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Effect of pH on the Passive Behavior of 6061 Al Alloy in Borate Buffer Solutions

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Abstract- The passive behavior of 6061 Al alloy in borate buffer solutions of various pH values ranging from 8.2 to 5.0 have been investigated by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization curves revealed that 6061 Al alloy show excellent passive behavior in borate buffer solutions of various pH values ranging from 8.2 to 5.0. EIS results showed that the changes in the pH lead to two distinct behaviors in the EIS plots. The pH ranging from 8.2 to 6.4 result in an inductive loop when for smaller pH values (ranging from 6.2 to 5.0) there is not any loop exhibited. The absence of inductive loops and presence of the imperfect semicircle with large diameter when pH is 6.0 and 5.5, are related to formation of stable passive film. Moreover, it can be concluded that the passive film formed on 6061 Al alloy shows its best protective behavior when pH interval is 6.0 to 5.5, and if the pH is higher or lower than this interval the protective properties of passive film will decrease.

Keywords- Alloy, Passive film, Inductive loop, Borate buffer solution

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1. INTRODUCTION

Al is a structural metal having good corrosion behavior to the atmosphere and many aqueous solutions of various pH values ranging from 8.5 to 4.5 [1-4]. It is assumed that the passive film grown on Al and its alloys are composed of Al oxide, which is estimated at about 2-10 nm in thickness. Generally, this passive film forms an efficient barrier against the dissolution of metal and undergoes a passivity breakdown under certain conditions [5-7].

In the last decade, many studies investigated the electrochemical behavior and passivation of passive films formed on Al and its alloys. These studies indicated that the composition of the passive films depends on many variables such as, pH, presence of aggressive anions and aerating conditions. Also, these studies revealed that passive films formed on Al and its alloys under various conditions are correlated with different structures. In atmosphere, a thin film of Al oxide formed immediately is observed to be amorphous, while the passive film formed in aqueous solution is usually dense, coherent and compact [8-13].

Generally, 6061 is one of the most widely used grades of Al alloys. This alloy is good compromise between corrosion resistance and mechanical behavior. Also, this alloy has a wide range of applications such as sheet metal working, fins and tubes for heat exchangers, welded boiler work, and marine applications [14].

Although many studies have been published on the passivity of Al and its alloys, there is still lack of knowledge on the effect of pH on the electrochemical behavior of the passive film formed on 6061 Al alloy. Therefore, EIS measurements of 6061 Al alloy in buffer borate solutions of various pH values ranging from 8.2 to 5.0 have been carried out in this work.

2. EXPERIMENTAL PROCEDURES

Chemical composition of 6061 Al alloy used in present investigation is shown in Table 1. All samples were ground to 2000 grit and cleaned by deionized water prior to the tests. Also, the buffer borate solutions of various pH values ranging from 8.2 to 5.0 were used as the test solutions at 25±1°C.

Table 1. Chemical compositions of 6061 Al alloy

Elements	Mg	Si	Fe	Mn	Zn	Ti	V	Cu	Cr	Al
6061 Al alloy /wt%	0.09	0.70	0.35	0.02	0.06	0.01	0.01	0.23	0.19	Bal

The electrochemical measurements were performed in the following sequence:

(a) Potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV s^{-1} starting from -0.25 V (*vs*. E_{corr}) to 1.0 $V_{Ag/AgCl}$.

(b) EIS test at open circuit potential (OCP) and AC potential with the amplitude of 10 mV and normally a frequency range of 10 kHz to 10 mHz.

Prior to electrochemical measurements, working electrodes immersed at OCP in buffer borate solutions to form a steady-state passive film (approximately 2 h). All electrochemical measurements were performed in a conventional three-electrode flat cell. The counter electrode was a Pt plate, and all potentials were measured against Ag/AgCl in saturated KCl.

The validation of the impedance spectra was performed by checking the linearity condition, i.e. measuring spectra at AC signal amplitudes between 5 and 15 mV (rms). Moreover, each electrochemical measurement was repeated at least three times. All electrochemical measurements were obtained using Autolab potentiostat/ galvanostat controlled by a personal computer. For the EIS data modeling and curve-fitting method, the NOVA impedance software was used.

