

Identification of organic corrosion inhibitors suitable for use in rechargeable alkaline zinc batteries

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Abstract

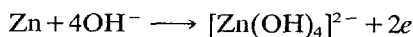
Inhibition of the corrosion of zinc in aqueous alkali by various organic compounds has been tested. The rates of hydrogen evolution due to the metal corrosion in these inhibitor environments have been monitored at 25 °C for a number of days. Except for a few of the tested compounds, all inhibited zinc corrosion to varying degrees. Inhibitor performance under electrochemical conditions has been checked for selected compounds that showed appreciable corrosion inhibition in the previous test. Thus zinc polarization is followed with and without these inhibitor environments under potentiostatic conditions. Corrosion potential and current density have been observed to play vital roles in determining suitable performance of inhibitors under battery situations. Inhibitor environments where zinc has produced nearly the same corrosion current density as in the standard (corrosion current density without an inhibitor) have performed well in battery situations. In such cases improved single and accumulated cycle capacities have been recorded in battery situations.

Keywords: Alkaline zinc batteries; Corrosion inhibitors; Organic inhibitors; Rechargeable batteries

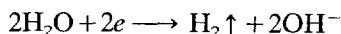
1. Introduction

Zinc is a preferred metal for many battery systems because of its favourable technological and economic features stemming from its high equivalent weight, high half-cell voltage, high energy density, high theoretical capacity density of 820 Ah kg⁻¹ and abundance in many forms.

However, the metal undergoes anodic dissolution with concurrent cathodic evolution of hydrogen in aqueous alkali. The corrosion potential of the metal in a solution of KOH is a mixed potential [1] with the partial oxidation reaction being:



while the partial reduction mechanism is given by:



This corrosion process leads to loss of valuable capacity in alkaline zinc batteries, resulting in reduced

shelf life. The corrosion rate can be measured either by electrodic investigations, for example, galvanostatic measurements of the kinetics of hydrogen evolution, or by volumetric measurement of hydrogen evolution as a function of time, reflecting the rate of corrosion.

Due to the detrimental effect of corrosion on battery performance, numerous attempts have been made over the years employing special additives, both organic and inorganic, adding them to the active mass of the anode mix to check the corrosion. These additives are observed to function through different mechanisms.

Beneficial inorganic inhibitors are found to be mainly oxides of heavy metals that are more noble than zinc [2] and have high hydrogen overvoltages. These metal oxides are believed to function either by forming layers of considerable thickness on the metal surface or by forming films through reaction with the protected substrate [2]. Organic inhibitors are usually considered to inhibit corrosion in metals by their adsorption at the metal surface. This adsorption phenomenon can be caused by π -bond orbital adsorption, electrostatic adsorption or chemisorption [3].

Inhibitors for use in secondary zinc batteries need to provide passivation of the zinc surface when the battery is not in use and equally to prevent passivation

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when the battery is in use, leading to enhanced cycle life.

It must be admitted that these criteria cannot easily be met by many inhibitors. Under electrochemical conditions the inhibition mechanisms as outlined above can be interfered with, the consequences being that some inhibitors may be effective only under cell-equilibrium (no load) condition with the inhibitor influence removed or deteriorating with cycling.

These limitations to the function of inhibitors call for assessment of their performance outside battery situations and in electrochemical environments that simulate real battery situations.

The use of polarization curves as a means of studying the corrosion of metals has been extensively documented [4]. Galvanostatic and potentiostatic designs have been found to work well.

2. Experimental

Three experimental stages have been adopted in this work. Attention has been focused on organic corrosion inhibitors. The criteria used for their selection are their good hydrophobic and nucleophilic properties, which favour the adsorption mechanisms mentioned earlier for corrosion inhibition.

A preliminary corrosion-inhibition test was conducted on selected organic compounds outside battery situations. This was followed by an electrochemical test on suitable inhibitors and finally a confirmatory inhibition test in real battery situations.

