

## Effect of (50% Isopropanol – 30% Methanol – 17% Xylene) Mixture on Corrosion Behavior of Pure Al and its Alloys in Simulated Fuel

**Dr. Rana A. Majed**

Materials Engineering Department, University of Technology/ Baghdad  
Dr.rana\_afif@yahoo.com

**Majid H. Abdulmajeed** 

Materials Engineering Department, University of Technology/ Baghdad

**Slafa I. Ibrahim**

Energy and Renewable Energies Technology Center, University of Technology/Baghdad

**Saja A. Abdul Maged**

Materials Engineering Department, University of Technology/ Baghdad

**Zahra`a S. Al-Saffar**

Materials Engineering Department, University of Technology/ Baghdad

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### Abstract

This work involves studying the effect of adding (50% Isopropanol – 30% Methanol – 17% Xylene) mixture on corrosion behavior of pure Al and its alloys in simulated fuel at room temperature. The results of electrochemical measurements indicate that the addition of this mixture lead to decreasing in corrosion rate values for pure Al and its alloys.

Electrochemical measurements were carried out by potentiostat at weep rate of 3 mV/sec to estimate the corrosion parameters using Tafel extrapolation method, in addition to cyclic polarization test to know the pitting susceptibility of materials in tested medium.

Generally, the cathodic Tafel slope ( $b_c$ ) were increased after adding mixture. But the anodic Tafel slopes ( $b_a$ ) were decreased except for Al-Cu alloy. The small anodic slope indicates the presence of a film on the surface of the tested material, which is less permeable and can even obstruct the metal dissolution reaction but still permits an electrochemical reaction to occur. This behavior can be achieved by the electronic density on oxygen atoms in alcohols.

**Keyword:** Al and its alloys, fuel, corrosion resistance.

**تأثير خليط (50%Isopropanol – 30%Methanol – 17%Xylene) على السلوك التآكلي للالمنيوم النقي وسبائكه في الوقود الصناعي**

الخلاصة

يتضمن هذا البحث دراسة تأثير اضافة خليط (50% Isopropanol–30% Methanol– 17% Xylene) على السلوك التآكلي للالمنيوم النقي وسبائكه في الوقود المحضر مختبرياً عند درجة

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

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حرارة الغرفة، وتبين نتائج القياسات الكهروكيميائية بان اضافة هذا الخليط تؤدي الى تقليل معدل سرعة التآكل للالمنيوم النقي وسبائكته.

اجريت القياسات الكهروكيميائية بالمجهد الساكن عند معدل مسح 3ملي فولت لكل ثانية لتقدير متغيرات التآكل بطريقة تافل الاستقرائية بالاضافة الى اختبار المنحني الحلقي لمعرفة حساسية المادة للتآكل في الوسط المحضر. لوحظ عموماً بان ميول تافل الكاثودية ازدادت بعد اضافة الخليط وان ميول تافل الانودية قد قلت ما عدا لسبيكة المنيوم-نحاس. ان النقصان في ميل تافل الانودي يدل على وجود غشاء واقى على سطح المادة المعدنية والذي يكون اقل نفاذية ويعيق تفاعل الذوبان المعدني وتلعب الكثافة الالكترونية على ذرات الاوكسجين في الكحول دوراً كبيراً في تعزيز الغشاء الواقى.

## INTRODUCTION

Corrosion inhibitors are used in conventional gasoline to retard corrosion in metal fuel systems components. Higher alcohols can be used to prevent or minimize phase separation in water – contaminated alcohol/gasoline blends. The prevention of phase separation would have definite benefits for overall drive ability as well as in corrosion of water – sensitive components such as aluminium. Others additive can be add to fuel such as acid neutralizers to protect surfaces against various chemical attacks, surface treatment of engine by treating the crankshaft with soft nitriding and by plating the cylinder bores with chrome, and shorter lubricant oil change intervals for preventing oxidization and deterioration are contained in the oil [1].

There are many studies concerned with corrosion of metals in fuel. Hamilta and co-workers [2] studied corrosion performance of Al-Si-Cu alloys in a synthetic condensed automotive solution, while other works [3,4] studied the corrosion in alcoholic fuels. Nie et al. [5] studied corrosion behavior of metallic materials in Ethanol-Gasoline alternative fuels.

