Developments and Improvements in Zebra Nickel Sodium Chloride Batteries

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Abstract

During last 4 years research work has continued at MES-DEA to improve the composition of the positive electrode of sodium nickel chloride "ZEBRA" battery. The energy improvement programme begun in 2000 and resulted in 2003 in the improvement of the specific energy of the battery from 94 Wh/kg (C type cell) to 120 Wh/kg (P type cell).

The principal gain in energy with the P type cell, was obtained by changing the chemical composition of the positive electrode.

The continuous development in MES-DEA brought in 2007 as result, the cell type X, with a new positive electrode offering improved specific energy in combination with fast charge regime, thus widening the application spectrum of ZEBRA batteries

Compositional changes to the positive electrode have been made to significantly increase in stability.

The paper describes the changes in chemical composition and the electrical data are discussed through the performance comparison between C, P and new X type.

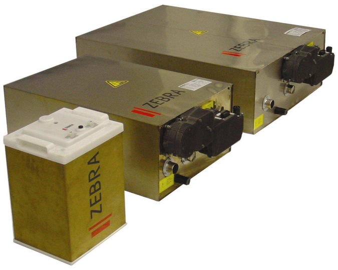
Keywords: "ZEBRA", "Battery", "Chemical Changes", "Nickel Sodium Chloride" "Electrical data".

0. Foreword

Zebra batteries are produced at MES-DEA Stabio, Switzerland.

MES-DEA is part of CEBI group and this year will bring the production capacity up to 2000 batteries/year.

1. Introduction



The ZEBRA cell has a central positive electrode mainly consisting of Nickel and sodium chloride plus some additives and a liquid electrolyte tetrachloroaluminate contained within a beta alumina tube electrolyte. The cell works in a range of temperature between 270°C-350°C and during charge sodium ions formed in the central positive electrode moves through the wall of the beta alumina tube to form the liquid sodium negative electrode which is contained by a square section mild steel case. A schematic of the cell is shown in figure 1.

MES-DEA during this years has developed three different type of granules showed in table 1 .

In order to have batteries with a specific energy of 120 wh/h was necessary to develop in 2003 the P type granules. This type of granules has shown in extreme condition a loss in capacity and the impossibility to accept fast charge (30A to 80% SOC).

