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Time Effect of Graphene Coating in between Metallic Layers of Copper in Nickel on Corrosion Behavior for Carbon Steel in Saline Water

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Abstract

The study was an experimental investigation for time 10, 20, and 30 min effect of graphene coating in between metallic layers of copper-nickel on corrosion behavior for carbon steel saline water. And Surface finishing for substrates was P320, P600, and P1200 mesh until mirror shiny surface before coated by metallic layers Cu – Cu – Ni reinforced with concentrations 0.25, 0.5, 1and 2 g/l graphene. First, X-ray diffraction, scanning electron microscopy associated for carbon steel & graphene and Microscopic test for coated specimen. The techniques were performed to study effect of saline water (3.5%) on the corrosion behaviors. Open circuit potential, tafel polarization, cyclic potentiodynamic polarization and impedance.

The results revealed that the types of corrosion were pitting corrosion, where the highest protections against corrosion were at 20 min with concentration 1 g/L graphene coating with P600 and P320 mesh. The results also showed the time increasing led to increasing for protection efficiency, decreasing for corrosion rates, increasing for polarization resistance, and decreasing for porosity percentage. Between metallic layers coating reinforced with concentrations 0.25, 0.5, 1and 2 g/l graphene.

1. Introduction

The multilayer metallic coatings lead to the proposal's enormous potential for improvement in performance relative to single-layer coating. [1], and corrosion is a significant reason for decay in industrial parts. So the advanced coatings improve in properties in their morphological, electrical, thermal, and mechanical characteristics [2],[3], Gr is applied as a corrosion inhibitor for metals. where a monolayer and multilayer graphene-coated onto metal surfaces have excellent barriers to oxygen diffusion, that renders the underlying metal inert from environmental oxidation [4]–[8].So, graphene-based anti-corrosion coatings are used to improving surface properties of a substrate [9], [10]. Gr consists of carbon atoms that are strongly bonded to form a hexagonal network, graphene has been generating sustained interest for many fields [11], [12].Cu-plating is used with both Ni and Cr plates and is considered to be the most preferable coating surface due to its ability to be spreader in a uniform layer and ductile with no pores with the advantage of polishing capability if several layers are used [13].Ni-plating can be used as a protecting agent against corrosion that can in the abrasion applications, resisting agent against the corrosion also as smoothing substance for other materials [13], [14].Multilayer chromium, nickel, and copper on the carbon steel, lead to copper and nickel are initially anodic versus chromium and become cathode versus carbon iron, when the electrolyte reaches the inner layer, galvanic corrosion take place [15].Resistance of a metal to electrochemical degradation was increasing by a coating of Cu with Gr. So, electrochemical characterization in aggressive CL environment shown changes in development of anti-corrosion coatings by using graphene layers [16]–[18]. Ni-graphene coatings provide corrosion resistance, which solves corrosion protection problems in the oil and gas industry [19],[20],[21]. Electrochemical for coating multilayer graphene improve the corrosion resistance of a Cu-Ni alloy [15], [22]–[24]highlight why it is important. It should define the purpose of the work and its significance.

The current state of the research field should be reviewed carefully, and key publications cited. Please highlight controversial and diverging hypotheses when necessary. Finally, briefly mention the main aim of the work. As far as possible, keep the introduction comprehensible to scientists outside your particular field of research.

2. Materials and Methods

2.1. Materials

2.1.1. Specimens of carbon steel ST37-2

Carbon steel ST37-2 is produced by the Arab Company for Special Steel (Arkosteel) in Saddat City –Egypt with the following characteristics, Chemical analysis is measured at SPECTRO MAXX at EVACO Co. in 10th of Ramadan city, Egypt. Which is shown in the following table 1.

Table 1 Chemical composition of steel (37.2).

Chem. Ele's.	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Al	Co	Fe
%	0.12	0.30	0.42	0.014	0.01	0.04	0.003	0.02	0.05	0.02	0.003	99

- Scanning electron microscope (SEM) of carbon steel fig.1.

2.1.2. The characterizations of graphene oxide:

Graphene oxide was purchased from the company "Graphene laboratories ,Inc., indiamart , India " Color : broan,Thickness : 1 atomic layer- at least 60 %,Flake size : 0.5 – microns, Composition : Carbon 97%,Oxgen (20 %),Single layer graphene oxide solution ,Item no: sgraphene -001 ,which, it is prepared by Hummer's method which is oxidized graphene formed from oxidizing crystal graphite with a mixture of sulfuric acid, sodium nitrate, and potassium permanganate. Graphene Oxide is represented in fig 1 (b) graphene oxide characteristics as FE-SEM image, (c) graphene oxide characteristics as EDX spectroscopy analysis, and (d) graphene oxide characteristics as XRD pattern.
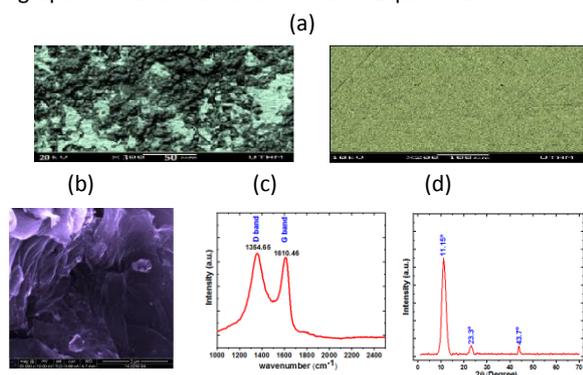
(a)

(b)   (c)   (d)

Fig 1 a- Scanning electron microscope (SEM) of carbon steel ,b–d; graphene oxide characteristics as, (b) FE-SEM image, (c) EDX spectroscopy analysis, and (d) XRD pattern of graphene oxide.

2.2. The schematic diagram of research sequence for metallic layers coated with graphene:

The searches can be summarized in the following preparation of specimens of the substrate, preliminary 5 samples for metallic coating, electroplating of graphene oxide, testing morphology of coating, and potentiodynamic scan all are represented in fig.2.The schematic diagram of the research sequence for metallic layers coated with graphene.

