

Corrosion Behavior of Some Metals and Alloys in Synthetic Condensed Automotive Solution

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Abstract

This work involves studying the corrosion behavior of some metals and alloys in condensed synthetic automotive solution (CSAS) at room temperature by Potentiostat at scan rate $3 \text{ mV}\cdot\text{sec}^{-1}$. The results show that stainless steel and copper are more stable than other materials (Al, Brass) in CSAS because the chromium oxide which formed on Steel surface and cupric oxide which formed on the Cu surface respectively. While brass may be attacked by aggressive ions and selective leaching can occur. Aluminium produce instable oxide layer compared with chromium and cupric oxides.

The corrosion parameters show that the materials take the following sequence for corrosion potentials E_{corr} as follow. While corrosion current density (i_{corr}) values take the sequence differ from the behavior of potentials as follow:

$-E_{\text{corr}}$ (mV) Al > Brass > SS 304 > Cu > SS 316L

i_{corr} ($\text{mA}\cdot\text{cm}^{-2}$) SS 304 > Brass > Al > Cu > SS 316L

The later results shows that SS 316L more resistance than other materials to corrosion in CSAS, and Al & Cu more resistance than brass & SS 304. The values of R_p take the following sequence for various materials:

R_p ($\Omega\cdot\text{cm}^2$) SS 316L > Al > Cu > Brass > SS 304.

Cyclic polarization curves of various materials show the agreement with the results of potentiodynamic behavior.

Key word: Corrosion in Fuel, potentiodynamic test, Al, Cu, Brass, and Steel.

1- Introduction

Widespread use of biodiesel and ultra-low sulfur diesel (ULSD) fuels has raised corrosion concerns in the engine manufacturing, fuel storage and regulatory communities. Biofuels derived from vegetable oils or animal fat age rapidly during storage, leading to the formation of aggressive species that react with storage tanks or engine parts, causing corrosion. With ethanol blends, water separation (for E5-E20) and stress corrosion cracking (E85)

are the main concerns. ULSD is thought to be more corrosive than diesel fuels containing higher amounts of sulfur. Microbiologically induced corrosion (MIC) is also a potential problem in all fuel systems, since they provide a readily available food source to microorganisms, including bacteria and fungi.

Most metal components in automobile fuel system will corrode or rust in the presence of water, air or acidic compounds. The gasoline distribution system contains water, and additional moisture may collect in the automobile tank from condensation.

Gasoline may also contain traces of sulfur and organic acids. Gasoline has always been recognized as potentially corrosive [1].

There are many studies concerned with gasoline such as the effect of ethanol-gasoline blends on corrosion rate in the presence of different materials of construction used for transportation, storage and fuel tanks[2] and fuel pumps [3]. Hamilta and co-workers [4] studied corrosion performance of Al-Si-Cu alloys in a synthetic condensed automotive solution, while other works [5,6] in alcoholic fuels. Nie et al. [7] studied corrosion behavior of metallic materials in Ethanol-Gasoline alternative fuels. Eiman and Jehad[8] studied the relative performance of compression ignition engine using various blends of diesel – ethanol fuels. Alessandra Regina Pepe Ambrozin et al.[9] 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. Thus, metallic corrosion could be related to fuels and biofuels utilization. They observed that the ethanol is the most corrosive and gasoline the least.

2- Experimental Procedure

2-1 Material and Chemicals

Specimens of Metals and alloys were used in this work include (Al, Brass, Cu, Pb, SS 304, and SS 316L). These specimens were polished to mirror finish, degreased with acetone and rinsed with distilled water. The specimens were then insulated with hot mounting device (QX-MACHINE INLAY) China manufactured by using formaldehyde (Bakelite) at 138°C for 8 minute leaving the topside of the specimen exposed.

An electrolyte of condensed synthetic automotive solution[4](CSAS) [ammonium nitrate (0.077g/L), ammonium sulphate (1.017g/L), potassium chloride (0.1345g/L), ammonium hydroxide (0.33 ml/L) and 1M hydrochloric acid (5.8 ml/L)] was used in this study, these salts obtained from BDH Chemical Ltd. The pH of this solution was 3.3.

2-2 Electrochemical Cell

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

2-3 Instruments

Potentiodynamic and cyclic polarization measurements were carried out with WINKING MLab 200 Potentiostat from Bank-Elektronik with electrochemical standard cell. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate $3 \text{ mV}\cdot\text{sec}^{-1}$. Polarization experiments were started when the rate at which open circuit potential (E_{ocp}) 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.

