============== APPLIED ELECTROCHEMISTRY ==============
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Effect of the Electrolyte Concentration on the Reversibility of a Nickel Oxide Electrode in a Nickel–Zinc Battery

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Abstract—The degree of charging of a nickel oxide electrode composed of spherical nickel hydroxide in a nickel–zinc battery was studied in anodic oxidation of the electrode in KOH solutions of different concentrations, containing hydroxozincate ions.

The use of a nickel oxide electrode composed of spherical nickel hydroxide on a foamed nickel support (FNi NOE), instead of a metal–ceramic (MC) electrode, in nickel–cadmium (NiCd) and nickel–metal hydride (NiMH) batteries made it possible to markedly simplify the production process and raise by 30–50% their electrochemical parameters. At the same time, as applied to a nickel–zinc battery, NOE of the same type made longer the service life of the battery compared to similar batteries with metal–ceramic NOE (MC NOE) but gave no noticeable advantages in the energy storage capacity.

The achievable degree of oxidation of an NOE composed of spherical nickel hydroxide in its operation in NiCd and NiMH batteries is 0.85–1.0 in terms of the $Ni(OH)_2 \rightarrow NiOOH$ transition [1], whereas in forming of NiZn batteries with the same NOE, this parameter does not exceed 0.7–0.8 [2]. In the previously developed NiZn batteries with an MC NOE, the degree of its charging was virtually the same as that obtained in NiZn batteries (0.85–0.9). If an NOE composed of spherical nickel hydroxide is used instead of MC NOE, its low degree of oxidation leads to a necessity for raising the amount of the active paste per unit capacity and, consequently, to a decrease in the capacity ratio of the negative and positive electrodes. This, in the end, reduces the specific energy of an NiZn battery with FNi NOE to 60 W h kg^{-1}, i.e., to a level provided by a similar battery with an MC NOE [3].

The aim of this study was to reveal what processes limit the chargeability of an NOE composed of spherical nickel hydroxide on a foamed nickel support both in forming of an NiZn battery and in its subsequent cycling under the conditions of varying concentrations of KOH and hydroxozincate ions in the electrolyte.

A preliminary analysis of our previous publications [2, 3] demonstrated that the hindrance to egress of a proton (and an electron) in charging of an NOE under the forming conditions may be due to simultaneous intercalation of zinc(II) contained in the electrolyte into the $Ni(OH)_2$ structure. The intercalated zinc is not an active component involved in electrochemical processes in the subsequent operation of the electrode. However, it can affect the distribution and interaction of the other components (H_2O; OH^-, K^+, and CO_3^{2-} ions) in forming of the NOE structure. Its own position in the layered structure of nickel hydroxides may vary [4], which is reflected in the degree of ordering of the nickel hydroxide structure and in its formability [5].

Another reason may be the electrolyte composition and, primarily, the KOH concentration both during the forming cycles and in the subsequent reversible operation, because an electrolyte of lowered concentration is used in NiZn batteries in order to diminish the solubility of zinc. In the course of cycling, this concentration decreases to even greater, and considerably so, extent [3] because of the small volume of the electrolyte and use of materials containing an admixture of carbonates and oxidizable organic additives.

A number of studies have been concerned with the influence exerted by zinc as a stabilizing additive on processes that occur in NOE, including that directly devoted to the issue in question [4]. In this study, we examined the influence exerted by zinc on processes occurring in forming of the $Ni(OH)_2$ structure and its

stabilization under conditions of NOE cycling in KOH solutions of different concentrations.

It was shown that the achievable degree of charging of an NOE containing incorporated zinc is lower than that of an electrode containing no zinc, but is distinguished by high stability of its capacity under cycling conditions. As the KOH concentration in the electrolyte was raised from 2 to 8 M, the degree of charging increased from 0.7 to 1.0. However, these results were obtained on electrodes with a constant content of zinc [6% Zn/(Zn + Ni)], and, therefore, they do not reflect specific features of the processes that occur in an NiZn battery, with the content of zinc in the NOE steadily increasing and the KOH concentration in the electrolyte simultaneously decreasing.

