

High performance nickel–metal hydride battery in bipolar stack design

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Abstract

The consumption of fuel in cars can be reduced by using hybrid concepts. Even for fuel cell vehicles, a high power battery may cut costs and allow the recovery of energy during retarding. Alkaline batteries, such as nickel–metal hydride batteries, have displayed long cycle life combined with high power ability. In order to improve the power/energy ratio of Ni/MH to even higher values, the cells may be arranged in a bipolar stack design. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Accumulatorenwerke Hoppecke together with Kurt-Schwabe Institut für Mess- und Sensortechnik e.V. Meinsberg have continued previous [1–5] works to study the properties of Ni/MH batteries in a bipolar stack design. The aim of the development is focused on the applications of bipolar nickel–metal hydride batteries as power storage devices in the hybrid vehicles as well as in the modern power net structures in conventional cars. During recent years, PEM fuel cell systems have been discussed as alternative power supply for road vehicles. A major difficulty for these vehicles are the enormous cost of the membrane and the catalysts applied. As the size of a fuel cell system is determined by the maximum power needed to drive the vehicle, the cost of the fuel cell is a direct function of that quantity. Using a battery, the maximum power requirements are smoothed and energy may be recovered during retarding. In addition, several appliances in the vehicle need energy in order to start the fuel cell system by itself.

2. Bipolar design

The idea of arranging an electrochemical battery in a bipolar stack design originates from Volta's pile during the very beginning of electrochemical science, 200 years ago [6].

In contrast to a conventional battery design, a bipolar stack is assembled in such a way that the single sub-cells are connected together via electrochemically inert bipolar plates. The bipolar connecting materials should provide sufficient electrical conductivity, only a small contact resistivity to the adjacent active materials on both of the sides, and must not allow any electrolytic contact between the two sides.

In the past, there had been attempts to build bipolar units made in such a way that the electrodes are directly fixed to the bipolar plate. Such an arrangement is of advantage, if the electrode material can be pasted directly onto the bipolar plate (Fig. 1a). The disadvantage is the need to have production technologies that allow a simultaneous preparation of active materials on both sides of the material. An alternative method is the preparation of a bipolar plate in such a form, that the positive and negative parts of the electrode are located beneath each other (Fig. 1c). Such plates lead to a pseudo-bipolar stack design (Fig. 1d).

We have chosen the combination of separate electrodes with a bipolar plate as illustrated in Fig. 1b. The advantage of this, is that, the electrodes from standard production lines may be applied and electrode thicknesses may be larger than that achieved by pasting active materials to the bipolar plate itself.

The difficulties that have to be solved to realize a bipolar design lay in the contact resistivity, preventing electrolytic bridges between the sub-cells, construction problems and restricting the amount of the electrolyte and immobilizing it in the active parts of the cells.

In contrast to all other electrochemical couples, the Ni/MH systems offers some advantages for building a bipolar stack.

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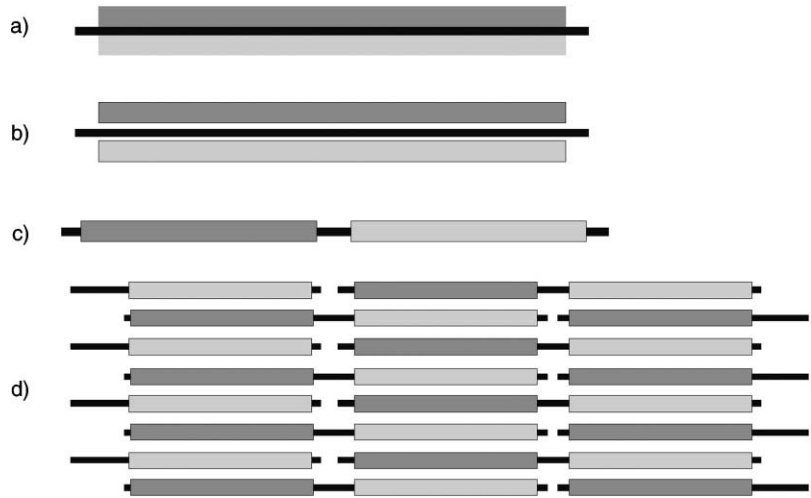


Fig. 1. Possible bipolar arrangements.

