EFFECT OF ADDITIVES ON THE CORROSION OF ZINC IN KOH SOLUTION

T KEILY and T J SINCLAIR

Procurement Executive — Ministry of Defence, Royal Armament Research and Development Establishment, Fort Halstead, Sevenoaks, Kent TN 14 7BP (Gt Britain)

Summary

The influence of electrolyte additions on the corrosion of zinc in alkaline solution has been determined using hydrogen evolution and polarization resistance techniques. Corrosion currents calculated from the data provided by the two methods differed in magnitude. The most effective of the inhibitors investigated were combinations of zinc oxide with one of several tetraalkylammonium compounds.

Introduction

The zinc electrode in alkaline solution has been studied in detail over the years, partly because of its extensive use in commercial primary and secondary cells. The attractive features of the Zn/KOH/MO electrochemical system applied to batteries include

(a) the rapid exchange process for the anodic reaction

$$Zn \rightleftharpoons Zn^{2+} + 2e,$$
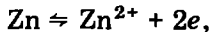
(b) slow, controllable gas evolution kinetics;

(c) relatively high discharge rates without passivation. These are offset by the tendency of the zinc anode to corrode on extended storage. One effective method of minimising oxidation of the anode has been to alloy it, principally with Hg [1, 2], although Al, Cd and Pb [3 - 5] have also been used. Saturation of the electrolyte with the discharge product, ZnO, is also widely used to decrease the corrosion rate of zinc in contact with concentrated KOH solutions. Other electrolyte additives which are reported to lessen zinc corrosion are EDTA [3], PbO, SiO$_2$ [5] and Ba(OH)$_2$ [6].

The use of electrochemical techniques in the estimation of corrosion potential (E_{cor}) and corrosion current (i_{cor}) is founded on the work of Tafel [7] who related overpotential (η) and applied current (i) in the equation

$$\eta = a + b \ln i$$

where a and b are constants. The relationship is valid provided that the reverse reaction is negligible and charge transfer controls the rate determining step. E_{cor} and ι_{cor} are derived from graphical plots of η against ln ι. When the linear parts of the anodic and cathodic curves are extrapolated, the intersection gives the value of E_{cor}. Overpotential and corrosion current are related by

$$\eta = \frac{RT}{\alpha nF} \ln \frac{\iota}{\iota_{cor}}$$

where α, n, F, R and T have their usual significance.

More recently, Stern and Geary [8] established a relationship between the slope of the tangent to the polarization curve at E_{cor} and the corrosion current, based on mixed potential theory Assuming that E_{cor} is remote from the reversible potentials of the redox processes and only charge transfer polarization is important, a corroding electrode system can be represented by

$$\frac{dE}{d\iota} = \frac{b_a b_c}{2.3\iota_{cor}(b_a + b_c)}$$

where b_a and b_c are constants similar to the Tafel parameters a and b The shape of the polarization curve has been analyzed by a number of workers [9 - 11], and other methods of studying corrosion rates — based on steady state [11 - 14] and transient [15 - 22] low polarization data — have been proposed. Several reviews of the range of electrochemical techniques used for the estimation of corrosion potential and corrosion current have been published [15, 20 - 22].

In this work, a range of additives in alkaline solution in contact with compacted pure zinc discs has been investigated. The results obtained from hydrogen evolution and polarization resistance experiments have been compared and evaluated to determine the effectiveness of the additives in corrosion inhibition.

Experimental

The zinc powder used in this work was supplied by ISC Alloys Ltd, Avonmouth, and was found to have 95% of the particles within the range 0.15 - 0 55 mm Slightly smaller, spherical particles were produced by shaking about 2 g of the powder in a vibrator mill for 5 minutes. Chemical analysis of powder samples established the composition as 99.95% Zn with < 0.005% of Fe, Pb, Cd or Hg Compacted zinc discs, measuring 12.8 × 1 5 mm and with effective surface areas of $1.70 \pm 0 05$ cm^2, calculated from surface profile scans, were prepared by compacting 1 g of powder in a small die with a hydraulic press for 2 min at a pressure of 10 MPa. Stock 8.8 ± 0 2 mol dm^{-3} KOH solutions were made by dissolving 'AnalaR' grade KOH

pellets in distilled/deionised water Additives were mixed with portions of stock solution either to saturation or to a maximum concentration of 0.1 mol dm^{-3}, except for ZnO which was always made up to 0 5 mol dm^{-3} strength Solutions were de-aerated by saturating them with H_2 gas and stored for at least 2 weeks in polythene containers before use

Gas evolution experiments were carried out with the specimen electrode discs sealed in glass bulbs fitted with a capillary side arm Approximately 18 cm^3 of solution were introduced into the bulb from a polythene wash bottle through the open capillary. A few drops of coloured kerosene were added to isolate the system from the atmosphere and to facilitate reading of the solution level in the side arm. The glass vessels were suspended in a water bath maintained at 298 ± 1 K and readings were taken twice daily with the aid of a cathetometer. A reference glass vessel containing a typical volume of gas under water, monitored fluctuations in the solution level with changing temperature and barometric pressure.

