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Corrosion Behavior of Anodized Pure Zinc in Sea Water

Abstract- *In the present work an electrochemical anodizations of pure Zn sheet result in the ZnO porous film structure in alkaline solution (15% ammonium florid) by using constant voltage technique at a range of (2-10) volt, for period time of 10 minutes at room temperature was studied .*
Atomic force microscope (AFM) used to investigate the topography and roughness of anodic film formed on the surface, it was found that the roughness of the anodic film is mainly depended on the anodizing voltage and its increase from 0.2 (as polished) to (2.9) nm after anodizing. Coating thickness also increases with an increase in voltage from 0 to 285 µm after anodizing. The corrosion behaviors of anodized and non-anodized of zinc specimens in sea water are obtained. The corrosion current density and corrosion rate are decreased with an increase in supplying voltage which increases anodic film thickness.

Keywords: *Anodizing, Zinc, Constant Voltage, Corrosion rate, Polarization*

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1.Introduction

Zinc oxide (ZnO) is a widely used in semiconductor with high bound energy (60 meV) [1]. It is also used in different instruments like sensors of gases, transparent electrode conducting (TEC) in thin films of solar cells sheets, surface audio wave and microphone applications. It's only electro-optical properties, especially, permit it's use as ultraviolet (UV) light-transmit diodes, also blue bright devices [2] , for this intention, wide articles was published towards to promote the band hiatus emission characteristics of the zinc oxide coating films [1-3].

Recently , many procedure were published to produce zinc oxide (ZnO) nanostructures, for instance vapor phase transmit [4, 5], metal organic, chemical vapor deposition [6–7], laser supply [8-9], thermal decomposition , a template-guide procedure , and chemical composition have been applied to product zinc oxide (ZnO) with hexagram shape, quantum points, nano tubes, nano wires, etc. These ZnO nanostructures in general produced by high temperature technique [4–10] by treatment procedure [11, 12]. Anodizing process is a famous way to produced self-organized structures with low dimension, like porous Al_2O_3, TiO_2, and ZrO_2. Suitable composition of produce zinc oxide (ZnO) nanostructures have an ability to get useful applications in producing materials with nanostructured shaps. Till now, little articles have reported a production procedure process to produce ZnO by anodization of zinc metal by applied high current density. Szpaek and Gabriel have explained the production of various ZnO structures by using different conditions in anodizing process [10-11].

Baugh [4] study the corrosion rate and polarization behavior of Zn in different aqueous solutions like NH4C1, $NaClO_4$ and Na_2 SO_4 media. The study confirms that the create of oxide surface film in weak acidic solution by differential conditions capacity measure over a broad range of frequency. The anodic coated layer work as protection film and their structure and composition are the important agent that define the photoelectric and electrical characteristic of the photo electrochemical solar cell. X-ray diffraction (XRD) results [5-7] have specified that the formation of anodic film layer on the metal surface with white color and its consist of ZnO as main composition of the surface which have a good properties of semiconducting.

Anodising is an electrochemical process that converts the surface of metals to an insoluble oxide coating. This coating film improves the corrosion rate and has wide applications such as decorative surfaces, a good basis for painting and othercoating methods, also special mechanical and electrical properties. Anodizing process has long been used

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in decoration and frilly metals surface or to increase the resistance of corrosion [1]. This operation is a high cost-effective process to create regular and a good adhesive thin films oxide on metal's surface [2] also the surface treatment is an important method used to increase a different types of nanostructures on numerous surface of metals, with the films produced widely used in various applications [3]. Metal oxides show a wide properties range of properties depending on interconnection between the reaction of metal ion and oxygen and the crystal structure of the metals.

Therefore, the oxides film formed on the metal surface have been the excellent materials in different purposes like light emitting diodes, varied types of transistors and solar cells [7].

The aim of the this work is to investigate the formation of zinc oxide film on zinc specimen by means of ammonium florid NH_4F (as electrolyte) in anodizing process using constant voltage technique and study the properties of the anodic coating layer and the effect of this layer on corrosion resistance.

2.Experimental work

I.Metal Preparation

Pure zinc sheet (99.98 % purity of 5mm thick) (chemical composition listed in Table 1), is used as working electrode in anodizing cell, the specimens were cut in to the desired size (3x2 cm). Zn sheet was immersed in acetone for 5 min.to remove oil, grease and common dirt. The specimens were rinsed in running water followed by distilled water to removal the traces of acetone on the specimen.

Metals	Zn	Al	Si	P	Cu
Standard by European Standard EN 988	98.81	0.22	0.06	0.26	0.65

Table 1: Standard chemical compositions of pure zinc.

The surface of the pure zinc was ground using emery paper up to 1000 grit to produce a flat surface. The specimen therefore has to be polished with 0.5 µm diamond paste on red felt cloth. The specimens were neatly cleaned by water, rinsed with acetone and dried under air then store in a disecater over silica jel.

