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Advances in ZEBRA batteries

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Abstract

ZEBRA batteries use plain salt and nickel as the raw material for their electrodes in combination with a ceramic electrolyte and a molten salt. This combination provides a battery system related specific energy of 120 Wh/kg and a specific power of 180 W/kg. With these data the battery is well designed for all types of electric vehicles and hybrid electric buses. The ZEBRA battery technology is industrialised in Switzerland where a new plant has a capacity of 2000 packs a year with expansion prepared for 30,000 packs a year.

Keywords: ZEBRA battery; Sodium–nickel-chloride system; High specific energy; Beta-alumina ceramic electrolyte; Electric vehicle; Hybrid electric bus

1. Introduction

The principle of the ZEBRA battery was invented in South Africa and the first patent was applied in 1978. BETA Research and Development Ltd in England continued the development and was integrated into the joint venture of AEG (later Daimler) and Anglo American Corp. 10 years later. The jointly founded company AEG Anglo Batteries GmbH started the pilot line production of ZEBRA batteries in 1994. After the merger of Daimler and Chrysler this joint venture was terminated and the ZEBRA technology was acquired in total by MES-DEA who industrialised it. The present production capacity is 2000 battery packs per year in a building designed for a capacity of 30,000 battery packs per year.

2. ZEBRA technology

ZEBRA batteries use nickel powder and plain salt for the electrode material, the electrolyte and separator is β''-Al_2O_3-ceramic which is conductive for Na^+ ions but an insulator for electrons [1].

This sodium-ion conductivity has a reasonable value of $\geq 0.2\,\Omega^{-1}\,cm^{-1}$ at 260 °C and is temperature-dependent with a positive gradient [2]. For this reason the operational temperature of ZEBRA batteries have been chosen for the range of 270–350 °C. Fig. 1 shows the cell and its basic reaction. There is no side reaction and therefore the charge and discharge cycle has 100% charge efficiency, no charge is lost. This is due to the ceramic electrolyte.

The cathode has a porous structure of nickel (Ni) and salt (NaCl) which is impregnated with $NaAlCl_4$, a 50/50 mixture of NaCl and $AlCl_3$. This salt liquefies at 154 °C and in the liquid state it is conductive for sodium-ions. It has the following functions, which are essential for the ZEBRA battery technology:

1. Sodium-ion conductivity inside the cathode
   The ZEBRA cells are produced in the discharged state. The liquid salt $NaAlCl_4$ is vacuum-impregnated into the porous nickel-salt mixture that forms the cathode. It conducts the sodium-ions between the β''-Al_2O_3 ceramic surface and the reaction zone inside the cathode bulk during charge and discharge and makes all cathode material available for energy storage. It also provides a homogenous current distribution in the ceramic electrolyte.
2. Low resistive cell failure mode
   Ceramic is a brittle material and may have a small crack or may break. In this case the liquid salt $NaAlCl_4$ gets into contact with the liquid sodium (the melting point of sodium is 90 °C) and reacts to salt and aluminium:

   $$NaAlCl_4 + 3Na \rightarrow 4NaCl + Al$$

   In case of small cracks in the β''-alumina the salt and aluminium closes the crack. In case of a large crack or break the aluminium formed by the above reaction shorts the current path between plus and minus so that the cell goes to low resistance. By this means long chains of 100 or 200 cells only lose the voltage of one cell (2.58 V) but can continue to be operated. The ZEBRA battery is cell failure tolerant. It has been established that 5–10%

