

Out of Africa

the story of the Zebra battery

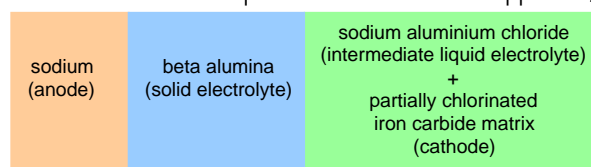
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As the title suggests, the Zebra battery had its origin in Africa. Perhaps a fitting description of the Zebra can be the following: a unique and robust creature that is equally at home in the dry, scorching plains of Central Africa where the temperatures can reach over 40°C in summer, as in the desolate, cold mountains of the Southern Cape where sub-zero temperatures are common during the winter months - and then it has a mighty good kick too!

The Zebra battery, which utilises only freely available and environmentally friendly materials for its functioning, has been highly successful in numerous electric vehicle and related tests conducted throughout Europe over more than a decade.

The Early Work: The early work on Zebra dates back to the mid-seventies when a group of scientists, headed by Johan Coetzer at the C.S.I.R. in Pretoria, South Africa, started investigations on partially chlorinated transition metal carbides and related interstitial hard metal compounds as positive electrodes in high energy density, high temperature secondary batteries. This development took place at a time when the other two leading high temperature systems: sodium sulphur and lithium iron sulphide were enjoying world wide attention. Prominent features of both these cell configurations have played a role in the final formulation of the first Zebra cell as shown in the sequence below.



Operating temperature: 250°C

The anodic half of the cell consists of liquid sodium in contact with the solid ceramic electrolyte, beta-alumina with the unique property of conducting sodium ions whilst acting as a total electronic insulator and electrode separator. This characteristic ensured achievement of 100% coulombic efficiency in a cycling cell.

Dissolution of the electro-chemically active cathode species in the molten salt of the lithium/iron sulphide cell contributed to capacity loss and self discharge in that system. The aim of the Zebra programme was to find an intermediate molten salt electrolyte, compatible with the chlorinated cathode, the beta alumina ceramic and showing no dissolution of the chlorinated transition metal during cell cycling.

Important contributions were made in this regard by Roger Bones and his colleagues at the Harwell Laboratories in the UK who joined the project in 1979. An investigation of the molten double salt $\text{NaCl} \cdot \text{AlCl}_3$ (melting point 155°C) showed that the transition metal chlorides FeCl_2 and NiCl_2 were highly insoluble in the melt as long as the molar ratio of 1:1 is maintained. More importantly, this neutral or basic melt composition was highly compatible with the ceramic electrolyte.

Early experimental cells constructed in the above way showed encouraging rate and reversibility characteristics. Chlorinated iron carbide electrodes achieving cathode utilisation figures of >0.35 Ah/g and >0.35Ah/cc of total metal were cycled for long periods showing good stability. While the sintered carbides and their analogues provided a good electronically conducting substrate for chlorination of the electrode, it was soon clear that this process would be impractical and was subsequently replaced by the more elegant approach, described later, which started from the pure metal itself.

The use of the intermediate molten salt electrolyte has proven to be beneficial in many ways. During the normal discharge reaction of the cell, anodic sodium reacts with the transition metal chloride to form sodium chloride and the pure metal. The open circuit voltage (OCV) for this reaction is 2.35V in the case of iron and 2.58V for nickel at about 250°C. The molten sodium aluminium chloride itself, however, can form a couple with the anode at a much lower OCV of

This reaction will occur when the iron or nickel cathode is fully discharged and the current flow is allowed to continue. It hence acts as an overdischarge buffer and is fully reversible provided overdischarge does not exceed 10% of the full capacity.

The above reaction also occurs in the event of fracture or failure of the ceramic electrolyte. The metallic sodium comes in direct contact with the melt and is rapidly consumed to precipitate a mixture of sodium chloride and aluminium metal. Although the reaction is exothermic, only a small rise in temperature is observed in practice mainly due to the porous matrix structure of the cathode. This process of rapid removal of free sodium when cell rupture occurs can contribute to enhance the safety characteristics of the battery.

