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# The Zinc-Air Refuelable Battery:

## Alternative Zinc Fuel Morphologies and Cell Behavior

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## ABSTRACT

Multicell zinc/air batteries have been tested previously in the laboratory and as part of the propulsion system of an electric bus; cut zinc wire was used as the anode material. This battery is refueled by a hydraulic transport of 0.5- 1-mm zinc particles into hoppers above each cell. We report an investigation concerning (1) alternative zinc fuel morphologies, and (2) energy losses associated with refueling and with overnight or prolonged standby. Three types of fuel pellets were fabricated, tested and compared with results for cut wire: spheres produced in a fluidized bed electrolysis cell; elongated particles produced by gas-atomization; and pellets produced by chopping 1-mm porous plates made of compacted zinc fines. Relative sizes of the particles and cell gap dimensions are critical. All three types transported within the cell and showed acceptable discharge characteristics, but a fluidized bed approach appears especially attractive for owner/user recovery operations.

## Introduction

Refuelable zinc/air batteries are "recharged" by an exchange of fluid cell reaction products for fresh zinc particles and zinc-depleted electrolyte. In electric vehicle applications, rapid refueling enables the vehicle to operate beyond the range limits imposed by its energy storage capability--allowing nearly continuous daily use. Employing fleet vehicles at high capacity factors allows rapid write-off of the initial cost. Lawrence Livermore National Laboratory (LLNL) has developed engineering prototype 6- and 12 cell batteries and demonstrated the capability for rapid refueling with 0.5-1-mm particles entrained in KOH electrolyte. Recently, a 6-cell zinc/air engineering prototype battery was successfully operated under sustained (5 hour) discharge conditions on an electric bus as part of a Zn/air-lead/acid parallel hybrid [1]. (The bus was loaned by Santa Barbara Metropolitan Transit District). This battery established operating feasibility of a multicell stack using the patented self-feeding configuration[2]. A process for zinc recovery was also investigated, which entails the deposition of zinc fines onto a non-adhering substrate followed by collection and pressing into pellets. [3]

This approach differs from reconstructable-anode zinc/air batteries in several important respects. Essentially all of the zinc fuel that is introduced into this battery is consumed to produce useful electricity. The battery can be brought from any state of discharge to 100% capacity without removal of unreacted zinc. Moreover, if the zinc recovery and refueling were accomplished using simple equipment operated at the fleet's home base, green-field industrial infrastructure and fuels transportation (required by centralized fuel recovery schemes) could be avoided altogether.

The work reported here fulfilled several objectives [4]: (1) Zinc particles fabricated by various techniques were tested for their ability to feed from hopper to cell and within the cell. (2) The shorting current that flows during refueling between adjacent oxygen-depleted cells through hoppers was determined. (3) The energy losses associated with standby corrosion of zinc were determined from the corrosion rates in the presence of cell materials.

## Zinc Fuel Pellets

LLNL invented a process for the manufacture of zinc fuel by compression of zinc fines within an electrolyte medium through use of a moving die to form 1-mm pellets of 60% density, which was reported earlier. [3]

Three new routes to battery fuel recycling were evaluated here. First, 1-mm zinc particles were grown in an electrowinning cell operated as a spouted bed and "seeded" with small particles. This process was developed at University of California at Berkeley for recovery of zinc or copper from ores. Prof. James Evans provided us with 0.75-1.0 mm, prolate ellipsoidal particles grown from 0.385 mm diameter cut wire seed in an electrolysis cell operated as a specially modified fluidized bed [5].

Eagle-Picher Co. fabricates porous zinc plates by compaction of zinc fines recovered from electrolysis of alkaline zincate solutions [6]. The process is used in manufacture of electrodes for various alkaline batteries. Samples of 7.6 cm diameter, 1-mm thick compacted disks of 60% theoretical density were furnished to us; we chopped the plates into 1-mm-thick, irregular fuel pellets for test. Two sieve grades were tested: 0.6-0.83 mm, and 0.83-1.2 mm.

