Electrochemical Behavior of Chemical Conversion of Coated Aluminum 1100Al in a Neutral Tartrate Solution

Khalid H. Rashid iD

Abstract

   1100 Al specimens were anodically oxidized in different concentrations of tartaric acid-tartrate solution (pH=7) in 1, 1.75, 3.25 and 4 wt % at temperatures of 30, 37.5, 52.5 and 60 ℃ by applying a range of potentials of 30, 37.5, 52.5 and 60 V at exposure times of 40, 47.5, 62.5 and 70 min.. These four variables are manipulated through the experimental work using Box – Wilson experimental design where second order polynomial model was proposed to correlate the studied variables with the thickness of anodic film of aluminum alloy (1100) to estimate the coefficients of the proposed polynomial adopted via statistica software. Optimum conditions for achieving the maximum film thickness are obtained from optimizing the above correlation and are found as follows: temp. = 44℃, acid conc. = 2.8 wt %, voltage = 43.6 V, time = 54.6 min.. Stagnate Solutions of 3, 5, 10 and 25 wt % Nacl at 25℃ have been investigated using polarization technique at optimum conditions for anodizing. The most important feature achieved was the great difference in behavior between the anodic polarization curves for bare and anodized aluminum in different concentrations of Nacl solutions. The corrosion rates for anodized specimens are lower than those for unanodized ones. The polarization behavior of anodizing specimens shows that the breakdown potentials are shifted to more noble direction than bare specimens which is more pronounced in 25 wt % Nacl solution due to anodizing.

Keywords: Aluminum Alloy (1100), Anodizing, Tartrate Solution, Neutral Conditions, Box-Wilson, Polarization.

التصرف الكهروكيمياوي الناتج عن أنودة سبيكةالمنيوم 1100 في محلول الترترات المتعادل

الخلاصة

تم أنودة نماذج من سبيكة الألمنيوم 1100 في تراكيز مختلفة من المحلول المتعادل لحامض الترتريك و ملح ترترات الأمونيوم في (1, 1.75 , 3.25 , 4)% وزنا عند درجات حرارة (30 , 37.5 , 52.5 , 60) ºم و جهود مسلطة بمدى يتراوح بين (30 ، 37.5 ، 52.5 , 60) فولت عند فترات زمن تعرض يتراوح بين (40 ، 47.5 ، 62.5 , 70) دقيقة . الأربع المتغيرات تم معالجتها من خلال تصميم التجارب العملية بأستخدام طريقة (Box - Wilson) لربط المتغيرات أعلاه بمعادلة من الدرجة الثانية تشير الى العلاقة بين المتغيرات الأربعة وسمك طبقة الانودة لسبيكة الألمنيوم (1100). من خلال أيجاد معاملات المعادلة المتعددة الحدود المقترحة و المعتمدة في البرنامج الإحصائي (Statistica analysis) . تم تحديد الظروف المثالية للحصول على أعلى قيمة لسمك الطبقة بواسطة أختيار الأفضل للمعادلة المتعددة الحدود من الدرجة الثانية وكانت 44ºم درجة الحرارة و 2.8 % وزنا تركيز الحامض و 43.6 فولت جهد مسلط و 54.6 دقيقة زمن تعرض. أستخدمت محاليل كلوريد الصوديوم الساكنة بتراكيز (3 , 5 , 10, 25) % وزنا عند درجة حرارة 25 ºم التي درست بأستخدام تقنية الأستقطاب عند الظروف المثلى للأنودة.

* Chemical Engineering Department, University of Technology /Baghdad

الميزة الأكثر أهمية التي أنجزت كانت الأختلاف الكبير في السلوك بين منحنيات الأستقطاب الأنودية لنماذج الألمنيوم المحمية وغير المحمية في محاليل كلوريد الصوديوم ذات التراكيز المختلفة . في العموم لوحظ بأن معدلات التاكل للنماذج المحمية أقل من النماذج غير المحمية. ويشير سلوك الأستقطاب للنماذج المحمية بأن جهود الأنكسار (التنقر) أزيحت بأتجاه الأكثر نبلا (الأتجاه الموجب) مقارنة مع المعدن الأصلي نتيجة الأنودة وأكثـــــر وضــــــوحا فـــــي محلـــــول الصـــــوديوم ذات التركيـــــز 25 % وزنـــــا.

