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Corrosion Behavior of Copper in Chloride Media

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Abstract: The electrochemical behavior of copper in 0.05 M HCl and 0.05 M NaCl carried out at open-circuit potential and at constant anodic potential after one hour has been investigated using electrochemical impedance spectroscopy (EIS) at 20 °C, 40 °C and 60 °C. The formation of copper chloride (CuCl) film does not protect copper from dissolution in the chloride media. The physical properties of the passive film such as, polarization resistance (R_p), capacitance (C), loss factor (%P), Warburg diffusion coefficient (W) and Kugel diffusion constant (k) were obtained from EIS measurements. Also, the radii of the pores formed as a result of anodic polarization have been calculated.

Keywords: Copper, NaCl, HCl, impedance (EIS), corrosion.

1. INTRODUCTION

The behavior of metals and alloys in aggressive media depends on many factors such as the chemical composition, the stability of the oxide film, metallurgical and processing parameters, and the effectiveness of any applied protection [1]. Copper and copper alloys are widely used in industrial applications due to many factors such as an excellent corrosion resistance, superior electrical and thermal conductivity, and mechanical workability. Thus, copper is widely used in heating and cooling systems, a conductor in electrical power lines, and pipelines for domestic and industrial water utilities including sea water. Corrosion products have a negative effect on heat transfer, causing a decrease in heating and cooling efficiency of the equipment. Due to the wide application of copper and copper alloys, the corrosion of copper and its inhibitions in a wide variety of media, especially when it contains chloride ions, have been discussed and reviewed in a large number of articles [2-8].

Chloride ions are very aggressive ions to copper and its alloys, due to the tendency of the chloride ion to form an unstable film (CuCl) and soluble chloride complexes ($CuCl_2^-$ and $CuCl_3^{2-}$) [9]. Thus, even trace amounts of chloride ions can cause corrosion problem to copper. Copper and its alloys are used for piping and delivery of water for domestic and industrial purposes. These pipes are frequently employed in a medium where chloride ions are present [10]. For this reason, corrosion of copper in a wide variety of media, particularly when they contain chloride ions, have attracted the attention of many investigators [11-14].

In aqueous chloride solution and at anodic potentials ≤200 mV, copper electrode undergoes dissolution-precipitation mechanism [15], leading to the formation of a diffusive compound $CuCl_2^-$ and precipitate CuCl on the surface as the concentration of $CuCl_2^-$ reached saturation limit. In previous work [16, 17], Kugel diffusion impedance element (K) was used to interpret the formation of the porous layer which results from the destruction of the passive layer or which is formed by pitting corrosion. The Kugel diffusion impedance element (K) is composed from the nonlinearly diffusion of the corrosion products (ions) as a result of the formation of a porous layer at the surface of the electrode. The Kugel impedance (Z_K) of element K is given by [18]:

$$Z_K = \omega/[(2\pi f)^{1/2} + k^{1/2}] \quad (1)$$

where ω is the angular frequency (=2πf), f is the frequency, and the constant k is given by:

$$k = D_i/r^2 \quad (2)$$

where D_i is the diffusion coefficient of ions inside pores with radius r [16, 19].

Other type of diffusion is called Warburg diffusion (or linear diffusion). It composed from the diffusion of ions or corrosion products to or out of the electrode surface, depending on the type of the electrochemical process which takes place at the electrode surface. The impedance of the linear diffusion depends on the type of the transferred species and on the value of the applied potential. At high frequency, the value of the Warburg impedance is small, since diffusion reactants do not have to move very far. Whereas at low frequency, the reactants or products have to diffuse further. The value of Warburg impedance (Z_W) is given by [18]:

$$Z_W = W/(2\pi f)^{1/2} \quad (3)$$

where W is the Warburg coefficient, which is inversely proportional to the square root of the diffusion coefficient (D), as shown by Eq. 4 [20]:

$$W = RT/2^{1/2}n^2F^2cD^{1/2} \quad (4)$$

where R is the ideal gas constant, T is the Temperature, n is the number of electron, F is the Faraday constant, c is the concentration (which depends on the concentration gradient through the pors), and D is the diffusion coefficient.