Eiman and Jehad [6] studied the relative performance of compression ignition engine using various blends of diesel – ethanol fuels. Alessandra Regina Pepe Ambrozin et al.[7] studied metallic corrosion related to mineral fuels and biofuels utilization. The utilization of these fuels implies their closer contact to metallic materials, which comprise vehicle, storage, and transportation systems [7]. Thus, metallic corrosion could be related to fuels and biofuels utilization. They observed that the ethanol is the most corrosive and gasoline the least. Shosmith studied the release of the majority of radionuclides from spent nuclear fuel under permanent disposal conditions which controlled by the rate of dissolution of the  $UO_2$  fuel matrix. This study discussed the mechanism of the coupled anodic (fuel dissolution) and cathodic (oxidant reduction) reactions which constitute the overall fuel corrosion process and published observations on fuel corrosion under disposal conditions were discussed [8]. Nobuo Otsuka [9] studied effects of fuel impurities on the fireside corrosion of boiler tubes in advanced power generating systems. He investigated thermodynamic equilibrium calculation relating fuel chemistry with flue – gas composition and volatile condensate deposits. Corrosive impurities such as sodium, potassium, chlorine, and sulfur, inevitably involved in fuel were considered in the calculation.

The aim of this work is to evaluate the efficiency of isopropanol, methanol and xylene mixture with 10.7 vol.% to improve corrosion resistance of pure aluminum and

its alloys in simulated fuel at room temperature by electrochemical measurements using potentiostat.

## Experiments and Procedure

### Material and Chemicals

Specimens of pure aluminium and its alloy were polished to mirror finish, degreased with acetone and rinsed with distilled water. The specimens were then insulated with hot mounting leaving (1 cm<sup>2</sup>) area exposed to electrolyte. The chemical analysis of experimental alloys is shown in table (1) by spectromax in State Company for Inspection and Engineering Rehabilitation (SIER)–Ministry of industry and minerals.

An electrolyte of condensed synthetic automotive solution [2] [ammonium nitrate (0.077 g.L<sup>-1</sup>), ammonium sulphate (1.017 g.L<sup>-1</sup>), potassium chloride (0.1345 g.L<sup>-1</sup>), ammonium hydroxide (0.33 ml.L<sup>-1</sup>) and 1M hydrochloric acid (5.8 ml.L<sup>-1</sup>)] was used in this study, these salts obtained from BDH Chemical Ltd. The pH of this solution was 3.3. Mixture of isopropanol, methanol and xylene with 10.7 vol.% were added to improve corrosion resistance, this mixture increases octane number according to the following equation [10]:

$$\text{Octane number} = \sum_i X_i a_i \quad \dots\dots(1)$$

where  $X_i$  and  $a_i$  are the volume fraction is the octane number of component  $i$ .

### Electrochemical Cell

The electrochemical standard cell used in this work was locally fabricated according to the ASTM standard G5-94 [11] with provision for working electrode (Al and its alloys), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an SCE reference electrode.

### Instruments

Potentiodynamic and cyclic polarization measurements were carried out with WINKING M Lab 200 Potentiostat from Bank-Elektronik. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 3 mV.sec<sup>-1</sup>. Polarization experiments were started when the rate at which open circuit potential ( $E_{oc}$ ) changed was less and more 200mV.

The main results obtained were expressed in terms of the corrosion potentials ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ) in addition to measure the Tafel slopes by Tafel extrapolation method. From the values of Tafel slopes and corrosion current density, the polarization resistances values can be calculate according to Stern-Geary equation. While experimental parameters for cyclic polarizations were obtained directly from SCI electrochemical software of potentiostat.

## RESULTS AND DISCUSSION

The variation of open circuit potential ( $E_{oc}$ ) with time for all experimental specimens in simulated fuel in the absence and presence of mixture was shown in Figs. (1) and (2). The potential of the samples was as a function of time in order to study the evolution of the film chemistry as it came to equilibrium with solution. As a result, the electrochemical reactions at this interface vary with time. The data of open circuit potential ( $E_{oc}$ ) that listed in the Table (2) indicate that addition of (50%Isopropanol –

30%Methanol – 17%Xylene) mixture little shift  $E_{oc}$  toward noble direction, this mean there are some reactions can occur between the metallic surface and components of mixture accelerate the stability of film formed on the surface.