Electrochemical measurements were carried out with a Wenking model ST72 potentiostat and ancillary PPT70 voltmeter, SMP72 scanning potentio-meter and VSG72 voltage scan generator modules Current/time curves were recorded on a Tekman model TE220/2 chart recorder. The electrochemical cell, based on a design described by Powers [23], was machined from PTFE The working electrode lay in the horizontal plane to facilitate visual obser-vation with a Leitz stereomicroscope at 6 3 - 63× magnification. The refer-ence and counter electrodes were calomel and platinum, respectively, and the effective surface areas of the working and counter electrodes were 0 7 and 12 0 cm^2 The volume of solution required to fill the cell was 15 cm^3.

After the cell was assembled and filled with electrolyte solution, it was connected to the potentiostat and usually left for 24 h at the rest potential of the zinc/electrolyte couple (measured with regard to the calomel elec-trode) to reach stability Two types of data were collected firstly, the cur-rent responses to polarizations of ±5 mV imposed on the working electrode, either in discrete 1 mV steps or by continuous variation, were monitored on the chart recorder, and secondly, cyclic sweep voltammograms were obtained between +0 6 and —0.4 volt with respect to the rest potential at a sweep rate of 0 5 mV s^{-1} All measurements were made under quiescent solution condi-tions at room temperature

Results and discussion

Gas evolution experiments

Prior to the main series of gas evolution experiments, the effect of vary-ing the zinc disc preparation procedure on the quantity of gas liberated was investigated. The zinc corrosion rates of (a) unmilled compacted, (b) milled compacted, (c) solid, and (d) commercial amalgamated (Mallory Batteries Ltd, Crawley) discs in 8.8 mol dm^{-3} KOH solution at 298 K are contained in Fig. 1 The amount of gas evolved from the amalgamated (10% w/w) disc
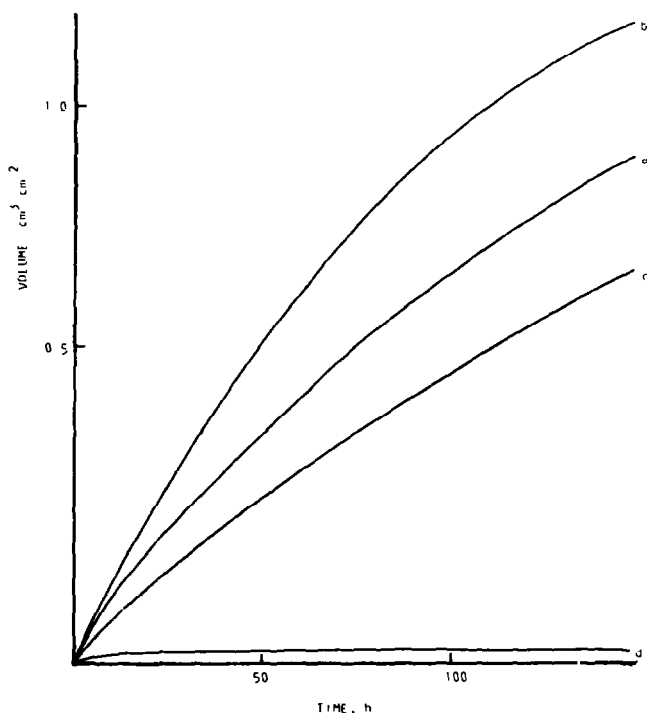
Fig 1 Hydrogen evolved from zinc in 8 8 mol dm^{-3} KOH solution using (a) compacted, (b) milled, compacted, (c) solid, (d) amalgamated discs

was small. Compacting the zinc powder at high pressure gave an essentially solid disc and the total gas volume was reduced by about 40% compared with the porous disc. This agreed reasonably well with the estimated effective surface area increase of a compacted disc over a solid disc of the same dimensions (30%). Milling the powder to a near-spherical particle shape before it was compacted into discs appeared to increase the corrosion rate under these experimental conditions. Unmilled, compacted discs were used in all the subsequent work.

Conversion of the hydrogen evolution data for zinc in 8.8 mol dm^{-3} KOH solution gave a corrosion current of 6 9 μA cm^{-2} (Table 1) This agreed with the result obtained by Mansfield and Gilman [3] for zinc in 6 molar KOH solution (7 μA cm^{-2}) and was reasonably close to the theoretical value of 13 μA cm^{-2} quoted in their paper

A list of the additives studied is contained in Table 1 with the concentration of each in solution. The majority of compounds was available as laboratory reagents but 'Aromox' and 'Ethoduomeen' were proprietary surfactants obtained from Armour Hess Chemicals Ltd. With the exception of the solutions containing quinol (dark brown), 3-aminophenol (light brown), 'Ethoduomeen' and 8-hydroxyquinoline (yellow) the solutions were colourless. Table 1 also contains selected corrosion rate data from the experiments conducted over 150 h