3- Results and Discussion

The electrochemical reactions at the interface vary with time. Fig. (1) shows the open circuit potential vs. time measurements for experimental metals and alloys in condensed synthesis automotive solution CSAS. The data of open circuit potential (E_{oc}) that listed in the Table (1) indicate that experimental materials take the following sequence:

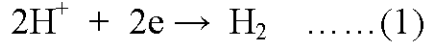
$-E_{oc} \text{ (mV)}$ Al > Brass > SS 304 > Cu > SS 316L

These results show that stainless steel and copper are more stable than other materials in CSAS because the chromium oxide which formed on Steel surface and cupric oxide which formed on the Cu surface. While brass may be attacked by aggressive ions and selective leaching can occur. Aluminium produce instable oxide layer compared with chromium and cupric oxides.

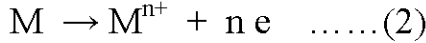
During anodic or cathodic polarization, or at open circuit, ion transfer reaction of metal ions and oxygen ions will take place. A clear process is the anodic corrosion of a passive metal in the steady state. In such a case, metal ions travel through the oxide film with a constant rate and are transferred 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[10].

The potentiodynamic polarization curves for experimental metals and alloys are shown in Fig. (2). This figure shows the main two behavior of

materials in active region, the lower section represent the cathodic reaction of reduction of hydrogen because of acidity of the medium as follow:



While the upper section represent the anodic reaction where the oxidation of metals can occur according to the following reaction:



The corrosion parameters listed in Table (1) show that the materials take the same sequence of E_{oc} in its behavior of corrosion potentials E_{corr} as follow. While corrosion current density (i_{corr}) values take the sequence differ the behavior of potentials as follow:

$$-E_{corr} \text{ (mV)} \quad Al > Brass > SS 304 > Cu > SS 316L$$

$$i_{corr} \text{ (mA.cm}^{-2}\text{)} \quad SS 304 > Brass > Al > Cu > SS 316L$$

The later results shows that SS 316L more resistance than other materials to corrosion in CSAS, and Al & Cu more resistance than brass & SS 304 .

The values of R_p are presented in Table (1) that calculated according to equation 3. These data indicate that the polarization resistance takes the following sequence for various materials:

$$R_p = \left(\frac{dE}{di} \right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c) i_{corr}} \quad \dots\dots(3)$$

$$R_p \text{ (}\Omega\text{.cm}^2\text{)} \quad SS 316L > Al > Cu > Brass > SS 304$$

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. Cyclic polarization curves of various materials show in Fig. (3), these curves indicate that cyclic behavior was agreement with the results of potentiodynamic behavior. Cyclic polarization of SS 316L gave reverse scan at the reverse potential more noble than forward potential and the reverse curve shift to lower current densities. Copper gave the reverse scan is same of the forward scan leading to corrosion resistance in CSAS and no chance to pitting corrosion. Aluminium gave the same behavior of SS 316L , but at more negative potential values. 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.

4- References

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Table (1): Corrosion parameters of metals and alloys in synthetic condensed automotive solution at room temperature.

Materials	(E_{oc}/mV)	(E_{corr}/mV)	i_{corr} $\mu A.cm^{-2}$	Tafel slope ($mV.dec^{-1}$)		Corrosion resistance $\times 10^3$ ($R_p/\Omega.cm^2$)
				$-b_c$	$+b_a$	
Al	-459	-430.3	3.44	135.9	156.2	9.173
Brass	-22	-41.4	6.89	104.7	129.8	3.652
Cu	+63	+53.6	2.26	90.8	88.1	8.591
SS 304	-10	-29.1	13.39	114.3	164.8	2.189
SS 316L	+294	+197.2	0.442	55.6	154.6	40.17

