

ZEBRA batteries, enhanced power by doping

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Abstract

The ZEBRA battery, based on the reaction sodium + nickel chloride \leftrightarrow sodium chloride + nickel, is well known for its high energy density of 118 W h/kg (cell) or 87 W h/kg (battery system including battery box and all peripheral equipment). The power density was increased in a first step by implementing a clover leaf-shaped ceramic electrolyte instead of the round tube electrolyte. A further improvement of the power density was achieved by doping of the positive nickel/nickel chloride electrode with iron, resulting in constant peak power of the battery system of 170 W/kg. The mechanism of the doping is described. The doping has no adverse effect on cycle life as a life test with presently 1100 nameplate cycles shows and this test is continuing. © 1999 Elsevier Science S.A. All rights reserved.

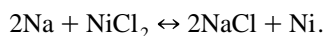
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1. Introduction

The ZEBRA battery is well known for its high energy density [1,2], but for car application, the battery has also to exhibit a high power capability as it is required by the car industry and tabled in the USABC requirements. Therefore, during the last 2 years, the development of the ZEBRA system was directed to the increase of the power density.

2. The ZEBRA system

The ZEBRA system is based on a very simple cell reaction:



In the charged state, sodium and nickel chloride are available and during discharge sodium reacts with nickel chloride to form nickel and sodium chloride. During charging, the reverse reaction will occur. This happens in a cell which is shown schematically in Fig. 1. Since sodium is one reactant, it is necessary to apply a sodium ion conductor as electrolyte. The best sodium ion conductor presently known is β -alumina which is a solid ceramic electrolyte

and this solid electrolyte separates the negative electrode from the positive electrode.

In the cell, between the cell case and the electrolyte, there is the negative compartment with sodium and inside the ceramic electrolyte, which is manufactured as a tube with one closed end, the positive electrode is located. The positive electrode is nickel chloride in a matrix of nickel powder to obtain the electronic conductivity. A nickel strip located in the middle of the positive electrode serves as a current collector.

There is a solid electrode as well as a solid electrolyte in the cell and therefore, additionally, a liquid electrolyte is necessary to make the positive electrode work together electrochemically with the solid electrolyte. This liquid electrolyte is a molten salt: sodium aluminium chloride. Due to the solid electrolyte which only exhibits sufficient conductivity at higher temperatures, the cell is operating at about 300°C.

The manufacture of the cells is easy because the cells will be manufactured in the fully discharged state. That means according to the reaction only nickel and sodium chloride (common salt) are present. For manufacture, the parts of the cell are mounted together with the ceramic into the cell case. The positive mass nickel and salt are filled into the positive compartment inside the ceramic electrolyte, then the molten sodium aluminium chloride, the second electrolyte, is added. Afterwards, the cell is com-

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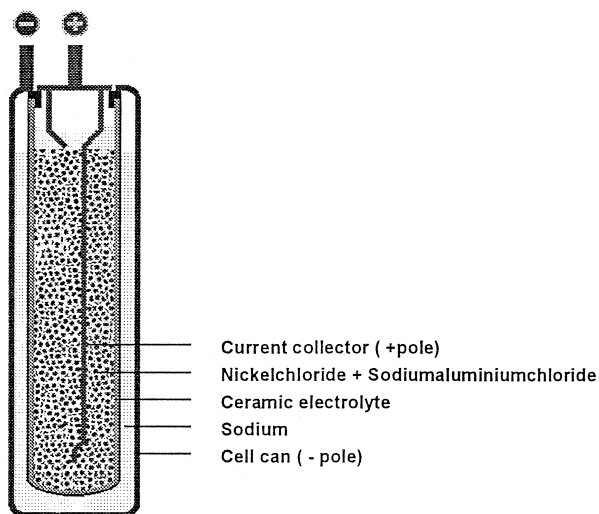


Fig. 1. ZEBRA cell.

pletely sealed by welding. The sodium is formed during the first charging in the negative compartment.

This cell has a very high cell voltage of 2.58 V. In order to obtain batteries from these cells with a voltage of around 300 V which is now fixed for car applications, about 110 to 120 cells must be connected in series. These strings can also be connected in parallel to get the capacity demanded. Inside the battery box, which is a vacuum-isolated box, the cells are densely packed. ZEBRA batteries are built up as a whole system. Not only the battery itself, but also peripheral equipment is included; peripheral equipment like the cooling box, the interface box with the main switches for the car and the battery management system.

