

Corrosion kinetics of battery zinc alloys in electrolyte solutions

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Abstract

Corrosion of sheet samples of zinc alloys and zinc of 99.995% purity has been studied in alkaline and weakly acid chloride electrolyte solutions. The samples were subjected to the initial surface treatment, mechanical or chemical, and the rate of their corrosion in electrolyte solutions with no access to oxygen was measured over the span of 30 days by monitoring the volume of evolved hydrogen. Structural properties of the surface layers of zinc samples were studied using X-ray diffraction technique. The corrosion kinetics of zinc in various media is related to zinc alloy composition, state of the sample surface, as well as to the effect of organic inhibiting agents added to the electrolyte solutions. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Corrosion inhibitors; Corrosion kinetics; Electrolyte solutions; Surface structure; Zinc alloys

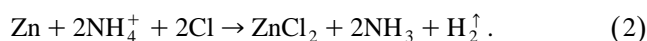
1. Introduction

Zinc and its alloys have attracted increased interest over the years because of their application as electrode materials in alkaline as well as chloride batteries. The interest has been focused on the relationship between material properties and the chemistry involved in dissolution and passivation of zinc electrodes. It has been found that these processes are greatly influenced by the state of the metal surface. Hence, a constant search for new agents and techniques modifying the surface properties of electrode materials and a growing demand for proper raw materials. Two procedures are commonly used to modify the surface properties. One of them consists in using various corrosion inhibiting agents adsorbed specifically on zinc surface, the other in subjecting the metal surface to an initial chemical or mechanical treatment. Despite numerous experimental data there is still a lack of conclusive information on the significance of such factors as the surface purity, homogeneity, smoothness, oxidation, and their role in a particular electrolyte solution. This is often due to the fact that in chloride batteries zinc is used in the form of the massive material, whereas in alkaline batteries it is used as powder. The use of the same form of samples is necessary to study the influence of preparation of the sample surface on the corrosion process in various electrolytes.

It is well known that the dissolution of zinc in an ionogenic medium is associated with gas hydrogen evolution as represented by the reaction:



For aqueous chloride electrolyte solutions in dry cells the reaction is given by:



The evolution of hydrogen associated with zinc corrosion is a spontaneous and unavoidable process conditioned by thermodynamic requirements [1]. In an alkaline medium the standard potential of the zinc electrode $E_o(\text{Zn}/\text{ZnO})$ is -0.420 V, whereas in weakly acid chloride solutions $E_o(\text{Zn}/\text{Zn}^{++})$ it is -0.763 V.

Borstel and Spahrber [2] have found that the rate of zinc corrosion can be slowed down only by the use of a suitable kinetic barrier. This can be achieved by a number of possible means. One of them is to alloy zinc with small concentrations of metals from groups III to V of the periodic table of elements, e.g., In, Ga, Al, Pb, Bi, and combination thereof [3] to modify the rest potential of zinc in electrolyte. Another approach consists in modifying the electrolyte composition with additives of organic inhibitors, that are absorbed on zinc surface at 'kink sites'. These organic additives fall into two classes. The first one involves substances interacting with the metal molecules, the second one comprises compounds interacting with the oxides present on the metal surface [4]. It is obvious that

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Table 1
Characterization of zinc sample

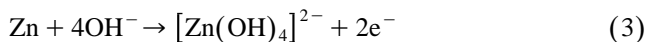
Code	Sample	Characterization of the investigated material			Article
		Main alloy components			
		% Pb	% Cd	% Mn	
1	Zn sheet	(0.0002)	(0.0024)		Zn sheet 99.995%, rolled, Poland
2	ZnPbCd sheet	0.92	0.026		Zn sheet for As battery type, Poland
3	ZnPbCd cans	0.46	0.058		PXE alloy, cans R14, Belgium
4	ZnPbMn cans	0.44	0.002	0.03	PMA alloy, cans R14, Belgium
5	Zinc cans-1	0.0008	0.0007		Zinc cans R12, Poland
6	Zinc cans-2	0.132	0.024		Zinc cans R12, Poland
7	Zinc cans-3	0.83	0.01		Zinc cans R12, Poland

this interaction is affected by contaminations present on the metal surface and as a consequence the rate of zinc corrosion is affected too.

Maja et al. [5], who studied the effect of some organic inhibitors on zinc corrosion in NH_4Cl solutions report that the corrosion process in these solutions is strongly affected by the oxide/hydroxide layers forming on the metal surface in the presence of oxygen. The corrosion is even more affected if oxygen is present in electrolyte of lower pH. Boto and Williams [6,7] have shown, that in electrolytes of pH lower than 5.6, or in the presence of complexing agents no oxides are formed and the reduction of oxygen is controlled by diffusion.

Inhibiting properties of some organic compounds in relation to zinc have been explained in terms of orbital adsorption of Π type bonds, electrostatic adsorption, or chemisorption [8]. Hence, it is obvious that the quality of zinc surface is of great importance to the inhibitor performance.

In alkaline media the kinetics of hydrogen evolution is strongly affected by products of zinc dissolution, which cover the metal surface. The process of their formation was proposed by Dirkse and Hampson [9]. Potential of zinc corrosion in KOH solution is a mixed potential [10] determined by partial oxidation of zinc:



and the reaction of reduction which is given by:



Which of these factors exercises control over the effective process depends on the solution composition, i.e., on the type of additives and the concentration of OH^- ions.

