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Project: Storage Technologies for Hybrid Electric Buses

Subject: ZEBRA Battery

Electrochemical Energy Conversion and Storage Systems Group

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Table of Content

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- **General**

One of the promising future batteries for electric propulsion of vehicles is the sodium/nickel chloride or ZEBRA (Zero Emission Battery Research Activities) battery. Despite some disadvantages with respect to the high temperature, the advantages with respect to specific energy and energy density are such that, especially in applications where the battery is used on a more or less continuous basis e.g., in delivery vans and taxies, it is an interesting candidate battery [1].

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 can be designed for all types of electric vehicles and according to [2] for hybrid electric buses, however the power density compared to other available technologies such as NimH should be improved.

The original development of the system was started because of the high energy density that could be achieved. Batteries are now currently being produced that are >100Wh/kg for the complete ZEBRA system ie cell pack, battery housing, cooling system, management system etc. This enables pure electric vehicles to have ranges greater than 120 miles and with the present power density of >150W/kg these EV's have a performance similar to IC, Internal Combustion powered vehicles. The chemistry, design and construction of the system also give many other very important benefits that contribute to the life, reliability, abuse resistance, safety and general wide applicability of ZEBRA.

The sodium/nickel chloride cell, like the sodium sulphur cell from which it evolved, consists of a liquid sodium negative electrode separated from a positive electrode by a sodium ion conducting solid electrolyte, beta alumina. It differs from the latter in that, a second, liquid electrolyte, is necessary to allow the rapid transport of sodium ions from the solid nickel chloride electrode to and from the ceramic electrolyte. The melting point of this salt (157° C) determines the minimum operating temperature of the cell but optimum performance is obtained in the temperature 270-350° C. At these temperatures, the beta alumina electrode contributes only a minor component to cell resistance [3].
The cell construction is shown schematically in Figure 1.

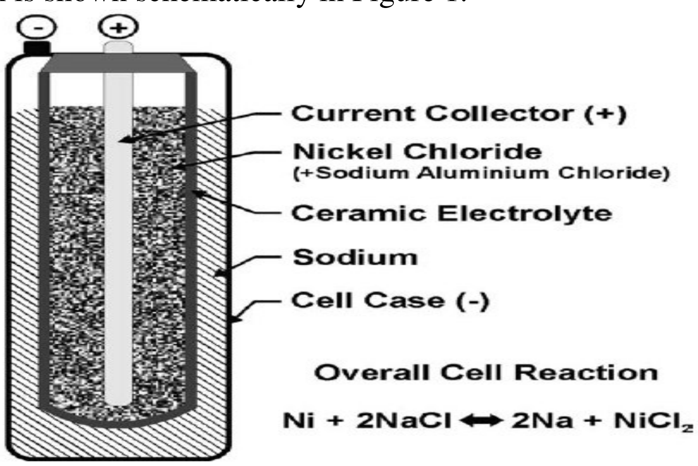

Figure 1. Zebra cell

The general behavior of a zebra cell can be realized by its simple and basic cell reaction, however, for some limiting factors and on the other hand improvement plans of the battery many types of additives have been applied to the zebra battery.

- **Electrical Parameters**

Vehicle trials with the first sodium/nickel chloride ZEBRA batteries indicated that the pulse power capability of the battery needed to be improved towards the end of the discharge. A research program [4] led to several design changes to improve the cell which, in combination, have improved the energy density of the battery to greater than 150 Wh kg^{-1} at 80% depth of discharge. Bench and vehicle tests have established the stability of the high power battery over several years of cycling. The gravimetric energy density of the first generation of cells was less than 100 Wh kg^{-1}. Optimization of the design has led to a cell with a specific energy of 120 Wh kg^{-1} or 86 Wh kg^{-1} for a 30 kWh battery.

Recently, the cell chemistry has been altered to improve the useful capacity. The cell is assembled in the over-discharged state and during the first charge the following reactions occur: at 1.6 V: $Al + 4NaCl = NaAlCl_4 + 3Na$; at 2.35 V: $Fe + 2NaCl = FeCl_2 + 2Na$; at 2.58 V: $Ni + 2NaCl = NiCl_2 + 2\ Na$. The first reaction serves to prime the negative sodium electrode but occurs at too low a voltage to be of use in providing useful capacity. By minimizing the aluminum content more NaCl is released for the main reactions to improve the capacity of the cell. This, and further composition optimization, have resulted in cells with specific energies in excess of 140 Wh kg^{-1}, which equates to battery energies>100 Wh kg^{-1} [4].

