

*Full Paper*

## **Investigation of the Electrochemical Behavior of the Anodically Passive Films Formed on Zirconium**

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**Abstract-** This study determined the semiconductor character of the anodically passive films formed on zirconium in 0.5 M NaOH (pH=13.3), estimated the dopant levels in these films, and estimated the passive film thickness as a function of the film formation potential. Mott–Schottky analysis revealed that the anodically passive films displayed n-type semiconductive characteristics, where oxygen vacancies and cation interstitials preponderated. Based on the Mott–Schottky analysis, it was shown that the calculated donor density increased with increases in formation potential. Moreover, the results indicated that the thickness of the anodically passive films increased linearly with the film formation potential.

**Keywords-** Zirconium, Passivation, Electrochemical impedance spectroscopy (EIS)

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### **1. INTRODUCTION**

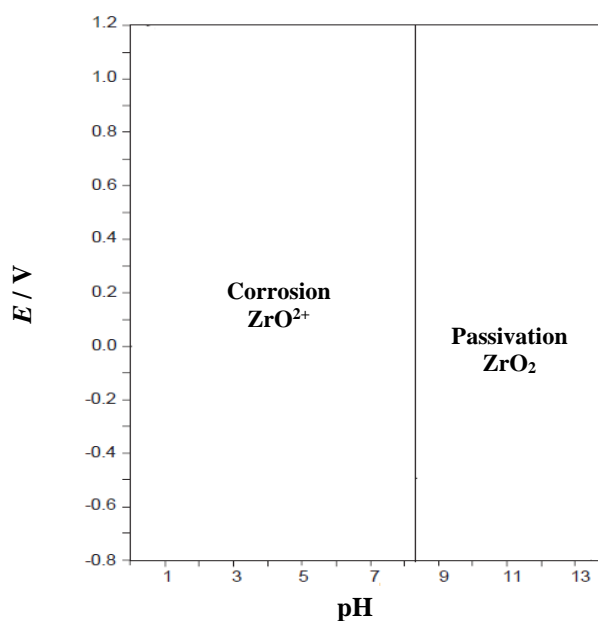
Zirconium is an active metal, normally exhibiting very stable passivity. Based on the theoretical potential–pH diagram of this metal (Fig. 1), at pH values ranging from 8.2 to 14.0 (passive domain) the surface film formed on zirconium is protective [1]. The passive film (ZrO<sub>2</sub>) formed on zirconium is known to exhibit semiconducting properties, because of its non-stoichiometric nature. It has been found that at potentials more positive than the

corrosion potential, passivation of the zirconium occurs [2–5]. Generally, the Mott–Schottky analysis has been shown to be an important in-situ method for the investigation of the semiconductor properties of passive films [6–8].

In the last decade, a large number of studies have explained the corrosion and passive behavior of the passive films on zirconium [9–14]. However, little information has been available about the effect of formation potentials on the semiconductive behavior of the passive film formed on zirconium.

The point defect model (PDM) [15–17] provides a microscopic description of the growth of the passive film, as well as an analytical expression for its semiconducting properties. Indeed, the diffusivity of the point defects is a key factor for describing the transport of point defects and then the kinetics of passive film growth.

Despite the extensive works published on the passive films, there is a lack of studies on the density and diffusivity of point defects in the passive films formed on zirconium. In this work, electrochemical impedance spectroscopy (EIS) and Mott–Schottky analysis of the zirconium have been performed to determine the semiconductor character of the passive film formed on zirconium, estimate the dopant levels in this film, and estimate the film thickness as a function of the formation potential. The ultimate goal of this study is to model experimental data within the PDM.