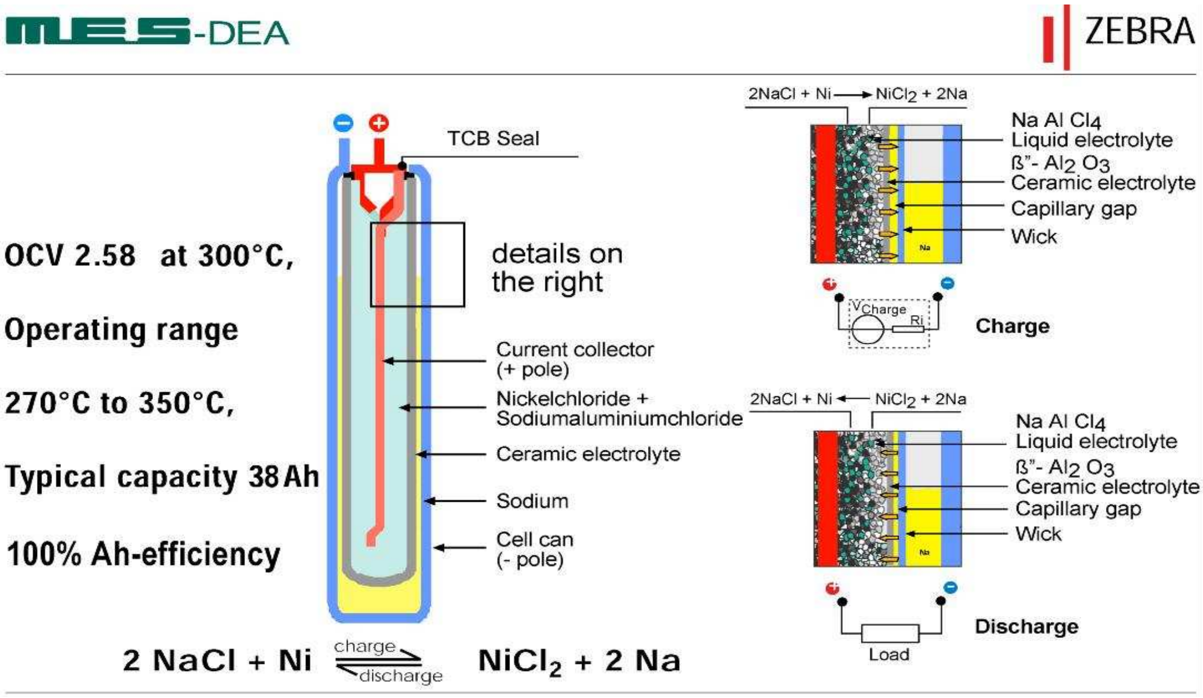


Figura 1: ZEBRA Cell Design

Cell Characteristics	**ML3C**	**ML3P**	**ML3X**
Capacity	32Ah	38Ah	38Ah
OCV	2.58V	2.58V	2.58V
Deep Disc. Cy. Stability	Very Good	Good	Very Good
Normal Charge	10A: 2,67V/cell	6A: 2,67V/cell	10A: 2,67V/cell
Fast charge	30A: 2,85V/cell	NO	NO (To be defined)
Regen. breaking	3,1V/cell, 60A, 4%SOC	3,1V/cell, 60A, 4%SOC	3,1V/cell, 60A, 4%SOC
Voltage Max generator	2,85V/cell up to 70%SOC, then 2,58V/cell from 80% to 100%SOC	2,67V/cell up to 70%SOC, then 2,58V/cell from 80% to 100%SOC	2,67V/cell up to 70%SOC, then 2,58V/cell from 80% to 100%SOC

Table 1 : ZEBRA ML3 Cell Characteristics

2. Chemical Changes

The active material are contained within the positive electrode which is made up of aluminium, sodium halides, nickel and iron. The main chemical changes with the previous generation of electrode are:

1. Introduction of small quantities of Iron Sulphide
2. New type of nickel powder made by Inco which has a higher surface area
3. Double content of Sodium Iodide

2.1 Introduction of small quantities of Iron Sulphide

Figure 2 shows the maiden charge for the ML3P and ML3X cells. Notice the presence of an extra reaction between 2.2V and 2.35V caused by the sulphur in the X granules. Again on discharge the presence of sulphur gives an extra discharge plateau Sulphur has been added to the nickel Zebra cell to stabilise the capacity. It was shown that without sulphur the nickel metal grain size grows rapidly on cycling. Recent post mortem works on the nickel powder by scanning electron microscopy (SEM) in secondary electron imaging mode (SEI) and by energy dispersive X-ray and XRD analysis confirmed that the presence of sulphur gives a very high surface area.The role of the sulphur has been debated in the past (ref.1**)** but the mechanism is still not clear.

