Sealed Ni–Zn cells, 1996–1998

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Abstract

Progress with sealed Ni–Zn cells in the period 1996–1998 is reviewed. No dramatic improvements stemming from R&D on cells were observed. Presently, the cells of Energy Research (ERC) seem to be the best and most widely used. © 2000 Elsevier Science S.A. All rights reserved.
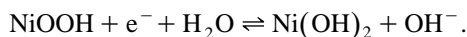
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1. Introduction

The nickel–zinc (Ni–Zn) cell undergoes the following electrochemical reactions:

$$Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$$

and

$$NiOOH + e^- + H_2O \rightleftharpoons Ni(OH)_2 + OH^-.$$
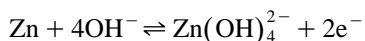
In the sealed system, the electroreduction of oxygen — a necessary condition for the sealing of cells — must also proceed. During the charging of a cell, and particularly during its overcharging, the oxygen, which is evolved at the positive electrode, must be electroreduced at the negative to prevent an increase of the internal cell pressure.

This paper is a review of contributions dated 1996–1998. Earlier works have already been reviewed several times [1–5].

2. Cell components

2.1. Anodes

No great progress with the negative electrode has been observed in recent years. The electrodes are invariably prepared, either by pasting or by pressing of the active mass. The main problems of Zn electrodes remain to be solved, viz. shape change during cycling, dendrite growth during charging, passivation of electrodes, and the evolution of hydrogen on electrodes. Which of these problems were addressed?

In the patent of Charkey [6,7], in dealing with sealed Zn secondary batteries, a Zn electrode, with a decreased solubility due to the use of an electrolyte with a low KOH concentration, is described. A Zn anode comprises a Zn active material (ZnO, Ba(OH)$_2$ or Sr(OH)$_2$) and a conductive matrix including a metallic oxide (PbO, Bi$_2$O$_3$, CdO, Ga$_2$O$_3$, and Tl$_2$O$_3$), which is more electropositive than Zn. The additives mentioned prevent the obvious shape changes of Zn electrodes.

The Russians [8] reported a remarkable service life of 450–500 cycles at Zn electrodes using additives (depassivators and surfactants). The effect of additives in the active mass is often studied. Shivkumar et al. [9] found that the addition of HgO is favourable, not only due to its known property that it influences the hydrogen overvoltage, but also because it minimises corrosion and shape change of electrodes. As to TiO$_2$, its effect surpasses the effect of HgO. For Pb$_3$O$_4$, the corrosion behaviour, as well as aging, is fairly good. However, this additive imparts a disadvantage of Pb being deposited on the counter electrode, which would be a setback from the battery point of view. Besides the ZnO and Ca(OH)$_2$ addition to powdered zinc used in pressed and sintered electrodes, the effect of other additives on the performance of Zn electrodes in Ni–Zn batteries was studied [10,11]. The references [10,11], unfortunately, give neither details nor results.

A decreased shape change, a smaller dendrite growth, and hence, a higher cycle life, were observed at electrodes provided with current collectors covered with lead [12].

Jacus and Rose [13,14] recommend the copper alloy containing preferably 1–6% Si as a material for current

collectors; the alloy mentioned is less susceptible to irreversible oxidation than the known brass current collectors.

Ionomers (i.e., polymers with ions) in contact with Zn impede strongly the dissolution of the Zn discharge product in an electrolyte, by which means the dendrite growth and the shape change of electrodes are reduced [15]. This was confirmed by the scanning electron microscopy of the surface of Zn electrodes before and after 50 charge/discharge cycles. A low-cost zinc ionomer, derived from styrot–acrylic acid copolymer, has been used in Zn electrodes. These Zn ionomers display excellent film formation and excellent stability in alkaline solutions.

Ohms et al. [16] used in Ni–Zn cells, with the RECOM principle (i.e., sealed cells), Zn electrodes provided with a copper foam collector filled with a mixture of ZnO with an added $Ca(OH)_2$, and with a small amount of PbO and PTFE. The ratio $Ca(OH)_2/ZnO$ corresponds to the composition of the compound $CaZn_2(OH)_6 \cdot H_2O$. The Ampere hour capacity of negatives in cells is fourfold towards the capacity of positives.