2.1. Inhibitor test outside battery situations

The apparatus [5] used consisted of vials and U-shaped capillary tubes fed with mercury. These act as manometers. The vials are joined to capillary tubes with colludin. Eight such set-ups were housed in a cabinet constructed of polystyrene foam, except for the front which was made up of glass. At the background of each set-up was affixed a graduation on the wall for reading the mercury levels. Temperature control was through an electric bulb controlled by relays as hot air was blown from it during operation. The experimental temperature was within 25 ± 1 °C. Tested inhibitors were divided into three groups. Refer to Table 1 for the list of inhibitors.

Anode gels similar to those to be used in battery situations were prepared with the following compositions: zinc (Canada Hg free) powder 62.0%; zinc oxide (Merck) 3.4%; magnesium oxide (Merck) 2.0%, α -cellulose (Fluka) 1.0%; starch (Farinex 267) (Avebe) 1.0%; 12 M potassium hydroxide (Riedel-de Haen) 30.0%; inhibitor. Except for α -diphenylglyoxime, which was tested in 0.1% concentration due to an observed

detrimental effect at higher concentrations, all other inhibitors were applied in 1.0% concentration. The standard composition was the same, except 12 M potassium hydroxide was 31.05% with no inhibitor addition.

5.0 g of anode gel were fed into the vials and covered with 9 M potassium hydroxide to predetermined minimum and maximum levels. Filled vials were connected to airtight capillary tubes. As corrosion occurs with subsequent hydrogen evolution, the mercury levels rise as a function of the rate of corrosion. Levels of rise were monitored at 24 h intervals and the corresponding pressures calculated using a computer program.

2.2. Electrochemical investigations on inhibitors

Compounds that showed appreciable extents of zinc corrosion inhibition were subjected to electrochemical investigations. The set-up here consisted of an electrochemical cell, a laboratory potentiostat (Wenking model LB 81) and a milliammeter. The electrochemical cell consisted of a 2 cm \times 2 cm zinc strip (pickled in dilute HCl, thoroughly cleaned and ground with 600 mesh abrading paper) serving as the working electrode, a platinum counter electrode, a saturated calomel reference electrode (SCE) and 50 cm³ of 1 M potassium hydroxide as electrolyte.

Tested inhibitors were α -diphenylglyoxime 0.1%, 2,4-dinitrophenol 1.0%, polyethylene glycol(200) 1.0%, polyethylene glycol(600) 1.0%, tripropylene glycol 1.0% and diaminepyridine 1.0%. Except for the standard (containing no inhibitor), all electrochemical test cells contained these inhibitors added directly to the electrolyte.

A potential scan was carried out starting at -1400 mV versus SCE (region of active zinc dissolution and hydrogen evolution) and stepped up at approximately 1 mV per second to -1600 mV.

Corresponding values of current were read from a milliammeter. Recordings were made at intervals of 10 mV with the electrolyte stirred at 150 rpm using a magnetic stirrer. The average test temperature was 22 °C. To assess the influence of inhibitor on zinc corrosion, polarization curves were plotted for pure zinc, with and without inhibitor environments.

2.3. Inhibitor test in real battery situations

Standard 'AA-size' cells were constructed in the laboratory with the same anode compositions as outlined earlier. Inhibitors tested here included α -diphenylglyoxime 0.1%, tripropylene glycol 1.0%, diaminepyridine 1.0%, polyethylene glycol(600) and polyethylene glycol(200) 1.0%.

The cathode composition for each cell was: electrolytic manganese dioxide (Kerr-McGee) 83.0%, graphite (Lonza KS 44) 9.5%, acetylene black (I.C. carbon No.

Table 1
Tested inhibitors

Group 1	Group 2	Group 3
α -Diphenylglyoxime	<i>p</i> -Nitrobenzoic acid	Polyethylene glycol(200)
Tripropylene glycol	4-Nitroaniline	Polyethylene glycol(600)
4-Chlorophenyl ethanol	2,4-Dinitrophenol	α -Diphenylglyoxime
<i>o</i> -Phenyl urea	4-Aminonaphthaline sulfonic acid	
2-Isopropylphenol	Diaminepyridine	
4- <i>tert</i> -Butyl phenol	<i>o</i> -Phenylenediamine	
1,2-Diethyl benzene	Benzidine	
Benzyl		

3) 0.5%, PTFE MP1100 (Du Pont) 0.3%, 1 M potassium hydroxide 6.7%.

