

Alkaline high power batteries in a bipolar stack design

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Received 08 January 2001; accepted 09 January 2001

Abstract

For several applications, batteries with a high power/energy ratio are required. In order to meet these requirements, alkaline batteries based on fibre structures and hydrogen storage negative electrodes that are arranged in bipolar stacks, can be used. The bipolar stacks are designed to provide comparatively high voltages, e.g. 12, 36 and even 110 V. These stacks display electrochemical characteristics of a typical battery but are able to provide high power densities. This paper compiles data obtained from such storage units. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nickel/metal hydride batteries; Bipolar stack designs; Applications/electric vehicles

1. Introduction

Nickel/metal hydride (Ni/MH) batteries are considered to be a substitute to the widely used nickel/cadmium accumulators. In comparison to nickel/cadmium accumulators a higher energy density can be obtained. For large cells in industrial applications the costs resulting from the use of the expensive hydrogen storage alloys play an important role in the acceptance of such batteries.

Therefore, one way for economic application consists in a special design that enables high power rates but with moderate or even small battery capacities. The aim of our investigations was to increase the power/energy ratio of a Ni/MH battery. Potential fields for applying such bipolar nickel-metal hydride batteries are power equalising, modern net structures for automotive applications and electric hybrid vehicles.

Conventional batteries are made of single cells connected in series. Thus, each cell is equipped with passive material such as cell walls, connectors etc. Looking back to the very beginning of electrochemical energy storage, Volta's pile was designed to obtain high voltages by connecting cells together via bipolar connecting plates [1]. We have tried to use the ideas of such a concept to build an accumulator based on the electrochemical nickel-metal hydride couple. The

advantage of this design is that the cross-section for the electric current collectors is the same size all over the bipolar stack. There is no need for highly conducting support structures in the electrodes. The connecting bipolar plate can be made from an extremely thin metal foil or another electronically conducting material. The bipolar plate has to provide sufficient electronic contact but also has to prevent any electrolytic bridges between adjacent sub-cells (our term for the unit cell in a stack).

In the past, several attempts have been made to realise such a concept of bipolar stacks. Several difficulties involved have so far prevented a wide technical solution. The reasons are as follows:

- Losses of power due to contact resistivity.
- Electrolytic bridges between sub-cells because of spilling or creeping of electrolyte.
- Limited amounts of the electrolyte in the sub-cells.
- Problems with the sealing of adjacent sub-cells.
- Differences of gas pressure in the sub-cells.
- Corrosion of the bipolar plate due to the electrolyte.

It has been shown that electrochemical systems based on simple ion transfer and not involving the electrolyte in the overall cell reaction are favoured for use in bipolar stack designs. As electrolytic resistivity will strongly influence the stack behaviour, we expected that the Ni/MH couple would perform better than cells with non-aqueous electrolytes. At the moment, hydrogen storage alloys of the AB₅ type can

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provide comparatively low equilibrium pressures at given state-of-charge and temperature. Accumulatorenwerke Hoppecke and Kurt-Schwabe-Institut für Meß- und Sensortechnik e.V. Meinsberg have a joint programme to study the bipolar Ni/MH storage systems, continuing former work [2–5] at Deutsche Automobilgesellschaft mbH.

2. Experimental

Fig. 1 displays a scheme of the bipolar arrangement. Bipolar stacks were built using positive electrodes prepared using fibre structure technology at Hoppecke Batterie Systeme GmbH, in a manner rather similar to the conventional production of positive electrodes for FNC batteries. The differences lie in the specific amount of active material related to the electrode size and the smaller thickness of the bipolar electrodes.

Depending upon the demanded power output required, the electrode thickness of bipolar cells can be varied between 1 and 0.5 mm. Most of our stacks are made from 0.7 mm positive electrodes. As all cells are discharge-limited by the positive electrodes, it is necessary to make the electrodes very uniform with respect to their capacity. The laboratory stacks were based on electrode areas of 72.5 cm^2 giving an electrical capacity of about 1.7 Ah.

Larger stacks with capacities of about 7 Ah are under construction for extended field tests. Non-woven polyamide or poly-hydrocarbons can be used as separators. The bipolar connecting plate is made of nickel. Negative electrodes were prepared in the laboratory using a commercial hydrogen storage alloy and pasted with a binder onto a metallic support. Stacks have been built in plastic as well as metallic containers of appropriate size. The electrolyte is KOH of a

concentration of 8.5 mol l^{-1} . The stacks are equipped with sensors for temperature and gas pressure (Fig. 2).

