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New developments on high power alkaline batteries for industrial applications

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Abstract

Alkaline batteries have been in use for about 100 years. They display excellent life cycle characteristics and are extremely reliable in many industrial applications. This paper gives an overview of new developments at Hoppecke based on fibre structure electrodes in the fields of nickel/cadmium (Ni/Cd) and nickel/metal hydride (Ni/MH) batteries for industrial applications.

Keywords: Nickel/cadmium accumulator; Nickel/metal hydride accumulator; Modular batteries; Bipolar design; Hybrid vehicle; Alkaline battery

1. Introduction

Hoppecke Batterie Systeme GmbH (HBS) is engaged in the production and development of nickel/cadmium (Ni/Cd) batteries based on a special metalized fibre material for the electrode structure.

In the plant in Hoppecke FNC-batteries (named according to fibre Ni/Cd electrodes) based on a technology developed by Deutsche Automobilgesellschaft mbH (DAUG) have been built since the early 1980s.

Electrodes of this type offer a lot of advantages in comparison to conventional alkaline battery electrodes. HBS GmbH (formerly DAUG-Hoppecke) is producing these batteries for several fields of industrial application. The advantage of the fibre structures electrode lays in their ability to contact the active components of the electrode intensively and durably. Having a porosity of about 90%, the metallized fibre structure is still flexible and elastic so that volume changes of the electrodes will be tolerated without losing active material. As the fibre material can be produced in various thickness, the performance and electric capacity of the electrodes can be tuned in a wide range to meet the requirements of the user of the batteries in the best way.

Even extreme demands of battery performance and safety can be met and cells of this type have been applied in automatic guided vehicles (AGV), railway application, mining lamps, electric vehicles, hybrid cars, airplanes (e.g. Boeing 777) and even in space research (low earth orbit). FNC-batteries produced by HBS have been successfully used in numerous applications in all parts of the world. The production process is arranged in a closed material cycle and minimises waste and side product formation. Batteries will be completely recycled after serving for many years.

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2. FNC-cells

2.1. Electrode structure

The fibre structure electrodes are produced from a special metallized polypropylene felt. The amount of nickel precipitated and the thickness of the felt are optimised for the different fields of application, Fig. 1. The metallized fibres form a three-dimensional structure to contact the active electrode particles but stay elastic to tolerate the volume changes during cycling.

The main advantages of the fibre electrode technology are:

- The same electrode technology can be applied for different types of electrode.
- Performance of electrodes can easily be tuned in wide ranges to the demands.
- FNC offers an extended calendar and cycle life.
- Advanced production technology without any harm to the environment.
- FNC batteries have been successfully used in stationary and mobile applications (AGV, UPS, traction, mining, aircraft, space research).

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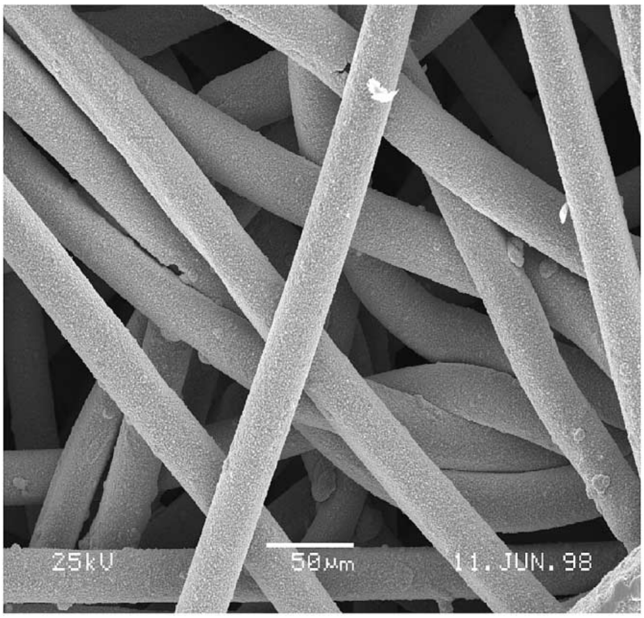

Fig. 1. Fibre electrode structure.