2.2.1. Cu- Ni- Metallic coating with Gr preparation processes

Preparations of specimens of substrate take place with the operations cutting, holing, grinding, emery, polishing, removal of grease, oxides and salts. Prior to the deposition of the coatings on Carbon steel 30X100X3mm dimensions were polished with struers® papers silicon carbide grades 320, 600 and 1200 mesh until a mirror shiny surface, Preliminary 5 samples were used to identify the suitable Cu, Cu and Ni plating conditions fig.2. for reach the appropriate conditions for the research five samples to reach the research, Electroplating of graphene oxide coating is achieved by 44 ml of deionized water and 308 ml of acetone to dissolve the graphene oxide for 90 min in the ultrasonic 100 watt – 40 kHz to activation then added to electrolytes with different ratio 0.25,0.5,1and 2 g/l . Therefore, the graphene oxide is coating by electroplating between the coated metallic layers of Cu, Cu and Ni with two similar electrodes by the cell is represented in fig.2.
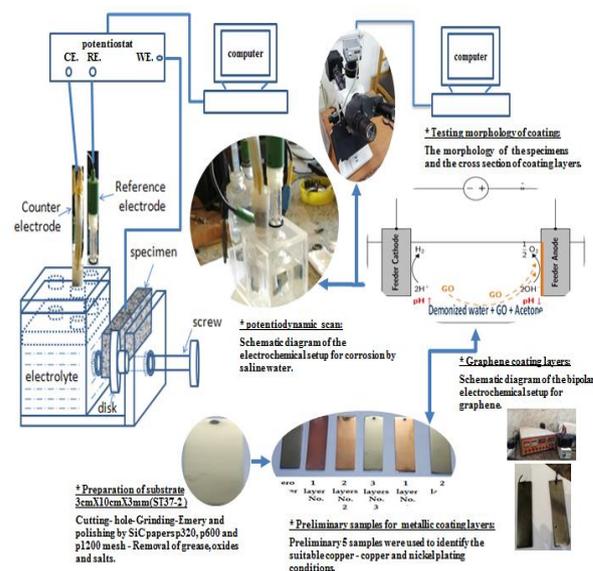

Fig 2 The schematic diagram of research sequence for metallic layers coated with graphene.

2.2.2 Experimental setup design for testing morphology of coating:

The morphology of prepared specimens are tested by the optical microscope CIM® with digital camera moticam2300–3.0MPixel USB2.0,USA shows morphology of the specimens and the cross section in fig 2.

2.3. Electrochemical measurements

2.3.1. Experimental setup design for testing corrosion of coating

The corrosion of prepared specimens are tested by the designed cell which consists from three electrodes reference calomel electrode Rf (HI 5412), Pt counter electrode and specimen. They are immersed in saline water as electrolyte as shows in the fig 2.

2.3.2. The corrosion techniques

An electrochemical process is electrochemical corrosion monitoring techniques are based on the corrosion of metals in solutions of electrolytes. Where, the electrochemical techniques are suitable for corrosion of metals in media with high electrical conductance. And also, if corrosion reactions have an electrochemical nature, electrode potential, electric current and electrical

resistance formed on the metal surface are the main characteristics of corrosion. So, we measure these three parameters characterize and monitor the corrosion of metals in electrical conductive media[25].

The corrosion techniques were tested by Gamry (PCI4/300®) instrument ,U S A where, the various factors were achieved on the corrosion behavior of carbon steel 37-2 coated by metallic layers (copper-copper-nickel) reinforced with graphene by the following techniques:

2.3.2.1 Open circuit potential, Eoc:

For gamry's software, the open circuit potential, Eoc is the equilibrium potential assumed by the electrode in the absence of electrical connections to the electrode. So, all potentials are specified as the potential of the working electrode with respect to the reference electrode "vs. Eref"or this open circuit potential "vs. Eoc". So, the equations used to convert from one form of potential to other shown in following:

E vs. Eoc = (E vs. Eref) - Eoc

E vs. Eref = (E vs. Eoc) + Eoc

The potentials are versus Eref or versus Eoc, the sign is used positive a potential, which, more anodic it is.

2.3.2.2 The Tafel polarization test:

Potentionstat records an applied current to cell that provides an increase in potential. Where, potential drives a reaction at the anode or cathode, is observed a current. That is, a potential where a total anodic current equals a total cathodic current is an open-circuit potential (Eoc), a potential swept across a range and a current is measured. [26].

Corrosion occurs at a rate specified by the equilibrium between opposing **electrochemical** reactions. First is the anodic reaction, metal oxidizes, releasing electrons into the metal. Second is the cathodic reaction, a solution form (usually O_2 or H^+) is reduced, removing electrons from the metal. By equilibrium of two reactions, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs. The two reactions can happen on one metal or on two dissimilar metals (or metal sites) that are electrically connected [27].

2.3.2.3 The electrochemical impedance spectroscopy (EIS):

By, applying an AC potential to an electrochemical cell and then measuring the current through the cell to get electrochemical impedance [28], [29].

The impedance attitude of coating is explored where most paint coatings degrade with time, resulting in an attitude more complex. After certain of time, water penetrates into the coating and forms a new liquid/metal interface under the coating. Corrosion phenomena can happen with the new interface. According to the simple equivalent circuit elements are Ccoat, the capacitance of coating, its value is much smaller than CdL, a double layer capacitance, with, units that are pF or nF, not µF. Rpore, pore resistance, and is the resistance of coating for ion-conducting paths develops in. The paths may not be physical pores full of electrolytes. On the metal side of the pore, an area of the coating has divided and a bore filled with an electrolyte solution has formed. with, very different than the bulk solution outside of the coating.Ru, electrolyte resistance, Rp, polarization resistance[29]–[31].

2.3.3. Corrosion Rate Measurement (mpy)

The rate of corrosion (C_R) is directly proportional with its corrosion current density (i_{corr}) in a given environment in according the relation [3], [32] :

$$C_R = 0.13 \times i_{corr} \times \left(\frac{e}{\rho}\right) \tag{1}$$

This equation calculates C_R in (m/y), e and ρ are equivalent weight and density of carbon steel, respectively. The data of corrosion rate indicate that the nanoparticle coatings led to decreasing in corrosion rate of carbon steel.

The applied coatings were evaluated by corrosion current densities for uncoated and coated specimens which, used to calculate protection efficiencies (PE%) as follows [33]:

$$PE\% = \left[1 - \frac{i_{corr_{coated\ specimen}}}{i_{corr_{uncoated\ specimen}}}\right] \times 100 \tag{2}$$

The best efficiency was for Cu-Ni-Gr coating. Surface porosity fraction evaluated by both potentiodynamic polarization and indentation measurements. and, the porosity percentage (PP%) is calculated by the following equation [33]:

$$PP\% = \left[\frac{R_{p_{uncoated\ specimen}}}{R_{p_{coated\ specimen}}}\right] \times 10^{\frac{-\Delta E_{corr}}{b_a}} \times 100 \tag{3}$$

So, the polarization resistances of the uncoated R_p, uncoated, the polarization resistances of the coated R_p, coated samples, the corrosion potential difference between them, ΔE_{corr}, and b_a is the anodic Tafel slope of the uncoated sample. The lowest porosity was found for Cu-Ni-Gr coating [33].

2.4. Microstructural characteristics of surface analysis

This was shown in the XRD diffractograms of GO/Cu-Ni coatings with concentrations; (a) 0.0, (b) 0.5, (c) 1.0 and (d) 2 (g/l) of GO on carbon steel fig.3.
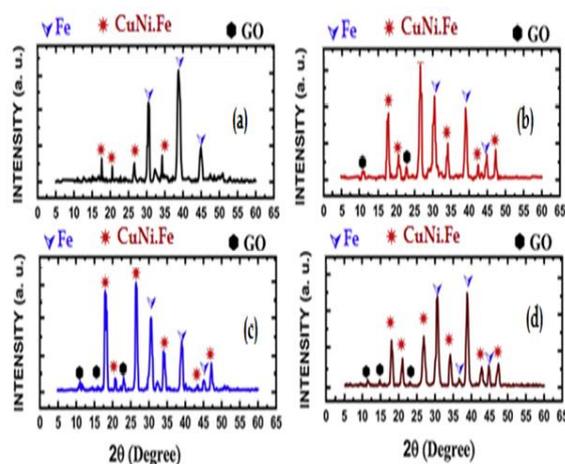

Fig 3 a–d; the XRD diffractograms of GO/Cu-Ni coatings with concentrations; (a) 0.0, (b) 0.5, (c) 1.0 and (d) 2 (g/l) of GO on carbon steel.