The open-circuit voltage and circuit current were measured immediately after construction of the cells. The cell cycle-life test was carried out on our computer-controlled test tower. Cells were cycled at a load of 4.2 Ω with 0.9 V cutoff voltage.

The charge condition was 1.7 V constant voltage taper current charge for 15 h. Single-cycle Ah capacities were recorded with accumulated Ah capacities calculated up to 40 cycles.

3. Results

3.1. Inhibitor test outside battery situations

With reference to Figs. 1 to 5, it is obvious that all inhibitors showed varying extents of corrosion inhibition except for 4-*tert*-butyl phenol, 4-nitroaniline and *o*-phenyleneamine, which promoted corrosion. The best inhibitors selected for further tests included: α -diphenylglyoxime, diaminepyridine, polyethylene glycol(600), polyethylene glycol(200), 2,4-dinitrophenol and tripropylene glycol.

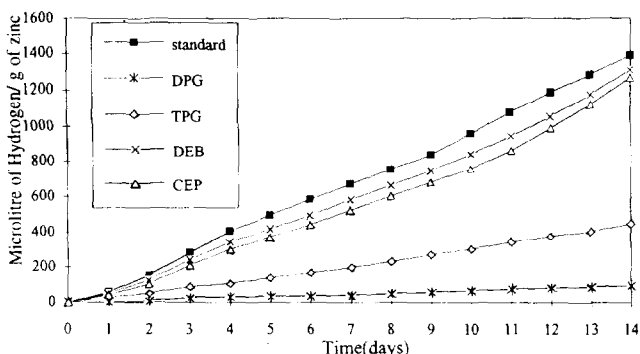


Fig. 1. Effect of group 1 organic inhibitors on zinc corrosion. Index: DPG, α -diphenylglyoxime; TPG, tripropylene glycol; DEB, 1,2-diethylbenzene, and CEP, 4-chlorophenyl ethanol.

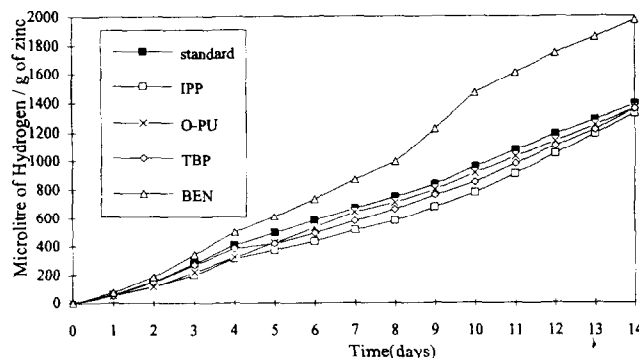


Fig. 2. Effect of group 1 organic inhibitors on zinc corrosion. Index: IPP, 2-isopropylphenol; O-PU, *o*-phenylene urea; TBP, 4-*tert*-butylphenol, and BEN, benzyl.

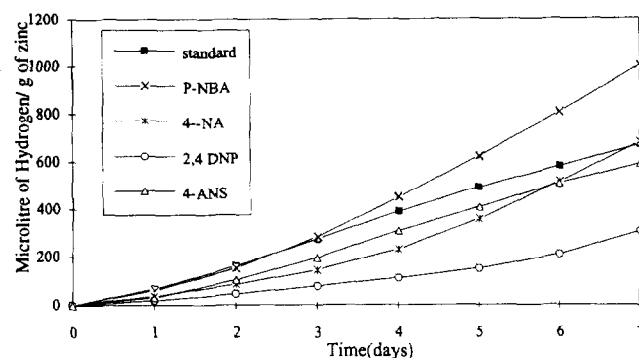


Fig. 3. Effect of group 2 organic inhibitors on zinc corrosion. Index: P-NBA, *p*-nitrobenzoic acid; 4-NA, 4-nitroaniline; 2,4-DNP, 2,4-dinitrophenol, and 4-ANS, 4-aminonaphthaline sulfonic acid.

3.2. Electrochemical investigations

Tafel plots of potential (E) versus $\log I$ (current density) for zinc in selected inhibitor environments produced quite interesting results and these are shown in Figs. 6 to 11.