TABLE 1

Effect of additives on the hydrogen evolved from zinc in alkaline solution

Additive	Concentration (mol dm^3)	Mean gas volume after 100 h (cm^3 cm^{-2} 10^{-2})	Mean gas evolution rate at 100 h (cm^3 cm^{-2} h^{-1} × 10^{-2})	Corrosion* current (µA cm^{-2})
—	—	56 ± 5	0 47 ± 0 04	6 9
Zinc oxide	0 5	29 ± 3	0 33 ± 0 03	3 9
Barium hydroxide	<0 5	42 ± 5	0 38 ± 0 05	—
Zinc oxide/barium hydroxide	0 5/<0 05	15 ± 4	0 08 ± 0 002	—
Tetraethylammonium bromide	0 1	49	0 35	—
Zinc oxide/tetraethylammonium bromide	0 5/0 1	5	0 05	—
Tetraethylammonium hydroxide	0 07	45 ± 10	0 30 ± 0 05	—
Tetrapropylammonium hydroxide	0 1	32 ± 5	0 25 ± 0 04	—
Zinc oxide/tetrapropylammonium hydroxide	0 5/0 1	6 ± 1	0 05 ± 0 01	—
Tetrabutylammonium hydroxide	<0 05	24 ± 3	0 22 ± 0 03	3 3
Zinc oxide/tetrabutylammonium hydroxide	0 5/<0 05	4 ± 0 5	0 03 ± 0 005	1 2
Tetraphenylarsonium chloride	0 01	67	0 66	—
Zinc oxide/tetraphenylarsonium chloride	0 5/0 01	30	0 30	—
Silicone	0 05	30 ± 5	0 28 ± 0 05	—
Glycerol	0 1	55	0 53	—
Pyridine	0 1	56 ± 10	0 45 ± 0 1	—
Qunuol	0 1	30 ± 10	0 36 ± 0 1	—
8-Hydroxyquinoline	<0 05	52	0 53	—
Hexamine	<0 01	44	0 45	—
Triethanolamine	0 01	75	0 73	—
3-Aminophenol	0 1	~90†	~0 90†	—
Dibenzylamine	<0 05	~90†	~0 90†	—
'Aromox'	<0 05	~100†	~1 00†	—
'Ethoduomeen'	<0 05	~100†	~1 00†	—

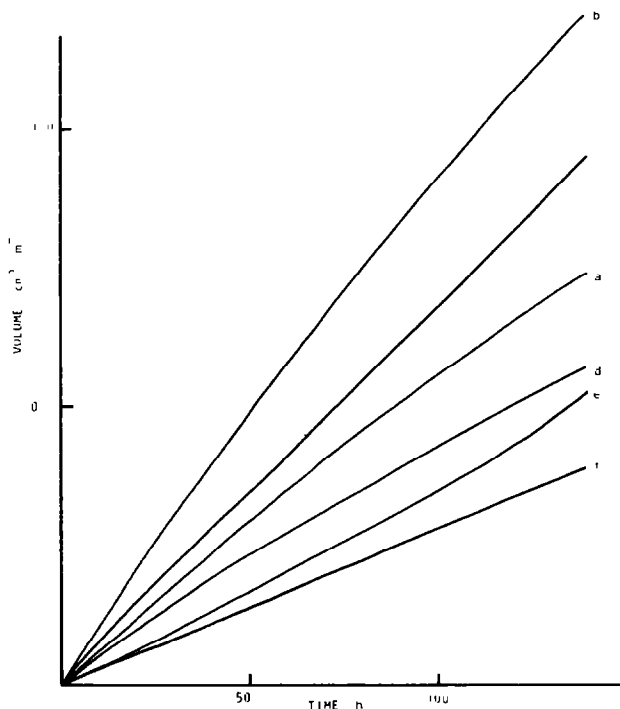*After 24 hours
†Extrapolated from 50 hours

Fig 2 Hydrogen evolved from zinc in 8 8 mol dm^{-3} KOH solution containing (a) no additives, (b) triethanolamine, (c) tetraphenylarsonium chloride, (d) barium hydroxide, (e) zinc oxide, (f) tetrabutylammonium hydroxide

Rapid corrosion, as defined by a hydrogen evolution rate twice that of the control solution, was found with alkaline solutions containing 3-amino-phenol, dibenzylamine, 'Aromox' and 'Ethoduomeen' after about 50 h The experiments based on these additives were discontinued at this stage The effect of other single additives in alkaline solution on the volume of hydrogen evolved from zinc is shown in Fig 2. Zinc oxide, barium hydroxide and additives based on quaternary ammonium compounds were found to inhibit zinc corrosion in 8 8 mol dm^{-3} KOH solution, although the improvement achieved was less effective than amalgamation of the metal surface

The curves obtained from solutions containing zinc oxide provided two pieces of information firstly, the volume of hydrogen evolved was less with zinc oxide (Fig. 2(e)) than without (Fig 2(a)), in agreement with the sub-stantial independent evidence available [2, 24]. The main reasons which have been offered in the literature to explain this observation are the reduced activity of water [24] and the limited dissolution of oxidation pro-duct [25] in zinc oxide saturated solution. Secondly, the rate of hydrogen evolution was found to increase with time (Fig. 4(d)), in conflict with most published data The reason for this has not been established although differ-ing conditions (e g , changes in solution composition with immersion time, ZnO and KOH concentration, amalgamation and the purity and physical form of zinc used) will affect the corrosion data to some extent.