Electrical tests were carried out with DIGATRON battery testing equipment. Some of the experiments were carried out in a climatic chamber so that the temperature of the air around the stack could easily be adjusted to various conditions.

An additional experimental set-up for three bipolar stacks was equipped with a fan to provide constant cooling. The same equipment was used for those experiments in which several bipolar stacks were connected to form units having a higher voltage or higher capacity. Thus, power systems with voltages up to 310 V were built and operated.

3. Electrochemistry of Ni/MH batteries

The electrochemistry of the Ni/MH system can be discussed as an ion transfer system with only hydrogen ions being used for the transfer of charges (Fig. 3).

At the negative electrode, an equilibrium between hydrogen stored in the alloy and the gaseous phase in contact to the electrode material is established. Therefore, gas pressure is changing depending on the state of charge of the negative electrode and the temperature. In a stack, the temperature of the sub-cells is never completely uniform, so the hydrogen pressure may differ between individual sub-cells. In order to solve this problem we have designed the stack in such a way that the gas pressure between the sub-cells is equalised.

During overcharging, the oxygen formed at the positive electrode limits the state of charge of the negative. In case of a deep discharge leading to a reversed voltage, the nickel hydroxide electrode may form hydrogen, but this is consumed at the negative. By this mechanism the negative

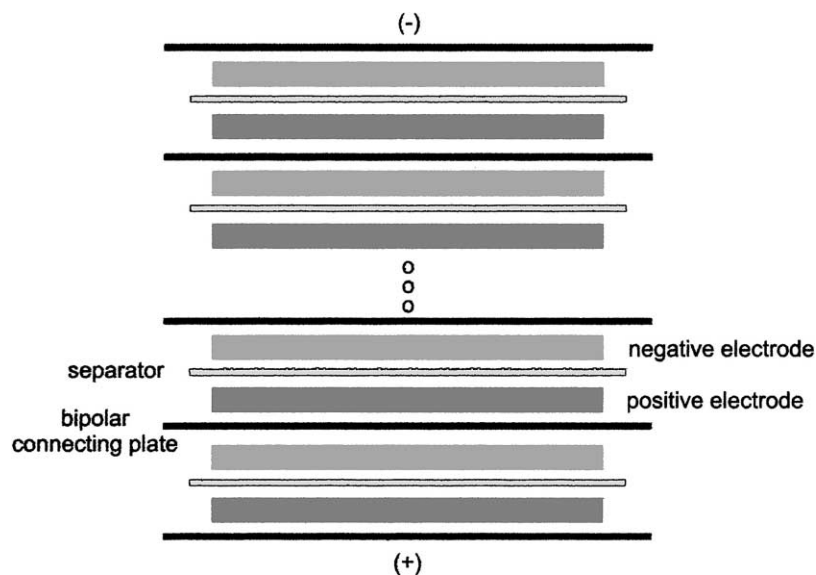


Fig. 1. Schematic diagram of a bipolar arrangement.



Fig. 2. Laboratory bipolar stack. 36 V, 1.7 Ah.

electrode is protected from oxidation as long as the current remains small.

4. Results

4.1. Constant current cycling of bipolar stacks

Apart from the higher voltage, the bipolar stacks display almost the same electrochemical behaviour as conventional Ni/MH cells. A significant difference lies in the arrangement of the electrodes. In conventional cells the electrodes are arranged in such a way that both sides of the electrodes contribute to the overall current. In a bipolar stack only one side of electrode is exposed to the counter electrode. As a consequence, the (geometric) current density of a bipolar electrode is twice that in a comparable conventional cell.

The pressure and voltage response during a typical cycle of a 12 V, 1.7 Ah bipolar stack is given in Fig. 4.

In practice, the internal pressure can be used to terminate the charging process. By doing so, the charging current can be increased. As an example, Fig. 5 demonstrates the voltage curves whilst cycling the stack at the 0.4 C rate of charge and 1 C rate of discharge, but limiting the stack pressure to 1.3 bar.

