Development of Ni–Zn cells

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Abstract

This paper describes experimental work relating to the development of long cycle life Ni–Zn cells. In all cases, these cells were constructed with a large excess of electrolyte such that, at the oxidized state, the greater part of the zinc was dissolved as zincate ions. Two cell types were investigated: cells with flowing electrolyte and cells with stationary electrolyte. The second type required a combination of additives in solution and pulsed current during charge in order to obtain good cycle life.

Résumé

Ce papier décrit les filières qui ont été suivies dans le but de mettre au point des accumulateurs Ni–Zn présentant une longévité satisfaisante en cyclage. Dans tous les cas étudiés, ces accumulateurs comportent un grand excès d'électrolyte afin que la majeure partie du zinc à l'état oxydé soit sous forme d'ions zincates. Deux voies ont été étudiées, l'accumulateur comportant un électrolyte soit circulant soit immobile. Ce second type d'accumulateur impose de coupler l'ajout d'additifs en solution à un régime de charge pulsée afin d'obtenir une longévité acceptable.

1. Introduction

For over 20 years the Ni–Zn battery has given rise to numerous studies aimed at making it operational. The Ni–Zn couple offers significant benefits as regards its technical and, above all, economic characteristics. Unfortunately, most of the studies have not resulted in a sufficiently useful life during repeated charging and discharging cycles. This situation is basically linked with the fact that metallic zinc reconstitution during recharging does not lead to compact deposits but to dendritic or powdered structures. Moreover, during the cycling procedure, a thickening of the negative plate bottom

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section is frequently observed, placing the separator under pressure and thereby promoting the generation of shorts. These phenomena as a whole result from the fact that the redox exchange between Zn and ZnO does not take place in a solid phase, but brings into play zinc as zincate ions dissolved in the alkaline electrolyte. After having analyzed the results of research performed previously, we studied a new approach which proved to be very promising.

2. Previous studies

Most foregoing studies had, in common, the use of a limited volume of electrolyte such that, at the end of charge, oxidized zinc is present, mostly as ZnO or $Zn(OH)_2$ and, to a limited extent, as zincate ions dissolved in the electrolyte. This option is selected since the following reaction:

$$Zn + 2NiOOH + H_2O \rightleftharpoons 2Ni(OH)_2 + ZnO$$
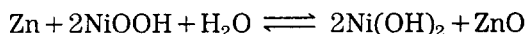
theoretically leads to a higher specific energy ($\simeq 340$ W h kg^{-1}) than the reaction characterized by:

$$Zn + 2NiOOH + 2KOH + 2H_2O \rightleftharpoons 2Ni(OH)_2 + K_2Zn(OH)_4$$
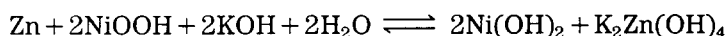
($\simeq 230$ W h kg^{-1}). In addition, the use of a small quantity of electrolyte results in an improved volumetric energy density (W h l^{-1}) and fast gas recombination kinetics — basic features for sealed batteries.

It is possible to classify into 5 categories the means by which the useful cycle lives of Ni–Zn cells may be increased:
- by the use of additives to the electrolyte [1–7]
- by the selection of separators able to delay dendrite growth [8–13];
- by the use of a variable charging rate [12, 14–20]
- by mechanical action on dendrites [18, 21–24]
- by the use of additives to the negative electrode.

Currently, Yuasa [25] appears to be the only company marketing low capacity, sealed Ni–Zn batteries ($\leqslant 10$ A h). This recently developed battery, incorporating a specially adapted separator, does not extend to more than 300 charge–discharge cycles. Confronted with the impossibility of obtaining a 1000-cycle useful life range for Ni–Zn batteries characterized by the use of electrolyte in small amounts, Sorapec studied the performance of Ni–Zn batteries operating with an electrolyte volume such that Zn in the oxidized state may be dissolved as zincate ions. It should be pointed out that batteries with vibrated plates [26, 27], which had an outstanding life, also operated with a significant electrolyte volume; however, the complexity of the vibration system limited interest on both technical and economic grounds.

