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Electric Fuel™ Zinc-Air Battery Regeneration Technology

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Electric Fuel™

Electric Fuel™ Zinc-Air Battery Regeneration Technology

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Introduction

The Electric Fuel Limited (EFL) zinc-air refuelable battery system is currently being tested in a number of electric vehicle (EV) demonstration projects, the largest of which is the 64-vehicle, two-year test sponsored chiefly by Deutsche Post AG (the German Post Corporation).

The EFL zinc-air battery system for electric vehicles comprises three linked system elements:

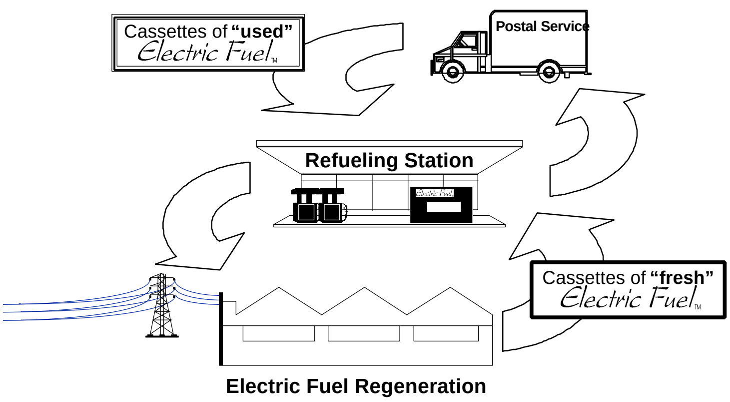
1. the on-board discharge-only zinc-air battery pack, which today is characterized by specific energy of more than 200 Wh/kg and specific peak power of 100 W/kg at 80% DOD (the specific peak power is projected to rise to more than 150 W/kg by 1998);

2. refueling stations for mechanical exchange of zinc anodes; and

3. zinc anode regeneration centers for centralized recycling of the zinc anodes.

The system elements are shown schematically in Fig. 1.

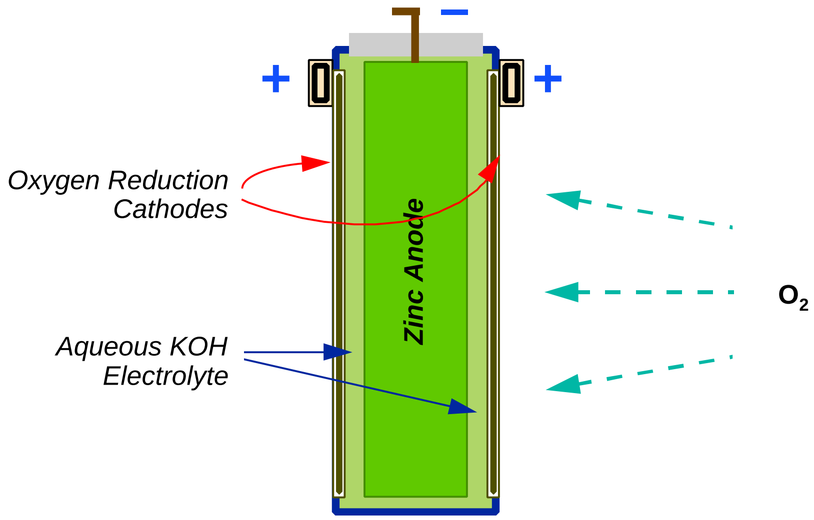
Figure 1. Schematic of Electric Fuel System Operation



This system has been the subject of various papers (1-6).

The cell comprises a central static replaceable anode bed of "Electric Fuel" which is a slurry of electrochemically generated zinc particles in a potassium hydroxide solution compacted onto a current collection frame and inserted into a separator envelope, flanked on two sides by the company's high-power air (oxygen) reduction cathodes. Cell capacity to 80% zinc utilization is 250 ampere hours in this design. The basic EFL zinc-air cell is shown schematically in Fig. 2.

