Open Circuit Potentials of Zinc Electrode in Buffer Solutions

M.M. El-SABBAH, MOHAMAD E. IBRAHIM, NADIAH S. MOHAMAD AND RABAB M. ABU-SHAHBA

Chemistry Department, Facultry of Science, Al-Azhar Univ., Cairo, Egypt.

Open-Circuit potential measurements of polished zinc electrode were carried out in buffer solutions over the entire pH range. In acid and alkaline buffers there is a general tendency for open circuit potential to drift with time towards more noble values. This behaviour may be attributed to the formation of isoluble layer of zinc oxide or hydroxide on the electrode surface, which increase the resistance of anodic areas, and therefore the potential becomes more positive. However, in high acidic and high alkaline solution, steady-state potentials are more negative than the immersion values,. This behaviour is expected considering the instability of zinc oxide or hydroxide in highly acidic and highly alkaline solutions. The results were interpreted in the light of the mixed potential theory of electrode processes. Hence, the theoretical potential-pH variation of 0.0059 V/pH was adequately explained.

The Oxide film formed on zinc electrode has a determinative influence in the protection of the metal from further attack. Consequently a number of investigations have been devoted to the study of the Characteristics of this film. The role played by OH^- in the dissolution and passibity of Zn was studied using diffuse light[1], anodic polarization[2], capacity of passivation film[3], potentiodynamic[4], galvanostatic[5], and potentiostatic[6], techniques. The corrosion and corrosion inhibition of Zn electrode in acid media and the effect of various ions were studied by authors[7-10]

The stability of ZnO and Zn $(OH)_2$ on the electrode was investigated by Zoubov and Pourbaix[11]. The potential-pH diagram constructed by the authors contains regions of passivity, immunity and corrosion.

The corrosion potential of Zn electrode was studied as a function of time and pH in different buffer solutions[13] The steady state potential varies linearly with pH of the solution according to:

$$E_{st.} = a - b \log [H^+] \quad \text{---------- (1)}$$

Where "a" and "b" are constants depending on the nature of the anions forming the buffer.

In the present investigation the open-circuit potentials of Zn electrode were measured till the attainment of steady state values, in buffer solutions covering the pH range 1-14.

EXPERIMENTAL

Spectroscopically pure Zn rods about 4.23 mm in diameter were made in the form of short rods fixed to pyrex glass tubes, with neutral wax, in a manner to obtain an area of $2.5cm^2$ of the electrode. Electrical contacts were made through thick copper wires, soldered to the end of the rods but not exposed to the solution. Before being used, the electrodes were adbraded successively to the finest grade by an emery paper, degreased with acetone and washed several times with re-distilled water.

A series of buffers in the pH range 1-14 (of clark and Lubs)[12] were prepared from AR chemicals and their pH were measured using digital pH meter.

A cell, Zn /Buffer solution : Sat KCl /Hg_2Cl_2 /Hg was set up using 50 ml buffer solution. Two salt bridges filled with the test solution are interposed between sat KCl and buffer solution to prevent diffusion of Cl to the zinc. Air bubbled through the buffer throughout the experiment. The cell voltage was measured to $\pm$? mV using digital voltmeter and continued till it was steady for 10 mts.

Each experiment was repeated several times with fresh solution and freshly abraded electrode to ensure reproducibility.

Weight loss experiments were carried out using Zinc coupons of 5x2x0.1 cm cut from sheets of zinc of the same specification as above. These were abraded, degreased, washed, dried, weighed and suspended in the test solution and weight loss measured after different intervals. Corrosion rate was calculated from average weight loss in three experiments.

All measurements were carried out at 25 ± 1°C

RESULTS AND DISCUSSIONS

Fig.1 represents the potential variation of zinc electrode in different buffers as a function of time. In almost all buffers from pH 2-10 there is a general tendency for the open-circuit potential to drift with time towards more noble values. This behaviour may be attributed to the formation of insoluble layer on the electrode surface of zinc oxide or hydroxide, which increases the resistance of anodic areas and therefore the potentials become more positive. However, in high acidic (pH < 2) and high alkaline solutions (pH > 13), steady state potentials are more negative than the initial values. This behaviour is expected because of the instability of zinc oxide or hydroxide in highly acidic and highly alkaline solutions.