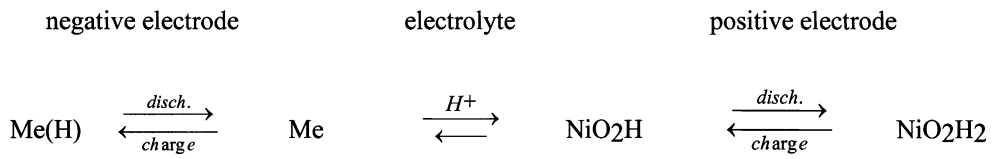


Fig. 2. Cell reactions in a Ni/MH cell.

The reasons are that the electrolyte is not directly involved in the electrochemical cell reaction (Fig. 2) and its amount can be restricted to the pore volume of electrodes and separators. This makes it easier to solve the problem of electrolytic creeping between the sub-cells. Another advantage is related to the nature of the negative electrode.

3. Metal hydride electrode and cell reaction

The negative electrode is made of an AB₅ storage alloy (grains visible in Fig. 3) located in a conducting structure. The electrode material contains a fibrillized binding agent as well as other additives.

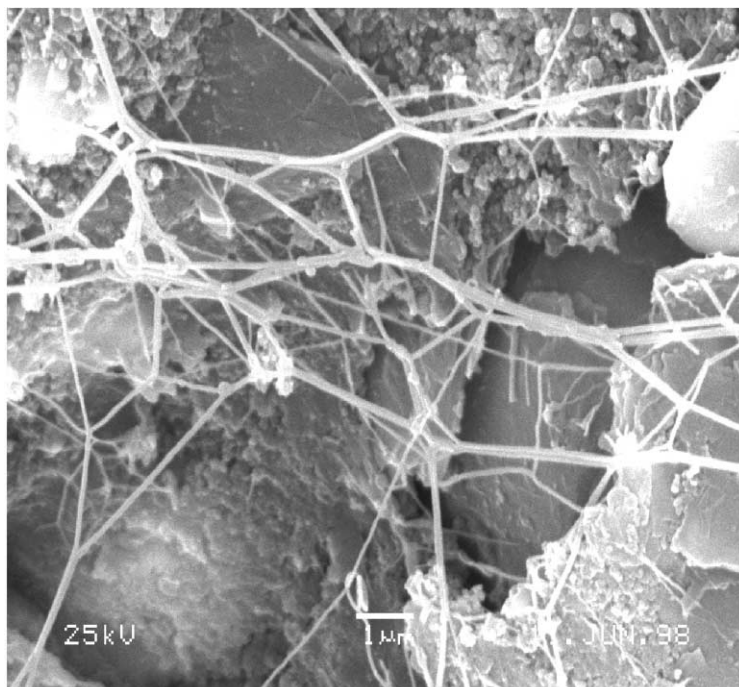


Fig. 3. SEM of the active material in the negative electrode (obtained from Institute of Chemistry, FH Holzminden).

In the course of the electrochemical reaction, the hydrogen ions are discharged at the surface of the storage alloy. The hydrogen is absorbed into the bulk of the storage material. As this process is related to the diffusion processes, the velocity depends strongly upon temperature.

Besides the electrochemical reaction, there is a phase equilibrium between gaseous hydrogen and the hydrogen distributed inside the storage alloy. This equilibrium follows approximately the van't Hoff isotherm with a heat of absorption of about 36 kJ/(mol H_2).

Kinetic hindrances occur due to the transfer of hydrogen from the surface to the bulk of the grains and from access of the gas to the metallic surface. The electrolytic wetting balance also influences the gas exchange. The kinetic hindrances result in a gas pressure higher or lower than the equilibrium value. Especially at the end of charge, the pressure rises considerably. At the end of discharge, the gas pressure is below atmospheric pressure. The cell design has to withstand these conditions (Fig. 4).

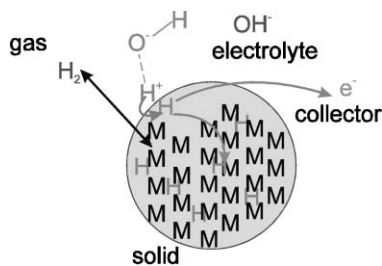


Fig. 4. Reaction paths of hydrogen in the storage alloy.

