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Electrochemical Behavior of the Passive Films Formed on Copper in Aqueous KOH Solutions

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Abstract- The electrochemical behavior of the passive films formed on copper in the alkaline solutions was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and Mott–Schottky analysis. In the Mott–Schottky analysis, no evidence for n-type behavior was obtained, indicating that the oxygen vacancies and the copper interstitials do not have any significant population density in the passive films. Also, this analysis revealed that with the decrease of solution concentration, the acceptor density of the passive films increased. The EIS plots indicated that the presence of two time constants, a high frequency incomplete semicircle and a low frequency rising arc. The EIS studies showed that the impedance value increased with decreases in solution concentration, which is consistent with the results of the polarization experiment.

Keywords- Copper, Mott–Schottky analysis, EIS, XRD, Passive films

1. INTRODUCTION

Copper are extensively used in industrial applications, corrosion prevention, power generation, and heat exchanger tubes. Therefore, there is a permanent interest in studying the corrosion and passivation of this metal in different conditions [1-5].

Generally, the passivation of copper in the alkaline solutions is of great interest because of the scientific importance of this phenomenon [6,7]. The passive behavior of copper in the

alkaline solutions has been investigated in relation to the protective characteristics of the passive films and the electrochemical production of copper oxide layers [8-12]. The characteristics of copper oxides are closely related to the composition of these films. The composition of the passive films formed on copper have been characterized by using different methods such as X-ray diffraction, X-ray photoemission spectroscopy, Raman spectroscopy, atomic force microscopy, scanning tunneling microscopy, and a quartz crystal microbalance. These studies indicated that the composition of the passive films depends on many variables such as applied potential, pH, presence of aggressive anions and aerating conditions [13-17].

In practice, there are industrial processes in which copper have to withstand the solutions of high and medium concentrations of hydroxides. Note that these concentrated solutions can affect the passive behavior. Therefore, it is important to pay attention to the behavior of copper in the alkaline solutions [17,18].

As can be seen from the short review above, a large number of studies have already been reported to explain the electrochemical behavior of the passive films on copper. However, little information about the effect of solution concentration on the semiconductive behavior of these passive films was available. The aim of this study is to research the electrochemical behavior of the passive films formed on copper in KOH solutions by using the EIS and Mott–Schottky analysis. Also, this work includes investigation of the passive region for the copper in KOH solutions, determination of the semiconductor character and estimation of the dopant levels in the passive film, as well as the investigation of the impedance behavior as a function of solution concentration.

2. EXPERIMENTAL PROCEDURES

Copper (99.96 wt.%) samples were polished up to 2000 grit and rinsed in distilled water and then dried with air just before each the electrochemical measurements. The alkaline solutions with different concentrations (0.600, 0.300, 0.030 and 0.003 M KOH) were used as the test solutions at 25±1°C. 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 0.9 $V_{Ag/AgCl}$.

(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.

(c) Mott-Schottky analysis was carried out on the passive films at a frequency of 1 kHz using a 10 mV ac signal and a step potential of 25 mV, in the cathodic direction.

Prior to all electrochemical, working electrodes immersed at OCP for 1000s to form a steady-state passive film. 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. 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. Finally, the structure of copper before and after immersion in KOH solutions were analyzed using the XRD (Philips PW-1800) with Cu K_α radiation (λ=0.1506 nm).

3. RESULTS AND DISCUSSION

3.1. XRD evaluations

Figs. 1 and 2 show the XRD patterns of copper before and after immersion in KOH solutions, respectively. As demonstrated in Figs. 1 and 2, the XRD patterns have three peaks which can be indexed to the diffraction from Cu(111), Cu(200), and Cu(311) lattice planes. Also, there is not any peak related to copper oxides in those patterns, which is due to the very small thickness (in few nanometers) of formed top layer.

