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Galvanostatic study of the breakdown of Zn passivity by sulphate anions

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ABSTRACT

The anodic behavior of Zn electrode in Na_2SO_4 solutions was studied by galvanostatic polarization technique. The polarization curves are characterized by a distinct arrest corresponding to ZnO formation, after which the potential rises linearly with time up to a well-defined value, the breakdown potential, at which the potential drops with time, down to more negative direction. This denotes the destruction of the passive film and initiation of pitting corrosion. It was found that, the breakdown potential, the time consumed till the breakdown potential and the rate of potential rise with time depend on the sulphate anions concentration, solution temperature and magnitude of the imposed current density. Addition of increasing concentration of phosphate, molybdate, tungstate or chromate anions causes a shift of the breakdown potential into the noble direction, indicating the inhibitive effect of these anions. The inhibitive effect of these inhibitors decreases in the order: $CrO_4^{2-} > WO_4^{2-} > MoO_4^{2-} > HPO_4^{2-}$.

1. Introduction

Zinc is a very important metal, used in a wide range of applications by various industries, e.g. as a construction material for roofs and facades in structural and civil engineering or as a sacrificial coating to protect iron and steel products from environmental corrosion attack in the steel producing and processing industry, especially the automotive industry [1,2]. Zinc is a very active metal so that it corrodes quickly in aqueous solutions [3]. For these reasons, the behavior of zinc has attracted the attention of several investigators in a wide variety of media [4–19]. The anodic and cathodic processes of zinc corrosion in aerated neutral solutions are dissolution of zinc and reduction of oxygen molecule [20], respectively, as

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{1}$$

and

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2}$$

Since, the solubility product of zinc hydroxide is markedly low, 3.0×10^{-17} [21], zinc hydroxide formed by a reaction of Zn^{2+} with OH^- precipitate on the surface of zinc substrate. The formed zinc hydroxide is followed by changing gradually to zinc oxide,

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{3}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{4}$$

resulting in the formation of a passive film [22]. Hence, the passive oxide film prevents zinc corrosion in the neutral solutions. However, zinc electrode suffers pitting corrosion when exposed to different aggressive anions [14,17–19,23–27]. Little is known about the passivity and passivity breakdown of zinc in nearly neutral aerated sulphate solutions [16,28].

The aim of the present study is to investigate the electrochemical anodic polarization behavior of Zn electrode and the breakdown of its anodic passivity in Na_2SO_4 solutions under some different conditions, e.g. concentration, solution temperature, and anodic charging current density. We also report the result of attempts to tolerate the breakdown of Zn passivity by using the sodium salts of phosphate, chromate, molybdate and tungstate as corrosion inhibitors.

2. Experimental

The zinc electrode was made from spec-pure zinc rod (Johnson-Matthey, UK). The electrode was fixed to a borosilicate glass tube with epoxy resin so that the total exposed surface area was $0.28\ cm^2$. Electrical contact was achieved through a thick copper wire soldered to the end of the zinc rod not exposed to the solution. Before being used, the electrode was abraded successively with finer grades emery papers. Then, it was rinsed with acetone and finally washed with triply distilled water.

The electrolytic cell used for galvanostatic polarization has a capacity of 250 mL. The Zn electrode and the main bulk of the solution were separated from the platinum (Pt) counter electrode using a G_4 sintered glass disc to prevent mixing of the anodic and cathodic reaction products. The cell has a double jacket through which, water at the adjusted temperature was circulated. A conventional three-electrode system was used. A platinum sheet was used as an auxiliary electrode, the working electrode was a zinc electrode

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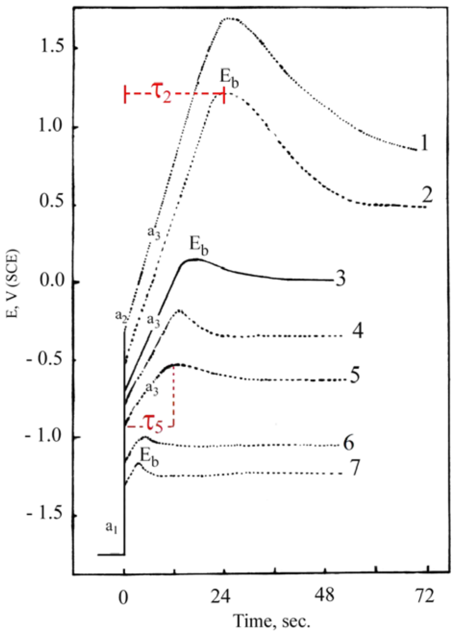

Fig. 1. Anodic polarization curves of Zn electrode in different concentrations of Na_2SO_4: (1) 0.0005 M, (2) 0.001 M, (3) 0.0025 M, (4) 0.005 M, (5) 0.01 M, (6) 0.05 M and (7) 0.1 M, at a current density 1.8 mA/cm^2 (pH 6.4, 25 °C).

and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary positioned close to the working electrode surface in order to minimize ohmic potential drop. Before carrying anodic polarization, the zinc electrode was subjected to cathodic pretreatment process for 10 min in the test solution with the same polarizing current density until reaching a constant potential value. This process was done to reduce any overlying oxides, that would form spontaneously on the metal surface before running the experiment [15,17,18]. The polarizing current was then reversed, and the potential was recorded as function of time (anodic polarization).

