

The Electrochemical Behavior of AISI 321 Stainless Steel in Alkaline Media

A. Fattah-alhosseini^{1*}, O. Imantalaib²

Faculty of Engineering, Bu-Ali Sina University, Hamedan 65178-38695, Iran

Abstract

In this paper, the electrochemical behaviour of passive films formed on AISI 321 stainless steel (AISI 321) immersed in 0.1 M NaOH + 0.1 M KOH solution was evaluated by different electrochemical techniques. For this purpose, passive films were formed at open circuit potential for 1 to 12 hours and then electrochemical measurements were done. The polarization curves suggested that AISI 321 showed excellent passive behaviour in 0.1 M NaOH + 0.1 M KOH solution. Mott-Schottky analysis indicated that the accepted densities were in the range of 10^{21} cm⁻³ and decreased with immersion time. Electrochemical impedance spectroscopy (EIS) results showed that the best electrical equivalent circuit presented two time constants: The high-medium frequencies time constant could be correlated with the charge transfer process and the low frequencies time constant was associated with redox processes taking place in the surface film. Also, EIS results showed that polarization resistance was increased with formation time from 1 until 12 hours, due to the thickening of passive film.

Keywords: Stainless steel; Passive film; Mott-Schottky; EIS.

1. Introduction

The durability of reinforced concrete is due to the excellent chemical stability of hydrated Portland cement and the passivity of steel in the alkaline (pH from 12.5 to 13.5) pore solutions in concrete¹⁾.

In recent years, there has been a growing interest in applying stainless steel reinforcement in concrete structures to increase the structures lifetime²⁾. Reinforced concrete applications have focused primarily on widely available austenitic stainless steels^{3,4)}. The replacement of mild carbon reinforcing steels with these corrosion-resistant stainless steels has been shown to decrease maintenance costs by 50% with projected service lives far greater than 100 years in even the most severe environments⁵⁾. Although stainless steel is more expensive than carbon steel, various procedures have been adopted; for example, the use of stainless steel rebars in critical areas, in closer contact with the aggressive medium, and the use of carbon steel rebars in the more protected parts of the structure. This combination is economically attractive due to the improved durability conferred by the stainless steel rebars²⁾.

The higher corrosion resistance of stainless steel is due to the presence of a very thin passivating and self-renewable protective layer formed on the surface. In neutral or alkaline solutions, this film is described

by a bilayer structure. The passive behaviour has been related with the formation of a complex oxide film consisting of a rich chromium-oxide/hydroxide inner layer and an iron-oxide rich outer layer⁶⁻⁹⁾.

The electrochemical behaviour of the passive films on stainless steels is an important factor which controls the passivity and therefore, the corrosion resistance^{10,11)}. This behaviour is dependent on several variables, including the chemical composition of the steel, temperature, immersion time, pH and composition of the electrolyte in which the films are grown¹²⁾. There are also several interesting studies focusing on the corrosion and passivation behaviour of the passive film formed in solutions simulating concrete of stainless steel¹³⁻¹⁶⁾.

However, there are limited systematic studies on the effects of immersion time on the passive behaviour of stainless steel. The aim of this paper was to investigate the influence of immersion time in a simulated concrete pore solution on the AISI 321 stainless steels under open circuit potential conditions using EIS. The use of open circuit potential conditions has the advantage that it really simulates the passivation process, thereby showing to be useful for passivation studies in stainless steel in order to obtain more real results. Polarization induces several changes in the outer layers of the surface film that may affect conclusions related to corrosion resistance. Also, in this work, Mott-Schottky analysis of AISI 321 stainless steels in a simulated concrete pore solution was performed and the defects concentrations were calculated as a function of immersion time. The relationship between the accepted density and immersion time has been discussed in order to understand the property of the passivation of AISI 321 stainless steels.