Of major interest is the behaviour of Ni/MH stacks at lower temperatures. In addition to the electrochemical reaction processes, the gas desorption and the mobility of stored hydrogen are retarded. As a consequence, the performance of Ni/MH cells is limited at these conditions. By optimising the electrode materials it is possible to extend the working range down to -20°C . In Fig. 6 curves at various temperatures of a bipolar stack discharging at the 1 C rate are given.

4.2. Pulse discharge and stack resistance

In some applications, higher currents are demanded. Normally these currents are demanded only for short time intervals. In Fig. 7 the voltage response of a 12 V bipolar stack is plotted versus time for different regimes of pulsed current. It can be seen that the major part of the voltage decay occurs in the early part of the pulse.

The stack shows a very small internal resistance. The value of the internal resistance is rather constant over a wide range of the state-of-charge (SOC) as seen in Fig. 8. In order to compare cells, the resistivity is normally given related to capacity and for each bipolar cell.

Using a 10 C dc current (17 A for a 1.7 Ah stack) after 1 s of polarisation, a resistance of about $20\text{ m}\Omega$ Ah or about

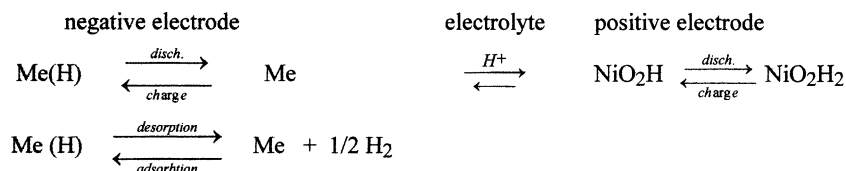


Fig. 3. Electrochemical and chemical reactions in a nickel/metal hydride cell.

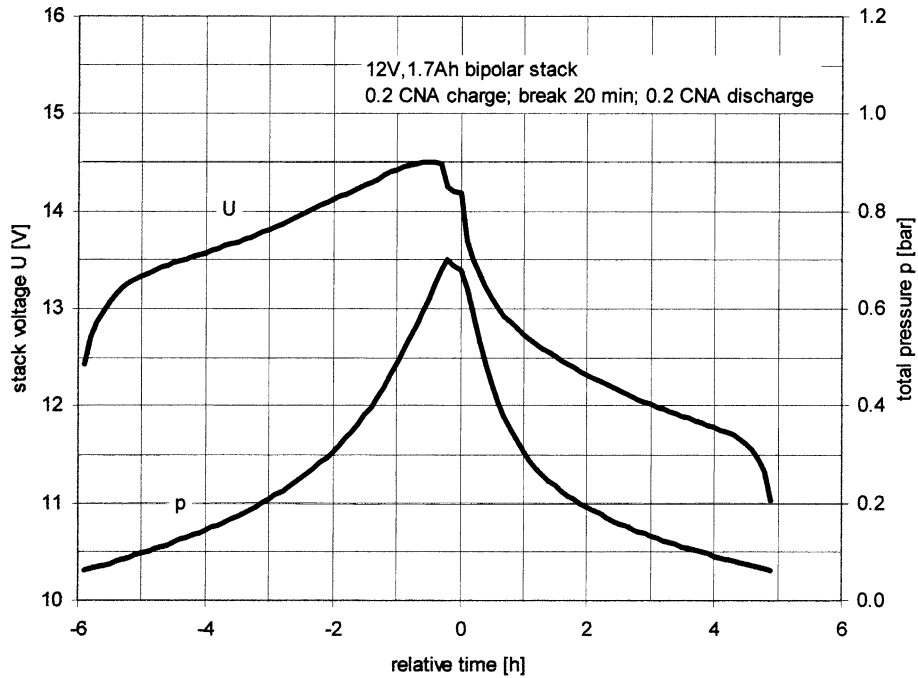


Fig. 4. Pressure and voltage during a typical cycle of a bipolar stack (12 V, 1.7 Ah).

0.86 $\Omega \text{ cm}^2$ per sub-cell can be computed from the voltage drop.

We were able to discharge stacks using current pulses up to the 30 C rate [6,7].

There is a certain change of the internal resistance during continuous cycling. At the beginning, the internal resistance decays slightly. After much cycling with high currents, an increase in resistivity was found after more than 600 cycles. It was caused by a partial (reversible) water loss from the sub-cells (See Fig. 9).