Introduction

It has been known that, when Al is anodically oxidized in neutral solutions in which oxide solubility is very low, adherent compact films of a thickness of 14 Å/V are formed[1]. Tartrate coatings on aluminum alloys have the advantage that they are easy to apply and that commercial information is readily available. However, the tartaric acid is normally harmful to body due to its toxicity [2]. The corrosion behavior of aluminum and its alloys is quite good in many aqueous solutions in the pH range of 4-9 due to the formation of an insoluble and protective aluminum hydroxide layer [1]. Nevertheless, the corrosion resistance decreases noticeably when the pH value changes away from the near neutral conditions as a consequence of the Al $(OH)_3$ layer dissolution.

Aluminum alloys are extensively employed as structural components in the industrial practice, and some surface treatments like anodizing are used to improve their corrosion behavior. However, no substantial improvement is obtained in the most severe conditions [3].

Anodizing may be used to enhance the corrosion resistance of aluminum and its alloys. An electrolytic process is used to thicken the surface film

And produce a hard, compact strong and highly adherent layer. Sealing has a great effect on the corrosion Resistance of the oxide coating. If the coating is not completely sealed, corrosion as well as staining may take place very rapidly. Conversely, properly sealed anodic coatings are being successfully used in the architectural field [1]. In general, the alloys with higher aluminum contents are more resistant to corrosion [4]. The characteristic of the coating layer obtained by anodizing process is very important since the alloy is used as an electric capacitor [1, 3].

After study on research and publication studies before, not found on any using of 1100 Al alloy but treating deal with another types of alloys. To know an idea of this research not found before and connect with scientific and applied modern subjects which serve the plan project scheme of development and from including of scientific and research dependent lines in department.

This work aims to study the electrochemical behavior of 1100 Al surfaces covered by a chemical conversion of coating obtained by anodizing process in a neutral tartaric acid-tartrate solution of (pH = 7) and compare the result with that of the same aluminum alloy surface not anodized at the optimum conditions obtained experimentally (temp. = 44ºC, acid conc. = 2.8 wt %, applied voltage = 43.6 V, time = 54.6 min.).

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Experimental Work

The working electrodes of (2×3 cm) aluminum 1100 Al in foil coupons of a tag shape were used as specimens. They were dipped in a solution of (20 g/l) HCl – (35 ml/l) H_3PO_4 at 85ºC for 3 min and then washed thoroughly with distilled water. The specimens were then immersed in solutions containing different concentrations of tartaric acid with ammonium hydroxide added to bring the (pH = 7) with stirring to temperatures of 30, 37.5, 52.5, and 60ºC. In this investigation, the corrosion behavior of resulting coating layer because of anodizing process and of the nonanodizing aluminum alloy is tested by immersion in stagnate Nacl solution of concentrations of 3, 5, 10 and 25 wt % Nacl solutions and using potential / current relationship recorded through polarization curves and potential as E_{corr} vs. exposure time during the corrosion test.

Open circuit potential (E_{corr}) was carried out in a cell described in Figure 1 and measured from off - circuit potential - time measurements and polarization was carried out in electrochemical cell with electrical circuit shown in Figure 2 which consists of three compartments for the working, counter and reference electrodes separated by narrow-porous frits. The counter electrode was a platinum electrode of (1.5×3.5cm), held by plastic plate set directly opposite to the working electrode.

The reference electrode was a saturated calomel electrode bridged by a laggin - Haber probe. The distance between the electrode surface and the laggin-Haber capillary was set to 1 mm to minimize the experimental error due to IR drop.

Table 1 presents a summary of the experimental conditions in terms of variables and their levels while Table 2 shows the number of experiments that must be done.

The potentiostate device using in this article is modern computerize type. And by this device we got the real corrosion potential (E_{corr}) (open circuit potential) with respect to reference electrode (SCE) that specified before. And take higher values and lower from this potential by automatic form and limitation restriction confinement control scan rate on device by rate 10 mV/min..

Reference electrode calibration was carried out by 30 % Kcl solution for activation.

pH meter calibration was carried out by using buffer solutions (4,7,9) before working start.

Controlling on temperature by using heater-stirrer magnetic plate and glass water bath pyrex type and using ordinary heater-stirrer with thermostat.

Rotation velocity was adjusted at very low speed 1 rpm for homogenous distribution to heat. And this value is fixed for all experiments.