4. Experimental results

4.1. Discharge characteristics

Several bipolar stacks with the voltages of 3.6 V (3 sub-cells), 12 V (10 sub-cells) and 36 V (30 sub-cells) have been built and investigated. The experimental stacks have a cylindrical shape to simplify their construction for the studies. The electrical contact resistance between the sub-cells is so small that it will not influence the stack behavior.

As mentioned earlier, the amount of electrolyte can be limited without having a drastic increase of resistance during the course of discharge. In Fig. 5, it is shown that only at the end of discharge, the stack resistance slightly increased. The origin of this increase is the polarization of the positive electrode and the effect can be found in other similar electrochemical systems (single cells Ni/MH and Ni/Cd).

Normally, the discharge of the sub-cells is limited by the capacities of the positive electrodes. As all the sub-cells are combined in series and the electric capacity of single sub-cells is comparatively small, the variation of the individual capacities of the sub-cells is of importance to the stack behavior. Even if it is attempted to furnish the electrodes in the stack with the same amount of active material, a certain variance of their electric capacities cannot be prevented. In the case of a voltage reversal of a single sub-cell, an electrochemical mechanism is available that prevents the failure of the complete stack. Under these conditions, hydrogen is produced at the nickel electrode. The hydrogen is transferred via the gas phase to the hydride electrode and is absorbed by the storage alloy. Thus, the metal hydride

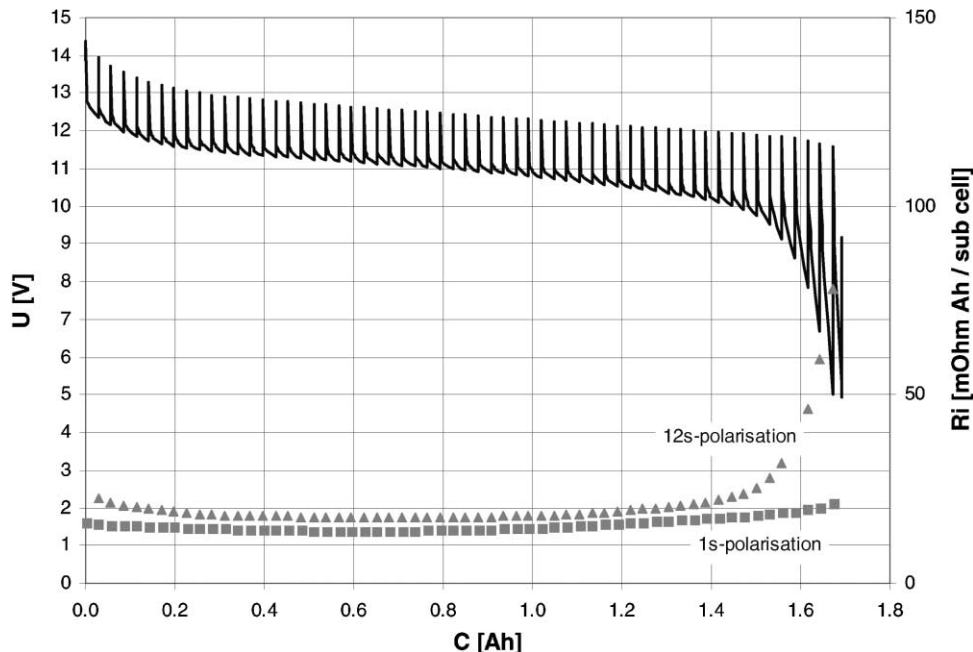


Fig. 5. Pulse discharge (5 C rate) and resulting specific resistivity (polarization after 1 and 12 s, respectively) of a 12 V, 1.7 Ah bipolar stack.