Correlation between corrosion of zinc in electrolyte solution and the storage time of batteries was investigated by Nartey et al. [11].

Irrespective of the pH of the electrolyte solutions the corrosion process is always accompanied by hydrogen evolution. Therefore the study of the kinetics of hydrogen evolution, i.e., measurements of the volume of hydrogen evolved vs. time, constitutes a simple method, which complements other experimental techniques [12] and pro-

vides a useful tool for the optimization of the electrode/electrolyte system in all chemical power sources using zinc as the anode material.

This work is a continuation of our previous study on the corrosion kinetics of zinc alloy powder in alkaline power sources [12,13]. Therein we presented the gasmetric method developed to investigate zinc corrosion and described the set used to measure the volume of the evolved hydrogen. The method makes it possible to minimize the influence of various methodical factors that can affect experimental results. We compared the obtained results with those provided by electrochemical techniques, including alternative current impedance technique [14], as well as with the storage tests results of alkaline batteries [15]. The study confirmed the applicability of the gasmetric method for testing zinc/electrolyte solution systems.

The objective of this work was to investigate how the corrosion kinetics of battery zinc alloys and pure zinc, in alkaline as well as weakly acid chloride electrolytes, is

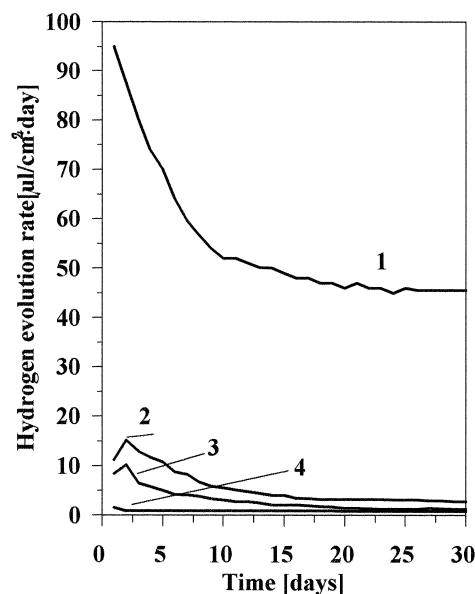


Fig. 1. Corrosion of zinc sheets and cans in 18% ZnCl_2 + 20% NH_4Cl solution. Effect of alloy composition: (1) zinc sheet 99.995%; (2) cans ZnPbCd; (3) cans ZnPbMn; (4) zinc sheet ZnPbCd.

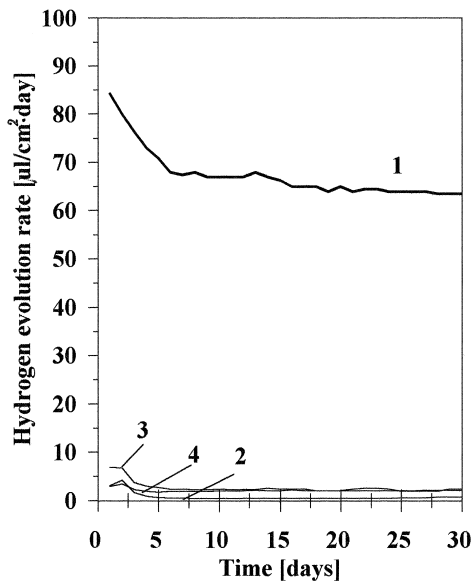


Fig. 2. Corrosion of zinc sheets and cans in 7 M KOH with zincates. Effect of alloy composition: (1) zinc sheet 99.995%; (2) cans ZnPbCd; (3) cans ZnPbMn; (4) zinc sheet ZnPbCd.

influenced by such factors as the alloy composition, state and treatment of the metal surface. The information is of interest both from a practical and a theoretical point of view. The samples under investigation were always of the same form to restrict the number of factors influencing the obtained data.

2. Experimental

The subject of this investigation were zinc alloys used in battery industry of composition given in Table 1 (metal

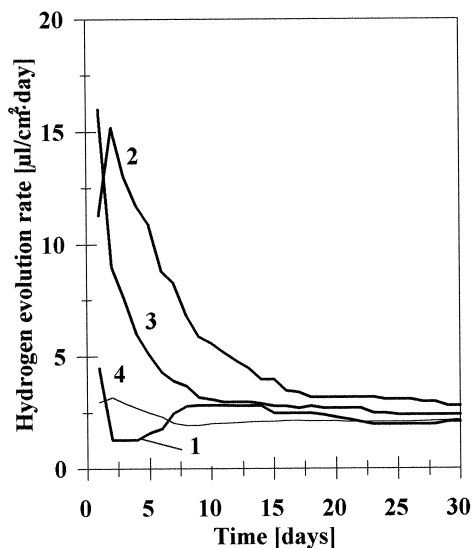


Fig. 3. Corrosion of zinc cans of ZnPbCd alloy. Effect of electrolyte solution: (1) ZnCl_2 ; (2) $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$; (3) NH_4Cl ; (4) KOH with zincates.