2.2. FNC-cell types

The various types of the electrodes are illustrated in Table 1. FNC cells are assembled to batteries of various voltages and capacity values. Due to the special electrode structure the service life is extremely high.

2.3. FNC-recom

During the 1980s and 1990s several attempts have been made at DAUG to improve the cells for an application in electric and hybrid vehicles, leading to the sealed cell system FNC-recom [1,2]. These cells had limited amount of electrolyte, spliced negative electrodes with a non-filled fibre structure to provide an enhanced gas transfer, and thus work at a pressure below that of the surroundings. These cells were able to be charged very fast and displayed a high energy density. They were successfully used in more than 100 electric and hybrid vehicles besides other applications, e.g. mining lamps, airplanes, etc.

2.4. FNC cells with reduced maintenance requirements (FNC A)

For some applications Ni/Cd batteries with special properties are demanded. These features are for stationary batteries (UPS): no charge equalisation, full recharge at a single voltage level, low operating voltage window, long service interval in terms of topping-up. Rather similar is the need of fast charge acceptance at low voltage levels for automatic guided vehicles (AGV). Energy density, reliability and topping-up intervals are of importance for other applications (e.g. railway) too.

The new FNC A design developed to meet these requirements [3] is based on an internal oxygen cycle that will reduce the state of charge of the negative electrode. The negative electrode is normally responsible for the limitation of charging at restricted charging voltage. The internal oxygen cycle also reduces water loss as most of the oxygen during overcharging is transferred to, and consumed at, the negative electrode. The cell design is shown in Fig. 2.

The design of the new FNC A, in principle, is based on the design of a standard vented FNC battery, with its positive and negative fibre structured electrodes. The electrode package is put into a so-called metal wrapping. In this special design, the electrodes are pressed together, reducing the distance between them. For FNC A, a special non-woven separator is used. This optimised separator has been chosen for suppressing dendrite growth as well as for transferring and storing of gas (oxygen).

There is no difference in the cell behaviour as long as the cells have not reached the overcharge phase. But during overcharge, the standard vented FNC shows a high rise in the cell voltage due to the polarisation of the negative electrode (hydrogen overvoltage). In contrast to this, there is no hydrogen overvoltage in a totally recombining system such as FNC-recom. With the new FNC A design, a good compromise could be achieved between properties of sealed and vented FNC design. Fig. 3 shows discharge curves of FNC A cells.

Table 1
Ni/Cd cells based on fibre electrode technology and field of application

	FNC X	FNC H	FNC M	FNC L
Power input/output	Very high	High	Medium	Low
Maximum current (CNA[a])	>7	<7	<3.5	<1
Typical discharge time demands (min)	0.5–5	0.5–5	10–300	60–600
Application	UPS, cranking, AGV	UPS, cranking, AGV emergency power	UPS railway, emergency power, motive power	Emergency power, railway, telecom, UPS
Cell resistivity (mΩ)	0.17–0.22	0.4–0.5	1.0–1.2	1.4–1.6
Electrode plate thickness (mm)	1.2	2.5	4.5	5.0
Electrode sizes (mm^2)	110 × 120	110 × 120	110 × 120	110 × 120
	110 × 160	160 × 180	160 × 180	160 × 180
			140 × 240	140 × 240

[a] CNA represents *nC* rate in A.