A further observation of significance was made when the above reaction occurred after cell failure. During the interaction of the melt with sodium, a low resistance pathway is created between the two electrode current collectors which acts like an internal short circuit and remains stable with further cycling of the cell. This process leads to a consistent low internal resistance value after cell failure. It has the important benefit that full-size batteries can be constructed in the form of a single, series-connected chain of cells to produce high terminal voltages. A single cell failure has no effect on the chain resistance and the overall terminal voltage value is reduced by the equivalent of only one cell.

The Zebra electrochemistry also shows an extremely good tolerance to overcharging. This results from the relatively low utilisation of about 30% of the available metal in the cathode. In the event of overcharging, the molten salt is electrochemically decomposed but no free chlorine gas is produced. Instead, more of the unused iron or nickel from the cathode matrix is converted into the metal chloride.

These most encouraging early results combined with the simple nature of the chemistry provided a sound foundation

and the necessary driving force to take the Zebra concept to the next level of development.

Formation of Beta R&D Ltd.: The beta alumina tubes used for the development of the ZEBRA cell had been supplied by a team who were developing the sodium sulphur battery at the British Rail Technical Centre in Derby. In January 1981, this programme was terminated and three members of the team: Jim Sudworth, Roger Tilley and Hamish Duncan led a management buy-out and formed Beta R&D Ltd. The new company began operating in January 1982. The company negotiated a contract with the Anglo American Corporation to develop the ZEBRA battery to the point of demonstration in an electric vehicle over an 18 month period. It was then that AAC disclosed that the new ZEBRA battery was based upon a sodium iron chloride cell in which the positive electrode was made by passing chlorine gas over iron carbide, and that the largest cell that had been made had just 5Ah of capacity. It was immediately obvious that this was not a viable manufacturing route and the chlorine was replaced by hydrogen chloride and the iron carbide by sintered carbonyl iron powder. In parallel with this work on iron, Roy Galloway was investigating the use of other transition metals as the positive electrode. Nickel which had the advantage of a higher open circuit voltage and only one valence state, looked very attractive, but could not easily be chlorinated. It was then that the first breakthrough in the search for a viable manufacturing route was made. Roy Galloway found that contrary to all expectations, a mixture of sodium chloride and nickel powder, when sintered at 800°C in hydrogen, gave an electrochemically active

electrode. This in effect meant that the cell was assembled fully discharged with the additional advantage that no sodium metal was needed, merely a conducting wick which would keep the electrochemically generated sodium in contact with the beta alumina tube. A metal shim wick made up of four interlocking segments of 0.1mm thick mild steel was developed by Mike Wright which together with a carbon based coating on the ceramic tube gave a sodium electrode capable of sustaining the highest discharge rates needed. One problem which was encountered was that part of the sodium metal generated on charge became trapped and inaccessible for electrochemical reaction, but this problem was solved by Johan Coetzer and Roger Wedlake who suggested the addition of aluminium metal to the positive electrode. This reacted with sodium chloride on charge generating sodium metal and sodium tetrachloroaluminate. This was not practical with a sintered electrode, but Mike Wright discovered that just mixing the metal powders with sodium chloride powder resulted in an electrochemically active system. This made it very convenient to incorporate the various additives which were developed to control capacity loss and resistance rise. Thus it was discovered that the sulphur needed for control of capacity loss could easily be incorporated as iron sulphide. The only disadvantage of this powder electrode was the tendency of the sodium chloride and the metal powders, which had a much higher density, to segregate during manufacture. This was overcome by Mike Wright who showed that by granulating the powders, the composition of each granule was identical and no further segregation recurred. This granule electrode could be used for both iron and nickel cells and for a time

The other potentially high cost component in the cell was the beta alumina solid electrolyte which was made from high purity aluminium oxide and required a complicated sintering process to control the grain size of the ceramic. Hamish Duncan suggested that if the starting material was boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) the conversion to beta alumina would be easier. This proved to be the case but the material didn't sinter to full density. Peter Barrow showed that the mixture of defect alumina (γ and δ) formed by dehydrating boehmite would be a better starting material. Using the boehmite route, a simple one peak firing method could be used. This is particularly important for large scale production as the previous two peak firing process could not be used in the tunnel kilns needed for mass production. Another advantage of this route was that the boehmite was relatively pure and considerably lower cost than the alumina used previously.

