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Electrochemical and Semiconducting Behaviour of a Brass Alloy in Borax Solutions

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Abstract
In this study, the electrochemical and semiconducting behaviour of a brass alloy in borax solutions under open circuit potential (OCP) was investigated. The OCP plots showed that the open circuit potential values in all solutions shifts towards positive amounts, which is an indicative of formation of the passive films. The potentiodynamic polarization curves revealed that the corrosion current densities decrease with decrease in concentration of borax solutions. The Mott–Schottky analysis indicated that the passive films displayed p-type semiconductive characteristics, where the metal vacancies preponderated. Also, the Mott–Schottky analysis revealed that with the decrease of solution concentration, the acceptor density of the passive films decreased. Finally, the electrochemical impedance spectroscopy (EIS) data showed that the decrease in solution concentration increases the impedance value.

Keywords: Brass; Polarization, Electrochemical impedance spectroscopy.

Introduction
The passivation behaviour of brass alloys in the alkaline solutions has been studied using various electrochemical measurements [1-6]. Also, the composition of the passive films have been confirmed by using different analytical methods such as X-ray diffraction, electron diffraction, X-ray photoemission spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, and a quartz crystal microbalance [7-10].
These studies indicated that the composition and performance of the passive films formed on brass alloys in aqueous solutions depends on variables such as applied potential, polarization time, and aerating conditions and pH. While there are reports on the passivation behaviour of brass alloys in the alkaline solutions, it seems that the passivation of these important alloys in the alkaline solution was not explored yet. There are industrial processes in which brass alloys have to withstand the solutions of high concentrations of hydroxides. Note that such concentrated solutions can affect very strongly the passivation phenomena. Thereby, it is important to pay attention to the electrochemical behaviour of brass alloys [11].
Only a few published papers discussed about the effects of solution concentration on the electrochemical behaviour of the passive film formed on copper and brass alloys was available. These papers usually studied the electrochemical behavior of the passive film formed on copper and brass alloys without consideration about the semiconductive behaviour, separately. But the objective of this paper is to research the electrochemical and semiconducting behaviour of the passive films formed on a brass alloy (Cu70/Zn30) in borax solutions by using the EIS and Mott–Schottky analysis.

2. Materials and methods
Chemical composition of a brass alloy (Cu70/Zn30) used in present investigation is shown in Table 1. All samples were polished up to 2000 grit and mounted by cold curing epoxy resin. The samples were then rinsed in distilled water and dried with air just before each test. The alkaline solutions with different concentrations (0.10, 0.07, 0.05 and 0.03 M borax) were used as the test solutions.

Table 1: Chemical compositions of the brass alloy (Cu70/Zn30) .

Elements	Zn	Ni	Fe	Mn	Al	S	Ag	Co	Si	Cu
Brass alloy /wt%	29.5	0.04	0.05	0.005	0.014	0.002	0.003	<0.01	<0.005	Bal

The electrochemical measurements were performed in a conventional three-electrode cell under aerated conditions. The counter electrode was a Pt plate, while the reference electrode was Ag/AgCl saturated in KCl. The electrochemical measurements were obtained by using a Autolab potentiostat/galvanostat system. Prior to the electrochemical measurements, working electrodes were immersed at OCP for 900 seconds to form a steady-state passive film. The potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV/s starting from -0.25 $V_{Ag/AgCl}$ (vs. E_{corr}) to 1.2 $V_{Ag/AgCl}$. The impedance spectra were measured in a frequency range of 100 kHz –10 mHz at an AC amplitude of 10 mV (rms). The validation of the impedance spectra was performed by checking the linearity condition, i.e. measuring the spectra at AC signal amplitudes between 5 and 15 mV (rms). Each the electrochemical measurement was repeated at least three times. For the EIS data modeling and curve-fitting method, the NOVA impedance software was used. The Mott-Schottky analysis were carried out on the 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

In Fig. 1, changes on the OCP of the brass alloy in borax solutions are shown. At the start of immersion, the open circuit potential is directed towards the positive amount. This trend is also reported for other brass alloys in the alkaline solutions which is indicative of the formation of the passive film and its role in increasing protectivity with time [12]. Fig. 1 also indicates that within 900 seconds a complete stable condition is achieved and the electrochemical tests are possible.