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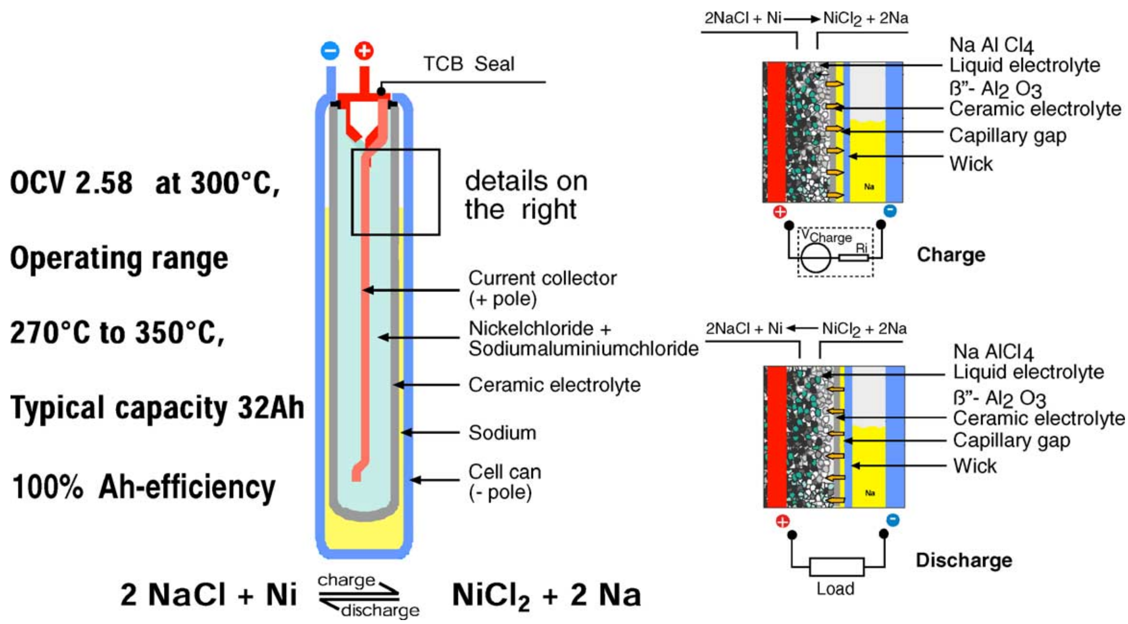

Fig. 1. Basic cell reactions.

of cells may fail before the battery can no longer be used. The battery controller detects this and adjusts all operative parameters.

This same reaction of the liquid salt and liquid sodium is relevant for the high safety standard of ZEBRA batteries: In case of the mechanical damage of the ceramic separator due to a crash of the car the two liquids are reacting in the same way and the salt and aluminium passivates the $NiCl_2$-cathode. The energy released is reduced by about 1/3 compared to the normal discharge reaction of sodium with nickel chloride.

3. Overcharge reaction

The charge capacity of the ZEBRA cell is determined by the quantity of salt (NaCl) available in the cathode. In case a cell is fully charged and the charge voltage continues to be applied to the cell for whatever reasons, the liquid salt $NaAlCl_4$ supplies a sodium reserve following the reversible reaction:

$$2NaAlCl_4 + Ni \leftrightarrow 2Na + 2AlCl_3 + NiCl_2$$

This overcharge reaction requires a higher voltage than the normal charge as illustrated in Fig. 2. This has three practical very welcome consequences:

(a) Any further charge current is stopped automatically as soon as the increased open circuit voltage equalises the charger voltage.
(b) If cells are failed in parallel strings of cells in a battery, the remaining cells in the string with the failed cells can be overcharged in order to balance the voltage of the failed cells.
(c) For a vehicle with a fully charged battery which is then required to go down hill there is an overcharge capacity of up to 5% for regenerative breaking so that the breaking behaviour of the vehicle is fundamentally unchanged.

4. Over discharge reaction

From the very first charge the cell has a surplus of sodium in the anode compartment so that for an over-discharge tolerance sodium is available to maintain current flow at a lower voltage as indicated in Fig. 2. This reaction is equal to the cell failure reaction but runs without a ceramic failure.

2.1. *ZEBRA cell design*

ZEBRA cells are produced in the discharged state so that no metallic sodium is to be handled. All the required sodium is inserted as salt. Fig. 1 shows the cell design.

The positive pole is connected to the current collector, which is a hairpin shaped wire with an inside copper core for low resistivity and an outside Nickel plating so that all

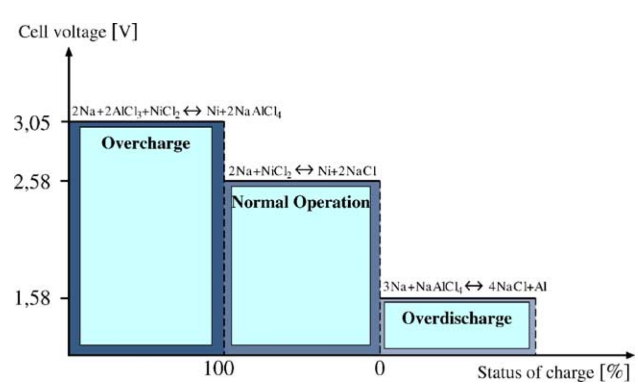

Fig. 2. Cell reactions at 300 °C. Theoretical specific energy: 790 Wh/kg (normal operation).