Both the immersion and the steady state potentials are found to depend on the pH. This can be shown in the potential-pH curves of Fig. (2). The variation of both immersion, and the steady state potentials in strongly acidic and strongly alkaline media can be considered as linear with a slope nearly equal to that of the hydrogen electrode system (viz. 0.059 V/pH unit at 25°C). This indicates that the nature of the cathodic reaction occuring at the electrode surface is mainly hydrogen ion discharge[11] viz.

$$2H^{+} + 2e \dashrightarrow H_2 \qquad (2)$$

The depolarization effect of oxygen manifests itself at pH = 6, which is indicated by the break observed on the curve, (pH 6-12). The immersion and the steady state values are pronouncedly shifted to less negative potentials compared to those obtained in highly acidic and highly alkaline solutions. Thus the reduction of oxygen participates in the overall cathodic reaction.

The scatter of the steady state and immersion potentials as indicated on the potential-pH curve (Fig. 2) show that the observed potentials lie within the domain limited by metal dissolution according to[11]:

$$Zn^{+2} + 2e \dashrightarrow Zn \qquad E_0 = -0.800\ V. \quad (3)$$

The steady state potentials approach from more negative to less negative values indicating the electrode is predominately under cathodic control and the cathodic areas increase at the expense of the anode sites. The magnitude of potential drift depends on the pH of buffer solution. The higher the pH of the solution the larger is this drift. However, in highly acidic and highly alkaline buffers, the steady-state potentials were approached from less negative values denoting

