Egyptian Journal of Petroleum (2015) **24**, 405–409

HOSTED BY

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com

FULL LENGTH ARTICLE

Semiconducting behavior of pure copper in alkaline solutions

A. Fattah-alhosseini [a,*], M.K. Keshavarz [b], A. Masomi [a], S. Marianaji [a]

[a] *Faculty of Engineering, Bu-Ali Sina University, Hamedan 65178-38695, Iran*
[b] *Department of Engineering Physics, Ecole Polytechnique de Montreal, Montreal, Canada*

Received 19 June 2014; revised 14 August 2014; accepted 2 September 2014
Available online 2 November 2015

KEYWORDS

Copper;
Mott–Schottky;
Passive film;
Alkaline solution

Abstract The corrosion resistance of passive film is correlated with its semiconducting properties, which can be measured by the Mott–Schottky analysis in high frequency domain. In this study, the semiconducting behavior of passive films formed on pure copper in aqueous NaOH solutions was investigated using Mott–Schottky analysis. The polarization curves suggested that pure copper shows comparable passive behavior in NaOH solutions with different concentrations. Also, the potentiodynamic polarization curves showed corrosion current densities reduction with decrease in concentration of NaOH solutions. In Mott–Schottky analysis, no evidence of *n*-type semiconducting behavior was found, indicating that oxygen vacancies and copper interstitials do not have a significant population density in the passive film. Also, this analysis indicated that with the decrease of NaOH concentration in the solution, the acceptor density of passive films increases.
© 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Copper is extensively used in industrial and corrosion prevention applications. This metal is the most common multicomponent construction material used in the chemical and petrochemical industries. Therefore, there is a permanent interest in studying the passivation of this metal in different corrosive environments. The passivation of copper in alkaline solutions is of great interest because of the scientific importance of this phenomenon [1–3].

During the last decade, the passivation behavior of the copper in alkaline solutions has been investigated in relation to the protective characteristics of passive films and the electrochemical production of copper oxide layers [4–6]. Studies on the copper oxide passive films using different characterization methods such as X-ray diffraction, and X-ray photoemission spectroscopy have indicated that the composition of the copper oxide passive films depends on many variables such as pH, presence of aggressive anions, and aerating conditions [7–9].

Generally, there are many industrial processes in which copper has to withstand corrosive conditions in solutions of high to medium concentrations of hydroxides while these concentrated solutions can affect the passivation behavior. Therefore, the passivation behavior of copper in the alkaline solutions needs to be fully understood [9].

The main objective of this study is to investigate the semiconducting behavior of passive films, formed on pure copper in NaOH solutions, by using Mott–Schottky analysis.

* Corresponding author. Fax: +98 8138257400.
E-mail address: a.fattah@basu.ac.ir (A. Fattah-alhosseini).
Peer review under responsibility of Egyptian Petroleum Research Institute.

http://dx.doi.org/10.1016/j.ejpe.2014.09.012
1110-0621 © 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute.
This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

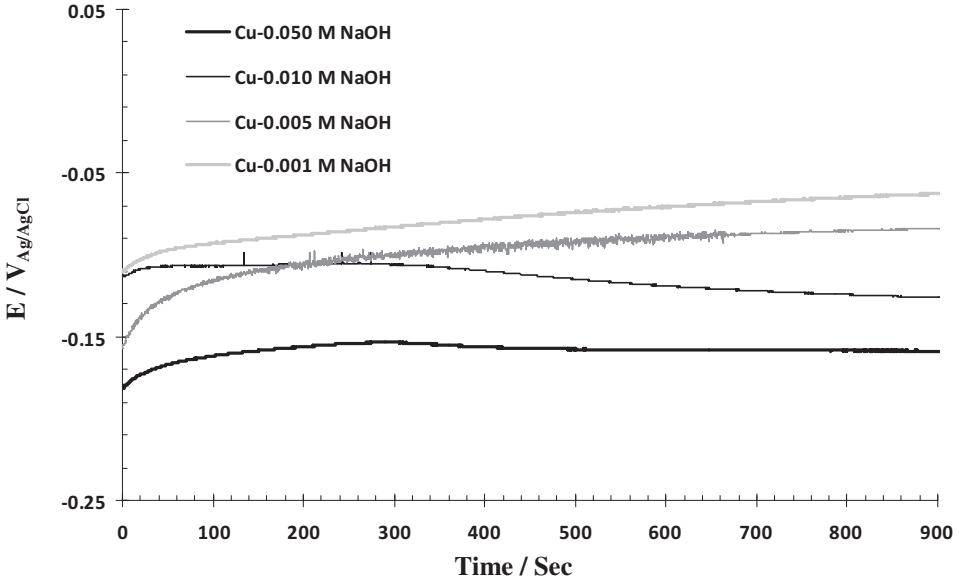

Figure 1 OCP plots of pure copper in NaOH solutions.