**Fig. 1.** Pourbaix diagram for zirconium–water system at 25 °C [1]

## 2. EXPERIMENTAL PROCEDURES

The zirconium (99.8 wt%) samples were polished up to 2000 grit, rinsed in distilled water, and then dried with air just before each of the electrochemical measurements. All electrochemical measurements were obtained in a conventional three-electrode flat cell under

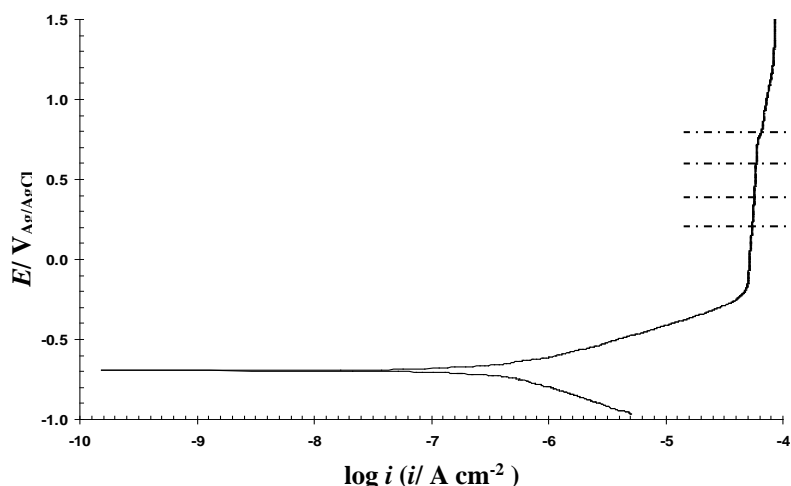
aerated conditions by using a  $\mu$ Autolab Type III/FRA2 system controlled by a personal computer. The counter electrode was a Pt plate, while the reference electrode was Ag/AgCl saturated in KCl. Also, the concentrated alkaline solution (0.5 M NaOH) was used as the test solution at  $25 \pm 1$  °C. Before potentiostatic film growth, the electrode was held at  $-1.2$  V<sub>Ag/AgCl</sub> for 5 min to remove the native oxide film. The potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV/s starting from  $-0.25$  V<sub>Ag/AgCl</sub> (vs.  $E_{\text{corr}}$ ) to 1.5 V<sub>Ag/AgCl</sub>. Four potentials within the passive region were chosen for potentiostatic film growth, EIS, and Mott-Schottky measurements: 0.2, 0.4, 0.6, and 0.8 V<sub>Ag/AgCl</sub>. Films were grown at each potential for 1 h to ensure that the system was in steady-state.

After each film growth period, EIS measurements were performed. The frequency was scanned between 100 kHz and 100 MHz and with an excitation potential of 10 mV (peak-to-peak). Mott-Schottky analyses were done by measuring the frequency response at 1 kHz during a 25 mV/s negative potential scan from each selected potential to  $-0.1$  V<sub>Ag/AgCl</sub>. For the EIS data modeling and curve-fitting method, the NOVA 1.7.8 impedance software was used.

### 3. RESULTS AND DISCUSSION

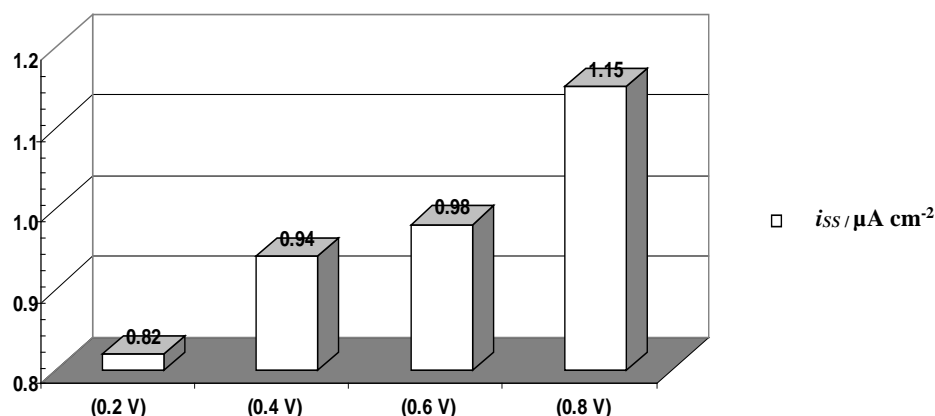
#### 3.1. Polarization measurement

Fig. 2 shows the potentiodynamic polarization curve of zirconium in 0.5 M NaOH. According to this figure, the current density was found to increase with potential during the early stage of passivation, and no obvious current peak was observed. Also, it was seen that the passive potential range extending from the corrosion potential. During the formation of the passive films on working electrodes, the evolution of the current density measured during the application of different potentials (0.2, 0.4, 0.6 and 0.8 V<sub>Ag/AgCl</sub>) in the passive domain.