The criteria for good inhibitor performance were the values of corrosion potential and corrosion current density [4] of zinc inhibitor environments. Results are shown in Table 2, where the anodic region refers to the potential region within which zinc was actively oxidized. Lower corrosion potential values in inhibitor

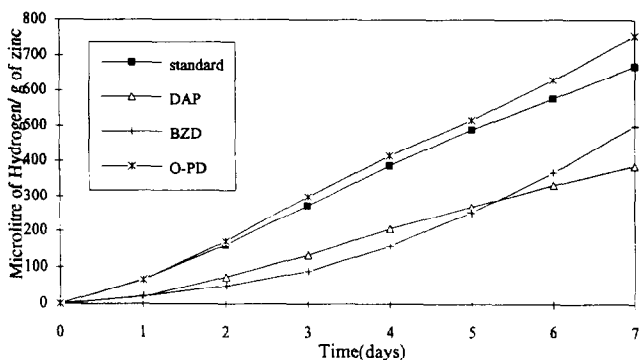


Fig. 4. Effect of group 2 organic inhibitors on zinc corrosion. Index: DAP, diaminepyridine; BZD, benzidine, and O-PD, o-phenylenediamine.

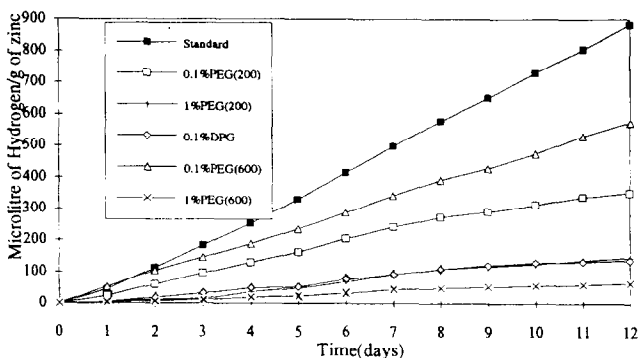


Fig. 5. Effect of group 3 organic inhibitors on zinc corrosion. Index: PEG(200), polyethylene glycol(200); PEG(600) polyethylene glycol(600), and DPG, α -diphenylglyoxime.

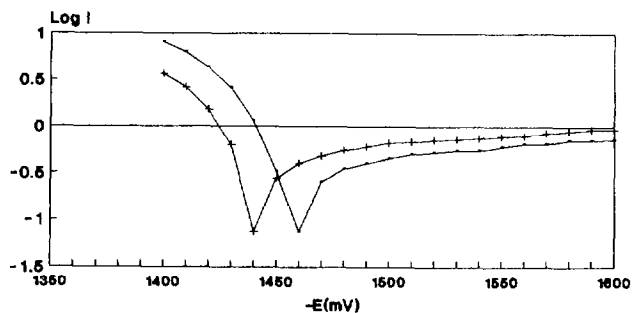


Fig. 6. Polarization curves for zinc showing the corrosion inhibition effect of 1% α -diphenylglyoxime in 1 M KOH (potentials vs. SCE): (●) pure KOH; (+) KOH+0.1% α -diphenylglyoxime.

environments confer some nobility on zinc. The lower current densities in the anodic region imply an inhibition of anodic dissolution of zinc. These properties have been shown by α -diphenylglyoxime, diaminepyridine, 2,4-dinitrophenol, polyethylene glycol(600) and polyethylene (200), as indicated in Table 2.

The high cathodic corrosion current density for 2,4-dinitrophenol seen in Fig. 8 probably arises from a reduction of the inhibitor at such potentials. An obvious colour change from light yellow to dark brown during the potential scan appears to confirm this.

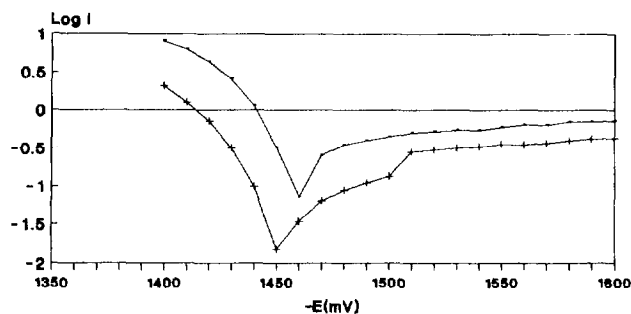


Fig. 7. Polarization curves for zinc showing the corrosion inhibition effect of 1% diaminepyridine in 1 M KOH (potentials vs. SCE): (●) pure KOH; (+) KOH+1% diaminepyridine.