3. Results and Discussions

3.1 Optical Observations of cross section and morphology for coating

3.1.1 Cross-sections and morphology of electroplating for 1, 2 g/l of Graphene at 10, 20 min for P320, P600and P1200:

For cross-section, the first layer was soft next to the substrate; the two layers Cu – graphene were hard spongy form, the two layers Cu – graphene brittle spongy form and Ni – graphene hard high strength spongy form with thickness 430.9 um, and for morphology, there were spongy form and had few cavities on surfaces of the coating fig 4.   (a)
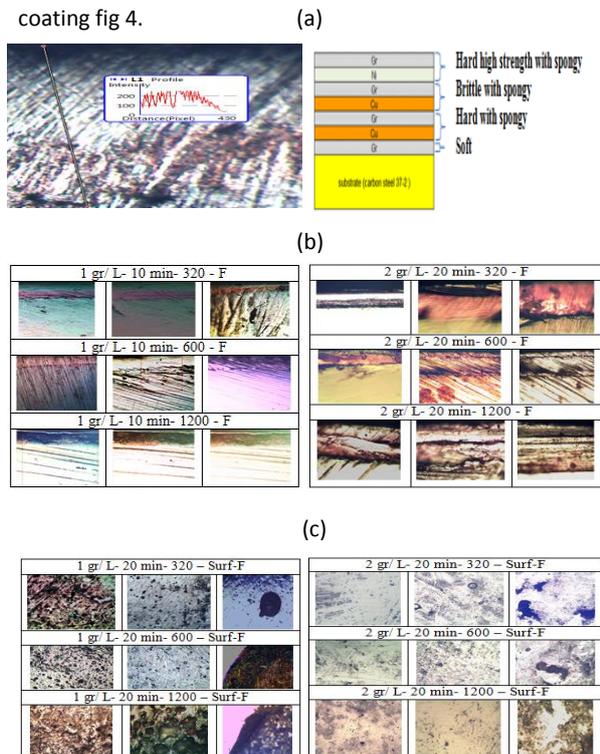

(b)

(c)

Fig 4 Cross-section and morphology of coating (a) sketch of layers with features with thickness, (b) cross-section and (c) morphology of coating for 1, 2 g/l graphene.

3.2 Open circuit potential, Eoc

The electrochemical measurements took place by Gamry PCl300/4 Potentiostat with a computer, three-electrode cell, a specimen as a working electrode with an active area of 1 cm2, a counter electrode, P_t, and reference electrode, SCE, used for our test.

3.2.1 The effect of layers coating on open circuit potential, Eoc of carbon steel

The open circuit potential, Eoc measured for the substrate, Cu-Ni coated on it, and Cu-Cu-Ni coated on it in fig 5. (a) the three layers lay in the region between No corrosion to corrosion region and substrate lays in corrosion region .

3.2.2 Effect of different times 0, 10, 20, and 30 min of graphene reinforced between Cu-Cu-Ni coated carbon steel during open circuit potential, Eoc

The open circuit potential, Eoc was measured for different times of Gr electroplating on Cu-Cu-Ni coated carbon steel where 20min electroplating goes from corrosion to No corrosion regions and the rest go to corrosion region as shown in fig. 5.(b) The relation between Voltage(V) and Time(S) for saline water of the open circuit potential, Eoc measured for different times

of Gr electroplating on Cu-Cu-Ni coated carbon steel.

Therefore, the research found that at 20 min. rising from corrosion activity region V ≤ - 0.35 towards no corrosion region occurred V > - 0.20,where The obtained experimental results are compared with results of K. Ollik and M. Lieder [10] with a good agreement. we found at 5 min still in uncertainty regarding corrosion activity region -0.35 ≤ V ≤ - 0.20 ,and at 10 ,30 min located in corrosion region within 300 (S) as shown in fig 5 (b).
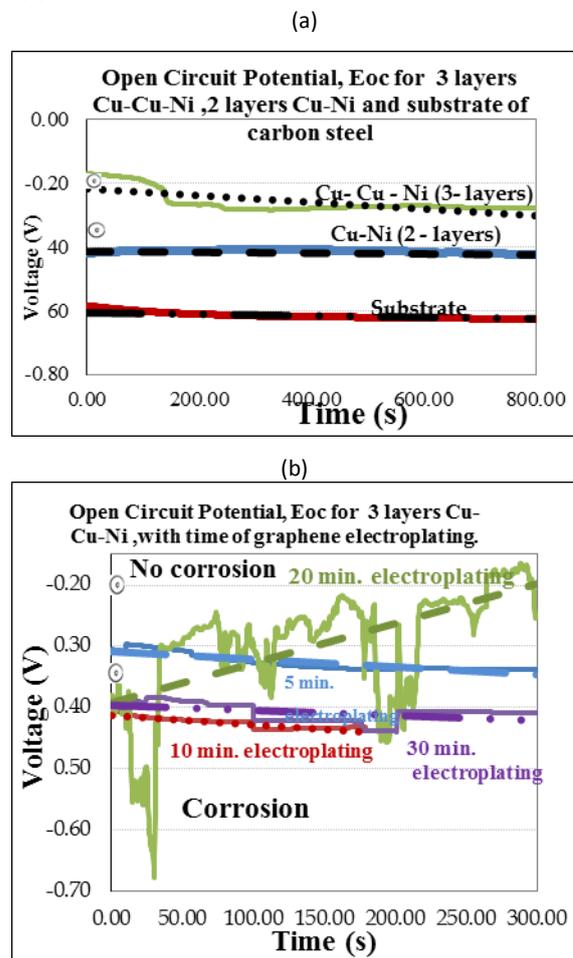
(a)

(b)

Fig 5 The relation between Voltage (V) and Time(S) for saline water (a) multilayer of Cu-Ni & carbon steel,(b) at different times of graphene electroplating on Cu-Cu-Ni coated carbon steel.

3.3 Tafel polarization test

The electrochemical measurements took place out by Gamry PCl300/4 Potentiostat with a computer, three-electrode cell, a specimen as a working electrode with an active area of 1 cm2, a counter electrode, Pt, and reference electrode, SCE, used for our test.

3.3.1 The effect of layers coating on tafel polarization test of carbon steel

Tafel polarization test measured for the substrate, Cu-Ni coated on it, and Cu-Cu-Ni coated on it. Therefore, the voltage of corrosion goes from -884 to -404 volt by coating as shown in fig. 6.(a) Tafel plot relation between Voltage (V) and Log(μA/cm²) for saline water of multilayer coating ,and Tafel polarization resistance shown in table 2.