3. RESULTS AND DISCUSSION

Figs. 1 and 2 show the potentiodynamic polarization curves for 6061 Al alloy in buffer borate solutions of various pH values ranging from 8.2 to 6.4 and 6.2 to 5.0, respectively . For all pH, the electrodes exhibit the same curve shapes similar to that reported previously [7, 15], where the current changes linearly around the rest potential manifesting cathodic and anodic Tafel behavior.

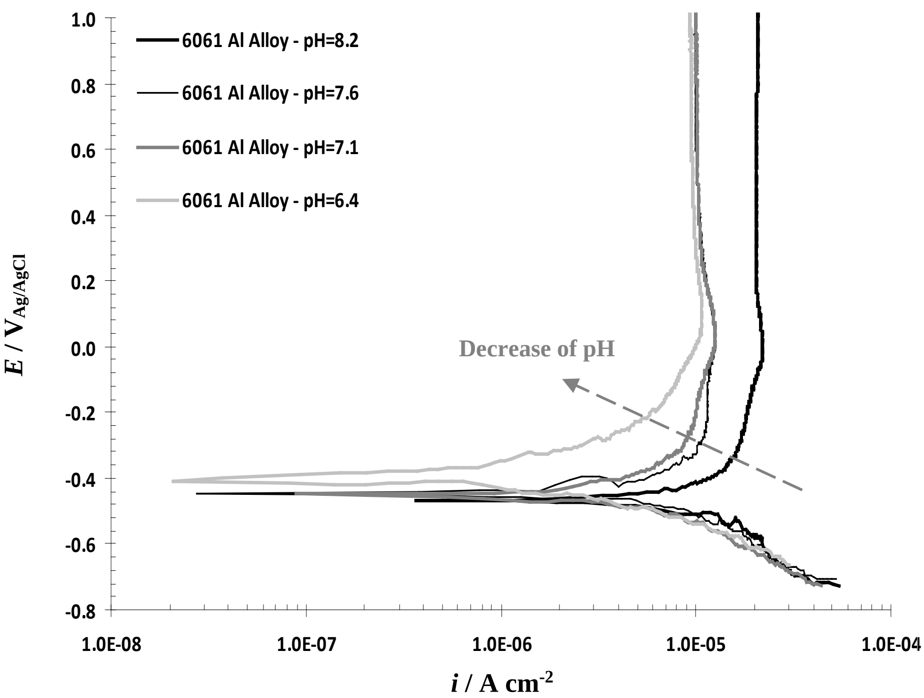

Fig. 1. Potentiodynamic polarization curves of 6061 Al alloy in buffer borate solutions of various pH values ranging from 8.2 to 6.4

