Nickel–zinc batteries with long cycle life

Alexandre P. Pavlov *, Ljudmila K. Grigorieva, Semen P. Chizhik, Vitaly Kh. Stankov

Avtouaz Company, suite 521B, 101 Prospect Mira, Moscow 129812, Russia

Abstract

The main problems concerning the nickel–zinc battery are described. A new method of destruction of dendrites in the nickel–zinc battery is proposed. This method is based on a thin high-porous nickel membrane inserted between the electrodes. The chemical reactions of dendrite destruction on this membrane are presented. Cycle life of more than 500 cycles has been achieved during the tests.

Keywords: Batteries; Dendritic growth; Membranes; Nickel; Zinc

1. Introduction

The creation of environmental-friendly chemical power sources becomes a very attractive task for scientists today. The widely-used nickel–cadmium batteries with long cycle life are gradually being replaced by other alternative power sources such as nickel–metal hydride, nickel–iron, nickel–zinc, etc. There is a great interest in the nickel–zinc battery which has a superior performance compared with both the lead/acid and the nickel–cadmium batteries.

However, the development of the nickel–zinc battery is time-consuming, because of the problems related to the solubility of the zinc electrode discharge products and the disparity in charging efficiencies between the nickel and zinc electrodes leading to dendritic growth and the failure of the battery [1,2]. In order to solve this problem, research has been done by means of the following methods:

1. addition of various species to the active mass of the zinc electrode aimed to prevent electrode crumbling and to suppress dendritic growth [3];
2. use of modified electrolytes improving the zinc morphology on cycling [2,4];
3. selection of separators stable under nickel–zinc battery operating conditions and suppressing dendritic growth [2,5–9], and
4. maintenance technology including methods of mechanical [10,11] or electrochemical destruction of dendrites [8,12].

The above-mentioned methods are partly efficient but they complicate significantly either the design of nickel–zinc battery or its maintenance.

For the time being, the main problem is the limited cycle life of the nickel–zinc battery due to dendritic growth. A satisfactory solution to this problem has not been found yet.

The authors have managed to increase of cycle life by the insertion of a thin high-porous nickel membrane (HPNM) between the electrodes [13]. In this work are described the design of the nickel–zinc battery and the processes occurring on the membrane. The results of the nickel–zinc battery tests are also presented.

2. Theoretical

The new element of our battery (HPNM) has perfect ionic and electronic conductivities, and is active in the electrolyte. When inserted in the nickel–zinc battery it has a strong effect on the operation of other elements, and it changes essentially their response to the processes taking place in the battery during operation.

HPNM inserted between two separators plays the role of an independent electrode which has no electrical contact with either the anode or the cathode. First of all, it is necessary to consider the overall electrochemical reactions that take place on the electrodes in the battery. Fig. 1 shows the fragments of the Pourbaix diagrams for nickel, zinc, oxygen, and hydrogen electrodes in alkaline electrolyte [14]. The nickel–zinc battery voltage is 1.7–1.8 V depending on the charge voltage [15,16]. This value exceeds considerably the stability with respect to water electrolysis (1.24 V). This effect cannot be
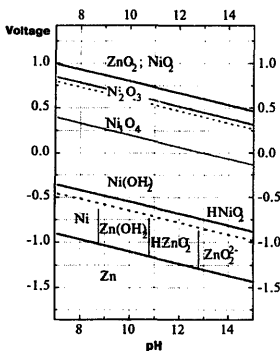
* Corresponding author.

Fig. 1. Pourbaix diagrams' fragments for nickel, zinc, oxygen and hydrogen electrodes in alkaline electrolyte. The Pourbaix diagrams [14] describe boundaries of electrochemical equilibria, electrode potential being plotted via pH of a solution.
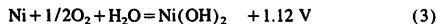
neglected. Therefore, it is necessary to study the role of oxygen and hydrogen during charge and discharge processes.

The basic undesirable phenomena that limit the application of the nickel–zinc battery occur during its charge, (i) the growth of dendrites on the zinc electrode, and (ii) electrolysis of water followed by oxygen formation on the nickel oxide electrode. Metallic zinc dendrites grow through the separator and their growth is faster when a 100% state-of-charge is achieved. At the final stages of the battery charge, oxygen releases and its amount makes up to 30% of the charge equivalent to that of the reserved in the battery. It dissolves in the electrolyte and is released to the atmosphere in case of excess.