During anodic or cathodic polarization, or at open circuit, ion transfer reaction of metal ions and oxygen ions will take place. A clear process is the anodic corrosion of a passive metal in the steady state. In such a case, metal ions travel through the oxide film with a constant rate and are transferred in an ion transfer reaction at the interface oxide/electrolyte. The rate of that passive film dissolution depends on the local potential drop at the interface, the pH and the activity of the metal ions at the oxide surface [12].

The potentiodynamic polarization curves for Al and its alloys in the absence and presence of mixture are shown in Figs. (3) and (4). These figures show the main two behaviors of Al and its alloys in active region, the lower section represents the cathodic reaction of reduction for hydrogen because of the acidity of medium as follow:



While the upper section represents the anodic reaction where the oxidation of aluminium can occur according to the following reaction:



Corrosion parameters are listed in Table (2) and (3) indicate that the sequence of corrosion potentials and corrosion current density as follow:

$-E_{corr}$	Al-Zn > Al > Al-Si > Al-Cu
$i_{corr}$ (in fuel only)	Al < Al-Si < Al-Cu < Al-Zn
$i_{corr}$ (in fuel + mixture)	Al < Al-Cu < Al-Si < Al-Zn

The corrosion current density ( $i_{corr}$ ) is a kinetic parameter and represents the rate of corrosion under specified equilibrium condition. Any factor that enhances the value of ( $i_{corr}$ ) results in an enhanced value of the corrosion rate on pure kinetic ground. The results of corrosion rate  $C_R$  are listed in Table (2) and (3) according to the following equation[13]:

$$C_R = 0.13 * i_{corr} * \left(\frac{e}{\rho}\right) \quad \dots\dots(4)$$

Where  $e$  is equivalent weight of Al (9 g) and  $\rho$  is density of Al (2.7g/cm<sup>3</sup>), these values were used for Al and its alloys.

The Tafel slopes were very much influenced in the presence of mixture. Generally, the cathodic Tafel slopes ( $b_c$ ) were increased after adding mixture. But the anodic Tafel slopes ( $b_a$ ) were decreased in the presence of mixture and cathodic Tafel have values higher than those of anodic Tafel slopes except for pure Al. It is inferred that the rate of change of current with change of potential was smaller during cathodic polarization than that during anodic polarization due to concentration polarization and reduction of oxygen can occur obtained from additive mixture.

The small slope indicates the presence of a film on the surface of the tested material, which is less permeable and can even obstruct the metal dissolution reaction but still permits an electrochemical reaction to occur [3,4]. It is known that the surface oxide on Al alloys permits the movement of ionic species and an electron or vacancy flux across it [3,4].

The polarization resistance ( $R_p$ ) was also determined from Stern- Geary equation, where [14, 15]:

$$R_p = \left( \frac{dE}{di} \right)_{i=0} = \frac{b_a * b_c}{2.303 * i_{corr} * (b_a + b_c)} \dots\dots(5)$$

where  $b_c$  and  $b_a$  are cathodic and anodic Tafel slop respectively. The values of  $R_p$  are presented in Table (2) and (3). These data indicate that the polarization resistance value increases in presence of mixture.

Cyclic polarization data were recorded by M Lab electrochemical laboratory system with electrochemistry software. Potentiodynamic measurements were carried out in order to determine the initiation and propagation of local corrosion, which is associated with the breakdown of passive protective film.

The breakdown potential ( $E_{br}$ ) is the one at which the anodic current increases considerably with applied potential. The potential, at which the hysteresis loop is completed upon reverse polarization scan, is known as the protective potential or repassivation potential. Breakdown potential is a sign of local corrosion but the measure of pitting susceptibility is the difference between the breakdown potential and the repassivation one. The protection potential represents the potential at the intersection of hysteresis curve with passive domain. Below this potential the propagation of existing localized corrosion will not occur.

