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Faradiac Impedance of a Heterogeneous Chemical Reaction and an Adsorption Process

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RESEARCH ARTICLE

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ABSTRACT

The electrochemical behaviour of stainless steel 302 has been investigated in 0.10 M K_2SO_4 solution using the impedance technique at several anodic potentials. Stainless steel 302 is passive up to 1300 mV, due to the main formation of Cr_2O_3. Above this potential stainless steel became active. Faradiac impedances of a heterogeneous chemical reaction and an adsorption process were discussed.

INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is widely used [1-4] to study the electrochemical properties of metals and alloys. Physical properties of a passive layer such as polarization resistance (R_p), capacitance (C), and a thickness of oxide layer (d) can be easily determined using the EIS technique. Furthermore, it has been pointed out [5,6] that the impedance of a heterogeneous chemical reaction Z_H and of an adsorption process Z_{ad} coluld be followed using EIS **(Figure 1).**

Z_H composed of a capacitance of an adsorbed (heterogeneous) speciesn (C_H), reaction inhibition resistance, (R_r) and of Warburg diffusion elements (W_1) and (W_2) while Z_{ad} contains the capacitance of an adsorbed material (C_{ad}) Warburg diffusion element (W) and diffusion resistance R_D. The main objective of the present study was to investigate the electrochemical behaviour of stainless steel in 0.10 M K_2SO_4 solution.
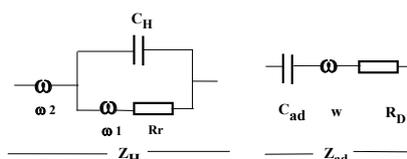
Figure 1. The equivalent electrical circuits of the Faradiac impedance of Z_H and Z_{ad} are shown below.

EXPERIMENTAL

The used stainless steel 302 consisted of iron with 3.42 wt% O, 0.57 wt% Si, 17.91 wt% Cr, 1.9 wt% Mn, 8.0 wt% Ni and 2.16 wt% Cu. An area of 0.78 cm² of the working electrode was exposed to 100 ml of 0.10 M K_2SO_4. The working electrode was successively abraded with emery paper up to 1000 grade and then cleaned with acetone. A platinum electrode served as counter electrode while the reference electrode was a saturated calomel electrode (SCE). The used glass cell is described elesewhere [7]. EIS measurements were followed in the frequency range $10^{-1} – 10^5$ H_z with an amplitude of 10 mV of using a computerized

impedance unit (IM5d produced by Kronach, Germany) after 30 min of anodic polarization at several selected anodic potenials. All patentials were measured against SCE at 25°C.

RESULTS AND DISCUSSION

Current densities for stainless steel in 0.10 M K_2SO_4 were measured at several potentials in the anodic range 300–1500 mV using the impedance unit. The variation of potential with current density is represented in **Figure 2.** It is clear from **Figure 2** that stainless steel is passive in the potential range 0-1300 mV due to the flow of very small current density values (nano- A and micro ampere scale) and it is active at potentials >1300 mV, as a result of flowing of very high current density values reaching 15.6 mA at 1500 mV.
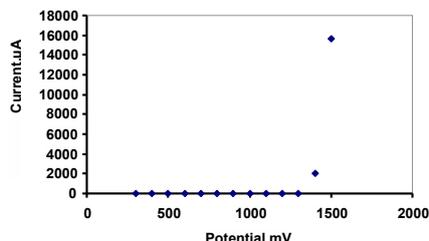
Figure 2. Variation of potential with current for stainless steel in 0.10 M K_2SO_4.

Two electrochemical equivalent circuit models were found to analyzed the measured EIS spectra for stainless steel in 0.10 M K_2SO_4 solution **(Figure 3)**.

Figure 3. Equivalent circuit models for stainless steel in 0.10 M K_2SO_4.

Models 1 and 2 were used to analyze the measured EIS spectra. Both models contained solution resistance (R_s) resistance of solution between the working and reference electrodes, and Young impedance

Young impedance [6] describes a heterogeneous passive oxide film at the electrode surface and it consists of a capacitance of an oxid film, (C), loss factor (P), which is a measure for surface roughness and time constant (τ).