In nickel hydroxide with a structure of the β-phase, zinc can be incorporated in amounts of up to 15% Zn/Ni or 10–12% Zn/Ni(OH)$_2$ [4, 6]. When zinc is accumulated in NOE in such amounts, the β-phase starts to decompose with the subsequent gradual transformation into the α-phase, and the interplanar spacing between Ni(OH)$_2$ layers grows from 4.6 to 7 Å [5], with simultaneous increase in the structural disorder [5, 6]. By contrast, the structure of nickel(II, III) oxides is more stable at a Zn/Ni(OH)$_2$ ratio less than 10%, compared with that in the absence of zinc, and provides a virtually constant degree of proton (electron) egress.

EXPERIMENTAL

We performed the study on NiZn batteries and prototypes of varied capacity with a nickel oxide electrode composed of spherical nickel hydroxide on a foamed nickel support.

FNi NOE was fabricated from nickel hydroxide with particles 10–30 μm in diameter. The starting active paste contained 53–53.5% nickel and admixtures of cobalt (5.4%) and zinc (3.4%), introduced in synthesis of nickel hydroxide.

As shown in [2], the degree of NOE charging obtained in forming cycles depends on the imparted charging capacity. Among the modes tested, the highest capacity was provided by that in which a capacity of 100–110% relative to the theoretical value for the Ni^{2+} → Ni^{3+} transition was imparted in the first cycle, and 120–140%, in the second.

Charging with an excess imparted capacity is accompanied by a change in the electrolyte composition, because nickel hydroxide is oxidized with consumption of hydroxide ions and release of water:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e. \qquad (1)$$

In the subsequent discharge, hydroxide ions are returned into the electrolyte and water is consumed, but not completely, because the charging capacity C_{ch} exceeds the discharge capacity C_d. As a result, the KOH concentration in the electrolyte may decrease to a varied extent, depending on the mode of battery forming.

The degree of NOE charging in the battery varied with the ratio of charging to theoretical capacity, C_{ch}/C_{th} (0.8–1.5), only slightly, from 0.65 to 0.75 [2]. Therefore, in order to obtain a noticeable effect in comparative analysis, forming was performed in this study at different C_{ch}/C_{th} ratios.

The degree of Ni charging obtained in the case when the charging is limited by the final voltage, $C_{ch} < C_{th}$, was determined as the C_d/C_{ch} ratio (current utilization coefficient), and that in charging with $C_{ch} > C_{th}$ imparted in the transition Ni^{2+} → Ni^{3+}, as the C_{ch}/C_{th} ratio (nickel utilization coefficient).

Table 1 shows that the degree of FNi NOE charging in prototypes with a cadmium counterelectrode exceeds by 15–20% that in prototypes with a zinc electrode. This fact confirms that hydroxozincate ions are involved in the formation of the NOE structure and affect the achievable degree of NOE charging.

Table 2 shows that two cycles are sufficient for forming of an FNi NOE. In the third and subsequent cycles, the capacity changes only slightly. It should be noted that the values obtained on prototypes are smaller than those for batteries, which is due to different electrolyte volumes per unit NOE capacity. Therefore, the results obtained in tests with prototypes are regarded as tentative.

To obtain the most contrasting, as regards the degree of charging, results, we carried out forming of prototypes with electrolyte of varied concentration under the most severe conditions with a C_{ch}/C_{th} ratio increased to 1.5 (Table 2). However, as the initial KOH concentration was raised from 7.0 to 8.5 M and forming was performed with a zinc counterelectrode, i.e., in the presence of Zn(OH)$_4^{2-}$ ions, the degree of charging increased by only 10%, and by only the 10th training cycle.

The variation of the electrolyte concentration in forming of FNi NOE during the forming cycles was determined for batteries with a capacity of 50 A h (C_{th} = 100 A h) at an initial KOH concentration in

Table 1. Degree of charging of NOE composed of spherical nickel hydroxide on an FNi support in forming in prototype batteries with cadmium and zinc electrodes. $C_{ch}/C_{th} = 0.88{-}0.95$

C_{th} of NOE, A h	Concentration of the starting electrolyte, M		Current density, A dm^{-2}		Capacity in cycling A h		Degree of charging
	KOH	LiOH	charging	discharge	charging	discharge	
Nickel–cadmium system							
0.89	7.2	0.93	0.48 (first stage	0.125	1st, 0.82	0.43	0.48
					2nd, 0.79	0.55	0.62
					3rd, 0.85	0.61	0.68
			0.24 (second stage)		4th, 0.80	0.56	0.63
					5th, 0.79	0.58	0.65
Nickel–zinc system							
0.89	7.2	0.93	0.48 (first stage)	0.125	1st, 0.82	0.32	0.36
					2nd, 0.79	0.45	0.50
					3rd, 0.85	0.50	0.56
			0.24 (second stage)		4th, 0.80	0.49	0.55
					5th, 0.79	0.49	0.55

