Review

Sealed nickel–zinc cells

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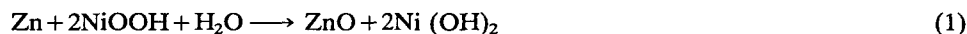*Institute of Chemical Technology, Technical University of Darmstadt, D-61 Darmstadt (FRG)*

Abstract

Problems of the preparation and the operation of secondary sealed Ni–Zn cells are considered. Attention is paid to the problems of the high solubility of the oxidation products of zinc in the electrolyte, the formation of Zn dendrites, the shape changes of the Zn electrode and the evolution of hydrogen and oxygen and their recombination. The state of the research and development of sealed Ni–Zn cells at some firms and institutions is reviewed.
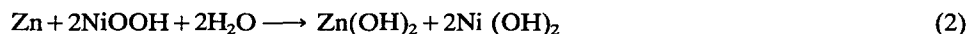
1. Introduction

The alkaline nickel–zinc accumulator was invented just 90 years ago and was patented by Mikhalovskii [1], a Russian investigator. Of the alkaline systems with a zinc anode, the Ni–Zn accumulator has one of the highest practical discharge voltages; its theoretical electromotive force is equal to 1.74 V and the theoretical specific energy is 373 W h/kg. In practice, up to 23% of this amount can be utilized at fairly high discharge rates. These properties, together with the moderate price of the electrode materials, make the accumulator attractive as a power supply for various electric appliances including electrotraction.
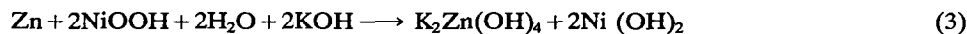
The principal cell reaction is

$$Zn + 2NiOOH + H_2O \longrightarrow ZnO + 2Ni\,(OH)_2 \tag{1}$$

or

$$Zn + 2NiOOH + 2H_2O \longrightarrow Zn(OH)_2 + 2Ni\,(OH)_2 \tag{2}$$

Since the products of anodic oxidation of zinc are soluble in the electrolyte (4–10 M KOH), the cell reaction can also be formulated as

$$Zn + 2NiOOH + 2H_2O + 2KOH \longrightarrow K_2Zn(OH)_4 + 2Ni\,(OH)_2 \tag{3}$$

In the case of reactions (2) and (3) the theoretical specific energies are 326 and 234 W h/kg, respectively.

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During anodic oxidation, zinc loses 4s2 electrons and its ions form sp3 hybridized orbitals, which are responsible for the formation of complex ions in concentrated hydroxides [2]. In addition to the current-generating process, several parasitic reaction proceed in the system, namely hydrogen evolution at the zinc electrode during charging

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \tag{4}$$

reduction ('recombination') of oxygen at the zinc electrode

$$O_2 + 2H_2O + 4e^- \longrightarrow 4\ OH^- \tag{5}$$
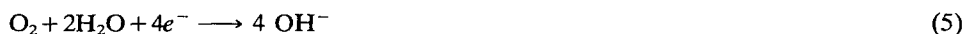
and its formation at the nickel oxide electrode

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^- \tag{6}$$

and ionization ('recombination') of hydrogen at the nickel oxide electrode

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^- \tag{7}$$

However, the rate of the latter process is very low [3]. Since zinc in alkaline medium is unstable, its corrosion proceeds with a non-negligible rate as

$$Zn + 2H_2O \longrightarrow Zn(OH)_2 + H_2 \tag{8}$$

Zinc hydroxide as a product of reactions (3) and (8) forms complex ions $Zn(OH)_4^{2-}$ up to saturation and afterwards it is precipitated as hydrated ZnO, which may cause passivation of the zinc electrode.

The corrosion of zinc is enhanced by the presence of impurities in zinc that lower the hydrogen overpotential, e.g. Co, Fe, Ni, Sb or Ge. On the other hand, it is hindered by the presence of metals that increase the hydrogen overpotential, e.g. Hg, Pb, Cd, In or Tl. Amalgamation of the zinc anode is a very effective means of suppressing the corrosion reaction.

Both electrode materials, zinc and nickel oxide, are in the centre of interest of battery researchers, since they are essential components not only for Ni–Zn but also for AgO–Zn, Ni–Fe, Ni–Cd and Ni–H accumulators and for primary cells with a zinc anode. They are therefore dealt with in detail in all monographs about electrochemical power sources, especially refs. 4–7 and also refs. 2, 8–12 as well as in proceedings of the symposia on power sources. The present article is devoted to problems concerning sealed Ni–Zn cells.

2. Preparation of electrodes

2.1. Nickel oxide electrode

Positive electrodes in Ni–Zn accumulators are usually prepared by impregnation of a porous sintered nickel support by the active material (so-called sintered electrodes). The technological details are given in the mentioned monographs. Since nickel is the most expensive component of Ni–Zn batteries (it constitutes more than 30% of their price), there have been many attempts to replace the expensive sintered electrodes by cheaper ones, with as far as possible the same parameters. Thus, plastic-bonded nickel oxide electrodes [13–16] were developed in the seventies. These were usually prepared by pressing or rolling the active material (a mixture of nickel oxide, graphite and plastic binder) onto a current collector (usually a nickel net). They were much cheaper and also lighter than commercial sintered electrodes, however their disadvantages were a limited cycle life, volume changes (swelling) and lower current-carrying capability.