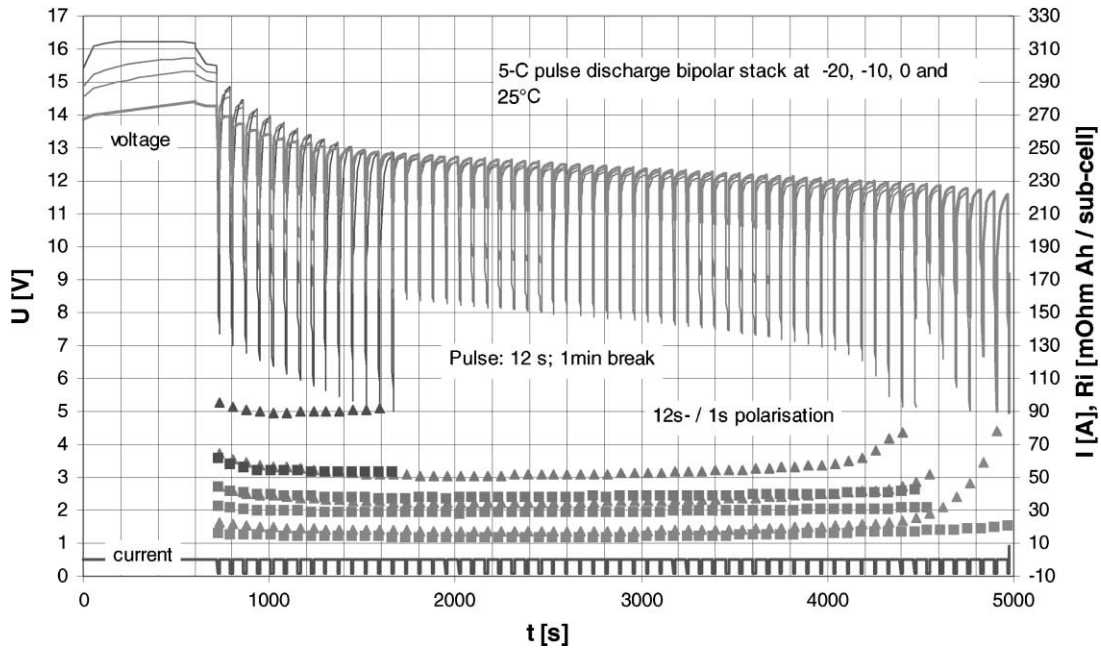


Fig. 6. Discharge curves at various temperatures.

electrode will not suffer a loss of hydrogen under these conditions. Even if hydrogen is only available at the surface of the storage alloy, it will protect the storage alloy from being oxidized. The result of a reversal of a sub-cell is only a loss of about 1.5 V of the stack voltage. A pressure increase is observed that may be used to indicate the undesired state of a sub-cell. If the current is not too high, and this does not happen regularly, the stack will withstand such abuse conditions.

4.2. Low temperature behavior

At low temperatures, the reaction at the hydride electrode becomes significantly retarded. By modifications of electrodes and stack design, the performance can be improved to allow pulse discharges at low temperatures. As an example, the discharge curve of a laboratory stack is given in Fig. 6.

For application in high performance systems, a stack is required that can be discharged with high specific currents.