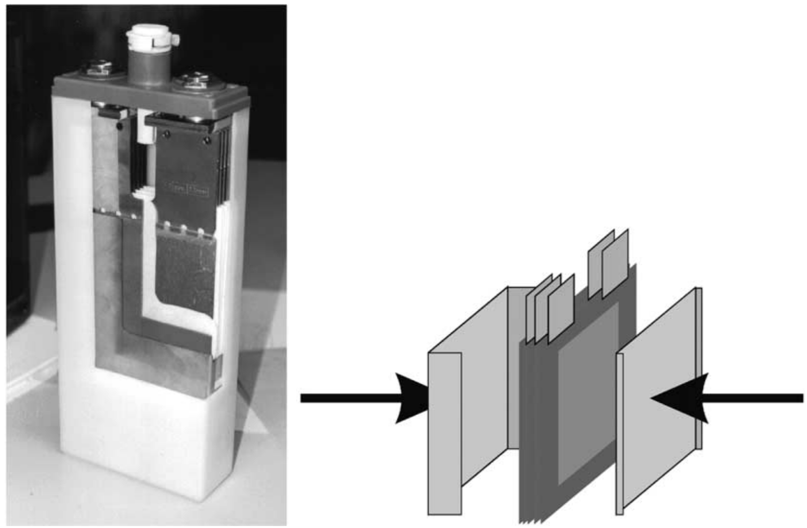

Fig. 2. FNC A: internal cell design and working principle.

2.5. Fields of application of FNC A

2.5.1. Railway application

A major field of application of alkaline cells is railway systems. Usually every wagon is equipped with a battery to provide energy for the time the generator does not operate.

FNC A cells provide a high level of safety, prolonged service intervals and higher energy densities compared to standard Ni/Cd cells.

Besides the application in the rolling stock, the new FNC A has already been applied for stationary power systems, e.g. railway crossings.

Due to the internal oxygen recombination, the charging voltage required is reduced and topping-up intervals can be prolonged. The results have been verified in a field test, where a battery had been operated in stand-by mode for more than 3 years in an outdoor cabinet. Although this battery had been operated at its maximum charging voltage of 1.5 V, it had lost an extremely low amount of water (about 0.01 g/Ah per day).

2.5.2. Automatic guided vehicles (AGV)

In advanced production technologies, a variety of material transport activities has to be realised, including storage of

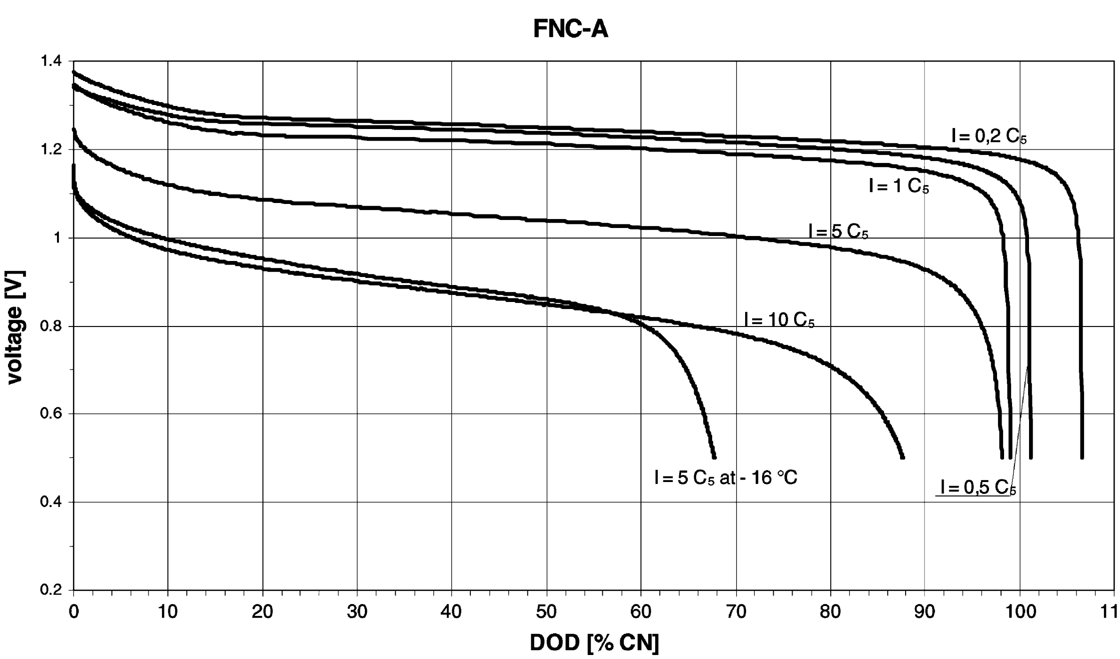

Fig. 3. Discharge characteristics of FNC A cells.

materials and products. This requires new logistic structures using computer-controlled and battery-driven transport vehicles.