**Fig. 2.** Polarization curve of zirconium in 0.5 M NaOH in the anodic direction

Fig. 3 shows the values of the steady-state passive current density ( $i_{ss}$ ) versus the formation potential. It was observed that the steady-state passive current density increased as the formation potential increased.



**Fig. 3.** Steady-state passive current density obtained during the potentiostatic growth of the anodically passive films on zirconium at different formation potentials for 1 h

### 3.2. EIS measurements

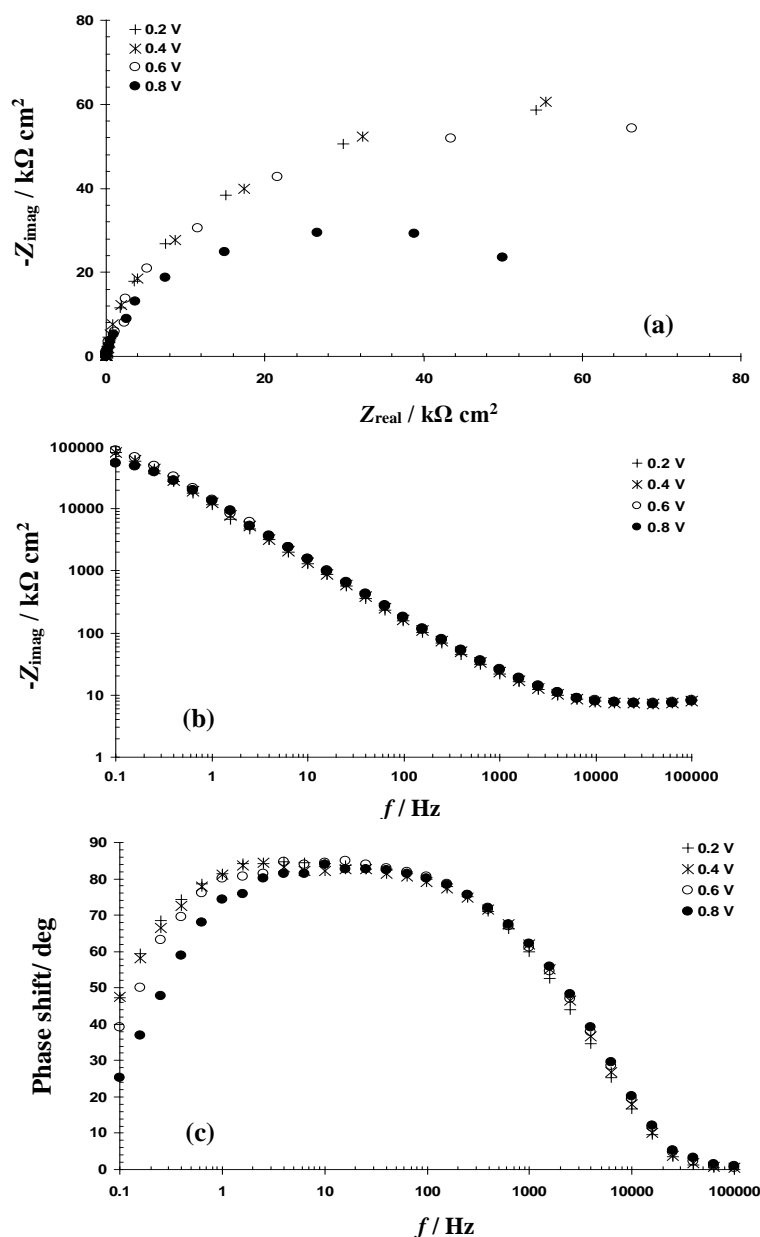
The EIS response of zirconium in 0.5 M NaOH was determined, and the results are presented as Nyquist and Bode plots in Fig. 4. In this figure, the Nyquist and Bode plots show a resistive behavior at high frequencies, but in the middle to low frequency range there was a marked capacitive response. Similar Nyquist plots for zirconium in 0.1 M NaOH solution have been reported by Jovic' [8]. The Bode-phase curves show one time constant (only one maximum phase lag at the middle frequency range). The phase angle values remained very close to  $90^\circ$ . This evolution revealed the formation and growth of a passive film. Also, the low frequency impedance decreased as the formation potential increased.

