

Zebra batteries

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(Received July 19, 1994; accepted July 21, 1994)

Abstract

By using molten sodium chloroaluminate as secondary electrolyte, a series of solid transition metal chlorides can be used as positive electrodes in cells with sodium as the negative and beta-alumina as the solid electrolyte. Nickel chloride is preferred and Zebra batteries based on this cell reaction have been developed to the pilot-line production stage. The batteries have a number of features which make them attractive for electric-vehicle applications. Thus, the cells can be assembled in the discharged state eliminating the need to handle liquid sodium. By locating the positive electrode inside the beta-alumina tube, square cell cases can be used giving maximum packing efficiency in batteries. The absence of corrosion in the cell leads to a long life and high reliability. For electric-vehicle applications safety is very important, and crash testing has shown that even serious damage to the battery in a crash situation would not present a significant additional hazard to the driver or passengers. The remaining technical challenges are to increase the specific power of the battery towards the end of discharge and to demonstrate that the processes, which have been developed for cell and battery production, are capable of meeting the cost targets.

Introduction

The term Zebra battery is used to describe a new class of secondary cells based upon the reaction between sodium metal and a transition metal chloride, typically nickel chloride [1, 2]. A beta-alumina solid electrolyte separates the anode and the cathode, and a liquid electrolyte, sodium tetrachloroaluminate, is necessary to mediate the transfer of sodium ions from the beta-alumina to the solid metal chloride. The cell operates in the range 250–350 °C, well above the melting point of the liquid electrolyte (157 °C) and in the region where beta-alumina is conductive enough to allow high power drains. The product of reactions is the metal plus sodium chloride.

Following demonstration of the first cells by Coetzer in 1978 at the CSIR in Pretoria, the Anglo-American Corporation of South Africa became involved, and the development of batteries capable of powering electric vehicles proceeded rapidly at Harwell and at Beta Research and Development Limited in the UK. Latterly, the Daimler-Benz group in Germany has become involved and together with the Anglo-American Corporation of South Africa, a joint venture company AEG Anglo Batteries has been formed to commercialize the battery.

Operating principles

Several of the first row transition metal chlorides offer attractive voltages versus sodium in the cell arrangement:

Na/beta-alumina/NaAlCl₄/MCl

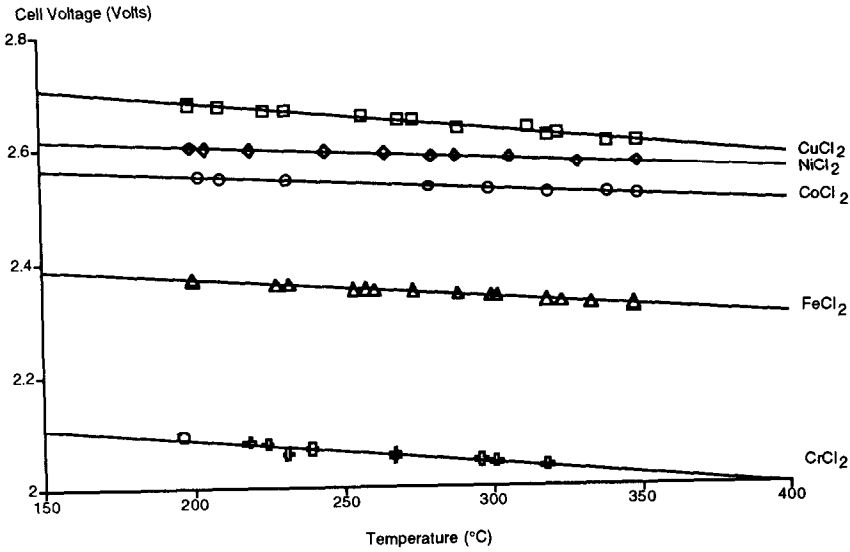


Fig. 1. Variation of e.m.f. with temperature for Zebra cells.