Although the effect of the tetraethylammonium ion on the corrosion of zinc in alkaline solution was found to be small in our experiments, tetrapropylammonium and tetrabutylammonium ions gave increasing inhibition of the corrosion reaction (Table 1) This trend suggests that steric factors, in this case the alkyl group chain length, are important in the mechanism of inhibition. Tetraphenylarsonium ion (with chloride counter-ion) was found to increase the corrosion reaction of zinc in respect of alkaline solution without additives. Mansfield and Gilman [3] reported that 10^{-3} molar tetraethylammonium perchlorate in 6 molar KOH solution increased the quantity of hydrogen evolved from zinc Although some inorganic anions (chloride, bromide) appear to have little effect on the corrosion of zinc in alkaline solution [3] as supported by the similar results obtained with tetraethylammonium hydroxide and tetraethylammonium bromide (Table 1), other anions such as iodide [1] and sulphide [3] increase the hydrogen discharge rate at metal surfaces Thus, the perchlorate ion may have influenced the result in Mansfield and Gilman's experiment. Combination of quaternary ammonium compound additions with 0.5 molar zinc oxide led to an appreciable decrease in the corrosion of zinc in alkaline solution (Fig 3) and markedly altered the rate curve (Fig 4(1)) This corrosion was one-tenth that of zinc in 8.8 mol
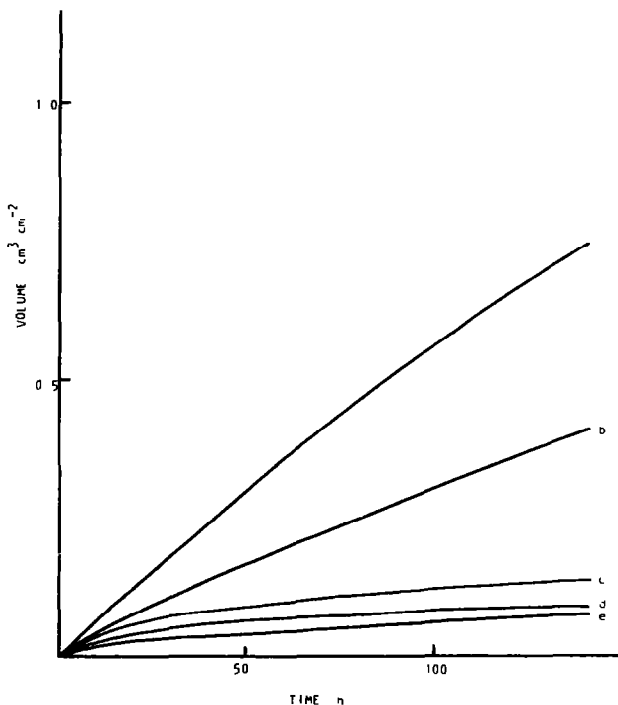

Fig 3 Hydrogen evolved from zinc in 8 8 mol dm^{-3} KOH solution containing (a) no additives, (b) zinc oxide/tetraphenylarsonium chloride, (c) zinc oxide/barium hydroxide, (d) zinc oxide/tetrabutylammonium hydroxide, (e) zinc oxide/tetraethylammonium hydroxide
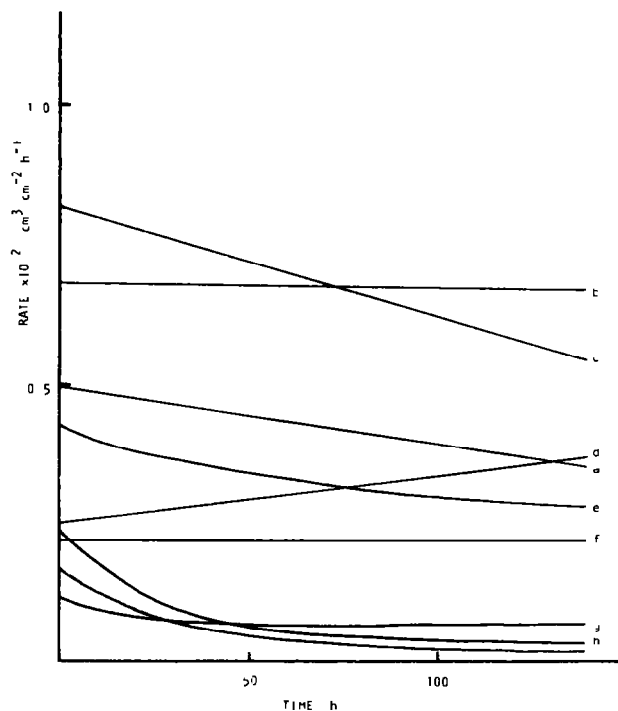
Fig 4 Change in rate of hydrogen evolved from zinc in 8 8 mol dm^{-3} KOH solution containing (a) no additives, (b) tetraphenylarsonium chloride, (c) triethanolamine, (d) zinc oxide, (e) barium hydroxide, (f) tetrabutylammonium hydroxide, (g) zinc oxide/tetraethylammonium hydroxide, (h) zinc oxide/barium hydroxide, (i) zinc oxide/tetrabutylammonium hydroxide