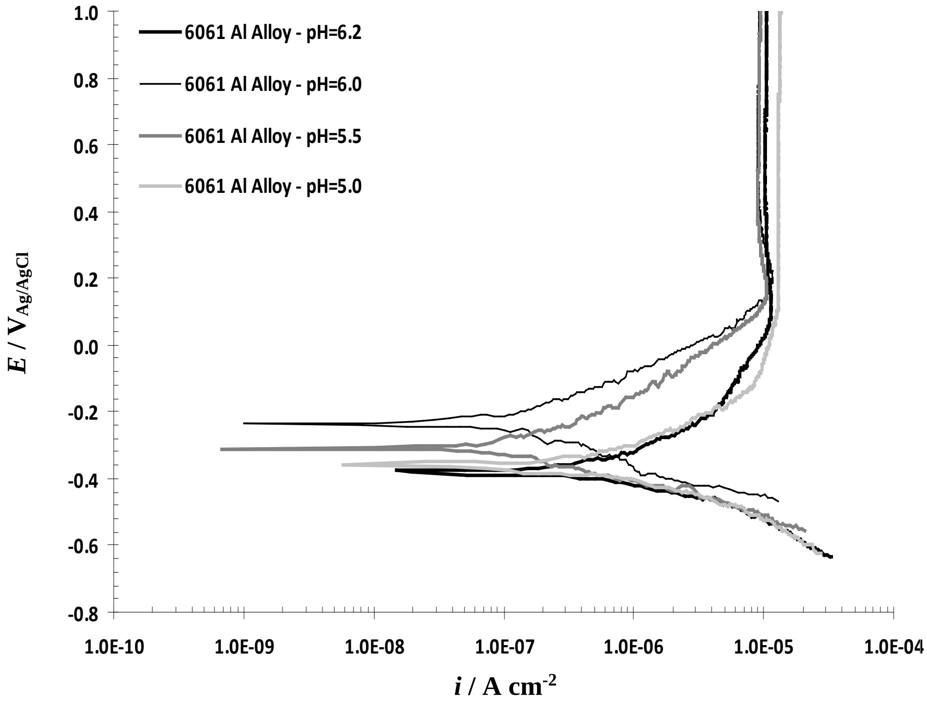

Fig. 2. Potentiodynamic polarization curves of 6061 Al alloy in buffer borate solutions of various pH values ranging from 6.2 to 5.0

As can be seen for all pH, a nearly constant passive current density was observed in the anodic potential region. It is clear that the passive current density appeared to be approximately constant only below the breakdown potential. By comparing the polarization curves in different pH solution, the current density was found to increase with potential during the early stage of passivation and no obvious current peak was observed in the anodic curve. Moreover, all curves exhibit similar features, with a passive potential range extending from the corrosion potential.

The corrosion current density (i_{corr}) was calculated by Tafel extrapolation of the linear part for the cathodic branch back to the corrosion potential [16]. The variation of the corrosion current density of 6061 Al alloy in buffer borate solutions are illustrated in Fig. 3. It is observed that the corrosion current density of this alloy decreases by reducing the pH from 8.2 to 5.5, while it increases when the pH reaches 5.

Figs. 4 and 5 present the Nyquist and Bode plots of 6061 Al alloy in buffer borate solutions of various pH values ranging from 8.2 to 6.4 and 6.2 to 5.0, respectively. These plots showed that the changes in the pH lead to two distinct behaviors in the EIS plots. As shown in Nyquist plots of 6061 Al alloy in buffer borate solutions, the pH ranging from 8.2 to 6.4 result in an inductive loop (Fig. 4a) when for smaller pH values (ranging from 6.2 to 5.0) there is not any loop exhibited (Fig. 5a). Indeed, the absence of inductive loops and presence of the capacitive semicircle with large diameter when pH is 6.0 and 5.5 (Fig. 5a), are related to formation of stable passive film. Generally, the diameter of capacitive semicircle was correlated with charge transfer resistance. An increase in the semicircle diameter indicates an increase in the passive film stability [17].

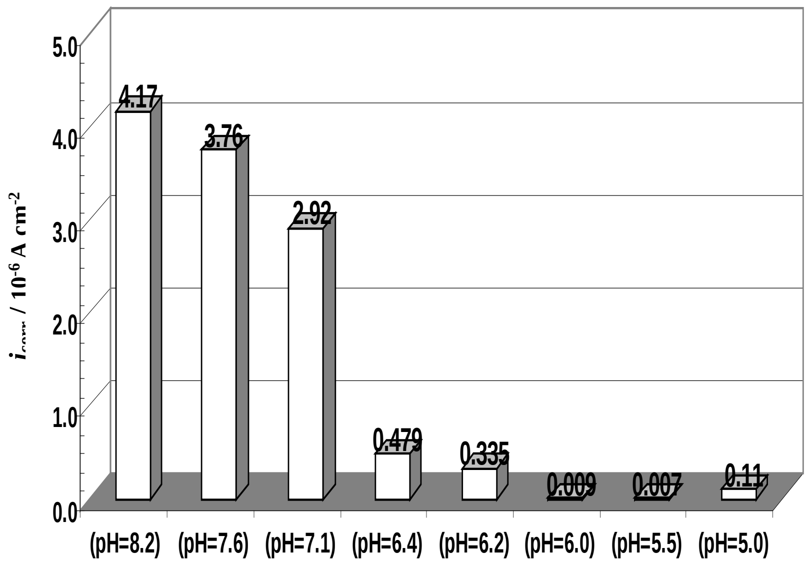

Fig. 3. Dependence of the corrosion current density on the pH of borate buffer solution

The increase in capacitive semicircle is correlated with thickening or compactness and stability of the passive film [11]. In Figs. 4b and 5b, it is observed that the overall impedance (especially in the low frequency domain) increases with decrease in the pH.