Table 2 Tafel polarization resistance results for substrate, 2 layers Cu-Ni, and 3 layers Cu-Cu-Ni coating in saline water

Tafel polarization Resistance	substrate	2 layers	3 layers
Lower Fit Limit (mV vs. Ref. (Pt))	-15.13	-12.51	-628.7
Upper Fit Limit (mV vs. Ref. (Pt))	31.37	138.5	950.7
Beta A (V/decade)	0.18	0.23	0.37
Beta C (V/decade)	0.15	0.23	0.14
Icorr (uA)	2.686	1.932	630.4
Ecorr (mV)	-844	-708	-404
Rp (ohms)	130.4	259.1	69.74
Corrosion Rate (mpy)	233.5	147	480.1
Protection Efficiencies	0	28	-23370
Porosity Percentage	0	1.40	5.76

3.3.2 Effect of different times 0, 10, 20, and 30 min for 0.5 g/l graphene reinforced between Cu-Cu-Ni coated on carbon steel for Tafel polarization test

Tafel polarization test measured for Cu-Cu-Ni coated by 0.5 g/l graphene at 0, 10, 20 and 30 min. At 20 min achieved for less corrosion ,where The obtained experimental results are compared with results of K. Ollik and M. Lieder [10] with a good agreement but,10 and 30 min achieved for more corrosion , the immunity (PE%) 99.7, 98.3 and 99.7 with (PP%) 1.76, 1.83 and 2.68 respectively for that condition as it shown in fig 6(b) the tafel plot relation between Voltage (V) and Log($\mu A/cm^2$) at 0,10,20 and 30 min. , shown in table 3.

Table 3 Tafel polarization Resistance results for 0.5 g/l of graphene10, 20and 30 min. electroplating for it between 3 layers Cu-Cu-Ni coating in saline water.

Tafel polarization Resistance	0.5g/l 10 min	o.5 g/l 20 min	0.5g/l 30 min
Lower Fit Limit (mV vs. Ref. (Pt))	-1.317	-443.8	-675.3
Upper Fit Limit (mV vs. Ref. (Pt))	1.056	1.045	773.7
Beta A (V/decade)	0.52	0.65	0.31
Beta C (V/decade)	0.48	0.29	0.16
Icorr (uA)	1055	801.3	653
Ecorr (mV)	-575	-457	-708
Rp (ohms)	103.2	109.8	68.85
Corrosion Rate (mpy)	803.4	0.6103	497.3
Protection Efficiencies	98.3	99.7	97.0
Porosity Percentage	1.83	1.76	2.68

3.3.3 Effect of different times 0, 10, 20, and 30 min for 1 g/l graphene reinforced between Cu-Cu-Ni coated on carbon steel for Tafel polarization test

Tafel polarization test measured for Cu-Cu-Ni coated by 1 g/l graphene at 0, 10, 20 and 30 min. At 20 min achieved for no corrosion,where The obtained experimental results are compared with results of K. Ollik and M. Lieder [10] with a good agreement but,10 min. and 30 min achieved for less corrosion , the immunity (PE%) 100, 98 and 97.0 with (PP%) 0 , 2 and 0.3 respectively for that condition as it shown in fig. 18. tafel

plot relation between Voltage (V) and Log($\mu A/cm^2$) for saline water at 0,10,20 and 30 min. the Tafel fitting ,E Log I and Tafel polarization Resistance shown in table 4.

Table 4 Tafel polarization Resistance results for 1 g/l of graphene10, 20and 30 min. electroplating for it between 3 layers Cu-Cu-Ni coating in saline water.

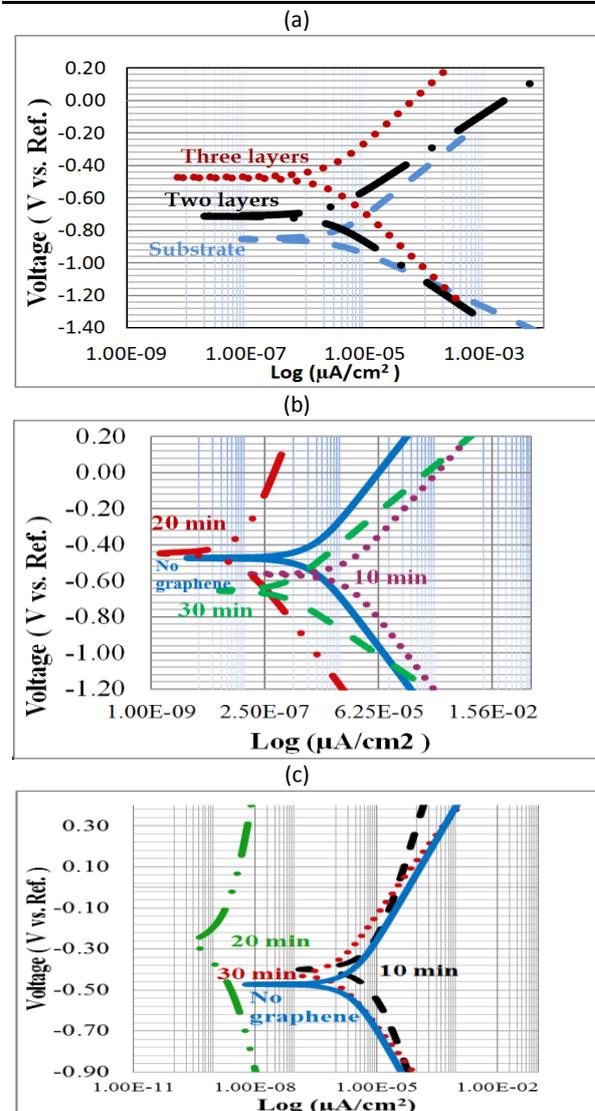| Tafel polarization Resistance	1 g/l 10 min	1 g/l 20 min	1 g/l 30 min
Lower Fit Limit (mV vs. Ref. (Pt))	-908.7	-1032	-430.8
Upper Fit Limit (mV vs. Ref. (Pt))	1.088	1326	184.3
Beta A (V/decade)	0.3682	1	1.7
Beta C (V/decade)	0.3589	1	0.4
Icorr (uA)	792.9	0	160.3
Ecorr (mV)	-399	-323	-421
Rp (ohms)	99.52	67069000	416.1
Corrosion Rate (mpy)	362.3	0	129.4
Protection Efficiencies	98	100	99.7
Porosity Percentage	2	0	0.3

(a)

(b)

(c)

Fig 6 The tafel plot relation between Voltage (V) and log ($\mu A/cm^2$) for saline water of measured for (a) multi-layers coating on carbon steel,(b) 0.5 g/l graphene at 0, 10, 20 and 30 min.,(c) 1 g/l graphene at 0,10,20 and 30 min electroplating on Cu-Cu-Ni coated carbon steel with & without graphene.