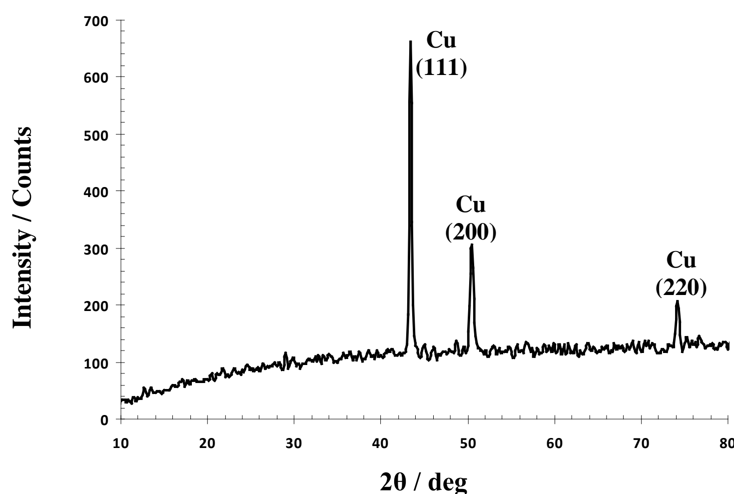

Fig. 1. XRD pattern of copper before immersion in KOH solutions

Comparing the relative intensity of the Cu peaks formed on copper in KOH solutions (Fig. 2) to that of the Cu peaks formed on this metal before immersion in KOH solutions (Fig. 1) indicates that in the sample which was immersed in the solution, the intensities of Cu(111), and Cu(200) peaks decreased and increased, respectively. Also, comparing the relative intensity of the Cu(200) and Cu(220) peaks formed on copper in KOH solutions indicates that the decrease in the solution concentration leads to higher relative intensities of these two peaks. Although the relative intensity of peak of Cu(111) planes did not have a significant change.