3.Anodizing procedure

The zinc specimen was attached to the positive terminal of the D.C. power supply where it becomes (anode) while the stainless steel sheet, was connected to the negative terminal to be (cathode). Figures (1) and (2) demonstrate a photo and a schematic outline for the entire structure of the anodizing process respectively.

The zinc object (anode) and cathode electrode are immersed in a solution of 15% NH_4F in the anodizing vessel. Before the power supply switched on, the voltage must be fixed at the desired value, when power supply switched on the current increased gradually and the voltage maintains at the fixed value for the remaining time of the experiment.

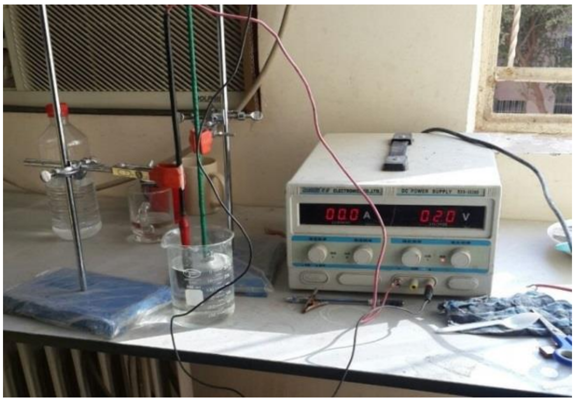


Figure1: Photograph of the complete assembly of the anodizing apparatus.

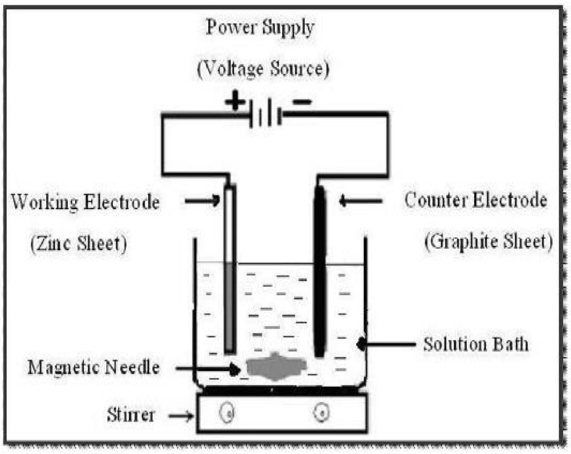


Figure 2: Schematic outline for the complete entire structure of the anodizing process.

When all necessaries conditions of experiment are set up, the power supply was switched on so that constant current was obtained .The parts were immersed in the electrolyte immediately when the power supply was switched on. Anodizing process provides a protection for the specimens from dissolution, also care have been taken during the loading specimen in order to prevent short circuit i.e. burning the surface.

the power supply was switched off at the end of the required anodizing time, and the specimen (anode) was removed from anodizing cell immediately to prevent the dissolution of anodic film. Running water used to rinsed the specimen followed by double distilled water to elimination the excess electrolyte on it, then dried in a furnace at 60 ^oC for 20 min. then store in disecater for 30 minutes.

The anodized specimens were analyzed with Atomic force microscope (AFM) and coating thickness measurement.

For estimation the corrosion rate, polarization system was completed by utilizing automated potentiostate sort MLAB200 in a 1-liter measuring glass comprising of working, counter and reference anodes. The working terminal was anodized and non-anodized pure zinc, held by steel rode intended to hold the samples, it was protected with shrinkage tube to give the awful contact and hold it steady in the cell. The counter (Auxiliary) terminal was a platinum electrode (Tacussel Pt-F05/30) situated specifically inverse to the (W.E) . Standard calomel electrode (SCE) was used as reference electrode and insert in Laggin-Haber tube. The dimension between the Laggin-Haber capillary tube and working electrode surface set at about 1 mm to limit the trial mistake because of IR drop; the polarization started beneath the consumption potential around 250mV in cathodic area and after that expanded with clear rate of 10 mV/min. to the anodic area possibilities. A thermometer was utilized to keep up the arrangement temperature inside 1^oC at room temperature as appeared in figures 3 and 4.The corrosion current density is measured from polarization curve in order to use in corrosion rates calculations. Corrosion rates are calculated using the following relationship (8):

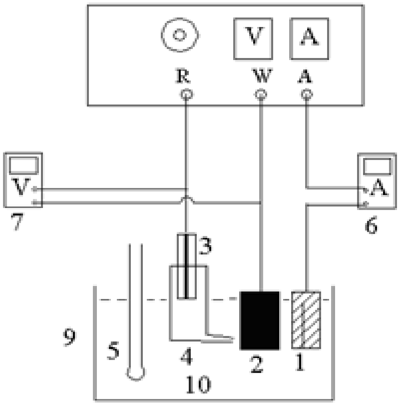
$$CR\ (mpy) = \frac{0.13\ *\ i_{corr} * E.W}{\rho}$$

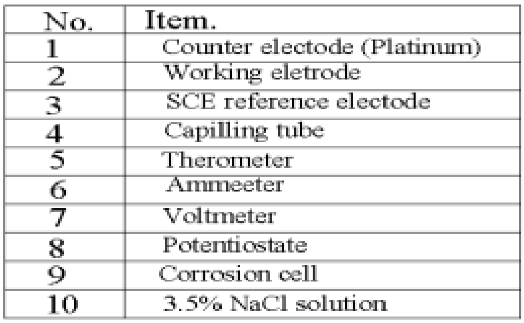
where:

i_{corr} : corrosion current density, $\mu A/cm^2$

E.W.: specimen equivalent weight (65 g. / equivalent).

