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The effects of silicate ion on the corrosion of zinc powder in alkaline solutions

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In the absence of zincate, silicate ion was found to have favourable effects on the corrosion rate of zinc powder in alkaline solution, as expressed by its gassing rate and polarization curve. The addition of zincate lessened the effect of silicate. Glass corrosion and silicate-zincate interaction in alkaline solution are also emphasized.

1. Introduction

For zinc powder suppliers and alkaline battery companies, the out-of-cell gassing test is one of the most meaningful quality control tests to measure the corrosion susceptibility of zinc. Although several gassing tests [1–5] are carried out in glassware with strong alkali at high temperature, no study has addressed the etching of glassware and the resulting effect of dissolved silica on the gassing rates and mechanism.

Contamination of test solutions by leached silicates from glassware has been found to interfere with equilibration of saturated ZnO solution [6]. Further investigation showed that the presence of silicate in 3 M KOH suppresses the passivation charge of zinc [7], because of the marked inhibiting effect of silicate on the rate of dissolution of zinc [8]. The effect was ascribed to adsorption of the silicate on the surface. Also it was shown that the addition of potassium silicate enhances the extent of active dissolution in a convective-dominated system [9].

Silicate ion has an inhibiting effect on the hydrogen evolution reaction (HER) on Ni [10] and Raney-Ni [11] in strongly alkaline solutions. For Ni, the effect is significant for concentrations higher than about $2\,\mathrm{g\,dm^{-3}}$ Si and current densities higher than $500\,\mathrm{mA\,cm^{-2}}$, while the inhibiting effect for $[\mathrm{Si}] > 4\,\mathrm{g\,dm^{-3}}$ on Raney-Ni appears at low current densities and may be attributed to a decrease in the exchange current density for the HER.

The work presented here considers the etching of glassware in gassing tests and the influence of the resulting dissolved silica on the gassing rate of zinc, the anodic oxidation of zinc and the HER on zinc in 9 M KOH.

2. Experimental details

Gassing tests were performed in glassware ($\sim 65\,\mathrm{cm^2}$ surface area) or polypropylene apparatus. Commercial alkaline battery-grade zinc powder was immersed in 36 wt % KOH (prepared by dilution of 45 wt % KOH, from Ricca Chem.) with or without potassium zincate (formed by adding 2 wt % Analar zinc oxide, 99.5% ZnO, to the electrolyte) and containing various amounts of sodium metasilicate ($\mathrm{NaSiO_3 . 9H_2O}$, ACP, 99.9%) in an oven at 93° C for 24 h. Hydrogen bubbles were collected and the corresponding volumes measured and reported (corrected to s.t.p. conditions). The zinc powder was a typical battery-grade material containing around 450 p.p.m. lead.

Electrochemical measurements were performed in a polypropylene cell at 25° C (rest potentials) or at room temperature (around 24° C, polarization curves). The effect of silicate on the rest potentials was estimated by measuring the potential difference between a zinc foil (zincate specific electrode) and the Hg/HgO reference electrode with a digital multimeter (Keithley 197). The cell potential became constant in the first minute following the addition of silicate solution. No difference was found between deaerated and aerated alkaline solutions. Polarization curves were obtained using a nickel foil counterelectrode, a Hg/HgO reference electrode and a zinc working electrode. The zinc electrode was electrodeposited zinc powder formed on $16\,\mathrm{cm^2}$ zinc foil at 800 mA for 1500 s in 36 wt % KOH–2 wt % ZnO. Potentiodynamic polarization curves were obtained using a PAR 273 potentiostat at a potential sweep rate of $1\,\mathrm{mV\,s^{-1}}$ from -1700 to -1300 mV (with respect to Hg/HgO).

In most of the experiments, ZnO was dissolved in alkaline solution to fix the initial zinc electrode potential and to maintain constant zincate activity over the duration of the gassing test or the polarization scan.

3. Results

3.1. *Etching of glassware*

It is well known that glass is attacked by alkaline solutions and silica passes into solution. The attack is facilitated by increase in temperature or increasing KOH concentration, but results may vary with different glasses [7]. Silica may pass into solution as metasilicate $\mathrm{SiO_3^{2-}}$, while polymerization and colloid formation are negligible in alkaline solution [8].

When gassing tests are performed in 36 wt % KOH–2 wt % ZnO at 93° C in Pyrex apparatus, the Si

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content after 24 h is found to be 1.81 g dm^{-3} Si (the standard deviation for 12 samples was 0.08 g dm^{-3}). In fact, the Si content increases linearly as a function of time for the first 24 h. The corresponding dissolution rate was estimated to be 4.1 mg day^{-1} cm^{-2}, in agreement with 5.6 mg day^{-1} cm^{-2} in 5 wt % NaOH at 100° C [9]. For the typical battery-grade zinc powder, the average gassing rate in such conditions was around 4.5 cm^3 mol^{-1} day^{-1} (s.t.p.).