Another development was the replacement of the expensive and heavy porous nickel support by various nickel or nickel-plated fibrous materials [17–22].

2.2. Zinc electrode

This electrode is usually prepared by pasting or rolling a mixture of ZnO, additives and an organic binder onto a current collector (a silver, copper or lead-plated copper net or an expanded metal) [23, 24]. In another method, a slurry of ZnO, additives and PTFE is formed into cakes on a vacuum filter table and the cakes are pressed on to each side of a current collector [25–27]. Other methods, used in special cases, are mentioned below.

3. Problems concerning Ni–Zn cells

Unequal charge acceptance is one of the basic problems of these accumulators. The charge acceptance of zinc electrodes approaches almost 100%, whereas that the nickel oxide electrode is about 90% owing to the parasitic reaction of oxygen evolution. Another problem is the formation of zinc dendrites during charging and overcharging of the zinc electrode causing short circuiting by penetration through the separator. Moreover, oxygen evolved at the positive electrode may cause oxidation and thus degradation of the separator material. This is often the case with separators containing cellulose.

Another serious problem is shape change of the zinc electrode during cycling. The principal cause for this phenomenon is the solubility of the discharge products of the zinc electrode in the strongly alkaline electrolyte. Shape changes are brought about by preferential dissolution of active material from the electrode edges during discharge, followed by redeposition in a more compact form at the electrode centre during charging. This results in a diminution of the active surface area of the electrode. The shape changes have been associated with non-uniform current distribution in zinc electrodes and with osmotic pumping.

Under certain conditions the zinc electrode tends to the passivation in the discharge phase. Only at a sufficient concentration of OH^- ions can zinc pass into the solution as $Zn(OH)_2$, otherwise a poorly soluble ZnO is formed causing electrode passivation. Therefore a sufficiently fast transport of OH^- ions to the zinc electrode is very important. Some additives are used to overcome passivation.

Much effort has been spent in suppressing the evolution of hydrogen at the zinc electrode. Many inhibitors are known, some of which are used in sealed systems (see below), where the evolution of hydrogen must be minimized, since its ionization at the nickel oxide electrode proceeds very slowly. Several means have been used to eliminate the disadvantages of the zinc electrode, namely:

(i) additives in the electrolyte, e.g. H_3PO_4, K_3BO_3, to suppress the formation of zincate ions;

(ii) additives in the zinc electrode to suppress the shape change (e.g. $Ca(OH)_2$);

(iii) use of auxiliary electrodes for ionization of hydrogen in sealed cells;

(iv) additives in the zinc electrode to suppress the formation of dendrites;

(v) modification of the charging regime;

(vi) development of improved separators resisting the penetration of dendrites and the transport of zincates;

(vii) adjustment of the proportion of active materials (a large excess of zinc).

Some of these provisions are essential for the realization of sealed Ni–Zn cells.

The overpotential of oxygen and the performance of the nickel oxide electrode can be increased by the addition of LiOH into the electrolyte and cobalt compounds into the active material; this also has a favourable effect on the mechanical and electrical properties of fibrous electrodes [21, 22]. Oxygen formed in sealed Ni–Zn cells during charging is reduced at the zinc electrode or at an auxiliary electrode.

The problems of sealed Ni–Zn cells will now be dealt with in more detail and it will be shown how they are solved in practical cells.

3.1. Problems of zinc oxide solubility in KOH solutions, shape change of zinc electrode and formation of zinc dendrites

All these problems are connected and for the solution of some joint measures may be used.

The solubility of zinc in the alkaline electrolyte can be suppressed by adding suitable compounds, whereby the cycle life of Ni–Zn batteries can be prolonged.

At the beginning of the seventies, Schneider and Dominiczak [28] made use of the old proposal of Langguth [29] and employed K_3BO_3 solutions as electrolyte in Ni–Zn accumulators with bipolar electrodes. Thus, they substantially suppressed the solubility of zinc and the formation of zinc dendrites. Also Eisenberg [30–32] recommended salts of a weak acid and a strong base, such as K_3BO_3, $NaBO_2$, Na_3BO_3 or K_3PO_4 for vented and sealed Ni–Zn cells. Addition of up to 10% of K_3PO_4 into the electrolyte has been patented in Japan [33]. Nichols et al. [34] replaced part of the OH^- ions in the electrolyte by F^- and borate anions. Furukawa et al. [35] recommended an alkaline electrolyte containing 5% KF. Adler et al. [36] also employed a mixture of KOH and KF in their experimental Ni–Zn battery. Cenek et al. [37] used 20% KOH + 10% KF electrolyte in vented Ni–Zn cells.

Jost [38] patented in 1969 an alkaline electrolyte for Ni–Zn cells containing carbonate, while Adler et al. [26, 27] used a solution of 2.5 M KOH, 2.5 M K_2CO_3 and 0.5 M LiOH or a solution of 3.5 M KOH and 3.3 M KF in their cells. Further, the solubility of ZnO in KOH was decreased simply by using electrolytes of a lower concentration [25, 39, 40].

The problems of shape change and dendrite formation bear direct relevance to the life expectancy of the batteries, and therefore they have been investigated in many laboratories. They are alleviated by suitable additives to the zinc electrode.