dm^{-3} KOH solution with no additives, but was still twice that observed for amalgamated zinc. Ramasamy *et al.* [1] studied the effects of tetramethylammonium hydroxide on the corrosion of zinc in alkaline solution containing zinc oxide and reported an increase in the hydrogen evolved. However, the quarternary ammonium hydroxide was added to the electrode mix which also included amalgamated zinc, mercuric oxide and a filler material.

Several supporting experiments were undertaken in this work to check the influence of changes in atmospheric pressure, ageing of the alkaline solutions, and attack of the glass vessels by the KOH solution. Analysis of solutions before and after experiments gave concentrations of elemental silicon of 10^{-3} and 3×10^{-3} mol dm^{-3} Cenek and Kouril [5] have reviewed the literature concerning silicon dioxide additions to alkaline solutions. At concentrations of about 10^{-2} molar, the corrosion of zinc was diminished. It was concluded that changes in concentration of silicon over the period of the experiments in this work were not likely to affect the results significantly. In two additional experiments, 8.8 mol dm^{-3} KOH solutions which had been stored in polythene for more than a year gave hydrogen evolution rates approximately 50% greater than the mean value quoted in Table 1 for fresh

solutions Barometric pressure and the level of a control cell containing only distilled water were monitored during another series of experiments. No significant relationship between the two factors was detected. The extreme readings taken from the control cell over the period of the experiment were equivalent to a volume of 0 01 cm^3, a value within the standard deviations calculated from the experimental data (Table 1). Finally, the analysed zinc ion content in one solution (0.22 $\times$ 10^{-3} mole) compared reasonably well with that calculated from the hydrogen evolved during the experiment (0.19 $\times$ 10^{-3} mole) as predicted from the stoichiometry of the reaction

$$Zn + 2H_2O + 2OH^- \longrightarrow Zn(OH)_4^{2-} + H_2$$
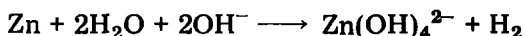
The large variations which occurred from experiment to experiment are shown by the standard deviations in Table 1. The curves in Figs 1 - 4 are average plots from between two and six experiments.

These hydrogen evolution experiments have shown that relatively small amounts (typically 0 05 mol dm^{-3}) of quaternary ammonium hydroxides added to 8 8 mol dm^{-3} KOH solution containing 0.5 mol dm^{-3} zinc oxide reduce the corrosion rate of pure zinc. In the following part of this paper correlation was sought between these results and those obtained using instrumental techniques.

Electrochemical experiments

The potentiostat and its associated equipment were used in conjunction with the electrochemical cell to investigate compacted zinc discs in 8 8 mol dm^{-3} KOH solution by (a) perturbing the rest potential of the couple by several millivolts and monitoring the resulting currents, and (b) recording cyclic sweep voltammograms over a wider potential range. The results obtained from these two methods are discussed separately since the former relates to corrosion current estimation and the latter to simulated electrode discharge/charge cycling.

(a) Initially, polarization resistance experiments were carried out to establish the sensitivity of the system to immersion time and to the type of scanning used. Typical results are shown in Fig. 5. The potentiodynamic curves were obtained directly with 'a' and 'b' recorded after electrode immersion times of 1 and 24 hours, respectively. The corrosion rate of zinc in 8.8 mol dm^{-3} KOH solution (related to the tangent to the curve at the origin) decreased with increasing immersion time, in agreement with the decreasing hydrogen evolution rate in Fig. 4. Although the dependence of mild steel and iron corrosion on immersion time in dilute acid solution has been reported using polarization resistance techniques [7, 12], no comparable data for zinc in alkaline solution were found in the literature.

