

APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Effect of Lanthanide Additives to a Nickel Oxide Electrode of a Sealed Nickel–Zinc Battery on the Self-Discharge and Hydrogen Pressure

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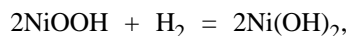
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Abstract—The influence exerted by addition of a nickel-based alloy containing lanthanides (La, Ce, Nd, Pr) to the active paste of a nickel oxide electrode on the self-discharge and hydrogen pressure in a sealed nickel–zinc battery was studied.

Proceeding with studies of gas evolution and gas absorption in a sealed nickel–zinc (SNIzN) battery with a nickel oxide electrode (NOE) made of spherical nickel hydroxide [1], we examined the influence exerted by addition of a nickel-based alloy containing lanthanides (La, Ce, Nd, Pr) to the active paste of a nickel–oxide electrode on the self-discharge and hydrogen pressure in an SNIzN battery. Lanthanide oxides were introduced into the active paste of an NOE in order to raise the utilization coefficient of the active paste in the NOE and improve its preservation [2]. Erbium, thulium, ytterbium, and lutetium oxides were found to be the most effective additives at an elevated temperature (75°C).

Nickel-based lanthanide-containing alloys exhibit a high absorption capacity for hydrogen [3]. The replacement of a cadmium electrode with an electrode composed of a nickel alloy with lanthanides, which can absorb hydrogen and desorb it upon polarity reversal, gave rise to nickel–metal hydride batteries. As the interaction of nickel metahydroxide NiOOH with hydrogen is accompanied by reduction of the nickel ion Ni³⁺ and oxidation of hydrogen



the influence of lanthanides on the self-discharge and hydrogen pressure in an SNIzN battery can be evaluated by a decrease in the NOE capacity and a change in the hydrogen pressure under cycling conditions.

EXPERIMENTAL

We introduced lanthanides into the active paste of an NOE in an amount of 1–2 wt % in the form of a nickel-based alloy containing La, Ce, Nd, and Pr. The study was performed on SNIzN batteries of the NTsG-25 type with an NOE composed of spherical nickel hydroxide [1]. The characteristics of the NOE studied in the batteries are listed in Table 1.

We determined the rated capacity of NOE by studying separate NOEs in prototype batteries. The electrodes were formed in two to three cycles, with a capacity equal to 1.1C_{th} of the positive electrode imparted in the first cycle, and 1.4C_{th} in the second and third cycles (C_{th} is the thermodynamic capacity). The zinc electrode contained 2 wt % CdO and 1 wt % PbO.

The open-circuit voltage U_{OC} of assembled batteries and the potential of NOE relative to a mercury

Table 1. Characteristics of NOE in NTsG-25 nickel–zinc batteries

Parameter	Content of alloy additive, wt %/g			
	0/0	0.5/1	1.0/2	2.0/4
Total amount of active paste, g	189	189	189	189
Ni + Co content, g	113	112	111	110
Capacity, A h:				
theoretical	51	51	51	50
rated	26	26	26	25

Table 2. U_{OC} of the batteries and the potential of NOE in the course of forming

Cycle	U_{OC} of battery, V				NOE potential, V			
	content of additive, wt %							
	0	0.5	1.0	2.0	0	0.5	1.0	2.0
Before forming	1.18	1.13	1.09	0.94		-0.19	-0.23	
First:								
after charging	1.85	1.85	1.85	1.85	0.51	0.50	0.50	0.50
after discharge	1.69	1.69	1.69	1.69	0.37	0.36	0.36	0.36
Second:								
after charging	1.84	1.84	1.84	1.84	0.45	0.50	0.50	0.45
after discharge		1.69	1.69					
Third, after discharge		1.79	1.80					

oxide electrode ($\text{Hg}, \text{HgO} | \text{OH}^-$) before the first forming charging depended on the content of the alloy in the active paste of the NOE (Table 2).

Table 2 shows that, before forming, the U_{OC} of the batteries decreases as the content of the additive in the active paste of NOE becomes higher. As the content of lanthanides increases, the potential of NOE shifts toward the negative direction and becomes more negative than the potential of the mercury oxide electrode. However, already after the first charging and during further discharge–charging cycles, the NOE potential becomes independent of the additive content and takes the characteristic value observed in the absence of an additive.

The open-circuit voltage and the charging–discharge characteristics of all the batteries under study become the same in the course of forming and cycling (Fig. 1).

The open-circuit voltage of batteries with NOE containing a lanthanide alloy (up to 2 wt %) and without additive varies in the course of storage in the same way (Fig. 2). However, the capacity in discharge after 29 days of storage of a battery containing 2 wt % alloy in the NOE is higher (Fig. 3). The loss of capacity in self-discharge is 30.6% for this battery and 36.0% for that containing no additive in its NOE. This result can be understood if we assume that the nickel-based lanthanide-containing alloy introduced into the active paste of the NOE is oxidized on its surface, but retains its ability to absorb hydrogen (Table 3).

Table 3 was compiled using data on self-discharge of ventilated nickel–zinc batteries, which is 10% in 30 days (2.5 A h) [4].

Calculation shows that the content of hydrogen in

the alloy after 29-day storage of an SNiZn battery (0.32 A h) is close to the value characteristic of the alloy used as the active paste in the negative electrode of a nickel–metal hydride battery.