Addition of $Ca(OH)_2$ increases the cycle life of Ni–Zn batteries [38, 39] by forming calcium zincate, $Ca(OH)_2 \cdot 2Zn(OH)_2 \cdot 2H_2O$, in the electrode, a compound of lower solubility than potassium zincate. This idea has been thoroughly studied by many authors [24–27, 36, 40–57].

Other additives preventing the shape changes and also improving the stability of Zn electrodes are Bi_2O_3, CdO, HgO, PbO, In_2O_3, $In(OH)_3$, Tl_2O_3, $Tl(OH)_3$, etc. [27, 43–45, 53–55, 57–71]. Suitable combinations of these compounds decrease the rate of hydrogen evolution at the zinc electrode. For example, more than 25 patents disclosed during the last five years by the firm Sanyo are devoted to the composition of zinc anodes for alkaline secondary batteries containing the above mentioned oxides or hydroxides. Ecological reasons force the manufacturers to decrease substantially the amalgamation of zinc, used as a remedy against the evolution of hydrogen.

Other recommended additives are carbon black, PTFE, carboxymethyl cellulose, dextrin, and other organic compounds. It seems, however, that small additions of Bi, Pb, Tl and In compounds are most advantageous since they are used most frequently.

In the sealed Ni–Zn cells the formation of Zn dendrites is not so critical as in vented cells. The conditions for dendrite growth are not so favourable with a starved electrolyte cell. According to the new findings [27] no dendrites were observed in sealed Ni–Zn cells. It was concluded that sealed cell operation tends to prevent zinc dendrite formation and propagation, thereby extending cell life.

Zinc dendrites are dangerous in every case for the incidental short-circuiting of the cell. On dendrites the first bubbles of hydrogen often appear. To suppress the prospective dendrite formation some effective methods used would probably be: additives (e.g. quarternary ammonium salts or ions of Pb, Cd, Bi, In and Tl), these elements are frequently used as additives in the zinc electrode; special charging regimes (e.g. charging with an asymmetrical a.c. accompanied with current pauses or charging with d.c. pulses [45, 72, 73]. A suitable separation system hindering the dendrite growth is, naturally, a necessary condition.

3.2. Problems with the evolution of oxygen and hydrogen

It has already been mentioned that oxygen is created on the nickel oxide electrode and hydrogen on the zinc electrode in advanced phases of charging. The first molecules of oxygen are evolved at the Ni oxide electrode due to a low oxygen overpotential considerably sooner than the charging of this electrode is finished (approximately at 70–80% charge) which causes an overpressure of oxygen. This overpressure increases continuously up to the end of charging (overcharging).

The hydrogen of electrolytic origin should appear in the gas mixture considerably later due to the access capacity of the zinc electrode. Unfortunately, before the full charging of Ni oxide electrode and therefore before the termination of charging, hydrogen is evolved in small amounts at the zinc electrode. This small amount of hydrogen is usually removed by the auxiliary catalytic electrode connected through a diode and a resistor to the positive electrode [45, 93, 95]. The hydrogen is absorbed and forms water by oxidation. The auxiliary electrode is a small sintered Ni plate doped with Pt and impregnated with PTFE. The location of the auxiliary electrode is visible in Fig. 1. The potential difference between auxiliary and positive electrode E_{AP} is suddenly changed at the end of charging (Fig. 2) since the auxiliary electrode
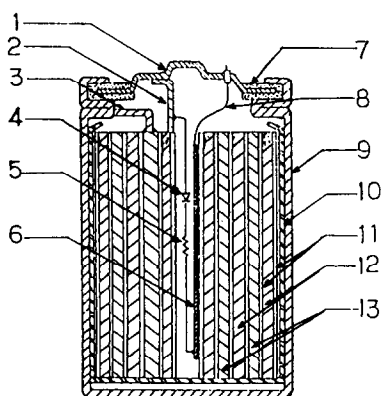

Fig. 1. Cross section of Toshiba long cycle life Ni–Zn cylindrical cell. 1, top metal cap of positive electrode; 2, positive metal lead; 3, negative metal lead; 4, silicon diode; 5, resistor; 6, auxiliary electrode; 7, insulating seal; 8, lead wire of auxiliary electrode; 9, outer negative can; 10, heat shrinkable tube; 11, separator; 12, Ni positive electrode; 13, Zn negative electrode.
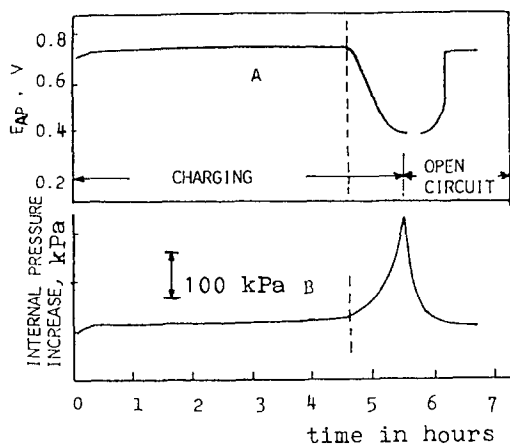
Fig. 2. Time dependence of potential difference between positive and auxiliary electrode (A) and the internal pressure during charging process (B).

is depolarized by oxygen formed at the positive electrode. At the same time, the internal pressure increases for the same reason. When the charging circuit is turned off and the oxygen is reduced at the Zn electrode, the potential difference recovers its initial value. During charging a constant current is applied until oxygen starts to evolve in the cell. Charging current cut off timing is determined by E_{AP}. The purpose of the diode is to maintain the activity of the auxiliary electrode by reducing unfavorable current flow to the positive electrode.

