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Design Changes to Improve the Specific Energy of the ZEBRA Battery

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Abstract

The sodium/nickel chloride (ZEBRA) battery has established itself as a leading electric vehicle battery and it is now entering series production at MES-DEA [1], [2]. The objective of a programme partly funded by the Swiss Federal Office of Energy is to improve the energy density of the Zebra battery to 120Wh/kg with no detriment to the well established characteristics of long life, safety, low cost and high power. A parametric study of all the principal components of the cells and battery enclosure has indicated where weight savings are possible. Compositional changes to the positive electrode and higher utilisation of the theoretical capacity have been made to significantly increase the nameplate capacity. Results are given for tests on the various improvements.

Keywords: Sodium-nickel-chloride, battery, energy density, range.

1 Introduction

ZEBRA batteries are currently being produced at MES-DEA in Stabio, Switzerland. A new building with 20,000m^2 of floor space was completed early in 2001 and equipment is now installed that brings the production capacity up to 2000 batteries/year. The building is designed to produce 33,000 batteries/year and an additional production capacity of 66,000 batteries can be added on the same site.

MES-DEA are part of the CEBI group of companies and the group's expertise in volume production has been applied to both the cell and battery resulting in significant weight and cost savings. The current production vehicle battery, the 18kWh Z5C, has a specific energy of 94 Wh/kg. This year a programme, partly sponsored by the Swiss Federal Office of Energy, to improve the specific energy of the Zebra battery was commenced. A target of 120Wh/kg was set to give existing Zebra powered electric vehicles an increase in range of around 25%.

2 Performance Status

The specification of the present 18kWh Z5 production battery without the battery management interface (BMI) is shown in Table 1. Improvements in specific energy have been demonstrated with other types of ZEBRA batteries. By increasing the size of the battery the cell energy density is not degraded as much as in smaller batteries. For large vehicle applications, such as buses where up to 12 Z5 batteries are used, an improved energy density can be achieved by simply increasing the battery size i.e. increasing the number of cells per battery pack. The weight and ease of handling limit the maximum size, the largest ZEBRA batteries built to date have been 43kWh, two batteries of this size have been delivered for testing in a military hybrid vehicle. Figure 1 shows the effect of battery size on specific energy.

For lower rate applications cooling is not required and several batteries have been constructed without the air cooling systems. Some of these batteries were not required to give high pulse powers and then a nameplate increase was also possible. Typically these batteries have a specific energy of ~115 Wh/kg. As the target improvement in this development programme was required to be demonstrated in existing small electric vehicles a specific power at 80% DoD of >150W/kg was still required. The simple modifications of removing the cooling and increasing the size of the battery were not applicable. The increase in specific energy has to come from reducing the weight of the cells and battery components and increasing the nameplate capacity.

Table 1:Specification of the present Z5C production battery

Type	unit	Z5-278-ML-64	Z5-557-ML-32
Capacity	Ah	64	32
Rated energy	kWh	17.8	17.8
Open circuit voltage	V	278.6	557
Weight	kg	189	
Specific energy	Wh/kg	94	
Specific Power	W/kg	169	
Peak power	kW	32	
Thermal loss	W	<110	
Cooling		Air	
Ambient temperature	° C	- 40 to + 50	
Dimensions (WxLxH)	mm	533 x 755 x 300	