A third possibility (melt produced shot) was also tested, although this approach would probably require industrial infrastructure and would not deliver the advantages of user/owner fuel recovery. Noranda Technical Center (Quebec) furnished particles of coarse zinc powder, fabricated by the gas-atomization of molten zinc. These particles were spindle-shaped, with rounded ends, smooth surfaces and length/width ratios of 4-8.

## Experimental system used in cell discharge studies

An experimental system was constructed for discharge tests using anode fuel produced by various techniques. The discharge cells were reconstructed from standard cell design developed and tested earlier. [1] The bipolar transfer plates of these cells were provided with acrylic windows to allow direct observation of the zinc particles within hopper and cell. These cells use porous gas diffusion electrodes catalyzed with Co-TMPP and supported on an Exmet screen current collector (Model AE-40, Eltech Research Company, Painesville OH). In these tests, we used silver-epoxy cement to affix the cathode current collector screen to the copper foil conductors soldered to the circuit board plates. This epoxy bond does not have the low resistance of soldered, pressure bonded or cold-welded connections and is not recommended for practical applications. Nevertheless, the epoxy allows non-destructive disassembly and reuse of the frames.

The experimental system is shown in Figure 1. Electrolyte flow was maintained at T = 50-60 °C and at rates of 4 ml/s to yield an average phase velocity of 0.5 cm/s; air flow was maintained at 60 ml/s (four-fold of stoichiometric.) At a discharge rate of 2 $kA/m^2$, this flow rate confines the maximum zincate concentration increase across the cell to 0.06 M, and the temperature increase to ~ 1°C. An active load (HP 30 A Power Supply) was used to control discharge rate, which allowed peak currents up to 50 A under reverse polarization. Electrolyte volumes were fixed at 1 liter; and discharge was generally continued at 20- or 35 A (with intermittent polarization sweeps) for eight hours, or until 250 Ah had been passed.

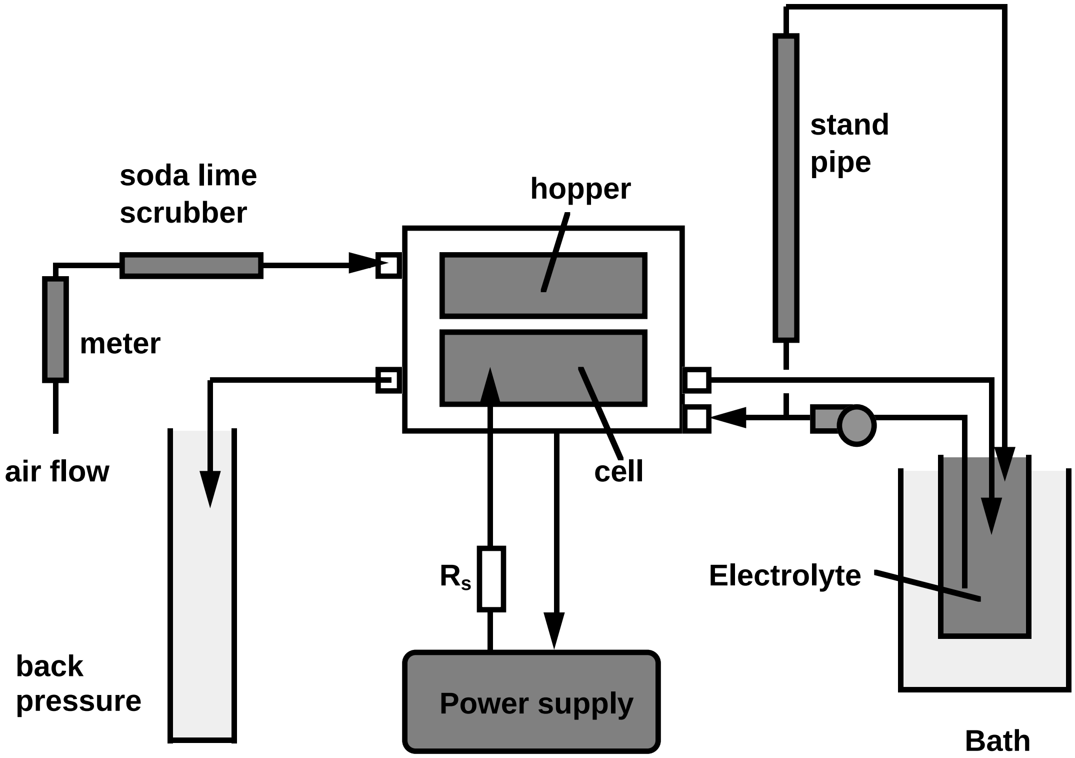

Figure 1. This experimental configuration was used in tests of alternative anode morphologies and in self-discharge and shorting tests.