Experiments were done in Na_2SO_4 solutions of different concentrations. The salts of Na_2HPO_4, Na_2MoO_4, Na_2WO_4 or Na_2CrO_4 were used as breakdown potential inhibitors. Electrolytic solutions were prepared from analytical grade reagents and triply distilled water. The pH measurements were conducted using an Orion Research Expandable Ion Analyzer EA 920. Measurements were carried out at a constant temperature, 25 ± 0.1 °C, except those related to the effect of temperature. The cell temperature was controlled using an ultra thermostat type polyscience (USA).

Each experiment was carried out in a freshly prepared solution and with a newly polished electrode surface. Polarization curves were recorded on a recording unit from Cole Parmer Instruments (USA). Scanning electron microscopy of the tested electrode was carried out using a Jeol Scanning Microscope JSM-T100 (Japan).

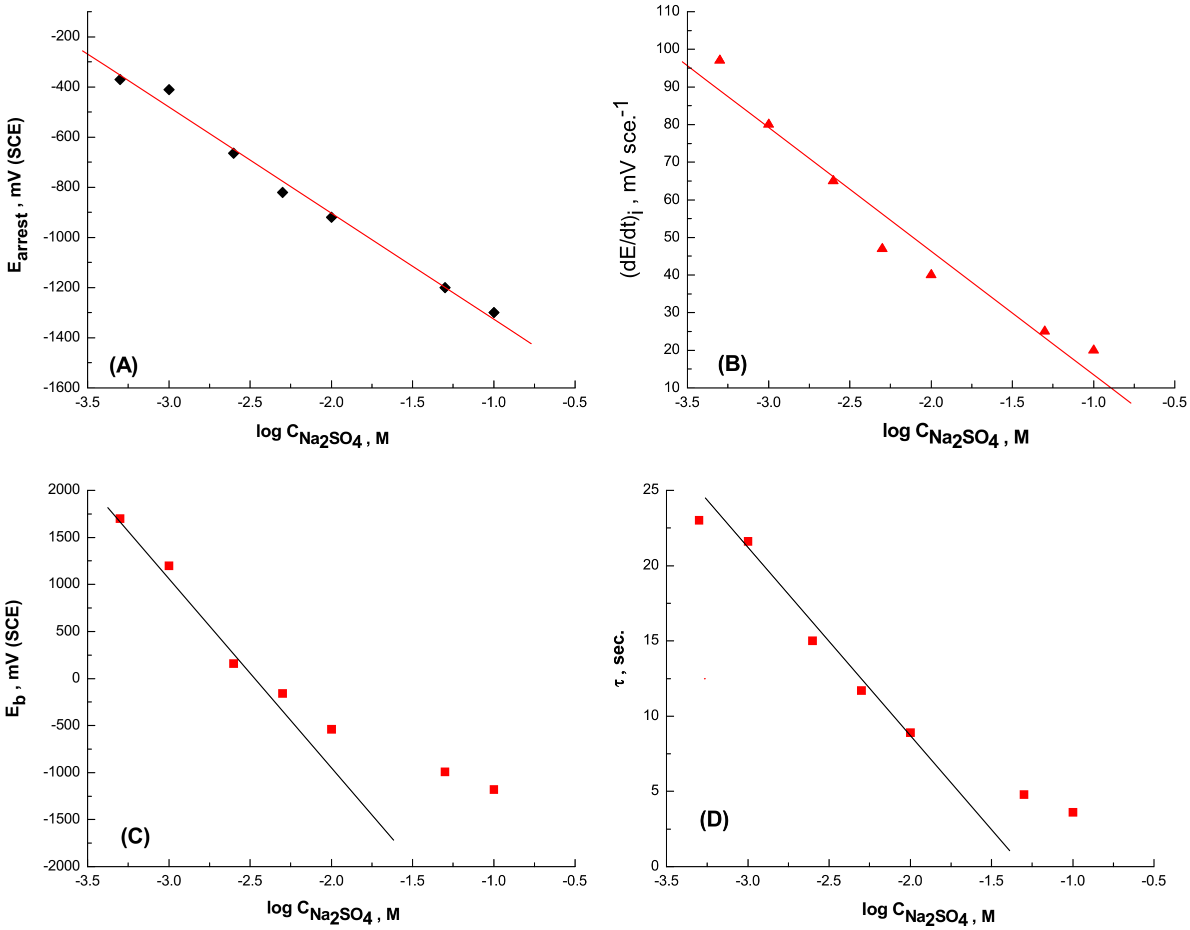

Fig. 2. Variation of (A) the starting potential of the arrest, E_{arrest}, (B) the rate of potential rise with time, $(dE/dt)_i$, (C) the breakdown potential, E_b, and (D) the duration time of the anodic arrest, τ, with the logarithm of the concentration of Na_2SO_4.