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For passive films formed on pure metal, the physical, chemical and mechanical properties can lead to a straightforward explanation of their protectiveness and stability [7]. The present study analyzes the stability of copper electrode in 0.05 M NaCl and 0.05 M HCl as a function of temperature and anodic potential using electrochemical impedance spectroscopy (EIS) technique. The technique provides the physical properties of the passive films such as capacitance (C) and polarization resistance (R_p).

2. EXPERIMENTAL

Electrochemical measurements were carried out in a standard three-compartment electrochemical cell [21] with platinum guaze as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the potentials in this study are referred to the SCE. The working electrode was a pure copper electrode having a purity of 99.98% with a radius of 0.75 cm, between measurements it was polished with emery paper (1200 grade), rinsed with distilled water and acetone, and wiped dry. EIS measurements were performed at the open circuit potentials and at constant anodic potentials of the samples investigated after one hour, and in the frequency range from 0.1 Hz to 10^4 Hz with *ac* voltage amplitude of ±10 mV. Measurements were performed at 20 °C, 40 °C and 60 °C. The electrochemical measurements were performed using a computer-controlled digital analyzer.

3. RESULTS AND DISCUSSION

By analyzing the shape of the measured spectra, an electrochemical equivalent circuit model was found by which a satisfactory simulation of all the spectra were possible. The corresponding equivalent circuit is shown in Fig. (**1**). It consist of the polarization resistance (R_p) in parallel to loss capacitance (C and P), with the Kugel diffusion impedance element (K), which is composed of two factors W and k, and the resistance of the solution (R_s) in series to the first two elements.

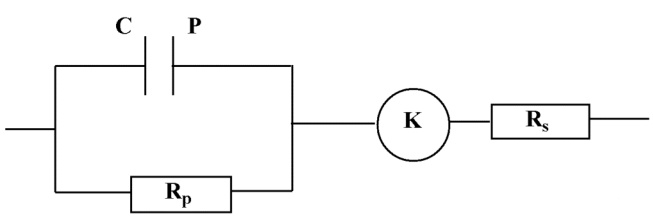

Fig. (1). Equivalent circuit model for copper in HCl and NaCl solutions.

3.1. Copper in 0.05 M HCl

A representative impedance spectra for the copper electrode in 0.05 M HCl at 20 °C at open circuit potential ($E_{o,c}$) and at 200 mV is shown in Fig. (**2**). Similar impedance curves were obtained at 40 °C and 60 °C (not shown). The results of simulation of all the measured impedance spectra for the copper electrode at these temperatures are given in Tables **1-3**.

The results summarized in Table **1** show that as the potential increases from $E_{o,c}$ to 800 mV, the current is increased. This increase in current values with potential indicates that the copper electrode in 0.05 M HCl is not passive, and undergoes dissolution, which was confirmed at the end of the experiment from the easily removable corrosion products. The surface of the sample was no longer smooth.