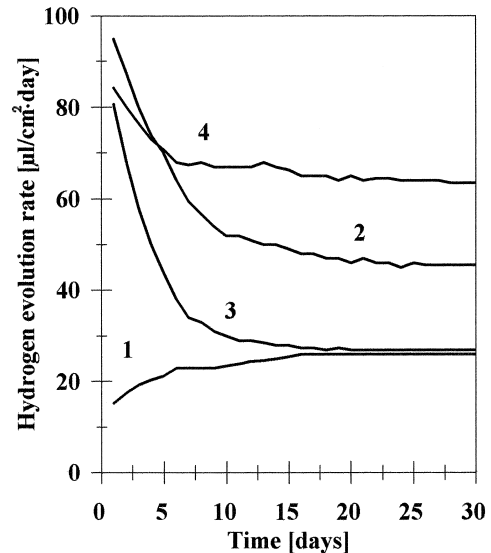


Fig. 4. Corrosion of zinc sheet 99.995%. Effect of electrolyte solution: (1) ZnCl_2 ; (2) $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$; (3) NH_4Cl ; (4) KOH with zincates.

sheets and cans) and zinc sheets of 99.995% purity. All samples were degreased. Some of them were etched in electrolyte solution for 30 days, some mechanically polished, some oxidated in an aqueous medium at 45°C for 24 h.

Several zinc sheets were lead plated in hot solution containing dissolved PbCl_2 . Chosen zinc samples were amalgamated using HgCl_2 in Cl^- solution or in solid HgO suspension in alkaline solution (at 45°C for 20 h). Surface active agents were added to electrolyte only after amalgamation with mercury chloride, or to measuring vessel simultaneously with HgO . Next the samples were placed into measuring vessels filled with electrolyte solution and

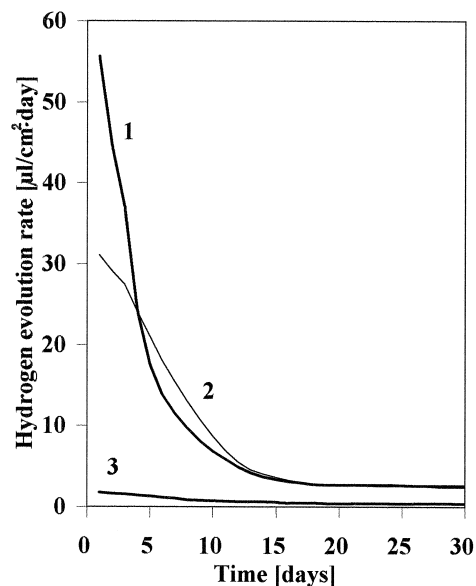


Fig. 5. Corrosion of zinc cans in 18% $\text{ZnCl}_2 + 20\%$ NH_4Cl solution. Effect of lead contents alloy: (1) 0.0008% Pb; (2) 0.13% Pb; (3) 0.83% Pb.

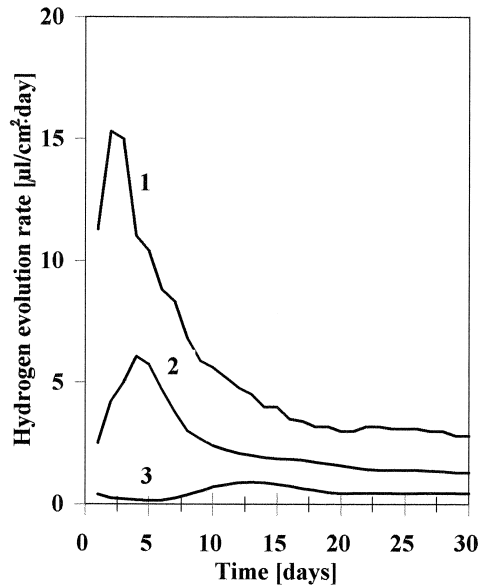
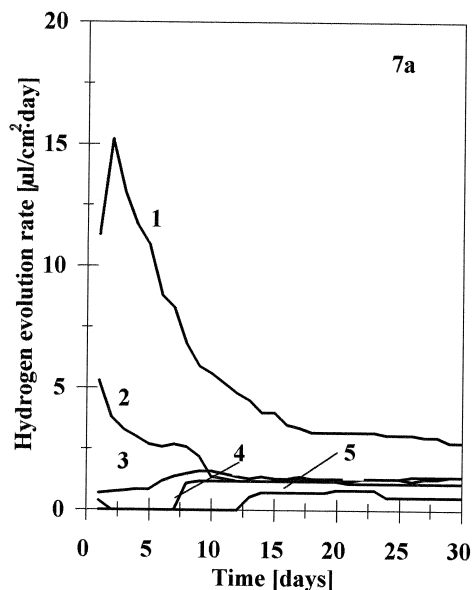


Fig. 6. Corrosion of zinc cans of ZnPbCd alloy in 18% ZnCl_2 + 20% NH_4Cl solution. Effect of surface leading: (1) 0 mg Pb/cm²; (2) 0.075 mg Pb/cm²; (3) 0.15 mg Pb/cm².

the volume of evolved hydrogen, with no oxygen access, was recorded using the method described previously [12].