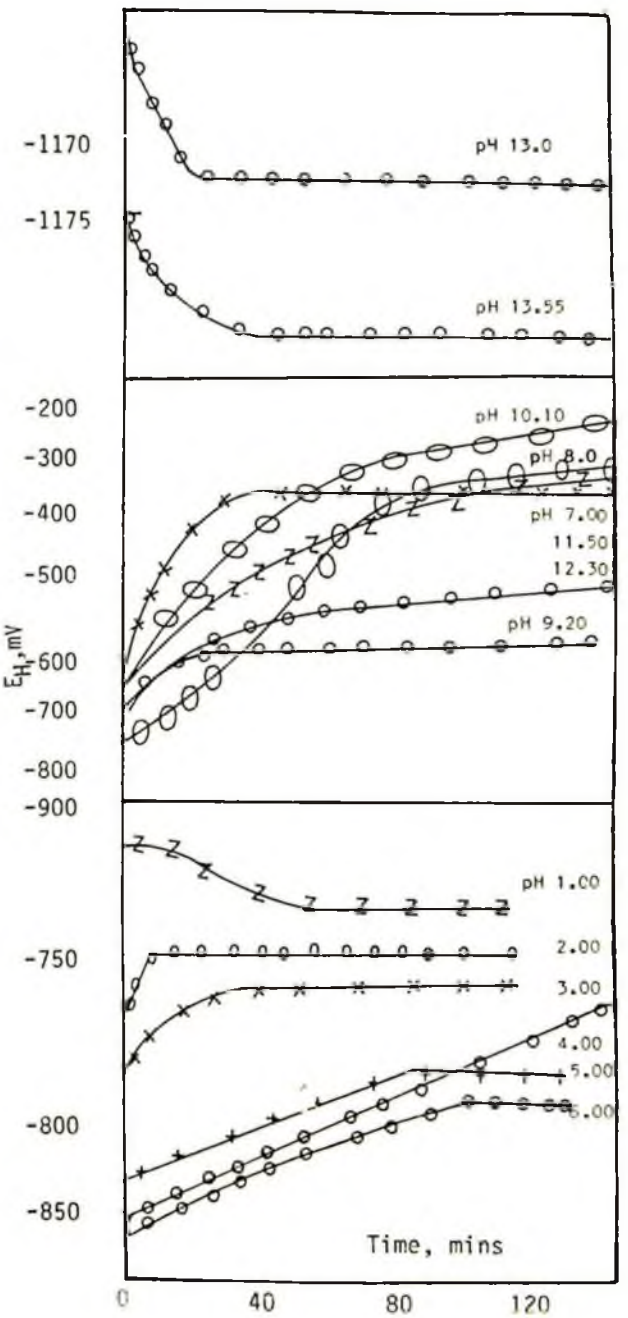


Fig. 1 Potential-time curves of Zinc-Electrode in buffer solution of pH 1-13.55

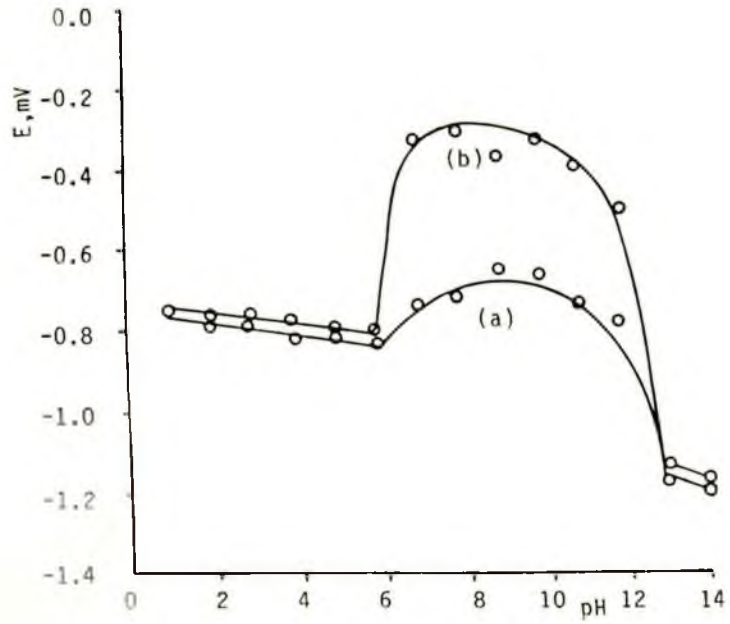


Fig. 2: Variation of the immersion potential (a) and the steady state potential (b) of Zn electrode as a function of pH.

the destruction of the preimmersion oxide film found on the surface of the electrode. These buffers promoted corrosion and the extent of corrosion acceleration depends on the nature and the pH of buffer. The corrosion products differ in acidic and alkaline solutions. Thus these products may be Zn^{+2} in acidic and zincate ZnO^{2-} or bizincate $HZnO_2^-$ in alkaline buffers as reported by Pourbiax[11].

The variation of the steady-state potential of the metal electrode with pH can be readily accounted for by considering that these potentials are mixed corrosion potentials governed by the partial anodic and cathodic reactions[13] dealt with as in the following:

$$M = M^{n+} + n\,e^- \qquad (4)$$

$$\text{and } H^+ + e^- = H \qquad (5)$$

The rates of anodic and cathodic processes can be expressed as:

$$i_a = k_a \exp(-\alpha_1 n_1 F E_{st.}/RT) \qquad (6)$$

$$\text{and } i_c = k_c\, C_{H^+} \exp(-\alpha_2 F E_{st}/RT) \qquad (7)$$

Where i_a and i_c = Current densities for anodic and cathodic reactions, respectively.

k = Reaction rate constant.
α = Transference coefficient.

