PITTING CORROSION CURRENT MEASUREMENTS ON Zn – ELECTRODE

N.S. Mohammed, M.B. Ibrahim, M.M.B. El-Sabbah and S.M. Abd El-Mataal

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr-City, Cairo, Egypt.

Pitting corrosion studies of Zn using some high molecular weight compounds (gelatin, soluble starch, polyvinyl alchol) and some simple amino acids (glycine, L-alanine, and L-valine) reveald that the pitting corrosion current and the concentration of the aggressive anion (CrO_4^{2-} or Cl^-) satisfy the relation:
$\log I_p = a + b \log C_{anion}$. where a and b are constants

The critical current density D_c corresponding to rapid passivation of Zn electrode in different pure alkaline solutions was studied by Iofa <1>, Landsberg and Bartlet<2>, Wojciak <3>, and others <4-7>. Their results reveald that the maximum current prior to passivation of anode was proportional to activity of $(OH)^-$. Abdul Azim and Shalaby <8> determined the quantity of electricity required for passivation in NaOH in presence and absence of various anions with different concontrations.

Mikhalenko and Flerov <9> found that the addition of styrene-maleic anhydride copolymers inhibits passivation.

In this study, the retardation of pitting corosion of Zn using high molecular weight compounds eg. gelatin, soluble starch and poly vinyl alcohol, was studied.

The effect of some simple amino acids as glycine, L-alanine and L-valine was also studied to elucidate the inhibition properties of these compounds on Zn electrode.

MATERIALS AND TECHNIQUES

Spectroscopically pure Zinc rods of ca 4.23 mm in diameter and short length were fixed to pyrex glass tubes in a manner to obtain an area of 2.5 mm^2 of the electrodes to be inserted in the solution used.

The simple electrolytic cell (Fig 1) consists of a 250 mL. pyrex glass beaker (A) containing 100 mL of the inhibiting solution, the zinc electrode and a glass stirrer. A second zinc electrode was enclosed in a glass tube (B) ending in a fine porosity, low resistance G_4 sintered glass disc.

The two compartments of the cell were charged with 0.01 M CrO_4^{-2} (inhibiting agent) solution to the same level. The two identical Zn electrodes were located in their positions and short circuited through Scalamp Galavanomater. Currents were observed to flow as a result of the uncontrollable surface conditions. These currents decayed to Zero after a few minutes. When this condition was established, a weighed quantity of sodium chloride was introduced into the main compartment (A) and the resulting current was followed as a function of time until the attainment of nearly steady values.

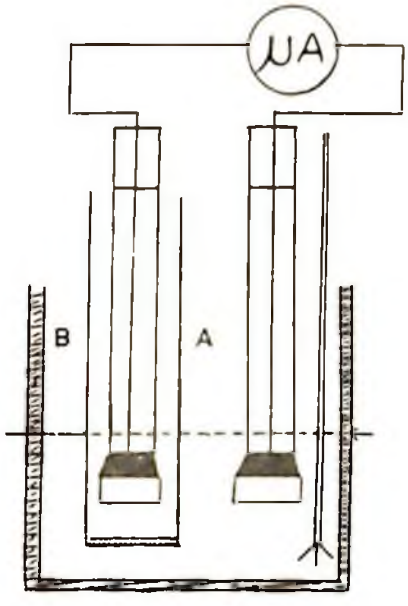


Fig. 1 Schematic representation of the electrical circuit and electrolytic cell used for measuring pitting corrosion currents.

The effect of the organic additives was substantiated by the addition of 0.1 M Cl^-

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solution containing increasing amounts of the additive to the CrO_4^{2-} solution. The resulting solution (0.01 M CrO_4^{2-}, 0.1 M Cl^- and X M of the additive), is in compartment (A). Then the current was followed till constant values.

Each experiment was done with freshly prepared electrodes and with new portions of the solutions and repeated to ensure reproducibility.

All measurements were carried out at 25°C ± 1.0.

RESULTS AND DISCUSSION

The variation of current flow as a function of time and Cl^- concentration is represented in Fig 2. These curves show that

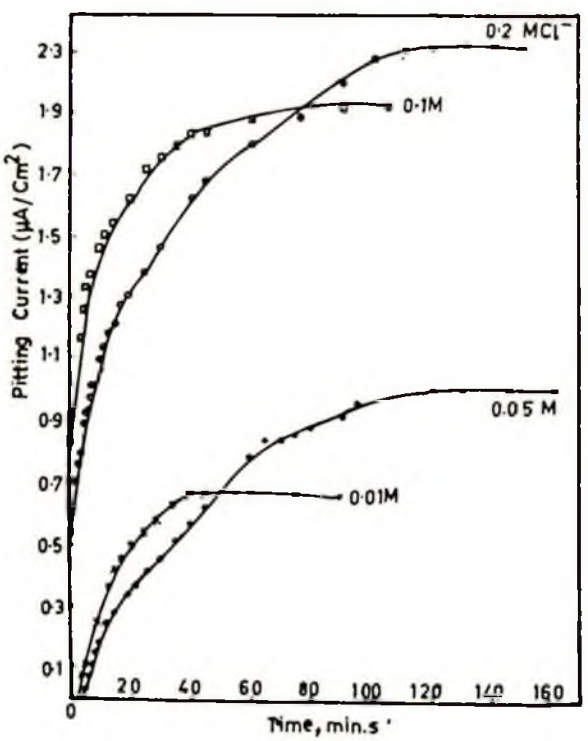


Fig. 2 Variation of the pitting corrosion current 10^{-2} M CrO_4^{2-} solution containing different concentration of NaCl.

the current increases with time reaching a limiting value (I_p). The value of this limiting current depends on the concentration of Cl^-. The effect of Cl^- on Ip shows the expected aggressivness of Cl^-. The pitting current and the concentration of Cl^- satisfy the relation:

$$\log I_p = a + b \log C_{Cl^-} \qquad (1)$$

where a and b are constants.