The following electrolytes were used in the experiment: 7 M KOH, 7 M KOH + 0.6 M ZnO, 30% ZnCl_2 (pH = 3.75), 18% ZnCl_2 + 20% NH_4Cl (pH = 3.88), and 26% NH_4Cl (pH = 4.09). Some of them contained additions of the surface active agents of ethylene–polyglycol type of different molecular mass (PEG 200, PEG 600) either fluoropolietyksyalkohol (FPA), or ether with ethylene oxide bond (EEO) (0.02 g of agent per 20 cm³ of electrolyte).



Samples of metal sheets had always the same surface area of 32 cm² and were investigated in the same volume of electrolyte of 20 cm³. This surface area is by about 50,000 times smaller than that of 1 g of zinc powder.

The experimental results obtained using gasmetric technique are presented graphically in Figs. 1–15.

We also studied the surface structure of the samples using X-ray diffraction methods. Measurements were carried out using the Philips X-ray diffractometer. Based on the analysis of the 8 diffraction lines (hkl: 203, 105, 114, 210, 211, 204, 006, 212) we determined the lattice constants a and c of hexagonal structure zinc alloys. Using the Hall method [16] we evaluated from the 001 reflex values of the internal stress, and from the ratio of integral intensities of lines 100 and 002 the surface texture with respect to theoretical value expected for the polycrystalline structure.

The results of structural investigations of the zinc samples surface are listed in Table 2.

3. Results

3.1. Influence of alloy additives, the state of the metal surface, and organic surfactants on the corrosion kinetic of zinc

The results of comparative studies of multicomponent zinc alloys and pure zinc in the form of massive samples shown in Figs. 1 and 2 reveal a significant difference between the behaviour of pure zinc and the behaviour of zinc alloys. Zinc alloys, however behave quite similarly

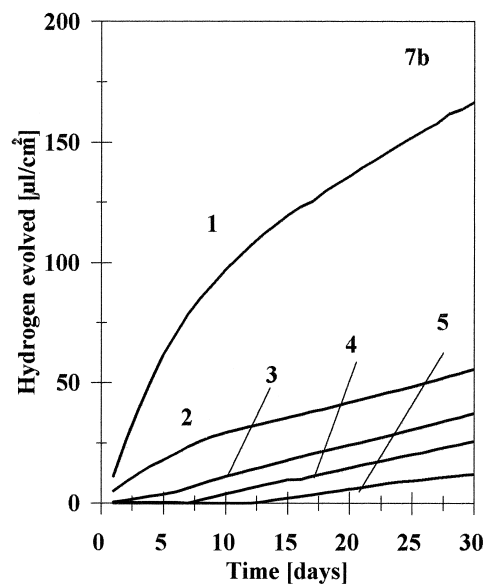


Fig. 7. Corrosion of zinc cans of ZnPbCd alloy in 18% ZnCl_2 + 20% NH_4Cl solution. Effect of surface treatment: (1) untreated surface; (2) polished surface; (3) etched surface; (4) oxidated surface; and (5) oxidated surface after polishing. (a) Show the effect of corrosion as hydrogen evolution rate; (b) monitored by total amount of hydrogen evolved.

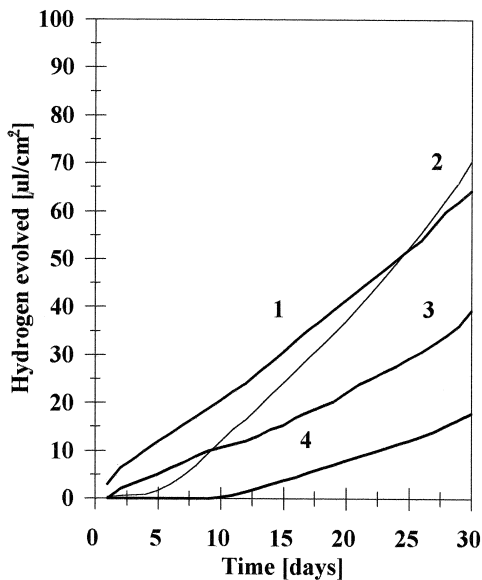


Fig. 8. Corrosion of zinc cans of ZnPbCd alloy in 7 M KOH with zincates monitored by total amount of hydrogen evolved. Effect of surface treatment: (1) untreated surface; (2) oxidated surface; (3) etched surface; (4) polished surface.

regardless of their composition. The evolution of hydrogen associated with corrosion of pure zinc in chloride as well as in alkaline electrolyte is 10 times higher than of zinc alloys. For all samples the first stage of corrosion is associated with a rapid hydrogen evolution, then the rate of the gas evolution gradually decreases to reach in 5 to 20 days a plateau (Figs. 1–6). The value of plateau is of 1–4 $\mu\text{l H}_2/\text{cm}^2$ per day, it is typical for the alloy composition and almost independent of the kind of electrolyte used

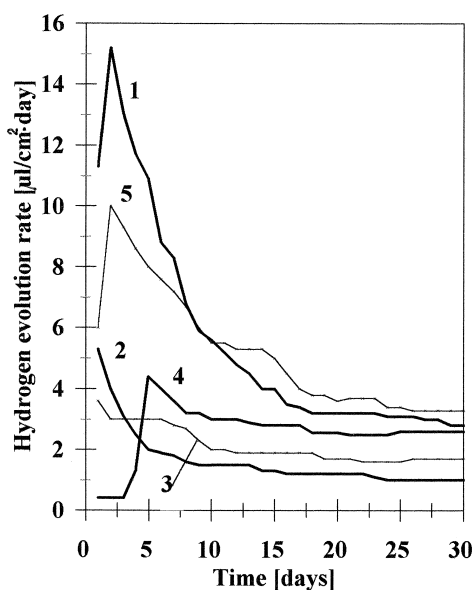


Fig. 9. Corrosion of zinc cans of ZnPbCd alloy in 18% ZnCl_2 + 20% NH_4Cl solution. Effect of surface active agents: (1) without agent; (2) PEG 200; (3) PEG 600; (4) EEO; (5) FPA.