3. Study of zinc electrode behaviour in a zincate medium

3.1. Experimental conditions
First, the influence of various parameters on the zinc deposit morphology was examined during electrode cycling. The preliminary experiments were

performed under the following conditions:
- a negative electrode (5 cm×5 cm) consisting of a steel strip with a 10 μm-thick cadmium coating and insulated edges
- a platinum counter electrode
- an electrolyte composition approximating to 8 M KOH + 2% sodium silicate + zinc (200 g l^{-1})
- a moderately agitated solution
- a temperature $\simeq 25$ °C.

3.2. Influence of current density

Preliminary testing in a Hull cell demonstrated that, for 15 min duration electroplating periods with low current densities ($i < 70$ mA cm^{-2}), deposits rapidly became spongy: i.e., non-adhesive foams (Fig. 1). For $i > 150$ mA cm^{-2}, deposits were relatively compact but dentritic (Fig. 2). For the 100 mA cm^{-2} density range, for an electrolysis time of less than 30 min, the existence of compact and smooth deposits was observed. Whatever the current density employed, with electrolysis times of more than 30 min, either spongy deposits ($i < 150$ mA cm^{-2}), or dendrites were always observed.

3.3. Influence of agitation

The greater the agitation, the more delayed is the formation of spongy deposits. However, agitation effects are only noticeable when convective effects are present close to the surface, greatly reducing the thickness of the diffusion layer.

3.4. Influence of additives in solution

The effect of various additives has been examined. Taking into account the fact that the formation of spongy deposits is accelerated by an elevation of temperature, all the tests have been effected at 45 °C; such a temperature
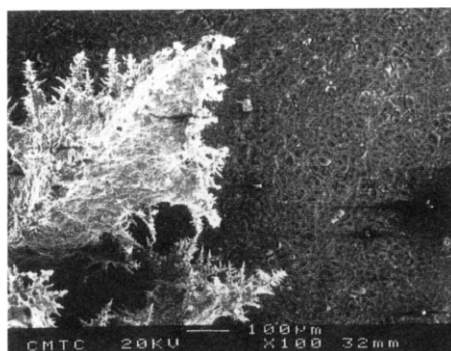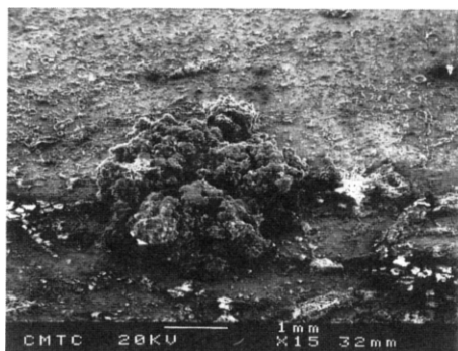
Fig. 1. MEB examination of non-adhesive zinc foams obtained at low current density (50 mA cm^{-2}).

Fig. 2. MEB examination of dendritic zinc deposit obtained at high current density (160 mA cm^{-2}).

amplifies the observed phenomena and facilitates the selection of the most active additives. Table 1 gives the electrolysis duration times, at a 30 mA cm^{-2} current density and with a stirred electrolyte, prior to the emergence of spongy deposits on zinc layers on a cadmium-plated substrate.

It will be seen that the best results are obtained with additives such as Pb^{2+} ions (at a 10^{-4} M level), the Casalis and the Shering brighteners, and the fluorinated compound, F1110. However, for long term tests, organic compounds, other than for the fluorinated F1110, are oxidized at the positive electrode.

Thus, additives suitable for Ni–Zn batteries are Pb^{2+} ions and fluorinated compounds (polyfluoroalcohol ethoxyl). With regard to the Pb^{2+} ions, we observed that the Pb^{2+} concentration must be within the 10^{-5}–10^{-3} M range. The initial Pb^{2+} concentration should therefore be limited to a value slightly less than 10^{-3} M in order that a residual concentration greater than 10^{-5} M exists at the end of charge. Taking into consideration the Pb^{2+} concentration range, and the fact that the electrolyte is unstirred (except for the bubbling on the positive electrodes at the end of charge), the depletion of Pb^{2+} ions is linked to the diffusion-limiting current and to the electrolyte volume per zinc electrode. Thus, the choice of a system in which all the zinc is solubilized in the electrolyte as zincate ions, which is possible with an electrolyte volume equal to 5 cm^3 (A h)$^{-1}$ favours the continued presence of the Pb^{2+} ions during the charging periods.