The glass corrosion equilibrium is assumed to be

$$SiO_2(s) + 2OH^- \rightleftharpoons SiO_3^{2-} + H_2O \qquad (1)$$

Silica dissolution progresses until the corrosion reaction equilibrium is attained. In the present case, the equilibrium is not reached in the first 24 h since the dissolution rate remains almost constant. This statement is supported by the fact the dissolution rate did not go to zero when 2 g dm^{-3} sodium metasilicate was initially dissolved in the solution; it was inhibited only by a factor 2. The constant alkaline corrosion rate of glass and the inhibiting effect of metasilicate have been reported previously [13].

It has also been shown that corrosion of asbestos-chrysotile in 40 wt % KOH at 120° C reaches an equilibrium when the Si content in solution is 2.0 g dm^{-3} [10]. For chrysotile, the equilibrium molar ratio Si : KOH is found to be 0.0071 at 120° C, whereas the glass corrosion equilibrium would exhibit a ratio greater than 0.01 at 93° C, presumably because of the lower stability of Pyrex in alkaline solution at high temperatures.

3.2. *Gassing rate*

Volumes of gaseous hydrogen evolved from immersed zinc powder were measured as a function of silicate and zincate concentrations and time in polypropylene apparatus. In the absence of zincate, the gassing rate (as given by the slope) appears to be fairly constant over the first 24 h (Fig. 1a), while silicate ion slightly reduces the gassing rate on 24 h. In the presence of zincate (2 wt % ZnO), it was found that the initial rate is quite similar to that in the absence of zincate but the gassing rate is not constant and slows down in the first 10 hours (Fig. 1b). Furthermore, dissolved silicate does not significantly affect the evolved hydrogen volume and the corresponding apparent gassing rate after 24 h. Gassing rates on 24 h are summarized in Table 1.

As reported above, the average gassing rate measured in glassware containing an average amount of 1 g dm^{-3} Si in 24 h was 4.5 cm^3 day^{-1} (s.t.p.). This compares with 5.1 cm^3 day^{-1} (s.t.p.) measured in the presence of 1 g dm^{-3} Si in polypropylene apparatus.

The favorable effect of silicate on zinc corrosion in KOH without potassium zincate was anticipated from the literature where it has been mentioned that silicates act as inhibitors to the aqueous oxidation of zinc [7, 8] and to the HER [10, 11]. However, it should be mentioned that zinc oxidation is not a rate determining step in the gassing mechanism which is largely determined by the HER [1–4]. On the other hand, the negligible influence of silicate in the presence of zincate was not anticipated. In the presence of zincate the attenuated effect of dissolved silicates on gassing rates may therefore be explained by (i) silicate-zincate interactions and a corresponding variation in the zincate activity, (ii) a change in the corrosion behaviour of zinc, (iii) a change in the HER kinetics on zinc, or (iv) a gassing inhibition which is largely dominated by the zincate effect.

3.3. *Electrochemical measurements*

3.3.1. *Rest potentials.*

Any interaction between silicate and zincate should be associated with a change in the free enthalpy or activity of zincate in alkaline solutions. The zincate activities may be measured by the equilibrium potential of the $Zn/Zn(OH)_4^{2-}$ electrode [15]. This potential is closely estimated by the experimental rest potentials of zinc with respect to Hg/HgO in alkaline solutions, since the exchange current density of this electrochemical couple is high [16].

The calculated equilibrium potential of zinc is − 1367 mV (against Hg/HgO) in 36 wt % (8.7 M) KOH, 2 wt % (0.34 M) ZnO at 25° C, estimating activity coefficients of zincate and KOH to be 57 and 7.5, respectively [16], and assuming negligible liquid-junction potentials between (36 wt % KOH + 2 wt % ZnO + silicate) solution and the 36 wt % KOH reference electrode [17] in the corresponding cell. Thus,

$$Hg\,|\,HgO\,|\,KOH(a_1)\,\|\,KOH(a_2),\ \text{zincate, silicate}\,|\,Zn \qquad (2)$$

where $a_1 = a_2$.

The rest potentials were found to be independent of silicate concentration in alkaline solutions (Table 2) and very close to the calculated values. This means that the formation of zinc silicates, such as metasilicate, $ZnSiO_3$, and dihydroxydisilicate $Zn_2\ (ZnOH)_2Si_2O_7$ does not occur in such solutions and that the silicate effect of gassing rate of zinc powder is not due to silicate–zincate interaction having a free enthalpy larger than 200 J mol^{-1}.