The performance data of ZEBRA cell and battery system are compared in Table 1, indicating that there is a big difference between cell and battery system values due to the addition of all the peripheral equipment. The energy density of the cells is close to 120 and of the battery system close to 90 W h/kg. The power density is defined at the magic value of 80% DOD and ZEBRA has reached

Table 1
Performance of ZEBRA cells and ZEBRA batteries

		Cell ML3	Battery including peripheral equipment
Energy density	W h/kg	118	87
	W h/l	275	139
Power density	0% DOD 30 s 2/3 OCV	W/kg 297	220
	80% DOD 30 s 2/3 OCV	W/kg 203	150
	80% DOD 30 s 2/3 OCV	W/l 473	240
	Efficiency (energy)	% 91	91
(12-h charge, 5-h discharge)			
Cycle life		up to 3000	up to 1700
Calendar life	years	> 5	> 5

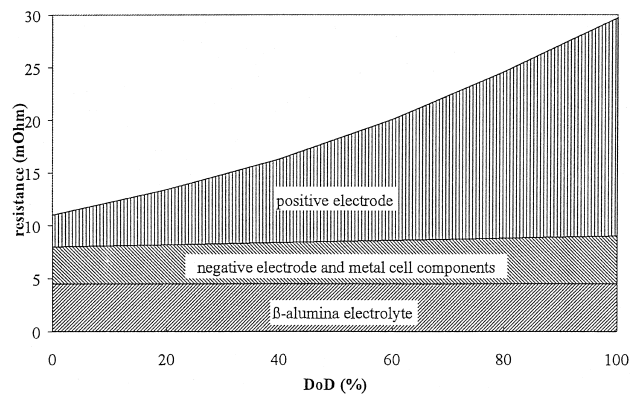


Fig. 2. Contribution of components to the resistance of a ZEBRA cell in a 2-h discharge (schematically).

about 200 W/kg at cell level and 150 W/kg at battery system level. While we had achieved the high energy density very early at the beginning of the ZEBRA battery development, it takes a lot of effort to bring the power density to this high value and make this power density even exceed 150 W/kg. Originally, using a round ceramic tube as electrolyte, we only got about 80 W/kg as power density, and the question was how to increase the power density.

3. Increase of power density

3.1. Geometric factors

Looking to the resistances vs. the depth of discharge, it can be seen that there are several contributions to the cell resistance: from the β -alumina, from the sodium electrode and the metal components, and from the positive electrode. Fig. 2 shows that the first two are constant but the resistance of the positive electrode is increasing with depth of discharge.

This is easy to explain because a solid electrode is used. If the reaction front moves from the ceramic into the inner part of the electrode, the ionic resistance of the second electrolyte becomes larger due to the longer distance which

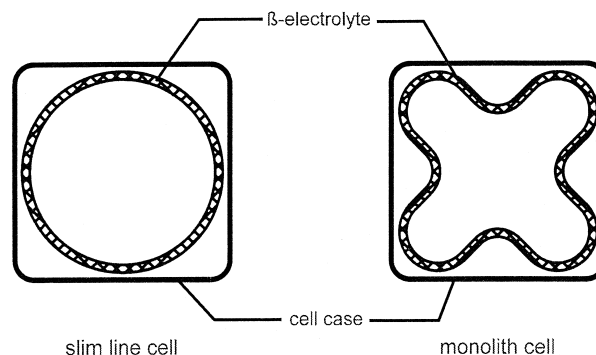


Fig. 3. Cross-section of old and new ZEBRA cells.

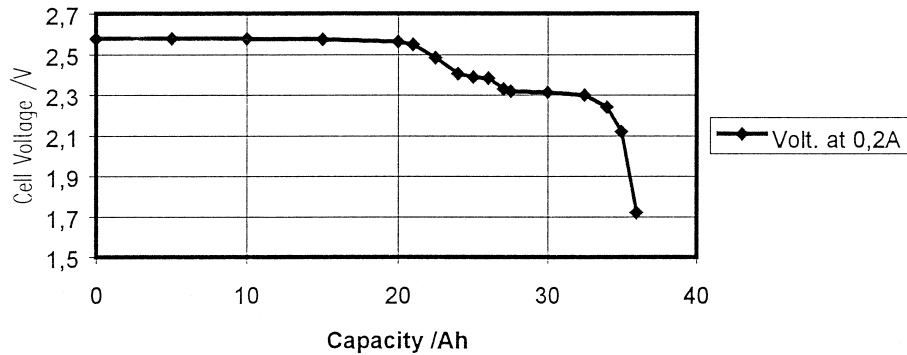


Fig. 4. OCV of a ZEBRA cell during discharge after pauses of 5 min (nameplate capacity: 26 A h).