3.3.4 The effect of time's coats for graphene multilayer's coating on the corrosion rate (mpy) and protection efficiencies PE (%) calculated from Tafel results

The variation of the corrosion rate in (mpy) and Protection efficiencies PE (%) for each time 0, 10, 20 and 30 min, where, the corrosion rate for 30 min. was the least 1.37 mpy with the biggest Protection efficiencies 98.39 % shown in table 5 and in fig 7.

Table 5 Effect of times' coating on the corrosion rate in (mpy) and protection efficiencies PE (%) for 1200 with 1 g/l graphene.

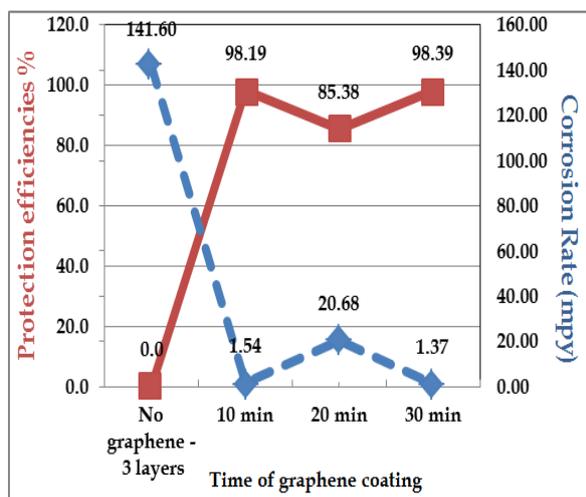| Factors	Corrosion Rate (mpy)	Protection efficiencies (PE %)
No graphene - 3 layers	141.60	0.0
10 min	1.54	98.19
20 min	20.68	85.38
30 min	1.37	98.39

Fig 7 Effect of times' coats on the corrosion rate in (mpy) and protection efficiencies PE (%) for 1200 with 1 g/l graphene.
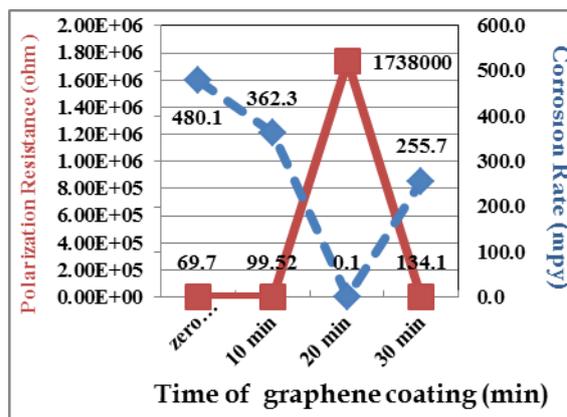
3.3.4.1 The corrosion rate (mpy),polarization resistance(Rp),porosity percentage PP (%) and protection efficiencies PE (%) for Times 0,10,20 and 30 min ,with 1200 -1 g/l specimens

The effect of the corrosion rate in (mpy), polarization resistance(Rp),porosity percentage PP (%) and protection efficiencies PE (%) for 0, 10,20 and 30 min , with1200 1 g/l ,Where increasing in surface finishing leaded to decreasing in corrosion rate with increasing in Polarization resistance shown in fig 8 (a), and the highest value at 20min was 1738000 (ohm) with the lost corrosion rate 0.1 (mpy) Also, Increasing in surface finishing leaded to decreasing in the porosity percentage with increasing in protection efficiencies, and the lost value at 20min was 0.0001 (PP%) with the highest value (PE%) 100 (%) as shown in fig 8 (b) for specimens ,where The obtained experimental results are compared with results of K. Ollik and M. Lieder [10] with a good agreement and shown in table 6

Table 6 The effect of Surface finishing for graphene multilayer's coating on the corrosion rate (mpy) , polarization resistance (Rp) ,porosity percentage PP (%) and protection efficiencies (%)for time 0, 10,20, and 30 min. with1200 - 1 g/l graphene as tafel polarization

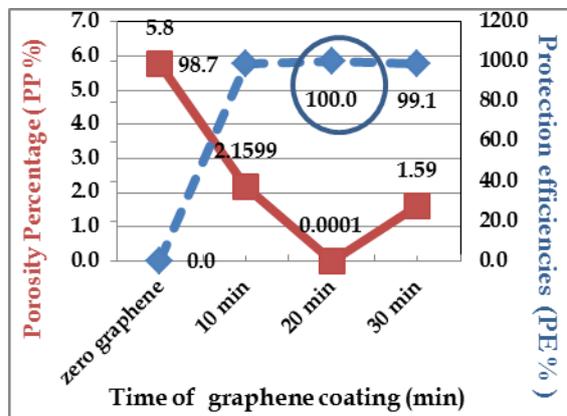| Factors	Corrosion Rate (mpy)	Rp (ohms)	Protection Efficiencies (PE%)	Porosity ercentage (PP%)
zero graphene	480.1	69.7	0.0	5.8
10 min	362.3	99.52	98.7	2.1599
20 min	0.1	1738000	100.0	0.0001
30 min	255.7	134.1	99.1	1.59

(a)

(b)

Fig 8 The effect of coating's concentration for graphene multilayer's coating on (a), the corrosion rate (mpy) and polarization resistance (Rp) (b),porosity percentage PP (%) and protection efficiencies (%)for Protection efficiencies PE (%) for Times 0,10,20 and 30 min ,with 1200 -1 g/l specimens

3.4 The cyclic potentiodynamic polarization

Cyclic potentiodynamic polarizations carried out by electrochemical measurements took place out by Gamry PCI300/4 Potentiostat with a computer, three-electrode cell, a specimen as a working electrode with an active area of 1 cm², a counter electrode, Pt, and reference electrode, SCE, used for our test.

3.4.1 Effect of coating Cu-Cu-Ni on carbon steel on cyclic potentiodynamic polarization:

Cyclic potentiodynamic polarization measured for Cu-Cu-Ni coated on carbon steel. Fig 9 (a) shown no pitting

with repassivation for the Cyclic potentiodynamic polarization plot relation between Log(µA/cm²) and Voltage (V) for saline water of multilayer coating ,and the Tafel fitting ,E Log I and Polarization Resistance ,where it shown Ecorr at -449 (mV) ,Icorr at 13.5 (µA) ,repassivation -92.22 (mV) and tafel corrosion rate 6.164 (mpy)with polarization resistance 151.5 (ohm).

3.4.2 Effect of different times 0, 10, 20, and 30 min for 1 g/l graphene reinforced between Cu-Cu-Ni coated on carbon steel with p1200 for cyclic potentiodynamic polarization

Cyclic potentiodynamic polarization measured for Cu-Cu-Ni coated on carbon steel. Fig 9 (b) shown pitting with repassivation, pitting with repassivation and no pitting without repassivation for 10,30,and 20 min respectively in Cyclic potentiodynamic polarization plot relation between Log(µA/cm²) and Voltage (V) for saline water of multilayer coating ,and the Tafel fitting ,E Log I and Polarization Resistance ,where it shown Ecorr at -285, -305 and -733 (mV) ,Icorr at 4.77, 4.06 and 112 (µA) ,repassivation -108.2 , -117.6 and 0 (mV) and tafel corrosion rate 2.181, 1.857 and 51.18 (mpy)with polarization resistance 115 , 123.8 and 124.3 (ohm) at 1 g/l p1200 10,30,and 20 min respectively in saline water of multilayer coating ,and the Tafel fitting ,E Log I and Polarization Resistance shown in table 7.