From the emergence of the ZEBRA battery several attempts have been done toward having better performance technically and economically. Hence, it is worth to mention at least the different terms for its design. At first, SL/09 cell was introduced with cylindrical Beta alumina; however, power loss due to the thickness of positive electrode at high depth of discharge led to emerge of beta alumina tube of cruciform cross section, the so called ML/1G. To reduce the dependence of the pulse power available on the DoD of a cell, a second positive electrode rather than a nickel based; iron based, with lower potential was practiced, ML/1F design. To have better performance, the current collector has been even changed from nickel to copper strips in order to reduce the ohmic resistance. This ML/3B cell design gave a pulse power of 190 W per cell at 5% DOD and 180 W per cell at 80% DOD. The last terminology that should be mentioned is ML/5 which is nothing else than a development of the current collector by increasing its surface area, reducing its weight, and changing the structure to make cell assembly easier. Fig. 2 illustrates the improvement in pulse power obtained for the different cell designs [3], [4].

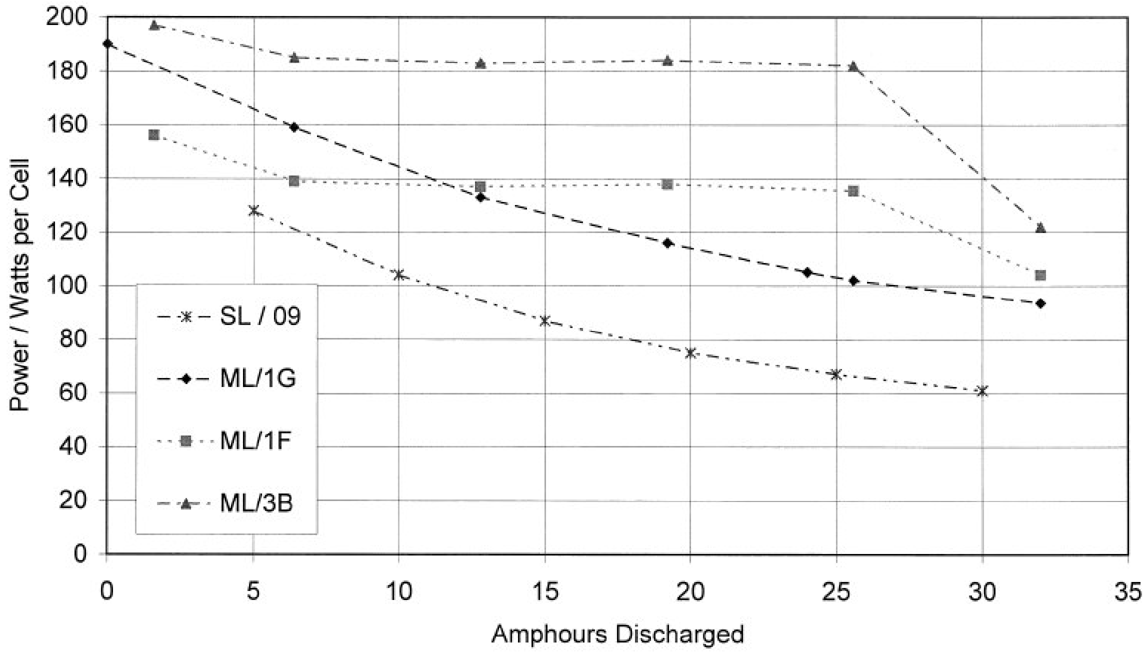

Figure 2. Plot showing the improvement in peak power performance for ZEBRA cell designs vs. DOD. Pulse power taken at 30 s, 2r3 of OCV.

Temperature: 295 to 3508C.

The sodium-ion, available in the cell, conductivity has a reasonable value of ≥0.2 Ω^{-1} cm^{-1} at 260° C and is temperature-dependent with a positive gradient. For this reason the operational temperature of ZEBRA batteries has been chosen for the range of 270–350° C. 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 [4]:

1. Sodium-ion conductivity inside the cathode
2. Low resistive cell failure mode
3. Overcharge reaction
4. Over discharge reaction

The last two mentioned factors are in fact can account for ZEBRA batteries' advantages [2], [4], since 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. 3. This has three practical very welcome consequences:

(a) Any further charge current is stopped automatically as soon as the increased open circuit voltage equalizes 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 braking so that the braking behavior of the vehicle is fundamentally unchanged.
On the other hand in over discharge mode, 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. 3. This reaction is equal to the cell failure reaction but runs without a ceramic failure.