Results and Discussion

The corrosion resistance of 1100 Al (before and after anodizing) was evaluated by following its corrosion potential. Figure 3 and Figure 4 show the open circuit potential of protected and unprotected aluminum alloy in 3, 5, 10 and 25 wt % Nacl solutions at 25ºC and immersion time of about 4 hours. It is clear that

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The effects of immersion time and concentrations of Nacl solutions on the electrode potential are illustrated in Figure 3 and Figure 4. It generally shifts to more positive direction in all concentrations of Nacl solutions studied, and this shift in potential is more pronounced in the order:

25 wt % Nacl > 10 wt % Nacl > 5 wt % Nacl > 3 wt % Nacl

Figure 3 shows that the potential increasing E_{corr} in open circuit potential after protection by a little amount with comparative with Figure 4 open circuit potential before protection, due to film Al_2O_3 formation was prevented electrolyte solution from attack basic metal surface.

Figures 5 and 6 show the anodic and cathodic polarization curves of unprotected and anodized 1100 Al in (10 and 25 wt %) Nacl solutions at 25ºC. In these figures it can be seen that 10^4 to 10^5 reduction in the anodic reaction rate of 1100 Al electrode for unprotected (not anodized) in (10 and 25 wt %) Nacl solutions.

It can be concluded the figures demonstrate stable passivity effects, this behavior is divided to three regions (active region, passive region, transpassive region). It is important to note that during the transition from the active to the passive region, a 10^3 to 10^6 reduction in corrosion rate is usually observed [5]. The actual cause for this unusual active - passive - transpassive transition is not completely known [5]. It's a special case of activation polarization due to the formation of a surface film or protective barrier which is stable over a considerable

range of oxidizing power and is eventually destroyed in strong oxidizing solutions [5].

Tafel curve in polarization diagram indicate to metal behavior, at time Al oxidize to positive Al ion with releasing electrons (anodic) and another time behave reduction behavior (cathodic) were Al ion take electrons and shifts to Al element, equation become
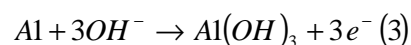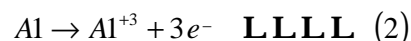
$$Al \Leftrightarrow Al^{+3} + 3\,e^- \quad \textbf{LLLL} \quad (1)$$
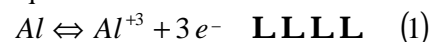
At potentials more positive than E_{corr}, corrosion rate increases, and reaches a maximum at the passivation potential of $E_{PP} = -0.3057$ and $- 0.497$ V.

The sudden drop in corrosion rate as a result of formation of a protective film is because the Al species become more thermodynamically stable than the Al^{+3}.

At passive zone, the current density is maintained at a low and steady level until the breakdown of the protective film begins at E_C (critical pitting or breakdown potential) $= -0.2002$ and $- 0.06312$ V.

Uhlig [6] reveals a scatter of values for this parameter E_C , it varies according to both metallurgical and environment conditions …etc.

It is believed that this gradual increase in corrosion potential is most likely the result of the formation of an insoluble and protective aluminum hydroxide layer according to the anodic reactions which takes place on the metal surface.

$$Al \rightarrow Al^{+3} + 3e^- \quad \textbf{LLLL} \quad (2)$$

$$Al + 3OH^- \rightarrow Al(OH)_3 + 3e^- \quad (3)$$

The published data reveal a scatter of values for the open circuit

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potential of aluminum ranging over several volts under identical experimental conditions [7, 8, 9].

It can be concluded that the variation in electrode potential with time depends on and is affected by material or alloy purity, surface treatment of the alloy and oxygen contact of the electrolyte…etc.

Suppressing the kinetic of anodic polarization curves at anodic sites on the surface is more pronounced in Nacl solutions of concentrations (3, 5 and 10 wt %) anodized specimens than Nacl solution of 25 wt % anodized specimens.

Figures 7 and 8 show the polarization curves of unprotected and anodized 1100 Al in (3 and 5 wt %) Nacl solutions at 25ºC showing unstable passivity. In these figures it can be seen that: The breakdown potential for 1100 Al in Nacl solution of concentration 5 wt % in Figure 7 is higher than that in Figure 8 due to the presence of oxide film on the anodized surface.