In the case of good access of oxygen to the negative electrode and fulfilment of other conditions the so-called oxygen cycle can start: the oxygen produced at the positive electrode passes across the separator to the negative where it is reduced. A certain balance between the amount of oxygen formed and the amount of oxygen reduced is established resulting in overpressure. The process of reduction of oxygen continues also in the open circuit state and in the discharge phase, and the overpressure in the cell falls.

In the case of a low rate of oxygen reduction on zinc (because of the diffusion limitations through the separators), auxiliary oxygen recombination electrodes with Ag–Hg or active carbon catalysts are used. The auxiliary electrodes are connected directly or over a resistor to the negative electrode [14, 74]. The oxygen recombination electrodes consist of a PTFE-bonded Ag–Hg catalyst on a Ag current collector and are wrapped in polyamide felt and radiation grafted polyethylene [74] or they are fuel cell electrode types with a PTFE film backing laminated to the back side to prevent flooding [14]. Both catalytic electrodes have higher hydrogen overpotentials than zinc which makes possible a direct connection without self-discharge of the negative electrode.

It seems lately that the problem of a suitable separator system with a sufficient oxygen diffusion rate to the negative electrode has been solved. Also the modification of the composition of the zinc electrode aids the prevention of hydrogen evolution so that recent experimental cells have no auxiliary recombination electrodes [27, 60, 61, 75, 76].

In spite of all measures for the prevention of gas evolution, in a sealed Ni–Zn accumulator one must cope with the evolution of oxygen and hydrogen and especially with their accumulation. While with small Ni–Cd accumulators total sealing is possible

—without any valve— with Ni–Zn sealed accumulators the valve must be a component of the accumulator. The situation is similar to that at sealed lead/acid accumulators. At a given overpressure of gases inside the accumulator the valve is opened and the accumulated gas can escape. A small valve (e.g. membrane type) is a simple device not complicating the accumulator; it contributes to the safety of operation. Examples of vents in Ni–Zn accumulators are visible on cells presented by Matsushita [60] and Toshiba [45].

3.3. Problem of separator system

A suitable separator system is essential for the good cycle life of Ni–Zn cells. It determines also the possibility of employing the oxygen cycle for removing the oxygen formed during the charging and overcharging of cells.

As mentioned above, the 'annoying' Zn electrode (in comparison with the 'good' Cd electrode) requires a specially reliable separator system with regard to preventing dendrite growth.

Some part of a separator system serves as an electrolyte retainer (electrolyte reservoir) since the porosity of electrodes is not sufficient to cover the electrolyte requirements of electrodes.

The separator system based on cellulose fulfils some requirements, however it is unsuitable for long-term operation since it is gradually oxidized to form carbonate in the electrolyte. The final result is a decrease of the cell voltage and a loss of the A h capacity of the positive electrode.

Much work has been carried out on separators for sealed Ni–Zn cells. Already in 1972 inorganic materials based on cerium oxyhydroxide bound with a plastic were used [13]. Thin foils prepared by the rolling technique were good separators as for the protection against Zn dendrites, however they substantially hindered the diffusion of oxygen to zinc so that the oxygen recombination rate was too low and hence auxiliary electrodes were used.

A similar situation was met with the use of commercial ZrO_2-on-asbestos separators and with radiation grafted polyethylene separators [74]. In 1978 microporous polypropylene foils were used as a separator [84]; later this material was more frequently applied [24, 26, 27, 48, 62, 69, 107], commonly traded as Celgard (Celanese, USA). Also non-woven nylon [45] and non-woven polypropylene fabric [43, 44] were used as separators.

The most common material used as an electrolyte retainer is the non-woven polyamide felt (e.g. Pellon). It is usually placed next to the positive electrodes. In cells working with the oxygen cycle, the separator system and the electrolyte retainer must not be fully flooded with the electrolyte so that the access of oxygen to the zinc electrode is possible.

4. Practical realization of sealed Ni–Zn cells

In the 1970s nickel–zinc cells were those developed for testing purposes in the USA (General Motors, Electrochimica Corp., Gould, Energy Research Corp. and Lawrence Berkeley) and in Japan (Tokyo Shibaura Electric Co., Sanyo Electric Co., Matsushita Electric Industrial Co., Toshiba Corp., Yuasa Battery Co. and Japan Storage Battery). The first cells usually contained auxiliary recombination electrodes, which have become superfluous nowadays because of the widespread use of additives in the zinc electrode and by the realization of the oxygen cycle.

4.1. Cells of Energy Research Corp.

This company was apparently the first one to publish the relevant research results. Kober and Charkey [77] (at that time at Yardney Electric Corp.) published results on sealed 4 A h cells in 1970. These cells were charged at constant voltage and on floating at 1.90 V for 30 day periods. The cells were then discharged at $C/2$ rate to determine if extended float adversely affected the available capacity. It was found that extended periods of time on float (total 120 days) had no effect on discharge capacity of sealed cells. The capacity retention of charged sealed Ni–Zn cells as a function of stand time was similar to that of Ni–Cd cells: the greatest loss of capacity occurred during the first few weeks.