4.3. Electrical cycling and thermal behaviour of bipolar stacks to an hybrid electric vehicle regime

In hybrid automobile applications the bipolar stack would be used to store or deliver energy steadily between the main energy source (internal combustion engine or fuel cell), and the consuming equipment. Using a powerful storage battery can reduce the peak power needed from the main energy supply and can store energy available from braking.

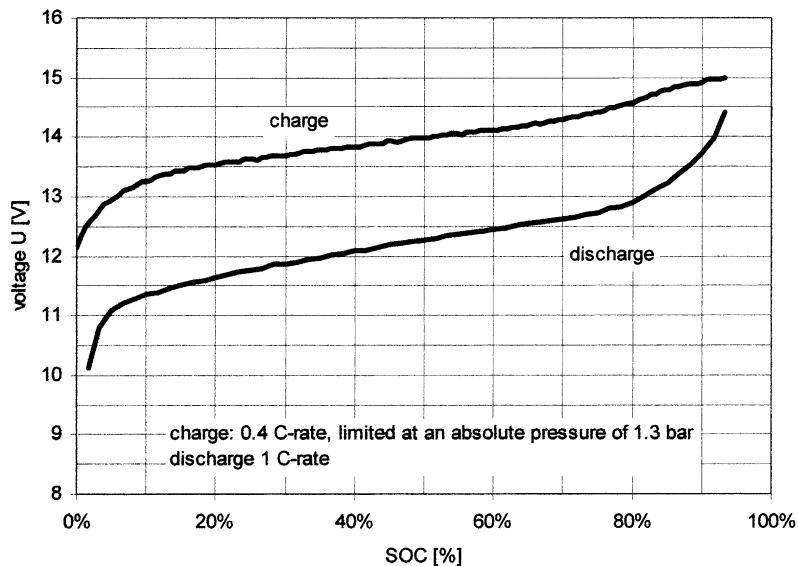


Fig. 5. Voltage of a 12 V, 1.7 Ah bipolar stack during 450 cycles of 0.4 C rate of charge, limited by a stack pressure of 1.3 bar and 1 C discharge.

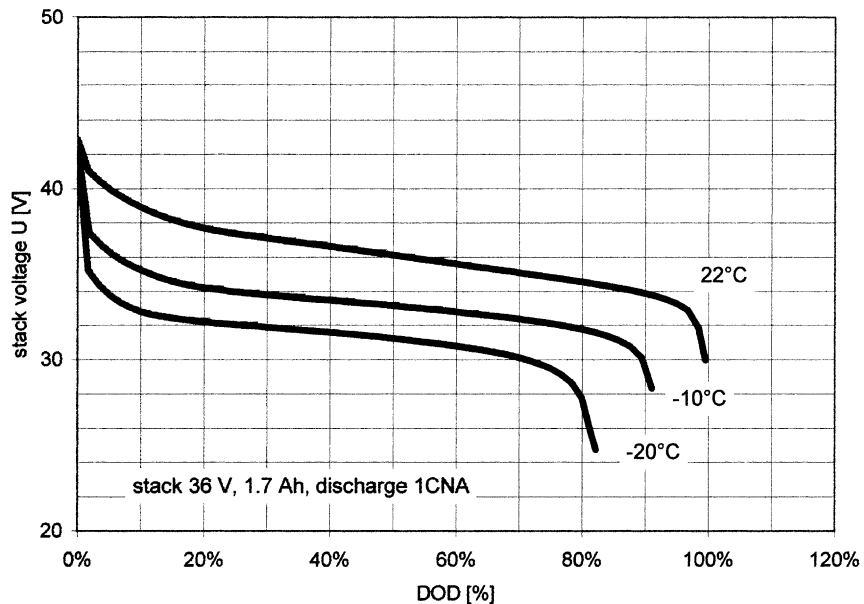


Fig. 6. 36 V, 1.7 Ah bipolar stack discharged at the 1 C rate at various temperatures.

As an example, we have designed a cycling sequence based on a 5 C rate of charge and discharge with a cycle depth of 10% from an initial 60% SOC. There are 5 s intervals between each charge and discharge. The sequence is repeated at least 100 times. This cycling sequence is shown in Fig. 10a.

During the repetitive cycling, a stationary state is achieved (Fig. 10b). The Ah efficiency was determined by measuring the remaining capacity after the cycling programme and it was very close to 98.7%. The energy efficiency amounted to about 90%.