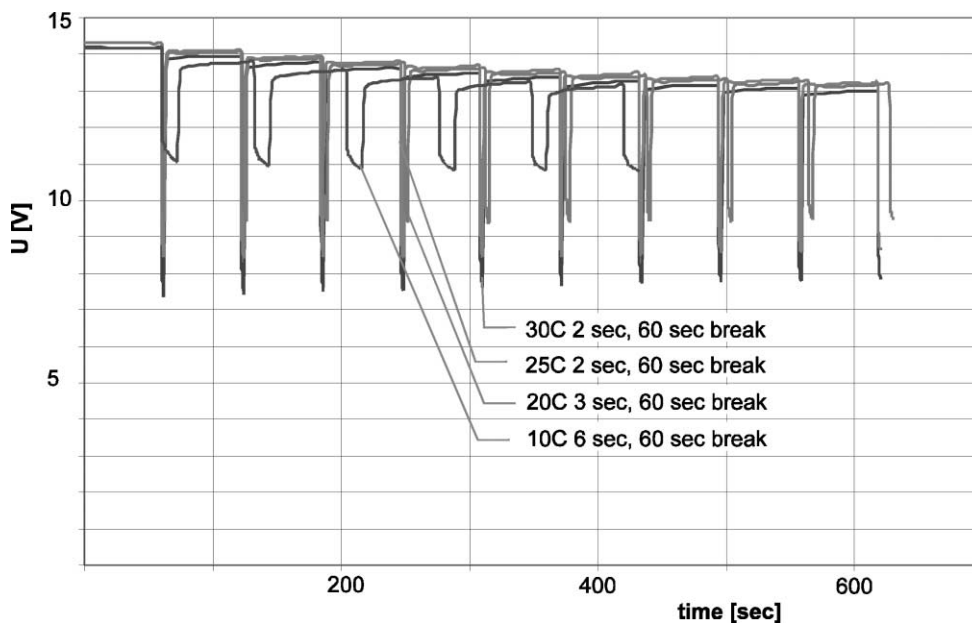


Fig. 7. Discharge curves with high current pulses 12 V, 1.7 Ah bipolar stack.

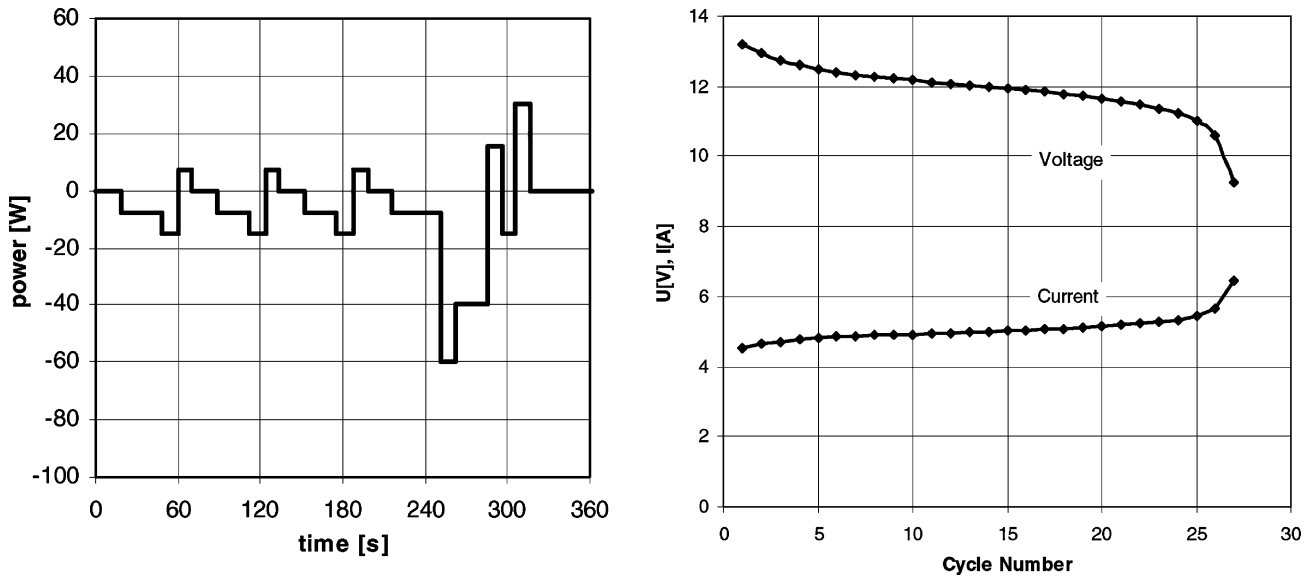


Fig. 8. DST pulse program scheme and voltage/current at the peak of 60 W pulse power as function of DST cycle number.

The advantage of the bipolar stack is the elimination of voltage losses due to connecting elements. However, it must be taken into account that the electrodes face the electrolyte single-sided. Depending upon the electrode dimensions, this may result in higher polarization losses for thick electrodes.

4.3. Pulse discharge

In a hybrid vehicle, the discharge is typically a pulse discharge with currents higher than 5 C. Such discharge curves are shown in Fig. 7.

A special investigation is the dynamic stress test (DST) cycling as illustrated in Fig. 8. During a complete cycle, the amount of charge drawn from the cell is larger than the recharged amount. Thus during cycling, the SOC is decreasing. The voltage measured at the highest discharge pulse is a measure of the performance characteristics of the stack.