The potentiostatic scanning experiments generated sets of exponential decay curves, similar to the schematic sketch overleaf, from which two measurements were taken. A 1 mV step imposed on the rest potential (a) of the electrode caused a transient maximum current (b) which fell to a steady value (c) after about 10 min These transient and steady state measurements,
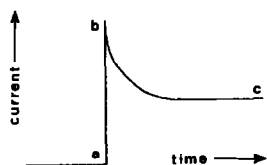
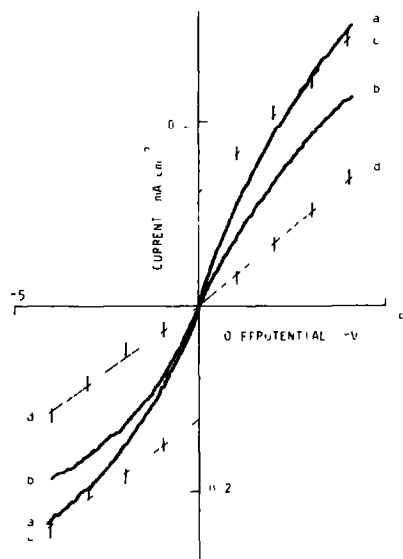taken after 24 hours immersion, are shown in Fig. 5 as 'c' and 'd' for ±4 mV in 1 mV steps.

Fig 5 Polarization resistance curves for zinc in 8 8 mol dm^{-3} KOH solution using (a, b) potentiodynamic scanning after 1 and 24 h immersion, (c, d) transient and steady state potentiostatic scanning after 24 h immersion

The slopes of the transient potentiostatic curves were close to that of the steady state curve, supporting the use of transient methods such as those proposed by Jones and Green [17] and Walter [18], and intersected the current axis at approximately ±0.12 mA cm^{-2}.

As expected, the potentiodynamic curve recorded after 24 h immersion lay between the transient and steady state potentiostatic curves but was distorted by mass transfer effects. Holding the potential for about 15 min at the end of the potentiodynamic sweeps resulted in a fall in the current to a value similar to the one obtained under steady state potentiostatic conditions at the same potential

Although E_{cor} is readily measured, manipulation of the current–voltage data is required before meaningful i_{cor} values are obtained. In the original treatment of polarization resistance data by Stern and Geary [8], it was assumed that E_{cor} was not close to either of the redox reversible potentials

For zinc in concentrated alkaline solution the metal dissolution process dominates the potential Mansfield and Oldham [26] introduced into the Stern–Geary relationship, written as

$$\frac{\mathrm{d}\iota}{\mathrm{d}E} = \iota_{\mathrm{cor}} \left(\frac{1}{b_{\mathrm{a}}} + \frac{1}{b_{\mathrm{c}}} \right),$$

the additional term

$$\frac{nF\iota_{01}}{RT}$$

where ι_{01} is the exchange current density of the zinc dissolution reaction and n, F, R and T have their usual meanings. Since ι_{01} for the $Zn/Zn(OH)_4^{2-}$ couple has been estimated to be 100 mA cm^{-2} [27], the additional term becomes much greater than the slope values from the current–voltage curves (7 8 and 0.031 mA cm^{-2} mV^{-1}, respectively) The observation that polarization curves are independent of large values of ι_{01} [3] means that we can omit the additional term containing the exchange current density for zinc on the grounds that the relative trends in the corrosion data are made clearer. The b_{a} and b_{c} values, related to the Tafel slopes of the anodic and cathodic reactions and calculated by Booker and Manohar [28], have been used to compute relative values of ι_{cor} from the Stern–Geary relationship. Our value of 0 36 mA cm^{-2} (Table 2) compares with the mean value of 0 37 mA cm^{-2} from the anodic and cathodic slopes from zinc in 6 molar KOH solution [28].

The tendency for the corrosion potential to shift in an anodic ('noble') direction when inhibiting substances like zinc oxide and tetrabutylammonium hydroxide were added to alkaline solutions (Table 2) agrees with the results of Mansfield and Gilman [3]. A change of +61 mV was found on adding 0.25 molar ZnO to 6 molar KOH solution compared with +50 mV for 0 5 molar ZnO in 8.8 mol dm^{-3} KOH solution. This effect can be explained by a lowering in the activity of water, thereby increasing the hydrogen overpotential [24], and by suppression of the zinc dissolution reaction [25].

It was clearly demonstrated from the hydrogen evolution data that additions of zinc oxide and tetrabutylammonium hydroxide, separately and together, to 8.8 mol dm^{-3} KOH solution significantly reduced the corrosion rate of zinc in alkaline medium (Table 1). The corresponding corrosion current density (ι_{cor}) values calculated from potentiodynamic polarization resistance data (Fig. 6, Table 2) were found to be very much greater, and the trend to lower corrosion rates with the additives less well defined. The differences in magnitude between the two sets of ι_{cor} values was partly due to the use of the potentiodynamic scanning mode which, as seen from Table 2, gave results about 3 times that of the steady state potentiostatic mode. It has been pointed out that the Stern–Geary equation is limited by a number of assumptions and approximations. One reason for the poor correlation be-