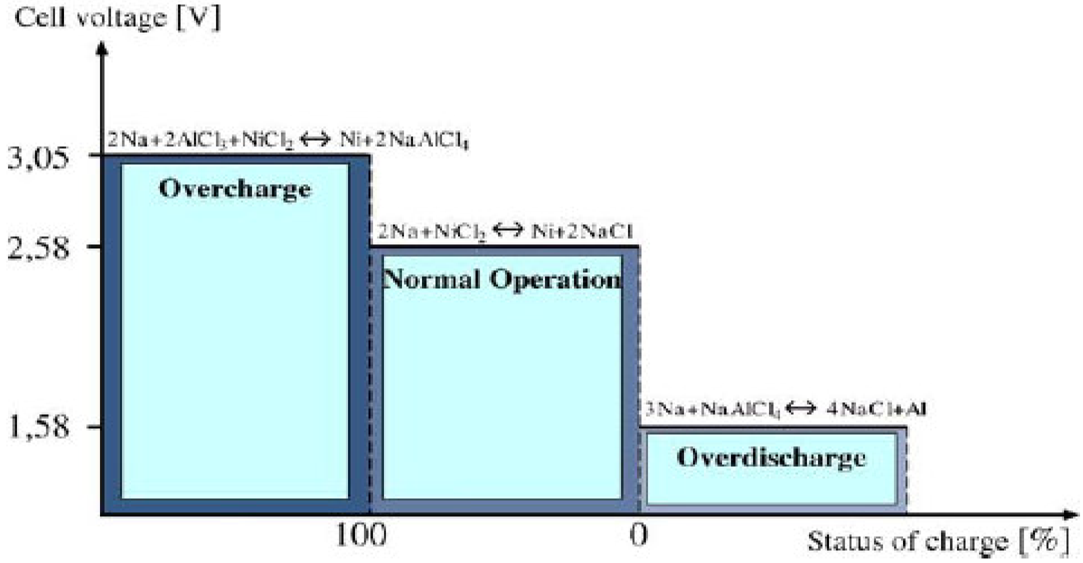

Figure 3.Cell reactions at 300 ◦C. Theoretical specific energy: 790 Wh/kg

To have an overview of ZEBRA battery types compared to other storage technologies an investigation result [5] is shown in Table1.

	VRLA	Nickel cadmium	Nickel metal hydride	Lithium ion	ZEBRA
Specific energy[a] (Wh kg^{-1})	34	45	65	110	120
Specific power[b] (W kg^{-1})	75	120	90	220	180
Self discharge per month (%)	8	20	30	10	None
Nameplate cycle life	500	1000	500	400	2000
Efficiency[c] (%)	70	80	80	85	90

Table 1. Comparison of different battery technologies

However, it is apparent that the above mentioned reference does not include all types of other storage technologies, for instance it can be possible also to consider high power cells esp. for NiMH and Li-ion batteries. As an amendment to above table it may worth to say that the specific power for NiMH and Li-ion can be realized in the range of 200-1500 and 80-2000 Wkg^{-1} respectively.
In the following, we will concentrate on the standard battery type the so called Z5 (Figure 4) which has 216 cells arranged in one or two strings. Between every second cell there is a cooling plate through which ambient air is circulated.
According to some tests performed by [2], 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 2.67V per cell for normal charge and 2.85V per cell for fast charge. Fast charge permitted up to 80% SoC. Regenerative braking is limited to 3.1V per cell and 60A per cell so that high regenerative braking rates are possible (Fig. 5).

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. 6). Obviously this is important for practical reasons something that we are seeking for.

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	

Figure 4. Z5C standard battery with main data

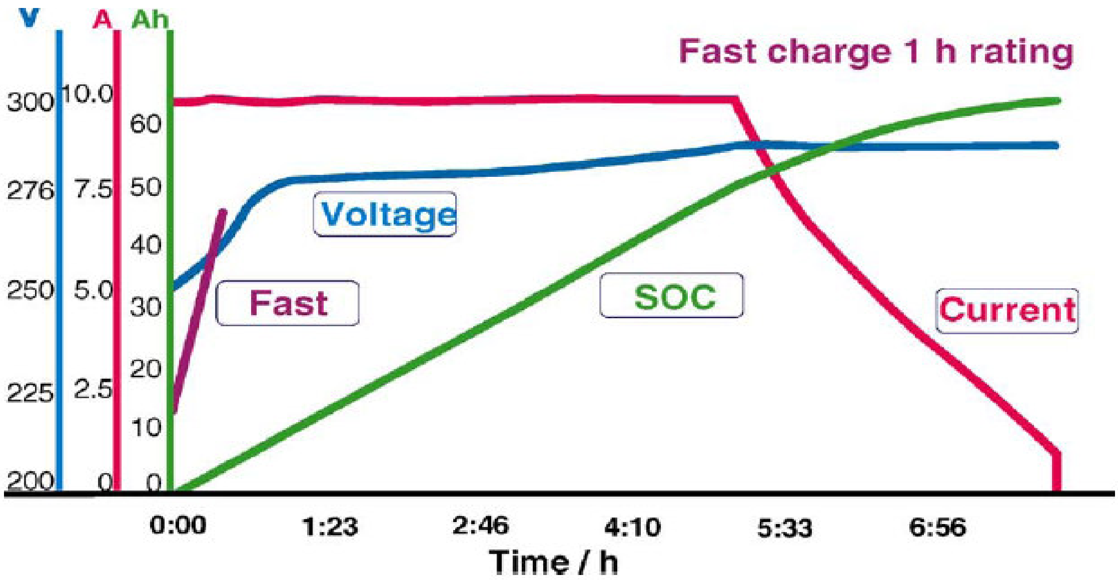

Figure 5. Z5C battery performance: normal IU-charge in 7.5 h. 2.67 V/cell at normal charge 2.85 V/cell at fast charge (up to 80% SoC).