Fig. 3. β″ ceramic with thermal compression bond (TCB) seal.

material in contact with the cathode is consistent with the cell chemistry.

The cathode material in form of a granulated mixture of salt with nickel powder and traces of iron and aluminium is filled into the beta-alumina tube (Fig. 3).

This tube is corrugated for resistance reduction by the increased surface and is surrounded and supported to the cell case by a 0.1 mm thick steel sheet that forms a capillary gap surrounding the beta-alumina tube. Due to capillary force the sodium is wicked to the top of the beta-tube and wets it independent of the sodium level in the anode compartment.

The cell case is formed out of a rectangular tube continuously welded and formed from a nickel coated steel strip (see below) and a laser welded bottom cap. The cell case forms the negative pole. The cell is hermetically sealed by laser welded nickel rings that are thermo-compression-bonded (TCB) to an α-alumina collar which is glass brazed to the beta-alumina tube.

2.2. ZEBRA battery design

ZEBRA cells can be connected in parallel and in series. Different battery types have been made with one to five parallel strings, up to 220 cells in series and 100–500 cells in one battery pack. The standard battery type Z5 (Fig. 4) has 216 cells arranged in one (OCV = 557 V) or two (OCV = 278 V) strings. Between every second cell there is a cooling plate through which ambient air is circulated (Fig. 5) providing a cooling power of 1.6–2 kW. For thermal insulation and mechanical support the cells are surrounded by a double walled vacuum insulation typically 25 mm thick. Light plates made out of foamed silicon oxide take the atmospheric pressure load. This configuration has a heat conductivity of only 0.006 W/mK and is stable for up to 1000 °C.

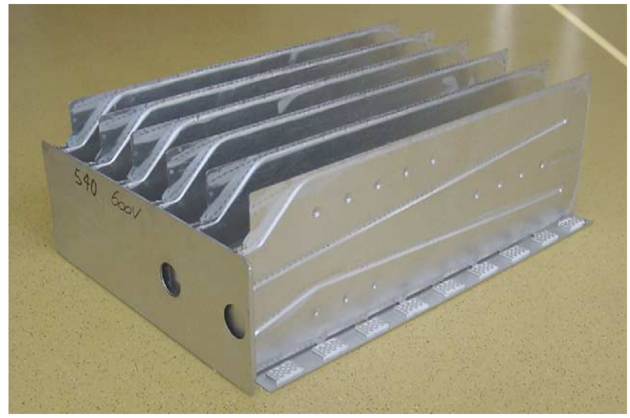

Fig. 5. Cooling plates.

2.3. Battery system design

Fig. 6 illustrates all components of the complete system ready for assembly. The ohmic heater and the fan for cooling are controlled by the battery management interface (BMI) for thermal management. Plus and minus poles are connected to a main circuit breaker that can disconnect the battery from outside. The circuit breaker is also controlled by the BMI.

The BMI measures and supervises voltage, current, status of charge, insulation resistance of plus and minus to ground and controls the charger by a dedicated pulse width modulated (PWM) signal. A CAN-bus is used for the communication between the BMI; the vehicle and the electric drive system. All battery data are available for monitoring and diagnostic with a notebook.

Type		Z5-278-ML-64	Z5-557-ML-32
Capacity	Ah	64	32
Rated Energy	kWh	17.8	17.8
Open Circuit Voltage 0-15% DOD	V	278.6	557
Max. discharge current	A	224	112
Cell Type/N° of cells		ML3 / 216	
Weight with BMI	kg	195	
Specific energy without BMI	Wh/kg	94	
Energy density without BMI	Wh/l	148	
Specific power	W/kg	169	
Power density	W/l	265	
Peak power 80% DOD, 2/3 OCV, 30s, 335°C	kW	32	
Ambient temperature	°C	-40 to +50	
Thermal loss at 270°C internal temperature	W	< 110	

Fig. 4. Z5C standard battery with main data.