* Corresponding author:

Tel: +98 916 1620892

Fax: +98 811 8257400

E-mail: a.fattah@basu.ac.ir

Address: Faculty of Engineering, Bu-Ali Sina University, Hamedan 65178-38695, Iran

1. Assistance Professor

2.M.Sc. Student

2. Experimental procedures

2.1. Test solution

Aqueous sodium-potassium hydroxide ($0.1 \text{ M NaOH} + 0.1 \text{ M KOH}$) solution was prepared to simulate the electrolytes contained in the pores of concrete¹⁴⁻¹⁶. The solution was prepared with double distilled water and used immediately after preparation. The temperature tested in all experiments was 20°C .

2.2. Stainless steels

The chemical composition of AISI 321 stainless steels used in the present investigation is shown in Table 1. All the as-received stainless steel samples were solution annealed at 1050°C for 30 min to homogenize the microstructure. Specimens of $10 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$ were cut and polished mechanically by abrading with wet emery paper up to 1000 grit size on all sides and then embedded in cold curing epoxy resin¹⁵. After this, the stainless steels were degreased with acetone, rinsed with distilled water and dried with a stream of air just before immersion.

2.3. Electrochemical tests

All electrochemical measurements were performed in a conventional three-electrode cell under aerated conditions. The counter electrode was a Pt plate, and all potentials were measured against Ag/AgCl. All electrochemical measurements were obtained using a uautolab potentiostat/galvanostat controlled by a personal computer.

Potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV/s . The impedance spectra were measured in a frequency range of $100 \text{ kHz} - 10 \text{ mHz}$ at an AC amplitude of 10 mV (rms). The validation of the impedance spectra was done by checking the linearity condition, i.e., measuring spectra at AC signal amplitudes between 5 and 15 mV (rms). Each electrochemical measurement was repeated at least three times. For EIS data modeling and curve-fitting method, NOVA impedance software was used. Capacitance measurements were carried out on passive films formed by immersion in the alkaline solution for different immersion times from 1 to 12 h. The capacitance tests were performed at a frequency of 1 kHz using a 10 mV ac signal and a step rate of 25 mV , in the cathodic direction.

3. Results and discussion

3.1. The open circuit potential vs. time

The open circuit potential of AISI 321 samples was

measured immediately after mechanical polishing of the surface in $0.1 \text{ M NaOH} + 0.1 \text{ M KOH}$ solution. As shown in Figure 1, after immersion, the potentials were negative, around -0.38 V . It was rapidly increased in the first 30 min, and then asymptotically tended towards the steady state after long exposure times.

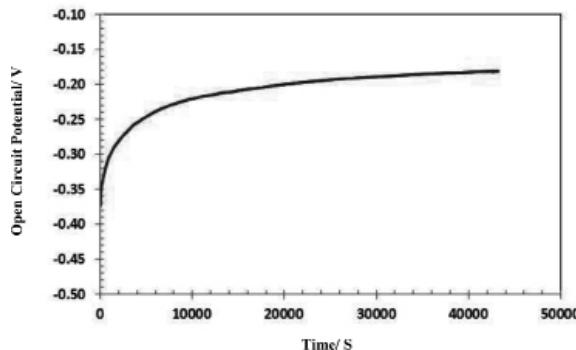


Fig. 1. Evolution of open circuit potential of AISI 321 immersed in $0.1 \text{ M NaOH} + 0.1 \text{ M KOH}$ solution.

3.2. Potentiodynamic polarization

Figure 2 shows the potentiodynamic polarization curves of AISI 321 immersed in $0.1 \text{ M NaOH} + 0.1 \text{ M KOH}$ solution from 1 to 12 h. According to Figure 2, by comparing the polarization curves in immersion time, the corrosion potentials of AISI 321 were found to shift slightly towards the positive direction with an increase in immersion time. For all curves, the current was increased with potential during the early stage of passivation and no obvious current peak was observed. Also, it was found that all curves exhibited similar features, with a passive potential range extending from the corrosion potential to the onset of transpassivity.