4.4. Electrical and thermal properties of bipolar stacks

Positive experiences with 12 V bipolar stacks have led to experiments with higher voltages. These stacks have a modified construction and allow an operation for extended experiments (Fig. 9). As most car manufacturers discuss 42 V power net technology, a 36 V bipolar stack with a cell capacity of about 2 Ah has been designed and operated. The specific electrical data correspond to that of the 12 V laboratory modules. From the view-point of a low weight design, even higher voltages would be preferred and could be realized.

As the electrical capacity depends upon the cross-section of the stack, the major advantage is the ratio of power to energy content. In order to meet the requirements of higher capacities, stacks can operate in parallel circuits.

The bipolar technique may be used for pulse cycling and load equalizing. It is possible to arrange bipolar stacks in series as well as in parallel to build larger batteries. A design was made for the battery structure, consisting of nine bipolar stacks (36 V). Assuming a capacity of about 7 Ah, an energy content of about 2.3 kWh and maximum power output of about 30 kW can be expected.

For larger battery units, the thermal conditions are of importance. Even if the cell resistivity is very low (about 20 mΩ Ah), heavy load cycling results in heating of the system. In order to operate batteries under these conditions, a thermal management system has to be incorporated. The effect of cooling the stack (12 V, 1.7 Ah) with a fan



Fig. 9. Bipolar stack design.

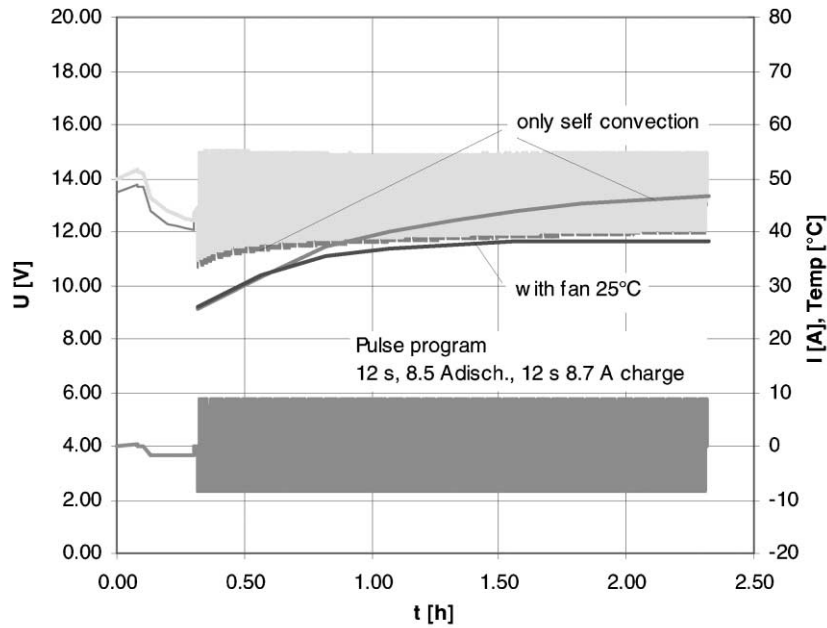


Fig. 10. Effect of cooling during pulse cycling of a bipolar stack.

in 25 °C environment is shown in Fig. 10. The pulse program (12 s, 5 °C) is adjusted in such a way that the battery maintains the state of charge during cycling.

Fig. 11 shows the temperature distribution (thermal imaging) after reaching a stationary state during another cycling experiment with the advanced cell stack. The experiment demonstrates that the stack can be operated using a thermal management system.

A more detailed analysis shows that the electrode package is under constant thermal conditions. The polarization (charging and discharging) is reduced at elevated temperatures.

Long-term experiments have proved that the battery system can be operated for several thousands of cycles. The characteristics (0.2 nominal capacity and 1 nominal capacity discharge) of a stack after about 1000 cycle experiments (different cycles of 80–100% of the nominal capacity)