The cruising course of an AGV includes periods of lower power demands and short intervals of high currents up to more than 10*C* rates (e.g. by lifting of heavy loads). In general, the batteries are working in a certain capacity window from 5 to 50% of the rated capacity. The fast recharging is limited by the voltage of the charging device. Immediately after charging the AGV resumes its operation in the production line. Due to their internal features FNC A provides a longer time of operation without the need for an equalisation charge of the batteries. As the charge efficiency of the negative electrode is slightly higher than that of the positive, the charging process at constant voltage conditions is practically limited by the potential increase at the negative. The possible recombination of oxygen in FNC A cells equalises the charge efficiencies of the electrodes [4].

2.6. Benefits of the new FNC A technology

- Enhanced charge acceptance at restricted voltage.
- Low internal resistance.
- Prolonged maintenance intervals (low water consumption).
- Enhanced energy density (volume, footprint, weight).
- Compact and mechanically stable design.
- Improved separation.
- Improved reliability and safety.

2.7. FNC A battery modules

The FNC A technique enables a relatively simple arrangement of single cells in a battery module with interconnected cell chambers. The difficulty consists in the sealing technique of the cells. Additional problems are related to the thermal behaviour. Welding techniques as well as the use of screws for the connections are available and have been successfully tested.

As an example an FNC A module of 75 Ah is shown in Fig. 4. A maximum capacity of 120 Ah can be arranged in a battery module of the same size. The modular battery combines the functionality of the FNC A design with the more compact arrangement.

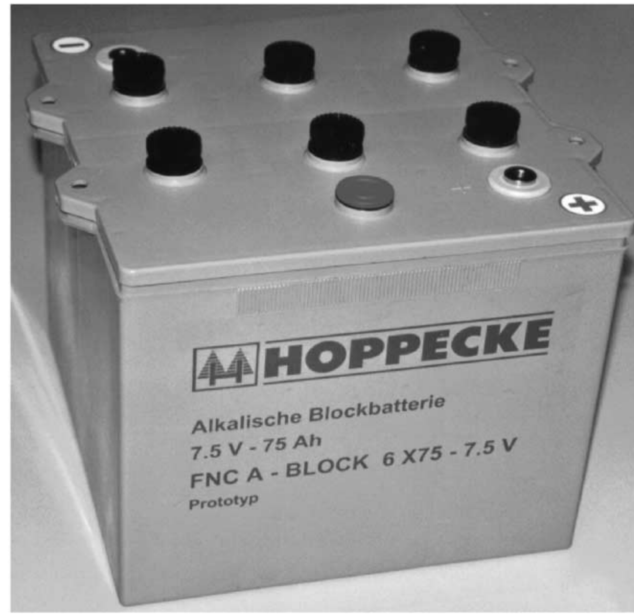

Fig. 4. FNC A battery module

2.8. High temperature telecommunication cell

Special requirements have to be met for batteries in telecommunication applications [5]. A special type of FNC-battery is designed for these applications at elevated temperatures. The cells can be built as single cells as well as compact battery modules [6].

In contrast to the FNC A cells special measures have been taken to prevent any oxygen reaction at the negative electrode. Thus, the cell is guarded against any tendency to thermal runaway at higher temperatures.

The higher operation temperature will cause a larger solubility of cadmium hydroxide in the electrolyte. This enforces additional measures to prevent dendrites.

The battery can be equipped with an automatic water refill systems as well as the so-called Aquagen® plugs (catalytic recombination of electrolyses gases to water). Both measures provide prolonged service intervals. The new composition of the electrodes provides an improved charging behaviour at low cell voltages at elevated temperatures.