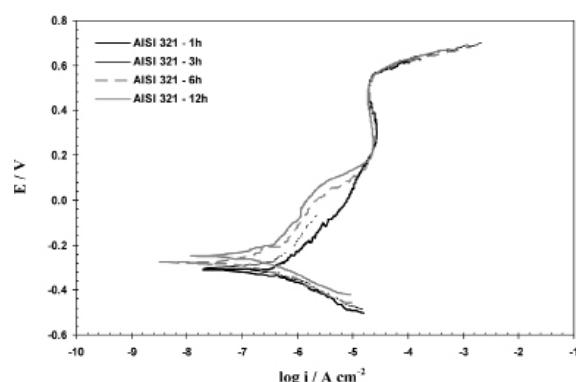


Fig. 2. Potentiodynamic polarization curves at 1 mV/s for AISI 321 in $0.1 \text{ M NaOH} + 0.1 \text{ M KOH}$ solution at different immersion times.

Table 1. Chemical compositions of AISI 321.

Elements	Cr	Ni	Mo	Mn	Si	C	Ti	S	Fe
AISI 321 / wt%	19.1	9.85	0.16	1.65	0.29	0.08	0.68	0.050	Bal

3.3. Mott-Schottky analysis

A previous study has proved that the outer layer of passive films contains the space charge layer and sustains a potential drop across the film. The charge distribution at the semiconductor/solution is usually determined based on Mott-Schottky relationship by measuring electrode capacitance, C, as a function of electrode potential E¹⁷⁻²⁶:

$$\frac{1}{C^2} = -\frac{2}{\epsilon \epsilon_0 e N_A} \left(E - E_{FB} - \frac{kT}{e} \right) \text{ for p-type semiconductor (1)}$$

where e is the electron charge (-1.602×10^{-19} C), N_A is the accepted density for p-type semiconductor (cm^{-3}), ϵ is the dielectric constant of the passive film, which is usually taken as 15.6), ϵ_0 is the vacuum permittivity (8.854×10^{-14} F cm $^{-1}$), k is the Boltzmann constant (1.38×10^{-23} J K $^{-1}$), T is the absolute temperature and E_{FB} is the flat band potential. The term kT/e is neglected because it is only about 0.025 V at room temperature. From Eq. (1), N_A can be determined from the slope of the experimental C^{-2} versus E plots, and E_{FB} from the extrapolation of the linear portion to $C^{-2} = 0$. The validity of Mott-Schottky analysis is based on the assumption that the capacitance of the space charge layer is much smaller than the double layer capacitance. Hence, the capacitance determined is mainly from the contribution of the space charge layer. This assumption is reasonable provided that the frequency is high enough (on the order of kHz)²⁷⁻³⁰.

Figure 3 shows Mott-Schottky plots of AISI 321 immersed in 0.1 M NaOH + 0.1 M KOH solution from 1 to 12 h. In the potential range of around 0.0–0.6 V, a linear relationship can be observed between C^{-2} and E. In the range of 0.0–0.6 V, the positive slopes suggest that all passive films formed on AISI 321 are p-type semiconductor.

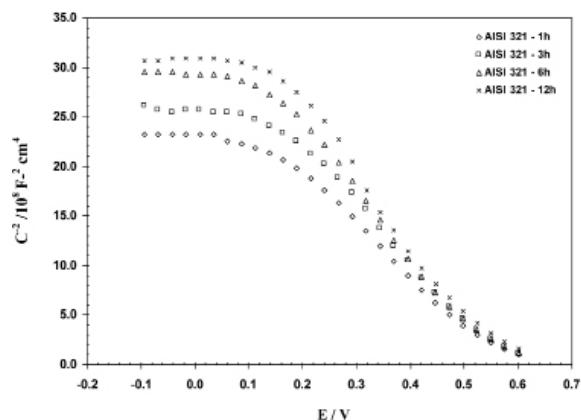


Fig. 3. Mott-Schottky plots of AISI 321 immersed in 0.1 M NaOH + 0.1 M KOH solution at different immersion times.

According to Eq. (1), the accepted density (N_A) can be calculated from the slope of the experimental C^{-2} versus E plots. Fig. 4 shows the calculated accepted densities for films formed on AISI 321 in 0.1 M NaOH + 0.1 M KOH solution. The orders of magnitude are around 10^{20} cm $^{-3}$, comparable to those reported in other studies^{15, 16}. According to Figure 4, for AISI 321, the accept densities were decreased with increasing immersion time. Changes in accepted densities correspond to the non-stoichiometry defects in the passive film. In this concept, the dominant point defects in the passive film are considered to be cation vacancies acting as electron acceptors.