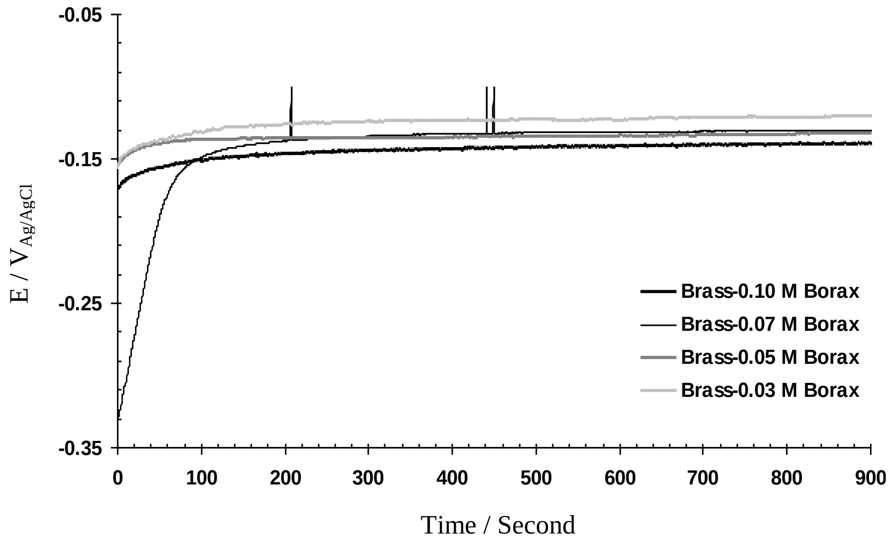

Figure 1: Open circuit potential plots of the brass alloy in borax solutions.

3.2. Potentiodynamic polarization measurements

Fig. 2 shows the potentiodynamic polarization curves of the brass alloy in borax solutions with different concentrations. By comparing the polarization curves in different solutions, the passive current densities were found to decrease with decrease in solution concentration. For all curves, the current density increased with the potential during the early stage of the passivation and no obvious current peak was observed. Also, all curves exhibit similar features, with a passive potential range extending from the corrosion potential to the onset of transpassivity.

The variation of the corrosion current density of this alloy in borax solutions are illustrated in Fig. 3. It is observed that the corrosion current density decreases with decrease in the concentration of borax solutions.

3.3. Mott-Schottky analysis

Generally, the corrosion resistance of the passive film was correlated with its semiconducting properties, which could be measured by the Mott–Schottky analysis in high frequency domain. According to the Mott–Schottky analysis, the space charge capacitance of p-type semiconductor was given by the following the Mott–Schottky relationship (1) assuming that the capacitance of the Helmholtz layer could be neglected [13-16]:

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

where e is the electron charge (-1.602×10^{-19} C), N_A is the acceptor density for p–type semiconductor (cm^{-3}), ε is the dielectric constant of the passive film (usually taken as 12 for copper alloys [11]), ε_0 is the vacuum permittivity (8.854×10^{-14} F cm^{-1}), k is the Boltzmann constant, T is the absolute temperature and E_{FB} is the flat band potential. The Flat band potential can be determined from the extrapolation of the linear portion to $C^{-2} = 0$ [13-16].