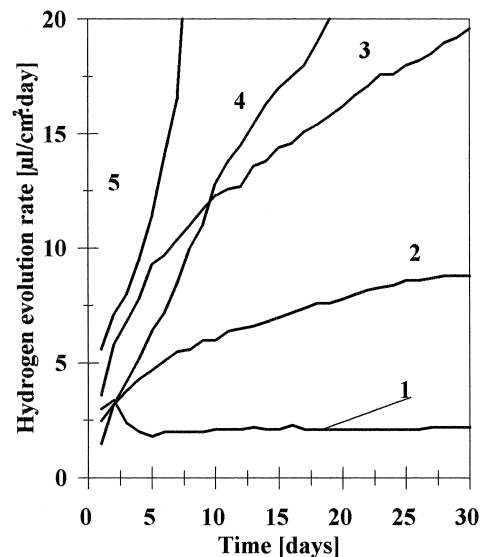


Fig. 10. Corrosion of zinc cans of ZnPbCd alloy in 7 M KOH with zincates. Effect of surface active agents: (1) without agent; (2) PEG 200; (3) FPA; (4) EEO; (5) PEG 600. Surface of zinc without treatment.

(Fig. 3). For pure zinc after 30 days of reaction the rate of hydrogen evolution is of 30–80 $\mu\text{l H}_2/\text{cm}^2$ per day, depending on the electrolyte (Fig. 4). The value of plateau and time needed to reach it depends mainly on the composition of zinc alloy and electrolyte (Figs. 1–4), also on the kind of metal, that covers zinc surface, e.g., Pb (Figs. 5 and 6), Hg (Figs. 12–15).

We have found, that the corrosion process of zinc samples not subjected to the initial surface treatment depends not only on the alloy composition but also on the type and composition of the electrolyte used. For zinc alloy sheets cleaned by polishing, etching in electrolyte,

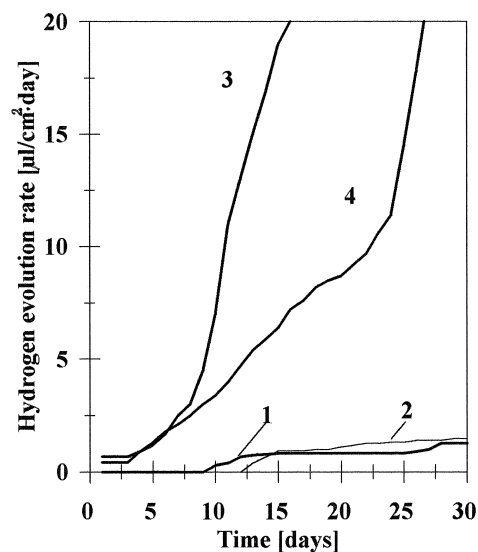


Fig. 11. Corrosion of zinc cans of ZnPbCd alloy, mechanically polished, in 7 M KOH with zincates. Effect of surface active agents: (1) without agent; (2) PEG 200; (3) PEG 600; (4) EEO.

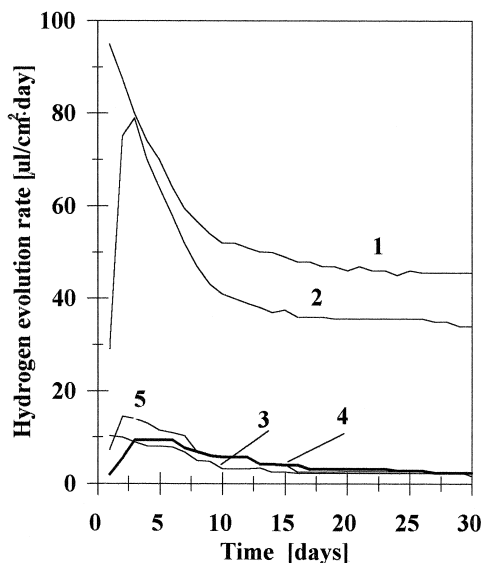


Fig. 12. Corrosion of zinc sheet 99.995% in 18% $\text{ZnCl}_2 + 20\% \text{NH}_4\text{Cl}$ solution. Effect of Hg amalgamation and PEG200 additive: (1) without additives; (2) PEG200; (3) 0.078 mg Hg/cm^2 ; (4) 0.78 mg Hg/cm^2 ; (5) 0.156 mg $\text{Hg}/\text{cm}^2 + \text{PEG200}$.

oxidated (by oxygen from air in presence of distilled water) one observes a substantial lowering of the amount of hydrogen evolved during the first stage of corrosion, and as a result a general decrease of the volume of hydrogen evolved, especially in chloride electrolyte (Fig. 7a,b).