Moreover, as shown in the Bode phase plots (Figs. 4c and 5c), the phase angle maxima is lower than 90°; such behavior can be explained as a deviation from ideal capacitor behavior. Indeed, the constant phase angle element (Q) is used to replace the pure capacitance element (C) to reflect the non ideal capacitance bahavior, involving surface heterogeneity, surface roughness and so on. Q is defined in impedance representation as Eq. (1) [18]:

$$Y = Y_0 (j\omega)^n \qquad (1)$$

Where Y_0 is the constant show for Q (Ω^{-1} cm^{-2} s^n), ω is the angular frequency (rad s^{-1}), j is the imaginary number and n is the Q exponent. The factor n, defined as a Q power, is an adjustable parameter that always lies between 0.5 and 1. When n=1, the Q describes ideal capacitor; for 0.5 b n b 1, the Q describes a distribution of dielectric relaxation times in frequency space; and when n=0.5 the Q represents a Warburg impedance with diffusion character.

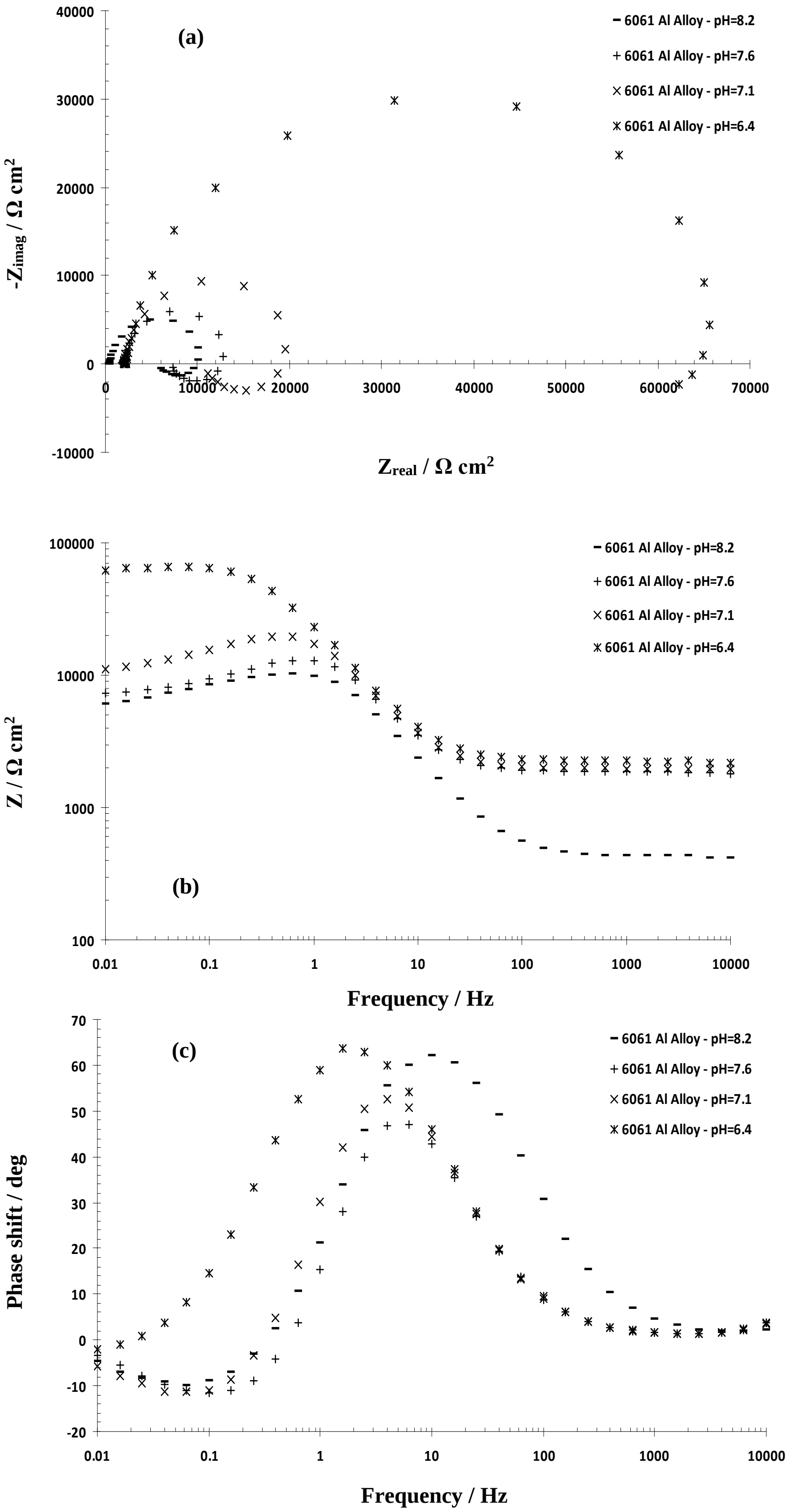

Fig. 4. Nyquist and Bode plots of 6061 Al alloy in buffer borate solutions of various pH values ranging from 8.2 to 6.4