## Results of discharge tests with alternative zinc anode materials

In all cases, the electrolyte became cloudy within a few minutes of the start of discharge in initially zinc-free electrolyte. The second phase product was found by X-ray diffraction to consist of zinc oxide (zincite). Upon conclusion of the tests, the spent electrolyte separated rapidly (~10 minutes) into a relatively clear supernatant fraction and a precipitate, the boundary between the two being sharp. The occlusion of the electrolyte by solid reaction products is estimated to be minimal: at 160 Ah/liter electrolyte loading, the reaction product would occupy less than 5% of the electrolyte volume (assuming the density of zincite).

Salient results of tests with (1) fluidized bed product, (2) chopped compacted plate and (3) irregular particles of gas atomized zinc are shown in Table 1. The last two entries in the table are for previous tests with 0.5-0.75 mm cut wire (as right cylinders having equal length and diameters). The entries summarize respectively the best results in single 80-cm$^2$ cells and the 6-cell multicell results (average cell polarization is taken as 1/6 the total battery polarization).

In general, the fluidized bed product and chopped plate did not feed with the same facility as the cut wire or gas-atomized particles. While the fluidized bed particles settled continuously within the cell, gaps developed in the bed; undisturbed particles also failed to fall from the hopper into the cell, being restricted by the narrow 2.5 mm by 2 cm long channel between hopper and cell. (The channel was reduced to 2.5 mm from 3.0 mm by assembly error). The smaller sieve fraction of the chopped plate effectively translated within the cell, but the larger fraction (0.85-1.2 mm) would not feed from hopper to cell. There was some disintegration the compacted fines within the cell. The atomized shot particles fed continuously from hopper to cell, at a rate roughly proportional to time-integrated current (total charged passed); the rate of displacement corresponds to a packing density of roughly 60% of theoretical.

Three potentially significant differences between the cut wire (tested on the moving bus) and the morphologies tested in the laboratory are (1) particle size, (2) surface irregularities roughness, and (3) vibrations due to road travel and pumps. The cell was designed with an entry gap of 3 mm and tested with favorable results on cut wire of smaller dimensions: 0.5- or 0.75 mm. The wire surfaces remained smooth and rounded throughout discharge. The fluidized bed product had porous surfaces which were not fully dense, and the porous chopped plate particles were of irregular shape. It is expected the nearly-spherical fluidized bed product would flow freely from hopper to cell if the cell entry gap and adjoining channels were enlarged to about 4 mm.

**Table 1. Salient Results for Tests with Alternative Fuel Morphologies.**

| *Pellet type* | *Size mm* | *Final loading Ah/liter* | *Cell Resistivity at Ah/liter loading* | *Comments* |
|---|---|---|---|---|
| Spouted bed spheres (UCB) | 1 | 170 | 2.0 Ω-cm$^2$ / 125 Ah/liter | Hopper-to-cell feed impeded |
| Compacted fines (Eagle Picher) | 0.6-0.83<br>(0.83-1.2) | 250 | 1.9 Ω-cm$^2$ / 47 Ah/liter<br>1.6 Ω-cm$^2$ / 160 Ah/liter | larger sieve did not feed |
| Atomized shot (Noranda) | | 160 | 1.5 Ω-cm$^2$ / 70 Ah/liter<br>1.8 Ω-cm$^2$ / 173 Ah/liter | hopper feed ~ charge passed [2] |
| Cut wire | 0.5 | 125 | 0.6 Ω-cm$^2$ / 125 Ah/liter | single cell results[1] |
| Cut wire in 6-cell stack | 0.5-0.75 | <55 | 2.1 Ω-cm$^2$ / <54 Ah/liter | Ag-epoxy connectors |

[1] polarization measured on screen embedded in air electrode.