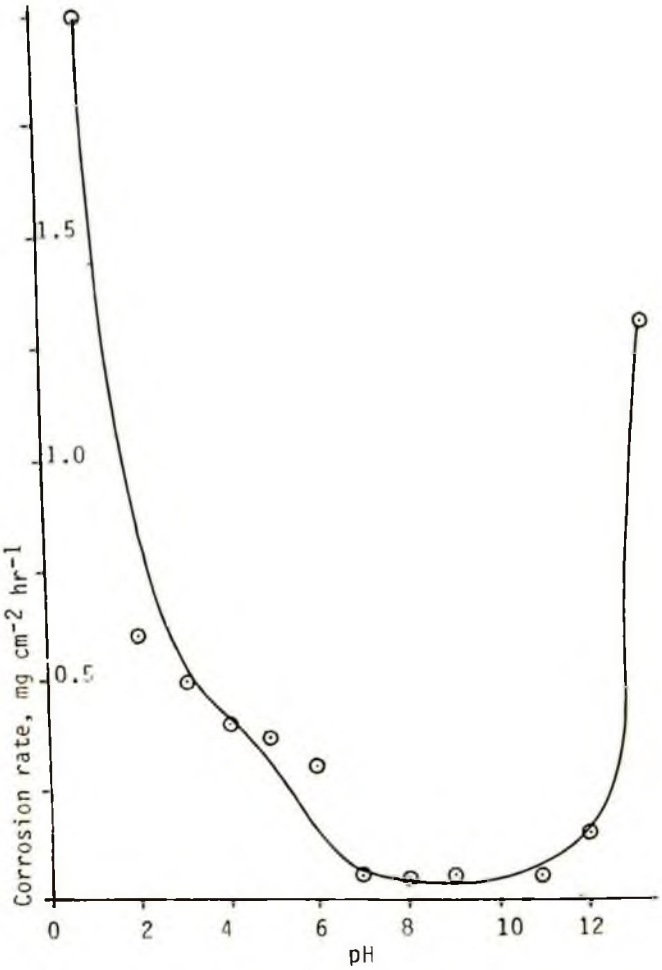


Fig. 3: Variation of corrosion rate of Zn-electrode as a function of pH.

$E_{st.}$ = Steady state potential.
C_H^+ = Concentration of H^+ in solution.

and a and c refers to anodic and cathodic reactions respectively. At equilibrium, $i_a = i_c$. Accordingly, $k_a \exp(\alpha_1 n_1 F E_{st.}/RT) = k_c C_{H^+} \exp(\alpha_2 F E_{st.}/RT)$ ---------- (8)

From equation (8) it directly follows that

$$E_{st.} = \frac{2.303\,RT}{BF}\log\frac{kc}{ka} - \frac{2.303\,RT}{BF}pH$$

$$= \frac{0.059}{B}\log\frac{kc}{ka} - \frac{0.059}{B}pH \text{----------(9)}$$

Where $B = (\alpha_1 n_1 + \alpha_2)$.

Equation (9) describes the experimental results, and shows that the slope of E_{st} - pH curve equals that of $H_2/2H^+$ system (59 mV) only when the term B amounts to 1. Such a case was recorded for Zn electrode in high acidic and high alkaline buffer solution (Fig. 2.). That the Zn electrode corrodes in highly acidic and highly alkaline

solutions and remain passive in the pH range 6-12 is supported from weight loss measurements (Fig. 3).

REFERENCES

1. K. Huber, Z. Electrochem., 48(1942) 26.
2. R.D. Armstrong and M.F. Bell , J. Electroanal. Chem and Interfacial Electrochem, 55 (1974) 201.
3. Z. ya Nikilina, Zhur, Priklad, Khim (J. Applied Chem.) 31(1958) 218.
4. T.P. Dirkse and N.A. Hampson, Electrochem Acta, 17(1972) 387; S.M. Afd. El-Haleem, Br. Corr. J. 11(1976) 215.
5. Z. Vorkapic and D.M. Drazic , J Electrochem. Soc. 121(1972) 1385.
6. Wojciak, Waclaw, Beltowska, and Brazezi, Mat. Przyr. Pr.chem. 12(1971) 35; C.A. 75(4) (1971) 29191.
7. Shams El-Din and M.G.A. Khedr, Metalloberflache , 25(1971) 210.
8. E.V. Semina and V.I. Shebeslov, electrokhimiya, 14(1978) 886; C.A. 89 (20) (1978) 170794.
9. M.G. Alvarez and J.R. Galvele Corrosin (Hauston) 32(1976) 285.
10. Drazic Dragutin and M. Zecevic , Hem Drus Belgrad, 40 (1978) 141 ; C.A. 89 (6) (1978) 50424 z :
    F.I. Kukoz and I.D. Kudryavtseva; Ingibiroranie passivirovanie met, 66 (1976) ; C.A. 91 (10) (1979) 80789 F.
11. M. Pourbaix , Atlas of Equilibria in aqueous solutions, pergsmon press (1966)
12. H.T.S. Britton , Hydrogen ions vol.I Chapman and Hall(1948) P 301,303, 306, 310.
13. S.M. Sayed, Egypt J chem. 21 (6) (1978) 431.