The problems with the evolution of gases are evidently not fully solved in the Korean-sealed Ni–Zn cells. It is not only oxygen that is liberated during charging, but also hydrogen, by the corrosion of the Zn electrodes. In the 25 A h cells, an overpressure of hydrogen of 1–2.8 atm is observed. The amount of hydrogen evolved is dependent on the amount and type of corrosion-inhibiting additives (HgO, PbO, In_2O_3). The overpressure of hydrogen impacts the ionization of oxygen on the Zn electrodes [17].

Chang et al. [18] studied in detail the passivation of Zn electrodes. They found that a higher concentration of the alkaline electrolyte affects the passivation potential, and therefore, the passivation of electrodes. In 8.5 M KOH, a relative thick passivation film is formed, whereas in 1 M KOH, the film is thinner. The passivation is slowed down by the addition of Hg, Pb, and Cd, to the Zn mass.

Doo et al. [19] measured the electrochemical impedances of porous Zn electrodes at different stages of charge (SOC). Instead of a simple RC circuit, they used the Davidson–Cole model which considers the porosity of an electrode. The impedance spectrum of the Zn electrode is dramatically changed during the shorting of a cell, and therefore, the impedance technique is a good diagnostic method for determining the charge state of Ni–Zn batteries.

2.2. Cathodes

A method for fabricating lightweight nickel oxide electrodes has been developed at Lawrence Berkeley National Laboratory [20]. Substrate materials of high porosity (FN 090 Nickel Felt Sorapec and Fibrex 50/50) are electrochemically impregnated with Ni and Co nitrates (galvanostatically at 35–50 mA/cm^2, pH = 3). Electrodes, using the Fibrex substrate, were very stable (400 cycles) with

specific capacities of 91–93 mA h/g in highly alkaline electrolytes ($\sim$ 7 M KOH).

The cells of Deutsche Automobil Gesselschaft (DAUG) [16] are provided with fibrous nickel oxide electrodes with a capacity of 1.6 A h. These electrodes are connected with hydrogen-recombinating electrodes.

2.3. Electrolytes

Electrolytes with reduced alkalinity are still sought for Ni–Zn cells. Potassium hydroxide of molarity 3.2–4.5, saturated with ZnO, and with 2 M KF, 2 M K_2CO_3, and 0.5 M LiF additives are recommended by Adler et al. [21] as a tentative optimum. A similar concentration of KOH (3.5–5 M), saturated with ZnO, was used in the DAUG cells [16]. Taucher-Mautner and Kordesch [22] used, however, somewhat more concentrated KOH solutions (7 M). KOH, 8.6 M, is applied in Japanese cells [23].

2.4. Separators

The separation system often determines the life of cells. It is necessary to separate both anodes and cathodes, and, in addition, to use a suitable carrier of an electrolyte as its reservoir. Also, in the new papers about sealed Ni–Zn cells, materials which have been proven and well-tried are mentioned: non-woven Nylon (Pelon) and polyolefine membranes (Celgard), which are always in several layers [24]. In the DAUG cells [16], the TiO_2 deposited in a polyethylene matrix serves as a main separator and a fleece from hydrophilic polypropylene fibers as an electrolyte carrier. Again, cellophane was used [23].

3. The cell studied

3.1. Samsung Advanced Institute of Technology (SAIT; South Korea)

SAIT has continued with the development of cells described earlier [5]. In 1996, it published results on cells designated for electric vehicles [25]. Single cells of capacity 180 A h and voltage 1.6 V were used, besides modules 50 A h–8 V and 80 A h–6.4 V. At the cell level, a specific energy of 70 W h/kg and a life of 300 cycles at 80% DOD were measured. The range of an electrovehicle equipped with modules was almost 200 km for one discharge of cells. Both modules were tested as power sources for scooters and new versions of electrovehicles.

3.2. Lawrence Berkeley National Laboratory (USA)

An optimized electrolyte with a reduced alkalinity containing F^- and CO_3^- ions was used in the experimental cells with a capacity of 1.4 A h. The cycle life perfor-

mance of cells is 425–460 cycles to 80% of initial capacity compared to 75–100 cycles for the conventional highly alkaline electrolyte [21].