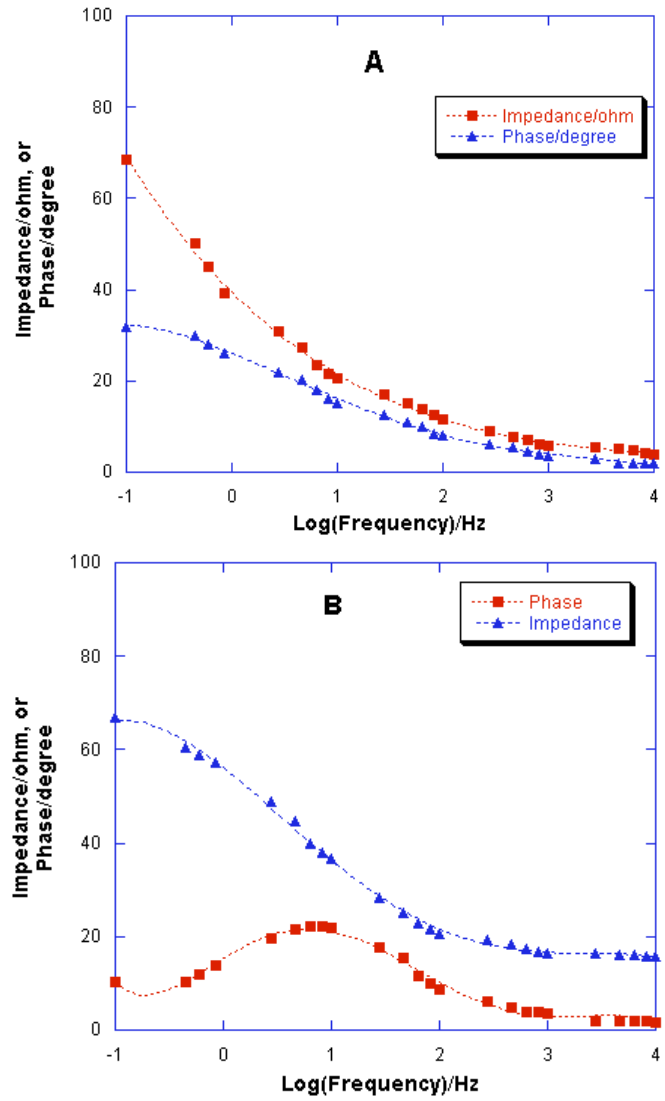

Fig. (2). Impedance plots for copper in 0.05 M HCl at 20 °C: (**A**) at $E_{o,c}$; (**B**) at 200 mV.

Table 1. Impedance Values for Copper in 0.05 M HCl Solution at 20 °C

Potential (mV)	Current (µA)	C (µF)	%P	R_p (Ω)	R_s (Ω)
$E_{o,c}$ (-53)	0.0	2040	6.7	4.91	11.0
0.0	199	1860	7.1	43.30	13.5
200	273	2990	8.3	15.40	15.0
300	1730	87.2	13.4	1.22	22.5
400	3290	39.2	14.4	1.08	32.5
500	3940	2.6	15.0	2.31	41.8
600	4210	1.2	17.2	3.49	50.2
700	4340	0.7	18.3	5.13	65.0
800	4600	0.1	19.3	16.30	66.3

Table 2. Impedance Values for Copper in 0.05 M HCl Solution at 40 °C

Potential (mV)	Current (μA)	C (μF)	%P	R_p (Ω)	W ($\Omega/s^{1/2}$)	k (s^{-1})	R_s (Ω)	r (m)
$E_{o,c}$ (-106)	0.0	973	4.5	58.1	*	*	9.7	*
0.0	767	395	2.5	9.3	*	*	10.2	*
100	2700	2050	2.9	4.7	*	*	17.4	*
200	4820	4510	2.8	2.1	*	*	27.3	*
300	5600	4850	2.9	2.1	88.7	338	39.0	$2.4x10^{-6}$
400	6060	6140	2.0	3.7	141.0	993	50.3	$1.4x10^{-6}$
500	6360	4970	1.9	6.6	277.0	3.12k	58.8	$8.0x10^{-7}$

*Very small value.

Table 3. Impedance Values for Copper in 0.05 M HCl Solution at 60 °C

Potential (mV)	Current (μA)	C (μF)	%P	R_p (Ω)	W ($\Omega/s^{1/2}$)	k (s^{-1})	R_s (Ω)	r (m)
$E_{o,c}$ (-145)	0.0	331	6.6	35.9	*	*	8.41	*
0.0	2140	611	0.10	2.7	*	*	8.85	*
100	3280	1790	0.2	6.4	*	*	15.7	*
200	5730	3360	0.4	3.2	*	*	22.4	*
300	7680	3960	0.9	2.0	130	2.2k	24.4	$9.5x10^{-7}$
400	8470	4240	1.2	2.0	164	2.4k	36.8	$1.9x10^{-7}$
500	9420	4790	1.4	3.0	219	3.3k	42.9	$0.8x10^{-7}$
600	11100	5370	1.5	2.5	273	6.3k	42.9	$5.6x10^{-7}$
700	10700	2930	1.6	23.5	433	7.8k	51.0	$5.1x10^{-7}$

*Very small value.