For chloride electrolytes the corrosion is markedly reduced if zinc sheets are initially etched in $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ solution (Fig. 7a,b). In this case the rate of hydrogen evolution corresponding to the plateau is low and independent of the electrolyte composition.

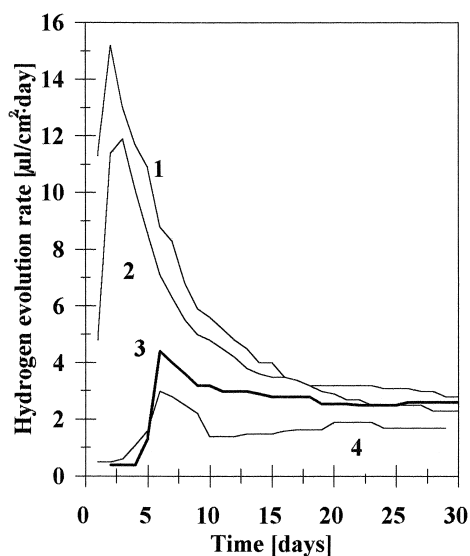


Fig. 13. Corrosion of zinc cans PXE (ZnPbCd) in 18% $\text{ZnCl}_2 + 20\% \text{NH}_4\text{Cl}$ solution. Effect of Hg amalgamation and EEO additive: (1) without additives; (2) 0.079 mg Hg/cm^2 ; (3) EEO; (4) 0.79 mg $\text{Hg}/\text{cm}^2 + \text{EEO}$.

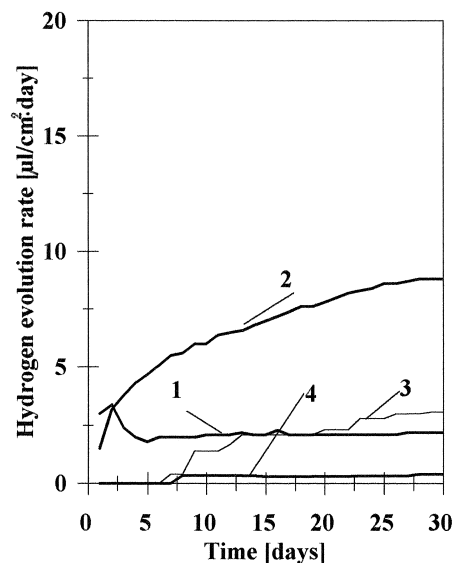


Fig. 14. Corrosion of zinc cans of ZnPbCd alloy in 7 M KOH with zincates. Effect of Hg amalgamation: (1) without additives; (2) PEG 200; (3) 0.076 mg Hg/cm^2 ; (4) 0.076 mg $\text{Hg}/\text{cm}^2 + \text{PEG 200}$.

The X-ray methods show (Table 2) that structural parameters of surface layers, such as texture of zinc grains and coefficients of the second order inner tension of samples subjected to mechanical or chemical treatment differ markedly from those obtained in the case of untreated samples.

The coefficient of the inner tension is closely related to production technology and its values are influenced only to a small degree by additional treatment of some samples. It is obvious that processes of rolling zinc sheets or pressing zinc cans should cause internal stresses and result in large texture of grains on surface layers. Texture coefficients

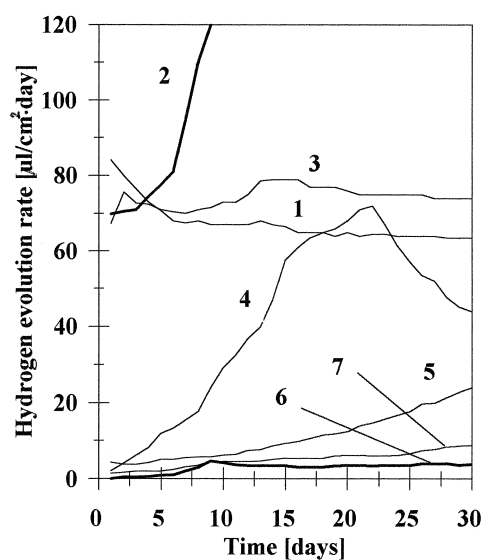


Fig. 15. Corrosion of zinc sheet 99.995% in 7 M KOH with zincates. Effect of Hg amalgamation and PEG 200 or EEO additive: (1) without additives; (2) PEG 200; (3) EEO; (4) 0.078 mg Hg/cm^2 ; (5) 0.156 mg Hg/cm^2 ; (6) 0.468 mg Hg/cm^2 ; (7) 0.156 mg $\text{Hg}/\text{cm}^2 + \text{PEG 200}$.