Table 7 Cyclic potentiodynamic polarization scan results for the effect of time 10, 20, and 30 with concentration 1 g/l of graphene p1200 between 3 layers Cu-Cu-Ni coating in saline water.

min	Tafel fitting								E Log I			polarization Resistance			
	Icorr (µA)	Ecorr (mV)	Esec.corr (mV)	Erpass (mV)	Eprot (mV)	Epit (mV)	difference	corrosion rate	Ecorr (mV)	Icorr (µA)	corrosion rate	Icorr (µA)	Ecorr (mV)	Rp	corrosion rate
10	4.77	-285	0	-108.2	-90.76	-15.85	285	2.181	-285	3.802	1.737	558.4	-285	115	255.2
20	112	-733	0	0	211.2	0	733	51.18	-733	80.59	36.83	717.9	-733	124.3	328
30	4.06	-305	0	-117.6	-92.4	-7.73	305	1.857	-305	2.661	1.22	663	-305	123.8	303

3.4.3 Effect of different times 0, 10, 20, and 30 min for 1 g/l graphene reinforced between Cu-Cu-Ni coated on carbon steel withp600 and p1200 for cyclic potentiodynamic polarization
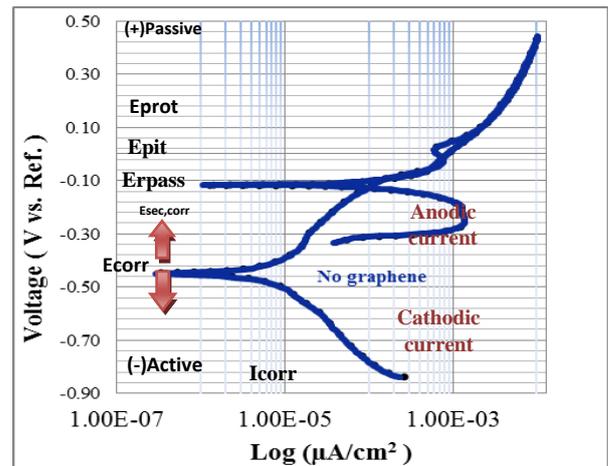
Cyclic potentiodynamic polarization measured for Cu-Cu-Ni coated on carbon steel. Fig 9 (c) shown no pitting without repassivation, pitting with repassivation and pitting with repassivation for 20,10,and 30 min respectively in cyclic potentiodynamic polarization plot relation between Log(µA/cm²) and Voltage (V) for saline water of multilayer coating ,and the Tafel fitting ,E Log I and Polarization Resistance ,where it shown Ecorr at -211, -285 and -305 (mV) ,Icorr at 4.58E-04 , 4.77 and 4.06 (µA) ,repassivation 0 , -108.2 and -117.6 (mV) and tafel corrosion rate 2.09E-04, 2.181 and 1.857 (mpy)with polarization resistance 1.17E+08 , 115 and 123.8 (ohm) at

1 g/l p600,p1200 and p1200 20,10,and 30 min respectively in saline water of multilayer coating ,and the Tafel fitting ,E Log I and Polarization Resistance shown in table 8.
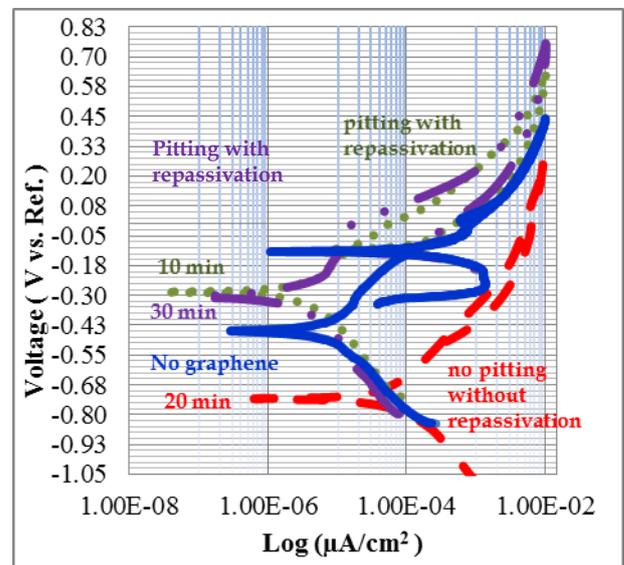
Table 8 Cyclic potentiodynamic polarization scan results for the effect of time 10, 20, and 30 with concentration 1 g/l of graphene at p600 and p1200 between 3 layers Cu-Cu-Ni coating in saline water.

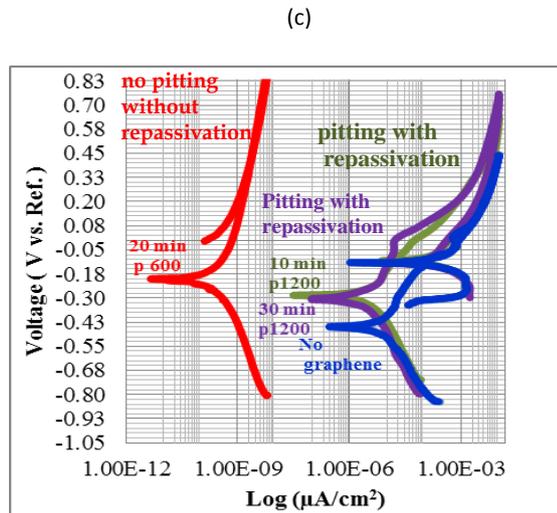| min	Tafel fitting								E Log I			polarization Resistance			
	Icorr (µA)	Ecorr (mV)	Esec,corr (mV)	Erpass (mV)	Eprot (mV)	Epit (mV) potential difference	corrosion rate		Ecorr (mV)	Icorr (µA) corrosion rate		Icorr (µA)	Ecorr (mV)	Rp (ohm)	corrosion rate (mpy)
10	4.77	-285	0	-108.2	-90.76	-15.85	285	2.181	-285	3.802	1.737	558.4	-285	115	255.2
20	4.58E-04	-211	-2.519	0	1.092	1.489	208.481	2.09E-04	-211	4.39E-04	2.01E-04	1.24E-03	-211.00	1.17E+08	5.66E-04
30	4.06	-305	0	-117.6	-92.4	-7.73	305	1.857	-305	2.661	1.22	663	-305	123.8	303

(a)

(b)

(c)

Fig 9 The Cyclic potentiodynamic polarization plot between Voltage(V) and log($\mu A/cm^2$) with saline water of measured for (a) multi-layers coating on carbon steel,(b) the effect of time 0,10,20,and 30 min at the concentration 1 g/l electroplating at p1200.,(c) for the effect of time 0,10,20,and 30 min at the concentration 1 g/l electroplating at p600 and p1200 on Cu-Cu-Ni coated carbon steel with & without graphene.