The type of behavior in the above figures is observed when cathodic process, E_{corr} is quite noble when the Al is completely passivated i.e., exhibition resistance to localized corrosion because of protection by the metal passive film.

E_{corr} for anodized aluminum 1100 Al shows a shift to more noble direction compared with bare specimens due to sharp anodic kinetic change because of anodized film formation.

Basheer [10] proved that the E_{corr} shifts to a more noble direction when anodizing process is applied to high pure aluminum.

Shaymaa [11] proved that the E_{corr} shifts to a more noble direction when anodizing process is applied to 7075 Al alloy.

Breakdown of potential of anodized specimen shifts to more noble direction due to the presence of oxide film on the anodized surface.

At potentials more negative than E_{corr}, the first region of all cathodic curves of unprotected is almost horizontal, characterized by a current density increasing rapidly with small variation in the applied potential. This is followed by an almost vertical region where the current density is practically independent of the potential, as also reported by Dibari and Read [12].

Hydrogen evolution on the cathode electrode is according to the following reactions:

$$H^+ + e^- \rightarrow H_{ads.} \quad \mathbf{LLLL} \quad (4)$$

$$H_{ads.} + H_{ads.} \rightarrow H_2 \uparrow \quad \mathbf{LL} \quad (5)$$
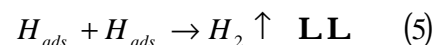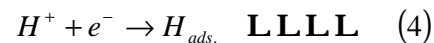
Table 2 shows the thickness of the oxide film of the 1100 Al specimens that was obtained in the experimental work. The specimens were designed according to the central composite rotatable design method by using Box-Wilson experimental design.

Conclusions

1- The potential difference increases to values (0.035, 0.039, 0.085 and 0.054 V) with decreasing in the concentration of Nacl solutions (25, 10, 5 and 3 wt %) respectively.

2- The cathodic branch of polarization curves is shown over a wide potential range that in the case of anodized specimens, the coating

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surface is more catalytic to the H_2 evolution reaction than on the unprotected surface, i.e., the anodized coating has an electronic resistivity of order:

Tartaric acid-tartrate solution anodized > Unprotected one.

3- The polarization data reveals that the final chemical conversion of coated oxide films formed under the above mentioned operating conditions is believed to behave as an insulating layer and have pronounced rectifying property.

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Table (1) Layout of experimental conditions

Variables	Levels				
Temperature (ºC)	30	37.5	45	52.5	60
Acid conc. (wt %)	1	1.75	2.5	3.25	4
Voltage (V)	30	37.5	45	52.5	60
Time (min.)	40	47.5	55	62.5	70

Table (2) Sequence of experiments according to control composite design.