ρ: Specimen density (7.14 g./ cm^3) .





No.	Item.
1	Counter electode (Platinum)
2	Working eletrode
3	SCE reference electode
4	Capilling tube
5	Therometer
6	Ammeeter
7	Voltmeter
8	Potentiostate
9	Corrosion cell
10	3.5% NaCl solution

Figure 3: Schematic diagram for potentiostat equipment.

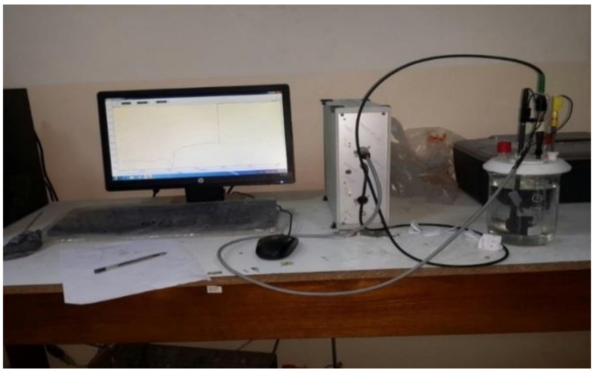


Figure 4: Potentiostat equipment for electrochemical test.

4.Results and Discussions

I.Coating Thickness Measurement

Eddy current testing process (coating thickness gauge TT260 ITALY made) was used to investigate the coating thickness, as shown in Table 2, the coating thickness increases with an increase in the supplying voltage due to the thick layer that precipitates on the low carbon steel surface.

Table 2 Coating thickness at different voltage supply.

No.	Anodizing Voltage Volt	Coating Thickness µm
1	as	0
2	2	197
3	4	232
4	6	240
5	8	270
6	10	285

Figure 5 demonstrates the effect of supplying voltage on film thickness of pure zinc. Thickness of (ZnO) is Increasing directly with the increasing in supplying voltage. Normally, the oxide film thickness increases to a maximum value at which higher voltage promote the oxygen reaction with pure zinc, i.e. to create the zinc oxide.

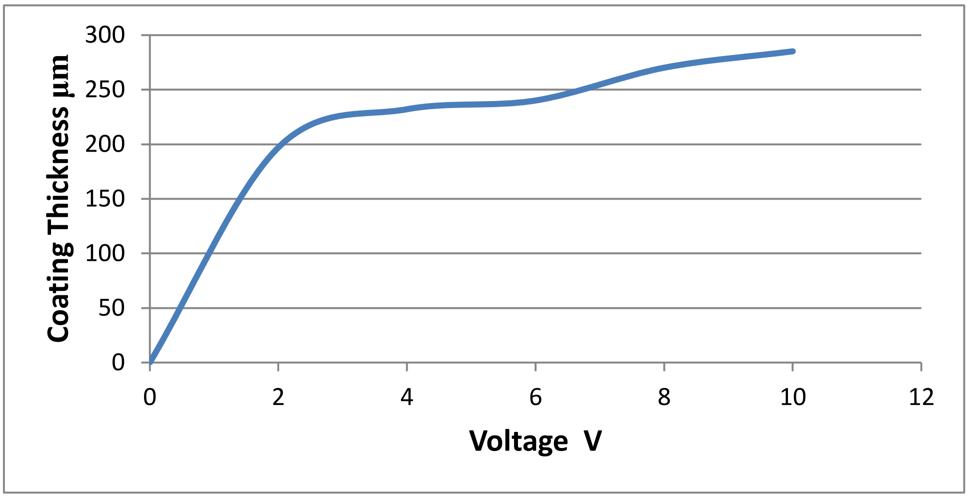


Figure 5: The effect of supplying voltage on film thickness.

N. Diomidis (9) indicated that an increase in anodizing voltage leads to increase the rate of growth of anodic film thickness when study the composition of coating film create on Zn by anodizing process by using Silicated based as electrolyte. This study also shows that the influence of hydrodynamics on the structural properties and corrosion resistance of the new film formed on the surface of the metal. The dissolution of the Zn base is observed to be desired for the precipitation of silicate-rich coating layers.

I.AFM Investigation

The roughness of surface film before and after anodization process was determined by AFM as shown in Figs. 6 and 7. The AFM image revealed that a rough film formed on the zinc surface after anodizing. The root mean square (RMS) roughness increases as the time increase due to the anodic layer formed on the surface. The type of this layer appears as spherical or semi-spherical. Precipitation process depends on surface cleaning.