Figure 2. Schematic diagram of EFL zinc-air cell



The EV batteries are built from 6.25 kWh blocks of 22 cells connected in series, with the blocks connected in suitable series and parallel arrangements according to the requirements of the vehicle, motor and controller. The battery contains subsystems for air provision and heat management. As configured for a Mercedes-Benz MB410 4.6-ton Deutsche Post vehicle (>1.5 tons payload), the battery comprises 24 blocks with a deliverable energy content of over 150 kWh, and weight (exclusive of presently unoptimized supporting trays) of 800 kg.

During cell discharge, zinc at the anode is consumed by conversion to zinc oxide, and at the cathode, oxygen from the air is electrochemically reduced to hydroxide ions. The overall cell reaction is:

$$2\ Zn + O_2 = 2\ ZnO\ (E_o = 1.65V)$$

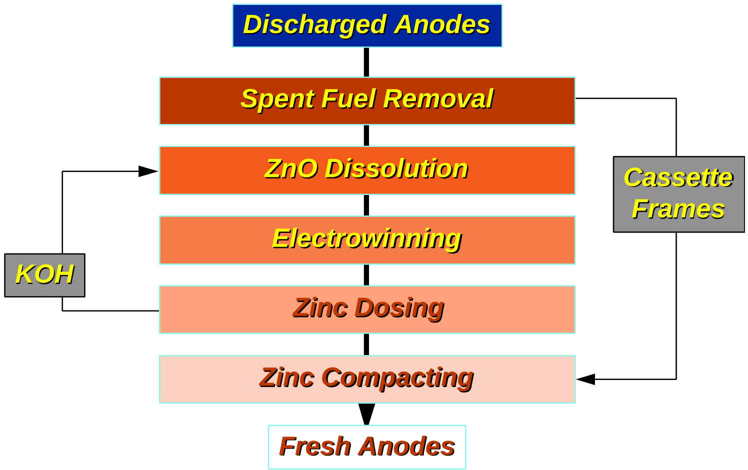
where E_o is the standard potential for the reaction. Theoretical specific energy according to the overall reaction equation is 1,350 Wh/kg. Demonstrated practical specific energy in various full size EV batteries of this design (around 200 Wh/kg), allow vehicle ranges per refueling in excess of 300 km. Nominal discharge voltage at the five hour rate is about 1.15 V per cell. Projected unit price of the EFL battery in volume production is about $75 per battery kWh.

The on-board battery is "refueled" or mechanically recharged by exchanging spent Electric Fuel "cassettes" - the zinc anode including current collector frame and separator envelope - with fresh cassettes. This is accomplished by an automated refueling machine that allows a zinc-air battery powered vehicle to “refuel” in an amount of time comparable to gasoline refueling. The depleted cassettes are electrochemically recharged and mechanically recycled external to the battery. With commercial implementation, regeneration of the cassettes will take place at centralized facilities serving regional networks of refueling stations. In this way the zinc anode recharging/recycling facility would assume a parallel role in a zinc-air based transportation system to that held by oil refineries in today’s fuel distribution system, without the negative environmental impacts of refineries or point-source pollution conventionally fueled vehicles (especially diesel).

Regeneration

The regeneration process is shown schematically in Fig. 3.

Figure 3. Schematic of Regeneration Process



This process as implemented in an automated facility in Bremen for the Deutsche Post fleet test, includes the following steps:

a. Disassembly, in which separator bags are removed from the anodes, and the zinc oxide discharge product (along with residual, undischarged zinc) is removed from the current collector frames.

b. Dissolution, in which zinc oxide is dissolved in a KOH solution to form a zincate-rich feed, according to the following equation:

$$ZnO + 2KOH + H_2O = K_2Zn(OH)_4$$

c. Electrowinning, in which the zincate solution is electrolyzed in an electrowinning bath according to the following equation:

$$K_2Zn(OH)_4 = Zn + 2KOH + H_2O + ½O_2$$

d. Reassembly, in which the electrowon zinc, together with residual (charged) metallic zinc, is compacted onto the current collector frame and the anode is inserted into a separator bag.