The rest potentials reported here are in agreement with values reported by Hendrikx *et al.* [16] and Boden *et al.* [17], but are more cathodic than those displayed by Sharma [15].

From plots of rest potentials as a function of zincate concentration in various alkaline solutions [15], it is deduced that rest potentials of solutions saturated with respect to ZnO are constant at − 1345 mV (against Hg/HgO), as compared to a value of − 1340 mV reported by Powers [18]. Theoretically, it may be demonstrated that at a given temperature the equilibrium potential of the Zn/zincate with respect to Hg/HgO should be constant in any KOH solution in equilibrium with ZnO and HgO solids [19]. This

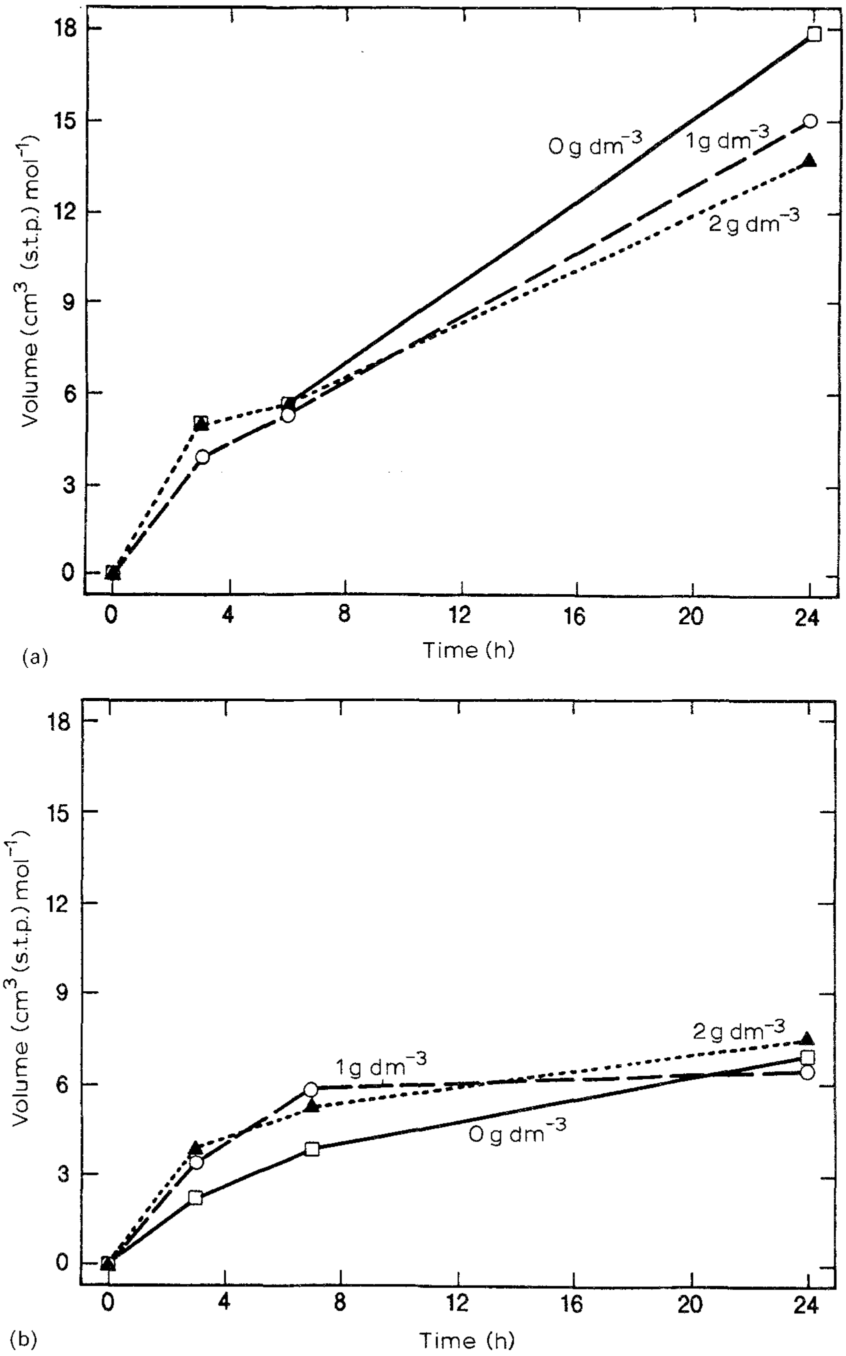

Fig. 1. Gassing volume evolved from zinc powder immersed in (a) 36 wt % KOH and (b) 36 wt % KOH, 2 wt % ZnO at 93° C as a function of time and Si content.