The roughness increases by increasing the supplying voltage of anodizing. Table 3 shows the effect of anodizing voltage on surface roughness. This may be due to rapid film growth with increasing applied voltage which enhances growth of nanoporous film. This can be shown in Figure 7.

A. chour, et.al. (10) Indicated in his study that the coating layer formed on the zinc surface is by anodizing process, consist of zinc oxide as mainly component and the surface becomes more rougher than the surface before anodizing due to the new layer create on the surface and the columnar structure becomes more obvious as the supply voltage value raises from 1.8 to 3.0 V. The increase in roughness of the surface film is due to the fact that the coating surfaces become nano-porous after electrochemical process.

Table 3: Roughness values for anodized pure zinc at different supplying voltage.

No.	Anodizing voltage Volt	Surface Roughness nm
1	as	0.2
2	2	0.9
3	4	1.3
4	6	1.7
5	8	2.2
6	10	2.9

Basheer [12] indicate that the roughness of the anodic film is mainly depend on the anodizing time and coating thickness, the ZnO layer create on the surface by anodizing process for magnesium alloy by alkaline solution at constant voltage.

Sami, and Basheer . [13], study the anodic layer formed on aluminum alloy (3003) by using (15% H_2SO_4) as electrolyte, the study shown that the micro hardness and surface roughness for the anodized samples are higher than that of un-anodized samples due to very much thicker oxide film created on the surface for anodized specimens, while atmospheric oxide film formed on the surface of un-anodized specimens. The anodic film was improved different properties like physical and chemical properties. And, the rates of corrosion for anodized samples are decreasing compare with un-anodized ones.

The polarization curves for anodizing alloy demonstrate that the breaks down potentials are transfer to more noble way compare with uncoated specimen because of anodizing process.

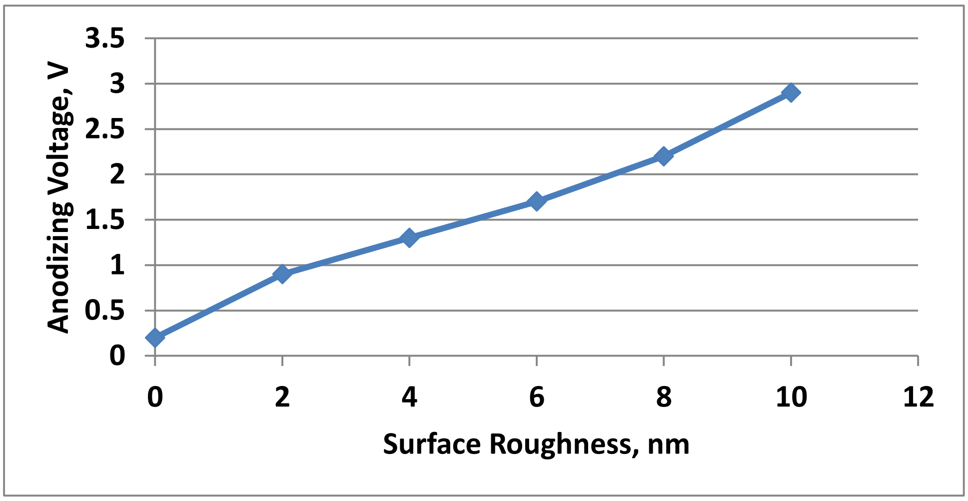
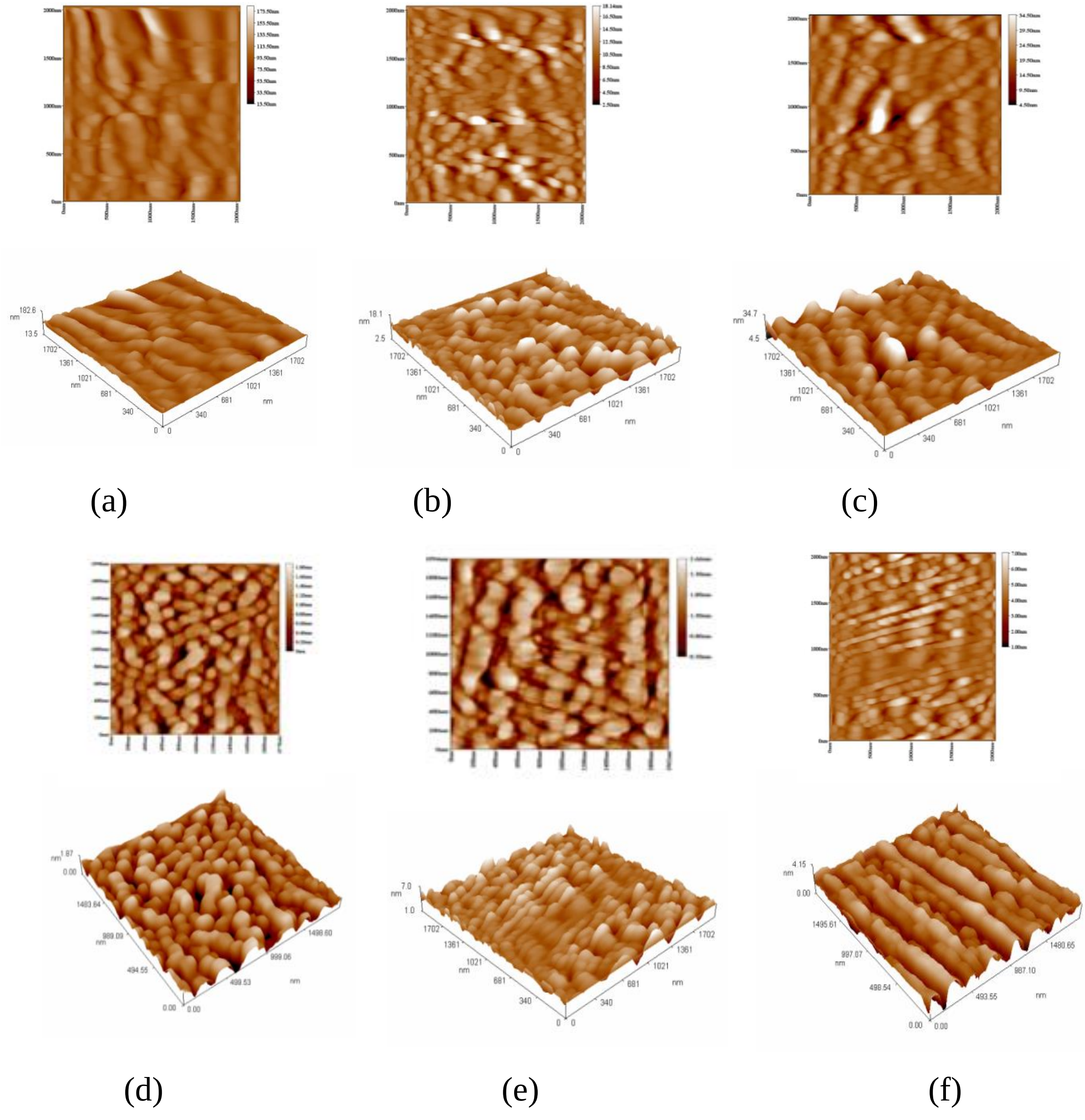