When compared with other nickel batteries such as nickel cadmium and nickel metal hydride the quantity of nickel used in the ZEBRA battery is very low. Thus for each kilowatt-hour of stored energy the ZEBRA battery contains one third the quantity of the nickel of the nickel metal hydride battery. Thus in large scale production when the dominant costs will be material costs, the ZEBRA battery will have a significant cost advantage over other nickel batteries.

Another important factor in cost is the lifetime of the battery measured in nameplate cycles. The ZEBRA cell has been shown to have an excellent lifetime - some modules have now exceeded 2,500 nameplate cycles and are still delivering their nameplate capacity (Figure 1). A 7kWh battery has completed 1600 nameplate cycles, equivalent to 3000 vehicle cycles (Figure 2)

The early cells which had mechanical seals utilising aluminium and graphite gaskets were contained in a double skinned battery box with evacuated thermal insulation. The end of the battery box was a plug of conventional insulation which could be removed to allow maintenance of the cell pack because at this stage in the development the reliability of the cells was poor.

Formation of AEG Anglo Batteries: In 1989 Anglo American Corporation formed this joint venture company with AEG with

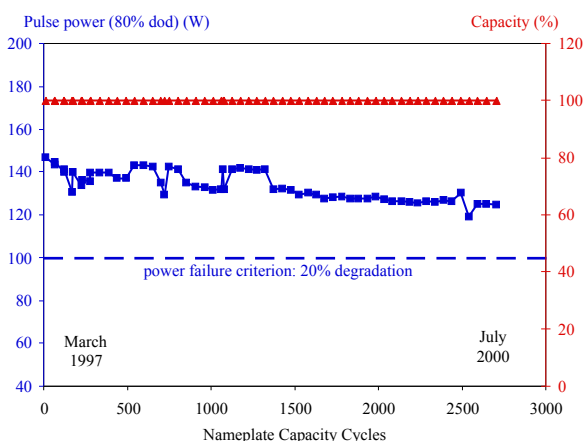


Figure 1. Life of Zebra cells

both cells were being developed. The iron cell had the advantage of low cost but the nickel cell was more stable and gave higher specific power. It was decided to concentrate development on the nickel cell and this determined the design of the cell with the positive electrode inside the beta alumina tube, as otherwise a nickel cell case would be needed and this would be much too expensive.

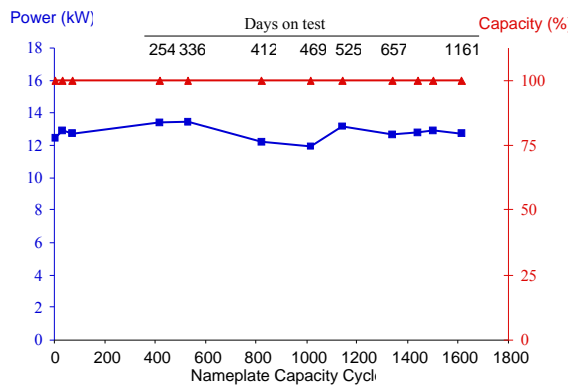


Figure 2. Life of Zebra batteries

the aim of industrialising the ZEBRA battery. At that time AEG was being absorbed into Daimler Benz who evaluated the battery for electric vehicle applications. The DB team led by Dieter Sahn suggested a re-designed cell with a higher power to energy ratio than the 100Ah cell then being used. This led to a smaller diameter and lower capacity (30Ah) cell which became known as the slimline cell. This cell had a new thermocompression bond seal in which nickel components were diffusion bonded to a metallised alpha alumina collar. Through AEG's input on quality control the reliability of the glass seal between the beta alumina and this alpha alumina component was increased dramatically and this, together with the new hermetic seal, allowed the re-design of the battery box as a totally sealed unit. This rugged construction conferred a high degree of safety on the battery and enabled it to pass all the safety tests devised by the European car companies. During this testing the battery was shown to be able to survive 30% overcharge as well as the normal crash tests.