Due to the energy losses while operating the bipolar stack, a temperature raise is observed. In order to provide for continuous operation, a thermal management system is required. In an experimental set-up the stack is exposed to a stream of air. The air originates from the surroundings at a rather constant temperature and flows over the cylindrical wall of the bipolar stack. The internal temperature of the stack was measured at the approximate top of the stack. After an initial period, the temperature becomes constant indicating that the heat produced in the stack is similar to the heat dissipated by the cooling device. Depending upon the

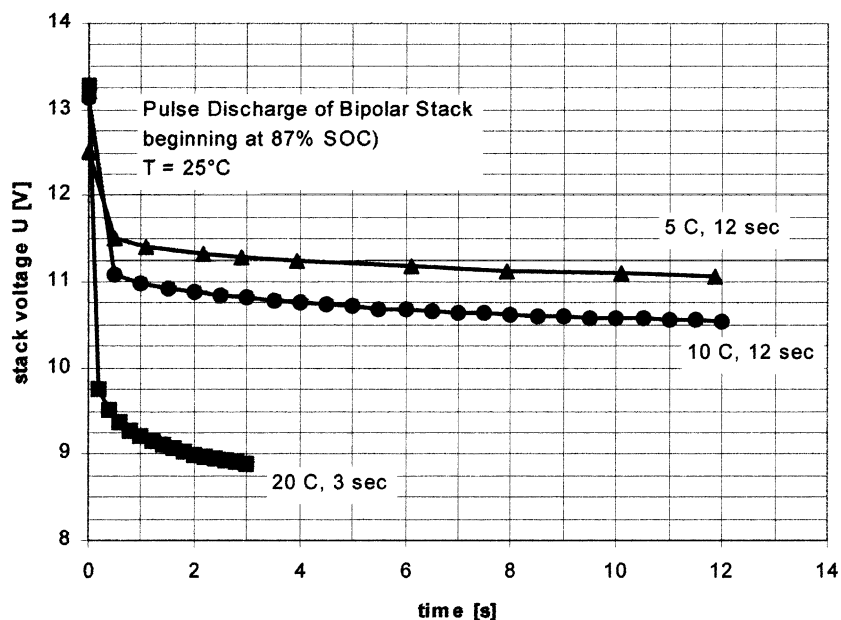


Fig. 7. Selected pulse discharge curves of a 12 V, 1.7 Ah bipolar stack.

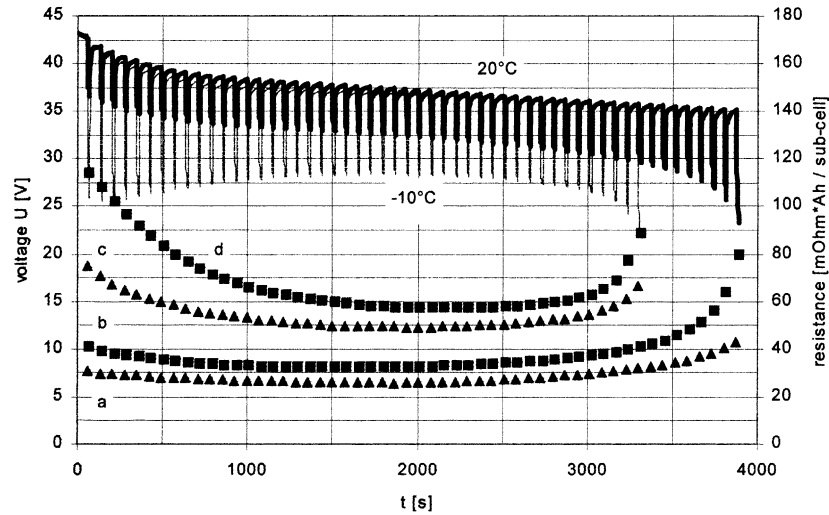


Fig. 8. 5 C Pulse discharges at the 5 C rate for a 36 V, 1.7 Ah bipolar stack at 20°C and at –10°C. Upper curves: voltage response at 20°C and –10°C. Lower curves show resistivity computed from: (a) 1 s polarisation, 20°C; (b) 10 s polarisation, 20°C; (c) 1 s polarisation, –10°C; (d) 10 s polarisation, –10°C.

temperature, the equilibrium pressure in the stack also reaches almost a steady value Fig. 11.