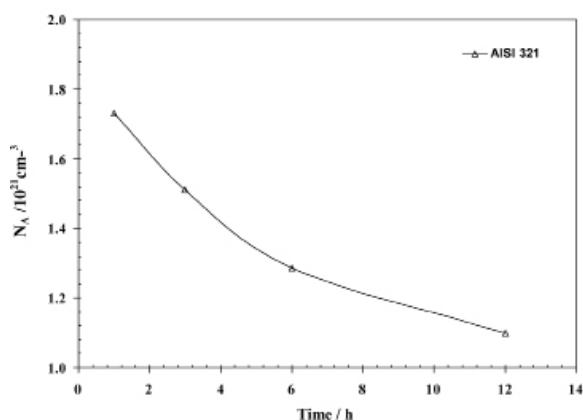


Fig. 4. Accepted densities of passive films formed on AISI 321 in 0.1 M NaOH + 0.1 M KOH solution, as a function of immersion times.

The Point Defect Model (PDM) postulates that passive films are bilayer structures comprising a highly defective barrier layer that grows into the metal and an outer layer formed via the hydrolysis of cations transmitted through the barrier layer and the subsequent precipitation of a hydroxide, oxyhydroxide, or oxide, depending upon the formation conditions. The outer layer may also be formed by the transformation of the outer surface of the barrier layer itself, provided that the outer layer is thermodynamically more stable than the barrier layer³¹⁻³⁴.

The PDM further postulates that the point defects present in a barrier layer are, in general, cation vacancies (V_M'), oxygen vacancies (V_O'), and cation interstitials (M_I^{z+}), as designated by the Kroger-Vink notation. The defect structure of the barrier layer can be understood in terms of the set of defect generation and annihilation reactions occurring at the metal/barrier layer interface and at the barrier layer-solution (outer layer) interface, as depicted in Figure 5^{31, 32}.

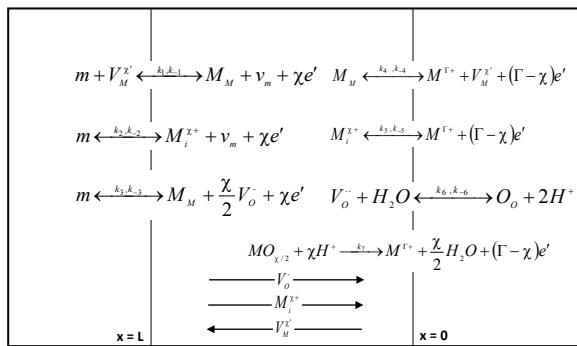


Fig. 5. Interfacial defect generation-annihilation reactions postulated to occur in the growth of anodic barrier oxide films according to the PDM. m = metal atom, M_i^{x+} = interstitial cation, M_M = metal cation on the metal sublattice of the barrier layer, and O_O^- = oxygen anion on the oxygen sublattice of the barrier layer^{31, 32}.

Cation vacancies are electron acceptors, thereby doping the barrier layer p-type, whereas oxygen vacancies and metal interstitials are electron donors, resulting in n-type doping. Thus, on pure metals, the barrier layer is essentially a highly doped, defect semiconductor, as demonstrated by Mott-Schottky analysis. Not unexpectedly, the situation with regard to alloys is somewhat more complicated than that for the pure metals, because the substitution of other metal cations having oxidation states different from the host on the cation sublattice may also impact the electronic defect structure of the film^{31, 32}.

3.4. EIS measurements

Figure 6 presents the EIS spectra of AISI 321 immersed in 0.1 M NaOH + 0.1 M KOH solution at open-circuit potential from 1 to 12 h. For AISI 321, the Nyquist plots diagrams displayed a capacitive arc that did not end at low frequency. The radius of the capacitive arc was increased with immersion time and it was related to the polarization resistance of the passive film. It is clear that the overall interfacial impedance was large ($\sim \text{k}\Omega \text{ cm}^2$) and increased with immersion time. This reflected the growth of the surface film and an enhancement of its protective behaviour as reported in the literature^{15, 16}.