The independent HPNM, which is a new element in the design of the separator, reacts with components of the solution. At the beginning of the charge, its interaction with dissolved oxygen is the most efficient process [17]. Nickel can chemisorb molecular oxygen as well as it can react to form oxides and hydroxides. Due to the developed surface area, HPNM is capable to absorb and fix chemically the oxygen formed. The processes that proceed on HPNM can be described as follows

$$Ni + 2OH^- = Ni(OH)_2 + 2e^- \quad +0.72 \text{ V} \quad (1)$$

$$2OH^- = 1/2O_2 + H_2O + 2e^- \quad -0.4 \text{ V} \quad (2)$$
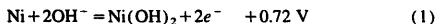
or as the overall reaction

$$Ni + 1/2O_2 + H_2O = Ni(OH)_2 \quad +1.12 \text{ V} \quad (3)$$

Because of the high value of the reaction potential, HPNM oxidation occurs spontaneously and it functions as an efficient absorber of oxygen dissolved in the electrolyte, thus protecting the other elements of the battery. It can be seen from the Pourbaix diagram that metallic nickel lies in the area of water stability and therefore the electrolysis with hydrogen release cannot occur under normal conditions. Thus, under the con-

ditions considered above, some stationary potential should exist on the HPNM that can be determined by the reactions (1)–(3).

Let us consider a case when a growing zinc dendrite has reached the surface of HPNM. As a result, nickel and zinc are in electrical contact, immersed in alkaline solution, covered with zincate ions. Such a pair represents a local element stimulating the zinc corrosion processes [17]. In order to find out details of the corrosion mechanism it is necessary to consider all possible electrochemical conversions and their relative role in the process. One can conclude that the locally short-circuited nickel–zinc pair will form a galvanic cell where the following overall reaction occurs

$$Zn + Ni(OH)_2 + 2OH^- = ZnO_2^{2-} + Ni + 2H_2O \quad (4)$$

with the surface potential equal to 0.5 V. This process occurs spontaneously and leads to zinc solvation [17]. It is clear that the solvation of the dendrite results in the destruction of its part being in contact with HPNM.

However, there is another mechanism of zinc corrosion in the same local element proceeding in parallel to that considered above. The question is about the hydrogen corrosion of zinc [17,18]. One can see from the Pourbaix diagram (Fig. 1) that, as opposite to nickel, the curve of zinc electrochemical balance in alkali is below that of the equilibrium potential of the hydrogen electrode. Hence, when nickel is short-circuited with zinc the latter shifts the potential of nickel to the negative voltage area, i.e. out from the boundaries of water stability with respect to electrolysis with hydrogen release. As a result the reduction of water on nickel becomes possible, according to equation

$$2H_2O + 2e^- = H_2 + 2OH^- \quad -0.82 \text{ V} \quad (5)$$

which is accompanied by solvation of zinc [3] on equation

$$Zn + 4OH^- = ZnO_2^{2-} + 2H_2O + 2e^- \quad (6)$$
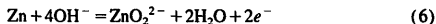
The overall reaction is

$$Zn + 2OH^- = ZnO_2^{2-} + H_2 \quad +0.4 \text{ V} \quad (7)$$

The potential of this process is comparable with the surface potential of reaction (4); they can, therefore, proceed simultaneously thereby accelerating solvation of the dendrites.

3. Experimental

Experimental research is carried out on nickel–zinc batteries with a capacity of 44 Ah. The batteries are assembled using a pressed zinc electrode and a sintered nickel oxide electrode. A cellulose film was used to separate the zinc electrode, the positive sintered electrodes were inserted in Kapron fibre packages. HPNMs manufactured under a special technology are inserted between the electrodes [13]. The membrane has the following characteristics: thickness: 100 μm, porosity: 60%, and pore size: 10 μm.