The values of the capacitance (C) have decreased with an increase in potential, due to the formation of thin film on the surface of the metal, which has been identified by Crousier *et al*. [15] as $CuCl_{(s)}$. The mechanism for the reduction processes of copper in HCl solution had been proposed by El-Sayed *et al*. [22]. This film is not strongly adsorbed on the surface of metal due to the flow of high current values, when potential was increased, the values of loss factor (%P), which is a measure of surface roughness [16] have increased, and this behavior indicates that the dissolution of the electrode is not homogeneous. Generally, the values of R_p are very small, due to the metal activity in this solution. The values of R_s increased remarkably with potential due to the accumulation of corrosion products on the surface of the electrode.

By a comparison of the behavior of copper in 0.05 M HCl at 20 °C with that obtained at 40 °C and 60 °C (Tables **1-3**), it can be noticed that the same trend was obtained at the three different temperatures. The activity of copper electrode increases as temperature increases. At 40 °C and 60 °C the components of K, which are the elements W and k, manifested itself at potential ≥ 300 mV. The presence of this element means that the surface of the electrode became porous. As reported by Al-Abdallah [16], the presence of Cl^- ions in solution and under anodic potential causes pitting corrosion. Tables **2** and **3** show that the values of Kugel diffusion constant (k), and Warburg impedance coefficient (W) increase with potential. The k values, which have the units of rate constant of first order kinetics, indicate that the rate of anodic dissolution of copper electrode increases with potential. Using the measured values of k and D_i (is equal $1.6x10^{-9}$ m^2/s for HCl) [19], the radius of the formed pores (r) were calculated and summarized in Tables **2** and **3**.

3.2. Copper in 0.05 M NaCl

A representative impedance spectra for the copper electrode in 0.05 M NaCl at 40 °C at open circuit potential ($E_{o,c}$) and at 100 mV is shown in Fig. (**3**). Similar impedance curves were obtained at 20 °C and 60 °C, not shown. The results of the analysis of these spectra are shown in Tables **4-6**. After cleaning the surface of the electrode, at the end of the experiment, a clear damage on the surface of the metal electrode has been observed.

The results summarized in Table **4** show that as the potential increases from $E_{o,c}$ to 1000 mV, the current is increased. An increase in current values indicates that the copper electrode in 0.05 M NaCl is active.

The values of C have decreased as potential increase due to the formation of thin film on the metal surface which has