EIS spectra for stainless steel were measured in newly prepared solution of 0.10 K_2SO_4 at 400 and 800 mV every 30 min for 210 min. **Figure 4** represents the analyzed impedance spectrum for the electrode at 400 mV after 150 min of anodic polarization. Similar EIS spectra were obtained for the rest of the measurements at 400 and 800 mV. The points in **Figure 4** are the measured values whereas the solid line connecting between the points is the result of simulation according to model 1 in **Figure 3**. The simulation was considered to be acceptable when the relative error in the values of impedance and phase angle shift is less than 2% and 0.3˚, respectively, using a computerized program for the simulation. According to **Figure 4**, the impedance line in the frequency range 10^{-1}–10^4 H_z is straight line with increasing impedance values as frequency decreases. The impedance values at frequencies >10^4 are independent on frequency, respresenting R_s. The phase angle shift curve shows a plateaue in the middle frequency region, indicating the presence [6] of Young impedance and Warburg diffusion element with 45° phase angle shift.
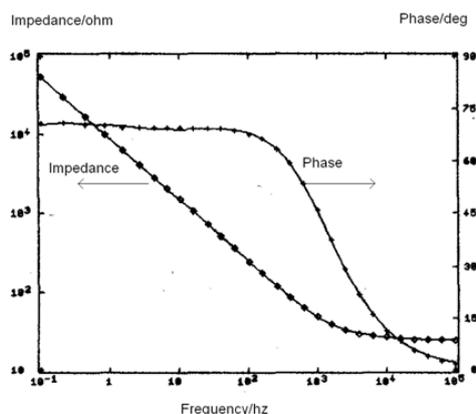
Figure 4. EIS spectra for stainless steel after 150 min of anodic polarization in 0.10 M K_2SO_4 at 400 mV.

In order to invesigate the effect of each element composing the electrical circuit, it is possible to change the value of any impedance element, keeping all the other values as obtained from the simulation, by 10%. For example W_1 in Z_H affect the EIS spectrum in the fequency range 1–10^3 H_z.

The analyzed impedance values of stainless steel at 400 mV in 0.10 M K_2SO_4 as a function of time are given in **Table 1**. According to this table, the values of current densities were very small (nA) and decreased with time. The values of C, describe the capacitance of the main passive oxide layer at the electrode surface, were decreased with increasing time, indicating a growth in the thickness (d) of the formed passive oxide film (mainly Cr_2O_3) according to equation 1[6]:

Table 1. Analyzed impedance values for stainless steel in 0.1 M K_2SO_4 at 400 mV according to model 1, **figure 3.**

Time min.	Current nA	C µF	P %	τ ns	C_H µF	R_r Ω	W_1 kΩs$^{-0.5}$	W_2 kΩs$^{-0.5}$
60	346	9.7	5.1	212	7.6	90	9.1	1.1
90	333	9.3	5.1	210	7.4	95	9.2	1.1
120	251	9.2	5.1	213	7.1	100	9.3	1.2
150	203	9.2	5.1	223	6.9	101	9.5	1.2
180	217	9.1	5.2	220	6.8	100	9.5	1.2
210	198	8.8	5.1	217	6.7	205	9.2	2.3

R_s=23.2 Ω

$$d = \frac{\varepsilon_\circ \varepsilon A}{\tau} \tag{1}$$

Where $\varepsilon_\circ$, ε and A are the permittivity of free space, dielectric constant of the oxide and the surface area of the electrode, respectively.