Table 2. Degree of charging of an NOE composed of spherical nickel hydroxide on a foamed nickel support in forming of prototype NiZn batteries with different initial concentrations of KOH in the electrolyte

Calculated capacity, A h	Cycle	Capacity, A h, at indicated initial KOH concentration, M		Degree of Ni charging at indicated initial KOH concentration, M	
		7	8.5	7	8.5
$C_{th} = 3.5{-}3.6$	Forming:				
	first	5.4/2.21*	5.4/2.18	0.62	0.62
	second	4.0/2.23	4.0/2.25	0.62	0.63
$C_{in} = 2.0$	Training:				
	first	2.4/2.06	2.4/2.08	0.56	0.58
	fifth	2.4/2.23	2.4/2.3	0.61	0.64
	tenth	2.8/2.21	2.8/2.34	0.63	0.68

* Charging/discharge capacity.

the electrolyte equal to 7 M and a C_{ch}/C_{th} ratio of 1.0 in the first and second cycles (Table 3). Even under these mild conditions, the electrolyte composition mainly changed during the forming cycles and varied only slightly in further cycling. In two forming cycles, the KOH concentration in the electrolyte decreased from 7 to 4 M in a charged battery, and to 5 M in a discharged one. In this case, the degree of NOE charging was 0.58–0.84. The high degree of charging obtained in these batteries is due to certain specific features of its operation.

The data in Tables 1–3 suggest that the impairment of the chargeability of FNi NOE in a NiZn battery is due to its forming directly in batteries and is asso-

ciated with the influence exerted on the forming β-Ni(OH)$_2$ structure by zinc being intercalated from hydroxozincate ions at a decreasing KOH concentration in the electrolyte.

The data obtained in forming of FNi NOE were confirmed in determining the cyclic life of NiZn batteries with varied KOH concentration. The initial concentration of 7 M decreased in the forming cycles to 5 M and remained at a level of about 4 M in further cycling (Fig. 1). The degree of NOE charging was in this case in the range 0.65–0.60 and decreased to 0.45 after 200 cycles because of the accumulation of zinc in NOE in amounts leading to degradation of the active paste. The total cycling life of the batteries was 300–350 cycles.

Table 3. Variation of the KOH concentration in the electrolyte in the forming cycles and the achievable degree of NOE charging in a Ni/Zn battery. Rated capacity 50 A h, initial KOH concentration 7 M

Cycle	State	Capacity, A h	Current density, A dm^{-2}	C_{ch}/C_{th}	C_d/C_{th}	KOH concentration, M
Forming:						
first	Charged	100	0.23	1.0		4.4
	Discharged	58.5	0.27		0.585	5.0
second	Charged	100	0.23	1.0		4.0
	Discharged	84	1.8		0.84	
Training:						
fifth	Charged	84	0.32	0.9		3.8
	Discharged	80	1.8		0.80	4.0

At an initial value of 6 M, the KOH concentration was in the range 4.0–3.0 after the forming (Fig. 1). The degree of charging was in this case about 0.5 till 200th–250th cycle, but the total cycling life may start to decrease in earlier cycles because the zinc electrode may be passivated at the specified lower-limit KOH concentration.
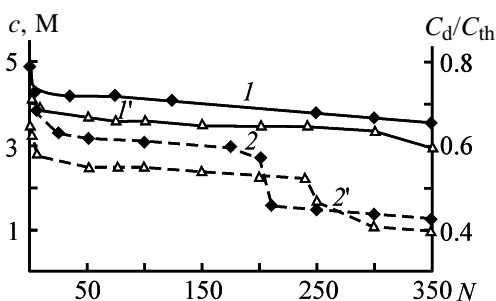
Fig. 1. Variation of (*1*, *1'*) the KOH concentration in the electrolyte and (*2*, *2'*) degree of charging of an NOE composed of spherical nickel hydroxide on an FNi support in the course of cycling of NTs-25 batteries. Initial KOH concentration, M: (*1*, *2*) 7 and (*1'*, *2'*) 6. (*N*) Number of cycles, (*c*) KOH concentration, and (C_d/C_{th}) degree of NOE charging; the same for Fig. 2.
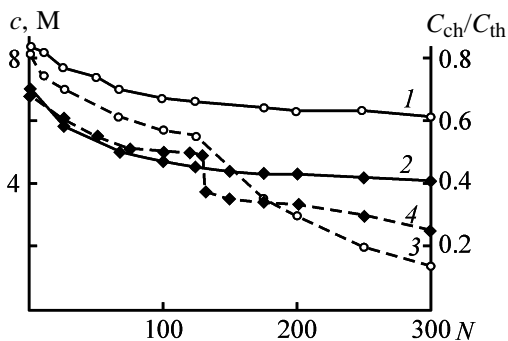
Fig. 2. Variation of (*1*, *1'*) the KOH concentration in the electrolyte and (*2*, *2'*) degree of charging of an MC NOE in the course of cycling of NTs-25 batteries. Initial KOH concentration, M: (*1, 2*) 7 and (*1', 2'*) 6.