Based on the Nyquist and Bode plots, the equivalent circuit shown in Fig. 5 was used to simulate the measured impedance data of zirconium in 0.5 M NaOH. This equivalent circuit was composed of:  $Q_{pf}$ , the constant phase element corresponding to the capacitance of the passive film;  $R_{pf}$ , the resistance of the passive film; and  $R_s$ , the solution resistance ( $R_s=7.8 \Omega$  for 0.5 M NaOH solution).

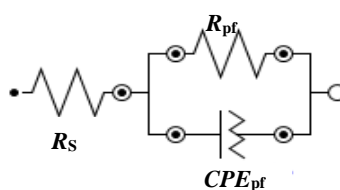
This equivalent circuit was composed of one time constant, as proposed by Jovic' [7,8] for describing the influence of the  $\text{ZrO}_2$  passive film's formation conditions on its properties in 1 M NaOH. The impedance of the constant phase element is presented using Eq. (1) [18–21]:

$$Z_Q = [C(j\omega)^n]^{-1} \quad (1)$$

Where  $n$  is associated with the roughness of the electrode surface. Fig. 6 shows the effect of formation potential on the resistance and capacitance of the passive film formed on zirconium in 0.5 M NaOH.

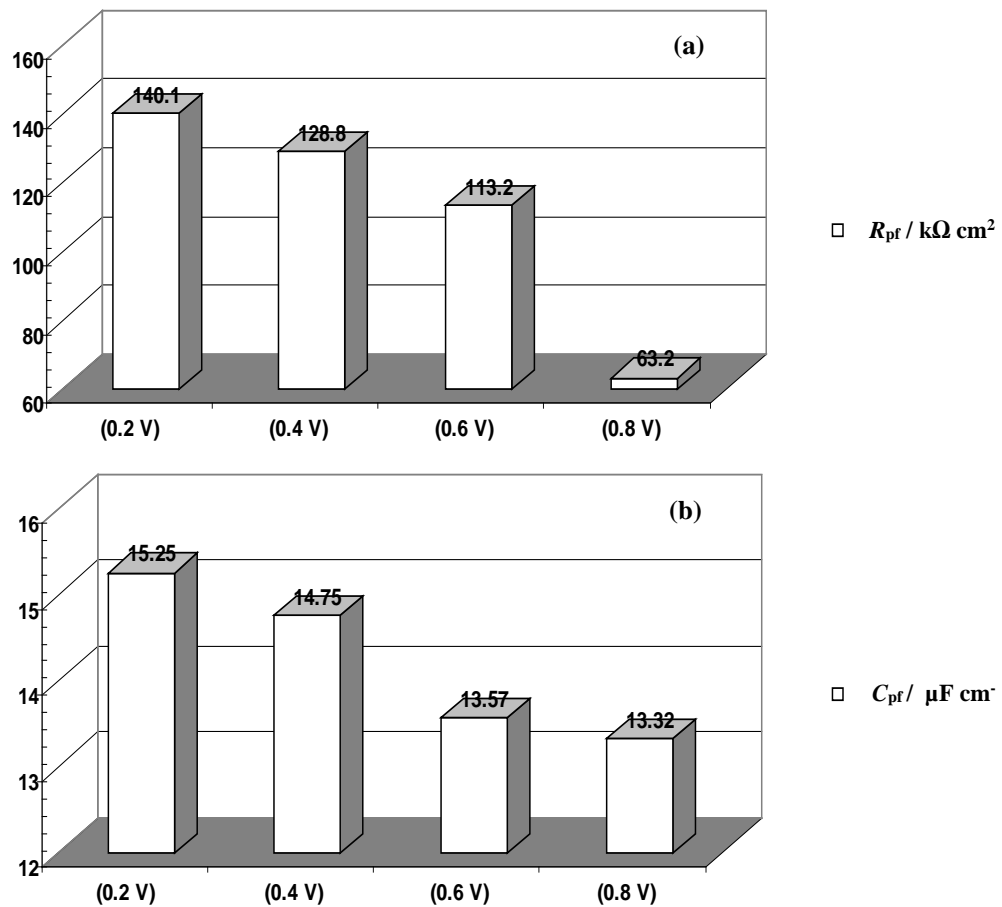


**Fig. 4.** (a) Nyquist, (b) Bode, and (c) Bode-phase plots of zirconium in 0.5 M NaOH, measured at different formation potentials



**Fig. 5.** The best equivalent circuit tested to model the experimental EIS data [7,8]

As can be seen in Fig. 6, passive film resistance and capacitance decreased as the formation potential increased.