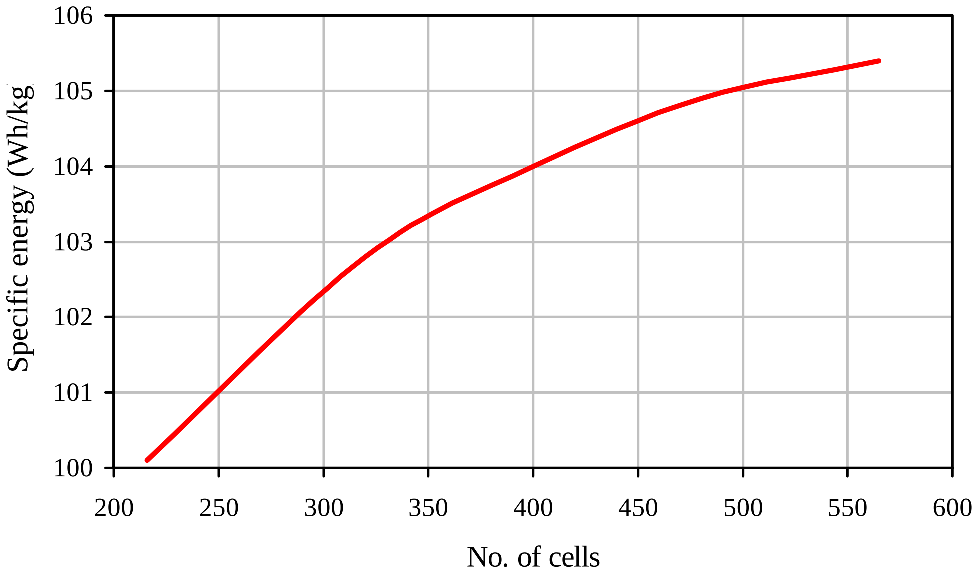

Figure 1 Effect of increasing battery size on specific energy

With any major changes to cells and batteries full qualification has to be undertaken. Reducing metal component weights could increase the cell resistance affecting available power. Safety and abuse resistance could also be affected. Increasing nameplate capacity increases the overall energy but the available power at deep depths of discharge and the long-term performance behaviour could be altered. Each change has to be carefully tested and qualified for performance, safety and long term stability.

3 Weight Reduction

3.1 Breakdown of ZEBRA component Weights

The major component weight breakdown for the present standard Z5C production battery is shown in figure 2. The cell component weight breakdown is shown in figure 3.

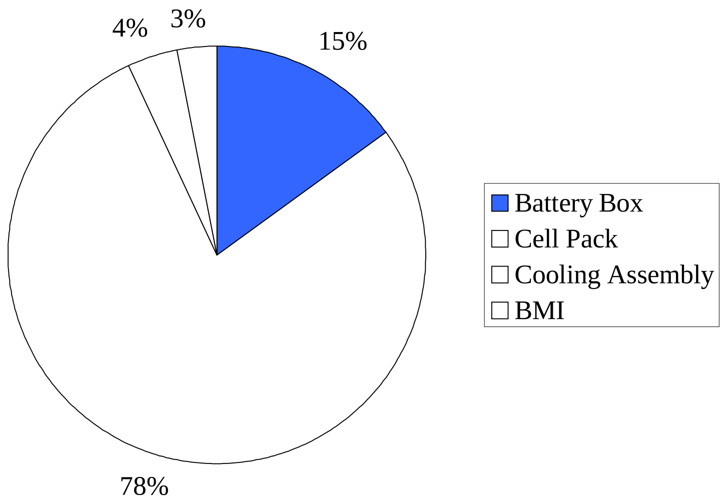

Figure 2: Weight breakdown of a Z5C battery

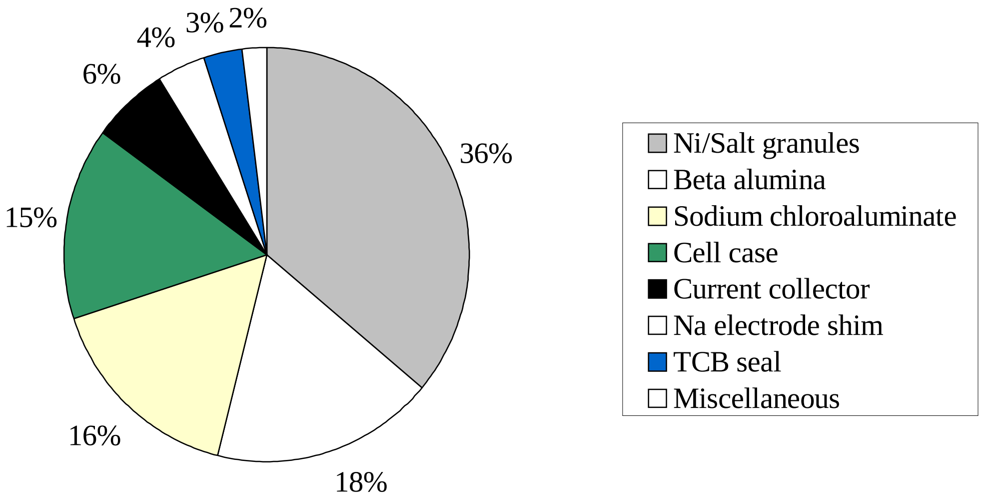

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Figure 3: Weight breakdown of an ML/3 cell

Reduction of the cell individual component weights has the largest effect on the overall battery weight. The cell pack as shown by figure 2 contributes to nearly 80% of the total weight.