Figure6: The effect of supplying voltage on film roughness.



(a) (b) (c)

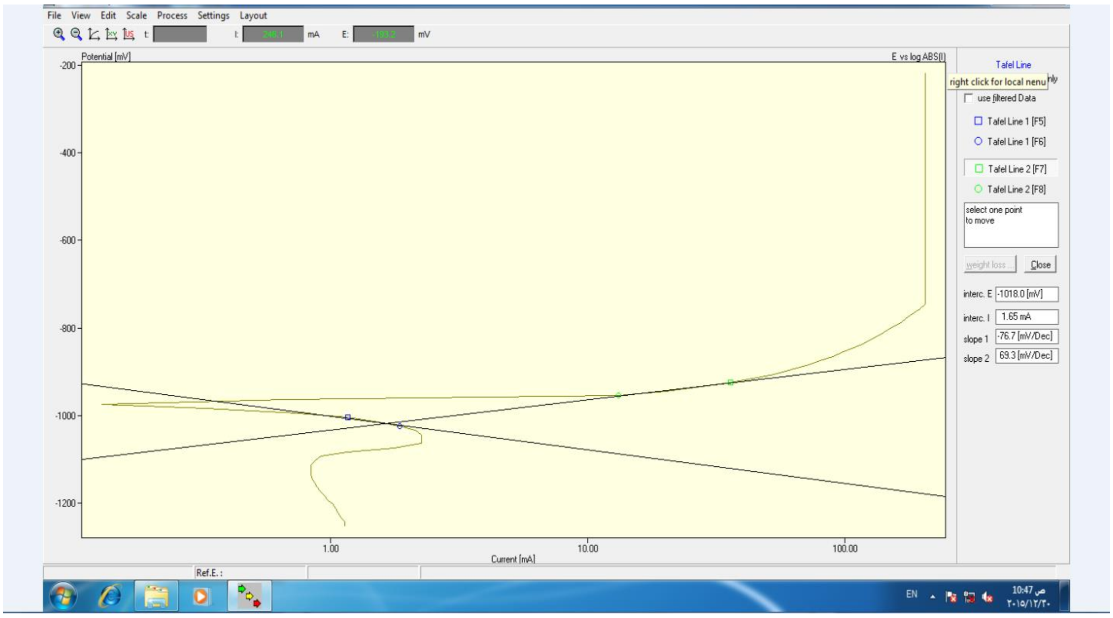
(d) (e) (f)

Figure 7: 2D and 3D AFM images for pure zinc with different supplying voltage (a) as polished (b) 2V (c) 4V (d) 6V (e) 8V (f) 10V

II.Polarization Measurement

Linear polarization measurements of anodized and non anodized zinc specimens in 3.5% NaCl solution are shown in figures (8-13). The polarization curves indicate the general behavior of cathodic and anodic regions. Tafel extrapolation method are used to calculated corrosion potential (E_{corr}) and corrosion current density (i_{corr}) , as shown in Table (4) and figure 14. It is obvious from Table (4) that the increase in supplying voltage for anodized specimens decreases the i_{corr} and corrosion rates. The extent of decrease in i_{corr} and corrosion rates is found to be a function of the anodized pure zinc with constant voltage, higher the supplying voltage, lower the values of i_{corr} and lower corrosion rate.