Literature proposes different models of equivalent circuits to interpret the impedance data on passive films formed on stainless steels in alkaline media. The simplest version involved the modeling of the system with an equivalent circuit composed by one time constant as proposed by Feng et al.^{35, 36} to describe the behaviour of AISI 316 stainless steel in borate buffer solution. This time constant was associated with the response of the passive film. However, as shown in Figure 7 this model could not fit the impedance data obtained in the present work.

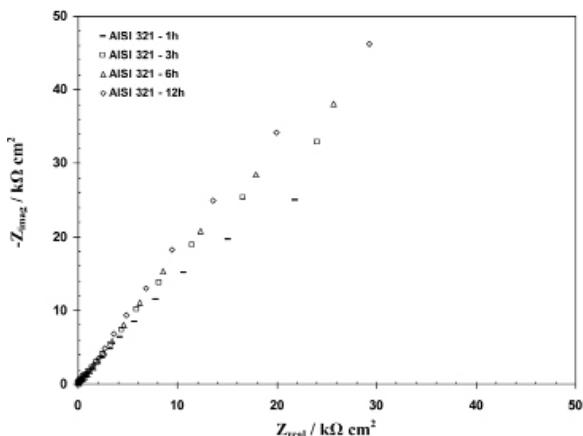


Fig. 6. Nyquist plots of AISI 321 in 0.1 M NaOH + 0.1 M KOH solution from 1 to 12 h of immersion.

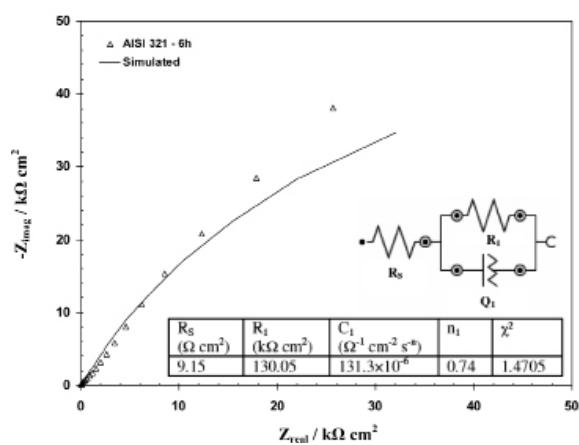


Fig. 7. The fitting results of typical Nyquist plots of AISI 321 in 0.1 M NaOH + 0.1 M KOH solution after 6 h of immersion using the simplest equivalent circuit.

The second version was the modeling of the system with an equivalent circuit composed by two time constant as proposed by Blanco et al.³⁷ to describe the passivation of austenitic and duplex stainless steels reinforcements in simulated pore solutions. This equivalent circuit, which was associated with charge transfer processes and a redox reaction on the material surface, provided a better fitting as shown in Figure 8.

The best version proposes an arrangement of two R-Q (constant phase element (CPE)) associations, as depicted in Figure 9.

This equivalent circuit has been reported as an excellent way to model the passivation of steels and stainless steels in alkaline media. This circuit presents two time constants. The interpretation suggested for the circuit elements is as follows: the high-medium frequencies (R_1 : charge transfer resistance, Q_1 : double layer constant phase element) time constant can be associated with the charge transfer process and the low-medium frequencies (R_2 , Q_2) time constant can be correlated with redox processes taking place in the surface film¹⁵. This equivalent circuit provided the best fitting as shown in Figure 10.