3.2 Cell Weight Reduction

The positive electrode (nickel/salt granules and sodium chloroaluminate) account for the largest proportion (52%) of the cell weight. Improvements to this electrode are discussed fully in section 4. The next largest contributions are the beta alumina 18%, the cell case 15%, current collector 6% and the sodium electrode shims 4%. A reduction in beta alumina thickness was investigated as this also gives other benefits besides saving weight. Thinner beta alumina reduces the cell resistance increasing energy and power. The volume available for the positive electrode is also slightly increased which increases the cell capacity.

Thinner beta alumina tubes were produced and the strength for handling during pressing and firing was acceptable with the average wall thickness reduced to 1mm. Unfortunately due to the production tolerances the wall thickness in certain areas of the tubes was as low as 0.8mm. This reduced the internal burst pressure of the thin wall tubes significantly which severely limited the over temperature capability of the cells. For the present production methods and cruciform shaped beta alumina tube it was concluded that the current average wall thickness of 1.25mm was optimised and no further weight saving is possible.

A reduction of cell weight by 4% was shown to be possible using a slightly thinner cell case and sodium electrode shims. The standard method of testing any cell changes is to build and electrically test cells in several 10 cell modules. Various cycling regimes are used to ensure that any changes are not detrimental to performance, long term stability, fast charge etc. Module testing showed that the thinner materials did not measurably change the cell performance.

The present production positive electrode current collector is made from nickel sheathed copper cored wire. A reduction in diameter of the copper in this composite current collector from 3mm to 2mm was also tested. Reducing the diameter did not markedly affect the cell resistance but the cell reproducibility was adversely affected. This effect was found to be caused by the reduction in surface area of the current collector and small nickel fins had to be added to increase the area and give satisfactory performance. Table 2 shows module test results comparing standard and reduced diameter copper cored current collectors with fins.

Table 2: Comparison of cell performance for standard and reduced diameter current collectors.

DOD	2mm Copper Core		3mm Copper Core	
(%)	Pulse (mΩ)	Continuous (mΩ)	Pulse (mΩ)	Continuous (mΩ)
2	7.9		7.9	
20	9.2	10.9	9.0	11.0
40	9.4	15.1	9.2	15.8
60	9.6	20.8	9.6	21.1
80	12.5	24.5	13.0	24.9
100	19.9	30.2	21.6	31.5

If the thinner cell case, thinner sodium electrode shims and the modified current collector were introduced then approximately a 6% weight saving would be achieved.

3.3 Battery Box Component Weight Reduction

Figure 5 shows the battery box component weight breakdown. The box components had recently been optimised by MES-DEA and a weight saving of around 26% had been achieved over the previous Z5B design. The scope for further weight reduction was therefore very limited and only two components, the insulation and heater were investigated. The present insulation boards have a density of 200kgm^{-3} and reducing the density saves weight and reduces the heat loss. The insulation board has to support the evacuated metal skins so only a small reduction to 180kgm^{-3} is possible. This change and use of thinner mica on the layered heater gives a weight saving of only 2% on the box components.

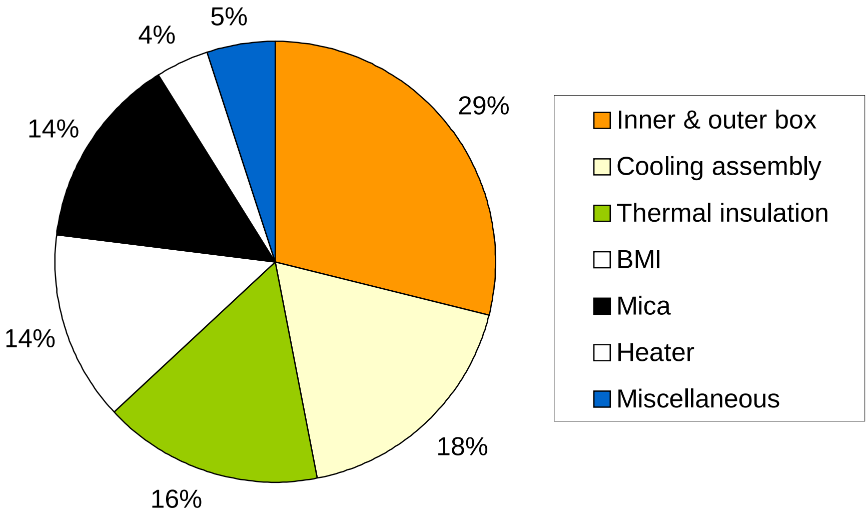


Figure 4: Z5C Zebra battery box component weight breakdown

4 Increasing Nameplate Capacity

The primary positive electrode reaction of the Zebra cell is that between nickel and sodium chloride. To reduce the dependence of the pulse power available on the DoD of the cell a second positive electrode reaction was introduced which has a lower potential. Iron was chosen since it has a slightly lower reaction potential and previous work had shown it to be stable in the ZEBRA system [3].