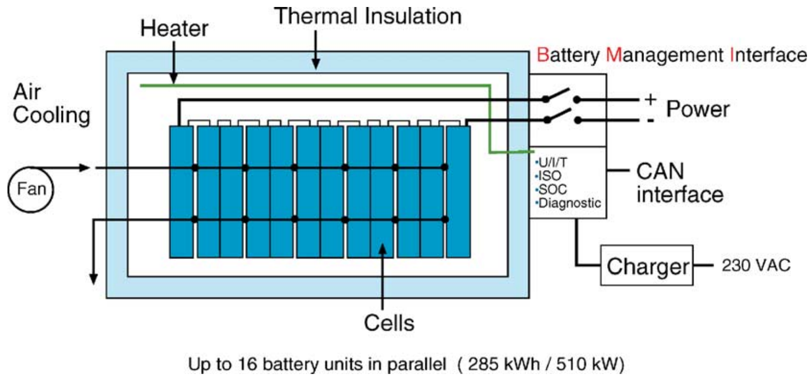

Fig. 6. ZEBRA battery system.

A Multi-Battery-Server is designed for up to 16 battery packs to be connected in parallel in a multi-battery-system with 285 kW h/510 kW using Z5C batteries.

2.4. Battery safety

Battery safety is essential especially for mobile applications having in mind that each battery should store as much energy as possible but this energy must not be released in an uncontrolled way under any conditions. It is required that even in a heavy accident there is no additional danger originated from the battery. On this background different tests like crash of an operative battery against a pole with 50 km/h (Fig. 7), overcharge test, over-discharge test, short circuit test, vibration test, external fire test and submersion of the battery in water have been specified and performed [3]. The ZEBRA battery did pass all these tests because it has a four barrier safety concept [4,5]:

1. Barrier by the chemistry
   In case of a heavy mechanical damage of the battery the brittle ceramic breaks whereas the cell case made out of steel is deformed and most likely remains closed. In any case the liquid electrolyte reacts with the liquid sodium to form salt and aluminium equal to the overcharge reaction described above. These reaction products form a layer covering the $NiCl_2$ cathode and thus passivate it. This reaction reduces the thermal load by about 1/3 compared to the total electrochemically stored energy.

Fig. 7. ZEBRA battery type Z12–Crash Test at 50 km/h.

2. Barrier by the cell case
   The cell case is made out of steel with glass brazed thermo-compression bonded seal that remains closed for temperatures up to about 900 °C.
3. Barrier by the thermal enclosure
   The thermal insulation material of the battery box is made out of foamed SiO_2 which is stable for above 1000 °C. In combination with vacuum like a thermo bottle it has a heat conductivity of only 0.006 W/mK. This value is increased only by a factor of three without vacuum. Beyond its primary function of thermal enclosure it is a protective container for all fault or accident conditions.
4. Barrier by the battery controller
   The battery controller supervises the battery and prevents it from being operated outside of specification.

3. ZEBRA battery performance

ZEBRA cells and batteries are charged in an IU-characteristic with a 6 h rate for normal charge and 1 h rate for fast charge. The voltage limitation is 2.67 V per cell for normal charge and 2.85 V per cell for fast charge. Fast charge is permitted up to 80% SoC. Regenerative breaking is limited to 3.1 V per cell and 60 A per cell so that high regenerative breaking rates are possible (Fig. 8).

The peak power during discharge, defined as the power at 2/3 OCV, is independent of SoC so that the vehicle performance and dynamic is constant all over the SoC range (Fig. 9). Obviously this is important for practical reasons.

3.1. Battery life data

Battery life is specified as calendar and cycle life. The calendar life of 11 years is demonstrated (Fig. 10). The cycle life is measured by the accumulation of all discharged charge measured in Ah divided by the nameplate capacity in Ah, so

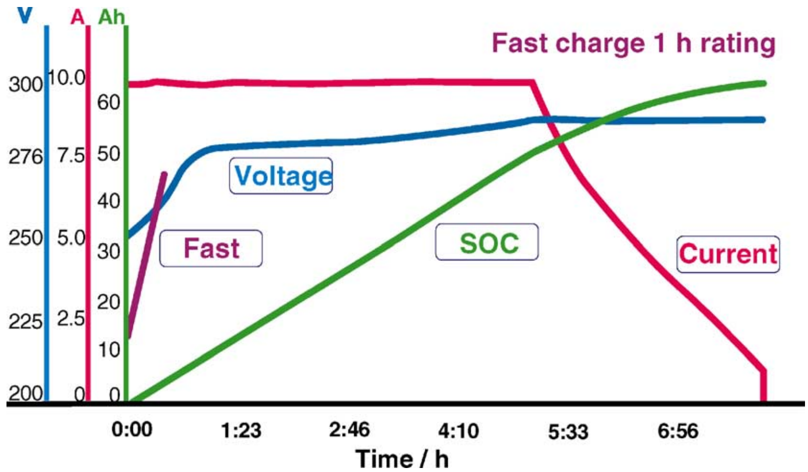

Fig. 8. Z5C battery performance: normal IU-charge in 7.5 h. 2.67 V/cell at normal charge 2.85 V/cell at fast charge (up to 80% SoC).