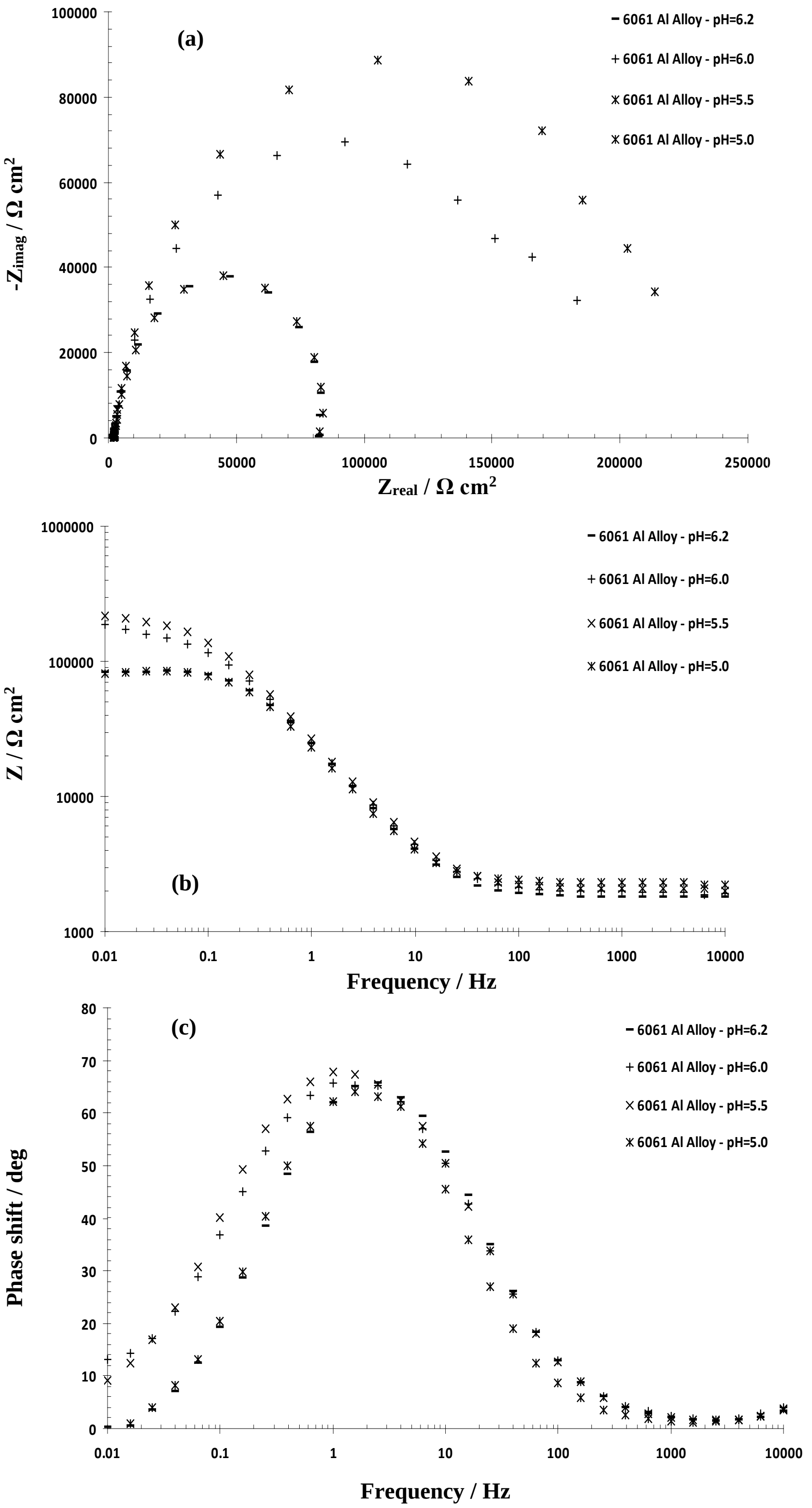

Fig. 5. Nyquist and Bode plots of 6061 Al alloy in buffer borate solutions of various pH values ranging from 6.2 to 5.0

According to the Nyquist and Bode plots of 6061 Al alloy in buffer borate solutions of various pH values ranging from 8.2 to 6.4 and 6.2 to 5.0, the equivalent circuits shown in Fig. 6 (a) [18,19] and (b) [11] was used to simulate the measured impedance data, respectively. The variation of the charge transfer resistance (R_t) obtained by applying two equivalent circuits (Fig. 6 (a) and (b)) is depicted in Fig. 7 to give detail information of the effect of pH on the passive film formed on 6061 Al alloy in buffer borate