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High performance nickel-metal hydride and lithium-ion batteries

U. Köhler*, J. Kümpers, M. Ullrich

NBT GmbH, Am Leineufer 51, D-30419 Hannover, Germany

Abstract

In comparison to pure electric vehicles (EV) the opportunities for hybrid electric vehicles (HEV) are much better, since range restrictions no longer apply and the interaction of the internal combustion engine and electrical drive bring increased energy efficiency and environmental friendliness. The batteries used in such applications must meet very high standards in terms of performance and service life. Although the battery capacity is smaller than for a purely EV, it needs to be able to generate far higher levels of power. The technical challenges of hybrid applications have led to the development of high-performance batteries. At the forefront of these is the nickel-metal hydride system (NiMH). With specific power and energy data in the range from 300 to 900 W/kg, 55 to 37 Wh/kg, respectively (based on cell weight), excellent charge efficiency and energy throughput levels of more than 10,000 times the nominal energy, the NiMH system comes very close to satisfying the needs of the HEV. Parallel developments with the lithium-ion system based on manganese spinel as cathode material show that, with specific power and energy levels above 1000 W/kg, 50 Wh/kg, respectively, this technology will also be able to play an important role in the future. Service life figures in terms of calendar life have been improved tremendously to about three years, but there is still a need for further improvement in order to meet the specifications of car manufacturers. For this reason, an increase of life span is the subject of intensive development work. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrical road vehicles can look back on a history of more than one hundred years. They made up a considerable share of vehicles in the early days of road traffic, but this share was soon lost in the face of the rapid progress made by vehicles equipped with internal combustion engines. The fundamental weakness of all electric vehicles (EV) lies in the battery required for energy storage. The energy storage capacity of batteries is unable to achieve the ranges attained by vehicles driven by internal combustion engines. Despite all the progress which has been made, not the least in the research and development activities conducted since the start of the 1990s, there has been no fundamental change in this regard. Significant technical advances have been made, but we are still far away from a product which is satisfactory in every respect [1,3]. The basic cause for the low storage capacity of electrochemical battery systems lies in the fact that their energy densities are much smaller than those of liquid hydrocarbons. This shortfall can only be compensated partially by the higher efficiency of the electrical system. The energy storage system would need to be at least ten times

*Corresponding author. Tel.: +49-511-9751830; fax: +49-511-9751801.

E-mail address: uwe.koehler@varta.com (U. Köhler).

larger in terms of volume and weight. These drawbacks in terms of volume and weight are compounded by high costs and customer inconvenience, reflected primarily in infrastructure aspects and charging times.

The systems which can currently be used on the markets for EV include the lead-acid battery, NiMH technology [1,7,9,10,14] and the high-temperature sodium-nickelchloride system. Lithium-ion batteries are the subject of intensive development work worldwide [16,17]. But even this most advanced system in terms of energy density, still lags well behind the energy densities possible with conventional petrol-driven vehicles. The basic advantage of hydrocarbon-based energy storage systems is also the reason for the newly awoken interest in fuel-cell technology. The general weakness of hydrogen-based systems was the fact that, in the past, they stored energy in the form of gaseous hydrogen. Storing energy in the form of methanol which releases hydrogen during subsequent use in the reformer comes a good deal nearer to resolving the problem and has resulted in considerable progress being made in this regard [19].

Because of the more sober view now being taken of the opportunities which exist for purely EV in the future, hybrid vehicles have once again become the focus of attention [2]. Linking internal combustion engines with electric drive systems offers a number of technical possibilities for constructing environmentally friendly, fuel-saving vehicles. One of the key components of the hybrid vehicle is the battery. Although the battery capacity is smaller than for a purely EV, it needs to be able to generate far higher levels of power. Since the use of batteries is currently also being discussed as a means for storing energy for future fuel-cell vehicles, the specific direction which battery development is taking here promises to be the most successful in the long run.

2. Nickel-metal hydride batteries

2.1. Background

Of all the new battery systems introduced world-wide, the NiMH system is generally regarded as the most technically mature [4–12,14,15]. This has meant that many of the latest generation of EV launched onto the admittedly small market have been equipped with batteries of this type (e.g. Toyota RAV4, General Motors EV1).