Table 1
Capacity of batteries at control cycles

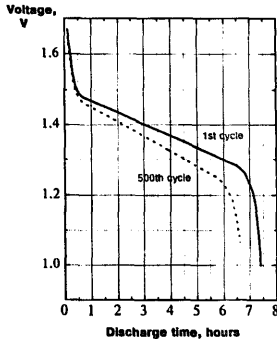| Cycle no.	1	50	100	150	200	250	300	350	450	500
Battery with HPNM capacity (Ah)	44	43	40	39	38	38	37	37	37	37
Conventional battery #1 capacity (Ah)	44	42	40	failed						
Conventional battery #2 capacity (Ah)	44	43	40	failed						
Conventional battery #3 capacity (Ah)	45	42	41	36	failed					

Fig. 2. Discharge curves of the HPNM-equipped battery during first and 500th control cycles; discharge current: 6 A.
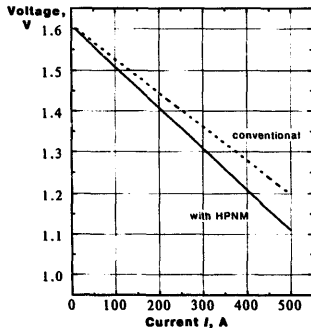

Fig. 3. Voltage characteristics for nickel–zinc batteries. The voltage was measured after the battery discharge by current I (horizontal axis) during 60 s.

The cycle-life tests of the nickel–zinc batteries are performed in the maximum charge state, which is the most favourable condition for the formation and growth of dendrites. The batteries are charged by a current of 6 A up to final voltage 2.0 V, and discharged by the same current during 1 h. Control cycles with 100% depth-of-discharge are fulfilled periodically on cycling (every 50 cycles). The batteries are discharged by the same 6 A current down to a final voltage 1.0 V. Three conventional batteries were cycled under the same conditions.

4. Results and discussion

Abrupt fluctuations of the potential that usually occur in the charge of nickel–zinc batteries were not recorded, because the zinc dendrites were not touching the positive electrode.

Table 1 shows the capacities of batteries with and without HPNM measured during the cycle life tests. The longest cycle life of the conventional batteries was 158 cycles.

One can see from the Table that the discharge capacity of the battery has slightly decreased after 500 cycles. The final voltage at ordinary cycling after the discharge by 6 A current was 1.64–1.69 V. The achieved cycle life was 500 cycles.

Fig. 2 shows the discharge curves of the nickel–zinc battery at the first and 500th control cycles. The voltage characteristics of nickel–zinc batteries with (and without) HPNM are shown in Fig. 3. One can see that HPNM inserted between the electrodes increases the internal resistance of the battery. Apparently, this increase is due to the diffusion resistance of HPNM.

5. Conclusions

The insertion of HPNM between the electrodes excludes the risk of electrodes shorting caused by dendritic growth. Growing dendrites are not capable to pierce the metal membrane because of its small pore sizes. In addition, when a zinc dendrite contacts the membrane an electrochemical solvation of zinc occurs.

The battery with HPNM has performed 500 charge/discharge cycles without failure.

The data obtained allow to conclude that HPNM increases essentially the cycle life of the nickel–zinc battery.

References

[1] J. McBreen, *J. Power Sources, 51* (1994) 37.
[2] V. S. Levinson, *Chemical Current Sources*, VINITI, Moscow, Soviet Union, 1975.
[3] Silver–zinc batteries, *Chemical and physical current sources, TC-22 Review*, Informelectro, Moscow, Soviet Union, 1973.
[4] Electrochemical power, *Rep. 3rd All-Union Scientific Conf., 19–21 Oct. 1989, Moscow, Soviet Union*, 1989.
[5] *US Patent No. 4 298 666* (1981).
[6] *Jpn. Patent No. 46-17 535* (1971).

[7] K. Bass, P.J. Mitchell. G.D. Wilcox and J. Smith, *J. Power Sources,* *35* (1991) 333.

[8] *Chemical Current Sources,* Energoatomizdat, Leningrad, Soviet Union, 1987.

[9] S. Thangadurai, N. Ven Katakrishnan, *Bull. Electrochem., 5* (1989) 107.

[10] *US Patent No. 3 923 550* (1976).

[11] *US Patent No. 4 684 585* (1987).

[12] A. Himy, O.C. Wagner, *J. Electrochem. Soc , 128* (1981) 330.

[13] *Russian Patent No. 94 028 153, H01M 10/24* (1994).

[14] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions,* Pergamon, London, 1966.

[15] T. Crompton, *Secondary Current Sources,* Mir, Moscow, Soviet Union, 1985.

[16] V.S. Bagotski, A.M. Skundin, *Chemical Current Sources,* Energoizdat, Moscow, Soviet Union, 1981.

[17] V.V. Scorchelleti, *Theoretical Bases of Metals Corrosion,* Himiya, Leningrad, 1973.

[18] L. Kish, *Kinetics of Electrochemical Metals Solvation,* Mir, Moscow, 1990.