The principle reversible cell reactions are :-

$$Ni + 2NaCl \rightarrow NiCl_2 + 2Na \qquad E = 2.58V \tag{1}$$

$$Fe + 2NaCl \rightarrow FeCl_2 + 2Na \qquad E = 2.35V \tag{2}$$

For most of the discharge the cell functions as a $Na/NiCl_2$ cell, however during a high current pulse when the working voltage falls below 2.35V the iron reaction augments the main nickel reaction. The iron reaction occurs near the front of the electrode where the cell has its minimum resistance. After a high power pulse the cell reverts back to the main reaction above 2.35V and the iron that has been produced is re-oxidised to iron chloride by nickel chloride. The iron chloride is then available for the next high current discharge.

It has been found convenient to assemble cells in the overdischarged state by including a small amount of aluminium powder with the appropriate amount of sodium chloride in the positive electrode mix. On the first charge the reaction that occurs is:-

$$Al + 4NaCl \rightarrow NaAlCl_4 + 3Na \qquad E = 1.6V \tag{3}$$

This is a reversible reaction but it occurs at too low a voltage to be energetically useful. However it does provide several other useful functions, one of which is to act as a pore former that ensures full charge acceptance on the maiden charge.

For the present production cell the available reversible capacity is more than 40Ah, but for electric car applications power considerations restrict the specified nameplate capacity to 32 Ah. This conservative figure allowed for some capacity fade which was originally anticipated over the lifetime of a battery in a vehicle. In fact, capacity stability has been excellent for long term tests simulating electric vehicle type discharge profiles. Figure 5 shows that full capacity is available for a module which has completed more than 7000 cycles (3000 nameplate cycles) over 4 years of typical electric vehicle driving cycles as specified by Mercedes Benz [4]. This supports the case for increasing the specified capacity of the existing production ZEBRA cell with no modification.

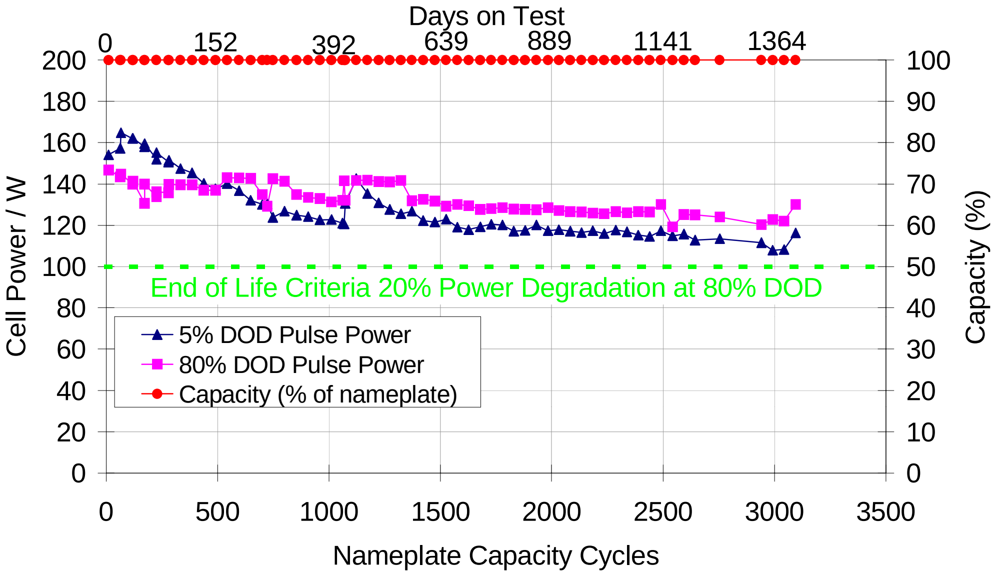


Figure 5 : Cycle history for 10 ML/4 cell module running in excess of 3000 nameplate cycles

Of the minor additives in the positive electrode, the cell capacity is most sensitive to the aluminium content. Reducing the aluminium content releases salt for the main cell reaction and hence improves capacity, while increasing the aluminium content reduces the capacity but makes the electrode more porous.

