosion, graphene and tin coated samples preserved their electrical conductivity but the uncoated sample lost its conductive properties. Unlike electrical conductivity, all of the samples showed poor wettability performance and their contact angle decreased severely, after being exposed to corrosion. Aluminum oxide and tin oxide occurred on the surface of samples at different quantities.

This study showed that, graphene has the potential to be a much better alternative as a coating material. It presented better electrical conductivity results than tin coating, the most widely used alternative in industry. It has better hydrophobic properties compared to its alternatives. After the corrosive conditions, even though the contact angle decreases dramatically, it still has higher degrees (roughly 3° higher than tin coated samples and 9° higher than uncoated samples) than other samples which is remarkable.

On the other hand, graphene has some shortcomings as a coating material and is not able to show its true potential yet. The most important shortcomings are graphene's low feasibility of mass production, coating and its low reliability as a coating material. But even for nowadays, lots of progress have been made.

In addition to these, almost 50% of our samples are failed due to the defects that occurred at the graphene surface. 80% of samples failed in corrosion test and wettability test because of the defects while none of the tin coated samples had any defects. However, there is a high potential to enhance the reliability against corrosion by increasing the amount of graphene layers.

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