4.4. Self discharge of a bipolar stack

The rate of self-discharge of a bipolar Ni/MH stack is mainly determined by two processes:

1. Decomposition of higher oxides in the positive electrode.
2. Electrolytic bridging across the bipolar plates and the walls between adjacent cells.

As is known from nickel/cadmium accumulators, the rate of self discharge depends upon the state of charge and the temperature.

At the beginning of our studies, electrolytic creepage between sub-cells was not completely eliminated. After improving the design, the self-discharge was reduced to the level found in discrete cell designs.

Fig. 12 gives the residual capacity of a fully charged bipolar stack following various periods on open-circuit at 25°C.

4.5. Changes to the negative electrode during cycling

It was observed that the negative electrode displays some changes during prolonged cycling [8]. After such experiments we have investigated the electrodes by scanning electron microscopy. The SEM photographs (Fig. 13a and b)

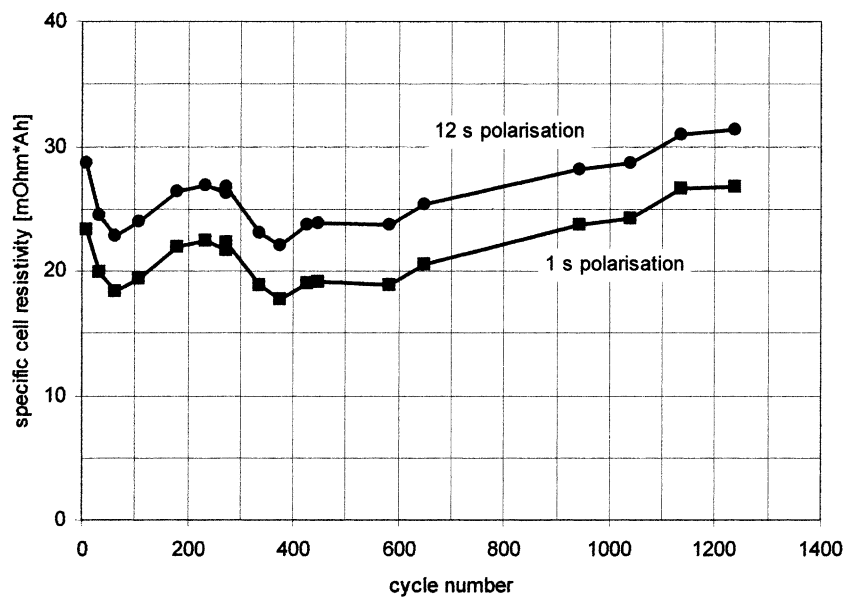


Fig. 9. Long-term specific resistivity of a sub-cell in a 12 V, 1.7 Ah bipolar stack. Data were computed at one and ten seconds into the fifth pulse of a 10 C pulse discharge sequence. Note that early variations are due to different cycling conditions.