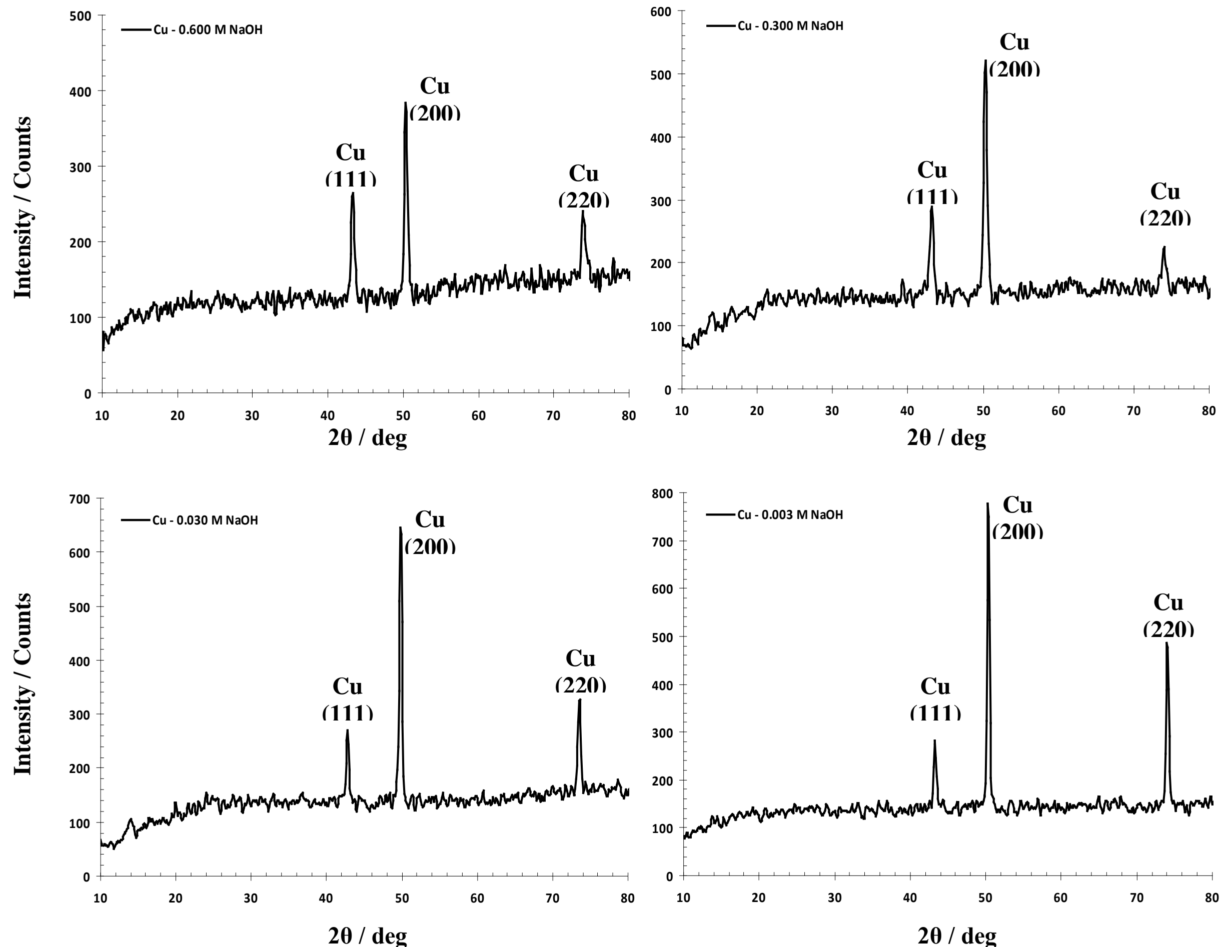

Fig. 2. XRD pattern of copper after immersion in KOH solutions

3.2. OCP and potentiodynamic polarization measurements

The OCP curves of pure copper in KOH solutions are demonstrated in Fig. 3(a). At the start of immersion, the open circuit potential is directed towards 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 protectivity with time [18]. The OPC curves show that within 1000 s a complete stable condition is achieved to implement the electrochemical tests.

Fig. 3(b) shows the potentiodynamic polarization curves of copper in KOH solutions with different concentrations. By comparing the polarization curves in different solutions, it can be found that the breakdown potentials decreased with solution concentration. The variation of the corrosion potential and the corrosion current density in KOH solutions are illustrated in Fig. 4. It is observed that the corrosion potential shifts towards the positive value with decrease in solution concentration. Also, the results show that the corrosion current density decreases with decrease in the concentration of KOH solutions.