Table 2
Structural parameters of the surface layers of zinc sheets samples^a

Sample no.	Lattice constants			Tension coefficient according Hall (OOL) ($e = (\Delta c/c) \cdot 10^4$)	Texture coefficient ($T = I_{(002)}/I_{(100)}$)
	a (Å)	c (Å)	c/a		
(1) Untreated	2.6648	4.9474	1.8565	1.41	17.9
(1) Polished	–	–	–	1.43	3.9
(2) Untreated	2.6647	4.9480	1.8568	4.87	9.0
(3) Untreated	2.6650	4.9480	1.8566	1.69	71.4
(3) Polished	–	–	–	1.70	3.1
(3) Chemically etched	2.6645	4.9465	1.8564	1.52	33.3
(3) Etched and polished	2.6643	4.9466	1.8566	3.52	3.6
(4) Untreated	2.6645	4.9433	1.8552	3.47	47.6
(4) Polished	–	–	–	3.98	2.8

^aSample no. as denoted in Table 1.

Lattice constants a and c are determined with an accuracy of ± 0.0002 Å; e —constant of internal stress of the second kind in direction of axis; $I_{(hkl)}$ —integral intensity of hkl X-ray diffraction line.

Theoretical value of T for polycrystalline sample of zinc without texture equals 1.32.

$T = I_{(002)}/I_{(100)}$) for these zinc alloys products amount to significant values whereas for polycrystalline samples of zinc with no texture its value is of 1.32. Usually for zinc powders T ranges from 1.6 to 2.5.

We have found that for zinc alloys sheets of similar chemical composition the value of the texture coefficient correlates with the corrosion resistivity of samples. Zinc alloys of lower T value are more corrosion resistant. It is therefore understandable why both polishing and chemical etching lower the rate of hydrogen evolution and the amount of the gas evolved (Fig. 7). This also explains why the sample No. 2 (Table 1) made of ZnPbCd alloy sheet is more corrosion resistant than other products of the same composition [15]. The explanation lies in the manufacturing process of this sheet, which gives product of very low texture coefficient ($T = 9.01$), close to values observed for samples subjected to additional treatment (Table 2).

The influence of organic compounds on the corrosion kinetics of zinc and its alloys is complex, going from H_2 inhibition to enhancement. It has been found, that organic compounds with bonds of ethylene oxide type present in chloride electrolytes do not markedly affect corrosion of unalloyed zinc sheets, regardless of the state of the sample surface or electrolyte composition. Thus, the corrosion of 99.995% zinc in chloride medium shows minimal susceptibility to the action of organic inhibitors (Fig. 12), contrary to the behavior of zinc alloys in the same medium (Fig. 9). In the latter case the presence of inhibitors markedly affects the first stage of hydrogen evolution. For zinc alloy sheets subjected to the initial surface treatment the corrosion is already slow, therefore the influence of inhibiting compounds is minor.

For zinc alloys in potassium hydroxide solution the corrosion process may be reduced by removal from sheets of the surface layer oxides (Fig. 8), contrary to pure zinc, where this treatment speeds up the corrosion twice. The initial oxidation of zinc alloy sheets results in an increase of the volume of hydrogen evolved by about 30%.

Contrary to chloride electrolytes, in alkaline solutions the organic surface active agents inhibit corrosion of zinc alloys only in some cases, i.e., for sheets mechanically cleaned or amalgamated. Inhibiting properties are shown only by organic compounds, which are weakly polymerized, soluble in aqueous solution, and quite stable in strong alkaline solutions. The use of other compounds can even accelerate the evolution of hydrogen (Figs. 10, 11 and 14). The detrimental role of oxide compounds present on surface of zinc alloys increases markedly if organic inhibitors are used in an alkaline medium. This manifests in increasing the rate of hydrogen evolution by 8–17 times (Fig. 10).

There is a marked analogy between the corrosion behaviour of zinc alloy sheets which is presented in this paper and zinc alloy powders in alkaline media containing additives of polyglycol type [12]. Some of polyglycols show inhibiting properties only after the surface of zinc grains is mechanically and chemically cleaned by mixing zinc paste in KOH medium [12,15].

3.2. Influence of amalgamation on the corrosion kinetics of zinc sheets in chloride and alkaline medium

Inhibiting properties of mercury, which was commonly used in the past to slow down zinc corrosion, constitute a mark reference for evaluation of other ecologically clean compounds.

We investigated the behaviour of ZnPbCd alloy and pure 99.995% zinc in chloride (18% $ZnCl_2$ + 20% NH_4Cl) and alkaline (7 M KOH + 0.6 M ZnO) electrolytes. We have found that the influence of surface amalgamation on the corrosion kinetics depends on zinc alloy additives. The more is the metal corrosion resistant the smaller is the influence of amalgamation. E.g., in the chloride electrolyte the corrosion of pure zinc sheets decreases by about 10–15 times for 0.078 mg Hg/cm² of surface. The increase of the amount of Hg to 0.78 mg Hg/cm² does not further influence the volume of hydrogen evolved per day. The

rate of hydrogen evolution is almost constant from the beginning of the process and not affected by polyglycol additives (Fig. 12). After investigation however, the surface of amalgamated sheets is more smooth and without dark spots.

For amalgamated ZnPbCd alloy in chloride electrolyte the volume of hydrogen evolved in 30 days is by about 30% lower than for non-amalgamated sheets. Daily amounts of the evolved gas are similar in both cases indicating similarity in the corrosion kinetics (Fig. 13). In chloride medium surface active agents are more effective in lowering the evolution of hydrogen (about 50%) than the surface amalgamation (about 30%).