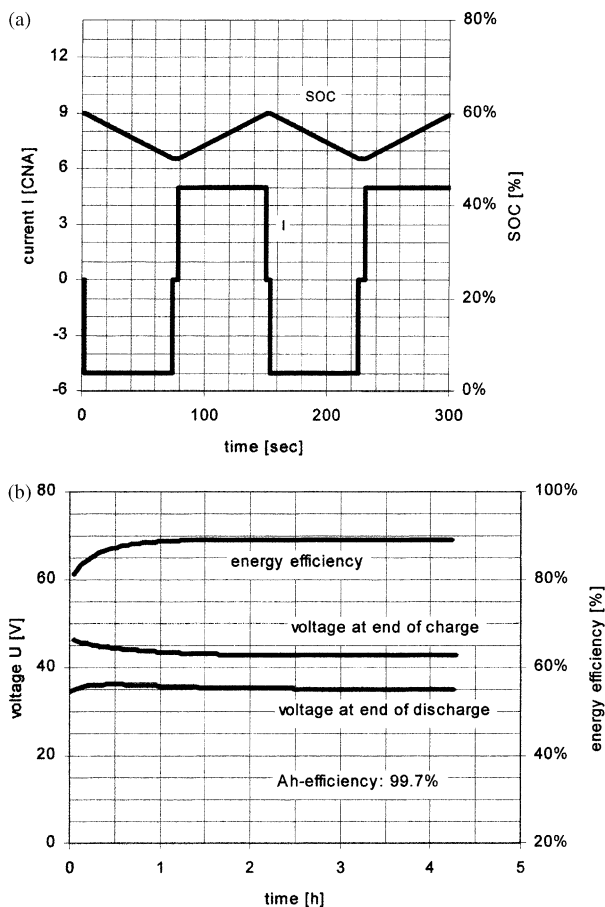


Fig. 10. (a) A 36 V, 1.7 Ah, bipolar stack initially at 60% state-of-charge on a regime representing a hybrid vehicle requirement. Cycling sequence: 5 C charge for 72 s. 5 s open-circuit, 5 C discharge for 72 s. 5 s open-circuit; (b) Hybrid cycles with a 36 V, 1.7 Ah bipolar stack, showing voltages and energy efficiency.

display some changes in the shape of particles of the storage alloy. It is likely that the particle size becomes reduced due to cracks formed as a result of mechanical tensions.

The reason for this could be the change of volume of the alloy during absorption and desorption of hydrogen. The change of particle size does not influence the electric behaviour. Single cell tests give a cycle-life expectancy at 25°C of more than 2000 cycles at 100% DOD.

5. Conclusions

Bipolar Ni/MH stacks are an appropriate device for electric power storage. They can operate with relatively high energy efficiencies. Discharges at low temperature are limited by transport processes. The properties of the stack can be tuned by variation in the electrode thickness in such a way that even high power/energy ratios can be obtained. Stacks of higher voltage can be built and operated. A way to overcome the limit of the restricted capacity of individual stacks may be by paralleling. The pressure in the stacks depends upon the state of charge of the negative electrode. For an application in hybrid vehicles, a thermal management system is needed to protect the battery from overheating. It has been shown that excess heat can be removed by an air stream arranged to flow constantly around the stack. The bipolar stack design could be an alternative for power storage in hybrid cars and the new automobile board net structures.

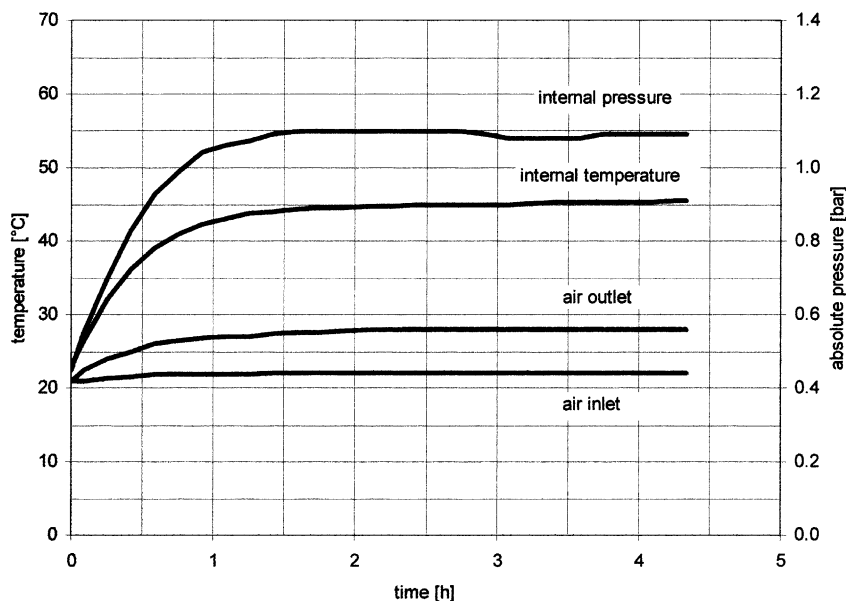


Fig. 11. Temperature and pressure profiles of a 36 V, 1.7 Ah bipolar stack during hybrid cycling in a experimental set-up with air-cooling (power consumption of fan: 0.9 W per stack). Ambient air temperature: 22°C.