Soon afterwards Energy Research Corp. [13, 78, 79] developed sealed Ni–Zn rechargeable batteries with a lifetime of at least 300 cycles at 63% DOD (depth of discharge). The 5 A h cells included ten pressed composite nickel oxide electrodes and eleven plastic-bonded ZnO electrodes. They were separated by one layer of Pellon polyamide (adjacent to the positives), followed by two layers of inorganic separators based on a metal hydroxide bound with PTFE. These could be characterized as layered structures containing loosely bound water of hydration, which facilitates proton transfer through the separator. The separator material was prepared from ultrafine particles of the particular compounds, blended with PTFE or with a plastic binder and worked into flexible sheets of various thickness and uniform porosity. The new inorganic separators were chemically more stable than the classical cellulose separators, prevented penetration of zinc dendrites and contributed to the increase of capacity maintenance. The cell electrolyte was 40% KOH with 1% LiOH as additive. The oxygen reduction rate at the zinc electrode was too low because of diffusion limitation due to the separators. Therefore, the cells were provided with two auxiliary electrodes containing Teflon-bonded electrocatalysts (Ag–Hg or active carbon). Such electrodes have a higher hydrogen overpotential than zinc, and so direct coupling through a resistor was possible without self-discharge of the Zn electrodes. The auxiliary electrodes were capable of sustaining reduction of oxygen at about the $C/10$ rate. After 70 h overcharging at 0.4 A the internal pressure in the cells with Ag–Hg and carbon catalyst was 187 and 374 kPa, respectively, and the gas phase contained as little as 1% of hydrogen. At the Ag–Hg electrode the reduction of oxygen proceeded through several steps to OH^- ions (with a 4 electron transfer) whereas on active carbon the products were OH^- and HO_2^- ions (with a 2 electron transfer). During a cycle life test with 62% DOD the best results were obtained with cells containing the Ag–Hg catalyst: the pressure build-up varied between 144 and 180 kPa at the 10th and 180th cycle. No zinc was found in the separator after 315 cycles, however the thickness of the zinc electrode increased by 32% and that of the positive by 20%. The major technological problem, the shape changes of the zinc electrode, was probably moderated by the addition of portland cement [80]. Electrodes containing 5–30% of portland cement attained 260 cycles with 70% of the initial capacity, whereas those without this additive sustained only 100 cycles.

4.2. Cells of Electrochimica Corp.

Besides large vented 225 A h accumulators, small 12 A h prismatic cells were also developed by this firm [32]. These contained four negative and three positive electrodes under starved electrolyte conditions. During cycle life tests, the DOD was 75–80% except for the 260th cycle where the cells were deeply discharged. The mean capacity decrease was 0.06 per cycle up to about 300 cycles. The current–voltage characteristics of fully charged cells were practically changeless during cycling up to

the 335th cycle and their internal resistance was 0.0175 Ω. A lifetime of 600–800 cycles seems realistic with regard to the stability of the zinc electrode (use of borates or phosphates as additives in the electrolyte [30–32]).

4.3. Cells of Gould

According to the patent literature [81, 82], the cells were cylindrical and the anode mix was blended with a styrene-butadiene binder. After complete discharge, almost no elemental zinc was present in the negative electrode. The separator consisted of several layers and the electrolyte support was placed between it and the cathode. Hydrogen formed during cell operation was oxidized on a catalyst (e.g. Ag) incorporated in the cathode. The internal pressure in the cells was low and no venting was necessary during high-rate cycling.

4.4. Cells of the Lawrence Berkeley Laboratory

Besides vented cells, hermetically sealed cells under starved electrolyte conditions have been studied during recent years [27]. Potassium fluoride or carbonate addition into the electrolyte was used to combat the shape changes of Zn electrodes. The construction of the sealed cells was similar to that of the vented cells: they contained pasted Zn electrodes, whose typical composition was ZnO 94%, PbO 2% and PTFE 4%; the current collector was a lead-plated copper stretch metal; the nickel oxide electrodes were of the sintered type, their capacity amounted to 1/3 of that of the negative electrodes and they were wrapped in a foil of Pellon 2524. The separator consisted of three layers of microporous polypropylene Celgard 3401, in which the Zn electrodes were wrapped and heat sealed. The electrode pack was pressed together at 27.6 kPa. The electrolyte contained 6.8 M KOH, 0.6 M LiOH and 0.78 M ZnO.

The cells were initially under vacuum, and after several cycles a steady pressure of about 100 kPa was attained as a result of the oxygen cycle (evolution of oxygen at the positive electrode at the end of charge and its reduction at the negative). The cells cycled at 100% DOD reached the test-termination criterion after 189 cycles showing only moderate shape change (as indicated by *in situ* X-ray photographs) and no visible dendrites. These are obviously destroyed by oxidation in the presence of oxygen as proposed by Stark [83] and as evidenced by the following observation. The cell was severely overcharged in the presence of an excess of electrolyte (2.5 M KOH, 2.5 M K_2CO_3, 0.5 M LiOH and 0.15 M ZnO) until many large dendrites appeared around the edges of the negative electrodes, and cycled in the sealed, starved-electrolyte condition. After several cycles all of the dendrites vanished except one which was coated with a white layer of ZnO. It is anticipated that sealed starved-electrolyte cells will suffer less dendrite short circuits than vented, electrolyte-flooded cells.