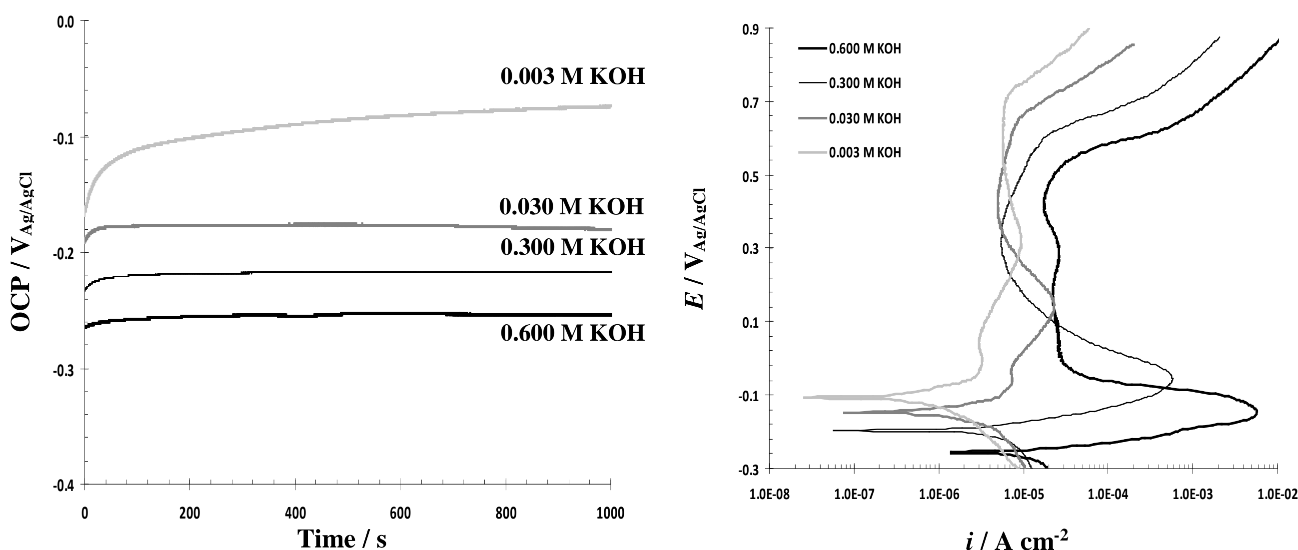

Fig. 3. OCP and potentiodynamic polarization curves of copper in KOH solutions

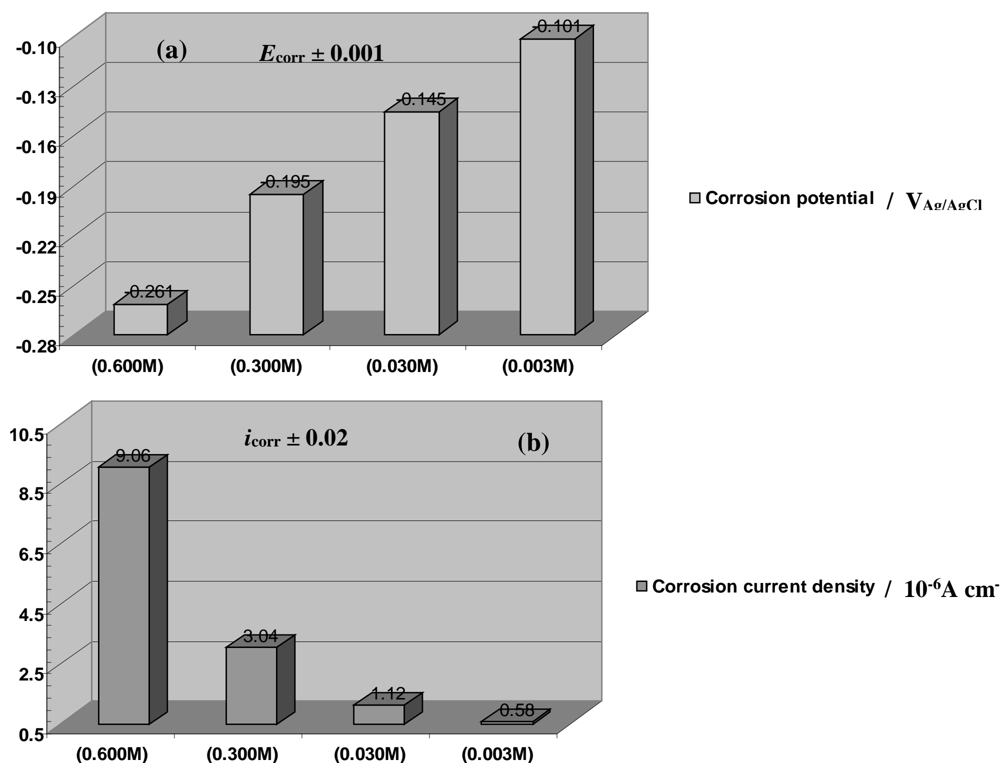

Fig.4. Variations of the (a) corrosion potential and (b) corrosion current density of copper in KOH solutions

3.3. Mott-Schottky analysis

Fig. 5 shows the Mott-Schottky plots of copper in KOH 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 and according to Eq. (1), acceptor density has been determined from these positive slopes [19-22]:

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

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 [17]), ε_0 denotes the vacuum permittivity, k, T, *and* E_{FB} are the Boltzmann constant, absolute temperature, and flat band potential, respectively [19-24]. The flat band potential can be determined from the extrapolation of the linear portion to C^{-2}=0. As it is shown, the flat band potential of this alloy increases when the concentration of solution decreases.