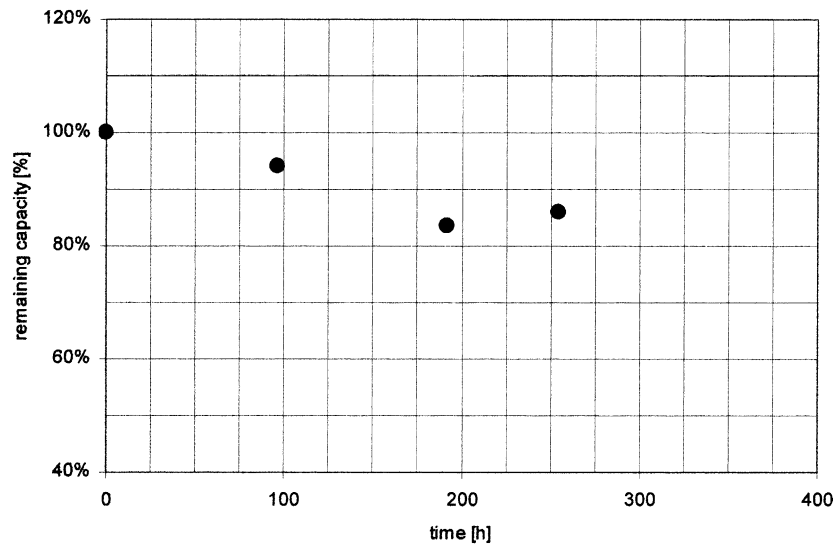


Fig. 12. 36 V, 1.7 Ah bipolar stack: self-discharge behaviour at 25°C.

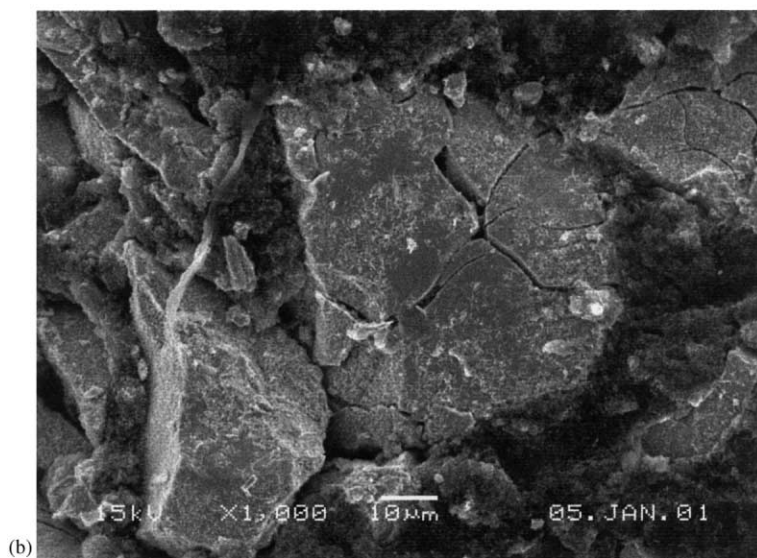
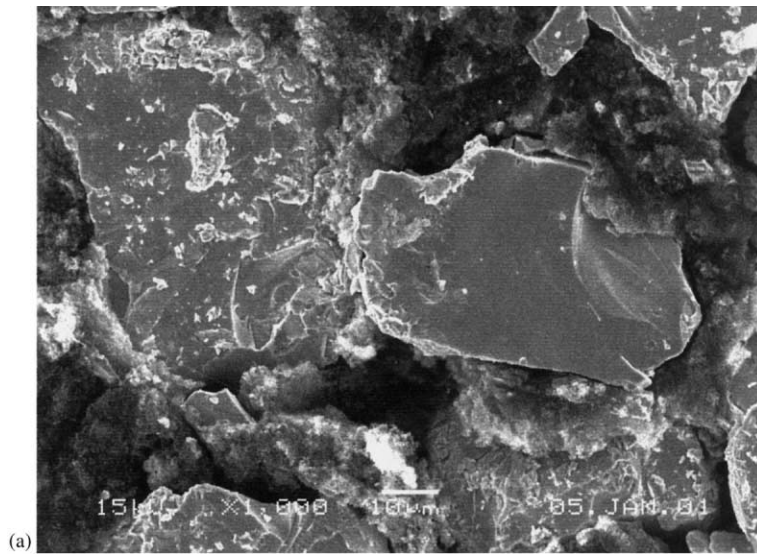


Fig. 13. (a) SEM of a fresh metal hydride electrode; (b) SEM of a metal hydride electrode after cycling.

Acknowledgements

The authors acknowledge the BMW (Bundesministerium für Wirtschaft, BEO 0329829 5) for financial support of these research activities and Dr. G. Sandstede for contributions and helpful discussion. The authors have to thank the Institute of Chemistry of FH Holzminden for the SEM investigations.

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