4.5. Cells of General Motors

McBreen [74] studied test cells assembled from two Zn electrodes (pressed from ZnO + 2% HgO) and three plastic-bonded NiOOH electrodes of dimensions 7.9 × 4.8 cm. The theoretical capacity of the positive electrodes was 2.4 A h and that of the negative electrodes was higher by a factor of 3.6. The cells contained two auxiliary electrodes for oxygen reduction placed vertically. They contained a PTFE-bonded Ag–Hg catalyst on a silver current collector. The electrolyte was 37% KOH saturated with ZnO and contained some LiOH. The separator was either commercial asbestos-supported ZrO_2 or radiation grafted polyethylene. Polyamide felt served as electrolyte carrier. The cells were cycled with the auxiliary electrodes on open circuit until the gas pressure exceeded the atmospheric. The auxiliary electrodes were then

connected to the negative terminal through a shunt. The internal pressure during cycling was about the same as at the end of the test (105 cycles), about 110 kPa, and the content of hydrogen increased somewhat (up to 38% in some cases). During the first few cycles, oxygen was completely reduced at the Zn electrodes. The cells served for studying the influence of $Ni(OH)_2$ and $Co(OH)_2$ in Zn electrodes on hydrogen evolution (no effect was found) as well as the influence of the capacity reserve of Zn electrodes on capacity maintenance.

Nickel–zinc cells were also studied at GM in the seventies as candidates for use in electric vehicles; sealed cells with electrodes up to 250 cm^2 area were developed. The Zn electrodes had a cheap current collector (Cu or low-carbon steel) and were prepared by a vacuum-table process [84, 85]. The positive electrodes were of a non-sintered type, lightweight and cheap. Microporous polypropylene and inorganic/organic materials served as separators, and the cells had a service life of about 200 cycles when operated at 1–3 h rate, 100 % DOD, to 80% of the initial capacity, or about 400 cycles to 60% of the original capacity. Cells with electrodes of 250 cm^2 area and of 125 A h capacity has a specific energy of 70–75 W h/kg. Their service life was 90 cycles under simulated conditions of city traffic, and a rapid improvement was anticipated.

Although no further data about sealed Ni–Zn cells were published, it is apparent that research and development at GM continue [25, 39, 86]. This is evidenced by studies of the formation and decomposition kinetics of calcium zincate in 20% KOH [39, 86], of shape changes of zinc electrodes [87], of the influence of KOH concentration on the service life of Ni–Zn cells [25, 40], of changes of the electrolyte composition during cycling [88], and of a new negative electrode prepared from calcium zincate [48].

4.6. Cells of Matsushita

Sealed cells with a sintered Ni cathode and a pasted Zn anode were developed at the beginning of the seventies [89, 90]. The anode was prepared from powdered ZnO with the addition of 1% $Ca(OH)_2$ and 0.05% sodium lignosulfonate mixed with an aqueous solution of polyvinyl alcohol. The separator was porous polyethylene impregnated with $Ca(OH)_2$ and cellophane. The cells were provided with a safety valve and a hydrophobized catalyst (graphite containing 1% of Pd). The electrolyte was 4–6 M KOH whose quantity corresponded to 1.9–2 ml per A h of theoretical capacity of the anode.

The cells were capable of charging at 1 h rate, during which a small overpressure was established in them. Batteries were assembled from five cathodes and four anodes with a capacity ratio 2:5. Their service life was 160 cycles (2 h discharge and 10 h charge to 150%), whereas similar cells containing less electrolyte showed only one half of the capacity already after 20 cycles.

Other patents [91, 92] refer to cylindrical cells with rolled (wound) electrodes. The inner wall of the battery case was coated with a special polymer film lining (ethylene–vinyl acetate copolymer, PVC, polyethylene, polypropylene and/or polyamide). This resulted in a four-fold decrease of the evolution of hydrogen after 100 cycles as compared to uncoated cell casing. Batteries described in the patents had a long service life. Small additions of In and/or Pb into zinc-amalgam based anodes were reported [60, 61] to prevent the formation of zinc dendrites and thus to ensure long cycle life of the battery.

4.7. Cells of Toshiba

Cylindrical sealed Ni–Zn cells with rolled (wound) electrodes were developed during the seventies [93, 94]. The cells contained an auxiliary catalytic hydrogen

electrode [45, 93, 95] described earlier (see Section 3.2). The capacity of 1.6 A h cells dropped by 38% after 75 cycles at 100% DOD.

A new charging procedure called open circuit voltage sensing method was developed by Toshiba [96]: the open circuit voltage (OCV) of the cell, which depends on the state-of-charge, was as follows. The charging proceeded in the pulse regime and the value of OCV after charging and a short pulse discharge was compared with that of a fully charged cell (Fig. 3). If the current OCV was lower than the final (present) value, the pulse charging continued until the full charge was attained. Thus, the method prevented the overcharge of the cell, which is harmful from the point of view of shape changes of the anode. In addition the discharge pulse seems to quickly dissolve Zn dendrites formed during the charging phase.

The problem of zinc dendrites was solved by applying a separator based on nylon non-woven fabric with poly(vinylalcohol) and boric acid. The separator had a low electrolytic resistance and resisted penetration of zincate ions.