| Exp. No.	Temperature (ºC)	Acid conc. (wt %)	Voltage (V)	Time (min.)	Film thickness, (Å)
1	37.5	1.75	37.5	47.5	10.99
2	52.5	1.75	37.5	47.5	7.93
3	37.5	3.25	37.5	47.5	6.99
4	52.5	3.25	37.5	47.5	5.93
5	37.5	1.75	52.5	47.5	4.99
6	52.5	1.75	52.5	47.5	3.995
7	37.5	3.25	52.5	47.5	2.99
8	52.5	3.25	52.5	47.5	1.99
9	37.5	1.75	37.5	62.5	2.98
10	52.5	1.75	37.5	62.5	2.99
11	37.5	3.25	37.5	62.5	3.96
12	52.5	3.25	37.5	62.5	4.98
13	37.5	1.75	52.5	62.5	5.87
14	52.5	1.75	52.5	62.5	6.91
15	37.5	3.25	52.5	62.5	8.95
16	52.5	3.25	52.5	62.5	9.68
17	30	2.5	45	55	1.98
18	60	2.5	45	55	2.11
19	45	1	45	55	2.11
20	45	4	45	55	3.44
21	45	2.5	30	55	4.22
22	45	2.5	60	55	5.06
23	45	2.5	45	40	6.22
24	45	2.5	45	70	8.33
25	45	2.5	45	55	9.66
26	45	2.5	45	55	9.66
27	45	2.5	45	55	9.66
28	45	2.5	45	55	9.66
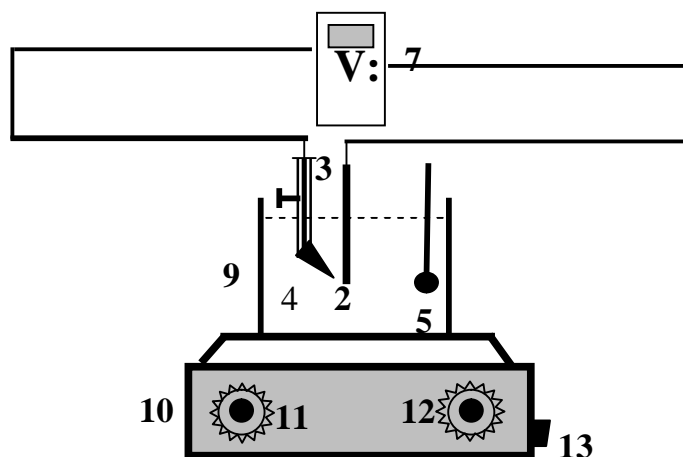
Figure (1) Schematic diagram for open circuit potential work
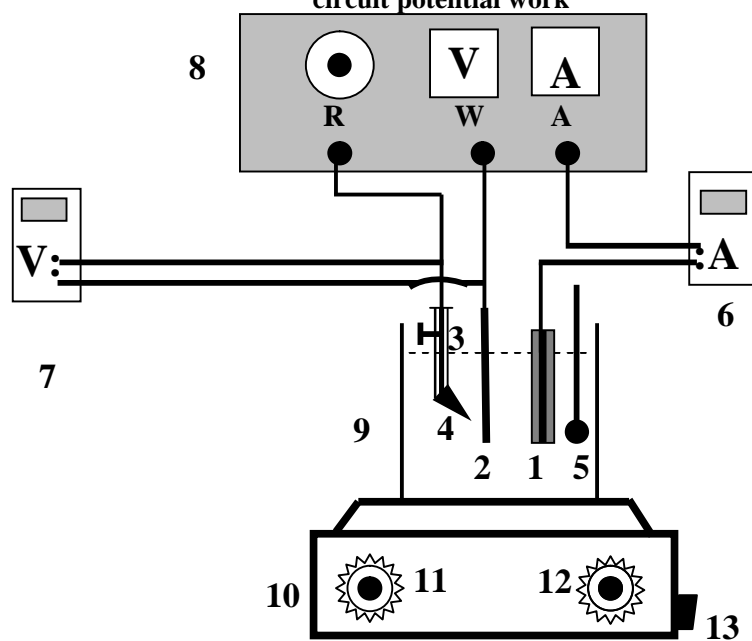
Fig

Figure (2) Schematic diagram for electric circuit for polarization work

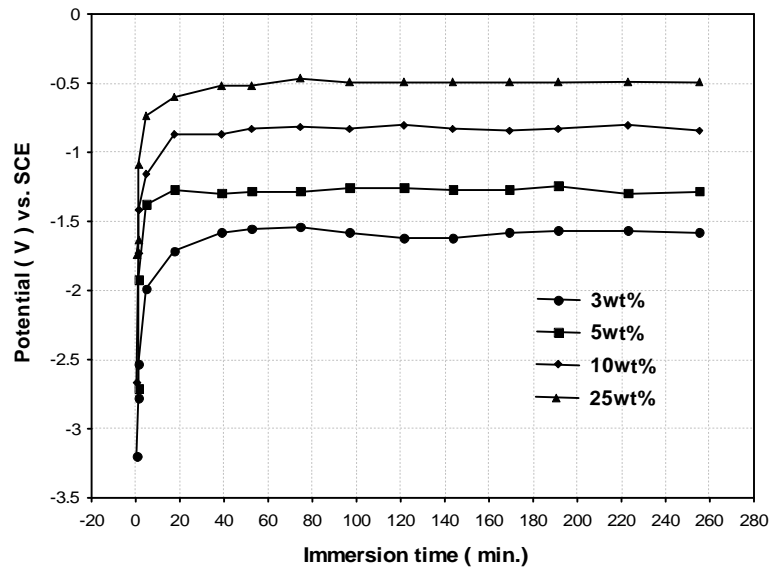|	
1 Counter electrode	2 Working electrode
3 SCE reference electrode	4 Capillary tube
5 Thermometer	6 Ammeter
7 Voltmeter	8 Potentiostate
9 Corrosion cell	10 Heater-stirrer magnetic plate
11 Thermostat	12 Stirrer regulator
13 Switch	