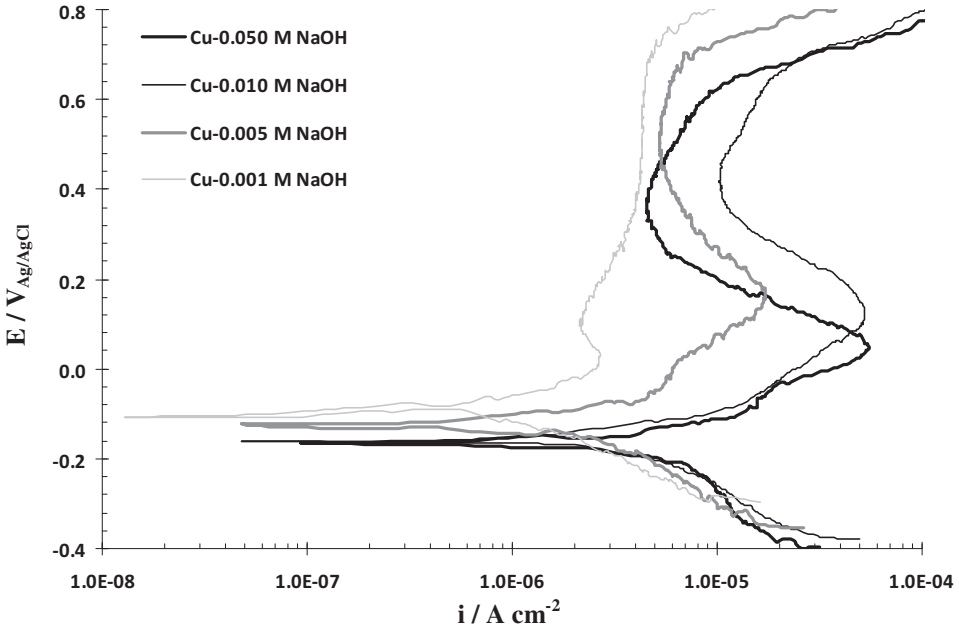

Figure 2 Potentiodynamic polarization curves of pure copper in NaOH solutions.

Furthermore, the point defect model (PDM) is used to determine the experimental data. This work includes investigation of the passive region of copper in NaOH solutions, determination of the semiconductor character, and estimation of the dopant levels in the passive films.

2. Experimental procedures

All pure copper (99.99 wt.%) samples were polished up to 1200 grit, rinsed in distilled water, and dried with air just before each electrochemical measurement. The electrochemical measurements were carried out in aerated alkaline solutions with four different NaOH concentrations (0.050, 0.010, 0.005, and 0.001 M) at 25 ± 1 °C using a conventional three-electrode flat cell.

The counter electrode was a Pt plate, while the reference electrode was Ag/AgCl saturated in KCl. Electrochemical measurements were obtained by using the μAutolab Type III/FRA2 system. Also, for the data analysis, the NOVA software was used.

Prior to electrochemical measurements, working electrodes were immersed at open circuit potential (OCP) for 900 s to form a steady-state passive film. Potentiodynamic polarization