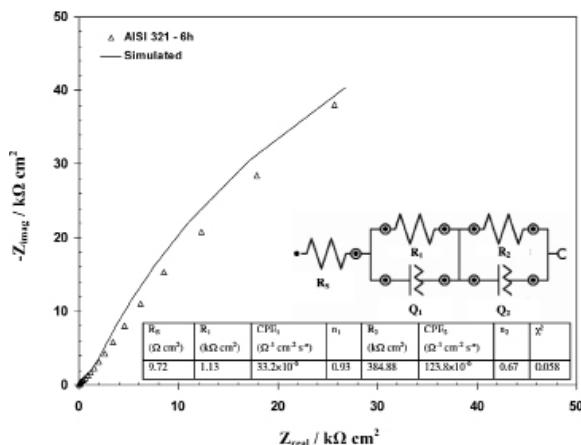


Fig. 8. The fitting results of typical Nyquist plots of AISI 321 in 0.1 M NaOH + 0.1 M KOH solution after 6 h of immersion using the second equivalent circuit.

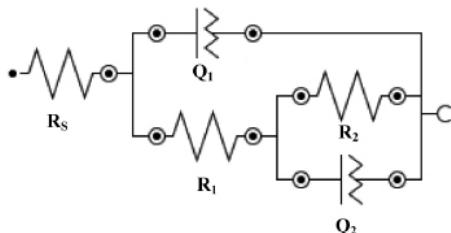


Fig. 9. The best equivalent circuit tested to model the experimental EIS data with two hierarchically distributed time constants¹⁵⁾.

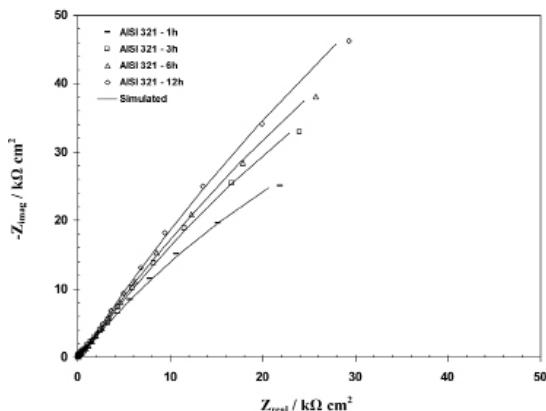


Fig. 10. The fitting results of Nyquist plots of AISI 321 in 0.1 M NaOH + 0.1 M KOH solution using the best equivalent circuit.

Table 2. Best fitting parameters for the impedance spectra of AISI 321 immersed in 0.1 M NaOH + 0.1 M KOH solution at different immersion times.

Time (h)	R_s ($\Omega \text{ cm}^2$)	R_1 ($k\Omega \text{ cm}^2$)	CPE_1 ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$)	n_1	R_2 ($k\Omega \text{ cm}^2$)	CPE_2 ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$)	n_2	χ^2
1	9.72	1.12	$10^{-6} \times 42.5$	0.93	179.91	$10^{-6} \times 149.4$	0.64	0.0526
3	9.81	1.15	$10^{-6} \times 39.9$	0.94	310.21	$10^{-6} \times 131.3$	0.66	0.0635
6	9.89	1.18	$10^{-6} \times 33.1$	0.93	384.88	$10^{-6} \times 123.8$	0.67	0.0583
12	9.84	1.19	$10^{-6} \times 31.5$	0.93	526.48	$10^{-6} \times 104.8$	0.68	0.0435

Table 2 presents the best fitting parameters (using the equivalent circuit depicted in Figure 9) obtained for films formed on AISI 321 immersed in 0.1 M NaOH + 0.1 M KOH solution from 1 to 12 h. With regard to the evolution with time, the fitting parameters R_1 and CPE_1 for films formed on AISI 321 were affected. The admittance of Q_1 was decreased from 42.5×10^{-6} to $31.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$, apparently very close to the values expected for a double layer capacitance. Also, the fitting parameters R_2 and CPE_2 were affected by the immersion time. R_2 suffered an important increase, whereas CPE_2 was decreased.

The values of CPE_2 and R_2 can be correlated with the redox processes that can occur in the passive film. The capacitance associated with CPE_2 can be determined from Eq. (2), where q represents the total amount of charge stored in the passive film and θ is the transformation degree achieved at a given electrode potential, E ³⁸⁾. A detailed analysis of redox capacitances is given in Conway's work¹⁵⁾.

$$C = q \frac{\partial \theta}{\partial E} \quad (2)$$

The transformation degree depends on the potential, which was the open circuit potential in this study. Therefore, it is possible to state that the decrease of the CPE_2 values with time indicated a diminution of the amount of charge susceptible to be transformed; thus, it accounted for the formation of more stable passive films as the immersion time was increased. Thus, the evolution of CPE_2 and the resistance R_2 with time could be observed, which increased about two or more orders of magnitude, thereby reflecting the formation of stable surface films with improved protective properties.