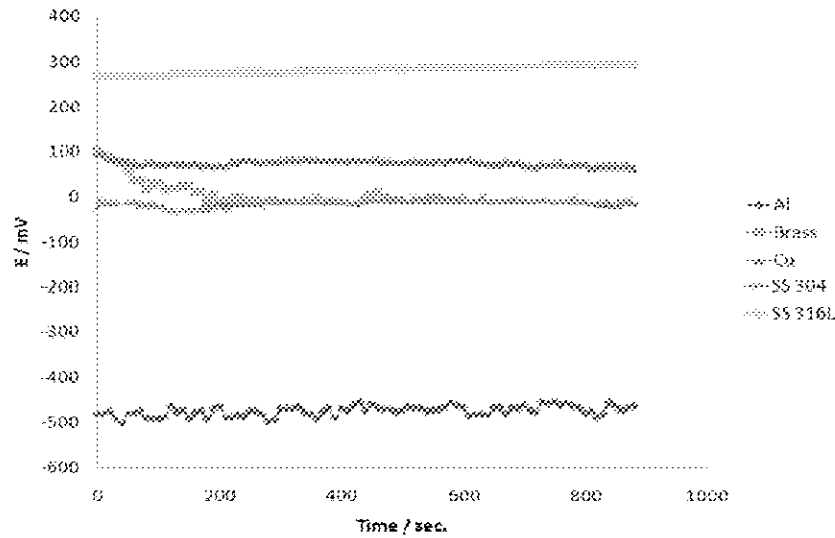


Fig. 1: Variation of open circuit potential – time for some metals and alloys in condensed synthetic automotive solution.

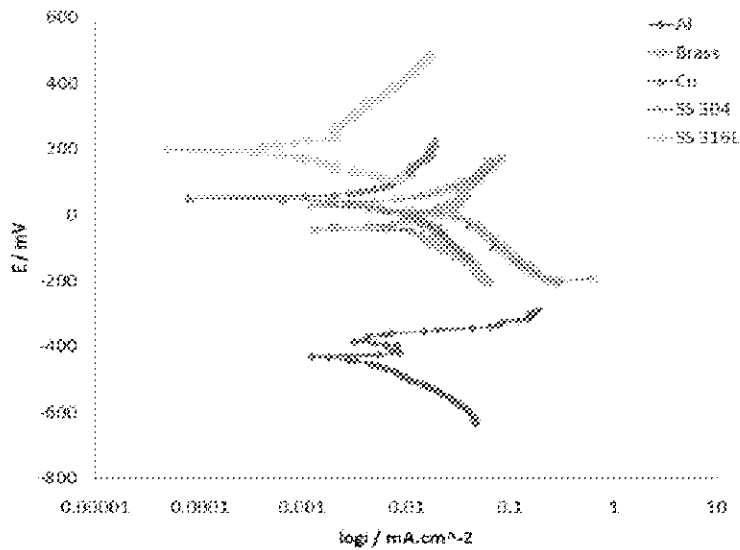


Fig. 2: Potentiodynamic polarization for some metals and alloys in condensed synthetic automotive solution.

