## 7.6 The Sodium Nickel Chloride "Zebra" Battery

### Introduction

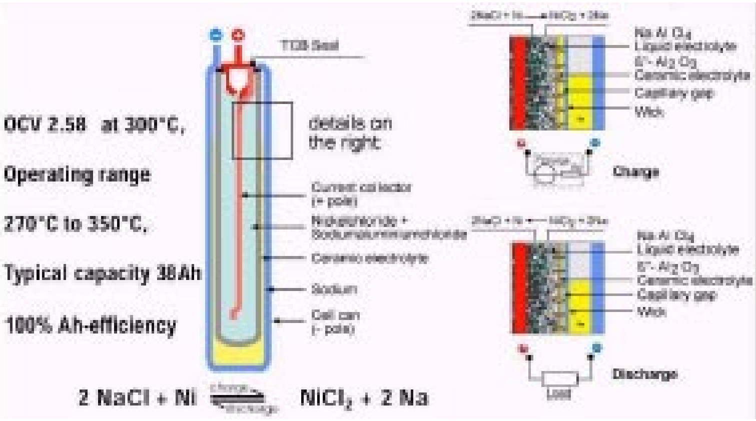
The "ZEBRA" Battery (Zero Emissions Batteries Research Activity) is a Sodium Nickel Chloride battery, manufactured in limited volume in Switzerland for EV applications. It is the only dedicated EV battery in production in the world today.

The technology was first developed in South Africa during the 1970s and 1980s. The major development then took place at AERE Harwell, who then entered joint development with AEG. AEG were later bought by Daimler Benz and then divested.

This technology is only manufactured today by the company MES-DEA GmbH, located in Stabio, Switzerland. MES-DEA bought the rights to the technology from AEG in 1999 after Daimler Benz divested itself of AEG in the late 1990s. MES-DEA built a new $66M factory in 2001 to manufacture the battery. The factory presently has an annual capacity of 30,000 units.

Figure 40 shows the functioning[1] of the Zebra cell.

FIGURE 40 ZEBRA CELL




The β-alumina ceramic electrolyte tube has the cross section of a clover leaf to increase the surface area available for ion transport between anode and cathode.

The finished battery package with control electronics has a specific energy density of 90 - 120Wh/kg (depending on format). Volumetric energy density is 166Wh/l. The theoretical specific energy of a cell is

1. From "ZEBRA Battery - Material Cost, Availability and Recycling", Dr. Galloway, Dr. Dustmann, MES-DEA GmbH, EVS 20, 2003.

790Wh/kg. The battery is robust, potentially inexpensive, available in a number of large EV formats and is a well tested technology. This specific energy density is about the same or better than current generation LiIon battery packs for EVs, available from SAFT or Sony. The Sony 32.4kWh LiIon battery pack in the 1999 Nissan Altra had a specific energy of 89Wh/kg. Existing SAFT LiIon EV modules have a specific energy of 110Wh/kg.

In comparison, the 9kWh LiIon battery provided by Valence Technology for retrofit into the Toyota Prius weighs 250 lbs, i.e. an effective specific energy density of only 80kWh/kg

The Zebra battery will withstand at least 1,000 100% DOD charge/discharge cycles including any type of partial charge/recharge and is also marketed by Rolls-Royce for demanding marine applications, including stand-by power in military submarines and surface vessels. It is an extremely robust and rugged battery capable of being used in demanding and harsh environments.

On rapid recharge, the Zebra battery can be 80% recharged in 75 minutes.

BMW used an earlier related technology (Sodium Sulphur) on their prototype E2 electric car in the early 1990s. Sodium Sulphur technology was developed by Ford in the 1960s and discontinued in the 1990s due to corrosion problems. Mercedes Benz announced that they would launch an electric version of the A Class in 1998 equipped with the NaNiCl battery. The Electric A Class would have had a range of 120 miles. The vehicle was not marketed. With the latest generation of Zebra battery, the range of the A Class EV would increase to 180 miles.

## Efficiency Comparison

The major perceived drawback of the Sodium Nickel Chloride battery is that it is a high temperature technology. The battery has to be maintained at an internal operating temperature of between 270˚C and 350˚C for efficient operation. While the battery is being used, this causes no energy penalty since the internal resistance of the Zebra battery coverts resistive losses to heat with 100% efficiency. All batteries have internal resistance and in all batteries, this internally generated heat has to be removed by a cooling system to prevent overheating.

Therefore in the case of the Zebra battery, the heat generated during operation can be used to maintain the temperature.