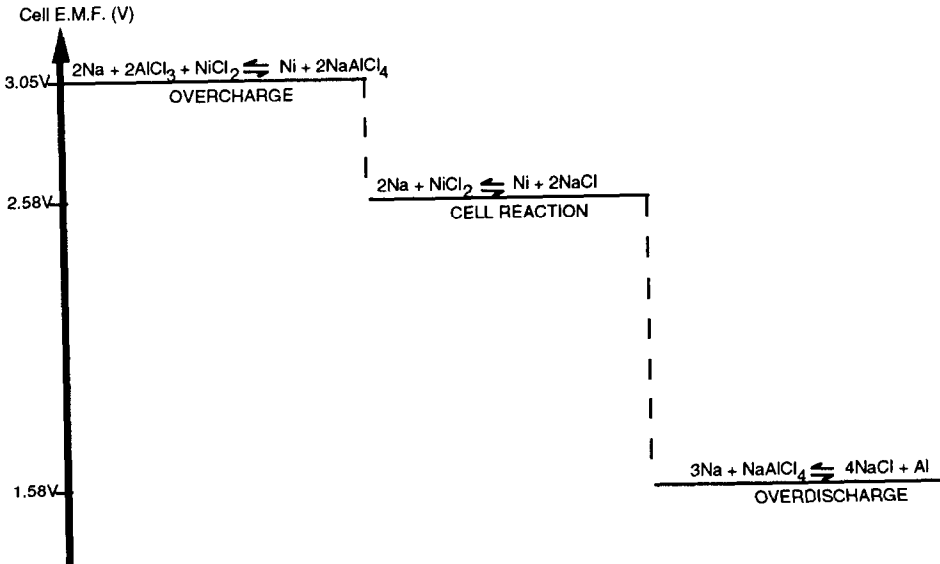
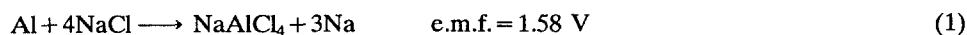


Fig. 2. Cell reactions.

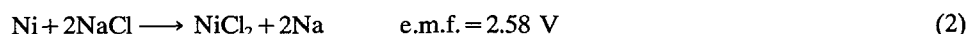
and Fig. 1 shows the experimentally determined variations of open-circuit voltage (OCV) versus temperature for a number of these. Both FeCl₂ and NiCl₂ have been extensively developed as electrode materials. FeCl₂ which gives an OCV of 2.35 V has the advantage of low cost but the cell chemistry is rather more complex [3-5].

NiCl_2 has the advantage of a higher OCV (2.58 V), which for a given internal resistance leads to higher maximum power and for this reason has been favoured for car application with its high power demand.

The cell reaction is shown in Fig. 2 from which it can be seen that overdischarge and overcharge reactions are possible. Use is made of the overdischarge reaction to allow the assembly of the cell without the addition of elemental sodium [6, 7]. A small quantity of aluminium which, on the first charge generates enough excess sodium to prime the sodium electrode, is added to the products of the discharge reaction – nickel and sodium chloride.



The main cell reaction involves chlorination of high surface area nickel powder with sodium chloride to form the nickel chloride positive electrode and sodium:



Sufficient sodium chloride is added to chlorinate more than 30% of the nickel, after which the overcharge reaction occurs in which sodium chloride is abstracted from NaAlCl_4 to give an AlCl_3 -rich melt.

Current status

Cell design and battery configuration

The cell design is shown schematically in Fig. 3. Two nickel components are sealed to a metallized alpha-alumina collar by thermocompression bonding [8]; the beta-alumina tube is then attached to the alumina collar by a glass seal. This subassembly can then be welded to the prismatic metal can. A metal wick inserted in the steel can, before the subassembly is welded in place, acts as the cathode for sodium deposition when the cell is charged.

The positive electrode is added as a mixture of nickel powder, salt and aluminium powder, and after addition of the molten sodium chloroaluminate the cell is sealed by welding on the positive terminal.

Every cell is tested by charging and discharging before assembly into a battery. This is done coulombmetrically so that all cells have the same capacity within $\pm 0.5\%$. The criteria for acceptance are: top-of-charge voltage; discharge resistance, and bottom of discharge voltage. The reproducibility of the cells is shown in Fig. 4 where the distribution of top-of-charge voltage is plotted.