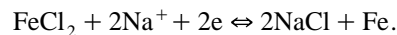
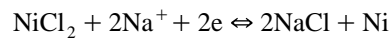
must be overbridged between reaction front and ceramic; that means an increasing resistance against depth of discharge. In order to reduce the cell resistance, action has been taken in changing the geometric factors: increase of the surface of the electrolyte ceramic and reduction of the thickness of the positive electrode. This could be achieved by changing the ceramic cross-section from round to a clover leaf shaped cross-section (Fig. 3). This new β -alumina electrolyte is called the monolith. In spite of this change, all external cell parameters and dimensions have been kept constant as well as the capacity of the cell [3].

This action increased the power density from 80 to 115 but the required 150 W/kg was not achieved.

3.2. Doping of the positive electrode

The geometric amendments alone have not been sufficient, therefore, a second measure has been introduced: the positive electrode Ni/NiCl₂ in the monolith cell has been

doped with iron [4]. Iron in the ZEBRA-system exhibits similar reactions to nickel:



During charge, the iron reacts with salt to form FeCl₂ and Na; during discharge, the reverse reaction takes place. The only difference between iron and nickel is the OCV: the nickel reaction has an OCV of 2.58 V, the iron reaction has 2.35 V, that means that the iron reaction occurs at a lower voltage than the nickel reaction. The OCV curve of a doped cell reflects this situation (Fig. 4). The OCV has been measured in a cell with 26-A h nameplate capacity during charge and discharge after a 5-min pause at each selected DOD value. It can be seen that the cell possesses about 24 to 25 A h nickel capacity, indicated by the nickel plateau and about 11 A h of iron capacity (iron plateau).

Looking to the resistances of the three different cells in Fig. 5, a very dramatic effect caused by the doping be-

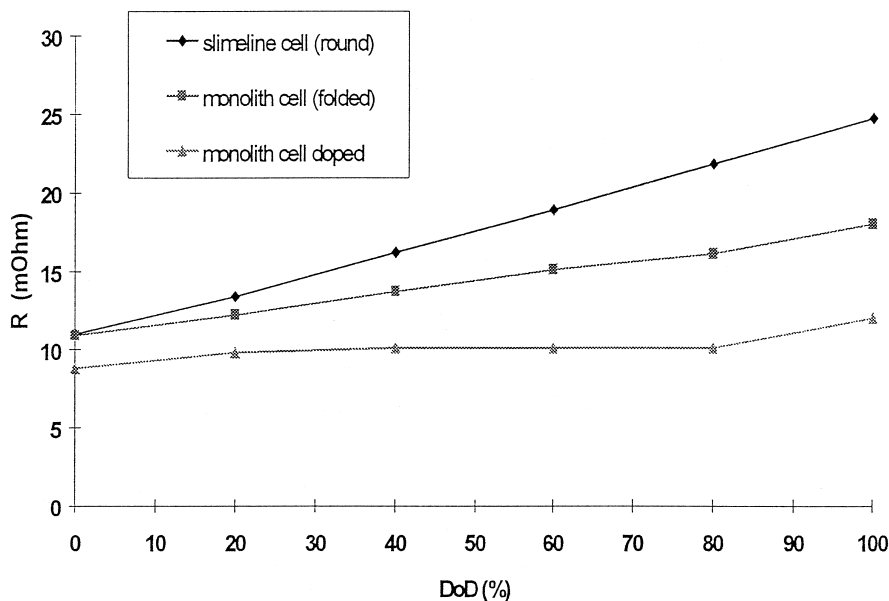


Fig. 5. Pulse resistance of different cell types in ZEBRA batteries.