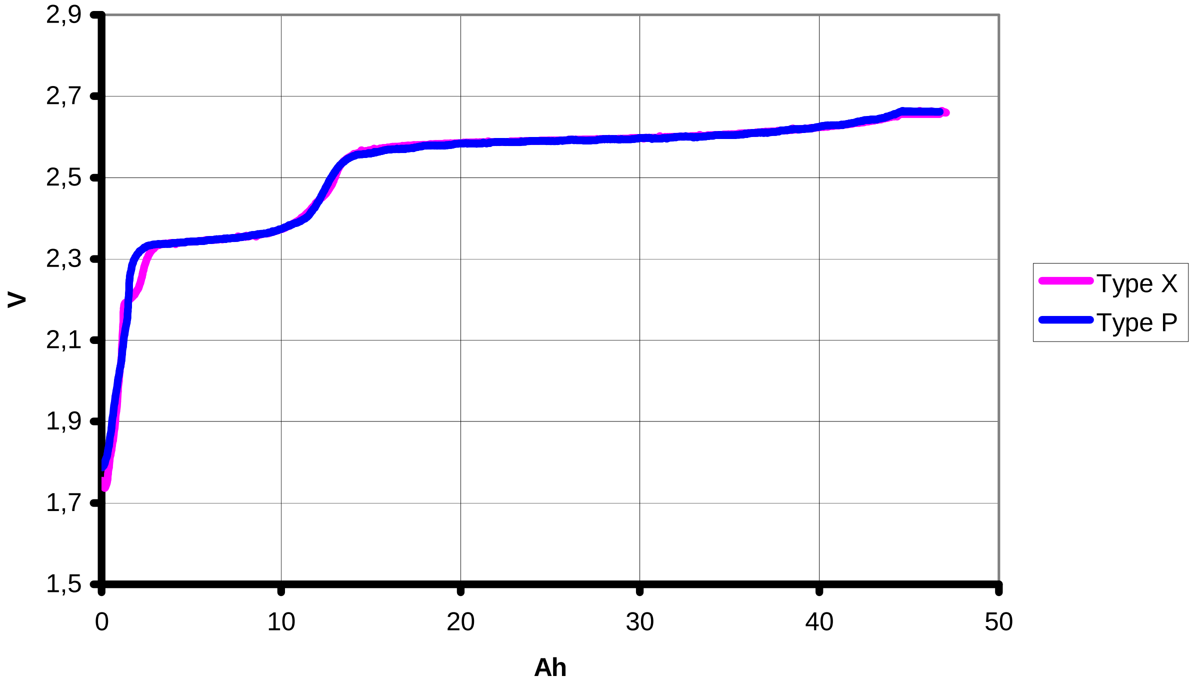


Figure 2: Maiden Charge 2.75A to 2.67V to 0.5A

2.2 New type of nickel powder made by Inco which has a higher surface area

An excess of transition metal is used mainly nickel, so that about the 30% of metal is involved in the charge-discharge reaction. The unused metal maintains the electronic conductivity. Higher surface area means more area for the cell reaction.

2.3 Double content of Sodium Iodide

The mixed Ni/Fe electrode developed at ZEBRA Power Systems to improve power required the addition of NaI to prevent increasing resistance with cycling. This deterioration was evident from the start of cycling. The amount of NaI was reduced significantly in 1999 with a change in granulation process. Now the right amount has been reassessed to optimise the stability of the cell in all charge situations.
NaI seems to enhance the $NiCl_2$ electrode in several ways.

- NaI enhanced the $NiCl_2$ electrode charge.
- Iodide acted as a charge transfer catalyst.

A possible mechanism was as follow to enhance charging
Electrochemical
$NiI_2 + 2NaCl \rightarrow NiCl_2 + 2Na + I_2$ V = 2.84V
Chemical
$Ni + I_2 \rightarrow NiI_2$

This suggest a benefit from NaI at higher voltage above 2.8V preventing an increasing of initial resistance during discharge.

3. Electrical Data and Life Testing

3.1 Fast Charge Bus Dynamic Stress Test

As charge acceptance at high rates is one of the major factors distinguishing the performance of ML3P and ML3C cells, this test demonstrate the difference between ML3P ML3C and x granules. Essentially this a ranking test where only a limited number of cycles to nameplate capacity are expected. A Dynamic Stress Test profile is applied with 70W peak power per cell repeated to 10%, 10%, 20%, 20% SOC with alternating Fast (2.85V, 30A to 80% SOC) and Normal (2.67V, 10A to 0.5A) charges. Every 33 of these cycles the module is re-characterised with a peak pulse power test to 0% SOC to observe the change in resistance. The initial resistance (95% SOC) is sensitive to this test and increases quickly. Figure 3 compares the 38Ah ML3P granule composition with the new 38Ah ML3X. The pass criterion is an increase of less than 20% in resistance after approximately 40 cycles The graph shows that the ML3P cells have doubled in resistance after 40 cycles whereas the ML3X cells have increased by only 2 mOhms after 60 cycles.