TABLE 1

Electrolysis duration times prior to emergence of spongy deposits on zinc layers on a cadmium-plated substrate

Additive	Time (min)
None	5
Gluconate	20
Casalis brightener	90
Ammonium heptamolybdate	15
Gelatin	10
Fluorinated compound 3 M FC 98	20
Fluorinated compound FC 128	20
Fluorinated compound FC 134	20
Triton	30
Shering brightener	>180
Fluorinated compound F 1033	15
Fluorinated compound F 1110	50
Fluorinated compound F 1176	15
Heliotropin	40
p-Anisaldehyde	15
Chlorobenzaldehyde	15
Nicotinic acid	5
Anisic acid	5
Pb^{2+} ions (10^{-4} M)	>210

In other respects, it has been confirmed that the beneficial effect of Pb^{2+} ions is maintained over several hundreds of cycles. Indeed, the major part of the Pb^{2+} ions being in the $Pb°$ state at the end of charge, the oxidation of $Pb°$ must occur during the discharge period, concurrent with the zinc oxidation.

3.5. Influence of charging current form

Although the use of a pulsed current charging procedure including, possibly, current inversion, has been specifically studied, research on this subject has rarely involved Zn in the presence of an excess of electrolyte. By contrast, many studies have been directed to the influence of pulsed current during charge for batteries constructed with a limited electrolyte volume [12, 14–17].

3.5.1. High current density pulses

In an initial series of experiments, the performance of the system was studied for high current density cathodic pulses. Indeed, it had been observed that with current densities in the 100 mA cm^{-2} range, deposits were neither spongy nor dendritic. In practice, since the nickel positive electrode associated with Zn cannot favorably have a surface capacity above 80 mA h cm^{-2}, the requirement for a steady charging procedure at 100 mA cm^{-2} would lead to a complete charge in less than one hour. Under these conditions, for a battery intended for electric vehicles, the charging currents would be excessive when the supply lines and the charging unit are taken into account. Further, difficult thermal exchange problems would be encountered. On the other hand, at the basic level, the use of a steady 100 mA cm^{-2} current density would quickly lead to concentration polarizations. For all these reasons, the application of a 100 mA cm^{-2} current density to the Zn electrode would require that the charging procedures be periodically interrupted. If, for practical reasons, a minimal 5 h charging duration (overcharge included) is adopted, the necessary rest period between each 100 mA pulse must be 4 times longer than the pulse duration. These rest periods contribute to a rehomogenization of the electrolyte. Also, it is advisable that the slope corresponding to pulse rise and fall be as steep as possible, so that the interval during which the electrode is subjected to low current densities (<80 mA cm^{-2}) is negligible by comparison with that corresponding to the 100 mA cm^{-2} rate. In addition to the stated charging schedule, it always seems well advised, as evidenced by several investigators, to periodically include a brief anodic pulse, the obvious role of which is to dissolve the dendrites as they start to grow.

The influence of the pulse duration was examined for the entire charging schedule (Fig. 3). The permanence of a smooth and compact deposit increased as the pulse duration decreased. Hence, results obtained with cathodic pulses of 1 s duration are poor, while they are good with pulses of a few milliseconds duration.
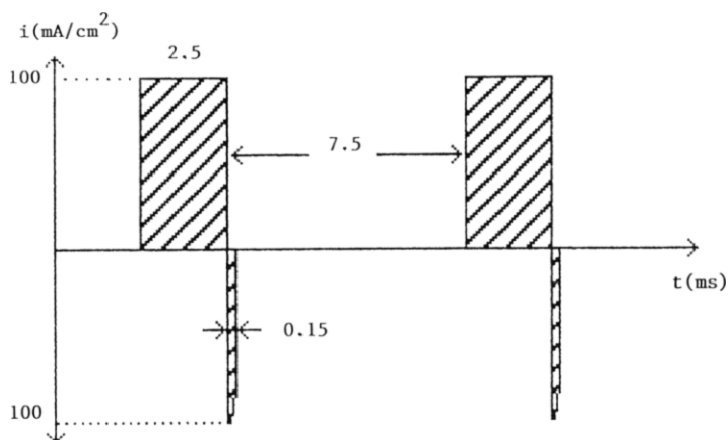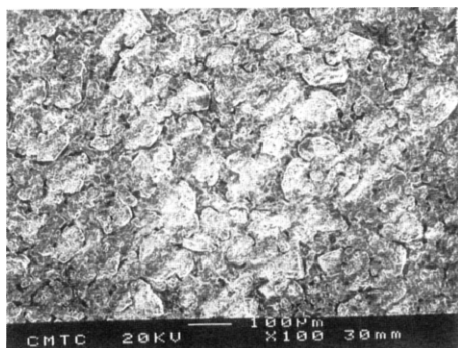
Fig. 3. High current density pulses.