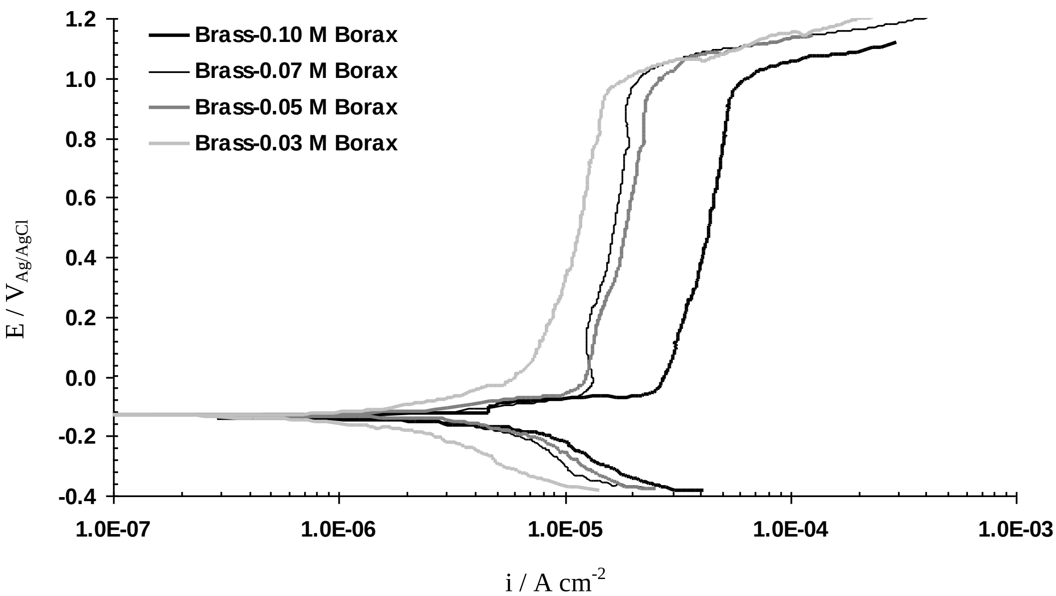

Figure 2: Potentiodynamic polarization curves of the brass alloy in borax solutions with different concentration

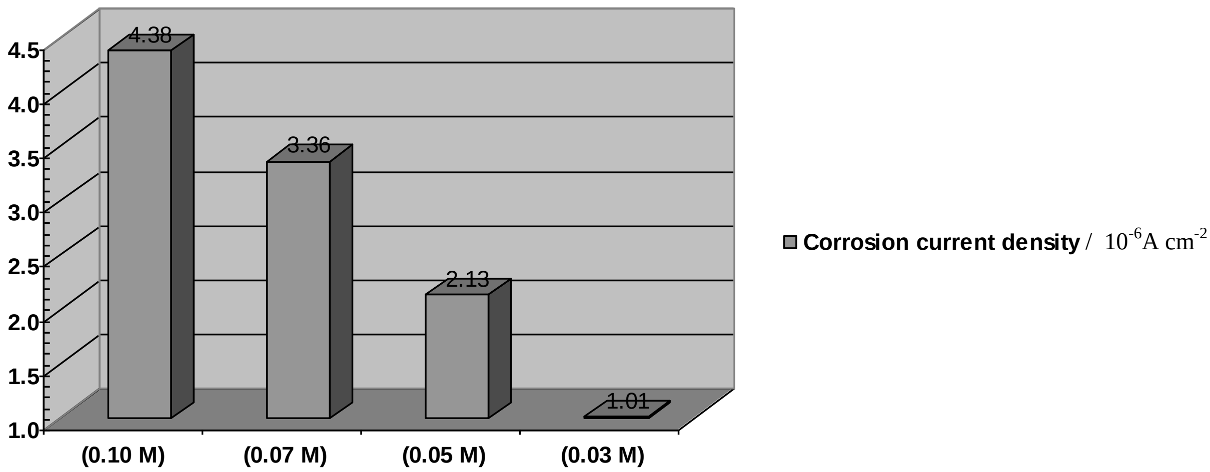

Figure 3: Corrosion current density of the brass alloy in borax solutions.

Fig. 4 shows the Mott-Schottky plots of the brass alloy in borax solutions. Firstly, it should be noted that for all concentration, the capacitances clearly increase with solution concentration. Secondly, all plots show one region in which a linear relationship between C^{-2} and E could be observed. The negative slope in this region is attributed to p-type behaviour, probably due to the presence of Cu_2O in the passive films [14].

It is reported [1] that the anodic polarization of the brass alloy involves the dissolution of Zn and Cu elements. The other studies of the behaviour of brass alloy in O_2-saturated and O_2-free solutions showed that the behaviour was dependent on the pH of the solutions. Indeed, the passivity is due to the formation of Cu_2O, which is relatively stable in the neutral and basic solutions. For brass, it is reported that when a passive layer grows at the OCP, the first step is the preferential dissolution of Zn from the alloy, leaving a copper-rich surface. Subsequently, the copper oxide formation begins [17].