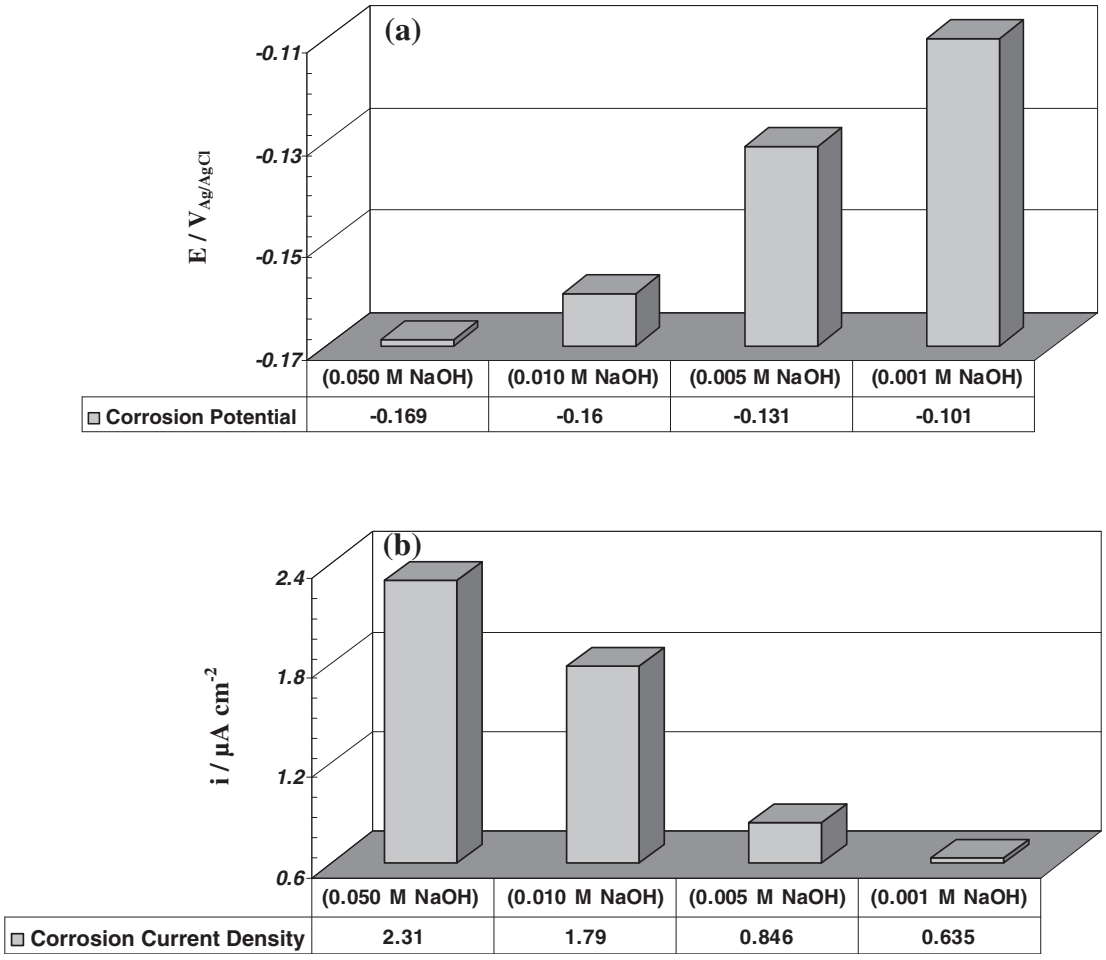

Figure 3 (a) Corrosion potential, and (b) corrosion current density of pure copper in NaOH solutions.

curves were measured potentiodynamically at a scan rate of 1 mV/s starting from −0.25 $V_{Ag/AgCl}$ (vs. E_{corr}) to 0.8 $V_{Ag/AgCl}$. Also, the corrosion current density was calculated by Tafel extrapolation of the linear part for the cathodic branch back to the corrosion potential. The Mott–Schottky analysis was carried out on passive films 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. OCP measurements

The OCP curves of pure copper in NaOH solutions are demonstrated in Fig. 1. At the start of immersion, the open circuit potential is directed toward positive values. This trend is also reported for copper alloys in alkaline solutions, which indicates the formation of passive film and its role in increasing productivity with time [10]. The OPC curves show that within 700 s a complete stable condition is achieved to implement the electrochemical tests.

3.2. Potentiodynamic polarization measurements

The potentiodynamic polarization curves of pure copper in NaOH solutions with different concentrations are illustrated in Fig. 2. By comparing the polarization curves in different solutions, it can be found that the breakdown potentials shift toward positive values with decrease in solution concentration.

The variations of corrosion potential and corrosion current density in NaOH solutions indicate that the corrosion potential moves toward positive values as the NaOH concentration decreases in the solution (Fig. 3(a)). In addition, the corrosion current density reduces with a decrease in the concentration of NaOH solutions (Fig. 3(b)).