solutions. It is observed that the charge transfer resistance of this alloy increases by reducing the pH from 8.2 to 5.5, while it decreases when the pH reaches 5. This trend is in good agreement with the variation of the corrosion current density (Fig. 3), which indicates that the passive film property is improved by decreasing the pH.

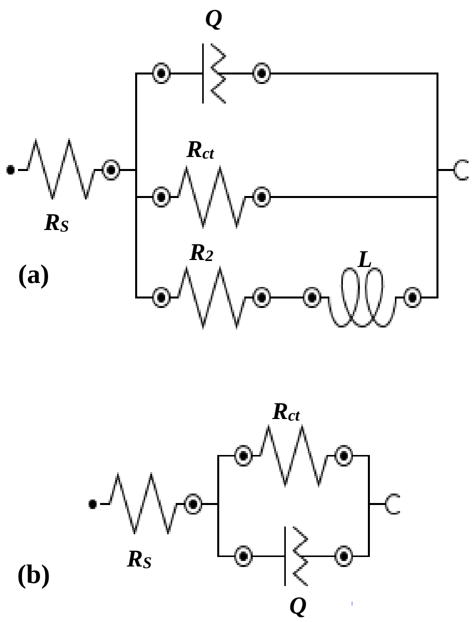

Fig. 6. Best equivalent circuits used to model the experimental EIS data of 6061 Al alloy in buffer borate solutions of various pH values ranging from (a) 8.2 to 6.4 and (b) 6.2 to 5.0

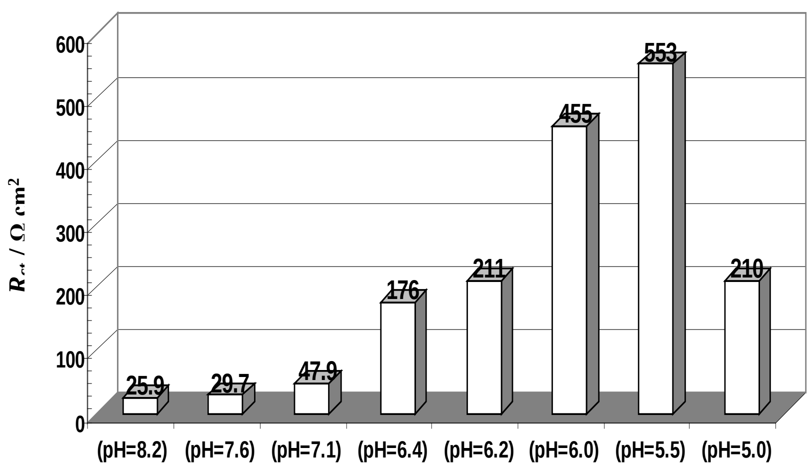

Fig. 7. Dependence of the charge transfer resistance on the pH of borate buffer solution