To optimise the electrode for power and energy a series of cells were tested with varying aluminium content in the positive electrode. These were compared by measuring the peak pulse power at various DoD for a 38 Ah increased capacity discharge, the standard production cell being 32Ah nameplate. The lowest resistance figure is obtained when the aluminium content is reduced to 70% of the normal production level. This is illustrated in figure 6 below.

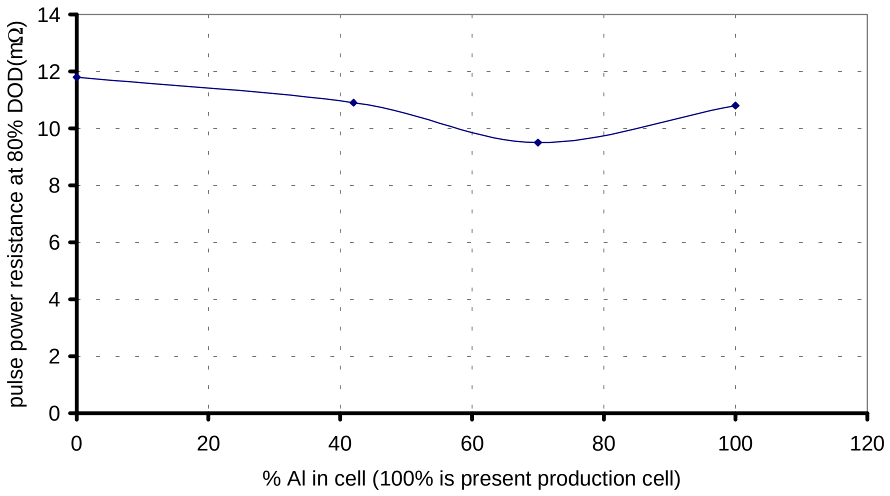
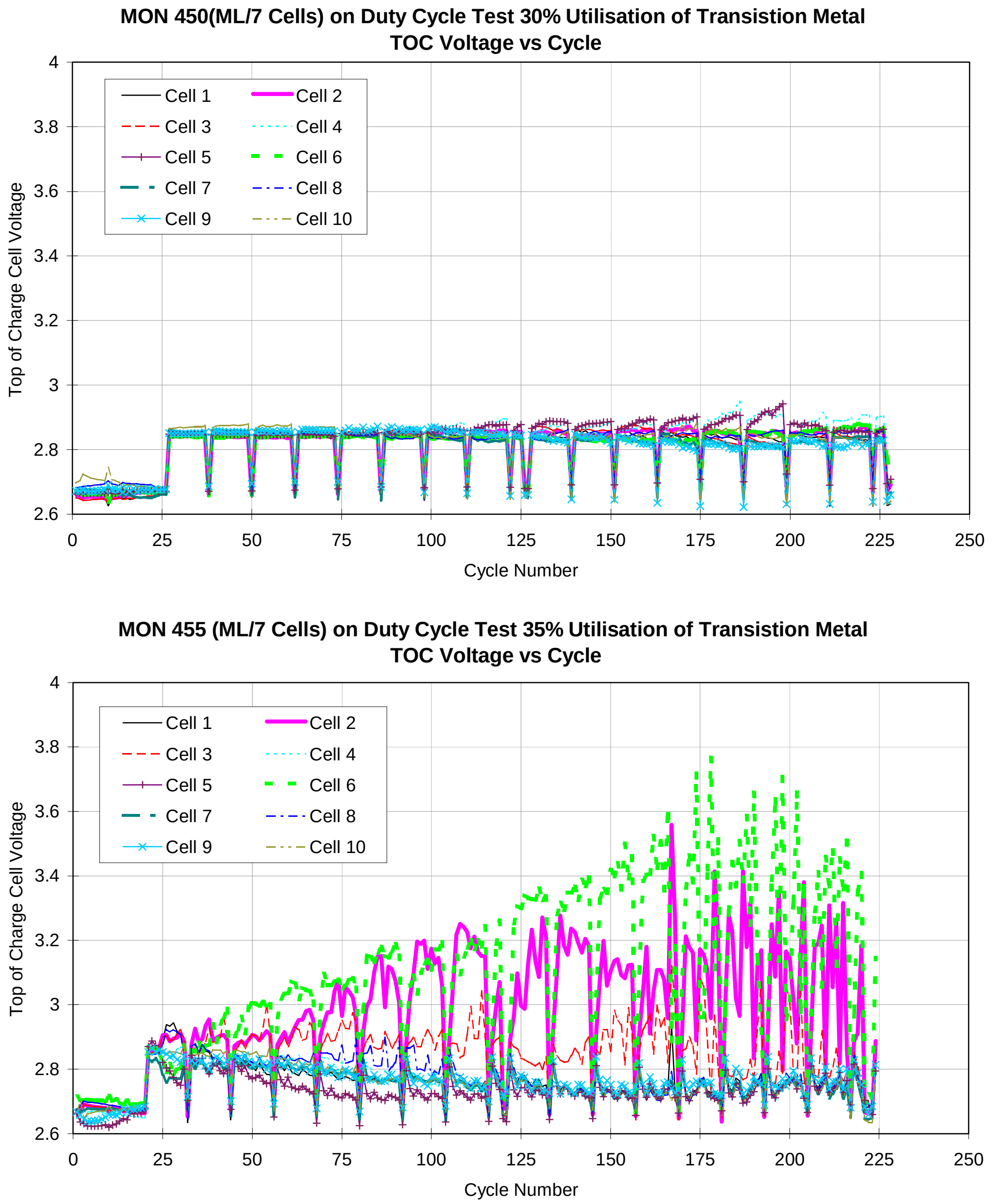