**Fig. 6.** Effect of film formation potential on the passive film resistance and passive film capacitance of zirconium in 0.5 M NaOH

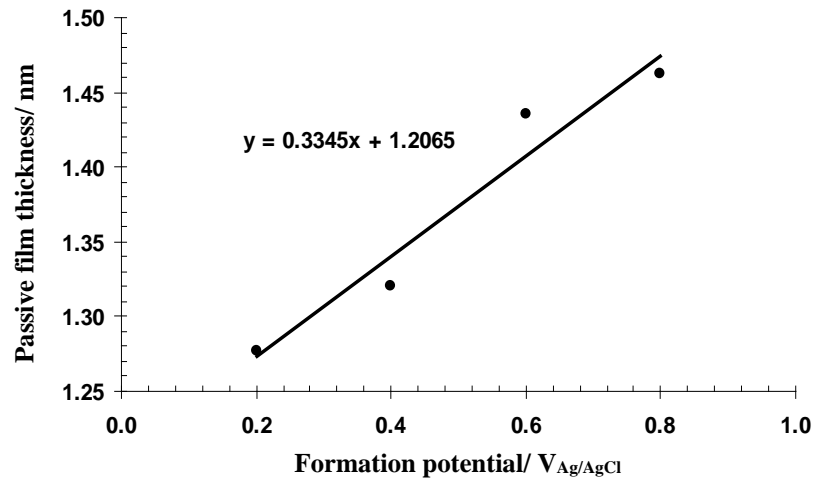
According to the equivalent circuit shown in Fig. 5, the passive film thickness ( $d$ ) can be calculated using Eq.(2) [2,4,22,23]:

$$d = \frac{\varepsilon\varepsilon_0}{C} \quad (2)$$

Where  $\varepsilon$  is the dielectric constant of the passive film ( $\varepsilon=22$  [2]),  $\varepsilon_0$  is the vacuum permittivity ( $8.854 \times 10^{-14}$  F/cm), and  $C$  is the total capacitance of the passive film. Generally, a change in the total capacitance of the passive film can be used as an indicator of change in the passive film thickness.

Therefore, the reciprocal capacitance of the passive film ( $1/C$ ) is proportional to its thickness, which decreases as formation potential increases. Fig. 7 shows a linear relationship

between the passive film thickness and formation potential. As can be seen in Fig. 7, the calculated thickness ranges from about 1.277 nm at  $E=0.2$  V<sub>Ag/AgCl</sub> to 1.462 nm at  $E=0.8$  V<sub>Ag/AgCl</sub>. Similar trend for zirconium in 0.1 M B(OH)<sub>3</sub>+0.001 M LiOH solution with or without hydrogen have been reported by Chen et al. [2].