[2] Level in hopper fell continuously with charged-passed, at rate corresponding to 60% packing density.

## Self-discharge of an oxygen-depleted cell during refueling

The battery is refilled by a hydraulic transfer of zinc fuel pellets entrained in zinc-depleted electrolyte flowing through fill tubes common to banks of cells. During refueling, it is expected that zinc particles should effectively short anode to cathode of adjacent bipolar cells, by forming bridges through these fill tubes. (This zinc and electrolyte bridge is removed before operation of the battery). To prevent catastrophic shorting during refueling, the flow of air into the battery must be discontinued, and any oxygen remaining in the cells must be consumed by discharge through a load prior to refueling. The low air volume in the cells (<100 ml/cell), results in a trivial energy loss of 0.13 Wh/cell or 0.03% of capacity.

An intuitively more important question concerns the discharge of a “zinc/water” cell shorted through zinc bridges between adjacent cells, according to:

$Zn + H_2O = ZnO + H_2$ (cathode) $E^\circ = 0.37$ V
(1)

To determine worst-case shorting currents, we measured a polarization curve for a Co-TMPP-catalyzed zinc/water cell (at operating temperature) in an oxygen-depleted cell and determined various "load lines" from the resistance of the particle-shunted cells (Figure 2). The intersection of various load and polarization curves give a self-discharge current density in the range of 3-5 $mA/cm^2$, corresponding to a power dissipation of 0.25 W/cell and a trivial energy loss of <0.02% of capacity during typical 10-minute refueling.

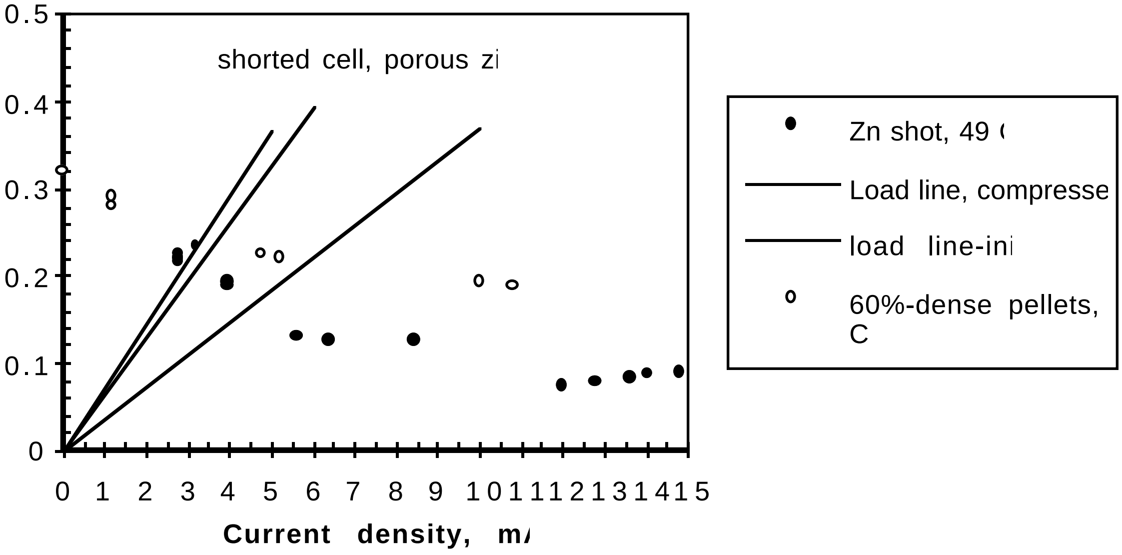

Figure 2 Polarization curves for oxygen-depleted zinc/water cells containing packed particle beds. Open data points, 0.6 mm compressed zinc pellets (60% dense; Eagle Picher) at T = 58 °C. Closed data points, gas-atomized coarse zinc powder, 0.6-0.83 mm (Noranda) at T = 49 °C. The dotted line is based on experiments with Eagle-Picher compressed zinc

pellets (T = 58 °C) for shorting between adjacent cells, while the solid and broken lines are for a range of resistance measured for cut wire (initial, and aged/compressed). Shorting current is estimated to be 3-5 mA/cm$^2$ at ~0.2 V.