potential (against Hg/HgO) is given by

$$E_r = -1297 - 29.6 \log (a^2_{KOH}/a_{zincate}) \quad \text{at } 25° \text{C} \qquad (3)$$

This means that $(a^2_{KOH}/a_{zincate})$ is constant in ZnO saturated alkaline solutions. From the solubility data of ZnO in alkaline solutions [20] and computation of corresponding activities [16], it is found that $(a^2_{KOH}/a_{zincate}) = 60$, corresponding to a calculated $E_{r(sat)}$ value of -1350 mV. From this ratio, it becomes

Table 1. Gassing rate (cm^3 (s.t.p.) mol^{-1}) of zinc powder in alkaline solution containing silicate and zincate ions

Zincate (wt % ZnO)	*Silicate (g dm^{-3} Si)*		
	0	*1*	*2*
0	16.3	13.6	12.3
2	5.6	5.1	6.1

Table 2. Measured rest potentials (E_r) and cathodic potentials at 1 mA cm^{-2} (against Hg/HgO) of the zinc electrode in 36 wt % KOH–2 wt % ZnO as a function of the silicate concentration at 25° C

Silicate concentration (g dm^{-3} Si)	*E_r (mV)*	*E_1 mA (mV)*
0	−1370	−1380
0.5	−1370	−1379
1.0	−1370	−1379
1.5	−1371	−1380
2.0	−1370	−1376

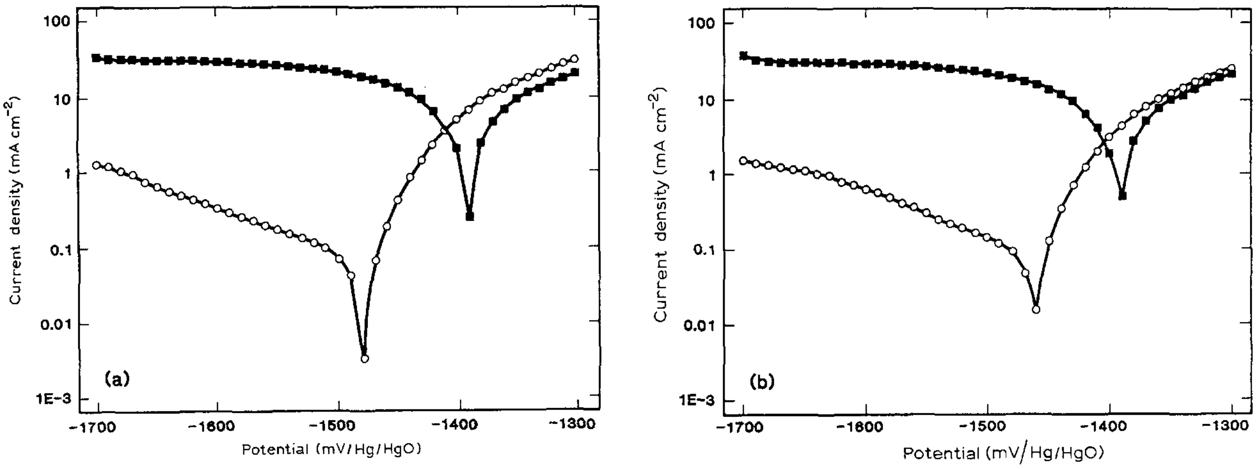

Fig. 2. Polarization curves of electrodeposited zinc powder in 36 wt % KOH with (■) and without (○) zincate at 24° C. The Si content was (a) 0 g dm^{-3} and (b) 2 g dm^{-3}.

easy to compute the activity and the corresponding activity coefficient of zincate in zincate saturated alkaline solutions.

3.3.2. Polarization curves. Cathodic polarization at 1 mA cm^{-2} of zinc electrode immersed in alkaline solutions containing zincate and silicates does not allow the evaluation of the effect of silicates on the HER (Table 1). Indeed, the resulting small polarization for such a poor electrocatalyst as zinc cannot be associated with the HER, so the polarization curves have to be measured.

In the absence of silicate, the polarization curve of electrodeposited zinc powder in 36 wt % KOH containing 2 wt % ZnO (Fig. 2a) is similar to that reported by Mansfeld and Gilman [21]. In the present case, the HER is completely hidden by the high limiting cathodic current (I_{lim}) associated with zincate reduction. Here, $I_{\text{lim}}/C_{\text{ZnO}} = 1.2$, as compared to 0.6 [21]. Without zincate, the polarization curve (Fig. 2a) is similar to that of Baugh *et al.* [22] where anodic polarization is ascribed to zinc dissolution and cathodic polarization is attributed to the HER. Assuming that the equilibrium zincate concentration is approximately 10^{-5} M [21], the zinc limiting current would be 12 μA cm^{-2}, which is much lower than the rate of the HER. Zinc dissolution is slightly decreased by zincate.

