THE EFFECTS OF AGEING PROCESSES ON THE OPERATION OF ALKALI-ZINC BATTERIES

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One of the greatest disadvantages of alkali-zinc batteries -- with cupric oxide electrodes (COE) and with air depolarization (AD) -- is the need for a large quantity of liquid electrolyte. Attempts to decrease the consumption of alkali by the use of the "secondary process" in the cells, i.e., by discharge without passage of zinc into solution, were unsuccessful because the zinc became passive [1, 2, 3]. The maximum concentration of zinc in the electrolyte, and, therefore, the duration of the "primary process", only depend (for a given alkali concentration) on the rate of the process of ageing of the electrolyte (by this is meant the spontaneous deposition of $Zn(OH)_2$ or ZnO from solution). The use of the "secondary process" depends primarily on prevention of passivation of the zinc anode, due to the ageing of the hydroxide (or oxide) film formed on its surface [2, 4].

In this paper we have investigated the kinetics of the ageing of "supersaturated" zincate solutions, as affected by a number of factors (nature of alkali, zincate and alkali concentrations, temperature, and various additives). We checked the effects of these same factors on the passivation of a zinc anode, in order to establish the relation between this and the ageing process. We also investigated alkali-zinc batteries of laboratory and industrial construction.

THE AGEING OF "SUPERSATURATED" ZINCATE SOLUTIONS

As "supersaturated" zincate solutions, we used spent COE electrolyte (with cupric oxide electrodes made by burning our binder), which had been in use up to the commencement of the "secondary process". The solution taken was placed in alkali-resistant glass test tubes, located in a water thermostat. Samples were taken systematically for the determination of zinc and alkali content.

Temperature had the most marked effect on ageing. The rate of ageing was so slow at low temperatures that the solution did not reach its equilibrium state, even after storage for several months (Table 1). Ageing was slowed down by increasing alkalinity of the solution and by decreasing concentration of zincate. Potassium zincate was the most susceptible to ageing, sodium zincate less so, and lithium zincate least of all (Fig. 1).

A pronounced effect on the ageing process was shown by the additives silicic acid and lithium compounds. In the the presence of these additives, solutions could be obtained with a high zinc content, ageing was retarded, and the equilibrium concentration of zinc was high. The action of these additives was manifest in zinc solutions of different alkalinities and at various temperatures, although their effect was more pronounced at higher temperatures (Table 1). Similar findings applied to sodium zincate solutions. A change was noted in the form of the equilibrium deposit, with the optimum amount of additive, in moderate concentrations of alkali. Thus, only the rhombic form of $Zn(OH)_2$ precipitated (up to + 40°) in the presence of SiO_3 , whereas the stable deposit was ZnO from solutions without additives.

PASSIVATION OF ZINC ANODE IN "SUPERSATURATED" ZINCATE SOLUTIONS

For this investigation we used a Ш -shaped vessel with separate anodic and cathodic cells. The cast anodes were cylindrical in shape. The electrolyte was prepared by dissolving ZnO in boiling concentrated alkali, with subsequent dilution. A fresh solution and new anodes were used for each experiment. The investigation was carried out in an atmosphere of air, in a thermostat.

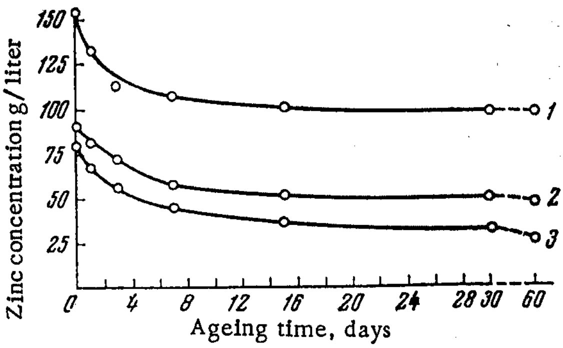

Fig. 1. Kinetics of the ageing of zincate solutions prepared from different alkalies. Temperature 20°. Total alkalinity 4.3 N. 1) Lithium zincate solution; 2) sodium zincate solution; 3) potassium zincate solution.

