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Electrochemical corrosion of zinc in sodium chlorite

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By means of electrochemical techniques, the corrosion of zinc and sodium chlorite deaerated aqueous solutions at room temperature was studied. An explanation for the formation of $Zn(OH)_2$ is given based on various solute species. Using these results and by scanning electron microscopy examination of the corrosion products formed, an overall reaction mechanism was proposed.

1. Introduction

Electrochemical oxidation of zinc has been studied with renewed interest [1] in recent years because of the possible commercial applications of Zn/air batteries and black zinc oxide coating for solar collector surfaces.

The anodic behaviour of zinc in alkaline solution, has been extensively studied [2–19]. The system of zinc in slight basic sodium chlorite solution has never been studied, except by Leij [16] who found that zinc in $NaClO_2$ containing alkaline solution, formed a coating of zinc oxide with a deep black colour and high corrosion resistance.

Fig. 1 is a distribution diagram for zinc hydroxide complexes. Referring to the Pourbaix diagram [20], the zincate ion $Zn(OH)_4^{2-}$ is one important species in KOH battery electrolytes. The tetrahedral structure of this zinc complex ion has been confirmed by previous investigation [21]. According to this distribution diagram for the zinc–water system, the species Zn^{2+}, $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ coexist in dilute basic solution, and the solid $Zn(OH)_2$ is the main zinc species in the pH range for 8 to 12.

Hampson the co-workers [22, 23] suggested a sequence of reactions for zinc in alkaline solutions. The effect of sodium chlorite on the mechanism of zinc hydroxide formation is unknown. The purpose of this study is to contribute to establishing the mechanism of corrosion of zinc in aqueous $NaClO_2$ and slight alkaline solution.

2. Experimental details

2.1. Material

The sodium chlorite content of the electrolyte solution was established iodimetrically as described by White *et al.* [24] and Hamilton and Simpson [25].

The zinc specimen was prepared from 99.99% zinc bar, cast and cut into pieces. The electrode was prepared by polishing with 600 grit SiC paper and was rinsed in distilled water before being transferred to the cells which were used by Chin and Venkatesh [26].

The electrode holder is designed to accept flat specimens. The rubber compression gasket between the specimen holder and the glass electrode holder ensures a leak-proof assembly. The area of specimen surface contact with cell solution is 1.07 cm^2.

2.2. Apparatus

Electrochemical measurements were obtained using a typical three electrode system. The electrodes consisted of the stationary flat zinc electrode (working electrode), a pair of counter electrodes and a saturated calomel reference electrode. A Princeton Model 173 potentiostat was used for the electrochemical measurement. Assembly of the apparatus used for electrochemical corrosion measurements was initiated by placing a known amount of sodium chlorite in a 1000 ml glass reaction vessel.

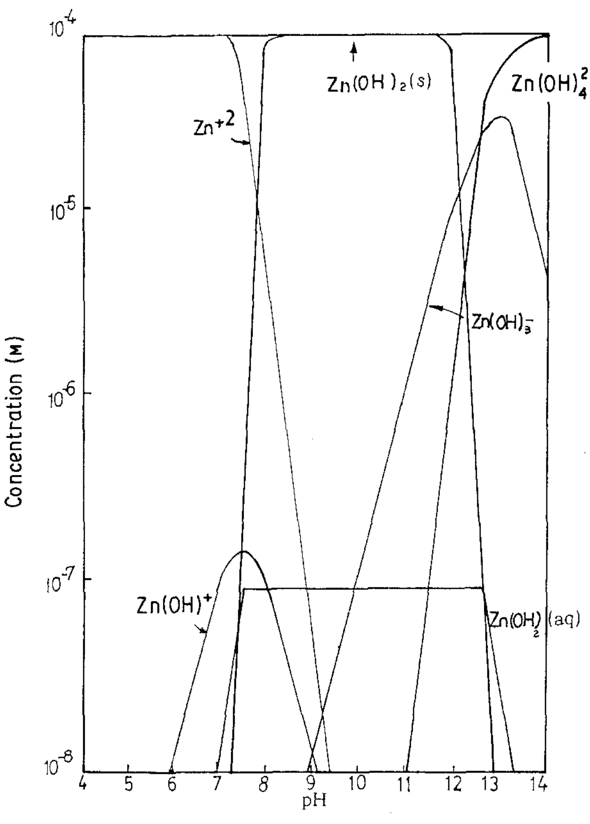

Figure 1 Variation of concentration of soluble and insoluble species with pH, Zn–H_2O distribution diagram (Total Zn(II) = 1×10^{-4} M).