The surface roughness of the electrode was not changed as it can be seen from the constant values of P. The values of the time constant (τ) were increased slightly from 285 ns at 60 min to 296 ns at 210 min of anodic polariztion, indicating a small decrease in the conductivity (σ) of the formed oxide film at the electrode surface according to equation 2[6]:

$$\sigma = \frac{\varepsilon_\circ \varepsilon}{\tau} \tag{2}$$

Newly prepared soltuin of 0.10 M K_2SO_4 is slightly basic and the pH of the solution at the end of the experiment was 7.1. The possible mechanisms [8] of anodic oxidation of a basic or slightly acidic aqueous solutions are shown in **schemes 1 and 2**, respectivly:

$OH^- \rightarrow OH_{ad} + e^-$ $H_2O \rightarrow OH_{ad} + H^+ + e^-$

$2OH_{ad} \rightarrow H_2O + O_{ad}$ $2OH_{ad} \rightarrow H_2O + O_{ad}$

$2O_{ad} \rightarrow O_2$ $2O_{ad} \rightarrow O_2$
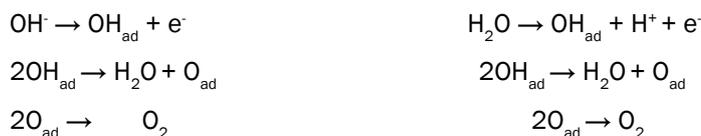
Scheme 1   **Scheme 2**

Scheme 1 explains the trend varaition of the values of Z_H components. With increasing time, the thickness of the adsorbed (due to the interacion between the negative OH^- and the positive electrode) species as a result of a decrease in the values of C_H. This behaviour is accomained by an increase in the values of W_1, W_2 and R_r. Due to the anodic oxidation of OH^- a concentration gradient of OH^- near the electrode appears, so the values of W_2 increases. Consequently, the values of W_1 of the adsorbed material (H_2O molecuels diffuse toward the solution) increase. The values of R_s were kept constant with a value of 23.2 Ω.

It is important to compare between the behaviour of stailess steel at 400 mV and at open circuit potetial (Eoc). The value of Eoc was -210 mV. At Eoc the analyzed impedance values of C, P, τ, C_H, W_2, and R_s were 19.2 µF, 5.1%, 207 ns, 26.2 µF, 623 Ω and 21.2 Ω respectively. A comparison between the analyzed impedance values obtained at Eoc with those obtained at 400 mV the followings could be obtained:

I.   The values of C and τ at Eoc are higher than the values obtained at 400 mV, because the surface of the electrode at Eoc was cleaned and abraded with emery paper.

II.   A weak adsorption process (weak interaction between the electrode and ions in solution) occurred at Eoc. As a result C_H presents only (with higer vallues than those obtained at 400 mV) and W_2 in the analysis. In this case C_H is better replaced by C_{ad}.

The analyzed impedance values for stainless steel in 0.10 M K_2SO_4 at 800 mV, according to model 1 **Figure 3**, are given in **Table 2**. The behaviour of stainless steeel at 400 and 800 mV is the same. Upon comparison between the values of similar impedance elements, under the same conditions, in **Tables 1 and 2** the following conslusions could be obtained :

I.   The values of the current densities at 800 mV are higher than the values of the current densities at 400 mV, leading to a higher rate of OH^- oxidation. Consequently, the values of C at 800 mV became smaller (due to an increase in the thickness of the oxide layer)

II.   Upon increasing anodic potential from 400 to 800 mV more adsorption of OH^- occurred, leading to smaller values of C_H which reftects a higher values of W_1 and W_2.

III.   Remarkably, the values of R_r at 800 mV are smaller than the values of Rr at 400 mV, indicating a more favorable oxidation process to occur at 800 mV.

Table 2. Analyzed impedance values for stainless steel in 0.1 M K_2SO_4 at 800 mV according to model 1, **Figure 3.**

Time min.	Current nA	C µF	P %	τ ns	C_{ad} µF	R_r Ω	W_1 KΩs$^{-0.5}$	W_2 kΩs$^{-0.5}$
60	192	10.0	4.7	285	9.3	10	6.4	0.65
90	124	10.0	4.7	285	9.0	16	66	0.68
120	92	9.7	4.7	288	8.8	20	6.6	0.69
150	94	9.6	4.7	292	8.6	20	6.6	0.70
180	72	9.5	4.7	295	8.6	24	6.7	0.73
210	67	9.4	4.6	296	8.5	30	6.8	0.75

R_s=23.2 Ω

Table 3. Analyzed Impedance Values for Stainless Steel after 30 min of anodic polarization in 0.10 M K_2SO_4 according to model 2, **Figure 3.**