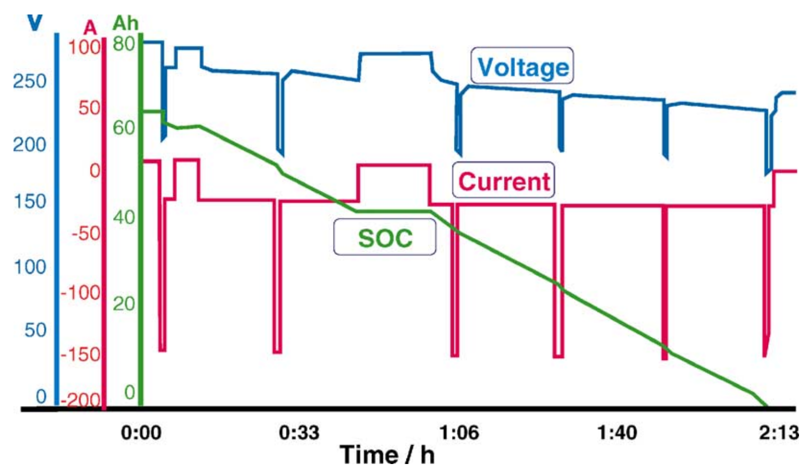

Fig. 9. Z5C Discharge—peak power at 2/3 OCV independent of SoC.

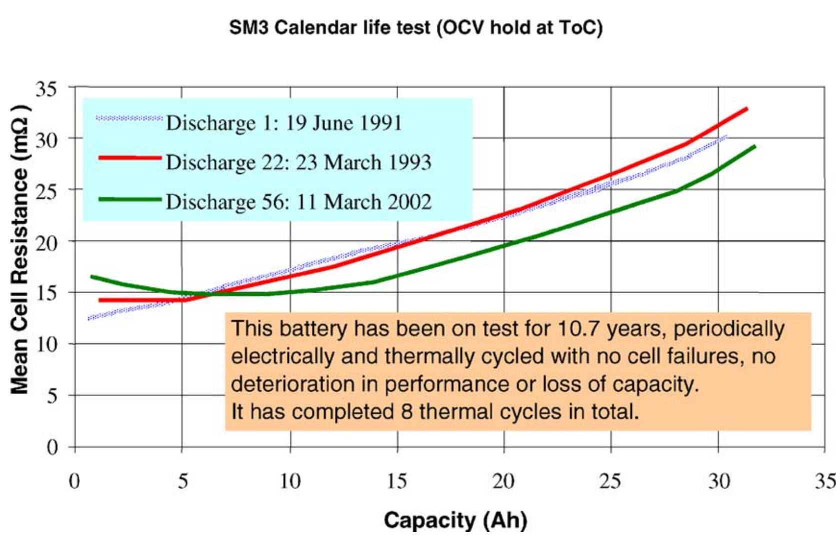

Fig. 10. Calendar life test—development of mean cell resistance.