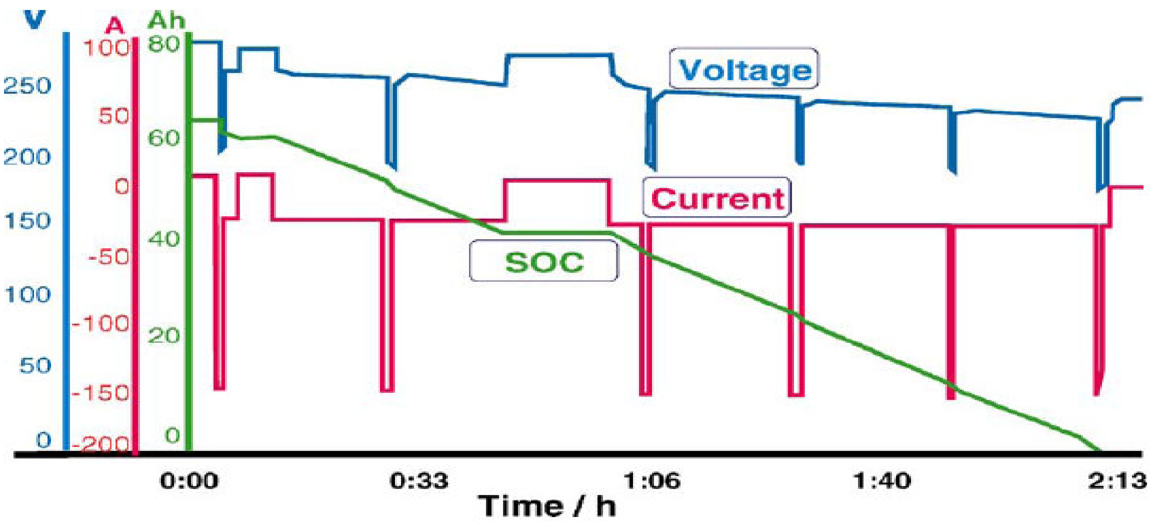

Figure 6. Z5C Discharge—peak power at 2/3 OCV independent of SoC.

- **Service Life**

The factors which determine cell life are: corrosion, resistance rise and capacity loss. In absence of electrical cycling, the ZEBRA cell degrades only very slowly as demonstrated by the performance of a small battery which was put on test in June 1991. This battery held at top of charge on open circuit and over the last 10 years has had 55 charge/discharge cycles and eight freeze/thaw cycles. As can be seen from Fig.7, the capacity is unchanged as the cell resistance [2],[3],[6].

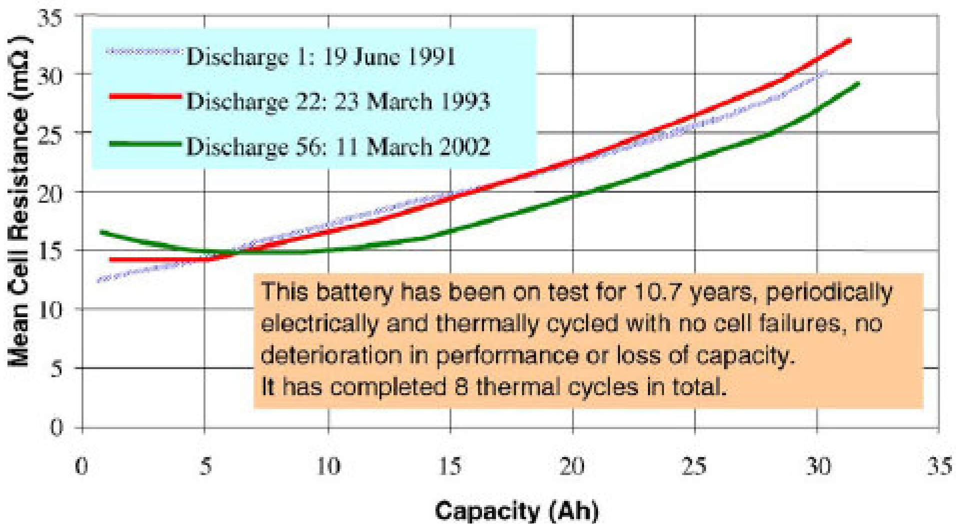

Figure 7. Calendar life test—development of mean cell resistance.