3.3. Mott–Schottky analysis

According to the Mott–Schottky analysis, the space charge capacitance of *p*-type semiconductors is given by the following Mott–Schottky relationship (Eq. (1)) assuming that the capacitance of the Helmholtz layer could be neglected [11–13]:

$$\frac{1}{C^2} = -\frac{2}{\varepsilon\varepsilon_0 e N_A}\left(E - E_{FB} - \frac{kT}{e}\right) \quad \text{for } p-\text{type semiconductors} \tag{1}$$

where e is the electron charge, N_A represents the acceptor density for *p*-type semiconductors (cm^{-3}), ε stands for the dielectric constant of the passive film (usually taken as 16 for copper alloys [9]), ε_0 denotes the vacuum permittivity, k, T,

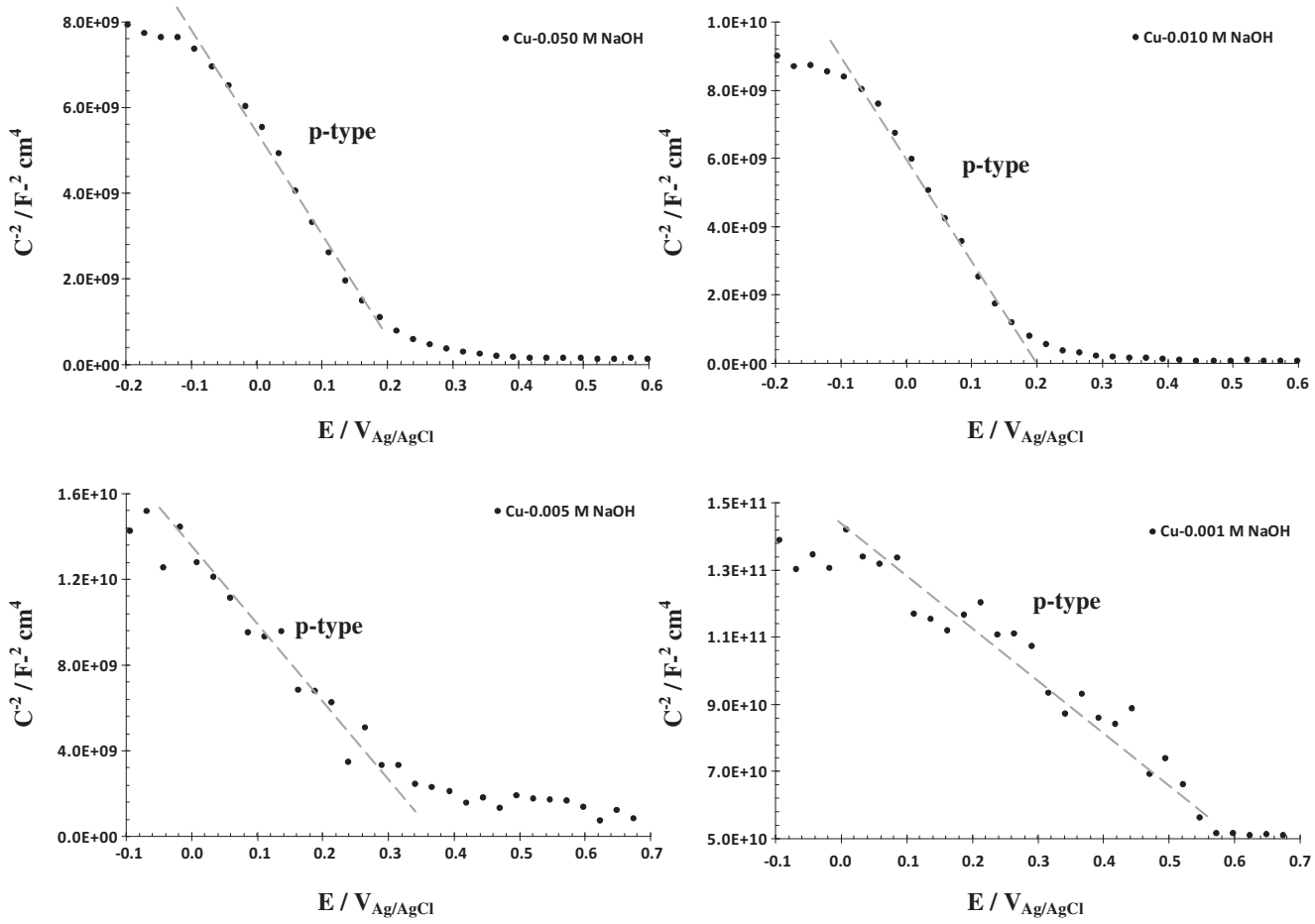

Figure 4 Mott–Schottky plots of pure copper in NaOH solutions. The electrodes are immersed at OCP for 900 s to form a steady-state passive film.