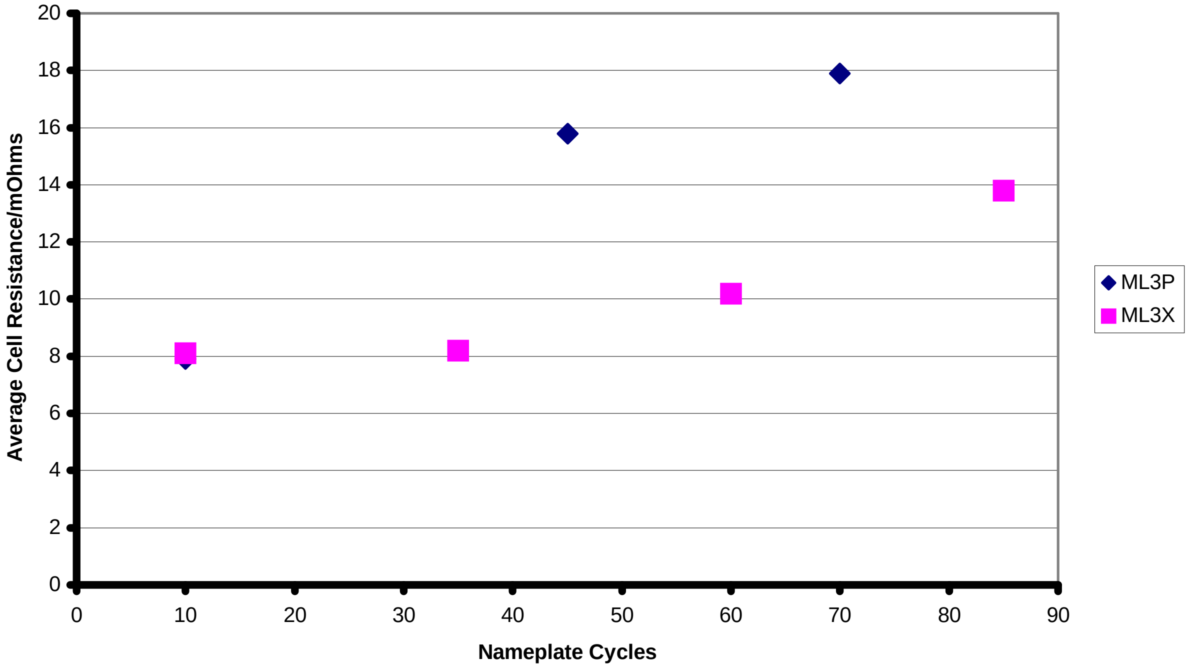


Figure 3: FCBDST Comparison of Pulse Resistance at 95% SOC

3.2 Vehicle Random Dynamic Stress Test

The Vehicle Random Dynamic Stress Test is regarded as a real life test but only 250 cycles to nameplate capacity are expected to be completed in the three months qualification period. Ten cells modules are cycled at an operating temperature of 295°C. A characterization cycle is performed ca. every 50 nameplate cycles. The characterization cycle consist of a C/2 discharge (19A) with peak power measurements performed at 95% SOC, 80% SOC, 60% SOC, 40% SOC, 20% SOC and 5% SOC. The pass criteria is that after 250 nameplate cycles the end life criteria (the end life criteria is defined as 20% of degradation of the maximum allowable values during Battery Acceptance testing) should not be achieved. The results in figure 4 shows the 95% SOC pulse resistance comparison.