The cycle life is measured by the accumulation of all discharged charge measured in Ah divided by the nameplate capacity in Ah [2], so 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. 8) from module tests and 1450 nameplate cycles from battery testing (Fig. 9) that simulated all real life operation conditions. The thermal insulation is stable for more than 15 years (Fig. 8).

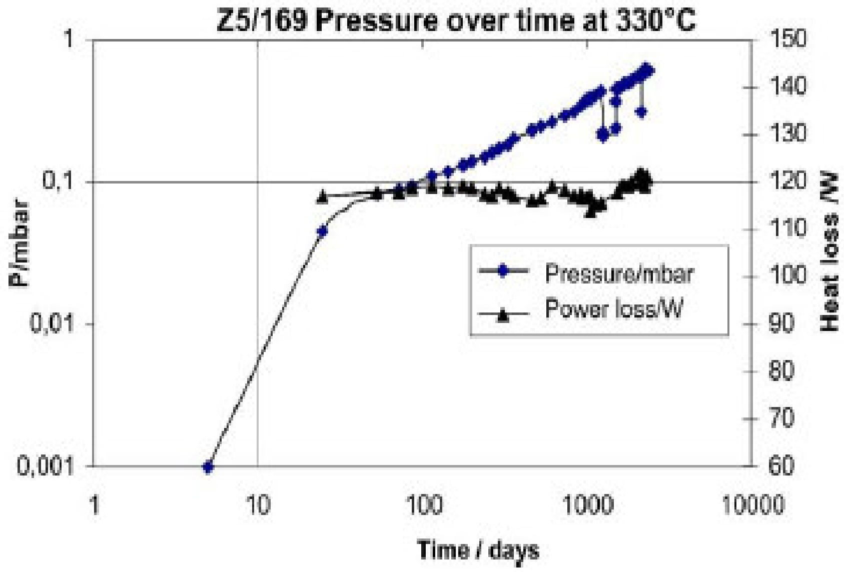

Figure 8. Calendar life test of battery tray insulation: pressure increase and heat loss.

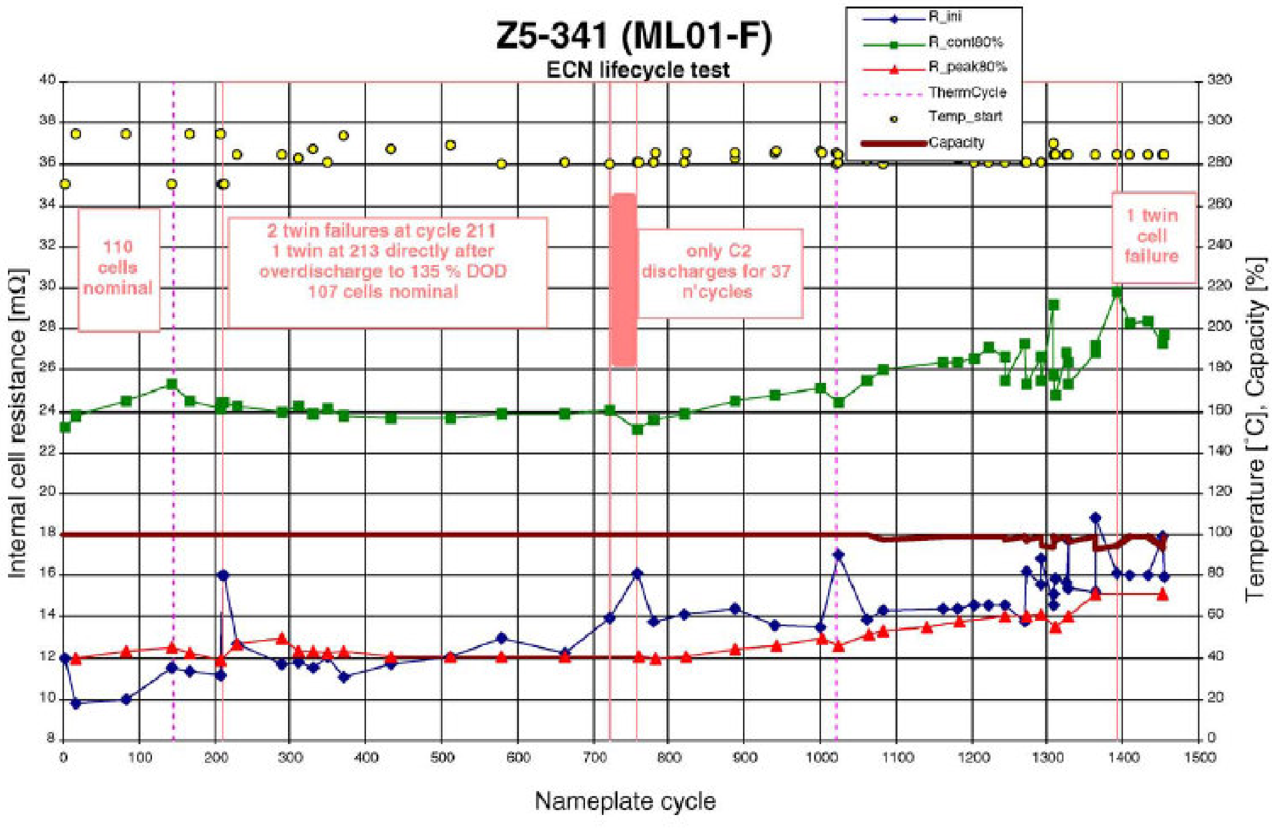

Figure 9. Life cycle test results of battery Z5-341.