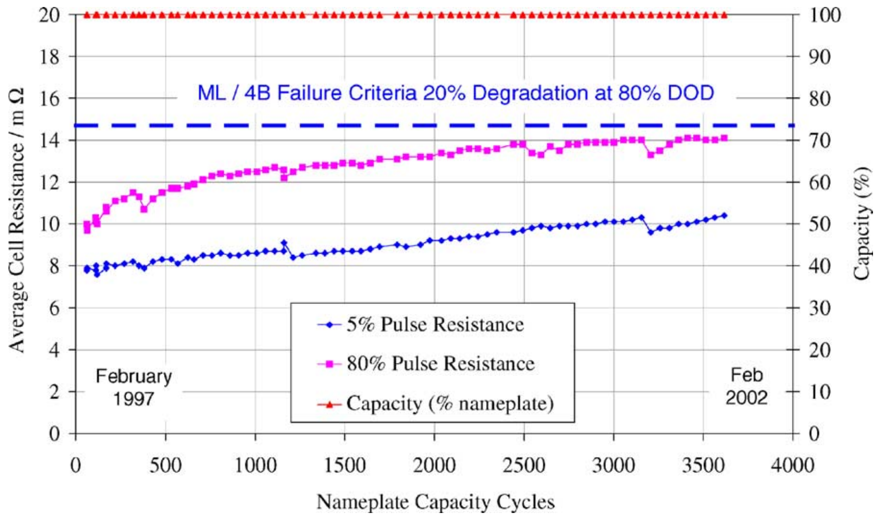

Fig. 11. Life cycle test results of ML/4B modules.

that one nameplate cycle is equivalent to a 100% discharge cycle. This is a reasonable unit because of the 100% Ah efficiency of the system. Furthermore 100% of the nameplate capacity is available for use without influence on battery life. The expected cycle life is up to 3500 nameplate cycles (Fig. 11) from module tests and 1450 nameplate cycles from battery testing (Fig. 12) that simulated all real life operation conditions. The thermal insulation is stable for more than 15 years (Fig. 13).

3.2. Recycling

Nowadays every product that is introduced to the market has to be recycled at the end of its usage. ZEBRA batteries are dismantled. The box material is stainless steel and SiO_2. Both of which are recycled into established processes. The cells contain Ni, Fe, salt and ceramic. For recycling they are simply added to the steel melting process of the stainless steel production. Ni and Fe contribute to the material