Fig. 4. MEB examination of a zinc deposit obtained with a pulsed current (5 mA cm^{-2}) and with Pb^{2+} additive.

In the case of a charging rate that included cathodic pulses of 3 ms duration, it was observed that the permanence of good deposits, during charging in the 6 h range, and alternating with discharges at the 0.5 C stationary rate (i.e., $\simeq 40$ mA cm^{-2}), is ensured when the electrolyte is under turbulent flow close to the zinc electrode.

The already observed beneficial effect of agitation is linked with a reduction of concentration polarizations upon both charging and discharging.

3.5.2. Low current density pulses

It does not seem possible, at current densities in the 5 mA cm^{-2} range, to maintain, simply by the use of a pulsed rate, a proper zinc electrode morphology during charge–discharge cycles. By contrast, the combination of pulsed charging and the addition of additives such as fluorinated compounds or Pb^{2+} in solution, leads to satisfactory results (Fig. 4). The electrode performance for cathodic pulses of a few seconds duration has received particular attention with a view to simplifying the charging unit. In all cases,

the electrolyte contained Pb^{2+} in 10^{-3} M concentration; between cathodic pulses, an anodic pulse of the same amplitude, but of a 20 times shorter duration, was inserted.

Two observations appear to be significant:
• It is essential that there is no rest period between pulses. The application of a 2 s duration pulse followed by an 8 s rest period (Fig. 5) leads to spongy deposits.
• Current densities for cathodic pulses should be between 3 and 10 mA cm^{-2}; outside these values, deposits are spongy. The values defined above probably vary according to the Pb^{2+} concentration at the electrode/electrolyte interface.

The detrimental effect of rest periods following 2–3 s cathodic pulses demonstrates that 'a compound', developing during the zero current periods, and initiating spongy deposits, is formed at the surface. By contrast, this compound would be destroyed by anodic pulses following immediately after cathodic pulses.

Recent studies by Saidani [28] and Wyart [29] support this hypothesis by adducing evidence of a 'sub-oxide' base. However, it would be helpful to know how a mechanism, which is already so complex, combines with the beneficial action of additives such as Pb^{2+}.

4. Construction of Ni–Zn batteries

On the basis of the above mentioned results, Sorapec studied and built several types of Ni–Zn battery conforming to two major designs:
• a Ni–Zn battery combining a pulsed charge at high current density and electrolyte flow,
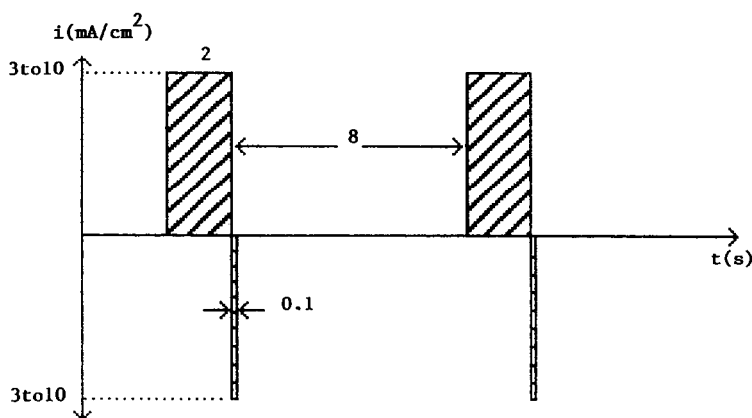• a Ni–Zn battery combining a low-current-density pulsed charge and additives in solution.

Fig. 5. Low current density pulses.

4.1. Ni–Zn battery combining a pulsed charge and electrolyte flow

During the period 1984–1986 Sorapec studied two battery types with flowing electrolytes.

The first type of Ni–Zn battery is characterized by the same electrolyte flowing in series-connected cells. In this case, the main problem concerns leakage currents which cause dendrite formation at the plate edges. It has been found (Fig. 6) that a periodic inversion of the electrolyte direction allows dissolution of the dendrites formed during the previous sequence; this dissolution is due to shunt currents. Tests made with 40 cells of 100 A h capacity have proved the efficiency of such a system; these cells were series-connected and more than 700 cycles have been obtained under these conditions.