In the presence of silicate, the polarization curves with and without 2 wt % zincate (Fig. 2b) remain qualitatively similar to those obtained without silicate. This means that it is not possible to evaluate any change in the HER kinetics when silicate ion is added in alkaline solution containing zincate ion.

From these polarization curves and rest potentials, several parameters have been quantitatively estimated (Table 3). First, the corrosion potential (E_{corr}) is almost independent of silicate concentration but depends on zincate. This shift of the polarization curve by about 80 mV is close to experimental and theoretical shifts reported by Mansfeld and Gilman in 6 M KOH [21]. It is equivalent to 60% of the shift estimated from change in equilibrium potential of zinc/zincate, because the corrosion potential in zincate-free solution is mostly determined by HER-zinc oxidation while in zincate solution it is determined by zincate reduction-zinc oxidation. This indicates that zincate would impact more on the corrosion behaviour than would silicate. Secondly, the equilibrium potential ($E_{\text{Zn/ZnO}}$) becomes less accurate in the absence of zincate, since its behaviour is non-Nernstian when the ZnO concentration is lower than 0.05 wt % [15, 17]. Thirdly, silicate has no significant impact on the limiting current for zinc deposition (I_{lim}) and on the Tafel parameters of the HER.

The Tafel parameters for the HER (Table 2) are slightly different than those for a smooth zinc cathode where the Tafel slope is 124 mV dec^{-1} and the exchange current density is 8.5×10^{-7} mA cm^{-2} [23]. This large difference in I_0 is ascribed to the high surface area of the "powder" cathode.

The effect of zincate on the Tafel parameters of the HER cannot be measured. By assuming that this effect is negligible, the corrosion current in various alkaline solutions is estimated by extrapolation from the HER Tafel line to the corrosion potential. Thus, the effect of silicate on corrosion of zinc in zincate-free and zincate alkaline solutions is found to be negligible (Table 3). The small effect of silicate on I_{corr} at 25° C agrees with the similar effect on the grassing rate at 70° C in the presence of zincate (Table 1). But this disagrees with the small favourable effect of silicate in the gassing test of zinc powder in zincate-free alkaline solutions.

In fact, although zinc corrosion is well explained by the mixed potential theory where zinc metal is oxidized to the zincate ion and water is reduced to hydrogen gas [21], polarization curves and corresponding estimations of general corrosion kinetics do not simulate localized corrosion induced during gassing tests [24]. In the absence of zincate, silicate reduces localized corrosion without influencing general anodic oxidation or hydrogen evolution; this suggests some local action on cathodic sites of microcells such as

Table 3. Electrochemical properties of zinc and Tafel parameters of the HER in various alkaline solutions

[*Si*] ($g\,dm^{-3}$)	[*ZnO*] (*wt* %)	$E_{(Zn/ZnO)}$ (*mV*)	E_{corr} (*mV*)	I_{corr} ($mA\,cm^{-2}$)	I_{lim} ($mA\,cm^{-2}$)	*HER**	
						b (*mV*)	I_0 ($mA\,cm^{-2}$)
0	0	−1385	−1479	0.070	–	173	4.7×10^{-5}
0	2	−1368	−1391	0.020	29.8	–	–
2	0	−1391	−1462	0.081	–	157	3.3×10^{-5}
2	2	−1370	−1392	0.029	28.9	–	–

* The reversible potential is −930 mV (against Hg/HgO). The standard error on *b* is 1 and 2 mV dec^{-1} and 0.2×10^{-5} and 0.4×10^{-5} mA cm^{-2} for 0 and 2 g dm^{-3} Si, respectively.

adsorption of silicate or effect of impurities. However, dissolved impurities, such as iron (< 2 p.p.m.), usually induce an activation process [25, 26]. In the presence of zincate, the corrosion kinetics are largely dominated by zincate while the effect of silicate becomes negligible, probably due to the effect of zincate on the adsorption of silicate. This means that silicate ion itself will reduce zinc corrosion in alkaline solution.

4. Conclusion

It has been shown that the effect of silicate ion on the corrosion rate of zinc powder in alkaline solution depends on zincate concentration. The favorable effect of silicate ion itself on the gassing rate vanishes when zincate is dissolved in alkaline solution.

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