2.9. Large-sized FNC cells

For special applications cells with high capacities up to 1500 Ah are demanded. FNC-MEGA LINE is designed for such stationary applications, e.g. power station back-up supply.

Although the performance type of the cells is only "L" (low) the design demands special internal measures to enable the unusual electrode format. The cell has several terminals to minimise voltage losses. A special problem of these large cells consists in thermal effects combined with high rate discharge. The cell is capable of being discharged in about 1 h with typical currents of ca. 1000 A. Cells have been tested in a working temperature window from −30 up to 50 °C. The cells can be equipped with electrolyte level indicators as well as with Aquagen® plugs (see Section 2.8) to control electrolyte consumption.

3. Nickel/metal hydride batteries in fibre technology

Accumulatorenwerke HOPPECKE is engaged in the development of nickel/metal hydride (Ni/MH) cells and batteries for industrial applications. The Ni/MH system shows very similar properties in terms of voltages and power characteristics to the Ni/Cd couple. It is considered as an alternative to the Ni/Cd system.

As the system can be discussed as a hydrogen shuttle battery it is possible to enhance the energy density by reducing the amount of free electrolyte. Due to the use of two insoluble electrode materials and reversible reactions, the electrochemical system is very stable with respect to cycling and the formation of dendrites is not a limiting factor of life-time expectancy. The application of AB_5 storage alloys instead of AB_2 provides a low equilibrium pressure of hydrogen in the cells as well as a expanded battery life. In contrast to the lithium ion shuttle system Ni/MH makes use of an aqueous electrolyte. Thus, for electrochemical reasons, the Ni/MH cells are more tolerant with respect to overcharge and deep discharge than lithium cells.

3.1. FNH battery modules

A battery in modular design can be used to increase energy density in comparison to single cell combinations. The use of the Ni/MH system results in an increase of the energy density of about 15% in comparison to Ni/Cd [6,7].

The major advantages are cycleability at high rates. Modules up to 140 Ah are under consideration. As an example, Fig. 5 shows a prototype of a Ni/MH 12 V module with 25 Ah. Each of the 10 cells is equipped with positive fibre structure electrodes and metal hydride (AB_5) negatives. The power behaviour of the prototype is designed as an X-type. By changing the thickness of the electrode the power/energy ratio can be tuned. The module was tested at low and elevated temperatures. From investigation of the single cells, a cycle life of more than 2000 charge transfers of the nominal capacity is expected. In the past Ni/MH batteries have been produced mainly as small rolled cells for electronic equipment. In addition, larger prismatic cells of higher capacity are known. The modular design is more compact and can easily be integrated into appliances. In Fig. 6, discharge curves (voltages and utilised charge) with 1*C* current at different temperatures are displayed.

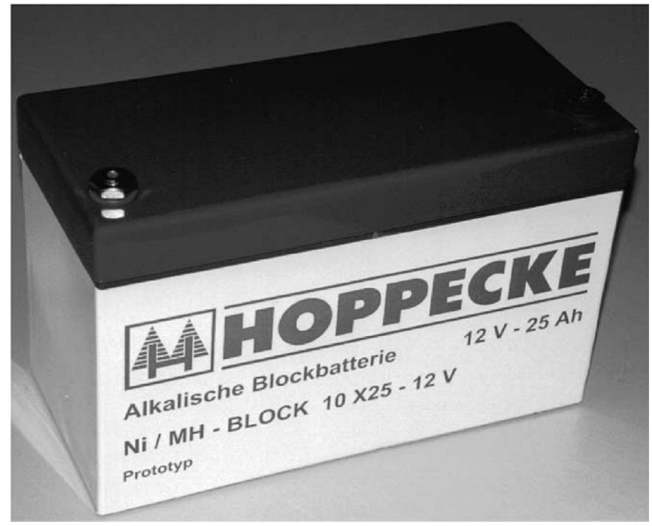

Fig. 5. Ni/MH battery module (12 V, 25 Ah).