Figs. (5) and (6) show the cyclic polarization of Al and its alloys in simulated fuel in the absence and presence of mixture.

These figures indicate that the potentials for the reverse scan curves are more negative than those for the forward scan. These results show a stable oxide film is formed during the forward scan. Also the hysteresis loop disappears in simulated fuel in the absence and presence of mixture, this means there are no chance to pitting corrosion, i.e., the materials did not show a breakdown potential.

The forward and reverse potentials for pure Al and Al-Si alloy became more noble in the presence of mixture, while became more active for Al-Cu alloy. The variation in forward and reverse potentials was observed for Al-Zn alloy in the presence of mixture.

**CONCLUSION**

Addition of (50%Isopropanol – 30%Methanol – 17%Xylene) mixture to simulated fuel increases the corrosion resistance of pure Al and three of its alloys include Al-Cu, Al-Si, and Al-Zn alloy. This mixture is also increased the octane number. The rate of corrosion takes the following sequence:

- C<sub>R</sub> in mpy** (in fuel only) Al < Al-Si < Al-Cu < Al-Zn
- C<sub>R</sub> in mpy** (in fuel + mixture) Al < Al-Cu < Al-Si < Al-Zn

Improvement of corrosion resistance due to electronic density on oxygen atoms in alcohols in addition to phenyl group which bulk molecule attractive to metallic surface and make as barrier to isolate the surface from fuel such as occur in sandwich theory of inhibition. Pure Al and its alloy did not show breakdown potential in simulated fuel in the absence and presence of mixture and the passive film was extended to more positive potentials in the presence of mixture.

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**Table (1): Chemical composition of Al-alloys.**

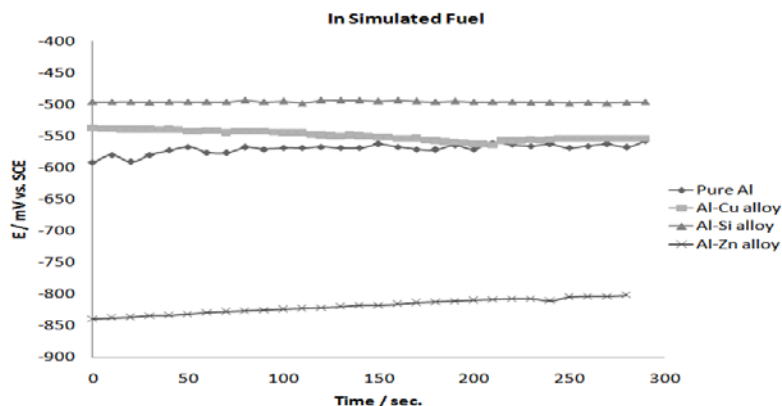
	Cu	Mg	Fe	Si	Mn	Zn	Ti	Cr	Pb	Ni	Al
Al-Cu	4.5	1.3	0.5	0.5	0.5	0.25	0.15	0.1	-	-	Bal.
Al-Si	1.01	0.344	1.05	12.74	0.195	0.49	0.03	0.043	0.1	0.04	Bal.
Al-Zn	1.5	2.5	0.5	0.4	0.3	5.5	0.2	0.25	-	-	Bal.

**Table (2): Corrosion parameters of Al and its alloys in simulated fuel at room temperature.**

Material	Open circuit potential (E <sub>oc</sub> /mV)	Corrosion potential (E <sub>corr</sub> /mV)	Corrosion current density (i <sub>corr</sub> /μA.cm <sup>-2</sup> )	Tafel slope (mV.dec <sup>-1</sup> )		Corrosion resistance x10 <sup>3</sup> (R <sub>p</sub> /Ω.cm <sup>2</sup> )	Corrosion Rate mpy
				-b <sub>c</sub>	+b <sub>a</sub>		
Pure Al	-551	-543.7	1.56	124.1	139.2	18.26	0.675
Al-Cu	-555	-460.4	11.50	60.7	46.9	0.999	4.980
Al-Si	-500	-478.0	5.89	104.0	85.5	3.459	2.550
Al-Zn	-801	-765.0	13.31	86.7	46.8	0.992	5.763