3.5 The electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) carried out using electrochemical measurements took place by Gamry PCI300/4 Potentiostat with a computer, three-electrode cell, a specimen as a working electrode with an active area of 1 cm^2, a counter electrode, P_t, and reference electrode, SCE, used for our test.

3.5.1 The effect of coating Cu-Cu-Ni on carbon steel on electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measured for Cu-Cu-Ni coated on carbon steel with saline water, which shown the equivalent circuit elements R.E., reference electrode, Ru, uncompensated resistance, CdL, double layer capacitance ,Ccoat, coating capacitance ,Rpore, pore resistance , Rp, polarization resistance(electron transfer resistance), W.E., work electrode see fig. 10, and fig. 10.(a) Nyquist plot relation between –Zimag (ohm)and Zreal (ohm).

The values of the equivalent circuit elements ,Rpore was 4.14E+03ohm, Rp was 1.31E+04 ohm, Ru , was the same 55.12ohm at p1200 and tolal R 1.73E+04 ohm as shown in table 9.

Table 9 The values of the equivalent circuit elements for Nyquist plot with no graphene between 3 layers Cu-Cu-Ni coating in saline water.

elements	Value	Error (+/-)
Rpore (ohms)	4.14E+03	70.37
Ccoat (F)	4.98E-06	5.11E-08
Rp (ohms)	1.31E+04	199.7
CdL (F)	4.38E-05	1.17E-06
Ru (ohms)	55.12	4.91E-01

3.5.2 Effect of different times 0, 10, 20, and 30 min for 1 g/l graphene reinforced between Cu-Cu-Ni coated on carbon steel with p1200 for electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measured for concentration 1 g/l of graphene between

Cu-Cu-Ni coated at 10, 20 and 30 min. on carbon steel p1200 with saline water as electrolyte. Fig. 10. (b)shown The Electrochemical Impedance Spectroscopy (EIS) Nyquist plot relation between –Zimag (ohm)and Zreal (ohm.

The values of the equivalent circuit elements Rpore the highest 3.03E+03ohm at 30 min the lowest 1.51E+03 ohm at 20 min, Rp , the highest 1.33E+04ohm at 20 min the lowest 8.90E+03ohm at 30 min , Ru , the highest 46.01ohm at 10 min, the highest total R 1.49E+04 ohm at 20 min,C 1.10E-5 (F) at 30 min and the lowest total R 1.20E+04 ohm at 30 min, C 6.07E-6 (F) at 20 min as shown in table 10.

Table 10 The values of the equivalent circuit elements for Nyquist plot with 1 g/l graphene at 10, 20 and 30 min between 3 layers Cu-Cu-Ni coating in saline water

Elem-ents	10 min		20 min		30 min	
	Value	Error (+/-)	Value	Error (+/-)	Value	Error (+/-)
Rpore (ohms)	2.77E+03	78.52	1.51E+03	20.64	3.03E+03	106.8
Ccoat (F)	39E-06	2.73E-08	2.93E-07	3.48E-09	4.67E-06	3.94E-08
Rp (ohms)	1.25E+04	164.3	1.33E+04	143	8.90E+03	148.1
CdL (F)	*5.22E-06*	1.24E-07	5.78E-06	9.69E-08	6.29E-06	2.21E-07
Ru (ohms)	46.01	36E-01	44.53	6.63E-01	42.69	2.82E-01

3.5.3 Effect of different times 0, 10, 20, and 30 min for 1 g/l graphene reinforced between Cu-Cu-Ni coated on carbon steel with p600 and p1200 for electrochemical impedance spectroscopy (EIS):

Electrochemical impedance spectroscopy (EIS) measured for concentration 1 g/l of graphene at 10, 20 and 30 min at p600 and p1200.where fig 10 (c) was shown electrochemical impedance spectroscopy (EIS) Nyquist plot relation between –Zimag (ohm)and Zreal (ohm).The values of the equivalent circuit elements Rpore the highest 3.03E+03ohm at 30 min the lowest 2.45E+03ohm at 20 min, Rp , the highest 1.94E+04ohm at 20 min the lowest 8.90E+03ohm at 30 min , Ru , the highest 46.29ohm at 20 min, the highest total R 2.19E+04 ohm at 20 min ,C 4.42E-5 (F) at 10 min and the lowest total R 1.20E+04 ohm at 30 min, C 3.70E-6 (F) at 20 min as shown in table 11.

Table 11 The values of the equivalent circuit elements for Nyquist plot with 1 g/l graphene at 10,20 and 30 min between 3 layers Cu-Cu-Ni coating in saline water

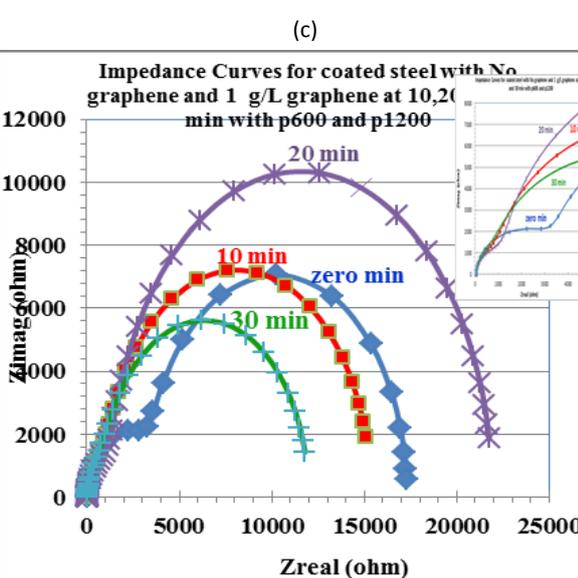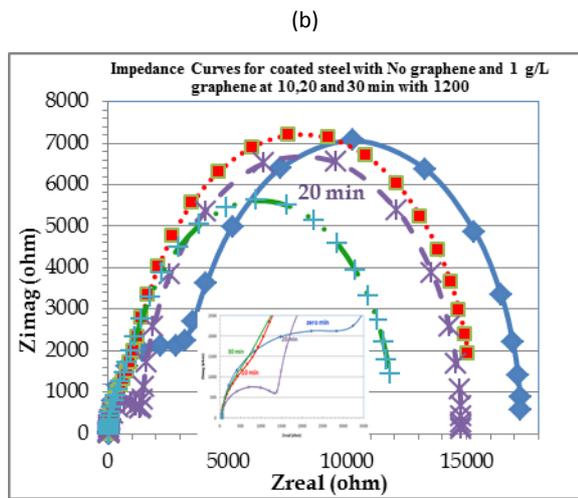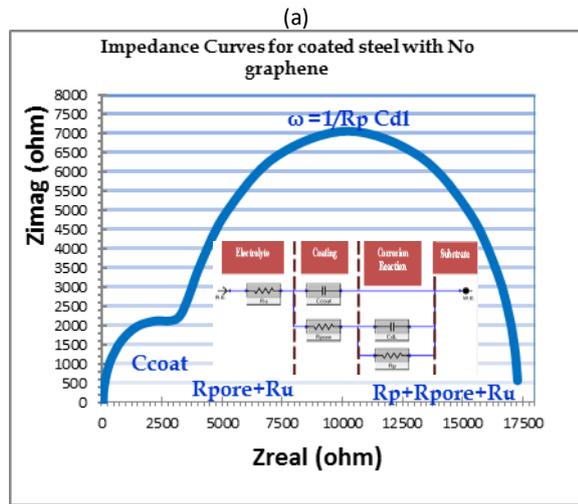| eleme nts	10 min p1200		20 min p600		30 min p1200	
	Valu e	Error (+/-)	Valu e	Error (+/-)	Valu e	Error (+/-)
Rpore (ohms)	2.77E+03	78.52	2.45E+03	51.93	3.03E+03	106.8
Ccoat (F)	39E-06	2.73E-08	1.04E-06	8.41E-09	4.67E-06	3.94E-08
Rp (ohms)	1.25E+04	164.3	1.94E+04	206	8.90E+03	148.1
CdL (F)	5.22E-06	1.24E-07	2.66E-06	4.34E-08	6.29E-06	2.21E-07
Ru (ohms)	46.01	36E-01	46.29	3.67E-01	42.69	2.82E-01