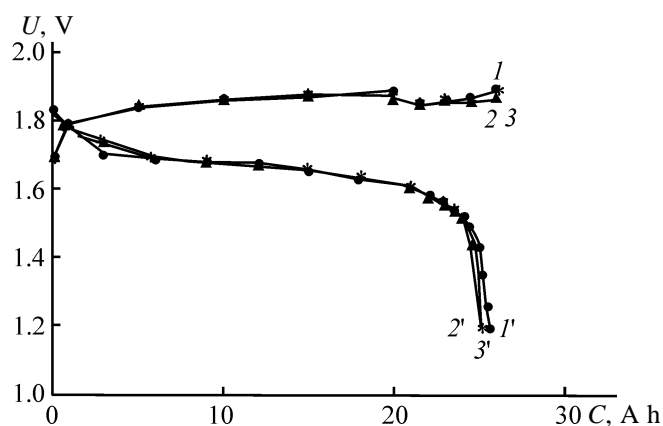


Fig. 1. Variation of the voltage U in ($1-3$) charging and ($1'-3'$) discharge in the ninth cycle of an NTsG-25 battery with a lanthanide alloy added to the NOE. (C) Capacity: the same for Fig. 3. Additive content (wt %): ($1, 1'$) 0, ($2, 2'$) 1, and ($3, 3'$) 2.

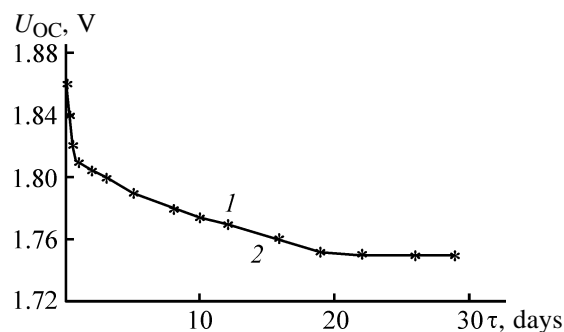


Fig. 2. Variation of U_{OC} in storage of charged NTsG-25 batteries (1) with addition of 2 wt % lanthanide alloy and (2) without additive. (τ) Time.

Table 3. Effect of the NOE composition on the self-discharge of NTsG-25

Battery	Capacity before (after) storage, A h	Decrease in capacity in storage, A h		Capacity of hydrogen absorbed by alloy, A h
		total	in oxidation by hydrogen	
NOE: without alloy additive	24.5 (15.7)	8.8	6.3	–
with alloy additive	24.5 (17.0)	7.5	5.0	1.3

In the course of cycling of an SNiZn battery, the pressure first increases and then reaches a constant value (Fig. 4). The maximum total pressure in the battery corresponds to the pressure of hydrogen and oxygen in charging, and the minimum pressure, to that of hydrogen in discharge. In the absence of an

alloy additive in the NOE, the hydrogen pressure in the battery was $(2.0\text{--}2.2) \times 10^2$ kPa, and the total pressure of hydrogen and oxygen, 2.8×10^2 kPa. In the case of an NOE containing the additive in an amount of 2 wt %, the hydrogen pressure in the battery was $(1.6\text{--}1.8) \times 10^2$ kPa, and the total pressure of hydrogen and oxygen, 2.2×10^2 kPa. Thus, the introduction of a nickel-based lanthanide-containing alloy in the active paste of an NOE made it possible to diminish the total pressure in an NTsG-25 sealed battery by 60 kPa, and the hydrogen pressure, by 40 kPa.

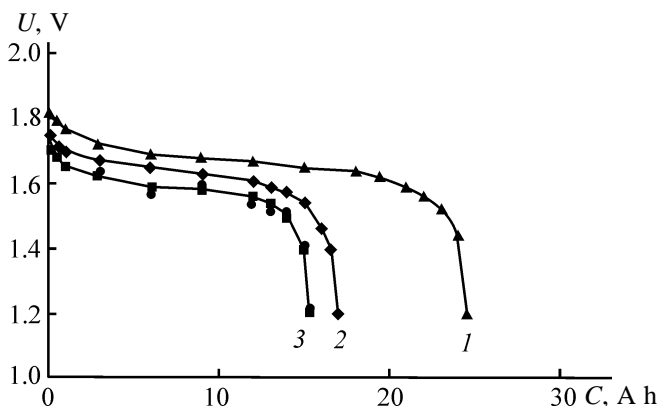


Fig. 3. Variation of the voltage U in discharge of NTsG-25 batteries (1, 2) with addition of 2 wt % alloy of lanthanides to NOE and (3) without additive (1) before and (2, 3) after storage for 29 days.

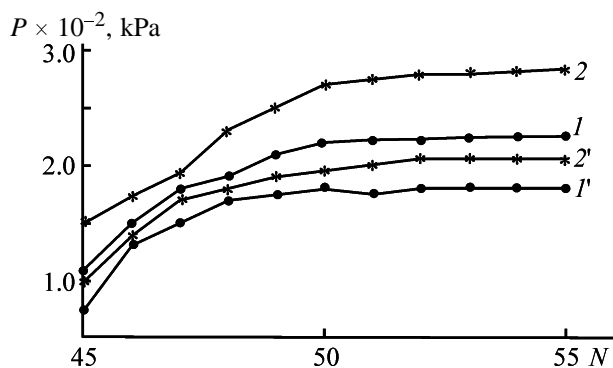


Fig. 4. Variation of (1, 2) maximum and (1', 2') minimum pressure P in an NTsG-25 battery (1, 1') with addition of 2 wt % alloy of lanthanides and (2, 2') without additive. (N) Number of cycles.

CONCLUSION

A nickel-based alloy containing lanthanides (La, Ce, Nd, Pr) introduced into a nickel oxide electrode retains its ability to absorb hydrogen. This leads to a decrease in the self-discharge of a sealed nickel–zinc battery in storage and makes lower the total pressure and hydrogen pressure in the battery in cycling.

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