Since its inception in 1990, the primary goal of the project has been to optimize the regeneration process, and especially the zinc electrowinning cell, in order to give a process set-up that could consistently provide fresh zinc with acceptable performance characteristics for the subsequent discharge. On the one hand, zinc with a high surface area, low apparent density, and dendritic morphology was required in order to provide high power levels (120 W per cell, equivalent to 100W/kg, at the end of discharge) and enable binderless compaction onto a current collector to give an adequately robust anode plate. On the other hand, the zinc corrosion rate should be minimal in order to achieve low battery self discharge rates, and the process should effectively allow for closed-cycle operation with minimal additives and effluents, with a means for utilization of the residual zinc returning in partially discharged plates.

The basic optimized electrowinning zinc conditions are summarized in Table 1.

Table 1. Optimized Electrowinning Conditions

Anodes	Nickel louvers
Cathodes	Magnesium plates
Current Density	100 - 200 ma/cm^2
Temperature	40° - 70° C
Electrolyte Concentration	7 - 8 M KOH
Zincate Concentration	30 - 40 gm zinc per liter

The electrolyte feedstock is compatible with the alkaline electrolyte composition in the discharge cell and has conductivity close to the maximum conductivity for KOH over this temperature range, assuring low ohmic drop. The dissolved zinc concentration of 30-40 gm/L (as zincate) is within the range of direct chemical solubility in KOH of zinc oxide, which is the major battery discharge product in the spent cassettes. This allows facile in-plant solubilization of incoming zinc oxide in minimum time and volume of depleted electrolyte feedstock.

In fact, the incoming spent fuel after mechanical removal of the anode frame and separator and breakup of the anode block comprises only zinc oxide and residual zinc. The zinc oxide is dissolved in excess depleted electrolyte feedstock and the remaining undissolved residual metallic zinc is separated off and retained for reblending with freshly electrowon zinc. The EFL system accordingly can deal with partially discharged plates without excessive energy loss.

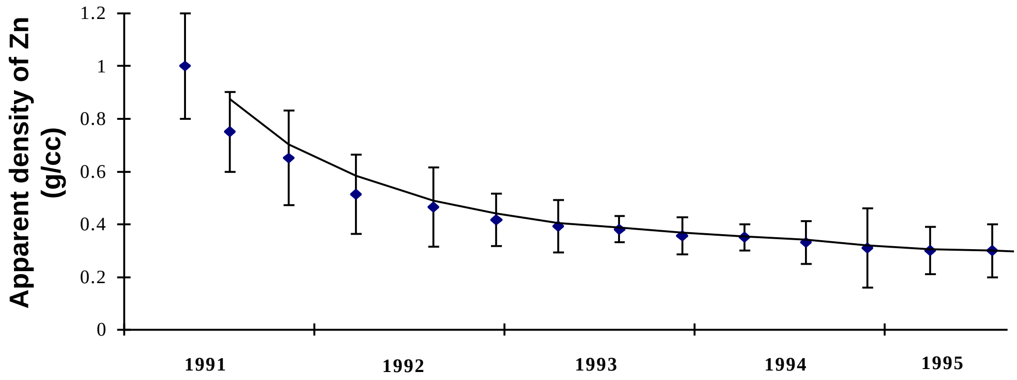
Certain details of the zinc electrowinning cell and subsequent processing are proprietary, but it can be said here that the anodes are nickel based with a louvered construction that directs evolving oxygen bubbles away from the anode-cathode interspace, thus maintaining a low ohmic drop. The cathodes are magnesium-based since zinc has been found to deposit with high coulombic efficiency and good dendritic morphology but with poor adhesion to this material. Due to the poor adhesion, the zinc can be easily recovered by periodic scraping with specially designed plastic scrapers without damage or spalling of the dendritic structure. The detached zinc sinks to the base of the cell where it can be periodically withdrawn as a slurry with KOH, for dosing and recompaction into fresh anodes.