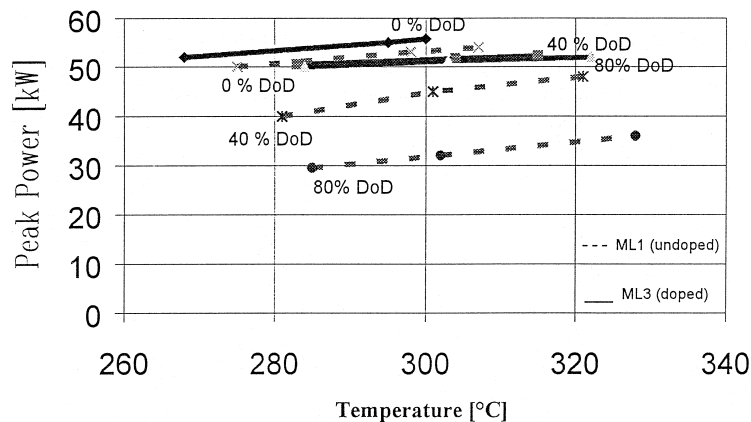


Fig. 6. Peak power of Z11-batteries (29 kW h) with doped and undoped ML-cells.

comes apparent. The upper curve represents the round cell, the curve in the middle represents the monolith cell, both without doping. In contrast, the resistance of the doped monolith is nearly constant at a very low value over the full range of DOD.

This behaviour is reflected in the peak power capability of cells and batteries. Fig. 6 shows the peak power curves of 29 kW h Z11 ZEBRA batteries with doped and undoped monolith cells in comparison. While the peak power of the doped battery stays above 50 kW even for the 80% DOD over the full range of the operating temperature, the peak power of the undoped battery drops to 30 kW at the end of discharge.

3.3. Mechanism of doping

The peak power and the peak resistances are measured in a C2 discharge with 30-s power pulses at 20%, 40%, 60%, 80% and 100% DOD (Fig. 7). Current and power during the pulse are adjusted in such a way that the voltage is kept at $2/3$ OCV. While the continuous resistance is increasing with DOD, the pulse resistance remains constant and is similar to the continuous resistance at 0% to 5% DOD. This can only be explained by the iron effect.

Assuming that the reaction front starts always at the inner surface of the ceramic and moves into the inner part of the positive electrode during discharge [5], the iron reaction at 0% to 5% DOD will occur close to the ceramic. This means that only a limited amount of FeCl_2 can be converted between 0% and 5% DOD. Considering the uniform distribution of the iron in the positive mass, about 0.45 A h of iron will be available for the peak power reaction of the FeCl_2 between 0% and 5% DOD. If the 30-s pulse of the main reaction is attributed to the discharge of FeCl_2 , about 0.4 A h of FeCl_2 located close to the ceramic will be necessary in order to obtain the low resistance.

In case of repeating the peak power pulses, the question is whether the resistance remains low or increases. Ten 30-s pulses with 30-s pause after each pulse showed a constant low resistance during all 10 pulses which corresponds to a DOD value between 0% and 5%. In spite of near all FeCl_2 has already been discharged during the first pulse in the electrode section (0%–5% DOD), this iron is again available for the next nine pulses as the low resistance values are showing.

In extending the pulse length from 30 s to 3 min, the resistance of the cell increases and at the end of the pulse,

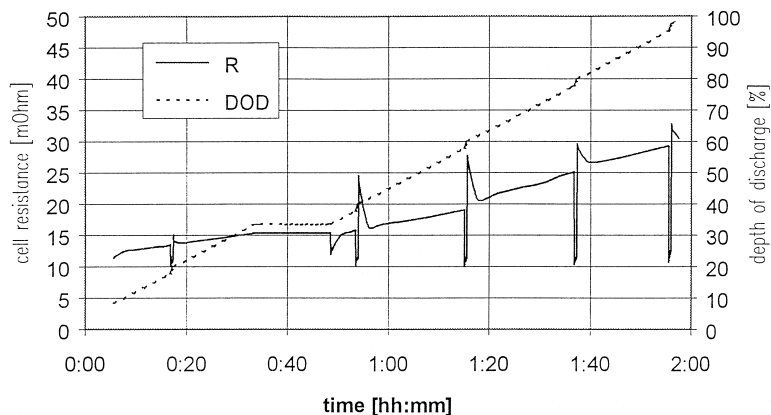


Fig. 7. C2 Discharge with 30-s peak power pulses of a Z5-battery (17 kW h) with doped monolith cells: cell resistance and DOD vs. time.