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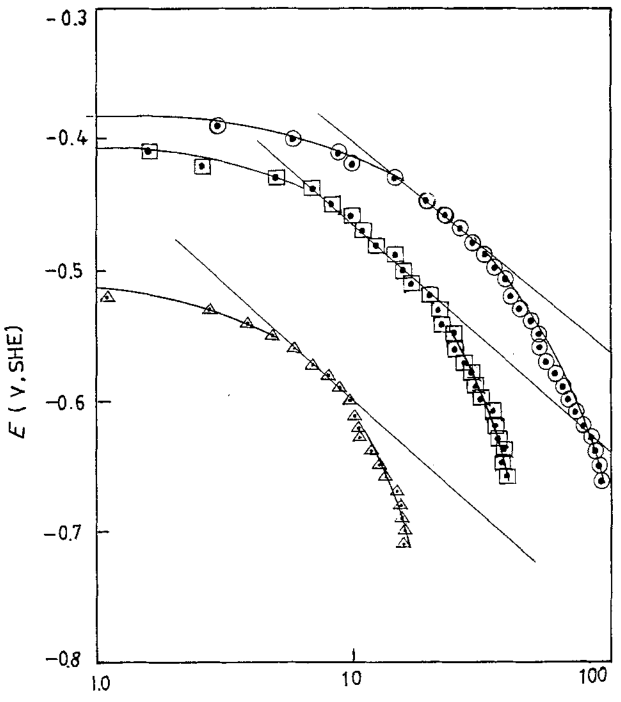

Figure 2 Cathodic Tafel plots for zinc in pH 11 solutions of various $NaClO_2$ concentrations. (△) 1 g litre^{-1}; (□) 3 g litre^{-1}; (○) 10 g litre^{-1}.

The potential between the zinc electrode and reference electrode was measured through a Luggin capillary which was placed as close as possible to the working electrode. All potentiostatic experiments were quoted with respect to the standard hydrogen electrode (SHE).

Electrochemical corrosion experiments were initiated by preparing 1000 ml of a solution containing a known amount of $NaClO_2$ and then was measured and adjusted to the desired pH values.

3. Results

3.1. Effect of $NaClO_2$ concentration

For pure zinc good and reproducible potentiostatic cathodic transients were obtained. Fig. 2 represents the Tafel lined obtained from the upper potential plateaux, pertaining to chloride ion reduction.

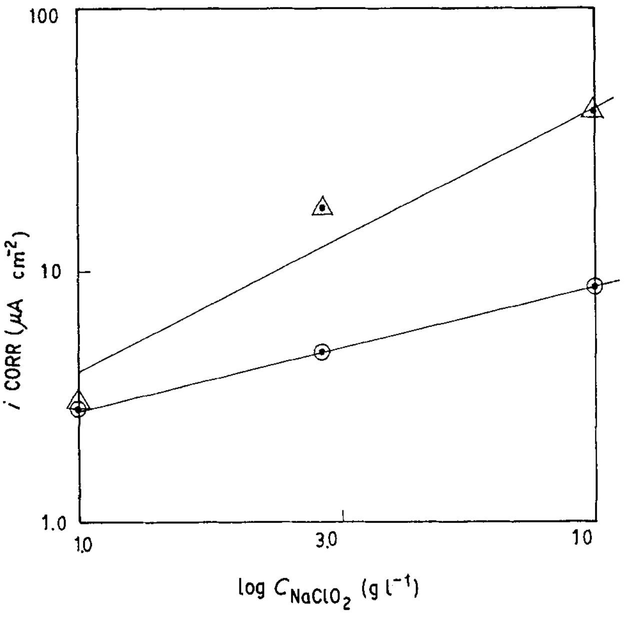

Figure 3 Concentration dependence of the corrosion current density (○) and the current density (△) at a constant potential of −0.5 V (SHE) in pH 11 for zinc in $NaClO_2$ solution.