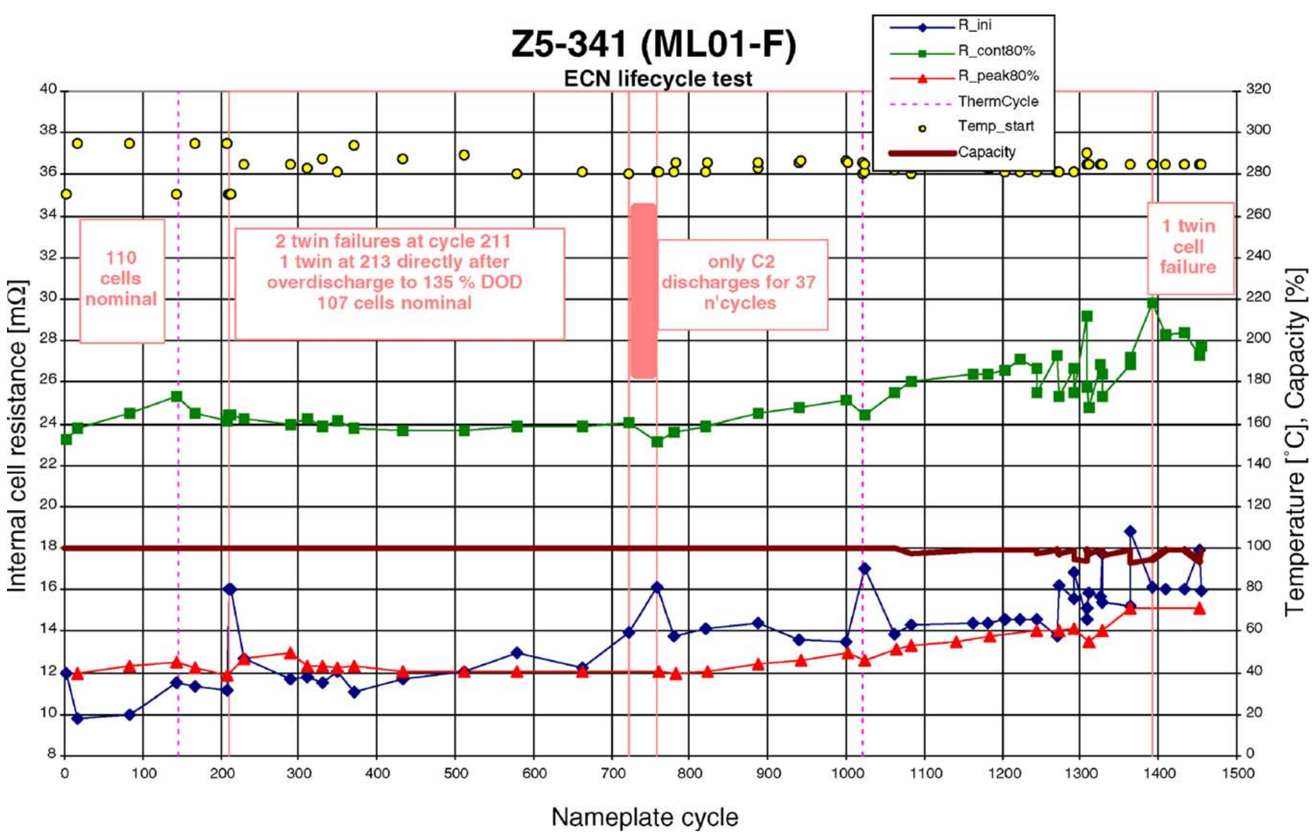

Fig. 12. Life cycle test results of battery Z5-341.

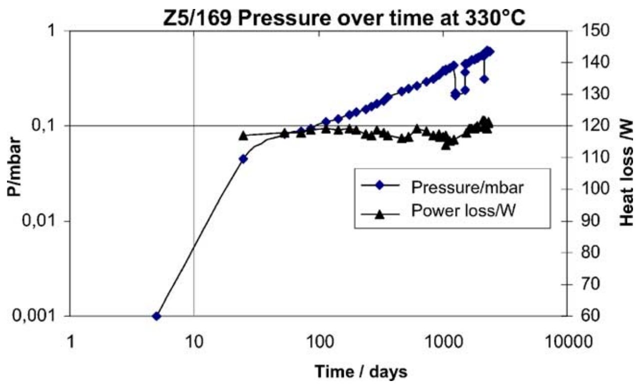

Fig. 13. Calendar life test of battery tray insulation: pressure increase and heat loss.

production and the ceramic and salt is welcome to form the slag. The recycling is certificated and cost effective.

4. Production

All ZEBRA battery production equipment is now concentrated in Stabio, Switzerland (the beta-powder line will move from Derby to Stabio before the end of the year 2002) with a production capacity of 2000 battery packs (equivalent to 40 MW h) per year. The plant is subdivided into three parts.

4.1. Ceramic production

A new rotary press has been installed and linked by a conveyor to the new shuttle kiln which is equipped with automatic handling systems for loading and unloading. After sintering the beta-tubes are moved to the cutting and inspection area by a monorail system that links all parts of the factory. A barcode system has been introduced for monitoring and backtracking of all production parameters from the start of ceramic powder production to the battery even after usage.

4.2. Cell assembly line

The cell assembly line has been supplemented by a continuously operating cell case line and the current collector welding line with a bending station and a brazing station which finishes the ready-to-use current collector. The new equipment is already designed for higher production in the next phase of production capacity build-up. This was also an important progress for cost reduction.

4.3. Battery assembly line

All battery components were redesigned for cost and weight reduction. New electrical test equipment and furnaces have been installed in order to increase the capacity for battery acceptance testing. The battery controller and its software is redesigned and tested. It includes a "Life-Data-Memory" which stores all relevant battery data during battery life like a black box.

5. Applications

The ZEBRA battery system is designed for electric vehicles, which require a balance of power to energy of about two, e.g. a 25 kW h battery has about 50 kW peak power. Other applications are electric vans, buses and hybrid buses with ZEV range (as shown in Fig. 14).

Fig. 14. Electric and hybrid vehicles equipped with ZEBRA batteries.

The present generation of ZEBRA batteries is not applicable for hybrid vehicles that have a small battery of about 3 kW h but high power up to 60 kW (a power to energy ratio of 15–20).

Recently also prototypes for stationary applications have been designed. These have great advantages in hot climate and for frequent cycling where the life span of conventional batteries is reduced such that the two to three times higher price of ZEBRA batteries is overcompensated by its much longer life resulting in lower life cycle cost and avoiding the exchange of batteries. For UPS applications the float voltage of 2.61 V per cell for ZEBRA has been established.

6. Summary

The first ZEBRA battery plant has been built in Stabio, Switzerland and the industrialisation of this battery technology has been started. A production capacity of 2000 battery packs (equivalent to 40 MW h) per year is established in the first phase. This has resulted in cost reductions that make life-cycle-cost of ZEBRA batteries less than those of lead-acid batteries. Recently, ZEBRA batteries have been adapted to other applications than electric vehicles in addition. Now electric vehicles are going to become an option for urban traffic about 100 years after their first period of success.

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