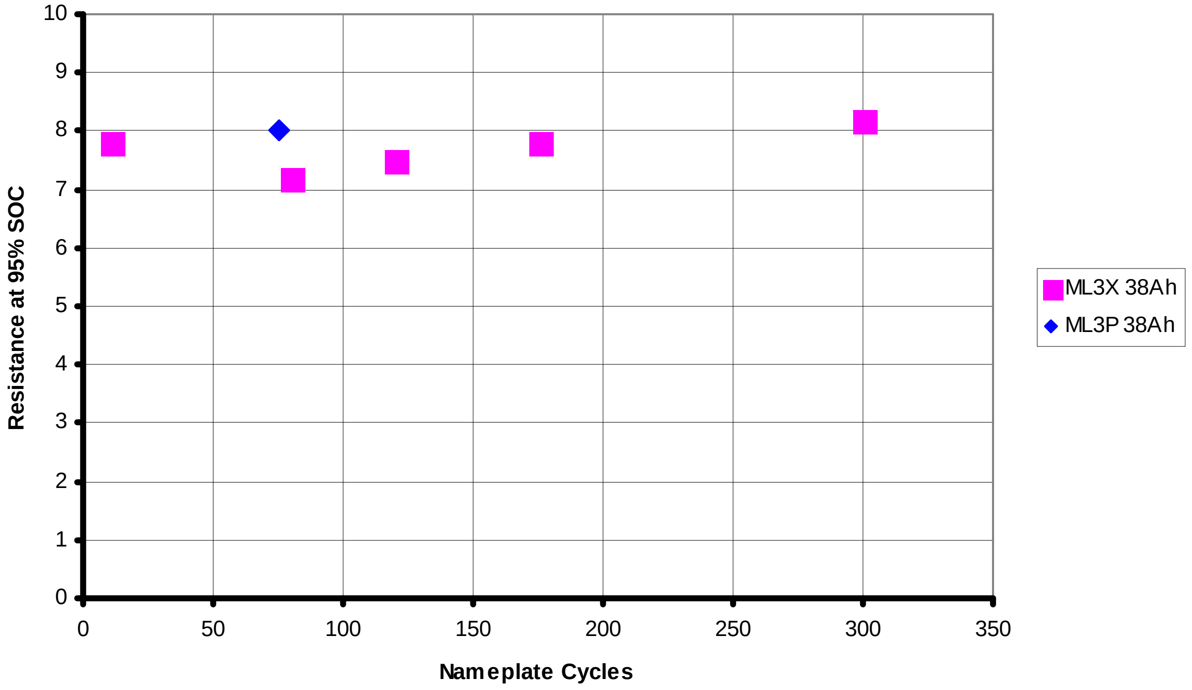


Figure 4: Vehicle Random Dynamic Stress Test. Pulse Power at 95% SOC
At 20% SOC the pulse resistances are shown in figure 5. The module is still cycling**.**