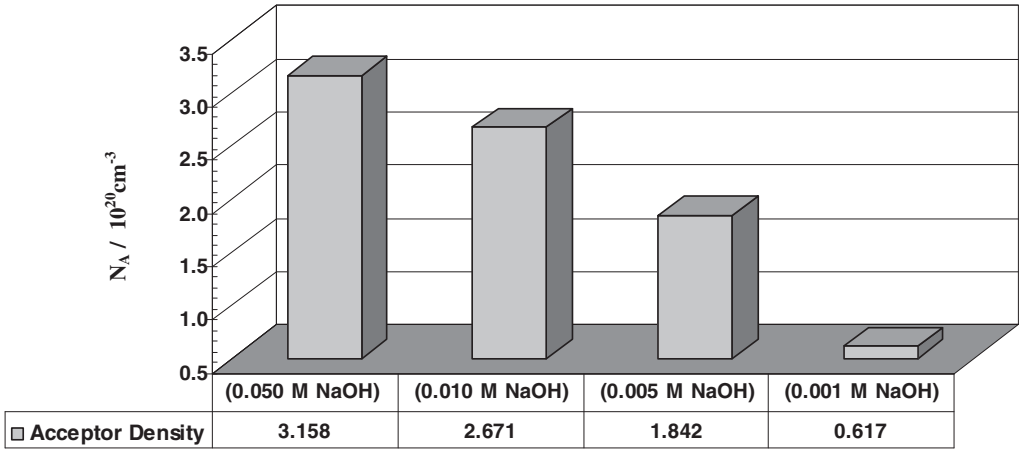

Figure 5 Calculated acceptor density of the passive films formed on pure copper in NaOH solutions as a function of concentration.

and E_{FB} are the Boltzmann constant, absolute temperature, and flat band potential, respectively [11–13].

Fig. 4 shows the Mott–Schottky plots of pure copper in NaOH solutions where by increasing the concentration of the solutions, capacitances clearly increase. Also, in all plots there is a region in which C^{-2} and E possess a somehow linear relationship.

The negative slope in this region is attributed to *p*-type behavior, due to presence of Cu_2O in the passive films [14]. Generally, passivity is due to the formation of Cu_2O,

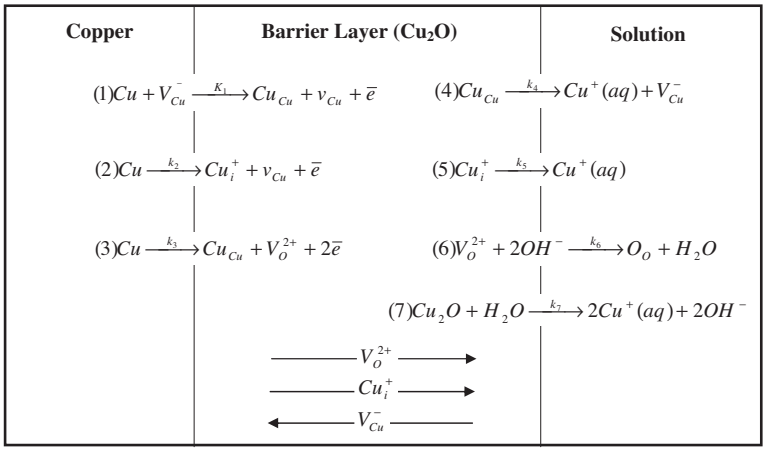

Figure 6 The modified PDM for passivation of pure copper in NaOH solutions. V_{Cu}^{-} = copper vacancy on the copper sublattice of the barrier layer, Cu_i^{+} = interstitial copper, Cu_{Cu} = copper cation on the copper sublattice of the barrier layer, V_O^{2+} = oxygen vacancy on the oxygen sublattice of the barrier layer, O_O = oxygen anion on the oxygen sublattice of the barrier layer, $Cu^{+}(aq)$ = copper cation in solution.

which is relatively stable in neutral and basic solutions. It has been reported that at open circuit potential when a passive layer grows on copper, there is a copper oxide formation [15].