(a)

(b)

(c)

Fig 10 Electrochemical Impedance Spectroscopy (EIS) Nyquist plot (a) coating Cu-Cu-Ni on carbon steel, (b) for 1 g/l graphene at 10,20 and 30 min. in multilayer metallic coating Cu-Cu-Ni on carbon steel p1200,(c) for 1 g/l graphene at 10,20 and 30 min. between Cu-Cu-Ni coated on carbon steel p600 and p1200 relation between –Zimag (ohm)and Zreal (ohm) in saline water.

3.5.4 Effect of different times 0, 10, 20, and 30 min coating for graphene between multilayer's metallic coating on (Coating's Rpore (ohms), Coating's Ccoat (F), Corrosion reaction's Rp (ohms), Corrosion reaction's CdL (F), and electrolyte's Ru (ohms)) by impedance

Effect of time coating for graphene between multilayer's metallic coating (Coating's Rpore (ohms), Coating's Ccoat (F), Corrosion reaction's Rp (ohms), Corrosion reaction's CdL (F), and electrolyte's Ru (ohms)) leaded to by impedance the following:

Increasing in time graphene coating from 0 to 30 min of graphene coating leaded to decreasing in coating's Rpore from 4142 to 1508 ohm, Corrosion reaction's Rp decreasing from 13100 to 8899 ohm, but at 20 min increasing to 1325 ohm, electrolyte's Ru decreasing from 55 to 43 ohm and decreasing in Coating's Ccoat from 5.E-06 to 3.00E-07 (F), decreasing Corrosion reaction's CdL 4.00E-5 to 5.00E-6 (F) as shown in table 12.

Table 12 Effect of time for graphene multilayer's coating on coating's Rpore (ohms), coating's Ccoat (F), corrosion reaction's Rp (ohms), corrosion reaction's CdL (F) and electrolyte's Ru (ohms) with impedance at 1200 surface finishing.

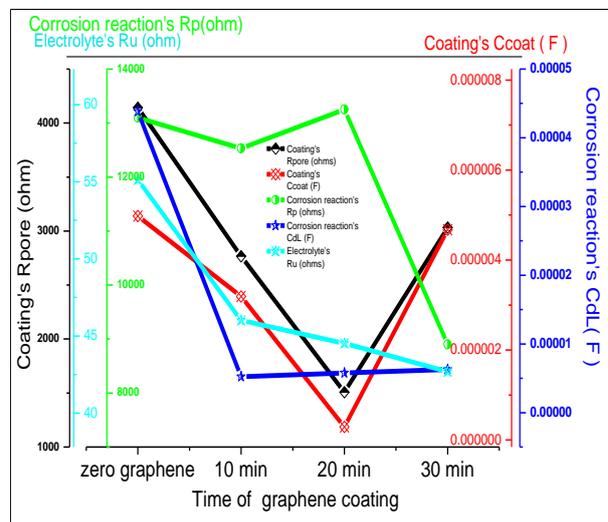| Factors	Coating's Rpore (ohms)	Coating's Ccoat (F)	Corrosion reaction's Rp (ohms)	Corrosion reaction's CdL (F)	Electrolyte's Ru (ohms)
0 min	4142	5.E-06	13100	4.E-05	55
10 min	2766	3.E-06	12530	5.E-06	46
20 min	1508	3.E-07	13250	6.E-06	45
30 min	3032	5.E-06	8899	6.E-06	43

The results were shown in fig 11.

Fig 11 The effect of coating's time for graphene multilayer's coating on coating's Rpore (ohms), coating's Ccoat (F), corrosion reaction's Rp (ohms), corrosion reaction's CdL (F) and electrolyte's Ru (ohms)with 1200 surface finishing.

4. Conclusions

Effect of studying different times 0, 10, 20, and 30 min for 1 g/l graphene reinforced between Cu-Cu-Ni coated on carbon steel 37.2 different surface finishing exposed to saline water Sodium Chloride (3.5 % NaCl) concentrations by weight :

1. The morphology of coating was spongier as shown in microscope in the inner faces than the outer faces of electrodes of the cells coating.

2. Protection Efficiency (PE%) were increasing from 0,98.7,100 and 99.1 % with increasing Time from zero,10,20, and 30 min respectively. Corrosion Rates (mpy) were decreasing from 480.1, 362.3, 0.1, and 255.7 mpy with increasing Time from zero, 10, 20, and 30 min respectively. Polarization Resistance (Rp) was increasing from 69.7, 99.52, 1738000, and 134.1 ohms with increasing Time from zero, 10, 20, and 30 min respectively. Porosity Percentage (PP%) were decreasing from 5.8, 2.1599, 0.0001, and 1.59 % with increasing Time from zero, 10, 20, and 30 min respectively. Between layers coating with concentrations 0.25, 0.5, 1and 2 g/l graphene. Where The obtained experimental results are compared with results of K. Ollik and M. Lieder [10] with a good agreement.

3. The types of corrosion were Pitting corrosion, where the highest protection against corrosion were at 20 min with concentration 1 g/l graphene coating for P600 and P320 mesh surfaces finishing were corrosion rate 0.001178 and 0.1072 (mpy), protection efficiencies 100,100 (PE %), porosity percentages 0.000001, 0.0001 (PP %) , polarization resistances 132400000, 1738000 (ohm).The next protection against corrosion was at 30 min concentration 0.5 g/l graphene coating with P320 mesh surfaces finishing were corrosion rate 0.1615 (mpy), protection efficiencies 99.7 (PE %), porosity percentages 0.4 (PP %) ,and polarization resistances 444.5 (ohm).

Conflicts of interest

There is no conflict interesting between authors and any person or authorities and the idea of research and its results own to the authors

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