3.2. Low temperature behaviour of FNH battery modules

In the past the utilisation of Ni/MH batteries had normally been limited by their restricted performance data at low

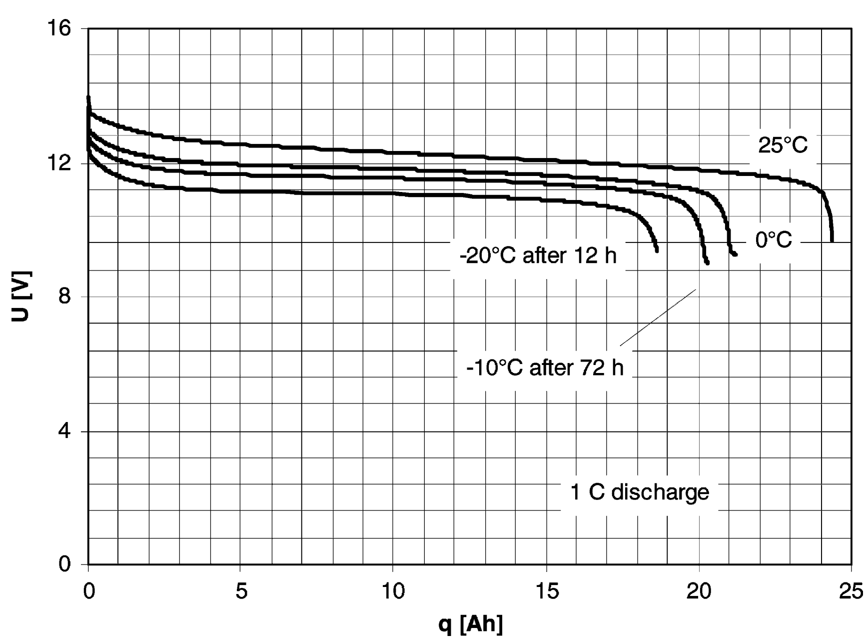

Fig. 6. Discharge characteristics of a 12 V, 25 Ah Ni/MH module.