The accurate control of capacity combined with the shape of the discharge curve (Fig. 5) gives protection against cells being driven negative in batteries. This can be understood by considering the effects of one cell failure in a series/parallel-connected battery. The lower voltage plateaux in Fig. 5, which probably correspond to reactions involving sulfur (added in small quantities to the positive electrode to stabilize the capacity [9]), cover several Ah of capacity. Thus, in a series-connected chain which continues to discharge, owing to circulating currents arising from imbalance, all the cells will discharge on to the lower voltage plateaux and the current will attenuate to zero, thus preventing the cells being driven negative and subsequently failing [10].

Batteries can operate with many failed cells because such cells have a resistance comparable to operating cells. For this reason, long series chains can be used in battery construction. Typical connection schemes are shown in Fig. 6, both of which have been used in batteries supplied to customers. The Z5 battery is one of a pair

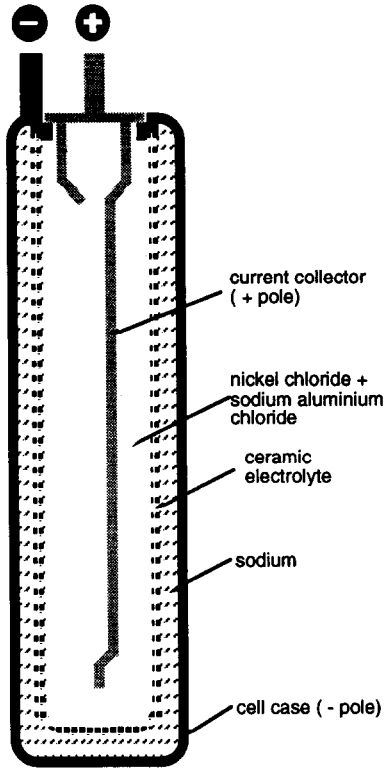


Fig. 3. Schematic diagram of a Zebra cell.

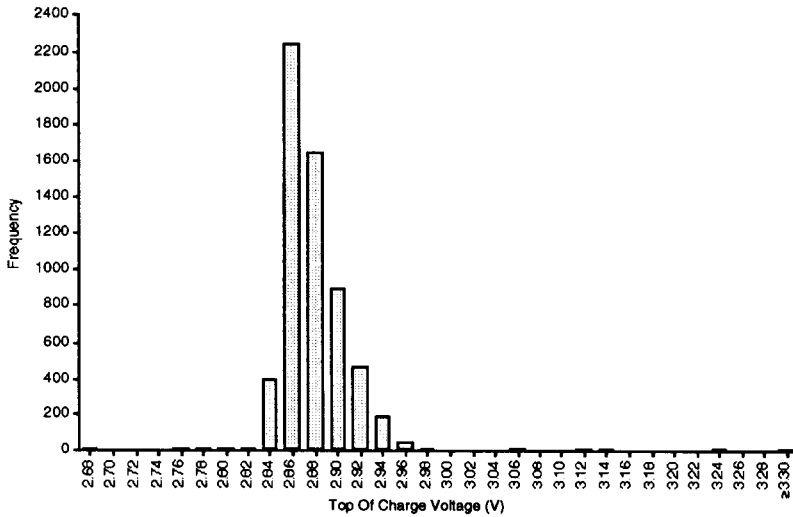


Fig. 4. Cell reproducibility: distribution of top-of-charge voltage.