However, when the vehicle is not in use, the battery will start to cool down. After about 4 hours, external heat has to be applied to maintain the temperature. The battery contains a heater which can be powered by the mains or powered by the battery itself. If the vehicle is left overnight it can be plugged in to both recharge it and to keep the battery hot. If the vehicle is left for more than 4 hours in a location without access to a source of mains power, the onboard DC heater switches on to maintain the temperature.

The key question in relation to other ambient temperature battery technologies is therefore:

- How much more life-cycle electrical energy does the ZEBRA battery use than ambient temperature batteries?

#### The Mendrisio Operating Trial

Between 1995 and the present, the Swiss town of Mendrisio has been operating an EV trial programme. The programme started with Peugeot 106 EVs equipped with a 14kWh NiCad battery pack, supplied by SAFT. The electric motor is a 20kW DC motor.

In 2001, a fleet of Renault Twingo electric cars powered by a 21.2kWh ZEBRA battery started operations. The motor is a 36kW AC induction motor.

The trial has been carried out under the auspices of the Swiss Federal Office of Energy and monitored independently by the local municipal authorities.

An important difference between the two vehicles is that the Peugeot 106s are equipped with a small gasoline heater for the passenger cabin, while the Renault Twingos use a 3kW electric heater powered by the main drive battery.

Operating results from this trial were presented by MES-DEA at the latest Electric Vehicle Symposium[1] in April 2005.

The table below summarises the characteristics of the two vehicles.

**TABLE 15** **MENDRISIO VEHICLE COMPARISON**

| | Peugeot 106 | Renault Twingo |
|---|---|---|
| Gross Vehicle Weight | 1350 kg | 1230 kg |
| Empty Weight | 1050 kg | 980 kg |
| Range at 50 mph | 50 miles | 75 miles |
| Heater | Petrol | 3kW electric |
| Battery | 14kWh NiCad | 21.2kWh |
| Motor | 20kW DC | 36kW AC |
| Avg. Energy Use | 0.41Wh/mile | 0.37Wh/mile |
| Fleet Sample Size | 15 | 5 |
| | | |

Over a two year period, the Peugeot 106 used an average of 25.8kWh of electricity from the mains per 100 km driven, or 0.41Wh/mile. Over a

1. “Mendrisio Operating Results using NiCd and ZEBRA Batteries”, EVS-21, Monaco, 2-6 April 2005

4 year period, the Renault Twingos have used an average of 23.2kWh/ 100km delivered from the mains, or 0.37Wh/mile.

These figures for the Renault Twingos equipped with the ZEBRA battery include use of the battery to heat the car in winter, not a trivial requirement in Switzerland. In fact, the winter consumption averaged 25kWh/100km versus 20kWh/100km in summer. In addition, the Twingos were equipped with winter tyres which increase rolling resistance, while the Peugeot 106s were not. There was no difference between winter and summer energy use by the Peugeot 106s for these same reasons.

With both vehicles, energy use per km decreases as the distance travelled per day increases.

The thermal energy loss of the ZEBRA battery when not in use is about 90W or 2.16kWh per day. However, in normal use the energy loss will be lower than this. Even if the vehicle was left unused with the battery plugged in for an extended period of time, the cost of this electricity to keep the battery at operating temperature would be minimal - less than 20 cents per day in Europe or the USA and would be equivalent to about 5 - 8 miles driving distance per day.

#### Conclusion

In normal everyday use, it does not appear that the ZEBRA Battery will use any more electricity than a NiCad system. There is so much variation in daily driving habits that the extra energy required to keep the ZEBRA battery hot does not appear to make much difference to overall energy efficiency.

The ZEBRA may in fact be superior to NiCad, since it has demonstrated slightly higher efficiency while also supplying cabin heat in winter and having higher resistance winter tyres.

## Cost Potential of the Zebra Battery

MES-DEA believe that the selling price of the ZEBRA battery would be $240/kWh in low volume production (10,000 units). At 100,000 units per year it is projected that the price would fall to $109/kWh.

In 2003, MES-DEA published a cost analysis[1] to justify these forecasts. The production cost breakdown of the ZEBRA battery is shown below.

1. ZEBRA Battery - Material Cost Availability and Recycling, RC Galloway, C-H Dustmann, EVS 20, Nov. 15 - 19 2003, Long Beach, CA.

**TABLE 16**

**ZEBRA BATTERY COST PROJECTION**

| | $/kWh | $/ Battery (21.2kWh) |
|---|---|---|
| Nickel | 17.75 | 376.30 |
| Other Internal Materials | 10.53 | 223.24 |
| Battery Case | 9.37 | 198.65 |
| Cell Manufacture | 13.82 | 292.98 |
| Case Manufacture | 9.37 | 198.65 |
| Controller | - | 250 |
| **TOTAL** | | **$1540** |

The total production cost is estimated at $1,540 or $73/kWh. MES-DEA assumed that the production cost would be 2/3rds of the selling price, giving an end user price of $109/kWh.