In addition to actual NiMH high-energy cells which have been developed with high specific energy of upto 80 Wh/kg, there are two product lines in particular which are attractive for hybrid vehicles.

2.2. High-power (HP) cells

A typical application for these cells is the propulsion battery of a conventional hybrid vehicle which has a specific range when used in purely electrical mode. High power levels, rapid charging and a long service life are all important for such applications. Due to the relatively high capacity values (>40 Ah) which the energy requirements bring with them, the cells are produced in prismatic form [9,12,14,15]. This construction form allows a relatively large cell surface, which is required for dissipating the heat losses occurring during battery operation.

The high requirements in terms of electrical power are met at the cost of the energy density which, at 55 Wh/kg and 150 Wh/l, lie far below the level of high-energy cells.

However, the load behaviour during discharging and charging is much better. Even when discharging with a 10 min current (6 C rate) more than 80% of the stored chemical energy can be converted to useful energy. The specific power lies in the region of 300 W/kg. Cells of the high-power type can be charged completely within 60 min. Partial charging up to around 80% is possible even within 10 min. Rapid charging is limited by the temperature and pressure rise in the cells resulting from exothermal hydride formation, losses generated by electrical resistance and the oxygen evolution occurring at the end of the charging process.

Hybrid buses are the primary application today for NiMH high-power batteries Fig. 1. Electrical operation allows the bus to travel completely free of exhaust gases in sensitive inner city areas. Under normal combustion engine operated drive the electrical propulsion system with the battery can provide extra power, e.g. for enhanced acceleration. Energy can be stored back into the battery when the vehicle decelerates.

2.3. Ultra high power (UHP) cells

Ultra high power cells with an even further increased power capability are probably the most important development for the long term [12,14,15]. They have been designed for "power assist" applications in state-of-the-art hybrid vehicles where the improvement in energy efficiency and the dramatic reduction in harmful waste gases is at the forefront of development work. Their use is also currently being discussed in new vehicle electrical supply systems supporting voltage levels of 42 V. The NiMH system has been further developed for these applications with a view to achieving a significant increase in power. UHP cells are currently available in prototype form, with capacities in the range from 3 to 26 Ah. Due to their relatively low capacities, these cells are produced in cylindrical form.

As an example Fig. 2 shows the discharge characteristic for a UHP cell with a capacity of 10 Ah. Even with a 30 C discharge (2 min), the full capacity is available at a voltage level of around 0.85 V. The maximum specific power output is in the region of 900 W/kg (SOC: 90%). Good values are



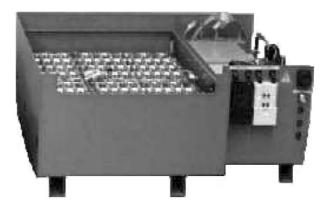


Fig. 1. NiMH high-power batteries (350 V/60 Ah) for hybrid buses.

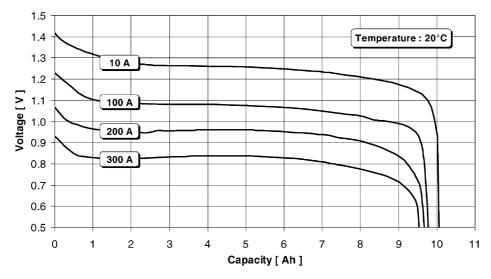


Fig. 2. Discharge characteristic of an NiMH-UHP cell with capacity 10 Ah.

also obtained for fast charging. The latest generation of UHP cells can be charged to levels in excess of 90% capacity within about 3 min (20 C rate). This corresponds to a maximum specific continuous power acceptance of ca. 1000 W/kg.

Fig. 3 shows a typical example of a power assist battery consisting of 200 UHP round cells with 10 Ah rated capacity. With a relatively low energy content of approximately 2.5 kWh, discharge powers in excess of ca. 55 kW can be achieved at normal ambient temperatures. In context of the overall system, this corresponds to a maximum specific discharge power of ca. 500 W/kg. Lower temperatures reduce the power capability due to higher internal resistance values, while performance increases slightly at higher temperatures.