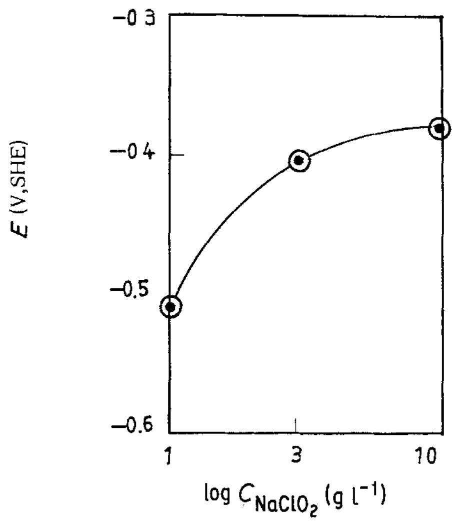

Figure 4 Corrosion potential against $NaClO_2$ concentration at pH 11 and deaerated solution.

Characteristic features are: (a) well-defined linear Tafel lines against root current density with slopes of 160 to 170 mV dec^{-1}; and (b) decrease of the polarization at a given current density with increasing concentration of $NaClO_2$. This produced the dependence of the current density on concentration at constant potential shown in Fig. 3 with the slope of the full log plot, the reaction order equal to one.

The corrosion current was obtained by extrapolating the straight lines to the corrosion potentials and the dependence of the obtained result on $NaClO_2$ concentration is also shown in Fig. 3. The dependence of the corrosion potential on $NaClO_2$ concentration is given in Fig. 4.

3.2. Effect of pH

The products of anodic dissolution and passivation of zinc electrode in the pH range from 8 to 12 is composed of both soluble and insoluble species. At pH less than 7, the most common species is soluble Zn^{2+}, at

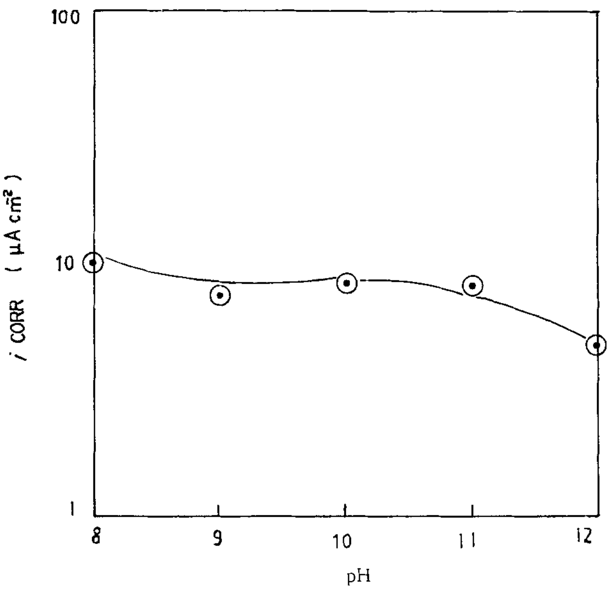

Figure 5 pH value dependence of the corrosion current density in deaerated $NaClO_2$ (10 g litre^{-1}) solution.

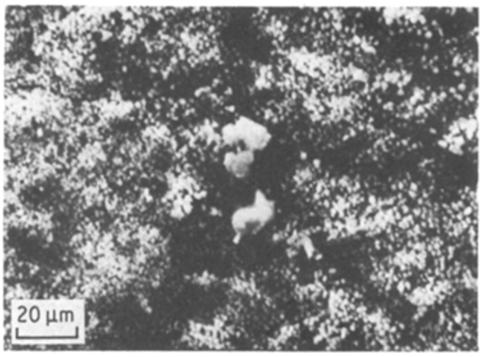

Figure 6 SEM view of a corroded zinc surface in pH 11 and $NaClO_2$ (10 g litre^{-1}) solution for 16 h.