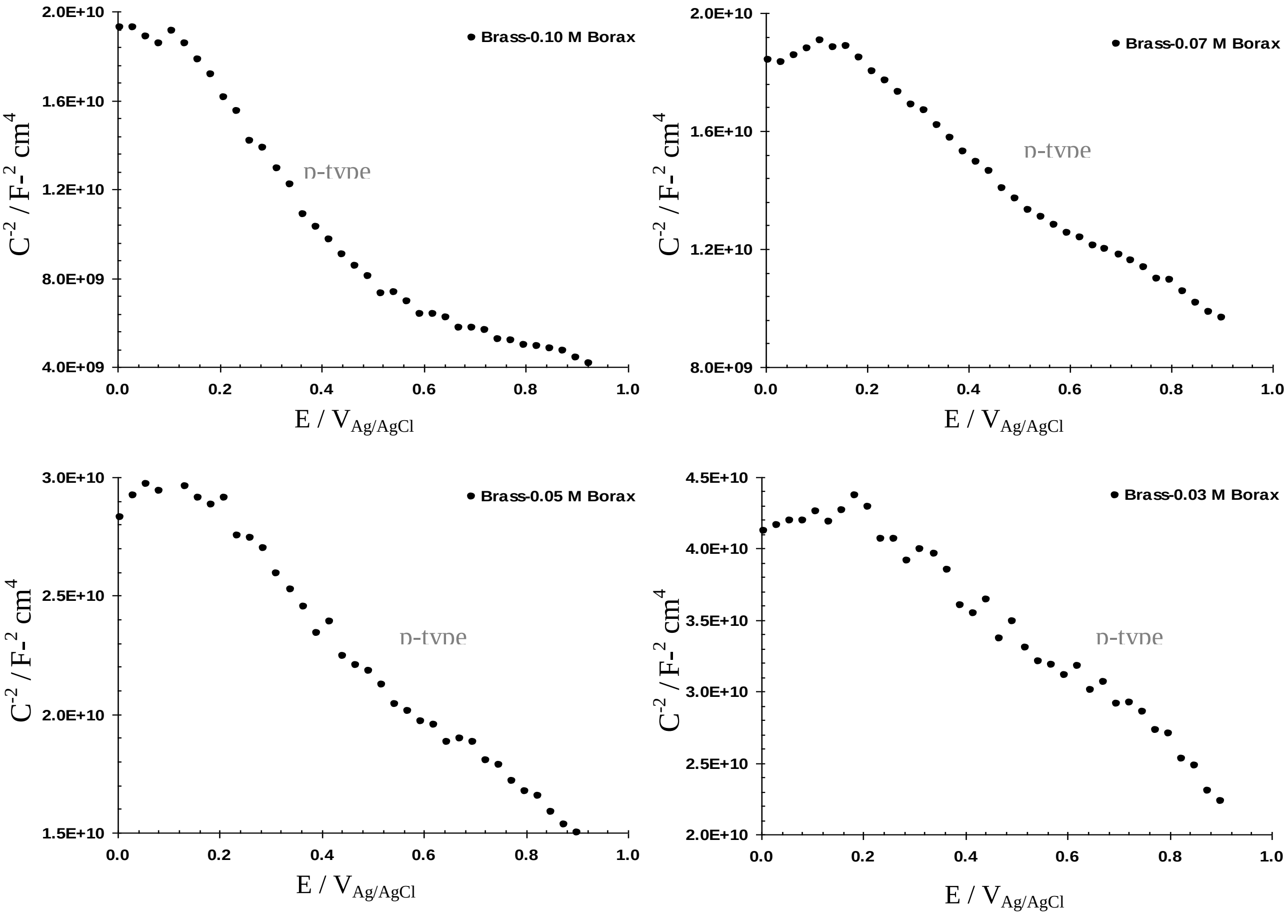

Figure 4: Mott-Schottky plots of the brass alloy in borax solutions. The electrodes are immersed at OCP for 900 seconds to form a steady-state passive film.

Fig. 5 shows the calculated acceptor density for the brass alloy in borax solutions. According to Fig. 5, the acceptor density increases with solution concentration. The changes in acceptor density correspond to the non-stoichiometry defects in the passive films. Therefore, it can be concluded that the passive film on the brass alloy is disordered. Based on the point defect model [18], the cation vacancies are electron acceptors, thereby doping the barrier layer p-type, whereas the oxygen vacancies and metal interstitials are electron donors, resulting in n-type doping. The orders of magnitude of N_A are around 10^{20} cm^{-3} and are comparable to those reported in other studies [14]. These high values of the calculated acceptor density can be attributed to a higher density of the Zn vacancies in the oxide films.