TABLE 2

Effect of additives on corrosion potentials and corrosion currents of zinc in alkaline solution

| Electrolyte additive	Immersion time (h)	Scanning mode	Corrosion* potential (V)	$\text{mean}\left(\dfrac{di}{dE}\right)_{E \to 0}$ (mA cm^{-2} mV^{-1})	Mean corrosion current (mA cm^{-2})
—	24	steady state potentiostatic	−1 625	0 031	0 36
—	24	transient potentiostatic	−1 625	0 035	0 41
—	1	potentiodynamic	−1 625	0 145	1 70
—	24	potentiodynamic	−1 625	0 085	1 00
Zinc oxide	24	potentiodynamic	−1 575	0 075	0 88
Tetrabutylammonium hydroxide	24	potentiodynamic	−1 600	0 032	0 36
Zinc oxide/tetrabutyl-ammonium hydroxide	24	potentiodynamic	−1 570	0 039	0 46

*Wrt calomel reference electrode
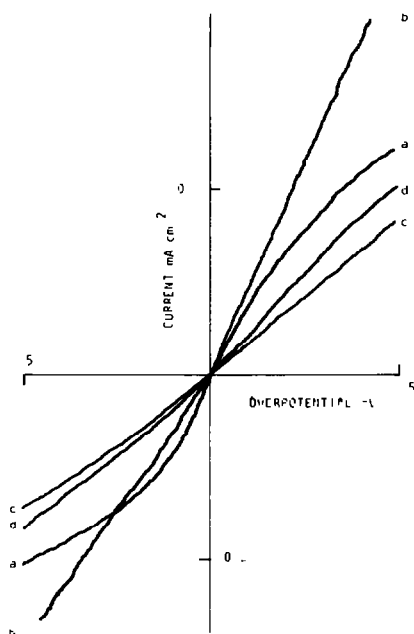
Fig 6 Polarization resistance curves for zinc in 8 8 mol dm^{-3} KOH solution containing (a) no additives, (b) zinc oxide, (c) tetrabutylammonium hydroxide, (d) zinc oxide/tetrabutylammonium hydroxide

tween the corrosion currents measured by the hydrogen evolution and the polarization resistance technique is the breakdown of the Stern–Geary treatment in multiple reaction systems such as alkaline solutions containing substantial quantities of zinc oxide. Thus, it is apparent from Tables 1 and 2 that there is no relation between the i_{cor} values for solutions without, and with, zinc oxide. However, comparison of the corrosion currents for these solutions with solutions containing tetrabutylammonium hydroxide is in reasonable agreement for the two methods.

(b) Battery discharge may be simulated in the laboratory by controlling the potential of an electrode and observing the resulting current. This potentiostatic technique has been applied to investigations of the zinc electrode in alkaline solutions containing additives.

The cyclic sweep voltammograms shown in Fig. 7 are representative of the profile for the zinc electrode in 8.8 mol dm^{-3} KOH solution when a sweep was carried out from the rest potential (a) first in the anodic direction to +0.6 V, then cathodically through the rest potential to —0.4 V and finally back to the starting potential. The voltammogram obtained from solutions without additives increased in a linear manner until, at an overpotential of +0.26 V, a maximum current was reached. The electrode surface had darkened (b) due to the formation of oxidation product at the electrode/electrolyte interface. At more anodic overpotentials the current fell as the passivating layer blocked the electrode surface (c). On the reverse part of the
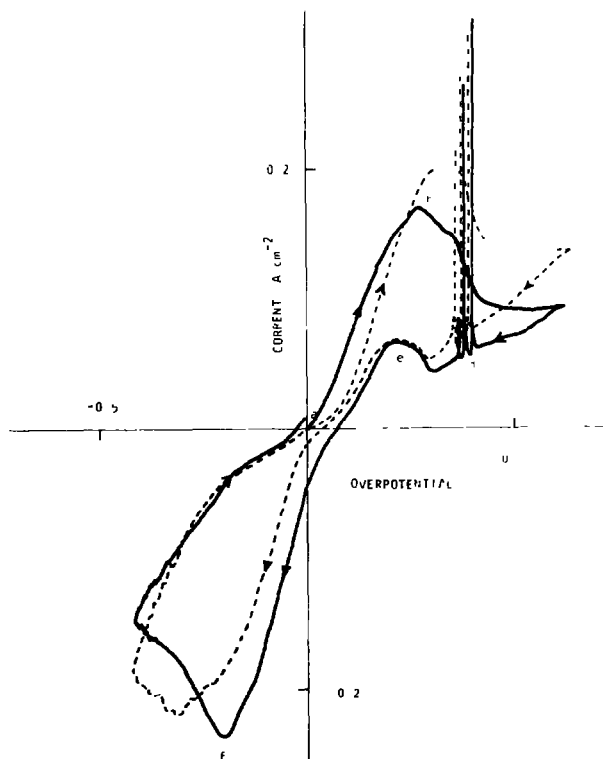
Fig 7 Cyclic sweep voltammograms of zinc in 8 8 mol dm^{-3} KOH solution containing no additives (——) and tetrabutylammonium hydroxide (– – –)

anodic sweep, rapid current fluctuations were noted between +0.38 and +0.34 V (d) attributed to structural/stoichiometric changes in the oxide layer Transient shadows traversed the surface at these current peaks. After passing through a maximum current value related to the anodic sweep peak but distorted by hysteresis effects (e), a cathodic limiting current was observed at --0.19 V (f) followed by vigorous hydrogen evolution at about - -0.30 V