Under normal operating conditions there are no life-limiting factors [6] associated with the positive and negative electrodes and the beta alumina ceramic electrolyte. Individual cells and modules (10 cells in series) have been cycled for many thousands of cycles, equivalent to 15 years use in an electric vehicle, with only a small change in performance and still being capable of giving the full nameplate capacity [6].

Figure 10 shows the performance of a module that has been tested for over 7000 electrical cycles (~3000 nameplate cycles over 4 years) [6], [7].

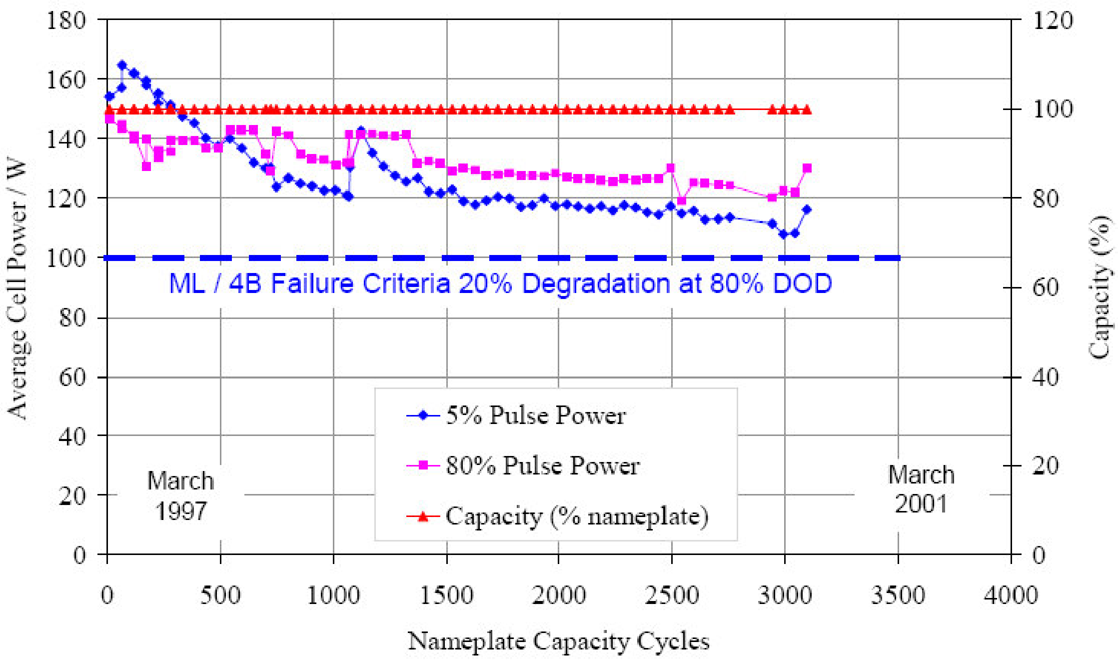

Figure 10. Performance on a Mercedes-Benz A-Class accelerated life test

- **Temperature Characteristics**

As it was mentioned in previous, the optimum operational temperature for ZEBRA batteries is in range of 270-350° C because at these temperatures, the beta alumina electrode contributes only a minor component to cell resistance [4].

In other words, 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 [8].

Although the high operating temperature can be a disadvantage in some application, particularly as SLI batteries which are small in size and whose use is intermittent, for many applications the high operating temperature is a definite advantage. Thus, the characteristics of a ZEBRA battery are almost independent of ambient temperature. The electronics components in BMI (Battery Management Interface) restrict the upper temperature limit to 70 °C. There is effectively no lower temperature limit [3].

Since ZEBRA batteries operate at ~300°C, there are no detrimental effects resulting from their use at extremely cold or hot ambient temperatures. For conventional battery systems, extreme temperatures require more elaborate thermal management or result in reduced battery performance. Besides, because of their high-temperature operation, ZEBRA batteries allow for the use of latent heat for fast cabin heating or window defrosting. But the thermal management needs for the high-temperature ZEBRA batteries are not quite ideal for electric vehicle-drive-systems. When not in use, zebra batteries typically require being plugged into a wall plug, or tethered, in order to be ready for use when needed. If shut down, a reheating process must be initiated that requires about one to 2 days to restore the battery pack to the desired 146 temperature, and fully charging the batteries. This reheating time can, however, vary depending on the SOC of the batteries at the time of their shut down, battery-pack temperature, and power availed for reheating. If shut down of the battery pack is desired, three to 4 days are usually required for a fully-charged battery pack to lose its heat significantly [5], [9].