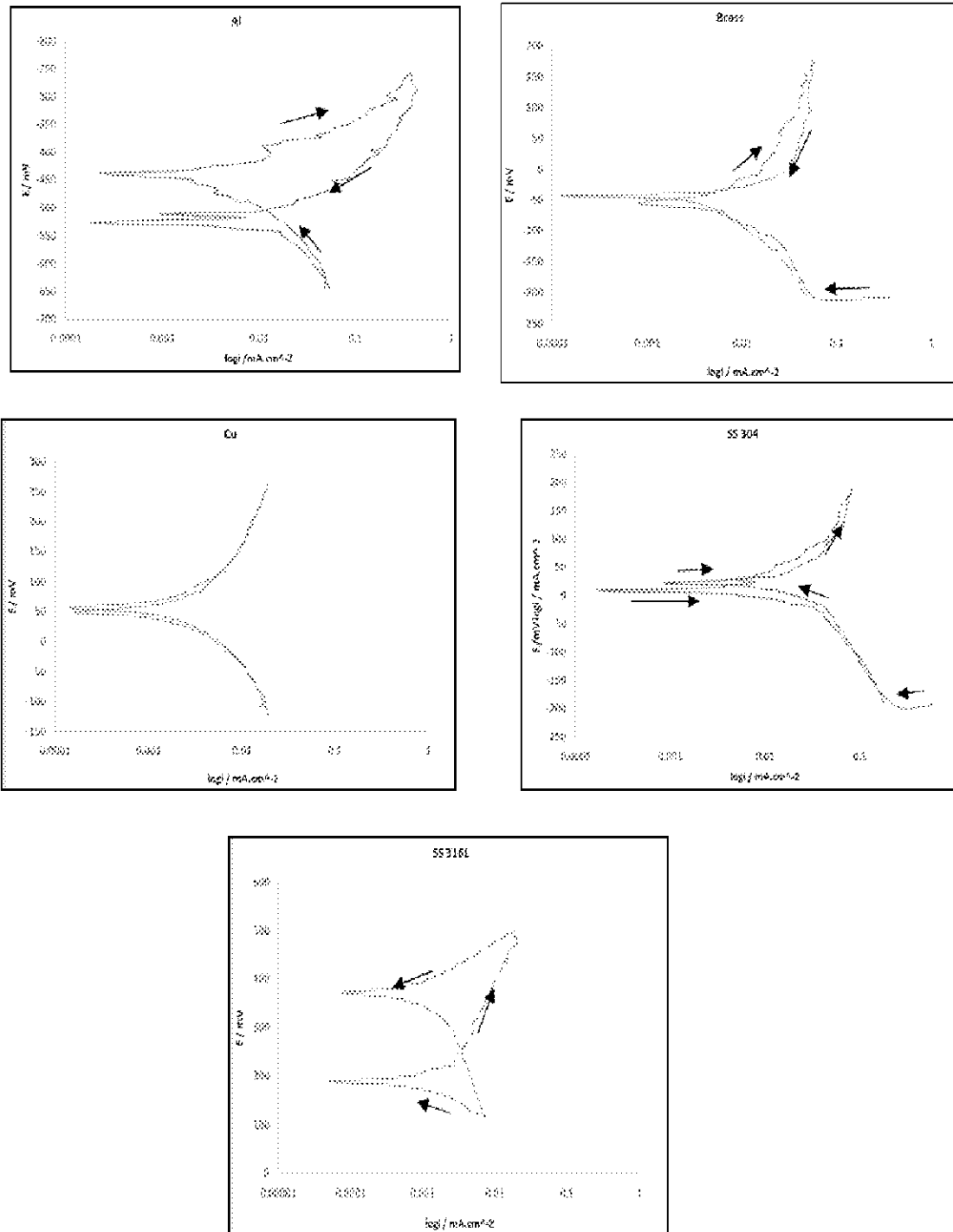


Fig. 3: Cyclic polarization for some metals and alloys in condensed synthetic automotive solution.

السلوك التآكلي لبعض المعادن والسبائك في وسط وقود المركبات المكثف الصناعي

م. سلافه إسماعيل إبراهيم

الخلاصة

يتضمن هذا البحث دراسة السلوك التآكلي لبعض المعادن والسبائك في وسط وقود المركبات المكثف المحضر مختبريا عند درجة حرارة الغرفة باستخدام المجهاد الساكن عند معدل مسح 3 ملم فولت/ثانية. وقد بينت النتائج ان الفولاذ المقاوم للصدأ والنحاس أكثر استقرارا من الألمنيوم والبراص في وسط وقود المركبات والذي يعزى الى اوكسيد الكروم المتكون على سطح الفولاذ واوكسيد النحاس المتكون على سطح النحاس في حين كان البراص أكثر تأثرا بالايونات المعادية بفعل النزح الانتقائي الحاصل . اما الألمنيوم فيكون طبقة اوكسيدية غير مستقرة مقارنة بأكاسيد الكروم والنحاس. بينت متغيرات التآكل المقاسة بان المواد المدروسة تأخذ تسلسل جهد التآكل التالي :

$$-E_{\text{corr}} \text{ (mV)} \quad \text{Al} > \text{Brass} > \text{SS 304} > \text{Cu} > \text{SS 316L}$$

بينما كانت قيم كفاءة تيار التآكل مختلفة في سلوكها وكما يلي:

$$i_{\text{corr}} \text{ (mA.cm}^{-2}\text{)} \quad \text{SS 304} > \text{Brass} > \text{Al} > \text{Cu} > \text{SS 316L}$$

وهذه النتيجة تبين مدى مقاومة الفولاذ 316 للتآكل أكثر من المواد الأخرى في وسط وقود المركبات وان الألمنيوم والنحاس أكثر مقاومة من البراص والفولاذ 304. أما تسلسل قيم مقاومة الاستقطاب فكانت كما يلي:

$$R_p \text{ (}\Omega\text{.cm}^2\text{)} \quad \text{SS 316L} > \text{Al} > \text{Cu} > \text{Brass} > \text{SS 304}$$

بينت منحنيات الاستقطاب الحلقي للمواد المختلفة توافقا كبيرا لنتائج منحنيات الاستقطاب الخطي.