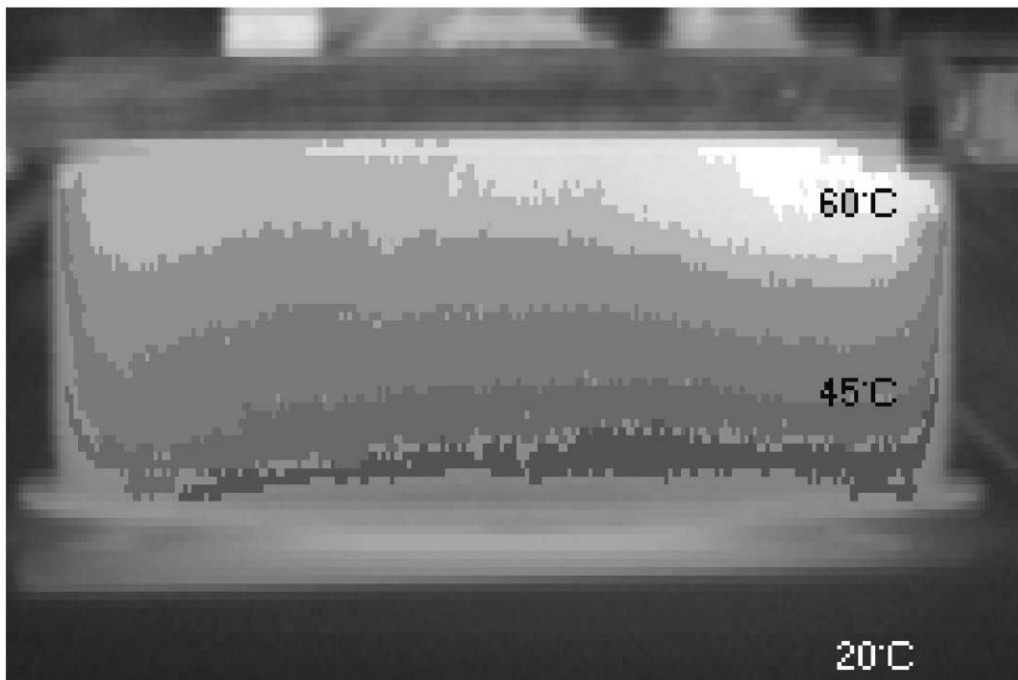


Fig. 11. Thermographic image after 1 h cycling at SOC of 40% (72 s cycle, 10% nominal capacity with $I = 10$ C).

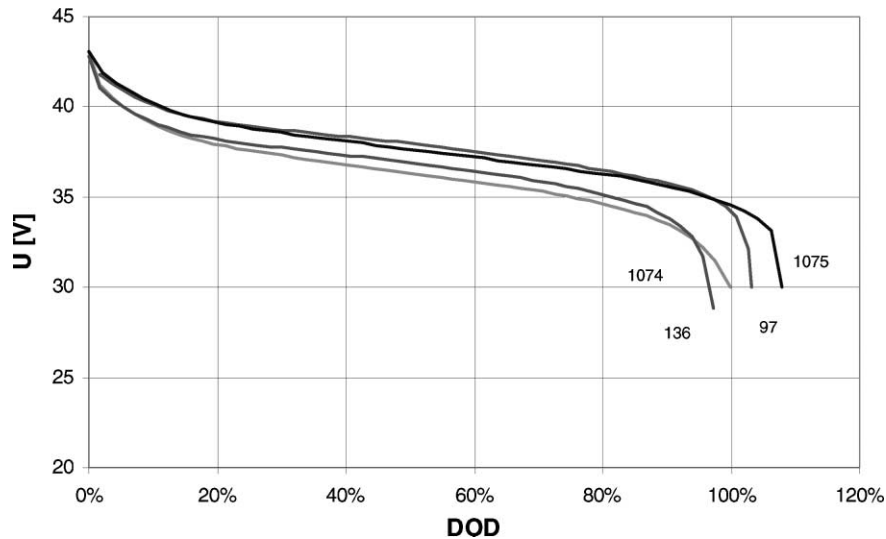


Fig. 12. Comparison of discharge characteristics of a bipolar stack after cycling (numbers indicate cycle number).

are compiled in Fig. 12 (related to the nominal capacity obtained with a 0.2 C discharge at the beginning of stack operation).

5. Conclusions

Bipolar Ni/MH stacks demonstrate excellent properties for high power applications. The power density can be extended up to values of about 1000 W/kg. They can be used in an extended range of temperature. Experiments have shown that the life time expectancy and cycling behavior make them an interesting alternative for an application in hybrid technology and new automobile power net structures.

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