Indeed, it can be concluded that the passive film formed on 6061 Al alloy shows its best protective behavior when pH interval is 6.0 to 5.5, and if the pH is higher or lower than this interval the protective properties of passive film will decrease.

4. CONCLUSIONS

The effect of pH on the passive behavior of 6061 Al alloy was studied in the present work. Conclusions drawn from the study are as follows

1. Potentiodynamic polarization curves revealed that 6061 Al alloy show excellent passive behavior in borate buffer solutions of various pH values ranging from 8.2 to 5.0.
2. EIS results showed that the changes in the pH lead to two distinct behaviors in the EIS plots. The pH values ranging from 8.2 to 6.4 result in an inductive loop when for smaller pH values (ranging from 6.3 to 5.0) there is not any loop exhibited.
3. The absence of inductive loops and presence of the imperfect semicircle with large diameter when pH is 6.0 and 5.5, are related to formation of stable passive film.
4. Moreover, it can be concluded that the passive film formed on 6061 Al alloy shows its best protective behavior when pH interval is 6.0 to 5.5, and if the pH is higher or lower than this interval the protective properties of passive film will decrease.

REFERENCES

[1] X. X. Zeng, J. M. Wang, Q. L. Wang, D. S. Kong, H. B. Shao, J. Q. Zhang, and C. N. Cao, Mater. Chem. Phys. 121 (2010) 459.

[2] K. Ishii, R. Ozaki, K. Kaneko, H. Fukushima, and M. Masuda, Corros. Sci. 49 (2007) 2581.

[3] K. C. Emregul, and A. A. Aksut, Corros. Sci. 42 (2000) 2051.

[4] S. S. Abdel Rehim, H. H. Hassan, and M. A. Amin, Appl. Sur. Sci. 187 (2002) 279.

[5] F. Rosalbino, S. Delsante, G. Borzone, and E. Angelini, Corros. Sci. 52 (2010) 322.

[6] B. Zhang, Y. Li, and F. Wang, Corros. Sci. 49 (2007) 2071.

[7] S. O. Gashti, and A. Fattah-alhosseini, Anal. Bioanal. Electrochem. 6 (2014) 535.

[8] F. J. Martin, G. T. Cheek, W. E. O. Grady, and P. M. Natishan, Corros. Sci. 47 (2005) 3187.

[9] L. Jinlong, L. Hongyun, and X. Jinpeng, Appl. Sur. Sci. 273 (2013) 192.

[10] L. Kobotiatis, N. Kioupis, and P. G. Koutsoukos, Corrosion (1997) 562.

[11] L. Jinlong, and L. Hongyun, Surf. Coat. Technol. 235 (2013) 513.

[12] B. Zhang, Y. Li, and F. Wang, Corros. Sci. 51 (2009) 268.

[13] K. L. Levine, D. E. Tallman, and G. P. Bierwagen, J. Mater. Proc. Techno. 199 (2008) 321.

[14] C. Vargel, and M. Jacques, Corrosion of Aluminum, Elsevier, (2004).

[15] Y. Liu, and Y. F. Cheng, J. Appl. Electrochem. 41 (2011) 151.

[16] G. T. Burstein, Corros. Sci. 47 (2005) 2858.

[17] C. M. Cepeda-Jiménez, P. Hidalgo, M. Carsí, O. A. Ruano, and F. Carreño, Mater. Sci. Eng. A 528 (2011) 3161.

[18] A. Fattah-alhosseini, A. Moradi, E. Moradi, and N. Attarzadeh, Anal. Bioanal. Electrochem. 6 (2014) 284.

[19] A. Fattah-alhosseini, and H. Farahani, Iran J. Mater. Sci. Eng. 10 (2013) 31.