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**Figure (3) Open circuit potential of protected 1100 Al in different
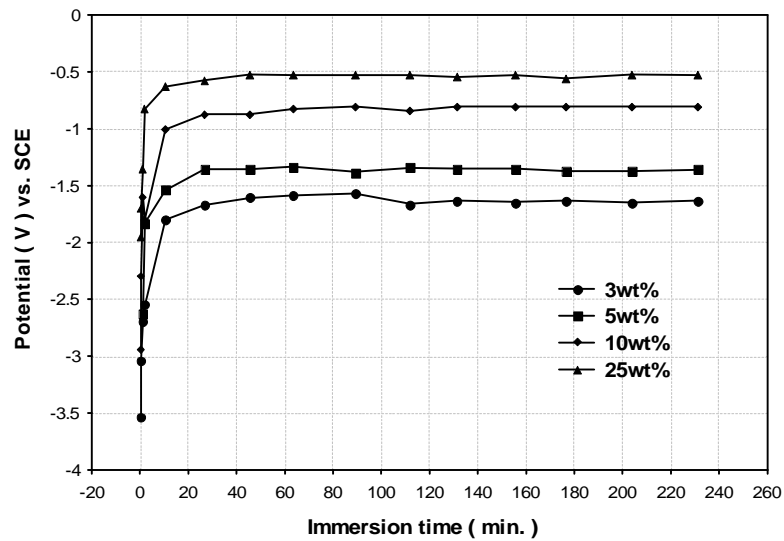Concentrations of Nacl solutions and 25ºC as a function of immersion time**

**Figure (4) Open circuit potential of unprotected 1100 Al in different
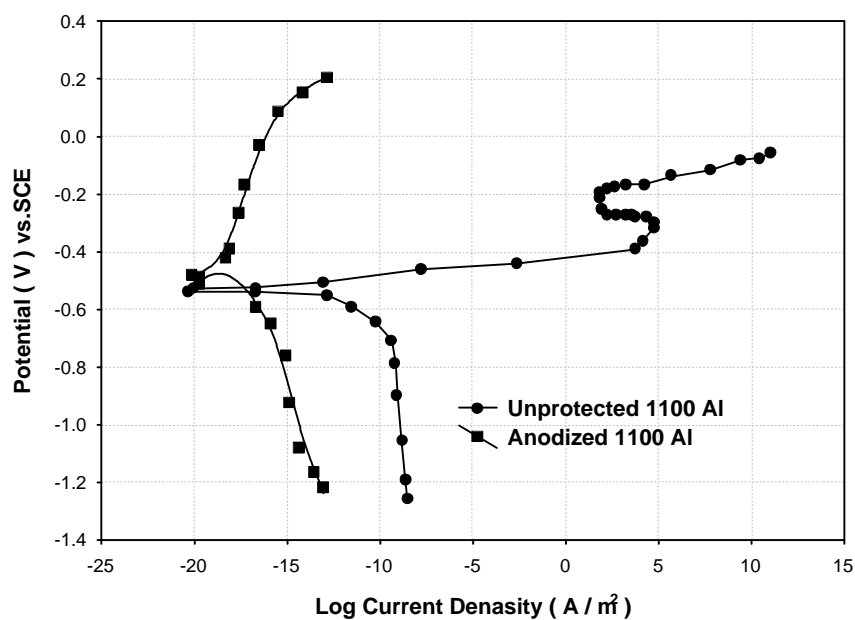concentrations of Nacl solutions and 25ºC as a function of immersion time**