The most expensive item in the ZEBRA battery is the Nickel metal used in the cathode. MES-DEA state that the NaNiCl technology makes much more efficient use of Nickel than NiMH or NiCd: 1.53kg of Ni is used per kWh of stored electricity compared to 6.8kg/kWh for NiMH and 3.5kg/kWh for NiCd. This is partly because the potential of the NaNiCl cell is 2.58V, more than twice the 1.2V of other Nickel systems.

Argonne National Laboratory estimated[1] in 2000 that the Nickel content per kWh of a LiIon high energy EV battery (using a nickelate $LiNiO_2$ cathode) would be 2.5kg/kWh.

**TABLE 17**

**COMPARATIVE NICKEL USE BY BATTERY**

| Battery | Nickel Use per kWh |
|---|---|
| NaNiCl | 1.53 kg/kWh |
| $LiNiO_2$ | 2.5 kg/kWh |
| NiMH | 6.8 kg/kWh |
| NiCad | 3.5 kg/kWh |
| | |

In practice, future Mixed Oxide cathodes using Mn, Ni and Co for LiIon EV batteries will probably use less Nickel than 2.5kg/kWh but it may still be the second metal in the cathode after Manganese, so it could be present in similar quantities to that used in ZEBRA technology.

1. "Costs of Lithium-Ion Batteries", Linda Gaines, Roy Cuenca, Argonne National Laboratory, May 2000

The current price of Nickel is between $7 and $8 per lb ($17.6/kg), which is $6/kg more than the cost used above in Table 16 by MES-DEA in 2003. This price increase will affect all Nickel based battery technologies[1] but there is no shortage of Nickel resources for increasing production in future if required. Global Nickel production is currently about 1.2M tonnes per annum with many new mines scheduled to open over the next 5 years. Global Nickel production would currently be sufficient to manufacture 37 million 21.2kWh ZEBRA batteries per year.

At current Nickel prices, the cost of the 21.2kWh NaNiCl battery above would increase to US$1,735, i.e. an end user selling price of $123/kWh.

The other main chemicals used in the ZEBRA battery are Iron, common salt (NaCl) and the inert mineral boehmite, a form of alumina. These substances are cheap and available in unlimited quantities. The total material cost is less than $40 per kWh.

The cost of the case is quite significant, since the battery requires good thermal insulation. The case is made of a double walled stainless steel box, containing a vacuum like a Dewar flask to minimise thermal conduction. However, the cost of the case rises at a lower rate than the size of the battery, so larger capacity batteries have a proportionately lower casing cost.

The cost of the controller is also independent of battery size, adding to the economy of scale as battery size increases.

Using MES-DEA’s methodology, a ZEBRA battery with a capacity of 42.4kWh would cost about US$3,640 to produce, based on a Nickel price of $18 per kg. Taking MES-DEA’s assumption that the production cost would be 2/3rds of the selling price, the price of a 42.4kWh ZEBRA battery would therefore be $5,461 or about $130 per kWh.

Even at today’s high Nickel prices, $130/kWh would be far cheaper than any competing battery technology, with the possible exception of Lead Acid.

If Nickel availability or price became an issue, the battery will work almost equally well with Iron instead of or partially replacing the nickel. In this case, the battery becomes a Sodium Iron Chloride battery. The cell potential is slightly lower (2.35V instead of 2.58V) but the operating temperature can be reduced from 300˙C to 250˙C. The cost of the battery could be reduced even further if iron was used instead of nickel. There would of course be no material supply issues at all with a $NaFeCl_2$ battery: practically unlimited quantities of this battery could be manufactured from iron and common salt. In fact, starting in 1998, later versions of the ZEBRA battery already used a 4:1 nickel to iron mix, along with some aluminium to improve overdischarge capability.

1. For comparison with the cost of NiMH batteries, See “Cost Analysis” on page 80.

## Safety

The ZEBRA battery must maintain an internal operating temperature of between 270˙C and 350˙C. In operation, the anode consists of molten sodium. The cathode consists of nickel chloride (or a mixture of nickel chloride and ferrous chloride) combined with molten sodium tetrachloroaluminate ($NaAlCl_4$).

Safety concerns are therefore frequently raised with regard to this technology, particularly since it contains molten sodium metal.

In 1998, the National Renewable Energy Research Laboratory (NREL) published[1] an independent safety study on the Zebra battery.