Unfortunately, the changeover system with is responsible for the periodic reversal of the electrolyte direction is complex, unreliable, and expensive.

The second approach studied at Sorapec is characterized by an electrolyte flowing independently in each element. However, since it was unrealistic to associate a pump and its engine with each element of the battery, we have included, in each element, a very simple pumping device with gear wheels,
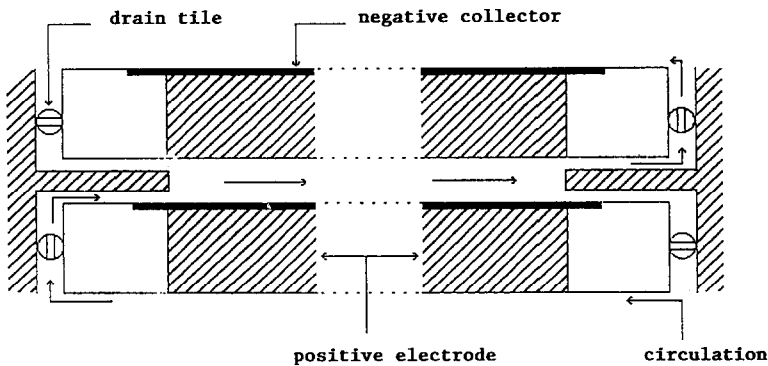

Fig. 6. Inversion system for the electrolyte direction.
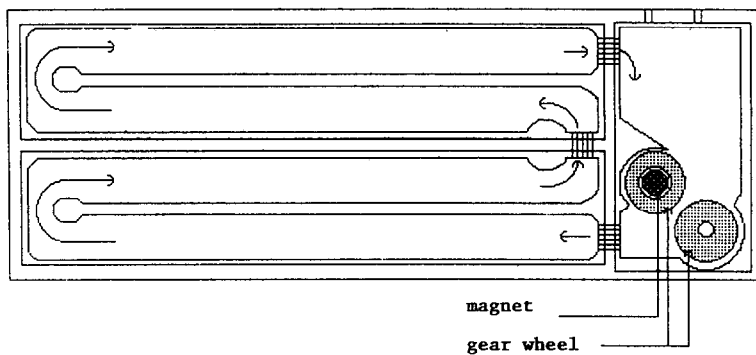

Fig. 7. Circulation system with magnetic coupling.

the rotor being associated with a circular permanent magnet. All the magnets are started by the rotation of an axis onto which are placed magnetized rings. A cavity located outside the cell stack allowed the device to be embedded in the battery block. Thus, propulsion is effected by magnetic coupling (Fig. 7).

Once again, we noted that decoupling occured as friction increased. This malfunctioning results in shutting down of the cells. Furthermore, this device, together with the preceding one, employs a large number of gaskets, which makes the whole system complicated and expensive.

4.2. Ni–Zn battery with a stationary electrolyte

Given the disadvantages associated with a flowing electrolyte system, further work has been concentrated on Ni–Zn batteries with a stationary electrolyte; in this case, good lifetimes are obtained using both a pulsed current during charging periods and additives in the electrolyte.

5. Characteristics of Sorapec Ni–Zn cells

In addition to the determination of the optimum charging rate and of the additives to be used, the correct operation when cycling Ni–Zn cells requires the implementation of very specific arrangements:
• the Zn electrode edges should be masked in order to avoid peak effects
• the geometrically active surface of the positive electrode should be slightly less than that of the opposite negative electrode. This arrangement overcomes detrimental field concentration effects at the electrode's edges
• the distance between the negative and the positive electrodes should be in the range 1.5–2 mm. This spacing should be maintained by an insulating structure that does not involve the partial masking of the electric field (should this occur, in places there would be current densities outside of the beneficial
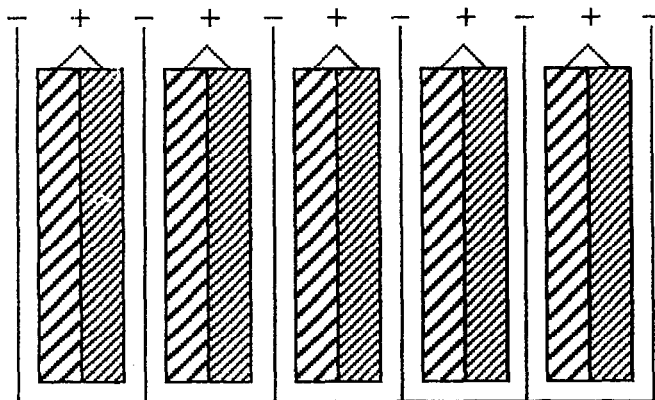