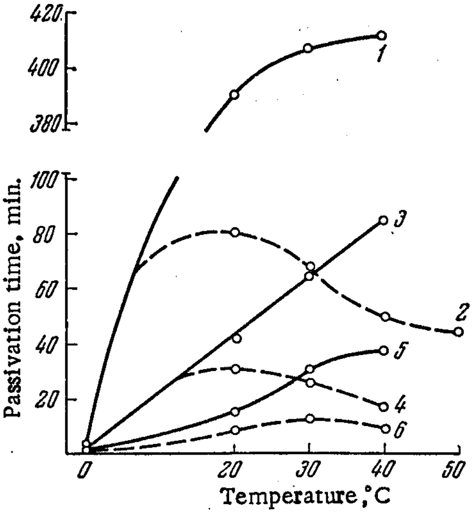

Fig. 2. Time for passivation of a zinc anode as a function of temperature. Anode current densities in amp/dm^2: 1), 2) 5.0; 3), 4) 6.0; 5), 6) 7.0. Electrolytes: 1), 3), 5) KOH_{total} 390 g/liter, Zn 103 g/liter, SiO_2 3.5 g/liter; 2), 4), 6) KOH_{total} 390 g/liter, Zn 103 g/liter

The relation between passivation time and temperature appeared, at first sight, to be anomalous, when using "supersaturated" zincate solutions without additives. Passivation took place more rapidly as the temperature of the zinc electrode was raised while the current was flowing, and the reverse effect was only observed at high current densities of at low temperatures (Fig. 2). The additives SiO_2^{3--} and Li^+ had a powerful influence on the passivation of the zinc anode, and, particularly, the former considerably retarded the passivation process. The effects of additives were most pronounced at the higher temperatures. At low temperatures, and high current densities, their effects were either less noticeable or even nonexistent.

INVESTIGATION OF THE WORKING OF ALKALI-ZINC BATTERIES

For this investigation we used laboratory prepared COE and AD batteries. The copper oxide electrodes were made from a mixture of CuO powder and metallic copper with a binder which burnt away. The AD electrodes consisted of plates cut out from VDTs batteries. We also used batteries of the type VDS-2-250.

It was found that the factors which had been shown to have a considerable effect on the ageing process of "supersaturated" solutions strongly influenced the working of alkali-zinc batteries. It was noted that a deposit was formed in the batteries sooner at higher temperatures. In the presence of the additives, silicic acid or lithium compounds, the working life of the batteries was increased, both up to the commencement of deposit formation, and up to the time of complete passivation of the anode (Table 2).

In batteries with KOH (s.g., 1.40), the presence of additives again considerably retarded the formation of a deposit; but it did not significantly affect the passivation of the zinc anode. The influence of additives was pronounced with electrolytes of lower KOH concentration (s.g. 1.20). Similar results were obtained with batteries containing a soda electrolyte, and also with AD batteries.

It was not possible to achieve stable working of the batteries by the "secondary process" with any electrolyte concentration. The introduction of additives to the electrolyte and the use of a Zn-Hg alloy anode improved the position but did not solve the problem completely. Experiments showed that there were possibilities, in this direction, for the use of a zinc powder electrode. The starting material for making such electrodes was either zinc powder, obtained by the electrolysis of zincate solutions, or zinc dust. The operation of a zinc powder electrode was found to be greatly influenced by its porosity. Electrodes pressed under high pressure (3-5 tons/cm^2),

TABLE 1

The Effects of Silicic Acid and Lithium Compounds as Additives, of Alkali Concentration, and of Temperature, on the Ageing of Zincate Solutions.