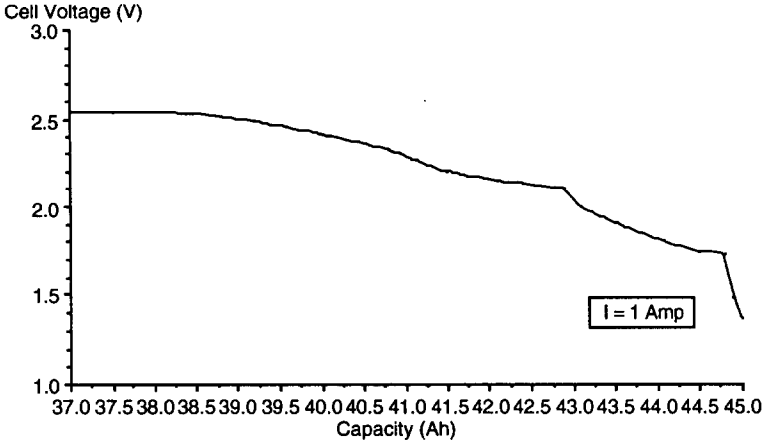


Fig. 5. Shape of end of discharge curve.

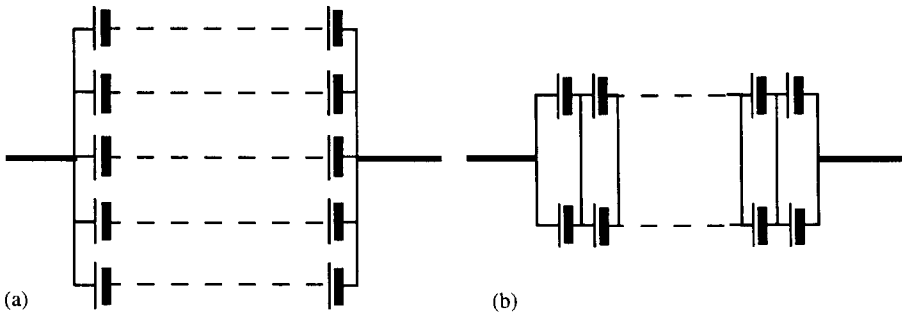


Fig. 6. Typical cell connection schemes: (a) Z5 battery, nameplate: capacity: 150 Ah, OCV: 113.5 V; (b) Z5 battery, nameplate: capacity: 30 Ah, OCV: 567.6 V.

of batteries installed in each of the Mercedes-Benz 190 cars which are operating on the island of Rügen, in Germany.

Battery design

In common with other high temperature batteries, it is necessary to insulate thermally the battery to minimize heat loss. This is achieved by the use of a double-skinned stainless-steel box in which 20–30 mm of insulation board is sandwiched between the two skins. Evacuation of this insulation ensures a low heat loss, and it has been shown that this vacuum is maintained for several years.

Because the positive electrode is contained inside the beta-alumina tube, it is possible to use a cell case of square cross section. This gives maximum packing efficiency and battery sizes can be changed in increments of 37 mm (cell width plus insulation) to meet customers' requirements. The battery is heated to the operating temperature by means of resistance heaters, and these are also used to maintain the battery at the minimum operating temperature. A cooling system is provided for high-rate discharge, and air or a liquid which is stable to temperatures up to 400 °C can be used.

Heating and cooling are automatically controlled by a microprocessor-based battery controller, which has the following functions: (i) control of battery temperature; (ii) charge control and integration for state-of-charge display; (iii) electrical insulation resistance monitoring; (iv) voltage control, and (v) fault detection and recording.

Battery characteristics

Specific energy and power

The specific energy of a Zebra battery suitable for powering electric cars approaches 100 Wh/kg and 160 Wh/l, a value which is high enough to meet the required daily range of a city car.

The specific power is typically around 150 W/kg and 250 W/l for a fully charged battery. Due to an increase in internal resistance during discharge, this power decreases. The capacity of the battery is virtually independent of discharge rate, as shown in Fig. 7 for a ten-cell module.

Life and reliability

A life of a least five years and 1000 cycles is required for electric-vehicle applications and the Zebra battery has the potential to meet this. To date, no wear-out mechanisms have been identified: significant corrosion does not occur and after 1000 cycles the battery capacity is still greater than 80% of the nameplate capacity. The longest lived battery is a 450 V, 13.5 kWh battery which was put on test in June 1991. The capacity and resistance are shown as a function of cycles in Fig. 8. The battery was fully discharged each cycle and charged at 2.5 kW (equivalent to the power of an on-board charger). No cell failures have occurred and the battery is still on test. Other batteries have been tested in electric cars and the test data are given in Table 1. The performance of these converted Mercedes-Benz 190 cars is shown in Fig. 9.