**Table (3): Corrosion parameters of Al and its alloys in simulated fuel containing mixture at room temperature.**

Material	Open circuit potential (E <sub>oc</sub> /mV)	Corrosion potential (E <sub>corr</sub> /mV)	Corrosion current density (i <sub>corr</sub> /μA.cm <sup>-2</sup> )	Tafel slope (mV.dec <sup>-1</sup> )		Corrosion resistance x10 <sup>3</sup> (R <sub>p</sub> /Ω.cm <sup>2</sup> )	Corrosion Rate mpy
				-b <sub>c</sub>	+b <sub>a</sub>		
Pure Al	-535	-491.8	1.54	65.1	67.2	9.323	0.667
Al-Cu	-547	-487.2	3.80	136.0	51.7	4.280	1.645
Al-Si	-497	-425.6	5.77	107.9	58.2	2.845	2.499
Al-Zn	-784	-748.3	12.42	288.9	42.5	1.295	5.378



**Figure (1): Variation of potentials with time for Al and its alloys in Simulated fuel in the absence of mixture.**

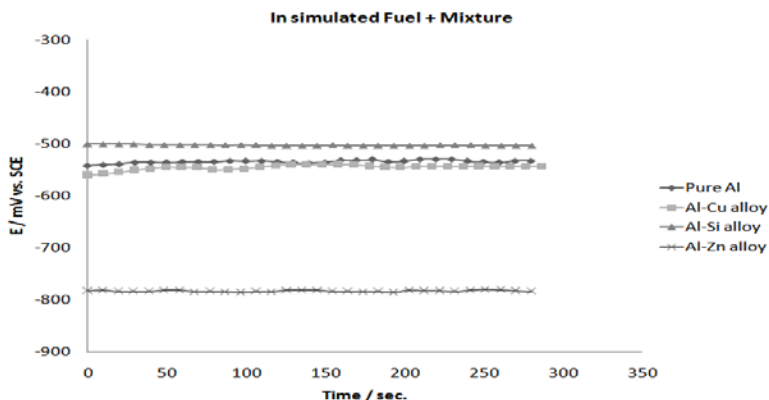


Figure (2): Variation of potentials with time for Al and its alloys in Simulated fuel in the presence of mixture.

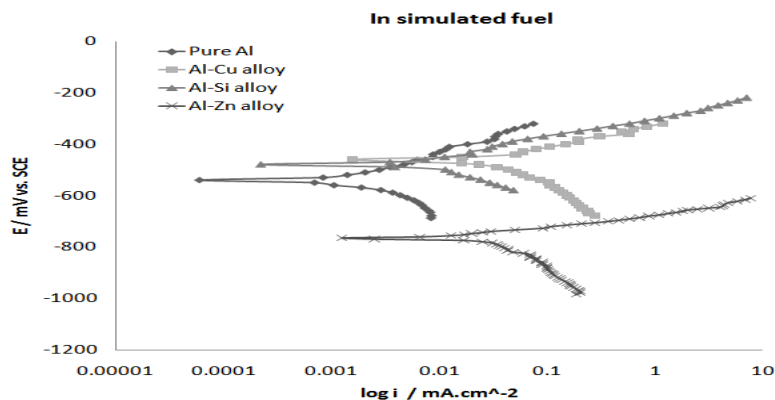


Figure (3): Potentiodynamic polarization of Al and its alloys in simulated fuel.

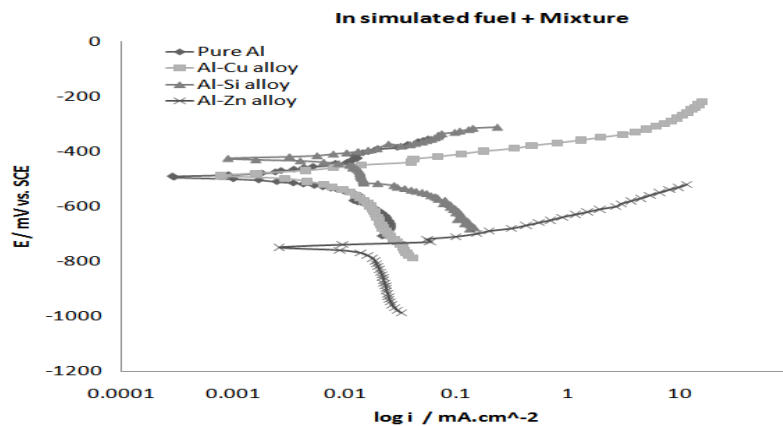


Figure. (4): Potentiodynamic polarization of Al and its alloys in simulated fuel in the presence of mixture.