The voltammograms for 8.8 mol dm^{-3} KOH solutions containing 0 05 molar tetrabutylammonium hydroxide were significantly different from the above case in two respects. Firstly, the initial part of the curve was distinctly curved, in agreement with the lower gradient found in the polarization resistance curves (Fig. 6), and secondly, the maximum current peak on the anodic part of the sweep was shifted to a more positive value by 0.07 V. This anodic shift has been recognised as enobling the metal and consequently lessening corrosion [3] and is in addition to the shift in the position of the rest potential in respect of the calomel reference electrode quoted earlier. A further manifestation of this anodic shift was found on the cathodic part of

the cycle where only small amounts of hydrogen were evolved at −0 4 V with tetrabutylammonium hydroxide in solution

The voltammograms recorded with solutions containing zinc oxide and zinc oxide/tetrabutylammonium hydroxide additives were similar to the alkaline solutions without additives and with only tetrabutylammonium hydroxide, respectively The surface changes associated with the transient currents observed between +0.38 and +0.34 V have been reported by Ramanathan [29] in similar studies. It is clear that the 's-skim' effect observed by this worker and the transient shadow have geometries dependent on the type of contact between the zinc electrode and the external conductor, and also on whether the solution is agitated or not The 's-skim' effect was produced because the contact lead was soldered to the centre of the reverse side of the electrode and the solution was stirred. In the experiments described in this work, the electrode was held in contact with a large metal surface under quiescent solution conditions A detailed explanation of this phenomenon is outside the scope of this work, but it is evident that the potential sensitive changes in the surface film are associated with the oxidation states and structure of the zinc oxide layer.

Conclusions

Gas evolution and electrochemical techniques have been used to establish the influence of electrolyte additions on the corrosion of zinc in alkaline solution. Corrosion currents calculated from the gas evolution results were lower than the uncorrected values obtained from the polarization resistance measurements. The most effective corrosion inhibitors for zinc in 8.8 mol dm^{-3} KOH solution were a combination of zinc oxide with one of several tetra-alkylammonium compounds

Acknowledgements

References

1 N Ramasamy, S Sarangapani, J P Nityanandan, S Venkatisan and V Aravamuthan, *Corr Sci*, *11* (1971) 873
2 L Z Vorkapic, D M Drazic and A R Despic, *J Electrochem Soc*, *121* (1974) 1385
3 F Mansfield and S Gilman, *J Electrochem Soc*, *117* (1970) 1328
4 F Mansfield, *Corr Sci*, *11* (1971) 557
5 M Cenek and O Kouril, *NASA Tech Transl F-14*, 693, 1973

6 C J L Booker and G Manohar, *Tech Note, City London Polytech* , June 1977

7 J Tafel, *Z Phys Chem* , *50* (1905) 641

8 M Stern and A L Geary, *J Electrochem Soc* , *104* (1957) 56

9 K B Oldham and F Mansfield, *Corros (Houston)*, *27* (1971) 434

10 G Palombarını, L Fellonı and G P Cammarota, *Corros (Houston)*, *29* (1973) 245

11 K B Oldham and F Mansfield, *Corros Scı* , *13* (1973) 813

12 F Mansfield, *J Electrochem Soc* , *120* (1973) 515

13 R L LeRoy, *Corros (Houston)*, *29* (1973) 272

14 R L LeRoy, *J Electrochem Soc* , *124* (1977) 1006

15 F G E Beetze and F P A Robınson, *Corros Scı* , *17* (1977) 195

16 S Barnartt, *Electrochım Acta*, *15* (1970) 1313

17 D A Jones and N D Green, *Corros (Houston)*, *22* (1966) 198

18 G W Walter, *Corros Scı* , *16* (1976) 573

19 K G Boto and L F G Wılliams, *J Electrochem Soc* , *124* (1977) 656

20 L M Callow, J A Rıchardson and J L Dawson, *Brıt Corros J* , *11* (1976) 123, 132

21 R L LeRoy, *Corros (Houston)*, *31* (1975) 173

22 G W Walter, *Corros Scı* , *15* (1975) 47

23 R W Powers, *Electrochem Technol* , *5* (1967) 429

24 T P Dırkse and R Tımmer, *J Electrochem Soc* , *116* (1969) 162

25 P Reutschı, *J Electrochem Soc* , *114* (1967) 301

26 F Mansfıeld and K B Oldham, *Corros Scı* , *11* (1971) 878

27 J P G Farr and N A Hampson, *J Electroanal Chem* , *13* (1967) 433

28 C J L Booker and G Manohar, personal communıcatıon

29 L V Ramanatham, *MSc Thesıs*, Cıty London Polytech , March 1975