The histogram demonstrated in Fig. 5 shows the calculated acceptor density for pure copper in NaOH solutions and indicates that the acceptor density increases with solution concentration. Changes in acceptor density correspond to the non-stoichiometry defects in passive films. Therefore, it can be concluded that the passive film on pure copper is disordered.

Based on the PDM [9,16], cation vacancies are electron acceptors, this leads to *p*-type conduction in the barrier layer, whereas oxygen vacancies and metal interstitials are electron donors, resulting in *n*-type doping. Ling et al. in a study on copper in anoxic sulfide-containing solutions [9], proposed the modified PDM for passivation of copper in NaOH solutions (as depicted in Fig. 6). In this modified PDM, the generation of oxygen vacancies at the Cu/Cu_2O interface (reaction (3)) and the flux of O^{2-} vacancy through the passive film, resulting from barrier layer dissolution, are essential for the film growth process. However, oxygen vacancies are electron donors, as are metal interstitials, and cannot be responsible for the *p*-type electronic character of the barrier layer. Thus, we are forced to conclude that the dominant defects in the barrier layer are the Cu(I) vacancies, which are electron acceptors, thereby the barrier layer is *p*-type doped as it is observed in Mott–Schottky analysis.

The density of acceptors (N_A) is of the order of magnitude of around 10^{20} cm^{-3}, which is comparable to those reported in other studies [13]. These high values of N_A can be attributed to a higher density of the Cu vacancies in oxide films.

4. Conclusions

The semiconducting behavior of the passive films formed on pure copper in NaOH solutions with different concentrations was investigated in the present work. The OCP plots showed that the open circuit potential shifts toward positive values, which is an indication of formation of passive films on pure copper. The polarization curves suggested that pure copper showed comparable passive behavior in solutions with different concentrations. Also, the potentiodynamic polarization curves showed that corrosion current densities reduce with a decrease in concentration of NaOH solutions. Mott–Schottky analysis indicated that the passive films displayed *p*-type semiconductive characteristics, where metal vacancies (over oxygen vacancies and interstitials) preponderated. Also, Mott–Schottky analysis showed that acceptor densities are in the order of 10^{20} cm^{-3}, which increase with solution concentration.

References

[1] Q. Zhong, L. Yu, Y. Xiao, Y. Wang, Q. Zhou, Q. Zhong, Adv. Mater. Res. 785 (2013) 928–932.
[2] N.H. El-Sayed, M.M. El-Rabiei, Egypt. J. Petrol. 23 (2014) 163–168.
[3] S.H. Sanad, A.R. Taman, Surf. Technol. 23 (1984) 159–166.
[4] R.M. Souto, S. Gonzalez, R.C. Salvarezza, A.J. Arvia, Electrochim. Acta 39 (1994) 2619–2628.
[5] M. Pérez, M. Sánchez, S. Barrera, R.M. González, R.C. Souto, A.J. Salvarezza, Electrochim. Acta 35 (1990) 1337–1343.
[6] M.M. Laz, R.M. Souto, S. González, R.C. Salvarezza, A.J. Arvia, Electrochim. Acta 37 (1992) 655–663.
[7] W. Kautek, M. Geub, M. Sahre, P. Zhao, S. Mirwald, Surf. Interface Anal. 25 (1997) 548–560.
[8] H.D. Speckmann, S. Haupt, H.-H. Streblow, Surf. Interface Anal. 11 (1988) 148–155.
[9] Y. Ling, M. Taylor, S. Sharifiasl, D.D. Macdonald, ECS Trans. 50 (2013) 53–67.
[10] W.A. Badawy, F.M. AI-Kharafi, Corrosion 55 (1999) 268–277.
[11] S. Maximovitch, Electrochim. Acta 41 (1996) 2767–2771.
[12] K. Nakaoka, J. Ueyama, K. Ogura, J. Electrochem. Soc. 151 (2004) C661–C665.
[13] K.-W. Cheng, W.-C. Lee, M.-S. Fan, Electrochim. Acta 87 (2013) 53–62.
[14] Q. Zhou, Y. Wang, Q. Zhong, Mater. Res. 399 (2012) 2067–2071.
[15] L. Yohai, W.H. Schreiner, M. Vazquez, M.B. Valcarce, Appl. Surf. Sci. 257 (2011) 10089–10095.
[16] D.D. Macdonald, J. Nucl. Mater. 379 (2008) 24–32.