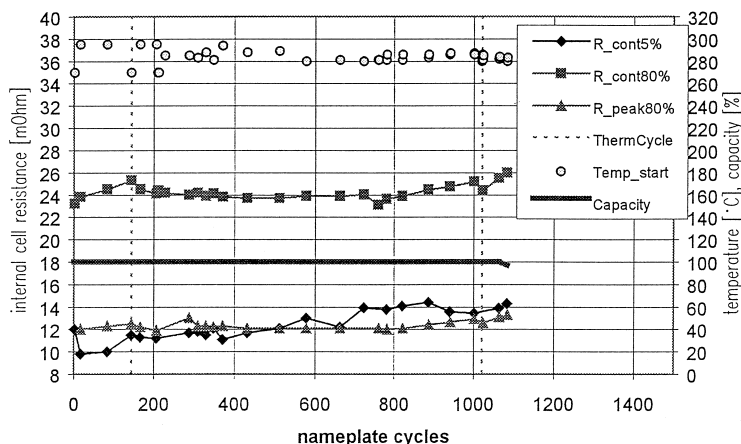
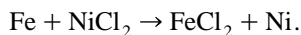


Fig. 8. Cycle life test (ECN regime) with a Z5-battery (17 kW h) with doped monolith cells: resistances at 5% and 80% DOD and capacity vs. cycles.

a resistance was reached which corresponds to a DOD value of about 20%. About 1.8 A h of the iron capacity are stored in the electrode section close to the ceramic which represents the extension of discharge to 20% DOD. During one pulse of 3-min duration, 2.4 A h have been discharged showing that about 75% of the discharged amount were related to iron and only 25% to nickel.

The results can be explained by the following mechanism. Two cells are built into the ZEBRA cell, the nickel cell and the iron cell, as paralleled cells. Due to the higher OCV, only the nickel cell is discharged at a low discharge rate, while the FeCl_2 does not take part in the reaction. As long as the cell voltage remains above the OCV of the iron cell, only nickel is discharged. If the nickel chloride is consumed, FeCl_2 will be discharged further until 100% DOD is achieved. This happens at the end of discharge during normal discharge rates. The two plateaux become visible.

During application of the peak power pulses, the voltage of the cell drops below the OCV of the iron reaction and both NiCl_2 and FeCl_2 will be discharged in parallel. That means that in a normal operation, up to a 2-h discharge rate only NiCl_2 will be converted while FeCl_2 remains available located close to the ceramic electrolyte as in the fully charged state. During the pulse, this FeCl_2 will mainly contribute to the reaction with the low resistance of the fully charged iron cell giving a high peak power. In repeating the pulses, the iron is again available with the low resistance and this can only be explained with a recovery of the FeCl_2 during the pause between the pulses. This recovery happens during low discharge current periods. Nickel chloride in the inner part of the positive electrode charges the Fe close to the ceramic to FeCl_2 . This internal electrochemical reaction is driven by the OCV difference:



The recovery of Fe to FeCl_2 occurs very fast, as long as NiCl_2 is available in the positive electrode. During the 10

pulses mentioned above, the Fe had recovered 10 times within the pauses.

By this simple measure, it was possible to increase the peak power of ZEBRA batteries to values of more than 170 W/kg, well above the required 150 W/kg.

4. Cycle life of doped ZEBRA batteries

Undoped ZEBRA batteries exhibited a very long life time of up to 1700 cycles and 5 years. The doping of the ZEBRA cells raised the question: What influence on cycle life has to be expected? Therefore, a cycle life test with a Z5 battery was performed which showed that doped monolith cells behave at least as well as undoped cells. Fig. 8 includes the result of this test: 1100 cycles have been achieved with stable capacity and only a slight increase in the continuous and peak resistances at 5% and 80% DOD. The battery is still on test.

5. Conclusion

The peak power could be raised from 80 to 170 W/kg mainly by the doping of the nickel cell with iron beside geometric adaptations of the ceramic electrolyte. This simple measure made ZEBRA fulfil the power requirements of the car industry which was confirmed in car testing. Furthermore, the doping showed no adverse effect on the cycle life of ZEBRA batteries.

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