Fig. 8. 60 A h Ni–Zn battery.

area). Good results have been obtained with cylindrical slugs distributed on the surface which reduce it only by a few percent.

Cells of 60 A h capacity have been built. They include 10 positive electrodes grouped in pairs and 6 negative electrodes (Fig. 8). The positive electrodes are manufactured by Nitech (a Sorapec subsidiary). They are characterized by the use of a fibrous collector electrochemically impregnated with nickel hydroxide. These electrodes offer a 180 A h kg^{-1} mass capacity (dry state).

Each nickel electrode has a 35–40 mA h cm^{-2} surface capacity. Its total surface is 150 cm^2, i.e., a 6 A h capacity. The electrolyte volume is equal to approximately 360 cm^3 per cell, i.e., 6 cm^3 $(A\ h)^{-1}$.

The charging procedure is characterized by a succession of cathodic pulses at a current density of 5 mA cm^{-2} (their duration is 2.75 s) and anodic pulses at 5 mA cm^{-2}, but of duration 0.15 s (Fig. 9). The discharge
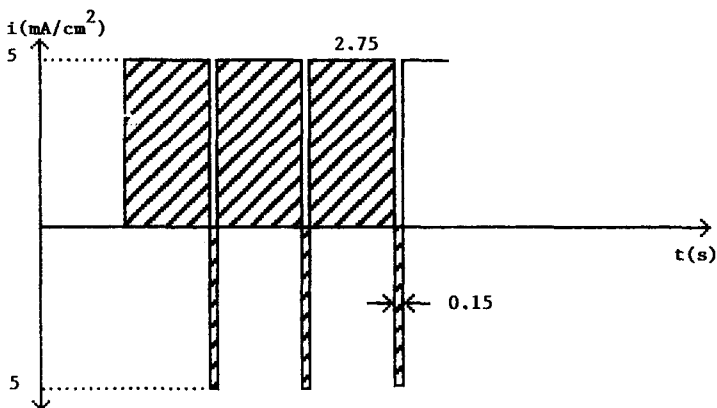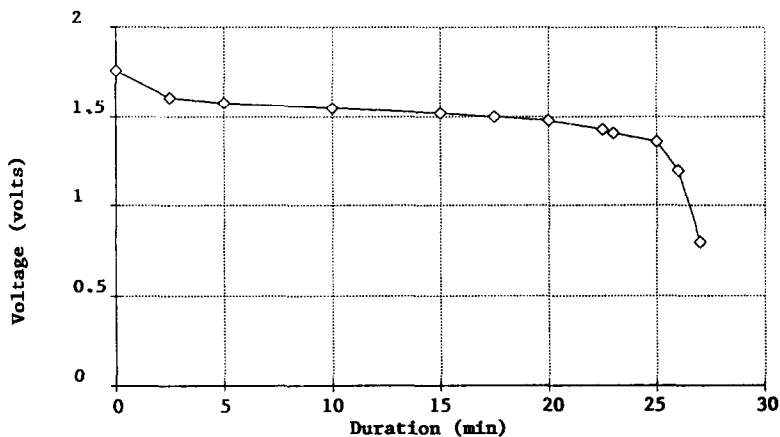
Fig. 9. Low current density pulses.