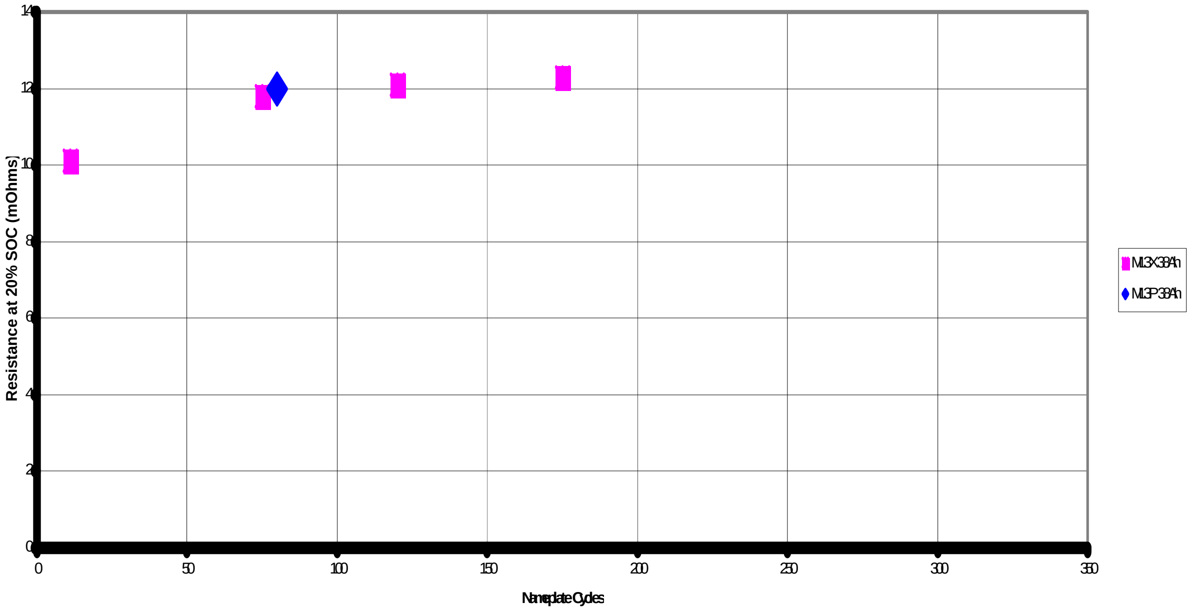


Figure 5: Vehicle Random Dynamic Stress Test. Pulse Power at 20%

3.3 Capacity Retention

This is a test to check capacity retention during deep discharge. ML3P cells have shown loss of capacity after few hundred cycles. The test regime is: Charge 2.67V, 10A to 0.5A; Discharge 223W (module) to 80% of NPC. The results are shown in figure 6. The module is still cycling.

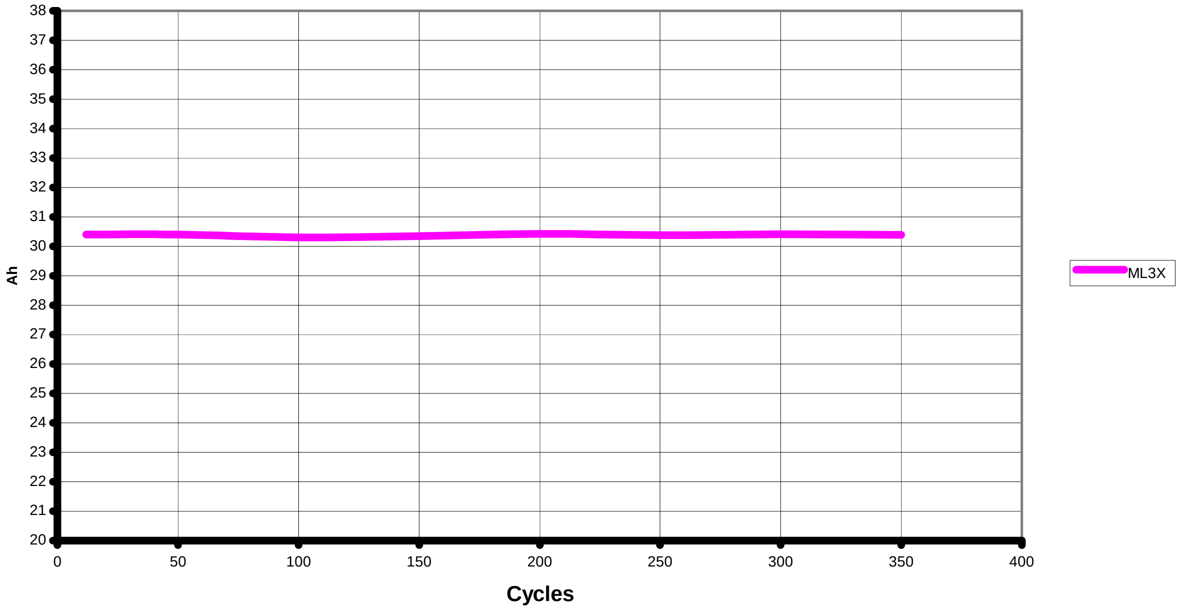


Figure 6: Capacity retention at 80% DOD

4 Conclusions

X type granules have shown the best specific energy, stability and allow Fast Charge.

The chemistry of the cell offers high flexibility giving us the chance to develop different recipes for different duty cycles.

The research work at MES-DEA is going ahead. New additives are under investigation to improve the performances of the ZEBRA cell.

5 References

[1] N. Nicholson "Beta Research and Development Internal Memorandum Number 25", 1988.