Polarization resistance, R_p ($R_p = R_1 + R_2$), where R_1 and R_2 were parameters from the fitting procedure, is commonly used as a measure of the resistance of a metal to the corrosion damage¹⁶⁾. The calculated R_p for the passive films formed on AISI 321 immersed in 0.1 M NaOH + 0.1 M KOH solution is shown in Figure 11. For AISI 321, after 1 h immersion, the R_p was around $170 \text{ k}\Omega \text{ cm}^2$, but it reached to $530 \text{ k}\Omega \text{ cm}^2$ after 12 h immersion.

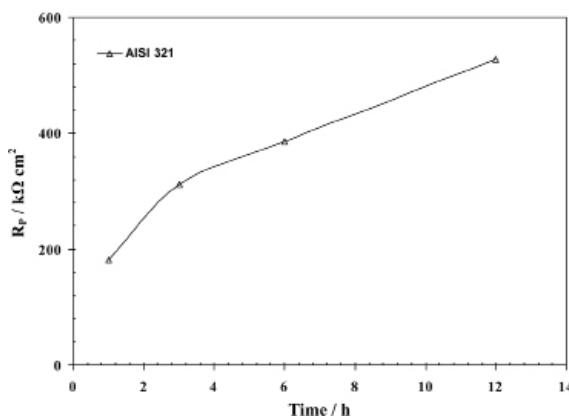


Fig. 11. R_p resistance from the fitting procedure for AISI 321 in 0.1 M NaOH + 0.1 M KOH solution at different immersion times.

4. Conclusions

The electrochemical behavior of the passive film formed on AISI 321 in 0.1 M NaOH + 0.1 M KOH solution at different immersion time was investigated in this study. Conclusions drawn from the present study are as follows

1. The OCP of AISI 321 rapidly was increased in the first 30 min; then asymptotically, it tended towards the steady state after long exposure times.
2. The polarization curves suggested that AISI 321 showed an excellent passive behaviour in 0.1 M NaOH + 0.1 M KOH solution.
3. Based on the Mott-Schottky analysis, it was shown that the accepted densities were in the range $1.0 - 3.0 \times 10^{21} \text{ cm}^{-3}$ and decreased with immersion time.
4. EIS results showed that the best electrical equivalent circuit presented two time constants: The high medium-frequencies time constant could be correlated with the charge transfer process and the low frequencies time constant was associated with redox processes taking place in the surface film.
5. For AISI 321, the overall impedance was increased with immersion time. This reflected the growth of the surface film and an enhancement of its protective behaviour.