Many additions for suppression of zinc dendrites were tested [45]: Bi_2O_3 combined with $Ca(OH)_2$ performed best. The electrodes for sealed Ni–Zn cells were prepared from a mixture of ZnO, Zn, Bi_2O_3 and $Ca(OH)_2$ bonded with PTFE and rolled onto a current collector.

The cells of sizes AA, C and D had capacities of 0.45, 1.5 and 3.5 A h and contained the mentioned type of anode and a sintered cathode. Cells of the size D attained 500 cycles by using the OCV sensing method.

Another patent of Toshiba [97] envisages the use of $LaNi_5$ in cylindrical sealed Ni–Zn cells for absorption of hydrogen, however catalytic hydrogen electrodes are apparently preferred.

4.8. Cells of Tokyo Shibaura Electric Co. [43, 44, 98]

Sealed Ni–Zn cells were composed of a plastic-bonded anode, sintered cathode, and non-woven polypropylene fabric as separator. The anode active material consisted
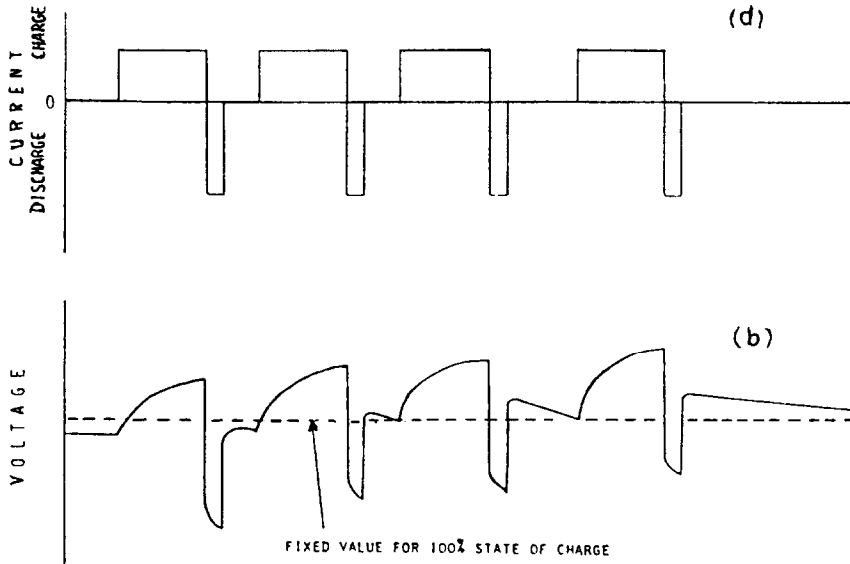

Fig. 3. Current and voltage change for open circuit voltage sensing method.

of ZnO, Zn, Ca(OH)$_2$, Bi$_2$O$_3$, powdered PTFE and a non-ionic surfactant (Triton X-100). The mixture was made up to a paste with water and spread on to a perforated Cu foil. The anode retained a sufficient quantity of electrolyte and had a favourable discharge characteristics. Cylindrical cells with similar electrodes were reported to have a capacity of 1.7 A h and service life of 100 cycles.

According to ref. 98 cells of size C and AA with nominal capacities of 1.5 and 0.45 A h were constructed and realized. At size C the specific energies of 37 and 35 W h/kg were reached at discharge with 300 and 600 mA respectively. These values are 50% better than for Ni–Cd batteries. The cells also showed a very good performance at low temperatures (-15 °C). It followed from the analysis of cell failures that failures were connected in all cases with the gasing (oxygen) of cells. The cells of size C were charged during cycling tests with 1 C rate only to 50% because the evolution of oxygen begins usually at 70–80% charge of a cell. In that case the life of 200 cycles was measured in contrast to 100% charge with only several tens of cycles. During the cycling test (at each cycle cells charged at 0.2 C rate up to 1.5 A h), 90% of the initial capacity was retained even after 200 cycles in the case of a light drain discharge (0.2 C). Also the shelf life of the batteries was relatively good: the amount of charge decreased to a 1/2 of the initial amount after 30 days at 25 °C. The charge reduction was associated with self-discharge of the nickel oxide electrode. The mentioned cells were recommended as power sources for electric tools, razors, tape recorder, toys, search lights, calculators etc.

4.9. Cells of Sanyo

Sealed Ni–Zn cells, according to patents of this firm, underwent a long development. Auxiliary catalytic electrodes, mentioned in the first patents [99–101] were based mainly on hydrophobized Pt or Pd on a nickel or carbon support, eventually in combination with LaNi$_5$ as absorbent [102]; they were usually placed on the wound electrode pack. In another patent [103] the Zn electrode was electrically connected to an electrode from a more noble metal, which was capable of reducing oxygen. A typical example was a Cd electrode formed from a mixture of powdered Cd, CdO and acetylene black. The ionic conduction between the Cd and Ni electrodes was prevented by a hydrophobic membrane. Addition of 1–7% K$_3$PO$_4$ into the electrolyte has been recommended [33].