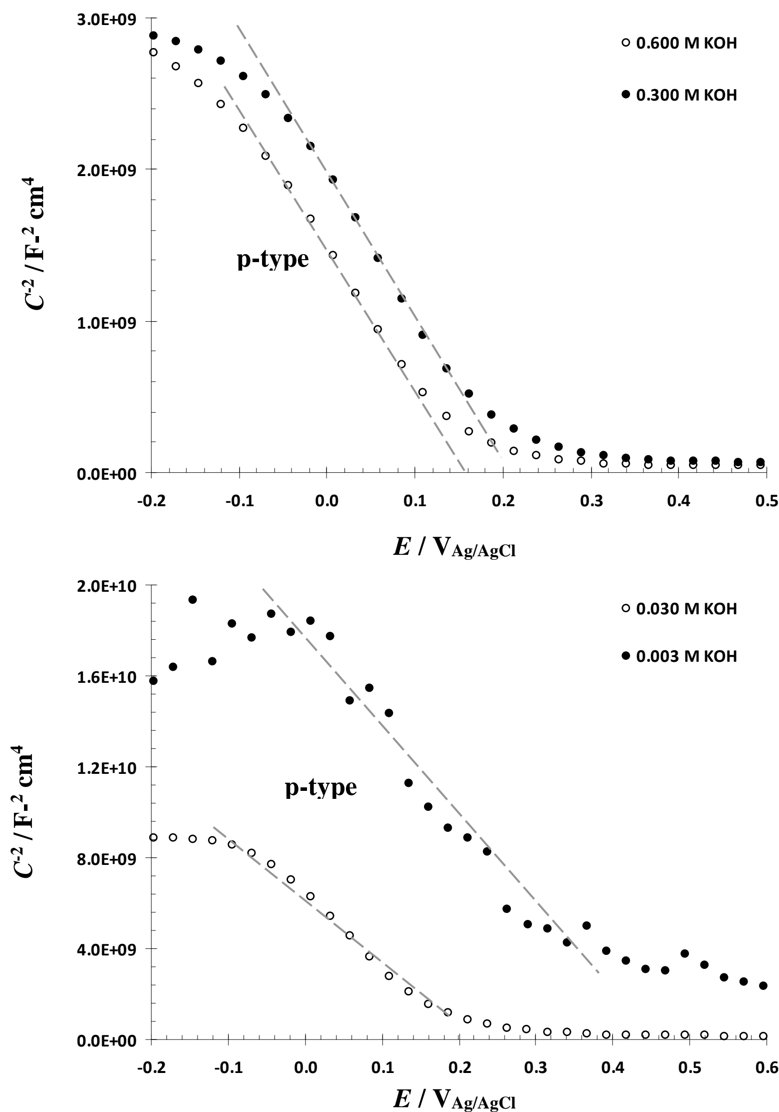

Fig. 5. Mott-Schottky plots of copper in KOH solutions

Fig. 6 shows the calculated acceptor density of copper in KOH solutions. According to Fig. 6, the acceptor density increases with solution concentration. The Changes in the acceptor density correspond to the non-stoichiometry defects in the passive films. Based on the point defect model [17,25], the cation vacancies are electron acceptors, thereby doping the barrier layer p-type, whereas the oxygen vacancies and the metal interstitials are electron donors, resulting in the n-type doping. The orders of magnitude of the acceptor density are around 10^{21} cm^{-3} and are comparable to those reported in other studies [23]. These high values of the acceptor density can be attributed to a higher density of the Cu vacancies in the passive films.

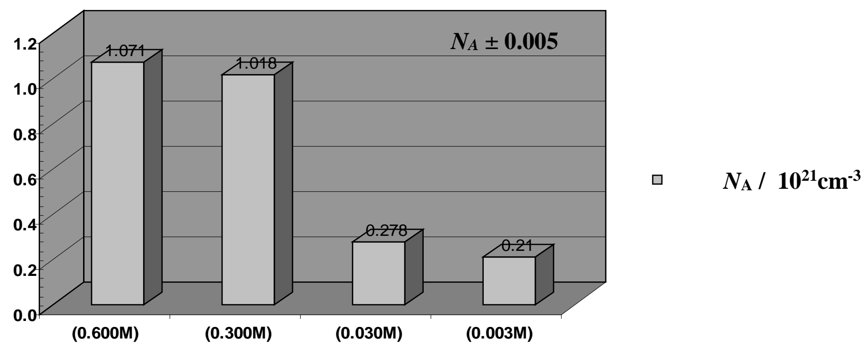

Fig. 6. Calculated acceptor density of the passive films formed on copper in KOH solutions as a function of KOH concentration