## Zinc corrosion during standby

The zinc fuel is subject to a slow corrosion during standby. This corrosion does not involve the air electrode, which is separated from the zinc by a porous membrane. Rather, a corrosion couple is established between zinc and metal parts (generally tin-plated) of the anode chamber. Appropriately, we measured the corrosion of zinc in contact with candidate metals and a ZnO saturated electrolyte at both ambient temperatures (long term standby) and elevated temperatures (during overnight standby) , in order to estimate the effect of corrosion on capacity loss.

Graduated glass pipettes (10 ml capacity) were sealed at the exit end then completely filled with zincate- and ZnO saturated electrolyte (125 Ah/liter), 20 g zinc particles (0.75 mm cut wire) and samples of metal foils or wires (area = 10 cm$^2$) in contact with the zinc. Corrosion rates were measured by the evolved gas over periods of 3-6 hours (57 °C); and up to 120 h (ambient T). The contacting metals were zinc (control), tin, various solders and copper. Complete results and analyses are reported earlier [4].

In all cases, the hydrogen evolution on the non-zinc current collector is controlled by the hydrogen evolution kinetics on the dissimilar metal; the corrosion rate of isolated zinc particles was small by comparison. In the control case (no current collector metal in contact with the zinc) the anode corrosion current density was insignificant (0.9 $\mu A/cm^2$ at 24 °C; 11 $\mu A/cm^2$ at 57 °C). When corrosion was scaled to 250 cm$^2$ cell size using the current collector area, corrosion values extrapolated for the tin-plated copper Exmet were 9.4 mA and <33 mA for 24- and 57 °C, respectively. If tin-plated copper is used as an anode current collector, the loss of zinc amounts to <7 Ah/month, or 1.75% of total cell capacity per month. At high temperature (57 °C), the capacity loss due to corrosion is negligible ( 0.02%), over the thermal time constant of the cell on standby (12 hours).

## Conclusions

Conclusions of this work are as follows:

None of the three forms of zinc fuel pellets (electrowon spheres, melt-formed shot and compressed zinc fines) can be ruled out on the basis of performance in the self-feeding cells. The failure of the fluidized bed product to feed from hopper into cell may be attributed to the small size of the interconnecting channel; this can be overcome by decreasing particle size or by increasing the width of the connecting channel or cell intake. The gas-atomized zinc shot showed the most fluid properties, and fed continuously from hopper into cell at a rate proportional to integrated current.

The discharge of adjacent cells by shorting under oxygen-depleted conditions is impeded by hydrogen cathode polarization and by the inter-particle resistance of the bed. The refueling energy consumption due to shorting is negligible: 0.02% of cell capacity is lost per recharge.

Self discharge of the zinc/air cell, resulting from the corrosion of zinc in contact with the metal anode current collector and basket is less than 2% per month, based on measurements of zinc corrosion in contact with metal components in the anode chamber. Overnight losses at ~ 57 °C are estimated to be small: <-0.02% of capacity for 12 hour period, during which the electrolyte remains relatively hot (>50 °C).

In stationary cells in the laboratory, the self-feeding cells (with 3 mm gaps) do not appear to accept particles of 1 mm dimensions or above, and even 0.8 mm particles may show difficulty in feeding if the particles are of spherical or planar shapes and have high coefficients of friction due to surface roughness or porosity. Particles in the range of 0.5-0.75 mm (e.g., cut wire) and 0.6-0.83 mm (gas-atomized coarse powder) tended to feed continuously. Vibrations are important in any friction-controlled, gravity-fed flow. A means of quantifying such vibrations (whether produced by roadway shocks, pump impellers, or some other mechanical means) should be developed and used in future tests of these cells, so that rigorous comparisons can be made.

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