These results determine the lower limit to the KOH concentration in the electrolyte, at which the NOE retains its working efficiency.

To reveal specific features of the processes occurring in FNi NOE in electrolytes with different KOH concentrations, we compared the data considered above with the results obtained in testing under similar conditions batteries with MC positive electrodes (Fig. 2). It can be seen that the degree of charging of an MC NOE formed separately in an electrolyte containing no zincate ions in the initial cycles exceeds that of a compacted NOE composed of spherical nickel hydroxide on a foamed nickel support at any of the initial KOH concentrations used (8.5–7.0 M). However, it decreases in the course of cycling just as the KOH concentration does. This dependence reflects the extent to which the capacity of batteries with MC NOE is unstable with respect to service life.

The results obtained in cycling of batteries with MC NOE at a KOH concentration of 8.5 M indicate that it is inadvisable to use an electrolyte of this composition in batteries with FNi NOE, because its forming will occur at a high concentration of $Zn(OH)_4^{2-}$ ions, which will shorten the cycling life of the battery.

Thus, introduction of zinc into FNi NOE stabilizes its capacity by making weaker its dependence on the electrolyte concentration, but the achievable degree of charging decreases in this case. The actually achieved degree of charging of FNi NOE under the conditions of forming in a NiZn battery is lower than that possible for NiCd and NiMH batteries and in NiZn batteries with MC NOE. This is due to the presence in the electrolyte of zincate ions involved in the transformation of the active paste at a decreasing KOH concentration.

As shown in [4], the zinc-containing active paste is formed in an electrolyte with a low KOH concentra-

tion (6–4 M) in the solid phase with a direct transition β-Ni(OH)$_2$ $\rightarrow$ β-NiOOH, for which the maximum degree of charging is 0.8. In this case, the specific capacity of FNi NOE is approximately equal to that of MC NOE because of the lower mass of the support of the former. A higher degree of charging is only achieved for a transition in forming via the γ-phase: $\beta_{(II)} \rightarrow \gamma \rightarrow \alpha \rightarrow \beta_{(III)} + \gamma$. For this phase to be formed in zinc-containing electrolytes, a higher KOH concentration is necessary, which is unacceptable for NiZn batteries.

CONCLUSIONS

(1) The degree of charging of a nickel oxide electrode on a foamed nickel support, obtained in forming in a nickel–zinc battery, does not exceed 0.7–0.85 of the calculated value corresponding to the transition $Ni^{2+} \rightarrow Ni^{3+}$, which is lower than the values obtained in nickel–cadmium and nickel–metal hydride batteries and in nickel–zinc batteries with a metal–ceramic nickel oxide electrode. This is due to the combined action of zinc introduced into the starting active paste of a nickel oxide electrode on a foamed nickel support and that contained in the electrolyte and to a decrease in the concentration of OH$^-$ ions.

(2) The degree of charging of a nickel oxide electrode on a foamed nickel support obtained in subsequent cycling of nickel–zinc batteries is 0.6–0.5 and varies within this narrow range as the KOH concentration in the electrolyte decreases. In this case, the nickel oxide electrode on a foamed nickel support has about the same specific capacity as that of a metal–ceramic nickel oxide electrode because of the lighter support.

(3) Comparison of the degree of charging of the nickel oxide electrode on a foamed nickel support with that of the metal–ceramic nickel oxide electrode, obtained under similar conditions, shows that zinc intercalated into the electrode on a foamed nickel support stabilizes the capacity of the electrode and makes it less dependent on the varying electrolyte concentration, but simultaneously depresses the level at which this stabilization occurs.

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