Potetial mV	Current A	C F	P %	τ ns	C_{ad} µF	W kΩs$^{-0.5}$	R_{ad} Ω
1000	5.62 µ	939 n	7.5	294	21.6	25.3	350
1100	13.5 µ	617 n	7.9	279	22.5	21.2	365
1200	25.3 µ	600 n	8.3	264	30.1	18.2	280
1300	52.6 µ	595 n	8.8	256	47.4	13.1	178
1400	2.05 m	5.75 µ	8.8	83	–	–	212
1500	16.5 m	28.8 µ	8.9	81	–	–	187

R_s=25 Ω

Figure 5 represents the EIS spectra for stainless steel in 0.10 M K_2SO_4 after 30 min of anodic polariztion at 1000, 1100, 1200, 1300, 1400 and 1500 mV with increasing anodic potentials, the curves of impedance and phase angle were shifted to lower values. The values of impedance are independent on frequency at low and high frequency regions and the plateaue at the phase angle curve is completely lost at 1400 and 1500 mV. Results of the analysis of of all measured EIS spectra in the potential range 1000-1500 mV according to model 2 **Figure 3**, are given in **Table 3.**
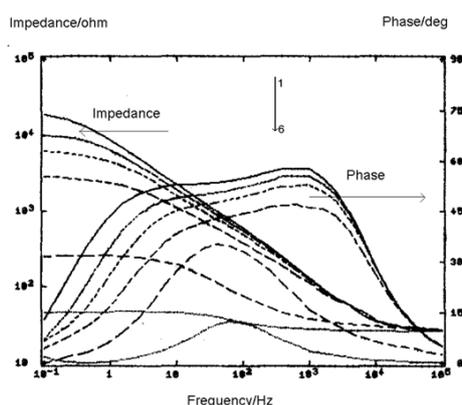
Figure 5. EIS spectra for stainless steel after 30 min of anodic polarization in 0.10 M K_2SO_4 at 1 1000;2 1100;3 1200;4 1300;5 1400;6 1500 mV

Faradiac impedance of the adsorption process, Z_{ad}, mainfests itself clearly in the analysis of the measured EIS spectra in the potential range 1000-1300 mV. Z_{ad} decribes simply the adsorption of species present in solution such as OH^-, SO_4^{2-} and H_2O.

In the potential range 1000-1300 mV an increase in potential is accompanied by an increase in the values of current densities. The values of C decrease with increasing potential and increasing in the current density values, indicating a growth in the thickness of the oxide layer. This behaviour could be discused as explained before when the potential had been increased from 400 to 800 mV. The % of P increases with increasing potential, indicating an increase in the surface roughness. The conductivity of the formed oxide film increases as the values of τ decrease. As a result of folowing of high current densities, the thickness of the adsorbed layer at the electrode surface increases through an increase in the values of C_{ad}, which is accompanied by a decrease in the values of W and R_{ad}. At 1400 and 1500 mV, stainless steell loss completely its passivity through a jump increase in the values of current densities and C as well as a sudden decrease in the values of τ (the electrode bcame well coductive).

Although anodic oxidation of OH^- or H_2O still occurs (pH of solution is 6.6) in the potential range 1000-1300 mV but the analysis of the measured spectra using model 1 **Figure 3**, was insatisfactory, probably due to the very high rate of anodic polariztion of OH^- or H_2O **scheme**. An attempt was done to combine both models together through series concetion of model 2 **Figure 3** with Z_H and R_s, the results of analysis were unacceptable specially under anodic polariztion at potentials less than 1000 mV, where the oxidation process is the rate determining step.

CONCLUSIONS

Stainless steel is passive in 0.10 M K_2SO_4 under anodic polarization up to 1300 mV by vertue of an increase in the thickness of the passive oxide layer. The measured EIS spectra under anodic potentials up to 800 mV could be easily anlayzed using the

Faradiac impedance of a heterogenous chemical reaction Z_H. The faradaic impedance of an adsorption process Z_{ad} could be used for analysis under anodic potentials $\geq$ 1000 mV.

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