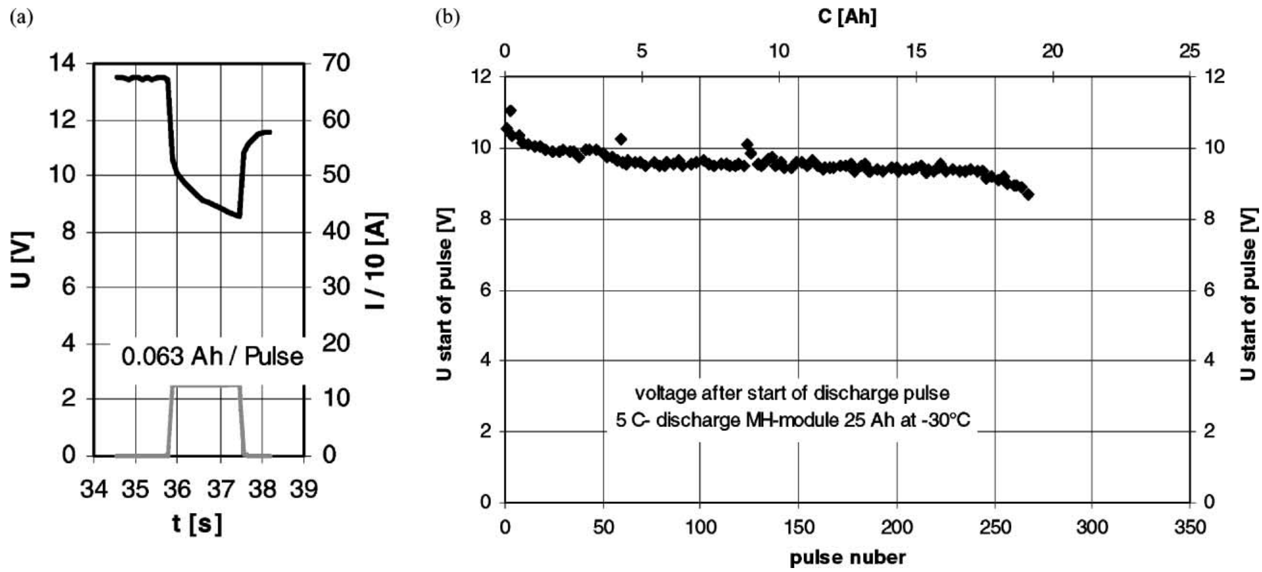

Fig. 7. (a) Pulse form and (b) low temperature pulse discharge (initial voltages during pulse discharge (2 s, 5C rate) at −30 °C) of a Ni/MH battery module (12 V, 25 Ah).

temperatures due to diffusion processes in the negative electrode. The new designed Ni/MH module has been improved to overcome this limitation.

By special modification we have been able to improve the low temperature performance as well as the behaviour at elevated temperatures. In Fig. 7a, the pulse discharge curve is shown. In Fig. 7b, the voltages at the beginning of the pulses are plotted versus the pulse number and the amount of charge. In that test about 75% of the nominal capacity is available in a pulse discharge (2 s, 5C rate) at −30 °C.

3.3. Behaviour at elevated temperatures

In addition the battery was cycled (0.2C rate) at elevated temperatures of 40 °C and even 50 °C for more than 4 months. Fig. 8 displays available capacity during 0.2C cycling.

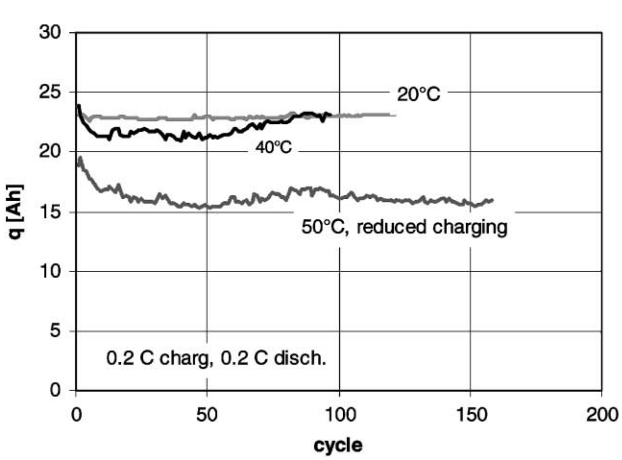

Fig. 8. Discharge capacity of a 12 V, 25 Ah Ni/MH module during cycling of at 40, 50 and 20 °C.

Measurements at the end of the experiment at normal, the temperatures indicate that there is no permanent loss of capacity. In the experiment at 50 °C charging was experimentally limited. This explains the lower value of the capacity available. At ambient temperatures a cycle-life of more than 2000 cycles (100% nominal capacity) has been found with laboratory single cells.

3.4. High power Ni/MH battery in stack design

The reactions and properties of the Ni/MH couple allow cells to be combined in a bipolar battery stack. In contrast to conventional batteries there are no cell walls and connectors attached to the single sub-cells [8]. The advantages of such an arrangement are higher energy densities and minimising of resistance losses. Aiming for high performances, power densities of about 1 kW/kg can be achieved. These are data close to those of super capacitors but display a rather constant discharge voltage level. The project in co-operation with the Kurt-Schwabe-Institut für Meß u. Sensortechnik (KSI) Meinsberg is supported by the German Ministry of Science and Technology (BMBF). Details are given in a separate paper [9].

3.5. Comparison of high power Ni/MH cells

The performance characteristics of differently designed Ni/MH systems is displayed in the following RAGONE-plot (Fig. 9).

This illustrates the possibilities to tune the battery data to the demands of the customer. The bipolar system has the highest ratio of power ability to energy content. Therefore, it may be used in a hybrid vehicle as a booster system. As it accepts charge also at high rates, energy from deceleration can be utilised for recharging.