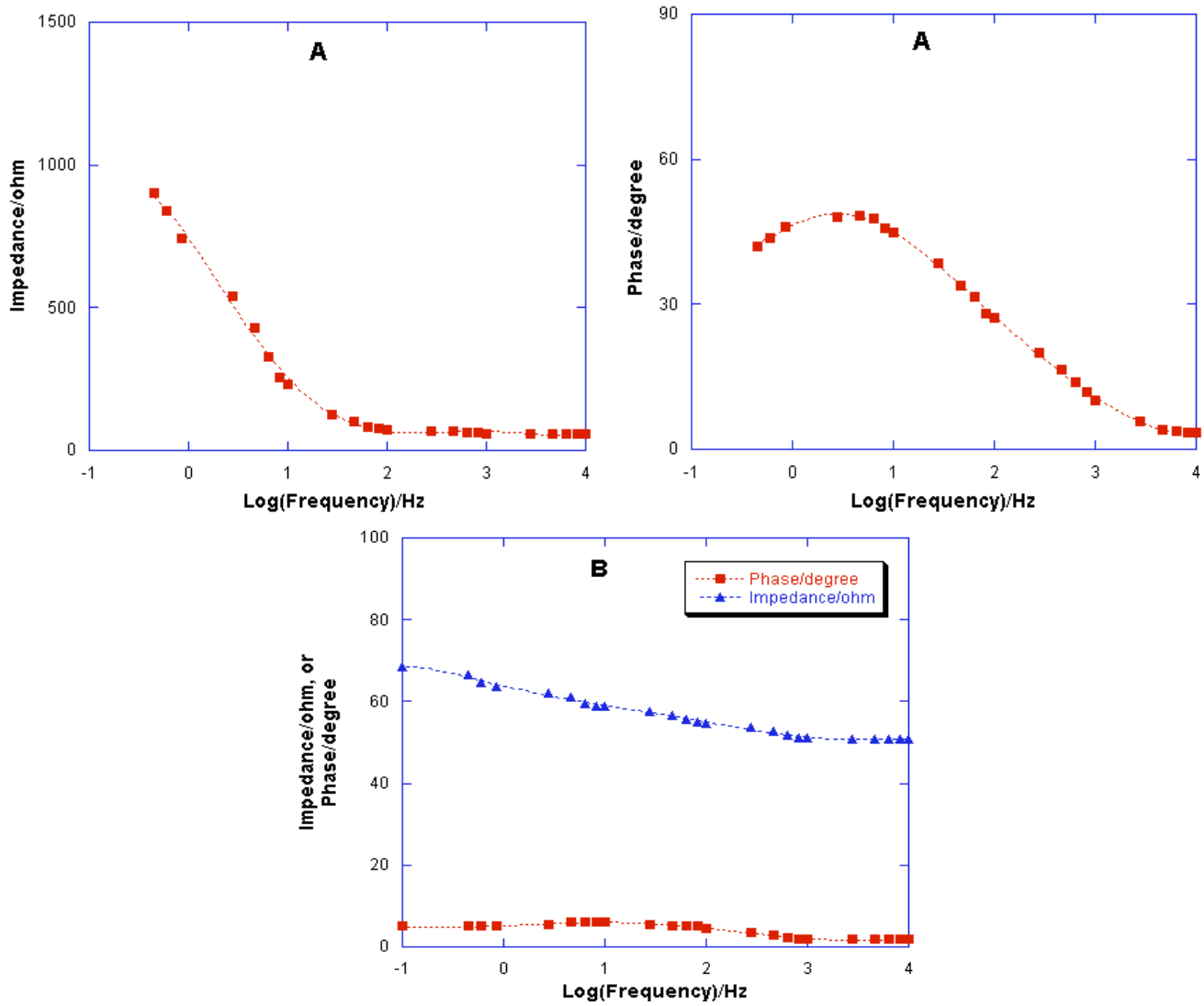

Fig. (3). Impedance plots for copper in 0.05 M NaCl at 40 °C: (**A**) at $E_{o,c}$; (**B**) at 100 mV.

Table 4. Impedance Values for Copper in 0.05 M NaCl Solution at 20 °C

Potential (mV)	Current (µA)	C (µF)	%P	R_p (Ω)	R_s (Ω)
$E_{o,c}$ (-68)	0.0	991	6.6	2.43	17.0
0.0	89	1330	6.7	11.60	71.2
100	630	6.90	12.2	6.06	89.4
200	1380	0.40	12.4	6.90	95.5
300	1890	0.90	12.5	10.50	109
400	3870	0.27	12.5	2.78	29.6
500	5930	0.25	12.7	2.97	29.1
600	6960	0.18	12.8	4.40	30.1
700	10700	0.16	12.9	3.72	28.8
800	12700	0.19	13.1	3.99	28.0
900	13600	0.13	13.3	3.04	28.6
1000	15200	0.12	13.5	3.94	28.8