2.4. Service life

The service life, either calendar life or cycle life is crucial for the cost-effectiveness of a battery system, particularly in

vehicle applications. Cycling endurance and the maximum capacity throughput figures are determined significantly by the specific charging and discharging conditions. Fig. 4 displays the tremendous influence of the depth of discharge to the achievable capacity throughput figures. The typical service life of NiMH cells operating under 1 h charging, 1 h discharging at 100% DOD lies in the order of 2000 cycles (drop to 80% of the initial capacity). Running the cells in a SOC operation window from 90 to 10% (SOC swing: 80%) brings about approximately double capacity throughput figures. UHP cells, in line with their design intentions, however, are only operated within a relatively small SOC range, though at very high charge/discharge currents. Cycling at a state of charge of around 70% is regarded as typical in this regard, a maximum of 5% of the capacity being charged and discharged for each cycle. Fig. 4 displays that under theses conditions more than 10,0000 times the capacity can be put through. Numbers in excess of 14,000 times were already demonstrated earlier with 1 Ah cells using the same electrode configuration [15].



Fig. 3. NiMH-UHP ("power assist") battery (250 V/10 Ah).

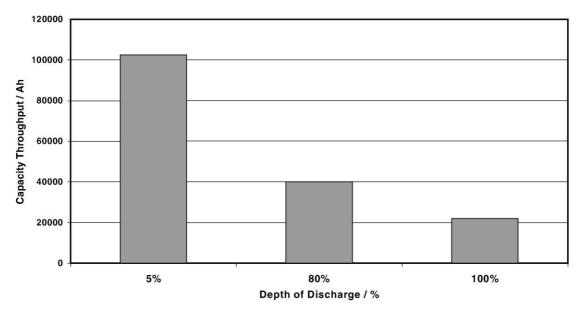


Fig. 4. Cycling endurance test with NiMH 10 Ah UHP cell: 5% DOD-cycling (SOC: 75-70%); Dch: 270 A (2.5% NC) + 20 A (2.5% NC); Ch: 50 A (5% NC) + rest periods (test still running), 80% DOD-cycling (SOC: 90-10%); Dch: 100 A (80%); Ch: 100 A (80%) + rest periods, 100% DOD-cycling: Dch: 10 A (100%); Ch: 10 A (100%).

3. Lithium-ion batteries

3.1. Background

Lithium-ion batteries are the most high-tech product on the portable batteries market. They are the batteries of choice in cutting-edge electronic appliances. The largest market for these batteries is the notebook computer market, followed by the cellular phone market. In these two markets in particular, the weight advantage of lithium-ion batteries is very evident. While NiMH portable battery cells have typical specific energies of 80 Wh/kg, the corresponding figure for lithium-ion batteries is more than 50% higher at 120–130 Wh/kg. Seen in terms of the volumetric energy density, the lithium-ion system displays no dramatic advantage. Both are more or less identical with cell-specific values of 200–300 Wh/l.

The weight advantage is the key factor that has made the lithium-ion system a highly attractive candidate for future energy storage systems in EV. While the current portable battery systems make virtually exclusive use of cobalt oxide for the cathode material, this is not possible in EV batteries due to availability and cost. For this reason, all efforts worldwide in this field are geared towards using cheaper materials [17]. Efforts were concentrated on a lithium-manganese spinel and immense progress has been made with this material over recent years.

As outlined at the beginning, the wide-scale use of lithium-ion batteries in EV cannot be envisaged at the current time, despite all the progress that has been made. This is due to the fact that, like all other battery systems, the energy density is still less than satisfactory. In addition, despite the use of inexpensive materials, the cost of a battery

with an energy storage capacity in the range 20–30 kWh would be prohibitive. NBT has therefore taken the decision to put its current development work on fully EV batteries on ice and, as with the NiMH system, to focus its efforts on developing high power batteries.

3.2. High-power lithium-ion cells

While the high-power NiMH system has already moved through the prototype stage and is moving towards series production, a similar development for lithium-ion is still some way in the future [16,17]. Nevertheless, the results which have been achieved to date are already indicative of the tremendous potential which this system also has for the high-power sector [18].