Figure 6: Effect of varying the aluminium content in the positive electrode.

The utilisation of the transition metal in the electrode is about 30% (~0.30Ah/g nickel/iron). Higher capacity cells have been tested by reducing the transition metal i.e. increasing the utilisation to 35% and adding more salt.

These cells were ranked for stability by rapid cycling as modules (12cycles/day) on a “hard” duty cycle regime with severe discharges and rapid one hour charges. After more than 200 cycles differences have emerged in the top of charge voltages for the two groups of cells. This effect is shown in figure 7.



MON 450(ML/7 Cells) on Duty Cycle Test 30% Utilisation of Transistion Metal
TOC Voltage vs Cycle

MON 455 (ML/7 Cells) on Duty Cycle Test 35% Utilisation of Transistion Metal
TOC Voltage vs Cycle

Figure 7: Effect of increasing the utilisation of the transition metal

The cells with utilisation at 30% have remained within a narrow band at the top of charge despite the arduous cycle regime. On the other hand at 35% utilisation (lower graph) the top of charge voltages show considerable divergence. This suggests the nickel has been overchlorinated. The conclusion is that only a small reduction is possible in the active metal in the positive electrode.

Changes to the other components in the positive electrode are also being assessed using this short term accelerated “ranking” test. The most promising positive electrode emerging from the above tests, the reduced aluminium content and slightly increased utilisation of the transition metal is being tested over a longer period of time using a typical electric vehicle duty regime. The new nameplate capacity will be 15 to 18 % greater than the present production cell.

5 Demonstration of improvements

To demonstrate the improvements it is intended to build several batteries and test them in vehicles starting early in 2002. The vehicles will be the MES-DEA converted Renault Twingo, which uses one Z5 Zebra battery and a Mercedes VITO van, which uses two Z5 batteries. Before building demonstration batteries as well as the extensive module testing all new designs of cells undergo full qualification testing. Tests such as overcharge, overheating, resistance after failure, freeze thaw testing etc have are being completed to ensure that the proposed changes do not affect the normal cell production and safety

Not all the performance improvements can be taken through to demonstration batteries within the scope of this programme. The cells and components have to be produced on the present MES-DEA production equipment. To incorporate some of these improvements the production equipment and tooling will require extensive modifications. Some of the more complex changes, such as the proposed current collector, will have to be decided upon based on the test results and cost/benefit considerations. Nevertheless the changes that can easily go through to batteries will give a substantial increase in specific energy.

6 Summary

Weight savings of around 6% in the cell components have been identified and tested in modules, without adversely affecting the normal performance parameters. Changes to the positive electrode composition and having a higher utilisation of the theoretical capacity has enabled the nameplate capacity to be increased by approximately 16%. Not all the tested improvements are to be demonstrated in vehicle batteries and the improvement in specific energy will not quite achieve the ambitious programme target of 120Wh/kg. The increase is however expected to be greater than 20% to around 115Wh/kg which translates to a sizeable increase in range for an electric vehicle.

7 References

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