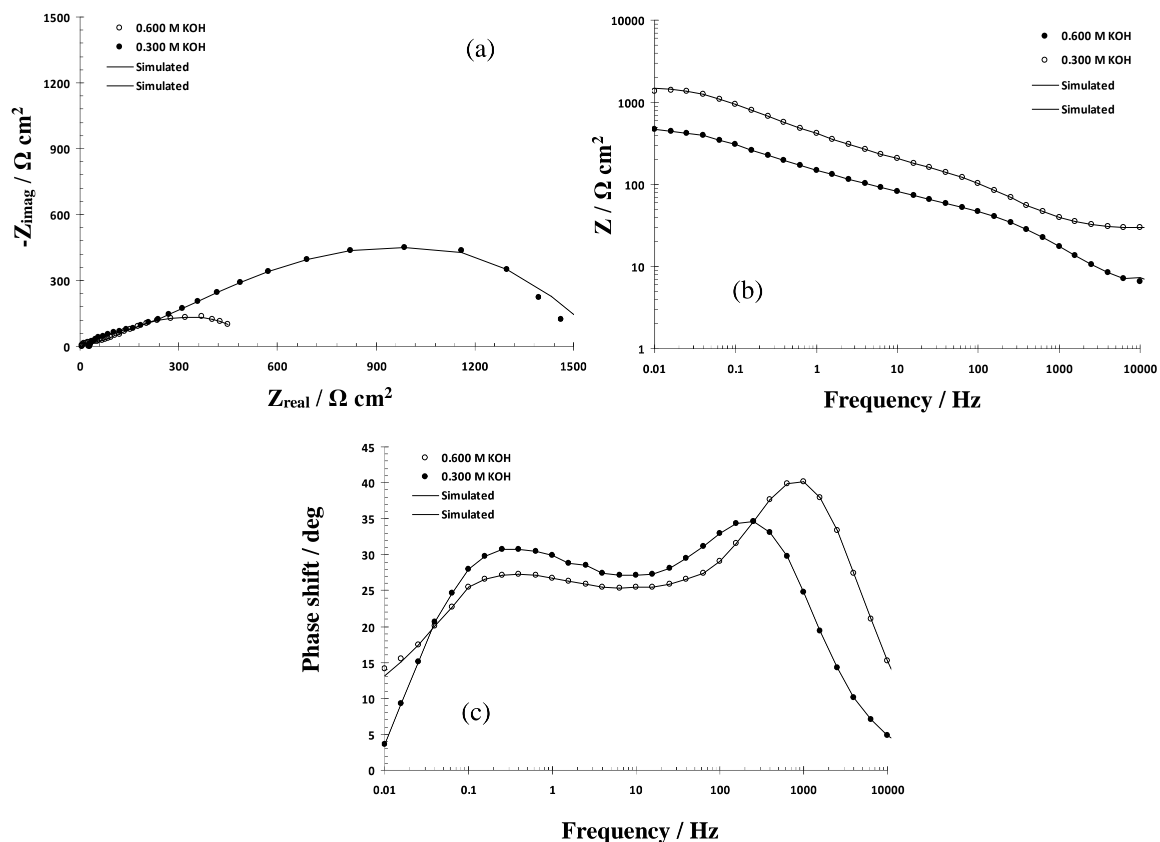

Fig. 7. Nyquist and Bode plots of copper in 0.600 and 0.300 M KOH solutions

3.4. EIS measurements

Figs. 7 and 8 present the Nyquist and Bode plots of copper in KOH solutions. The Nyquist plots (Figs. 7(a) and 8(a)) indicate the presence of two time constants, a high and a low frequency incomplete semicircle. In Figs. 7(c) and 8(c), all Bode phase plots show two phase maxima at the high and low frequencies.