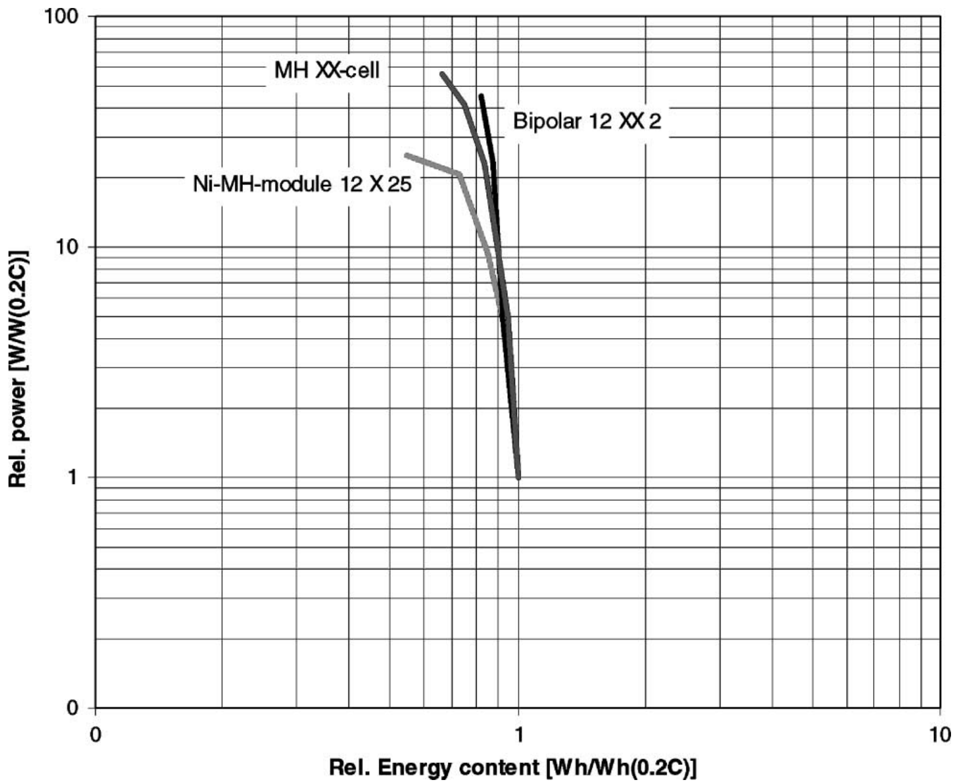

Fig. 9. Modified RAGONE-plot of differently designed Ni/MH systems.

3.6. Fields of application of industrial Ni/MH batteries

Ni/MH cells are ideal storage devices to be applied in the following cases:

- *High power applications*: Super capacitors lack voltage stability during charge transfer. That limits the amount of energy available. Ni/MH bipolar stacks are displaying defined voltage levels as is typical for batteries but they are also designed for high power/energy ratios.
- *Advanced board net structures*: Ni/MH batteries provide extended cycle life, fast rechargeability, reliability.
- *Hybrid combustion vehicles*: The Ni/MH system (FNH-recom) has already been applied in electric and hybrid vehicles.
- *Fuel cell hybrid vehicles*: Fuel cells in vehicles are not able to make use of braking energy and their costs are determined by the maximum power requirement (size of electrochemical interface). High power Ni/MH batteries can cut costs by smoothing the peak power and may be used to start-up fuel cell components at low temperatures.

4. Conclusions

There are several directions for the further development of alkaline batteries for industrial applications. Besides the conventional Ni/Cd batteries known for about a century more advanced battery designs have been found. Ni/MH batteries may be used for special applications as they have very similar properties compared to Ni/Cd. With respect to cycling behaviour and energy density Ni/MH may be favoured, but the different low temperature behaviour and the properties of the storage alloy has to be taken into account.

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