In alkaline solutions the deposition of mercury on the surface of pure zinc markedly lowers the corrosion rate during the initial period the corrosion rate so that it is comparable to the corrosion rate of zinc alloys. In the next stage the gassing of zinc free of alloying additives is markedly increased (Fig. 15). The inhibiting activity depends on the amount of mercury deposited. The corrosion of ZnPbCd alloy in KOH solutions is almost completely inhibited by HgO content, which corresponds to 0.45 mg Hg/cm² of surface (after HgO reaction with zinc for 20 h at 45°C). The same effect is observed for much lower concentrations of Hg (Fig. 14) in the presence of some surface active agents. This has been applied in production technology of alkaline cells.

4. Discussion

Gasmetric results illustrating the corrosion kinetics of solid, pure and alloyed, zinc samples indicate that corrosion process depends not only on alloy additions but also quite strongly on passivation of zinc surface, degree of order of zinc crystallites, and composition of electrolyte solution. Two-stage course of hydrogen evolution, as observed in pure electrolyte, is typical for zinc samples with untreated surface which is then coated with a layer of zinc oxide, usually additionally contaminated and scratched. Such state of surface promotes the occurrence and differentiation of local corrosion potentials, local cells emerge causing intensified evolution of hydrogen.

As the outer layer of a sample dissolves the role of these factors decreases till thermodynamic equilibrium is reached i.e., an appropriate level of surface passivation in a given electrolyte.

As follows from X-ray study of the structure of surface layer on zinc the two-stage kinetics of corrosion is also related to the degree of order of zinc crystallites. It should be noted here that although the depth of penetration of X-ray Cu K α radiation depends on the incidence angle but yet in the case of metallic zinc it may be felt to below 15 μm . Thus, the calculated values of structural parameters are characterizing the surface layer of zinc sample of that thickness. We have found that since there is some differ-

ence in the degree of order of zinc crystallites, expressed as the texture factor, between outer and deeper layers of a flat zinc sample, it affects the differences in corrosion kinetics. In the second stage the layer of lower value of texture factor T corrodes causing lesser and stable corrosion rate.

So it is evident that initial treatment of zinc surface by prolonged etching in electrolyte solution or by mechanical polishing improves corrosion resistance due to removal of impurities and simultaneous exposure of lower texture factor crystallites. These samples show low corrosion rate from the beginning of the experiment. As previously discussed in Section 1, the fact that at the second stage of corrosion the plateau value on the plot of hydrogen evolution rate depends on the presence of alloying elements in zinc as well as on the pH of electrolyte is self-evident because the two decide upon the corrosion potential of zinc in electrolyte. A given zinc alloy is distinctly affected by the pH of electrolyte only in the case of previously untreated samples. The plateau value of treated samples is almost pH-independent.

We consider whether the volume of hydrogen evolved at an early period of corrosion is liable to the presence of oxygen dissolved in electrolyte. An assumption of possible reaction between hydrogen in statu nascendi and residual oxygen in electrolyte could give explanation of almost negligible gassing rate observed for some samples at the initial stage of reaction. It could have substantial effect on the measurement data only for samples with really low corrosion rate from the very beginning of experiment.

Presaturation of electrolyte solution with zinc salts hinders the dissolution of corrosion products, delaying further corrosion of zinc. Lack of saturation causes a rise in the corrosion rate at the initial stage of the process until saturation of the solution is reached.

Surface amalgamation of pure zinc drastically depresses the corrosion process, playing a similar role as alloy additions. Both amalgamation and lead-plating of battery zinc alloys additionally inhibit corrosion but far less than in case of pure zinc for the correction of corrosion potential resulting from their presence is small. Inhibiting effect is related to the degree of surface coating with these metals.

Preliminary oxidation of zinc surface prior to placing the sample into a weakly acid chloride electrolyte suppresses corrosion, whereas in an alkaline medium intensifies this process. The oxide layer on zinc readily dissolves in an acid electrolyte, exposing the inner layer of lower texture factor where the corrosion process is running slower.

The maximum of corrosion reduction of the alloyed zinc in a given electrolyte solution may be achieved by suitable mechanical preparation of zinc surface so that it is smooth, clean and with the lowest possible texture factor. In the case of an alkaline electrolyte it is very important to have the zinc surface free of oxides, then the action of

organic surfactants as kinetic barrier for zinc corrosion becomes most effective.

5. Concluding remarks

The studies enabled us to evaluate some methods of zinc corrosion inhibition which are used in practice or described in the literature. A multistage character of corrosion observed for cast zinc samples is consistent with previous literature information; e.g., Suresh Kannan et al. [17] evidenced by weight loss measurements that zinc alloys with Mg, Al, and Pb in alkaline solution showed the corrosion rates over 20 h to be greater than those over 100 h. Ming Cai and Su-Moon Park [18], using spectrochemical techniques, revealed three different mechanisms of zinc passivation in alkaline solution. Results of this study on samples made of zinc casts instead of zinc powder enlarge the knowledge on the kinetics of zinc corrosion in alkaline and weekly acid electrolyte solutions. The results show that the corrosion resistivity of zinc depends strongly on the structure of its surface layer. The results are important for optimizing the production technology of anodic material for battery systems with zinc anode.

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