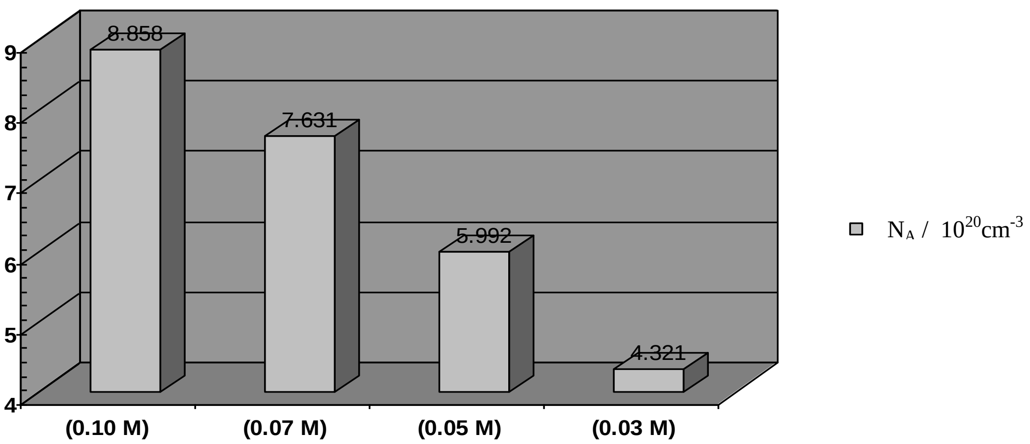

Figure 5: Calculated acceptor density of the passive films formed on the brass alloy in borax solutions as a function of concentration.

3.4. EIS measurements

Fig. 6 shows the Nyquist and Bode plots of the brass alloy at the OCP after 900 seconds immersion in borax solutions. The Nyquist plots (Fig. 6(a)) show that the decrease in solution concentration increases the impedance value, due to increase of the preferential dissolution of the brass alloy. Also, as it can be seen from Fig. 6(b), clearly the impedance (Z) increase with decrease in concentration of borax solutions.