KOH concentration N	Additive concentration, g/liter	Temperature, °C	Ageing time, days						
			0	1	3	7	15	30	60
			Zinc concentration, g/liter						
4,3	Without additive	+20	79,5	74,8	55,9	47,2	45,2	31,6	26,6
	5, $LiOH \cdot H_2O$		96,0	84,0	63,9	54,9	53,6	50,9	48,3
	1,75,SiO_2		91,9	84,2	73,5	63,8	60,7	53,5	52,5
7,0	Without additive	0	159,5	159,5	158	156,5	155	—	—
	10, $LiOH \cdot H_2O$		195,5	195,5	194	188,5	179	—	—
	7, SiO_2		214	214	204,5	201	186,5	—	—
	Without additive	+20	159,5	156	138	119	101	88,2	73,7
	10, $LiOH \cdot H_2O$		195,5	193	171	157	142,5	137	131
	7, SiO_2		214	206	188,5	171	155,5	144,5	142,5
	Without additive	+40	159,5	107	79,7	67,3	63	61,2	—
	10, $LiOH \cdot H_2O$		195,5	147,5	127	111,5	101	90,4	--
	7, SiO_2		214	196	177	168	156	151,5	—
9.5	Without additive	+20	211	207	181,5	151	121	103,5	94,8
	10, $LiOH \cdot H_2O$		252	250	246	239	232	223	217
	7, SiO_2		273	273	270	268,5	267	262	249

TABLE 2

The Effects of Temperature and Additives on the Working of Cupric Oxide Batteries, $i_a = 4.0$ ma/cm^2. Electrolyte KOH (s.g., 1.30).

Additive concentration, g/liter	Temperature, °C	Electrolyte used up, ml/amp-hr	
		Up to the start of deposit formation in battery	Up to complete passivation of zinc electrode
Without additive	0	6,1	4,8
	+20	9,0	6,2
	+40	13,0	8,8
10, $LiOH \cdot H_2O$	0	5,4	4,6
	+20	5,8	5,4
	+40	6,9	6,2
1,75,SiO_2	0	5,1	3,7
	+20	6,9	3,9
	+40	7,9	4,4
7,SiO_2,	+20	5,2	3,5
	+40	6,7	4,2

Note: The results in Table 2 are only comparative. They would not be the same at different electrode and volumetric current densities; but their relative order would be the same.

and having a porosity of about 18%, were mechanically strong enough, but became passive on discharge more rapidly than did monolithic electrodes. Pressing under relatively low pressures (250-300 kg/cm^2) required the use of a binder (polystyrene adhesive) to improve the pressing characteristics. The electrode was enveloped in a cellophane film. to protect it from mechanical disintegration in the electrolyte and to reduce the interaction of zince and alkali. Such electrodes could operate by the "secondary process" without passivation, with an electrolyte consumption of 1.0 - 1.5 ml/amp-hr.

DISCUSSION OF RESULTS

In our view, "supersaturated" zincate solutions have a dual nature. The zinc in such solutions can exist in either colloidal or ionic forms. The colloidal form can be produced, during discharge at a zinc anode, by the breaking away of separate particles of the hydroxide (or oxide) film which forms during discharge at the electrode surface [5]. These colloidal particles are subject to ageing in the course of time; the material of a micelle nucleus crystallizes, dehydrates, and changes into a less active form. This leads to spontaneous deposition of solid phase from the solution. The fact that the same factors affect ageing of the solution and passification of the electrode is evidence of a relation between these two processes. The process of passivation of a zinc anode in "supersaturated" zincate solutions is interpreted by me as follows: the hydroxide film, formed on the surface of a working zinc anode, is subjected to ageing. The change of the material of the anode film to a less soluble form, together with the continuation of the discharge process, lead to a gradual thickening of the film. With the development of the ageing to the formation of ZnO, which is the most compact oxygen compound of zinc, the film rapidly loses its porosity, and this leads to complete passivation of the electrode. The chemisorption of SiO_3^{--} or Li^+ ions, which have thick hydrated envelopes, into the inner layer of the zinc hydroxide (or oxide) micelle, reinforces the hydration envelop of the whole micelle. This confers greater stability on the colloidal particle. The retardation of ageing of the anode film, under the influence of an additive, also retards the passivation of the zinc anode. The reduced tendency of a zinc powder anode to passivation can be explained, in my opinion, by the renewal of its working surface after cessation of dissolution of the separate zinc grains, i.e., by the absence of a continuous anode film.

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