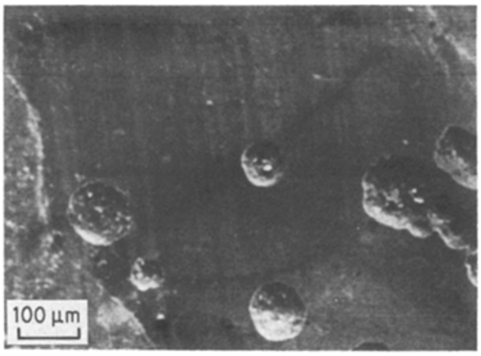

Figure 7 SEM view of corroded surface of zinc in pH 12 and $NaClO_2$ (10 g litre^{-1}) solution after anodic polarization.

pH greater than 8 and less than 12, the main product is solid $Zn(OH)_2$. The corrosion current densities of pH 8 to 12, deaerated $NaClO_2$ solutions are shown in Fig. 5. The dependence of corrosion current on pH 8 to 12 shows no effect, which is consistent with the other data provided by Tomlinson *et al.* [27]. The corrosion current of zinc in $NaClO_2$ solution is essentially independent of pH 8 to 12.

3.3. SEM examination

Among the electrolytes considered in this paper, the concentrated $NaClO_2$ is the most corrosive. Micrographs in Fig. 6 show the specimen after 16 h immersion in 10 g litre^{-1} $NaClO_2$ and pH 11 solution. The film appears partially white and grey in colour. Fig. 7 shows the specimen after anodic polarization in 10 g litre^{-1} $NaClO_2$, pH 12 solution appears with dissolution pits, this is probably due to the small amount of chloride ions present.

4. Discussion and conclusions

The exact mechanism of surface disintegration is presently not known in detail, but the observations made with zinc anodes in $NaClO_2$ solution, suggest a mechanism as follows. The zinc anode absorbs into its surface ClO_2^-, similarly as is proposed for NO_3^- [28] and BrO_3^- [29].

$$2Zn + ClO_2^- + 2H_2O \rightarrow 2Zn(OH)_2 + Cl^- \quad (1)$$

This action increases with increasing chlorite concentration, and is independent of pH.

These generally thin hydroxide films will vary in adherence and thickness, depending on the surface structure of the zinc electrode. There will be places where the film adheres well and thickly, causing partial passivation of the anode (see corner of Fig. 7). On application of an anodic current the weakest spots will be attached first and there the soluble species will go into solution, partially retaining the passive spots. Since the Zn^{2+} or $Zn(OH)_4^{2-}$ can be saturated in pH of 8 or 12, respectively, a precipitating process of $Zn(OH)_2$ can be followed.

The scheme outlined in Fig. 8 is proposed and is consistent with the zinc–water distribution diagram concerning "oversaturated" zinc species in solution. It explains the dissolved zinc concentrate increases in solution, the aqueous $Zn(OH)_2$ will be formed and then precipitated on the electrode surface.

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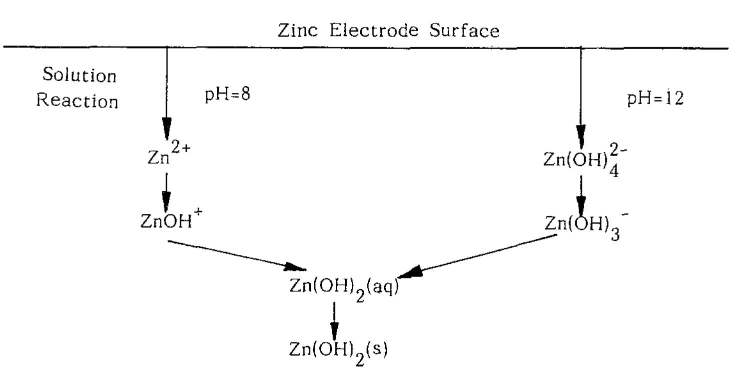

Figure 8 Summary of reactions to form $Zn(OH)_2$ (s) at the corrosion potential.

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