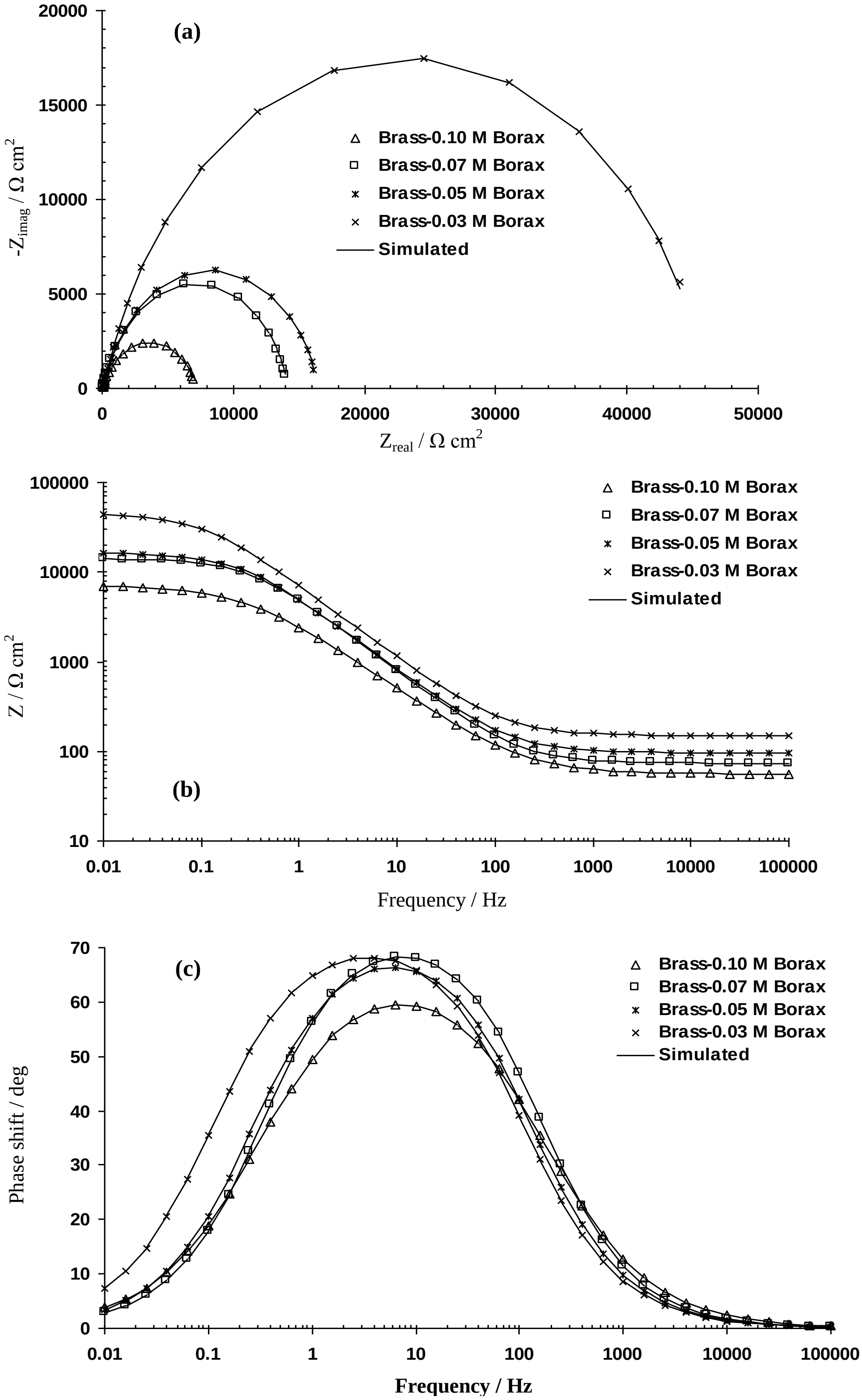

Figure 6: Nyquist and Bode plots of the brass alloy in borax solutions.

In Fig. 6(c), all Bode plots show one phase maxima at the intermediate frequencies. Also, the phase angle in the low-frequency range decreases, with reaching zero. Therefore, the equivalent circuit shown in Fig. 7 was used to simulate the measured impedance data on of the brass alloy in borax solutions. This equivalent circuit is composed of: R_s – solution resistance; CPE_{pf} – constant phase element corresponding to the capacitance of the passive film; R_{pf} – resistance of the passive film [19]. In the investigated frequency range (100 kHz– 10 mHz) contribution of the double layer, or reaction of oxygen evolution has not been detected and the capacitance and the resistance of the passive film dominate the overall process in the passive film. Eq. (2) used in all available software in which the CPE is treated as an independent component of the equivalent circuit [20]:

$$Z = R_s + \frac{R_{pf}}{1 + (j\omega)^n C_{pf} R_{pf}} \quad (2)$$

As shown in Fig. 6, this equivalent circuit could fit the impedance data. Table 2 presents the best fitting parameters obtained for the films formed on the brass alloy immersed in borax solutions. Fitting data shows that as the concentration decreases, the passive film resistance (R_{pf}) increases.

Table 2: Best fitting parameters for the impedance spectra of the brass alloy in borax solutions.

Borax Solutions	R_S (Ω cm^2)	R_{pf} (kΩ cm^2)	C_{pf} (μF cm^{-2})	n
0.10 M	55.6	7.12	85.75	0.836
0.07 M	73.6	14.14	39.54	0.846
0.05 M	96.1	16.45	37.91	0.830
0.03 M	149.2	46.24	29.75	0.826

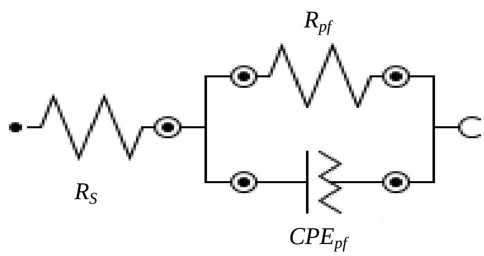

Figure 7: Best equivalent circuit used to model the experimental EIS data of the brass alloy in borax solutions.

Conclusion

The electrochemical behaviour of the passive film formed on the brass alloy in borax solutions were investigated in the present work. Conclusions drawn from the study are as follows

1. The OCP plots showed that the open circuit potential values shifts towards positive amounts, which is an indicative of formation of the passive films.
2. The potentiodynamic polarization curves showed that the corrosion current densities decrease with decrease in concentration of borax solutions.
3. The Mott–Schottky analysis indicated that the passive films displayed p-type semiconductive characteristics, where the metal vacancies (over the oxygen vacancies and interstitials) preponderated.
4. Also, the Mott–Schottky analysis showed that the acceptor densities are in the order of 10^{20} cm^{-3}, which decrease with decrease in concentration of borax solutions. These high values of the acceptor densities can be attributed to a higher density of the Zn vacancies in oxide films.
5. The EIS studies showed that the decrease in solution concentration increases the impedance value, due to increase of the preferential dissolution of the brass alloy.

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