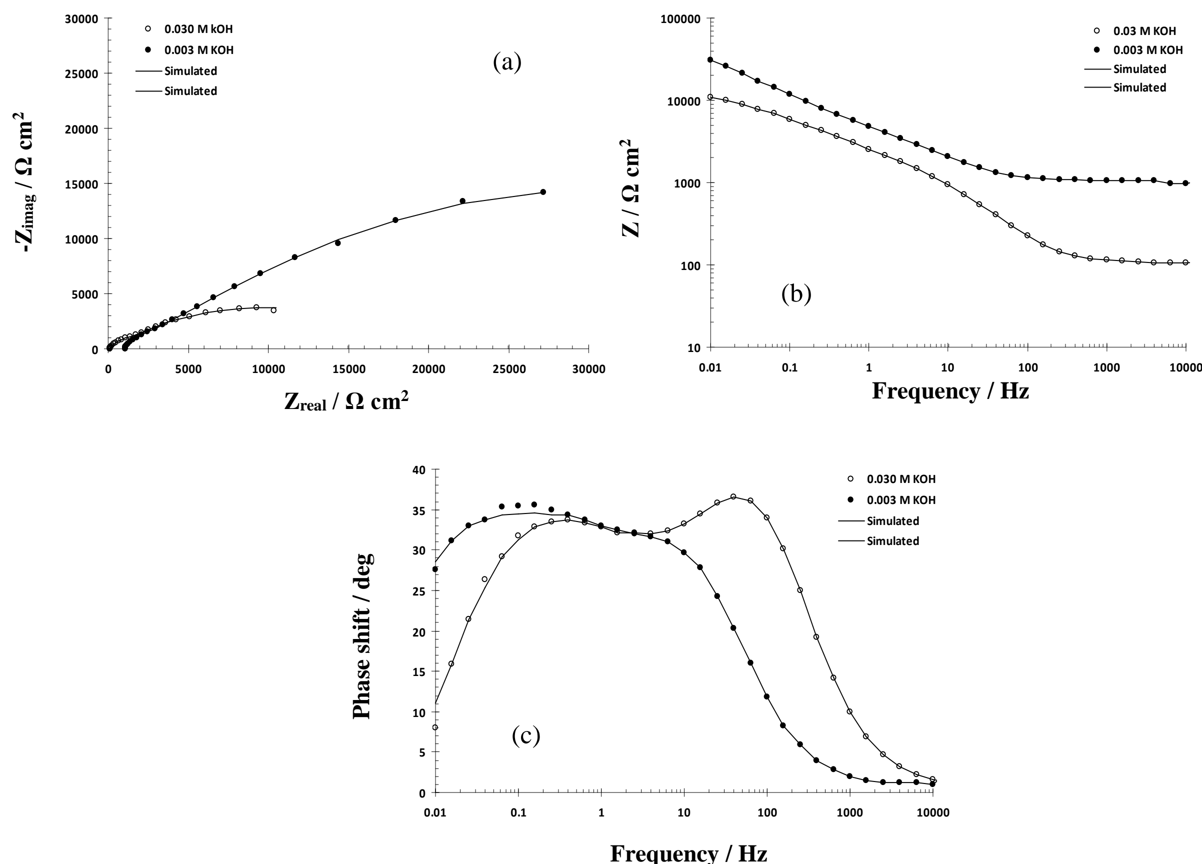

Fig. 8. Nyquist and Bode plots of copper in 0.030 and 0.003 M KOH solutions

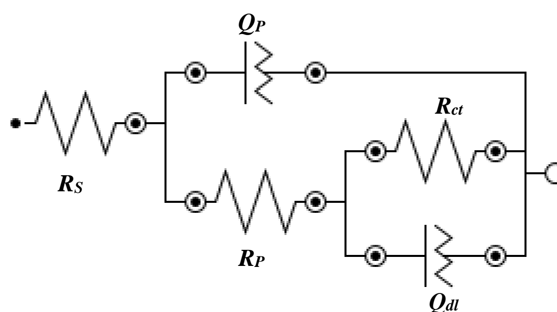

Fig. 9. Best equivalent circuit used to model the EIS data of copper in KOH solutions

Therefore, the equivalent circuit shown in Fig. 9 (with two time constants) was used to simulate the measured impedance data on copper in KOH solutions [2,26]. In this equivalent

model, Q_P the constant phase element of the passive film, R_p the passive film resistance, Q_{dl} the constant phase element of the double layer, R_{ct} the charge-transfer resistance, and R_S represents the solution resistance. As shown in Figs. 7 and 8, this equivalent circuit could fit the impedance data.

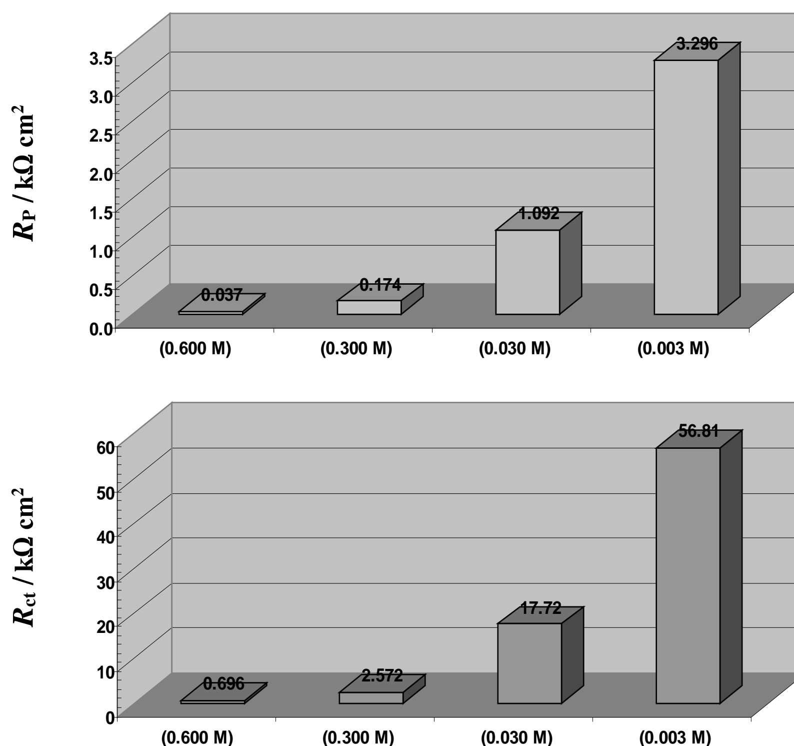

Fig. 10. Variations of the (a) passive film resistance and (b) charge-transfer resistance of copper in KOH solutions

The variation of the passive film resistance (R_p) and the charge-transfer resistance (R_{ct}) of copper in KOH solutions are illustrated in Fig. 10. It is observed that as the concentration decreases, R_p and R_{ct} increases. Therefore, the measured value of polarization resistance ($=R_p+R_{ct}$) increases with decreasing concentration of KOH solutions, indicating that the corrosion current densities decreases with decrease in concentration of solutions.