- **Self Discharge**

The sodium ion conducting beta alumina is an electronic insulator and as there are no chemical side reactions the cell is 100% coulombically efficient (Ah charge in = Ah discharge out). There is no self discharge and the cell is fully sealed and maintenance free (there is no overcharge gassing reaction as in lead acid). Accurate charge control and measurement are therefore easily possible and cell in series chains can not get out of step. These features also confer a high efficiency on the system [5],[10].

Although the cell has 100% coulombic efficiency, and therefore, has no self discharge, the base operating temperature of 270° C requires that even in a very well insulated battery box utilizing evacuated thermal insulation, some heat loss is inevitable and this can be considered as self discharge. It is not possible to quantify this as a percentage of capacity as it depends upon the operating cycle but it varies from 10% per day [3] if the battery is not used at all to zero for an intensively used battery in which the temperature never fall to 270° C. Keep in mind that, this self discharge does not lead to cells getting out of balance and there are, therefore, no adverse effects other than a reduction in the energy available.

- **Safety (Auxiliary Circuits)**

The Zebra cell has certain intrinsic safety features. If a cell is crushed and the ceramic electrolyte is fractured, the sodium metal reacts with the sodium chloroaluminate to form sodium chloride and aluminium. These products are non corrosive and do not have high vapor pressures. The cell can be over charged and overdischarged as described by the reaction shown in Figure 1. Cells are normally operated within the standard nickel /nickel chloride reaction range as they will degrade if repeatedly operated well into the overdischarge and overcharge regions. In extreme fault situation however, such as a charger malfunction, the overcharge reaction allows cells to overcharge safely. These features, combined with the ability to withstand freeze/thaw cycling, enables cells and batteries to be very abuse resistant [6].

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, 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 [2]. The ZEBRA battery did pass all these tests because it has a four barrier safety concept [2],[6]:

1. Barrier by the chemistry
2. Barriers by the cell case

3. Barrier by the thermal enclosure
4. Barrier by the battery controller

The battery controller the so called Battery Management Interface, BMI supervises the battery and prevents it from being operated outside of specification. Each battery has a microprocessor management system that continuously monitors voltage, current, temperature, and state of charge and computes the voltage, temperature and current limitations. The BMI communicates with the external load and charger via controller area network (CAN) bus system to ensure that action is taken to prevent abuse and messages are present over the CAN bus which can support a stand-alone vehicle display [6].

- **Recycling**

ZEBRA battery systems including the cell and box are dismantled. The box material is stainless steel and SiO2. 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 [2].

The US company, Inmetco has successfully recycled 20 ton loads of ZEBRA cells by adding them to their standard submerged arc smelting furnace to produce nickel containing remelt alloy used in the stainless steel industry. The ceramic and salt contained in the cells collects in and the slag and is compatible with their process. This is sold as a replacement for limestone used in road construction - nothing goes to landfill. Inmetco typically processes about 5000 tones of nickel based batteries per year. There is scope for increase as total nickel containing raw material throughput is in excess of 60,000 tones per annum. Thus there is ample recycling capacity as the ZEBRA battery production is ramped up [11].

- **Cost**

According to [5], the battery technologies that are the main contenders for automotive traction applications are listed in Table 2, together with representative cost values in Pound and effecting factors for each technology.

	VRLA	Nickel cadmium	Nickel metal hydride	Lithium ion	ZEBRA
Cost[d] (£ kWh^{-1})	105–175	200–300	250–350	250–1000	70–270
Cost affected by					
Overcharge capacity	Yes	Yes	Yes	Yes	No
Deep cycling	Yes	Yes	Yes	Yes	No
Maintenance	Yes	Yes	Yes	Yes	No
Ambient temperature	Yes	Yes	Yes	Yes	No

Table 2. Cost comparison of different battery technologies

Based on the [11], the total cost consists of 1. Material cost 2.Case cost 3. Battery system cost and 4. EV operating cost. In following, these cost evaluation are presented which are based on the information from MES-DEA Sa, Stabio, Switzerland

Material	kg/cell	kg/kwh	$/kg	$/cell	$/kWh
Ni (powder + sheet)	0.15	1.53	11.6	1.74	17.75
Iron (powder + sheet)	0.14	1.43	3.36	0.47	4.80
Copper	0.03	0.31	2	0.06	0.61
Halide salts	0.22	2.24	0.77	0.17	1.73
beta-alumina (boehmite)	0.14	1.43	2.38	0.33	3.40
Total	**0.68**	**6.94**	**4.08**	**2.77**	**28.28**