The corrosion potential increases in most cases in the noble direction with the increase in anodizing applied voltage. The observed positive shift (noble direction) in E_{corr} and the decrease in i_{corr} due to anodic oxide layer formed on the surface are shown in Table 4



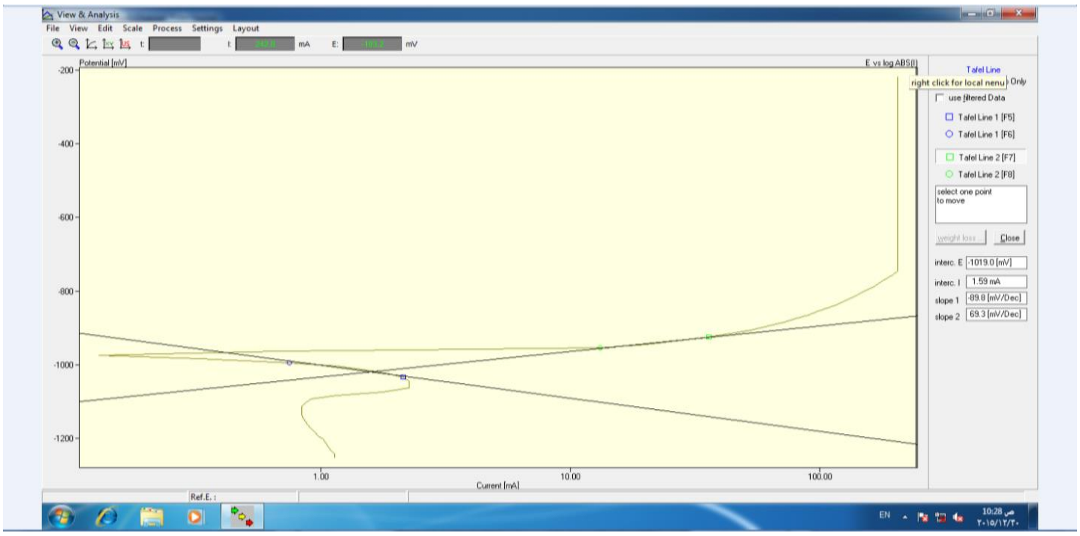
interc. E -1018.0 [mV]

interc. I 1.65 mA

slope 1 -76.7 [mV/Dec]

slope 2 69.3 [mV/Dec]

Figure 8: corrosion behavior of pure zinc before anodizing.



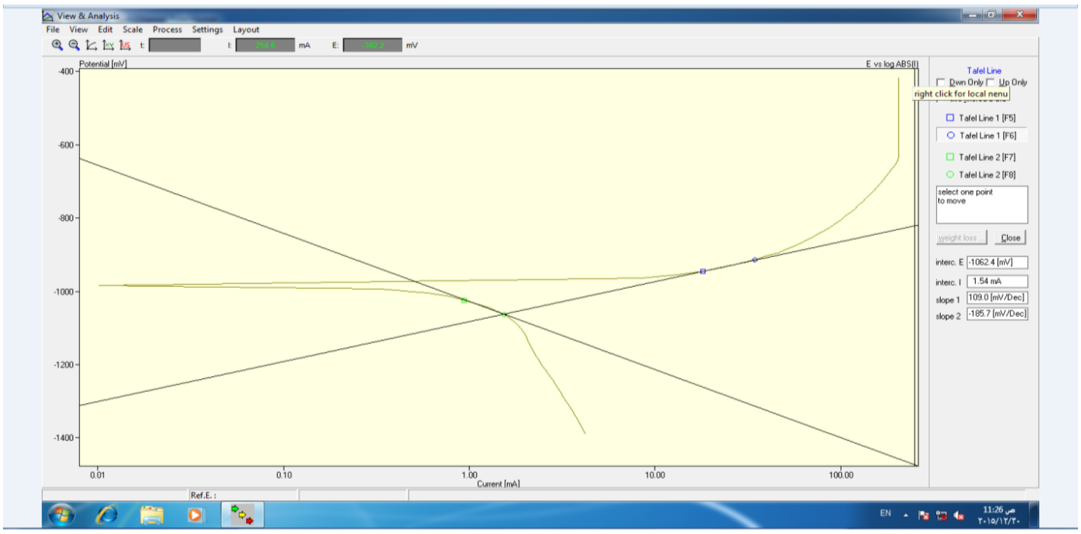
interc. E -1019.0 [mV]

interc. I 1.59 mA

slope 1 -89.8 [mV/Dec]

slope 2 69.3 [mV/Dec]