**Fig. 7.** Effect of formation potential on the passive film thickness of zirconium in 0.5 M NaOH

### 3.3. Mott–Schottky analysis

Fig. 8 shows the Mott–Schottky plots of zirconium in 0.5 M NaOH at selected formation potentials. As can be seen, clear  $C^{-2}$  clearly decreased as formation potentials increased. In this figure, the positive slopes are attributed to n-type behavior. Similar Mott–Schottky plots (with n-type behavior) for zirconium in 0.1 M B(OH)<sub>3</sub>+0.001 M LiOH solution with or without hydrogen have been reported by Chen et al. [2].

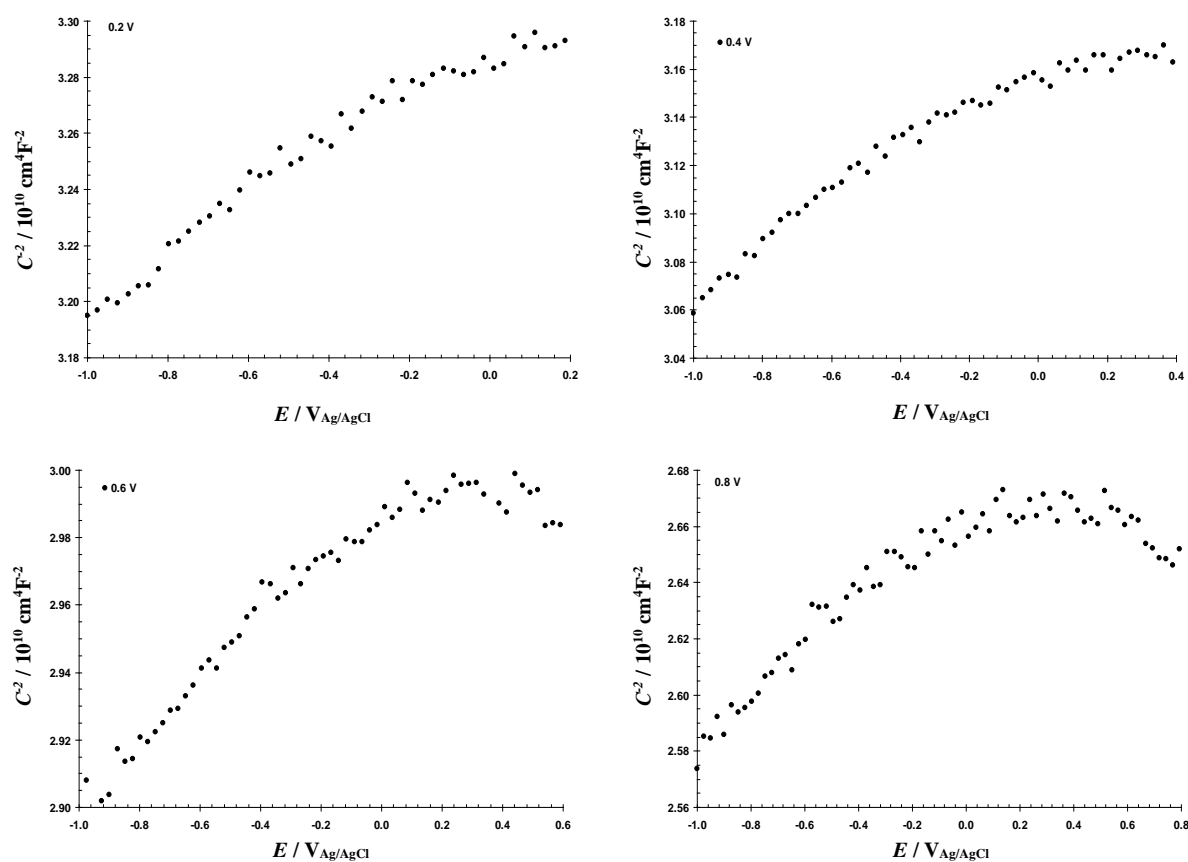
The positive slopes in this region are attributed to n-type behavior, and acceptor density was determined from these positive slopes according to Eq. (3) [2,21,22]:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left( E - E_{FB} - \frac{k_B T}{q} \right) \quad \text{for n-type semiconductor} \quad (3)$$