According to the patented manufacturing process [104], the sintered nickel oxide cathode is charged to 120–130% capacity prior to hermetization of the cell; the anode capacity is in a four-fold excess against the cathode [105]. Such a cell has a lower internal pressure during cycling, a slower pressure increase and a longer service life than control cells. Another patent [106] recommends charging of the cathode to 20% of the theoretical capacity of the anode prior to sealing; this results in an increase of the service life to 523 cycles compared to 358 cycles without this treatment (anode consisted of ZnO + 5% CdO; charging to 120% capacity, discharging to 1.2 V at 4 h rate). The cells did not leak.

The separator consists of two or more thin (10–40 μm) microporous foils (e.g. polypropylene) and a non-woven fabric (e.g. nylon) as electrolyte retainer [107]. The foil facing the cathode is made hydrophilic, that facing the anode is untreated. This ensures a service life of 410 cycles (to 75% of the initial capacity) and maximum internal pressure of 800 kPa after 100 cycles compared to 240–300 cycles and 600–3200 kPa for the control battery.

The anodes have some special features. The content of binder in the active material on both sides of the electrode is not the same [59]: the concentration ratio of the binder should be in the range 1:(1.05–1.2) and the overall concentration 5%.

A somewhat similar proposal refers to an anode [108] in which the inner layer (facing the centre of the cell) of the wound anode has a lower zinc content than the outer layer; the ratio of their zinc content should be 1:(1.1–1.75) and the Zn particles in the outer layer should be smaller. Such a structure of the anode leads to a longer cycle life.

A further improvement of the cycle life was achieved by additives in the zinc electrode [59, 76, 109, 110]. Many metal oxides were tested (TiO_2, V_2O_5, MoO_3, WO_3, Fe_2O_3, CuO, HgO, Al_2O_3, Ge_2O_3, In_2O_3, Tl_2O_3, SnO_2, PbO, Bi_2O_3). Combined addition of 2.5% In_2O_3 and 2.5% Tl_2O_3 into a pasted Zn electrode (in an R-6 type cell) proved best, causing an increase of the cycle life from 100 to 500 cycles. The oxides are reduced in the zinc anode to the metals, which have a high overpotential of hydrogen and cause negligible evolution of hydrogen (they act as corrosion inhibitors). The reduced metals form a metal net in the zinc electrode improving the conductivity of the Zn electrode and hence the discharge characteristic of the Zn electrode.

4.10. Cells of Yuasa

Information about maintenance-free sealed rechargeable Ni–Zn batteries was published in 1984 [111]. Their specific energy is 62 W h/kg, cycle life 100–140 or 320–360 cycles at 100 or 60% DOD, respectively. The anodes are made by rolling a layer of Zn, ZnO and PTFE on a Cu current collector; the cathodes are sintered nickel oxide electrodes and are enclosed in the separator together with an electrolyte carrier [112].

3 A h sealed Ni–Zn batteries contained two sintered Ni cathodes contacting an electrolyte support and wrapped in a separator (cellophane, polyamide or polyolefine foil), four anodes made from zinc or ZnO–PTFE mixture pressed on to a copper or silver current collector, and a KOH solution (density 1.30–1.40 g/cm^3), which occupied 90% of the pore volume of the cell components [113]. An electrolyte retainer covered the anodes on the sides facing the cathodes, while the other sides were in contact with a non-woven PTFE of polypropylene fabric. The discharge voltage of the battery was higher by 100 mV than that of the battery without a hydrophobic layer.

A similar sealed cell consisted of a nickel oxide cathode and one or two zinc anodes with a hydrophobic PTFE layer on the anode surface opposite to the cathode and a water-repelling non-woven PTFE fabric on the resin layer [114].

Still other Ni–Zn cells [115] contained Ni cathodes prepared by pasting a sintered Ni fibre mat with a mixture of 95% $Ni(OH)_2$, 5% Ni and polyvinylalcohol. Their specific energy was 70 W h/kg.

A maintenance-free Ni–Zn battery for portable equipment was developed in recent years [75]. The battery is shockproof, its specific energy is 57 W h/kg and service life about 200 cycles at 100% DOD.

To prevent the formation of Zn dendrites in sealed Ni–Zn batteries, the Zn anode on the end of the electrode stack has an oxygen-permeable layer attached to its side opposing the stack and the other side of the anode. Both sides of the other anodes in the stack are covered with an oxygen non-permeable electrolyte retainer [116].

A long cycle life is also expected in batteries with cathodes having a different overpotential of oxygen on different parts of the electrode stack and with anodes covered with non-woven hydrophobic layers [117].

Anodes having a current collector of a stable and cheap Cu–Sn alloy with a high overpotential of hydrogen are probably also suitable for sealed cells [118].

4.11. Cells of Japan Storage Battery

From the accessible literature [119] it is only known that this firm constructed a prismatic sealed cell PZ-60 with an output voltage of 1.6 V, capacity of 550 mA h and energy density of 163 W h/l.

5. Conclusions

Sealed Ni–Zn cells are prospective power sources particularly for portable electronic devices and electric appliances of a low power. Commercial cells must be provided with pressure release valves because of the possibility of Zn electrode gasing during the operation. The regulator controlled charging regime is considered for these cells. At present, reduction of oxygen on the Zn electrode (oxygen cycle) is not a great problem owing to the new separator materials. Also, dendrite formation in the sealed Ni–Zn cells is minimal. The addition of $Ca(OH)_2$ into the anode active mass appears beneficial. The application of sintered nickel oxide electrodes as positives is considered.

6. Acknowledgement

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