References

- [1] B. Elsener, D. Addari, S. Coray, A. Rossi: *Electrochim. Acta.*, 56(2011), 4489.
- [2] L. Freire, M.A. Catarino, M.I. Godinho, M.J. Ferreira, M.G.S. Ferreira, A.M.P. Simões, M.F. Montemor: *Cem. Concr. Compos.*, 34(2012), 1075.
- [3] D.B. McDonald, M.R. Sherman, D.W. Pfeifer, Y.P. Virmani: *Concr. Int.*, (1995), 65.
- [4] R.D. Moser, P.M. Singh, L.F. Kahn, K.E. Kurtis: *Corros. Sci.*, 57(2012), 241.
- [5] S.D. Cramer, B.S. Covino Jr., S.L. Bullard, G.R. Holcomb, J.H. Russell, F.J. Nelson, H.M. Laylor, S.M. Soltesz, , *Cem. Concr. Compos.*, 24(2002), 101.
- [6] N.E. Hakiki, M. Da Cunha Belo, A.M.P. Simões, M.G.S. Ferreira: *J. Electrochem. Soc.*, 145(1998), 3821.
- [7] M. Da Cunha Belo, N.E. Hakiki, M.G.S. Ferreira: *Electrochim. Acta.*, 44(1999), 2473.
- [8] K. Sugimoto, Y. Sawada: *Corros. Sci.*, 37(1995), 1809.
- [9] C.M. Rangel, T.M. Silva, M. Da Cunha Belo: *Electrochim. Acta* 50(2005), 5076.
- [10] C.O.A. Olsson, D. Landolt: *Electrochim. Acta.*, 48(2003), 1093.
- [11] S. Fajardo, D.M. Bastidas, M.P. Ryan, M. Criado, D.S. McPhail, J.M. Bastidas: *Appl. Sur. Sci.*, 256(2010), 6139.
- [12] A. Poursaei, C.M. Hansson: *Cem. Concr. Res.*, 37(2007), 1127.
- [13] L. Freire, M.J. Carmezim, M.G.S. Ferreira, M.F. Montemor: *Electrochim. Acta.*, 55(2010), 6174.
- [14] H. Luo, C.F. Dong, X.G. Li, K. Xiao: *Electrochim. Acta.*, 64(2012), 211.
- [15] R.S. Dutta, R. Purandare, A. Lob, S.K. Kulkarni, G.K. Dey: *Corros. Sci.*, 46(2004), 2937.
- [16] R.S. Dutta, G.K. Dey, P.K. De: *Corros. Sci.*, 48(2006), 2711.
- [17] A. Gildenpfennig, U. Gransberg, G. Hohlneicher: *Corros. Sci.*, 45(2003), 575.
- [18] D.D. Macdonald, A. Sun: *Electrochim. Acta.*, 51(2006), 1767.
- [19] M.G.S. Ferreira, N.E. Hakiki, G. Goodlet, S. Faty, A.M.P. Simões, M. Da Cunha Belo: *Electrochim. Acta.*, 46(2001), 3767.
- [20] N.E. Hakiki, M.F. Montemor, M.G.S. Ferreira, M. da Cunha Belo: *Corros. Sci.*, 42 (2000), 687.
- [21] E.M.A. Martini, I.L. Muller: *Corros. Sci.*, 42(2000), 443.
- [22] I. Nicic, D.D. Macdonald: *J. Nucl. Mater.*, 379(2008), 54.
- [23] K.S. Raja, D.A. Jones: *Corros. Sci.*, 48(2006), 1623.
- [24] J. Macak, P. Sajdl, P. Kucera, R. Novotny, J. Vosta: *Electrochim. Acta.*, 51(2006), 3566.
- [25] Y.X. Qiao, Y.G. Zheng, W. Ke, P.C. Okafor: *Corros. Sci.*, 51(2009), 979.
- [26] Y. Yang, L. j. Guo, H. Liu: *J. Power. Sour.*, 195(2010), 5651.
- [27] Y.F. Cheng, C. Yang, J.L. Luo: *Thin Solid Films.*, 416(2002), 169.
- [28] N. Li, Y. Li, S. Wang, F. Wang: *Electrochim. Acta.*, 52(2006), 760.
- [29] D.D. Macdonald: *J. Electrochem. Soc.*, 153(2006), B213.
- [30] D.D. Macdonald: *J. Nucl. Mater.*, 379(2008), 24.

- [33] M. Kamrunnahar, J. Bao, D.D. Macdonald: Corros. Sci., 47(2005), 3111.
- [34] Y. Zhang, D.D. Macdonald, M. Urquidi-Macdonald, G.R. Engelhard, R. B. Dooley: Corros. Sci., 48(2006), 3812.
- [35] Z. Feng, X. Cheng, C.g Dong, L. Xu, X. Li: J. Nucl. Mater., 407(2010), 171.
- [36] Z. Feng, X. Cheng, C. Dong, L. Xu, X. Li: Corros. Sci., 52(2010), 3646.
- [37] G. Blanco, A. Bautista, H. Takenouti: Cem. Concr. Compos., 28(2006), 212.
- [38] A. Collazo, M.J. Cristobal, X.R. Novoa, G. Pena, M.C. Perez: J. ASTM. Int., 3(2006).