3.3. Yuasa and Kyushu (Japan)

These Japanese institutions developed jointly the Ni–Zn batteries for electric vehicles [23]. One of the results is a Ni—Zn battery (nominal capacity 30 A h, nominal voltage 17 V, weight 8.4 kg, size $178 \times 166 \times 172$ mm^3) for scooters. Its specific energy amounted to 65 W h/kg. The life of the battery tested in the laboratory was 400 cycles. In city traffic, the scooter has a daily range of 20 km for one charge of the battery. According to the measured discharge profile, a maximum current of 80 A is observed. Batteries provided with different separators (Celgard, Celgard covered with Ni or Celgard + cellophane), with different additives, and with different electrolytes, were tested; in some of them, a life of 100 cycles was noted.

3.4. Energy Research (ERC; USA)

The basis of the success of ERC cells is the good control of the problems associated with Zn electrodes. Zinc anodes comprise either a Zn active material, ZnO and $Ca(OH)_2$ [26,27] or ZnO, $Ba(OH)_2$, or $Sr(OH)_2$ [6,7]. In the second version, the Zn anode is split into electrode assemblies separated by a porous hydrophilic element. Electrodes of both polarities are prepared by the rolling technique [24]. The ERC cells are able to supply over 60 W h/kg at 1 C discharge rate and a power of 450 W/kg at 12 C rate. At the same time, the life is higher than 600 cycles at 80% DOD and 11,000 cycles at 10% DOD [28]. ERC produces prismatic cells of 2–15 A h capacity. The battery for a hybrid electric vehicle [24], with a voltage of 220 V, was assembled.

The sealed Ni–Zn cells from ERC are presently the best ones obtainable, not only from the electrochemical point of view, but also according to other criteria (ecological, economical, etc.). It seems that the ERC cells are even used for applications in medicine as a power source for a left ventricular assist device, which is a surgically implanted pump assisting the heart in the circulation of blood throughout the body. The first-generation prototype Ni–Zn cells provide 60 W h/kg (73 W h/l), a weight saving of more than 35% in comparison with the lead–acid battery in current use [29]. Further optimization of this design will result in a projected energy density of 70 W h/kg by reducing the cell weight by 15%. The developed battery (size $24.4 \times 23.4 \times 61$ mm^3, voltage 11.6 V, weight 440 g) is a seven-cell unit. The battery delivers more than 600 deep discharge cycles. The developed batteries have important implications for both medical and non-medical applications.

3.5. Deutsche Automobil Gesellschaft (Germany)

DAUG — its research center in Esslingen — presented in 1997 Ni–Zn cells with the RECOM principle [16]. These cells are provided with two recombination electrodes for the removal of excess oxygen and hydrogen. For the time being, the laboratory cells, each with capacities of 1.6 A h given by the positive electrodes in Plexi cases, are tested. The cycling of cells is carried out at the 0.2 rate: charging factor 1.2, cut-off voltage 1.1 V. The decrease of capacity with cycling is practically linear: 0.08–0.13% per cycle. After 1100 cycles, the initial capacity fell to 0.45 A h due to the ''poisoning'' of positive electrodes by the deposited zinc.

3.6. Technical University Graz (Austria)

The prototypes of small cylindrical Ni–Zn cells of sizes AA (R 6) and C (R 14) were constructed in the Institute of Inorganic Technology [22]: the pelletized cathode MnO_2 mixture of commercial primary cells was substituted by a porous nickel electrode (usually sintered). The anode of cells is made of the gel mass of KOH + Zn powder or ZnO. The reliable separation system is formed by two layers of laminated cellulose and non-woven polyamide fabric. The cylindrical cells with an OCV of 1.8 V give capacities of 0.5 and 1.5 A h, respectively, depending on load, DOD, and cut-off voltage. The assumed life of cells is from 50 to 100 cycles (discharged to 0.8 V). Short-circuit currents of 10–15 A were measured. The slow (15–24 h) charge of cells is controlled (with constant voltage 1.9 V). Unfortunately, as for other nickel systems, the self-discharge of cells at elevated temperature is the same as for Ni–Cd or Ni–MeH cells.

4. Conclusions

Sealed Ni–Zn cells of ERC are clearly, at present, the best quality obtainable, and are widely used in practice.

Acknowledgements

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