Equation (1) was derived theoretically by Shams El-Din <10>, in which the constant b is given by

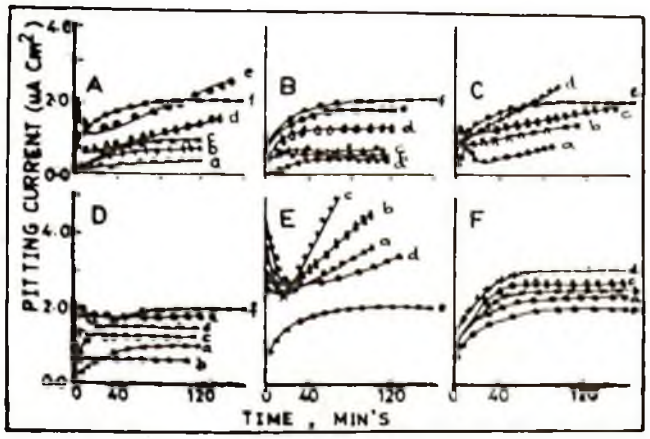
$$b = \alpha_1 n_1 / z_1$$

where α_1 is the transfer coefficient of the anodic reaction, n_1 is the number of electrons involved in the oxidation reaction and z is the valancy of the agressive ion. The magnitude of α depends on the nature of the electrode as well as on the type and concentration of the supporting electrolyte <10>. For electrode reactions governed by transfer across a single energy barrier, values ranging between 0.3 and 0.7 are commonly given <10>. Accordingly with n = 2 ($Zn \rightarrow Zn^{2+} + 2e$) and Z = 1 the term b assumes a value ranging 0.6 - 1.4. The value of b for 0.01 M CrO_4^{2-} solution is found to be 0.9.

In solutions containing small addition of Cl^-, no current flowed in the cell at the beginning of experiment; a short time elapsed before any appreciable current rise. As the concentration of the attacking agent is increased, this induction period becomes shorter. The current flows immediately in the cell containing large amounts of the Cl^- (Fig 2). This induction period is explained by Shame El-Din <10>, as the times required for Cl^- to undermine the passive layer and cause pitting.

Currents are measured with time in solutions of 0.01 M CrO_4^{2-} and 0.1 M Cl^- in the presence of increasing amounts of glycine, L-alanine and L-valine respectively (Fig 3A, B, C).

The classical current-time curves for measuring the pitting corrosion of zinc in case of L-alanine consists of two segments. The first shows an increase of current with time. The current reaches a limiting value which is refered to as the pitting current. An increase of the concentration of the additive results in a decrease in the pitting current signifying the retarding effect on the process. On the other hand when glycine is used, two different behaviours were recorded (Fig. 3A). In low concentrations of the inhibi-



A - a) 0.001M, b) 0.005M, c) 0.007M, d) 0.01M, e) 0.1M, f) Nil
B - a) 0.05M, b) 0.01M, c) 0.007M, d) 0.005M, e) 0.001M,f) Nil
C - a) 0.007M, b)0.05M, c) 0.001M, d) 0.01M, e) Nil
D - a) 0.1%, b) 0.5%, c) 0.01%, d) 0.005%, e) 0.001%, f) Nil
E - a) 2.0%, b) 0.5%, c) 0.05%, d) 5.0%, e) Nil
F - a) 0.005%, b) 0.02%, c) 0.1%, d) 0.2%, e) Nil

Fig. 3 Variation of the pitting corrosion current in (0.01M CrO_4^{2-}+0.1M Cl)solutions containing different concentrations of (A)Glycine (B) L-Alanine (C) L-Valine (D) Gelatin (E) Soluble Strach (F) Polyvinyl alcohol.

tor, curves similar to the classical ones were obtained. However, in solutions containing high concentrations of the additive a sharp current peak followed by a continuous increase in the pitting current was recorded. This indicates that glycine is more effective for the retardation of the pitting corrosion of zinc when added in low concentrations. Addition of L-valine, on the other hand, results in a continuous increase in the pitting corrosion current, Fig (3C). Hence the use of this additive as inhibitor for pitting corrosion of Zn in the prevailing conditions is not recommended.

Curves depicted in Fig (3 D,E,F) represent the affect of addition of gelatin , soluble starch and poly vinyl alchol on the pitting corrosion current of Zn in 0.01 M CrO_4^{2-} and 0.1 M Cl^- . In the case of the use of gelatin and poly vinyl alchol as additives, the current increases with time till the attainment of nearly constant value independent of time. The magnitude of this constant value is dependent on both nature and concentration of the additive. Only gelatin was found to retard the pitting corrosion of Zn electrode. This is shown by the low I_p values recorded in the presence of the additive. An increase of the concentration of the inhibitor results in a derease in the I_p value. Addition of soluble starch and poly vinyl alcohol accelerates the pitting corrosion of Zn. This was indicated from the increase of corresponding I_p value with addition of these additives.

As revealed from these results, among the addition agents used L-alanine and gelatin can be used safely as retardants for the pitting corrosion of Zn whereas glycine can be used only at low concentrations.

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