Safety and ruggedness

Zebra batteries have been subjected to a series of tests to demonstrate their ruggedness and safety. These include overcharge, short-circuit overheating, vibration and shock. Drop testing to simulate the effect of a severe road accident is an important

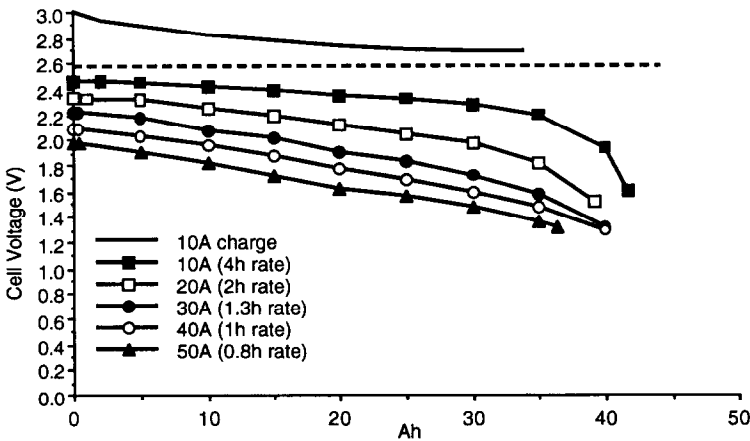


Fig. 7. Discharge performance at various rates.

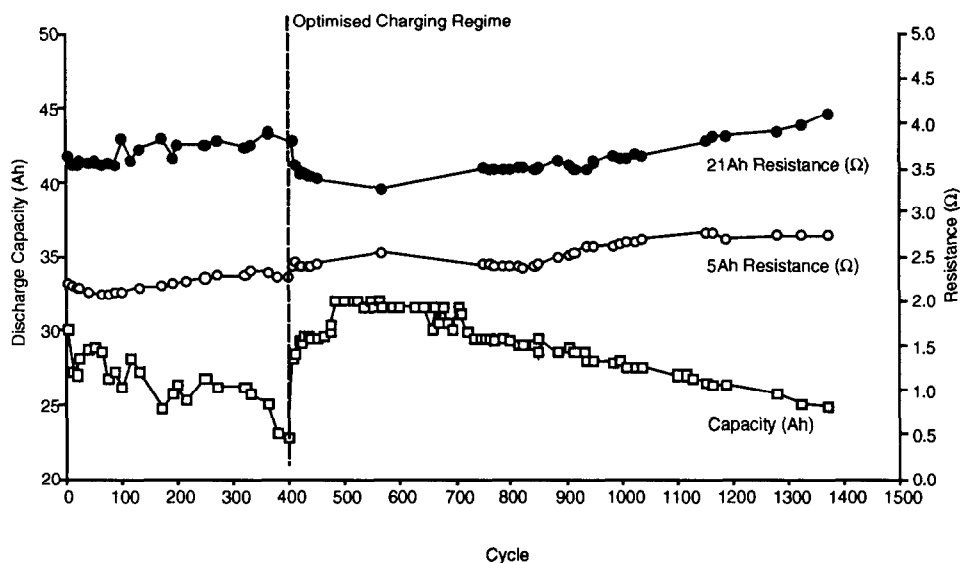


Fig. 8. Capacity and resistance vs. cycles for a 450 V, 13.5 kWh battery.