4. CONCLUSIONS

1. The potentiodynamic polarization curves revealed that the corrosion current densities decrease with decrease in concentration of KOH solutions.
2. The Mott–Schottky analysis indicated that the passive films displayed the p-type semiconductive characteristics, where the metal vacancies (over the oxygen vacancies and interstitials) preponderated.

3. Also, the Mott–Schottky analysis showed that the acceptor densities are in the order of 10^{21} cm^{-3}, which increases with solution concentration.
4. The EIS plots indicated the presence of two time constants, a high and a low frequency incomplete semicircle.
5. The EIS studies showed that the impedance value increased with decreases in solution concentration, which is consistent with the results of the polarization experiment.

REFERENCES

[1] P. Shi, Q. Wang, Y. Xu, and W. Luo, Mater. Lett. 65 (2011) 857.
[2] O. Imantalab, and A. Fattah-alhosseini, J. Mater. Eng. Perform. 24 (2015) 2579.
[3] Q. Zhong, L. Yu, Y. Xiao, Y. Wang, Q. Zhou, and Q. Zhong, Advanc. Mater. Res. 785 (2013) 928.
[4] M. M. Antonijevic, S. C. Alagic, M. B. Petrovic, M. B. Radovanovic, and A. T. Stamenkovic, Int. J. Electrochem. Sci. 4 (2009) 516.
[5] A. M. Alfantazi, T. M. Ahmed, and D. Tromans, Mater. Des. 30 (2009) 2425.
[6] J. Kunze, V. Maurice, L. H. Klein, H. H. Strehblow, and P. Marcus, Corros. Sci. 46 (2004) 245.
[7] G. Kear, B. D. Barker, and F. C. Walsh, Corros. Sci. 46 (2004) 109.
[8] D. W. Shoesmith, T. E. Rummery, D. Owen, and W. Lee, J. Electrochem. Soc. 123 (1976) 790.
[9] Y. Ashworth, and D. Fairhurst, J. Electrochem. Soc. 124 (1977) 506.
[10] R. M. Souto, S. Gonzalez, R. C. Salvarezza, and A. J. Arvia, Electrochim. Acta 39 (1994) 2619.
[11] M. Pérez Sánchez, M. Barrera, S. González, R. M. Souto, R. C. Salvarezza, and A. J. Arvia, Electrochim. Acta 35 (1990) 1337.
[12] M. M. Laz, R. M. Souto, S. González, R. C. Salvarezza, and A. J. Arvia, Electrochim. Acta 37 (1992) 655.
[13] D. W. Soesmith, T. E. Rummery, D. Owen, and W. Lee, J. Electrochem. Soc. 123 (1976) 790.
[14] W. Kautek, M. Geub, M. Sahre, P. Zhao, and S. Mirwald, Surf. Interface Anal. 25 (1997) 548.
[15] W. Kautek and J. G. Gordon, J. Electrochem. Soc. 137 (1990) 2672.
[16] H. D. Speckmann, S. Haupt, and H. H. Streblow, Surf. Interface Anal. 11 (1988) 148.
[17] Y. Ling, M. Taylor, S. Sharifiasl, and D. D. Macdonald, ECS Transactions 50 (2013) 53.
[18] W. A. Badawy, and F. M. AI-Kharafi, Corros. 55 (1999) 268.
[19] O. Imantalab, and A. Fattah-alhosseini, Anal. Bioanal. Electrochem. 7 (2015) 210.
[20] K. Nakaoka, J. Ueyama, and K. Ogura, J. Electrochem. Soc. 151 (2004) C661.

[21] K. W. Cheng, W. C. Lee, and M. S. Fan, Electrochim. Acta 87 (2013) 53.
[22] Y. K. Hsu, C. H. Yu, Y. C. Chen, and Y. G. Lin, J. Power Sources 242 (2013) 541.
[23] Q. Zhou, Y. Wang, and Q. Zhong, Advanc. Mater. Res. 399 (2012) 2067.
[24] L. Yohai, W. H. Schreiner, M. Vazquez, and M. B. Valcarce, Appl. Sur. Sci. 257 (2011) 10089.
[25] D. D. Macdonald, J. Nucl. Mater. 379 (2008) 24.
[26] C. Liu, Q. Bi, A. Leyland, and A. Matthews, Corros. Sci. 45 (2003) 1243.

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