In 1991 AAB set up a pilot line to produce batteries for market development. The ceramic sub assembly - a beta alumina tube sealed to an alpha alumina collar to which two nickel rings had been diffusion bonded - was produced in Derby together with the positive electrode granules and the sodium chloroaluminate liquid electrolyte. The cells were produced on an automatic transfer line in an AEG factory in Berlin and the batteries were built in an AEG factory in Ulm in Southern Germany.

The first cells made in the pilot line were the slimline cells described above but in parallel with the development of a properly engineered battery a major research programme was underway to increase the power to energy ratio of the cell. This led

to the development by Johan Coetzer and Tony Meintjes of a cell with a convoluted beta alumina tube which both increased the surface area and reduced the thickness of the positive electrode. This became known as the monolith cell. The challenge here was to produce this complex ceramic shape by isostatic pressing and firing in a gas powered kiln. In 1995 the plant

in Derby was extended by installing equipment to produce the new monolith ceramic. This meant installing an automatic dry bag press and a three cubic metre capacity gas fired top hat kiln. In addition continuous furnaces were installed to replace the batch furnaces used to produce the thermocompression bond seals, to calcine the beta alumina tubes and to form the sub assembly by glass sealing the tube to the alpha alumina collar. Almost all of the handling of the ceramic parts was automated. In Berlin it was necessary to change the station where the metal shims were fixed to the beta alumina tube as the shims had to be redesigned to fit the new convoluted shape.

The peak power available from the monolith cell at deep depths of discharge was increased by substituting some of the nickel with iron. This effectively results in an iron cell in parallel with the nickel cell which is normally fully charged by the nickel cell but which discharges when the cell voltage is pulled down below the iron potential of 2.35 volts. This means that the pulse power is almost independent of state of charge. A second improvement in power was obtained by the use of a composite copper cored current collector. The net result was to increase the pulse power of the cell to 200 W/kg. The improvements in specific power and energy are shown in Figure 3.

In the next ten years several battery types were developed in addition to the basic air cooled 17.5kWh battery (Z5): four liquid cooled 30kWh batteries Z8 and Z11 for BMW and Z7 and Z12 for Mercedes Benz. The Z12 battery was developed for the A class Mercedes and a small fleet of sixteen

cars was built, most of which are still in service. During this period the long life and high reliability of the ZEBRA battery was demonstrated. Several batteries exceeded five years life and 100,000 kilometres without any maintenance to the battery. This was partly due to the development of a sophisticated battery management system which because of the 100% coulombic efficiency of the ZEBRA battery was capable of keeping the cells within safe limits of charge and discharge. It also gave an accurate measure of the state of charge, which in the A class Mercedes was converted into a display of the remaining range available. Extensive use of ZEBRA powered vehicles has shown that the fact that the battery operates at an elevated temperature is an advantage rather than a disadvantage. The vehicle is independent of ambient temperature and operates hap-