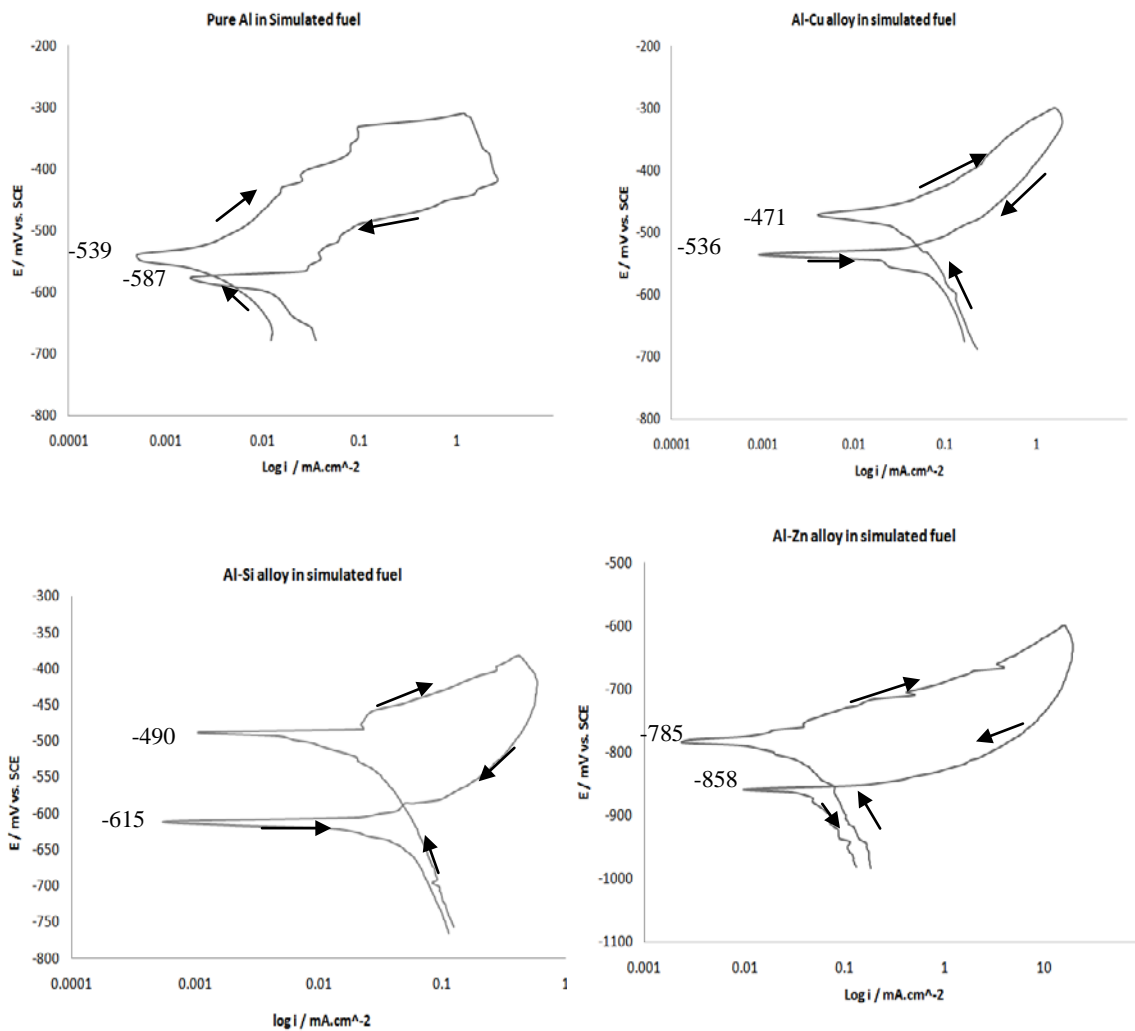


Figure (5): Cyclic polarization of Al and its alloys in simulated fuel in the absence of mixture.