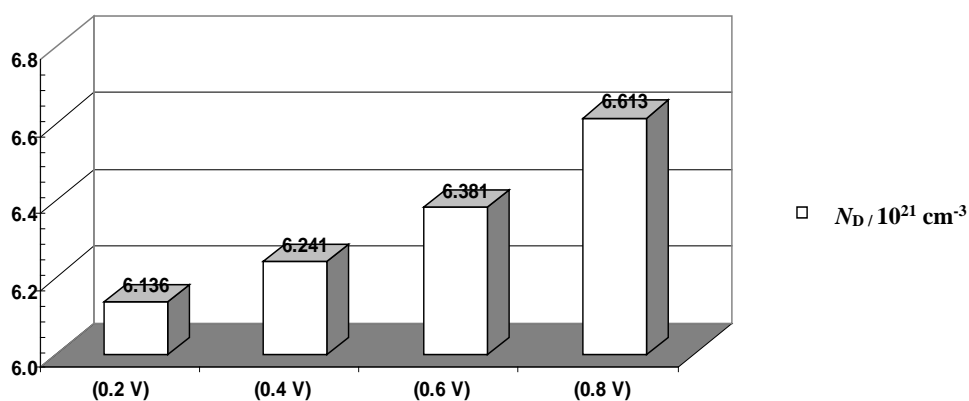
where  $e$  is the electron charge,  $N_D$  represents the donor density for  $n$ -type semiconductors ( $\text{cm}^{-3}$ ),  $k_B$ ,  $T$ , and  $E_{FB}$  are the Boltzmann constant, absolute temperature, and flat band potential, respectively [21,22].

Fig. 9 shows the calculated donor density of the passive film formed on zirconium in 0.5 M NaOH at selected formation potentials. The orders of magnitude are around  $10^{21}$   $\text{cm}^{-3}$  and

are comparable to calculated donor density of the passive film formed on zirconium in 0.1 M  $B(OH)_3+0.001$  M LiOH solution with or without hydrogen [2].



**Fig. 8.** Mott-Schottky plots of passive film formed at different formation potentials on zirconium in 0.5 M NaOH



**Fig. 9.** Donor densities of the passive films formed on zirconium in 0.5 M NaOH as a function of film formation potential



Also, it is clear that the orders of magnitude decrease with formation potential. Indeed, decreasing the formation potential give better conditions for forming the passive films with higher protection behavior, due to the growth of a less defective passive film.

According to the PDM [15–17], the flux of oxygen vacancy and cation interstitials through the passive film is essential to the film growth process. In this concept (n-type behavior), the dominant point defects in the passive film are considered to be oxygen vacancies and/or  $Zr^{4+}$  interstitials acting as electron donors.

#### 4. CONCLUSIONS

In this work, the electrochemical behavior of the anodically passive films formed on zirconium in 0.5 M NaOH was explored using EIS and Mott–Schottky analysis. Conclusions drawn from the study are as follows:

1. The Nyquist and Bode plots show a resistive behavior at high frequencies, but in the middle to low frequency range there was a marked capacitive response.
2. EIS results showed that the reciprocal capacitance of the anodically passive films increased as the formation potential increased.
3. The experimental data were interpreted in terms of the PDM for the passivity of zirconium in 0.5 M NaOH, assuming that the donors are defects including oxygen vacancies and cation interstitials.
4. Based on the Mott–Schottky analysis, it was shown that the calculated donor density increased as the formation potential increased.
5. The results showed that decreasing the formation potential offered better conditions for forming the anodically passive films with higher protection behavior, due to the growth of a less defective passive film.

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