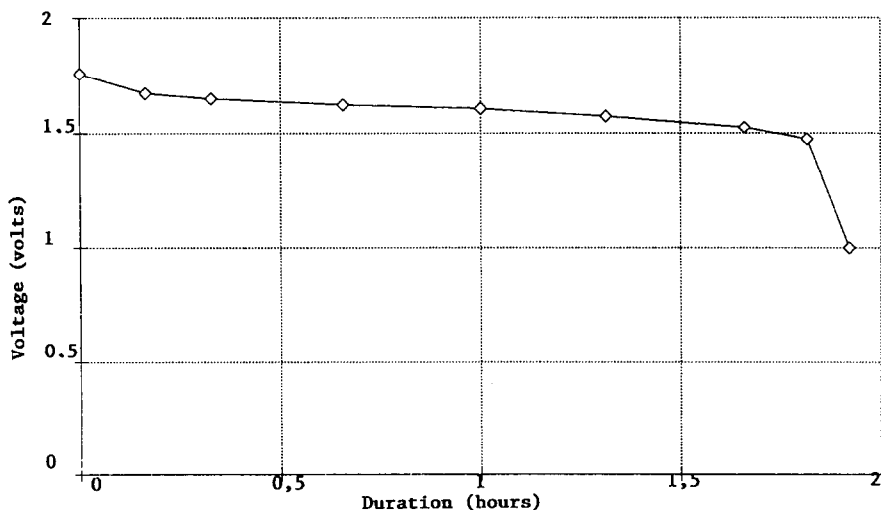Fig. 10. Ni–Zn battery — discharge at 2 C rate.

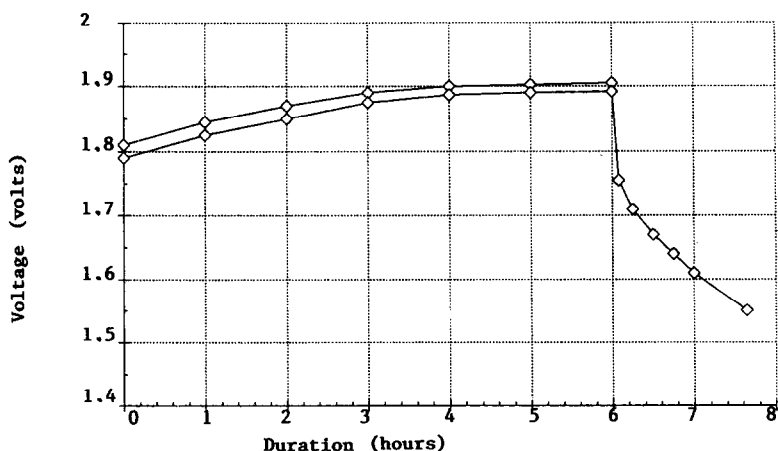Fig. 11. Ni–Zn battery — discharge at 0.5 *C* rate.

Fig. 12. Ni–Zn battery — charge–discharge cycle.

characteristics of these cells are shown in Figs. 10 and 11. For a discharge at the 0.5 *C* rate an average voltage of 1.6 V is observed. The cells were subjected to charging and discharging cycles (Fig. 12) whereby charging was performed at the 0.17 *C* rate with a 1.17 overcharge, and discharging at a 0.5 *C* rate with an 80% d.o.d.

The specific energy of these Ni–Zn cells reaches 57 W h kg^{-1}. To date, more than 1000 cycles have been obtained; the evolution of the cell capacity as a function of cycle life is given in Fig. 13. We are currently studying the construction of 140 A h cells for electric vehicles; in this case, the specific energy can reach 70 W h kg^{-1}.
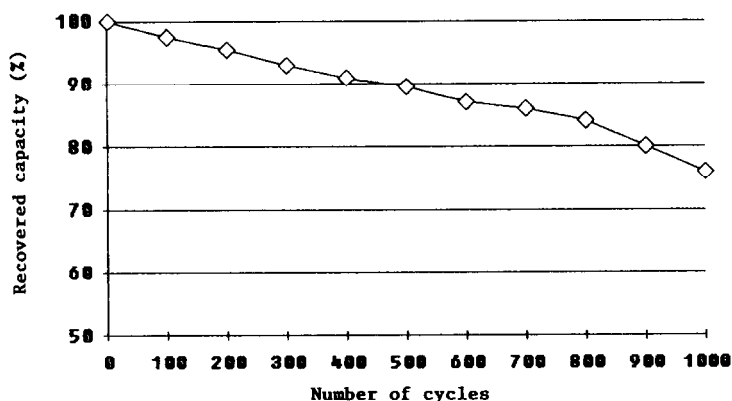
Fig. 13. Evolution of the recovered capacity as a function of cycle number for Ni–Zn cells. Charging rate, 0.17 C_5; overcharge factor, 1.17; discharge rate, 0.5 C_5; depth of discharge, 80%.

Acknowledgement

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