An electrowinning current density of 100-200 mA/cm^2 is adequate for good zinc morphology and compact plant dimensions under the operating conditions of Table 1 and, with anodes activated with electrocatalysts having a low overvoltage for oxygen evolution, an electrowinning cell voltage of 2.2V is achieved. This is important for reducing energy losses in the plant and achieving a high effective overall energy cycle efficiency for the EFL system compared with other advanced batteries.

Properties of the Zinc

Fig. 4 shows the improvement with time during the project as to apparent density of zinc in the slurry.

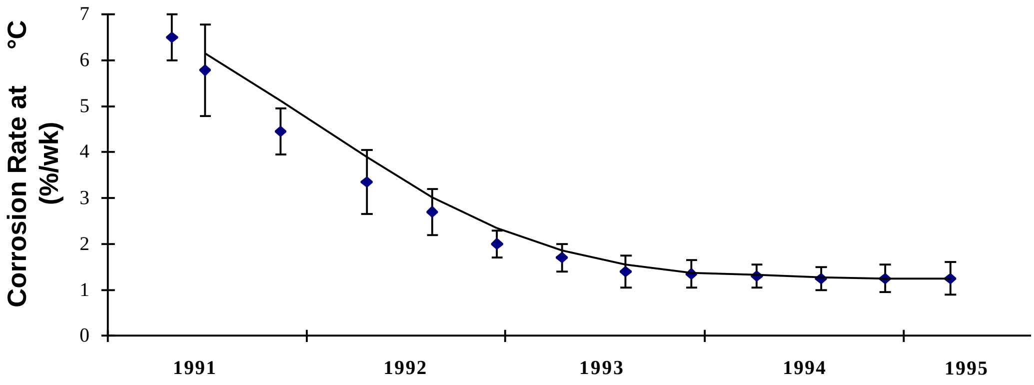
Figure 4. Improvement in apparent density of zinc over time



The low slurry density of 0.3 gm/cc (to be compared with the X-ray crystal density of regular bulk zinc of 7.14 gm/cc) is achieved with an effective B.E.T. surface area of around 1 m^2/g.

Fig. 5 shows the improvement with time during the project as regards the corrosion rate of the zinc. The corrosion rate of 1-2% /week at 30°C, which is the main contribution to zinc-air cell self-discharge, is comparable to self-discharge figures for lead-acid batteries for electric vehicles and significantly better than self-discharge figures for advanced batteries of the nickel-metal hydride and sodium-nickel chloride types.

Figure 5. Improvement in zinc corrosion rate over time



Implementation

To date, Electric Fuel has constructed demonstration regeneration plants in Bet Shemesh, near Jerusalem, and at Trofarello in Italy, each capable of regenerating 10 kg zinc per hour. The Bet Shemesh plant, opened in May 1995, has been used to produce zinc for vehicles being tested in the integration phase of the Deutsche Post's field test, and will continue to produce zinc for ongoing testing and demonstration of vehicles in Israel and elsewhere.

The Trofarello plant is being used to provide zinc for a small fleet of vehicles operated by the Italian energy company Edison SpA. Edison is a long-standing strategic partner of Electric Fuel and has licensed the technology for use in Italy, France, Spain and Portugal.

Construction of a scaled-up regeneration plant in Bremen, Germany, to produce 100 kg zinc per hour, was completed in early 1996. This plant, which is scheduled to come fully on-stream in mid-1996, is to supply zinc to support the fleet of 64 Deutsche Post EV's during its two-year field test of the zinc-air energy system. Design and construction was accomplished in cooperation with UHDE GmbH (Hoechst Consulting), and plant operating duties will be shared with Stadtwerke Bremen AG, the municipal utility of Bremen. Both companies have chosen to become Electric Fuel strategic partners in Germany.

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