The report found that “when subjected to extreme external influences simulating vehicle accidents, batteries do not appear likely to add additional significant hazards to occupants or emergency response personnel”. The cells are fail-safe to overcharging or overdischarging and are fabricated without the use of metallic sodium. Failure from exposure to high temperatures results in small hazards and they can be “safely and legally shipped in the cold state”.

The NREL commented that AEG Zebra (as it was then) felt that a breached cell was very unlikely to release sodium, since any trauma capable of breaching the cell would also break the ceramic electrolyte, binding all of the sodium into sodium chloride. No sodium had been released in any safety tests. However, the report did recommend that tests should be undertaken to determine if there were circumstances in which sodium could be released and what the effects would be.

The use of the battery in military and civilian submarines, including its proposal by Rolls Royce for nuclear submarines, indicates that any safety concerns have been satisfactorily resolved.

In March 2005, the UK oil well logging equipment company Sondex bought the rights to advanced Zebra battery technology under development by Beta R&D in the UK. They are using NaNiCl batteries to replace Lithium Ion in downhole equipment - a very harsh operating environment. They see Zebra batteries as being a more robust, reliable and cost effective alternative to LiIon. This also indicates that any reliability or safety issues with the technology have been resolved.

## High Temperature

Being a high temperature battery, the Zebra battery uses 90W of power to maintain its operating temperature if it is not used. The battery is plugged in to the mains to power an onboard mains heater when not in use and has a small onboard DC heater for use where mains power is not available. This requirement to keep the battery hot is not a problem

1. “Current Status of Health and Safety Issues of Sodium Metal Chloride (Zebra) Batteries”, D. Trickett, NREL, WW171000, November 1998.

in fleet utility or public transport operations and would not be a significant cost for private drivers. The battery heats up during operation so external heating only needs to start a few hours after shutdown.

On the other hand, the high temperature of the Zebra battery has the advantage that the poor cold weather performance of ambient temperature batteries, especially LiIon, is avoided. The Electric A Class developed by Mercedes used an oil cooled Zebra battery that could also provide instant cabin heating in winter. The Zebra Battery was found by Mercedes to perform equally well in an outside temperature range from minus 40˚C to +40˚C. Standard LiIon batteries are down to 50% capacity at -20˚C and experience a further sharp drop off in performance below that temperature.

If the battery is not required for an extended period, the heater can be switched off and the battery allowed to solidify. This freezes in the state of charge and no charge is lost while the battery is frozen. Unlike the earlier Sodium Sulphur battery, an unlimited number of freeze-thaw cycles can be performed without damage or loss of capacity. On thawing the full charge that was in the battery at time of freezing becomes available again. Therefore there is no self-discharge during idle periods, unlike NiMH. The battery takes 12 - 15 hours to heat up after it has frozen.

## Recent Developments

In September 2004, MES-DEA started an active commercial programme to convert the Renault Twingo and Smart Car to electric propulsion, equipped with the Zebra battery. These vehicles can be purchased from MES-DEA for about 18,000 euros. The Italian Government provide a 65% subsidy to people who buy an EV, which makes the vehicle an attractive proposition for the Italian market.

The Zebra battery has been selected by Th!nk Nordic for their new Th!nk Public 4 seater EV. The Indian electric car manufacturer Reva have also selected it for their proposed NXG city electric car. A number of US bus manufacturers also offer it as an option for hybrid or pure electric buses. The 3 UK Commercial EV programmes have all selected the Zebra battery.

The city of Lyon in France is operating 5 electric buses (45 passengers), each equipped with 8 Zebra batteries. As of July 2005, the city of Rome in Italy has ordered 36 electric buses equipped with the Zebra battery and has tendered for 400 electric taxis also to be equipped with this battery. Italy is particularly vulnerable to oil supply shortages since 73% of its electricity comes from thermal power stations, the majority of which are oil fired - not coal or natural gas.

## Conclusion

The ZEBRA battery has many advantages:

1. Energy density higher or equal to LiIon
2. Lowest Cost of any modern EV battery technology
3. Available, cheap and plentiful materials
4. Resistant to Overcharge and Overdischarge
5. Fail-safe to cell failure
6. Ruggedness
7. High calendar life
8. Undiminished low temperature performance

Its disadvantages:

1. 12 - 15 hours to thaw out after freezing
2. 90W energy loss while not in use

The battery is therefore finding particular application in public transport and utility operations where it can be put into continuous use and energy losses are minimised. However, the much lower cost of the NaNiCl technology compared to NiMH or LiIon means that for a 20kWh Zebra battery, it would take more than 50 years for the energy losses of the Zebra battery if kept permanently on stand-by to equal the extra cost of the other batteries.