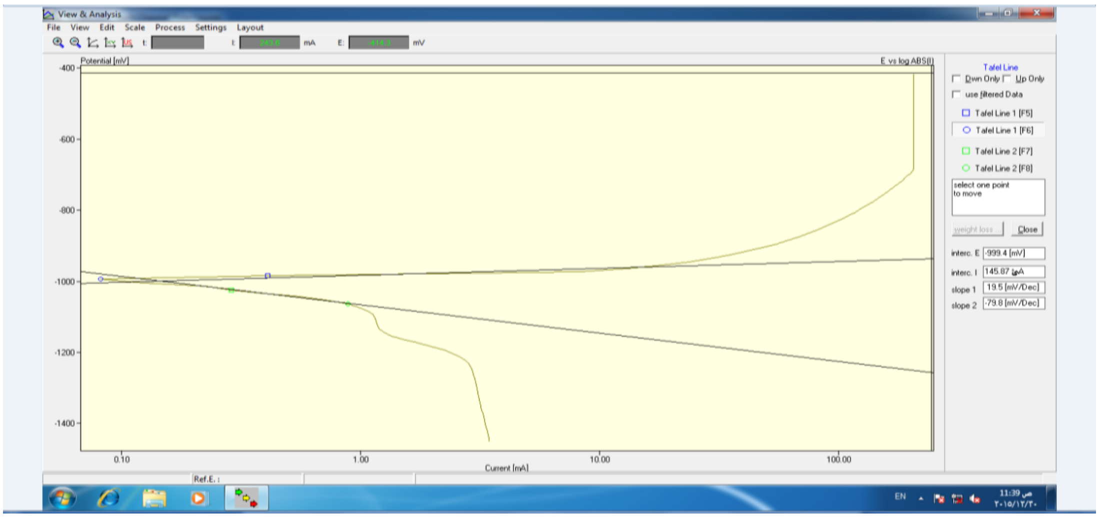
Figure 9: Corrosion behavior of anodized zinc at 2V.



select one point
to move

interc. E -1062.4 [mV]
interc. I 1.54 mA
slope 1 109.0 [mV/Dec]
slope 2 -185.7 [mV/Dec]

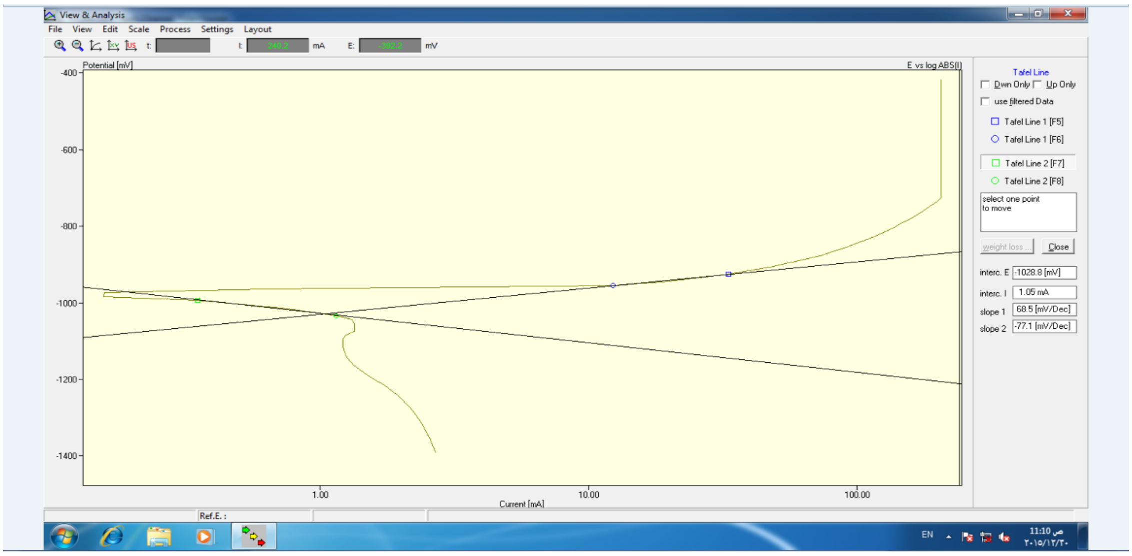
Figure 10: Corrosion behavior of anodized zinc at 4V.



select one point
to move

interc. E -999.4 [mV]
interc. I 145.87 µA
slope 1 19.5 [mV/Dec]
slope 2 -79.8 [mV/Dec]