Similar to developments with NiMH, development efforts concentrated on the relatively low cell capacities over the range of 5–20 Ah. The increase in power compared to high energy cells is achieved primarily through using thinner electrodes and materials better capable of withstanding high currents. A fundamental problem is the conductivity of the organic electrolyte which is around two orders of magnitude below that of aqueous media. The electrode stack arrangement used for prismatic cells has also been abandoned for cost reasons. Instead, a winding technology similar to that used with portable battery cells or coil-type capacitors is being applied.

Fig. 5 shows the discharge voltage behaviour of a lithiumion cell with a capacity of 6 Ah which is subjected to currents of 6–100 A. Even with a discharge current of 100 A (ca. 16 C rate), voltage values of over 2/3 of the rated voltage can still be obtained. The comparison with lithium-ion high energy cells can be seen from Fig. 6. While

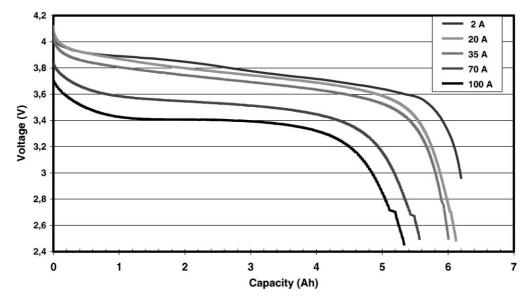


Fig. 5. Discharge voltage characteristic of a lithium-ion high-power round cell with a capacity of 6 Ah.

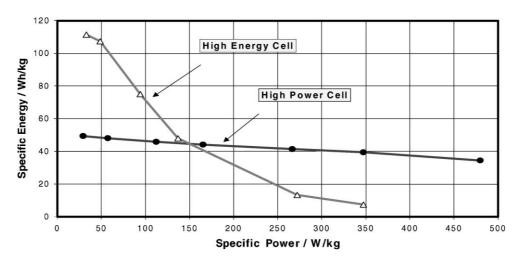


Fig. 6. Energy/power diagram (Ragone plot) for different Li-ion cell types.

the specific energy of a lithium-ion high-power cell of 55 Wh/kg is around half of that of a high energy cell, its power density is more than four times higher.

3.3. Service life

Lithium-ion batteries have a shorter service life than NiMH batteries, a fact which still is the major weakness of this system. The service life of lithium-ion batteries today is determined primarily by the calendar life. Depending on the cell type and cell size, service lives of two to four years can be achieved today under normal ambient temperatures. This is entirely adequate for most portable battery applications, but is not acceptable in vehicle applications where a minimum service life of five years is required. Over recent years, considerable progress has been made in the stability

of the materials used. There is, therefore, optimism that this problem can come closer to a solution over the coming months and years.

4. Conclusion

Efforts over recent years have seen considerable progress being made in NiMH systems in terms of performance. Specific power which comes close to the 1000 W/kg level signifies an increasing degree of competition for capacitor systems since [13], in addition to comparable power levels, they also offer an energy storage capacity which is around twenty times higher. Use in electric and hybrid vehicle prototypes demonstrates that the NiMH system can have a particularly interesting role to play in the future of vehicle

construction. Its particular strengths are to be found in its high gravimetric and volumetric power data. This makes this battery particularly attractive wherever small, powerful, quick-charge batteries are required.

The results achieved with the NiMH-UHP-technology not only support use of NiMH power assist batteries for future hybrid vehicles, but also open up additional fields of application for the NiMH system. Such applications include supply batteries for new 42 V-vehicle electrical systems.

In the field of development and production engineering, the lithium-ion high-power battery still lies several years behind the corresponding NiMH system for applications in the automotive sector. The results achieved to date nevertheless show that considerable potential exists in terms of power levels which it will be important to exploit in the future. Specific power levels up to 1500 W/kg with specific energy levels of up to 80 Wh/kg appear feasible. The main problem at the current time is the calendar service life, particularly under temperature conditions such as those that can be expected in automotive applications. It will be necessary to double the current service life in order to satisfy the needs of the vehicle industry.

Acknowledgements

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