Table 5. Impedance Values for Copper in 0.05 M NaCl Solution at 40 °C

Potential (mV)	Current (µA)	C (µF)	%P	R_p (Ω)	R_s (Ω)
$E_{o,c}$ (-150)	0.0	144	6.6	1.7k	36.3
-100	48.6	180	7.3	69.8	37.0
0.0	626	272	7.8	14.3	37.3
100	1310	1770	7.9	12.5	48.0
200	2540	2.17	8.5	4.3	51.8
300	3740	0.83	8.6	4.8	57.7
400	4490	0.79	8.9	8.3	62.4
500	4710	0.74	9.1	9.7	74.7
600	6090	0.31	9.8	14.9	75.0

been identified by Crousier *et al.* [15] as $CuCl_{(s)}$ and a green product $CuCl_2.3Cu(OH)_2$. The flow of high current indicates

Table 6. Impedance Values for Copper in 0.05 M NaCl Solution at 60 °C

Potential (mV)	Current (μA)	C (μF)	%P	$R_{p\,(\Omega)}$	W ($\Omega/s^{1/2}$)	k (s^{-1})	$R_{s\,(\Omega)}$	r (m)
$E_{o,c}$ (-145)	0.0	4.1	8.8	*	*	*	30.0	*
-100	92.9	64.6	8.8	63.2	*	*	29.1	*
0.0	1040	367	9.4	4.36	*	*	30.9	*
100	2150	529	9.7	15.8	335	11.2k	36.1	$4.23x10^{-7}$
200	3480	1120	9.8	162k	448	20.4k	40.9	$3.13x10^{-7}$
300	4620	1190	9.9	*	603	26.8k	49.1	$2.73x10^{-7}$
400	4700	966	9.6	*	1.09k	50.9k	55.2	$1.98x10^{-7}$
500	4750	330	10.0	*	6.43k	268k	60.8	$8.64x10^{-8}$
600	4830	283	10.1	*	9.15k	250k	62.8	$8.94x10^{-8}$
700	6560	253	9.8	*	9.61k	331k	66.7	$7.77x10^{-8}$
800	7940	213	9.9	*	11.8k	709k	68.3	$5.31x10^{-8}$
900	9410	198	9.7	*	12.4k	770k	69.6	$5.10x10^{-8}$

*Very small value.

a weakly adsorbed material at the surface of the metal. The values of P have increased from 6.7% at 0.0 mV to 13.5 at 1000 mV, due to an increase in the surface roughness of the electrode. As a result of anodic polarization, generally the values of R_p were very small due to the high metal activity.

The values of R_s were increased from $E_{o,c}$ to 300 mV due to the resistance of solution and resistance of corrosion products. At 20 °C, at potential ≥ 400 mV, the values of R_s were decreased and have an average value of about 28 Ω due to the separation of layers from the metal surface.

By a comparison of the behavior of copper in 0.05 M NaCl at 20 °C with that obtained at 40 °C and 60 °C (Tables **4-6**), it can be noticed that the same trend was obtained at the three different temperatures. The activity of copper electrode increases as temperature increases. The components of K, which are the elements W and k, manifested itself at potentials ≥ 100 mV at 60 °C, and increases with potential. The radius of the formed pores is summarized in Table **6**. Comparison between Tables **3** and **6** shows that the radius of the pores is smaller in presence of NaCl.

CONCLUSION

The corrosion behavior of pure copper was studied in 0.05 M HCl and 0.05 M NaCl solution by electrochemical impedance spectroscopy (EIS) at 20 °C, 40 °C and 60 °C. In both solutions, the increase in current values with potential demonstrated that the copper electrode in not passive and undergoes dissolution. From the values of loss factor (%P), this dissolution process is found to be homogeneous. The values of resistance of solution (R_s) are found to be increasing with potential, which demonstrated the resistance of the corrosion products. As an except in 0.05 M NaCl solution at 20 °C the valued of R_s was remarkably decreased to 28 Ω due to the separation of layers from the electrode surface. The EIS results showed that the corrosion mechanism for copper is the same in both media. The results of this work also demonstrated that EIS is a powerful technique to follow the change in corrosion mechanisms for copper in both media.

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