TABLE 1

Mercedes-Benz battery tests

Battery no.	A16	A19	A26	A44
Battery installed	26.07.1991	27.09.1991	28.01.1992	03.07.1992
Charge (Ah)	97847	78226	161095	63630
Nameplate cycles	544	435	895	354
Battery km	46798	33611	76934	26264
Lifetime (days)	1046	983	860	704
Number of failed cells	35	1	0	0
String 1	10	1	0	0
String 2	6	0	0	0
String 3	5	0	0	0
String 4	5	0	0	0
String 5	4	0	0	0
String 6	5	0	0	0

feature of the battery qualification procedure, and two types of test are used. The first test is to drop hot and fully charged batteries on to a one metre length of 'Armco' crash barrier standing upright, Fig. 10. This penetrates into the battery to a depth of two-thirds of its width. Some white smoke is emitted from the battery, and the internal temperature increases locally. The external temperature only increases noticeably in the region of the penetration. In the second test, a battery is dropped on to a semi-cylindrical steel body resulting in considerable distortion of the battery box. In both tests the terminal velocity is 50 km/h and in neither test has anything leaked out of the battery. These tests showed that there would be no danger to the driver or passengers even in a serious accident.

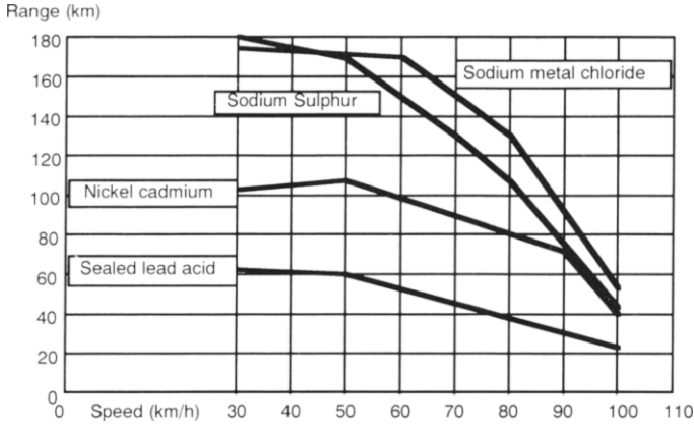


Fig. 9. Performance of Mercedes-Benz cars.

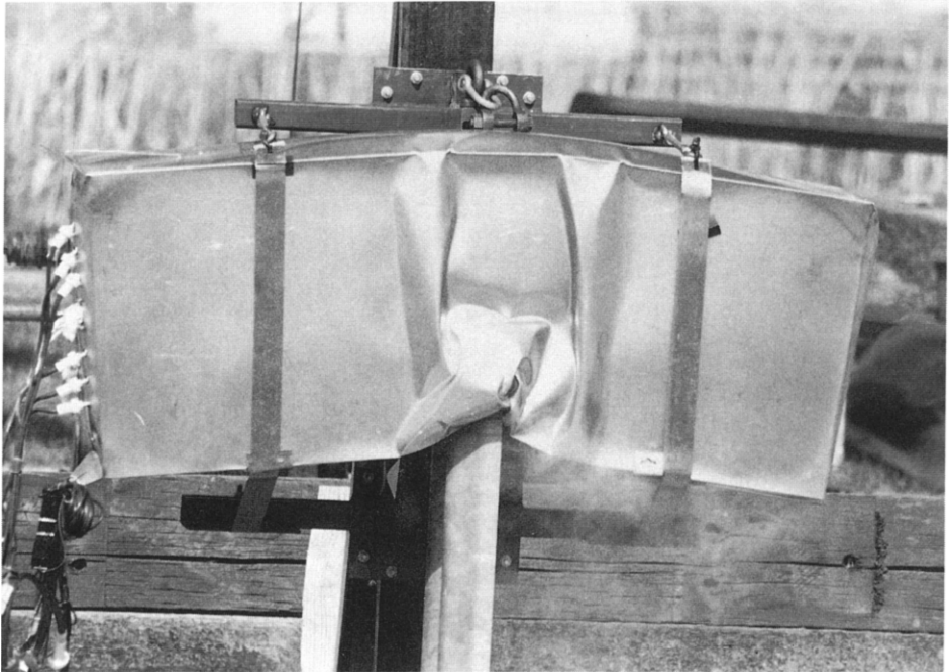


Fig. 10. Battery safety drop test.

A high-temperature battery must be capable of many freeze/thaw cycles as these will undoubtedly occur during the life of the battery from a variety of causes. At the present time all cells undergo four such cycles before they become operational, and several batteries have been cooled down and reheated in operation without any cell failures occurring. These tests have been done at different states-of-charge and this does not appear to be an important factor.