Table 3. ZEBRA Cell ML3P Material Cost

Material	kg/bat	kg/kWh	$/kg	$/bat	$/kWh
Stainlees Steel	18	0.85	3.2	57.6	2.72
Steel (cooling system)	7.5	0.35	1.5	11.25	0.53
Thermal isolation	7.5	0.35	12.5	93.75	4.42
Miscellenious	4	0.19	9	36	1.70
Total	**37**	**1.75**	**5.4**	**198.6**	**9.37**

Table 4. ZEBRA Battery Z5 (21 kWh) Case Material Cost

Part		$/kWh	Battery in $
Cells	Material tab 1	28.28	599.6
	Assembly	12.12	257.0
	Energy	1.7	36.0
Case	Material tab 2	9.37	198.6
	Assembly	9.37	198.6
Controller			250
Total		**72.63**	**1539.9**

Table 5. Cost Projection of a 21 kWh Mass produced ZEBRA Car Battery

Assuming that the battery production cost (Table. 5) are 2/3 of the selling price MES-DEA company has claimed that they end up with 2310 $ for a 21,2 kWh battery (109 $/ kWh).

- **Manufacturer**

ZEBRA batteries started full-sale commercial production in 2001 in a purpose built facility in Switzerland with a forecast capacity of over 30,000 batteries (equivalent to over 600MWh) per year, MES-DEA Company, only one company in the world! And the current production is 700 samples annually.

- **Practical Experience**

Several pure and hybrid electric battery buses with up to six Z5 batteries are in service in the Italian cities of Bologna, Florence, and Modena giving totally emission free operation [2], [3].

More precisely, Autodromo Electric Bus, Cito Electric Bus, EVO Electric Hybrid Bus, Man Electric, Bus and LARAG Wil Bus are of many practical experiences of ZEBRA batteries if we want to name a few.[2][3]

ISE offers a proven diesel hybrid system that compares favorably with competing diesel hybrids, particularly those offered by Allison and BAE Systems. During 2002 and the first half of 2003, ISE integrated three buses using a diesel system employing its proven Siemens components, under a $3.1 million contract received from New Jersey Transit (NJT). These systems were installed into three 40-foot Nova RTS buses, which were delivered to NJT between June 2003 and May 2004.

The Storage technology used in these diesel hybrid buses, Fig. 11, can be a choice between ultracapacitors, which are more efficient than competing battery-based energy storage subsystems, and advanced nickel sodium chloride ZEBRA batteries, which carry more energy per unit weight than the batteries used in competing hybrid drive system [12]. These systems were developed by ISE Corporation, USA and installed into three 40-foot, 12.2 meters, Nova RTS buses, which were delivered to New Jersey Transit, NJT between June 2003 and May 2004.

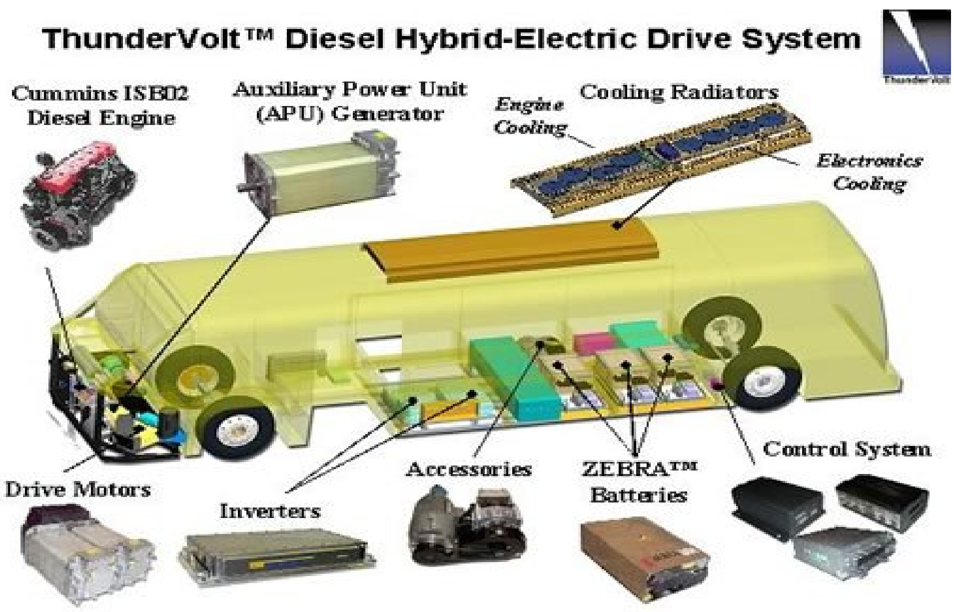

Fig. 11, Diesel hybrid drive system using ZEBRA and Ultracapacitor technologies

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