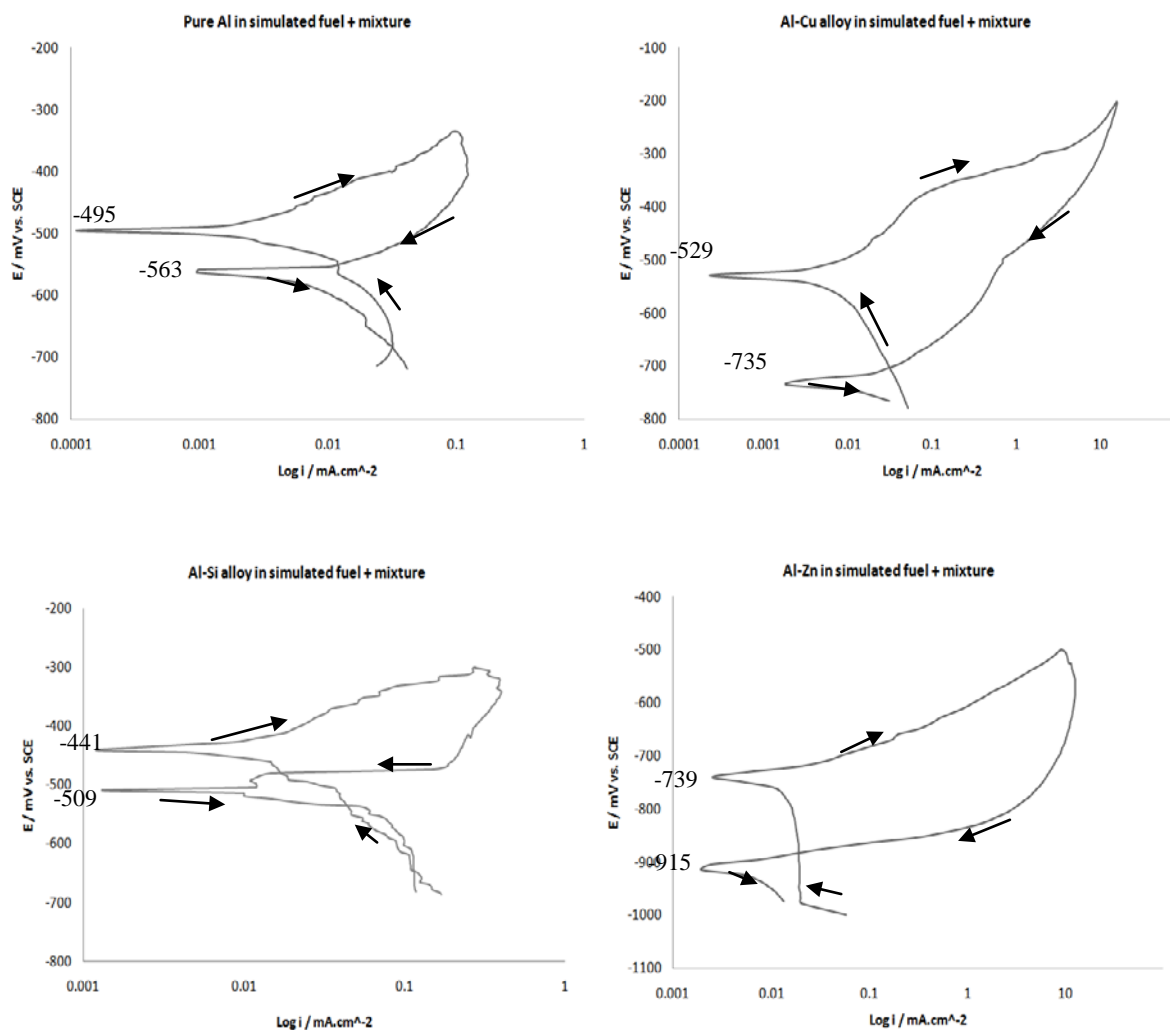


Figure (6): Cyclic polarization of Al and its alloys in simulated fuel in the presence of mixture.