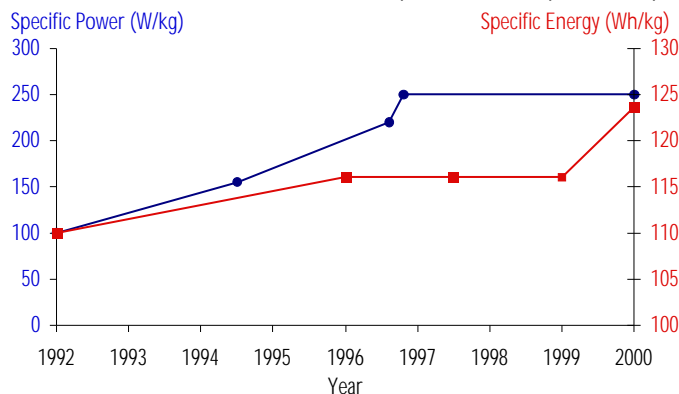


Figure 3. Cell Specific Power and Energy Improvements

pyly in southern California or the Arctic circle (Figures 4 and 5). The heat capacity of the battery can be used for cab heating. By extending the operating temperature range in winter down to 250°C cab heating can be provided in the severest climates for the whole of the discharge.

By 1998 AAB had taken the development of the ZEBRA battery to the point where it was ready to be put into production. The pilot lines in Derby and Berlin were producing batteries at the rate of up to twenty per month, the electric vehicles were performing very well and the customers were pressing for a commitment for volume production. At that time however, the two parent companies of AAB were redirecting their strategies away from peripheral activities and towards their core businesses. For a time it looked as though the project would be terminated but in early 1999 the whole of the ZEBRA battery business was sold to the company MES-DEA located in Stabio in southern Switzerland.

Renaissance of the ZEBRA Battery:

Carlo Bianco the owner of MES, a major supplier of components for the automotive market, had established MES-DEA to produce components such as motors, drive systems and brake systems for electric vehicles and had purchased several ZEBRA batteries for powering prototype electric vehicles. When the opportunity arose to purchase the ZEBRA battery technology he decided to build a new plant for the volume production of ZEBRA batteries in Stabio. The first phase of the building, which is almost complete, has 18000 m² of floor space (Figure 6). Production capacity in 2001 will be 2,000 batteries per year but the building is designed to produce 33,000 batteries per year and sufficient ceramic powder for 100,000 batteries per year. Phases two and three which would each add a production capacity of 33,000 batteries per year can be accommodated on the same site by extending the present building.

The cell assembly line in Berlin and the battery assembly line in Ulm were both transferred to an existing building in Stabio in May this year and are now producing batteries. The ceramic pilot line in Derby which produces the ceramic sub assembly, will be transferred in stages over the next two years, starting in January 2001 when the new building is ready. The purchase of a new multi cavity isostatic press, a nine cubic metre capacity shuttle kiln and a cutting and grinding station will bring the capacity of this ceramics plant up to the planned 2,000 batteries per year.

The MES expertise in volume production has been applied to both the cell and battery and significant cost and weight reductions have already been achieved. The new lightweight battery box design combined with an increase of 6% in the nameplate capacity of the cell has resulted in an increase in specific energy to 100Wh/kg. It is expected that in the near future the



Figure 4. Mercedes 'A'-class electric vehicle in Southern California

acknowledgments to Daimler Chrysler



Figure 5. Mercedes 'A'-class electric vehicle in the Arctic

acknowledgments to Daimler Chrysler

nameplate capacity of the cell will be increased by 13% to give a specific energy for the battery of 110Wh/kg.

When the new factory starts production in 2001, ZEBRA batteries will be available at an excellent price/performance ratio.

Three basic cell designs can be specified to produce batteries with heights of 210mm 264mm and 300mm suitable for installation in a wide range of electric vehicles. The battery management system has been integrated with the interface box into the BMI the battery management interface.

These basic batteries can be connected in

parallel with a multiple battery server to produce 544Ah battery systems operating up to 557V or 1088Ah at 278V. Around 200 vehicles from electric cars through vans to buses have covered several million miles in total. Some of these vehicles are pure battery vehicles but many of the buses are diesel battery hybrids with a battery range sufficient for operation in the city centre. The ZEBRA battery is an environmentally friendly power source available today for commercial fleets and soon to be available in volume production at a very competitive price.



Figure 6. ZEBRA battery production plant (Phase I) under construction