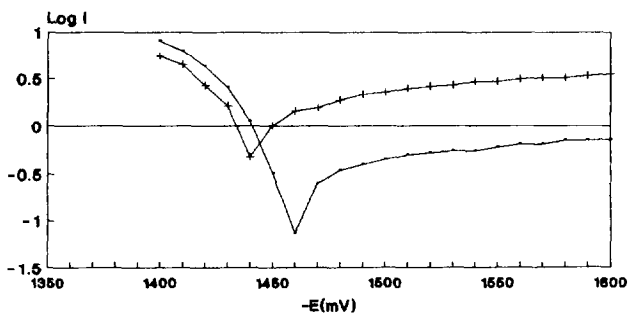


Fig. 8. Polarization curves for zinc showing the corrosion inhibition effect of 1% 2,4-dinitrophenol in 1 M KOH (potentials vs. SCE): (●) pure KOH; (+) KOH+1% 2,4-dinitrophenol.

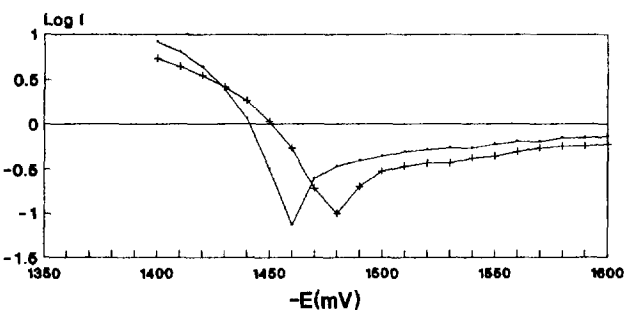


Fig. 9. Polarization curves for zinc showing the corrosion inhibition effect of 1% tripropylene glycol in 1 M KOH (potentials vs. SCE): (●) pure KOH; (+) KOH+1% tripropylene glycol.

3.3. Results of inhibitor test in battery situations

Selected inhibitors for this test included: α -diphenylglyoxime, diaminepyridine, tripropylene glycol, polyethylene glycol(600) and polyethylene glycol(200). 2,4-dinitrophenol was not tested in a battery situations due to its electrochemical instability.

With reference to Figs. 12 and 13, 0.1% α -diphenylglyoxime (higher concentrations when tested produced very low short-circuit currents, causing early passivation and cell failure), 1% polyethylene glycol(600) and 1% diaminepyridine showed better single-cycle life and accumulated capacity than the standard. The output from tripropylene glycol was lower than the standard. There was poor performance from polyethylene gly-

Table 2
Results of electrochemical test

Inhibitor	Corrosion potential (mV)	Corrosion current density (mA cm ⁻²)	Current density in anodic region (in relation to standard)
Standard	-1460	0.075	
0.1% α -Diphenylglyoxime	-1440	0.075	lower
1% Tripropylene glycol	-1480	0.100	not well defined
1% Diaminepyridine	-1450	0.150	lower
1% 2,4-Dinitrophenol	-1440	0.475	slightly lower
1% Polyethylene glycol(600)	-1430	0.075	lower
1% Polyethylene glycol(200)	-1450	0.146	slightly lower

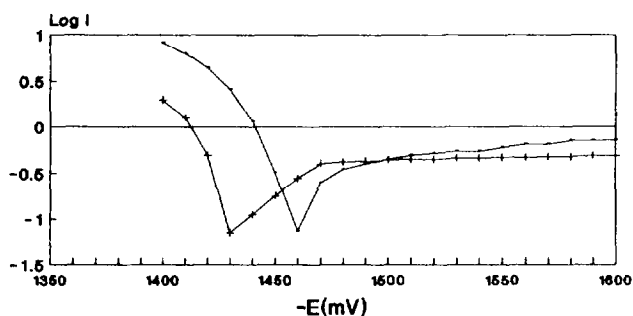


Fig. 10. Polarization curves for zinc showing the corrosion inhibition effect of 1% polyethylene glycol(600) in 1 M KOH (potentials vs. SCE): (●) pure KOH; (+) KOH+1% polyethylene glycol(600).