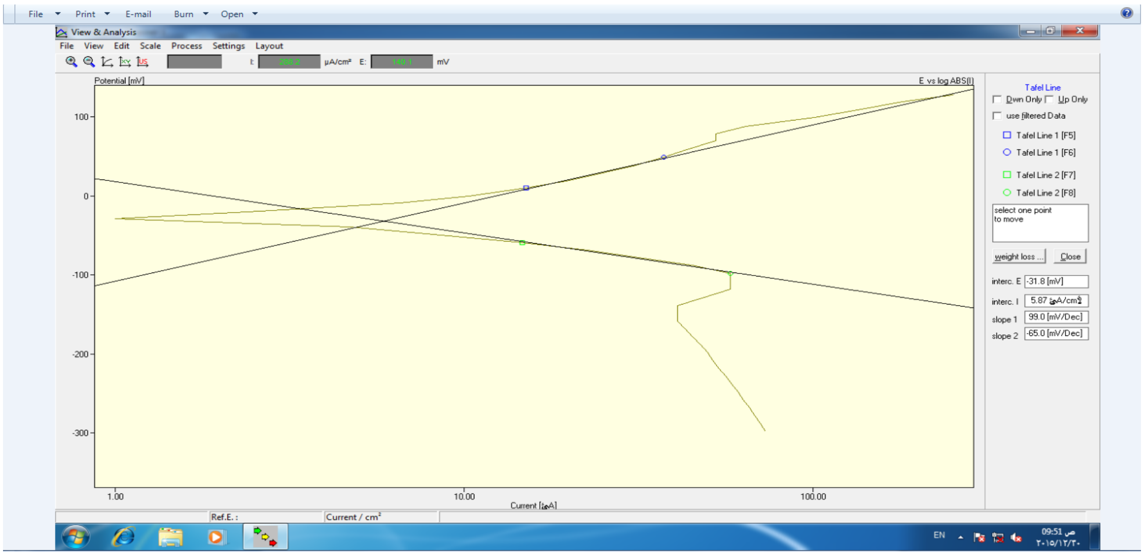
Figure 11: Corrosion behavior of anodized zinc at 6V.



select one point
to move

interc. E -1028.8 [mV]
interc. I 1.05 mA
slope 1 68.5 [mV/Dec]
slope 2 -77.1 [mV/Dec]

Figure 12: Corrosion behavior of anodized zinc at 8V.



I: 288.2 µA/cm² E: 140.1 mV

select one point to move

interc. E -31.8 [mV]

interc. I 5.87 µA/cm²

slope 1 99.0 [mV/Dec]

slope 2 -65.0 [mV/Dec]

Figure 13: Corrosion behavior of anodized zinc at 10V.

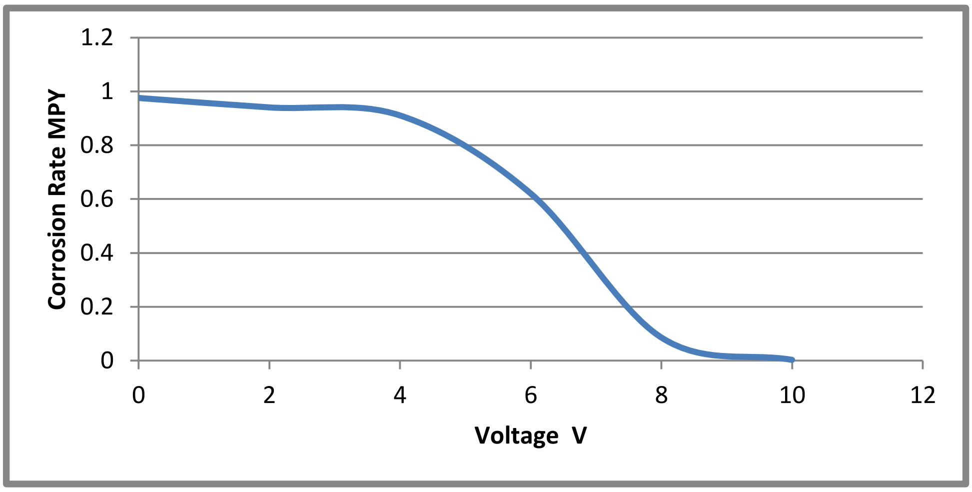


Figure 14: The effect of zing anodizing on corrosion rate

Table 4: Corrosion rate of anodized pure zinc at different supplying voltage.

No.	Anodizing Voltage Volt	Anodizing Time min.	I corr. mA/cm^2	Ecorr. mv	C.R. Mpy
1	as	10	1.65	-1018	0.976
2	2	10	1.59	-1019	0.941
3	4	10	1.54	-1062	0.911
4	6	10	1.05	-1028	0.621
5	8	10	0.145	-999.9	0.086
6	10	10	0.005	-31.8	0.003

Conclusions

Zinc material is protected from corrosion by anodic film at different voltage supply (2, 4, 6, 8 and 10 volt) at constant time which produced thick film of ZnO.

Corrosion resistance at 10 volt is improved due to its anodic film.

The anodic film create on the surface at 10 V has a rough surface and dark gray color, it mainly consisted of zinc oxide, also has the best corrosion resistance due to the higher coating thickness

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