Technical challenges

These are twofold: (i) to increase the specific power of the battery towards the end of the discharge and (ii) to demonstrate in the pilot phase that the processes, which have been developed for cell and battery production, are capable of meeting the cost targets.

The increase in internal resistance, which occurs during discharge, is the result of the way in which the positive electrode operates — a reaction front moves through the electrode starting at the beta-alumina interface on both charge and discharge [11]. This results in the ionic path through the melt getting longer and the ohmic resistance increasing. There are several ways of changing the cell geometry to reduce the electrode thickness. One possibility is to reverse the cell configuration, putting the positive electrode outside the beta-alumina tube. This is something which has been considered, however, even if this was a satisfactory technical solution, it would mean re-establishing the life and reliability data which have already been demonstrated for the central positive cell design. Other changes to cell design which retain the central positive configuration are being evaluated and show promise of being able to increase the specific power by up to 50% at 80% depth-of-discharge. The challenge is to adapt the cell production processes in a way which is cost effective.

The demonstration of the processes at pilot-plant level has begun and the areas where further development is required are summarized below.

The positive electrode powder is prepared by conventional means and the plant installed in the pilot line is capable of producing enough material for 2000 batteries per annum if run continuously. Scale-up to a rate of 15 000 batteries per annum can be achieved by using a larger version of the same equipment. This is commercially available.

The sodium chloroaluminate melt is presently made in 300-kg batches but for a large-scale production it could probably be procured from a chemical company, some of whom already manufacture it in ton quantities.

The production of the ceramic electrolyte starts with boehmite (aluminium oxide monohydrate) and sodium and lithium compounds as the raw materials, and these are converted to beta⁺-alumina powder by conventional ceramic processes such as calcination, milling and spray drying. The resultant powder is formed using an automatic dry bag press and the green tubes are sintered in a continuous firing process on an automatic line. The thermocompression-bonding process is operating at a high yield but our aim is to increase this to a level where it will not be necessary to check every seal for leak tightness. Both the glass sealing process and the thermocompression-bonding processes require automating. Although yields at each stage are quite high, further improvements are necessary as the cumulative yield for the whole process, which is of course the product of the yields at each stage, is still too low.

The assembly of the cell takes place on an automated transfer line. Laser welding is used throughout which requires tight tolerances for all components including the ceramic subassembly. To meet these tolerances at an acceptable cost is a major challenge. The indications are, from the limited operation to date, that this can be met.

Final assembly of the cells into a battery is possible once their performance has been checked by charging and discharging each cell. The use of sophisticated process control on the assembly line will be essential if this time-consuming step is to be eliminated. This will be the next step once the line is operating at the required level.

The making of the cell interconnections in this battery and the fabrication of the battery box is achieved by use of a robot welder. Further optimization of this welding process is continuing.

Commercial impact

Two distinct markets have been identified for the Zebra battery: industrial traction and automotive applications.

The advantages of this battery for the industrial traction market are: zero maintenance with corresponding high reliability, and increased specific energy allowing two-shift operation. A field trial in which a 50 kWh battery was installed in a fork-lift truck demonstrated those advantages over a period of one year. A similar application is for a free-roving mining vehicle one of which, equipped with two 17 kWh Zebra batteries, is at present undergoing trials with British Coal.

Although industrial traction represents a substantial market, the automotive market is potentially much larger. The California initiative in the USA has opened up the possibility of a market for electric cars and the Zebra battery has been identified as one of the candidate technologies by the California Air Resources Board. We now have over five years experience of testing Zebra batteries in electric vehicles, and several car companies are designing electric vehicles with power trains based on the Zebra battery. A government-sponsored trial has been in progress on the island of Rugen, in Germany, for more than one year, and Zebra battery powered vehicles currently outnumber all other types.

The Zebra battery will face severe competition, not least from the advanced ambient temperature batteries, but we believe that its unique combination of characteristics will guarantee it a significant share of what should be a very large market in battery terms.

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