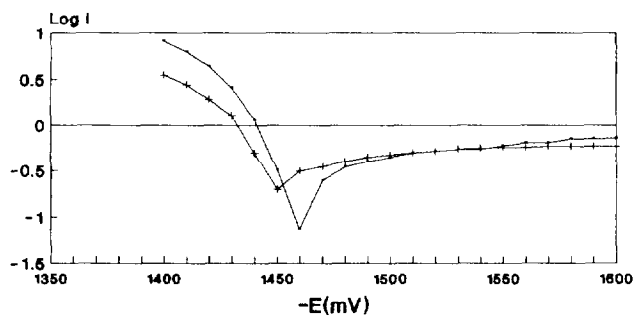


Fig. 11. Polarization curves for zinc showing the corrosion inhibition effect of 1% polyethylene glycol(200) in 1 M KOH (potentials vs. SCE): (●) pure KOH; (+) KOH+1% polyethylene glycol(200).

col(200). For this inhibitor, the level of zinc utilization at the first cycle was as low as 33.78% as against 41.62% for the standard. Cell deterioration with cycle number was quite fast, with the level of zinc utilization dropping to as low as 17.62% at the tenth cycle. Testing of this inhibitor was therefore discontinued.

4. Conclusions

The electrochemical investigations and testing of inhibitors in real cell situations have shown that inhibitors performing well in cell situations have lower corrosion potentials and current densities in the anodic

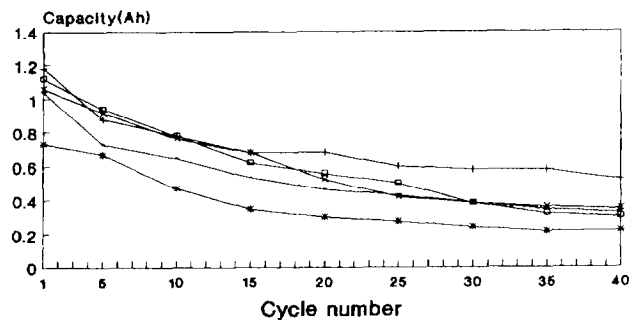


Fig. 12. Single-cycle capacity performance of cells containing organic inhibitors: (●) standard; (+) 0.1% α -diphenylglyoxime; (*) 1% tripropylene glycol; (□) 1% polyethylene glycol(600); (×) 1% diaminepyridine.

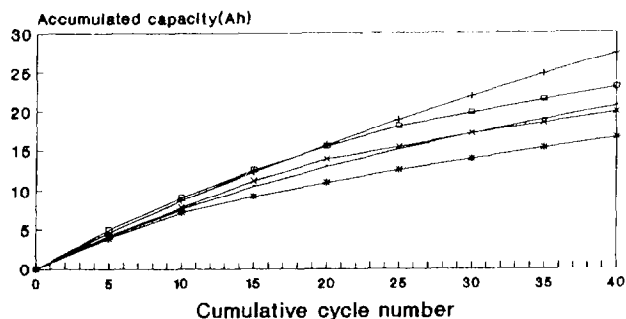


Fig. 13. Accumulated cycle capacity performance of cells containing organic inhibitors: (●) standard; (+) 0.1% α -diphenylglyoxime; (*) 1% tripropylene glycol; (□) 1% polyethylene glycol(600); (×) 1% diaminepyridine.

region than the standard. At the same time they produced corrosion current densities equal to the standard.

α -Diphenylglyoxime and polyethylene glycol(600) performed best in the cell situation and have shown these properties. All other inhibitors falling short of fulfilling these two conditions did not do very well in the cell situation, as can be seen by the results for tripropylene glycol and diaminepyridine.

It is thus obvious that the lowered corrosion potential imparts nobility to the zinc. The fact that the inhibitor also enables zinc to have the same corrosion current density as in the standard makes the zinc equally active

for electrochemical reaction. Organic inhibitors fulfilling these two conditions should perform well in real cell situations.

References

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