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Figure (5) Polarization curve of 1100 Al in an Nacl solution 25 wt %
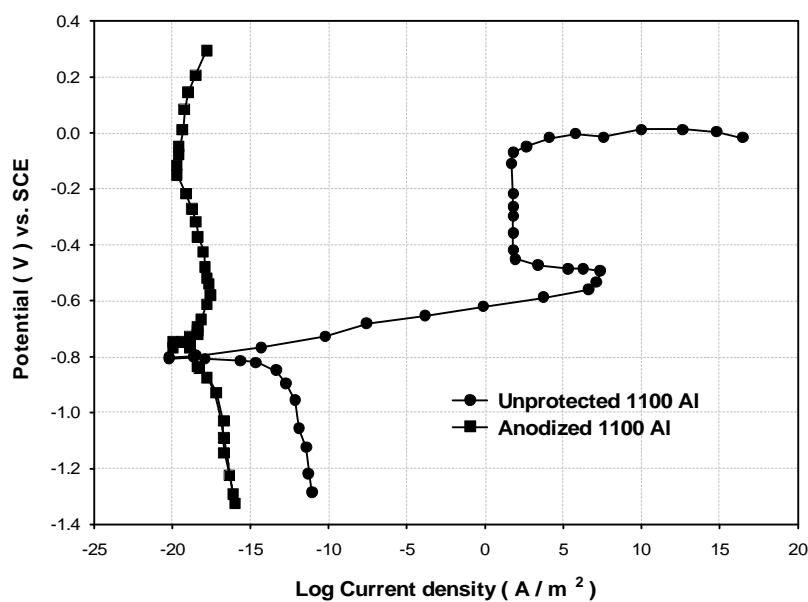

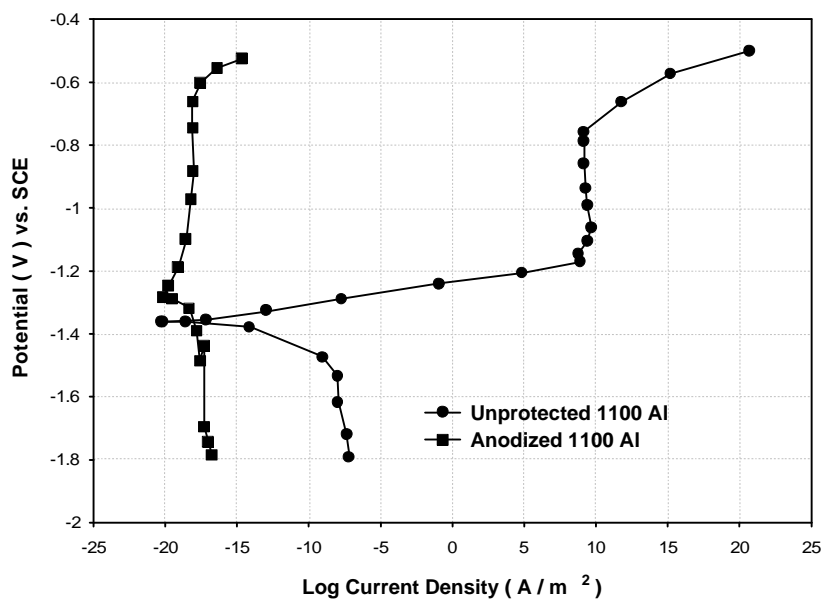**Figure (6) Polarization curve of 1100 Al in an Nacl solution 10 wt %**

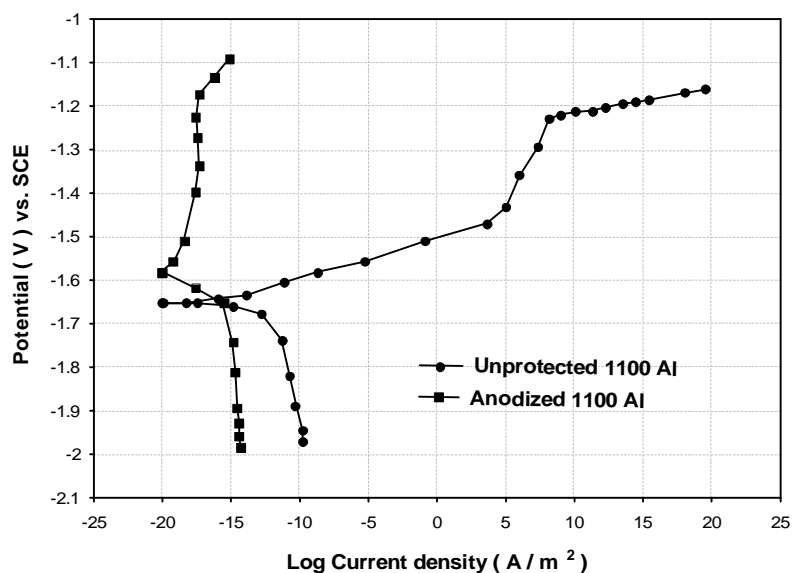**Figure (7) Polarization curve of 1100 Al in an Nacl solution 5 wt %**

Figure (8) Polarization curve of 1100 Al in an Nacl solution 3 wt %