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A New Concept in an Electrically Rechargeable Zinc-Air Alkaline Battery

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## A NEW CONCEPT IN AN ELECTRICALLY RECHARGEABLE ZINC-AIR ALKALINE BATTERY

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LBL has developed a new concept for an alkaline zinc battery that would overcome the cycle-life limiting phenomena characteristic of most zinc electrode concepts. The new concept is a flow-thru porous zinc electrode with recirculating supersaturated zincate solution. An alkaline zinc battery with recirculating zincate is not a new concept itself, but all of the prior systems used an inert (usually flat) current collector with recirculating zinc particles. The concept employed here uses an inert substrate having an open "honeycomb" type porosity onto which zinc is plated (and from which it is stripped) while electrolyte circulates through the open pores. Materials having this type of porous structure are commercialy available as either "metal foams" or "carbon foams". We have studied in some detail the use of copper foam-metal, shown in Fig. 1. The open honeycomb or retriculated structure is apparent; the nominal "cell" diameter is 0.2 cm and characteristic diameter of the filaments is ca. 0.4 mm. particular foam has a bulk density of 3% (97% porosity) of the bulk density of copper with a total BET surface area of ca.  $10^4 \ \mathrm{m}^2$  per  $\mathrm{m}^3$ . Using a 0.3 cm thickness, the internal surface area is roughly 30 times the superficial area, so the "true" current density for zinc deposition/stripping will be more than an order of magnitude lower than the nominal current density. Low

current density is known to promote uniform zinc deposition/stripping and should extend cycle-life. A full parametric study of the influence of current density, electrolyte flowrate, and zincate concentration on zinc distribution was conducted. Figure 1 shows the appearance of the electrode after the deposition of 160 mAh/cm² of zinc (at 10 mA/cm²), which appeared to be the maximum amount of zinc that could be deposited uniformly. The zinc deposit mirrored the cellular structure of the substrate and the distribution was found to be uniform and invariant with the number of cycles over a wide range of conditions of flowrate, zincate concentration and current density.

The new concept employed carbon materials exclusively as the structural elements of the electrode to minimize <u>both</u> cost and weight. An inexpensive transition metal oxide catalyst of proven stability was used to maintain the low cost. As a result of several man-years of effort at LBL, we have identified two types of carbon materials that can be used to form the structural elements having the required stability: 1.) graphite fibers woven into a "cloth" that serves as the current collector; 2.) a high surface area graphite powder formed by heat treatment of a carbon black. The latter was impregnated with a mixture of transition metal oxides to form the active catalyst. The electrode was fabricated by bonding the catalyst layer to one side of the graphite cloth, and a hydrophobic polytetrafluoroethylene (PTFE) film bonded to the other. The resulting polarization curves for these electrodes is shown in Fig. 2 at room temperature in 12 N KOH containing 200 g/l zincate. After 300 cycles, the electrode was still showing acceptable voltage in the current density region 10-20 mA/cm<sup>2</sup>.

Proof-of-principle experiments were conducted in 1.5 Ah zinc-air

prototype battery employing the new concepts in zinc and air electrodes described above. The design of the 1.5 Ah prototype is shown in Fig. 3. The cell was cycled at the three hour rate producing 1.2 volts on discharge, required 2.0 volts on charge, and operated satisfactorily for over 150 cycles. Based on the 1.5 Ah prototype performance characteristics, engineering design calculations were made for 32 kWh battery. These calculations project an energy density of 110 Wh/kg, peak power density of 140 W/kg, electrical efficiency of 60% and an attractive materials cost of < \$20 per kW. The prototype testing revealed a number of problem areas that a would have to be addressed in further studies using multi-cell prototypes: shunt currents in the electrolyte manifold; the effect of air electrode dissolution products in the electrolyte on zinc cyclability; component reliability.

### **Acknowledgment**

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the US Department of Energy under Contract No. DE-ACO3-76SF00098.

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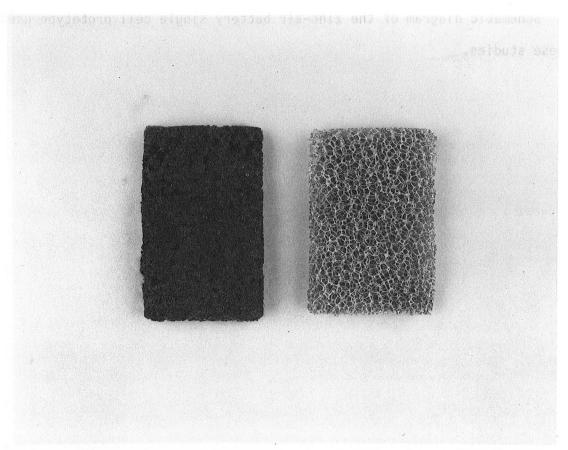
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#### Figure Captions

- 1. Photograph of the copper foam metal used as a substrate for zinc: (top) before zinc deposition; (bottom) after the deposition of  $160 \text{ mAh/cm}^2$  of zinc.
- 2. Polarization curves for bifunctional air electrodes fabricated from graphite materials with nickel-oxide and nickel-cobalt spinel oxide as

catalysts.

**3.** Schematic diagram of the zinc-air battery single cell prototype used in these studies.



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Fig. 1

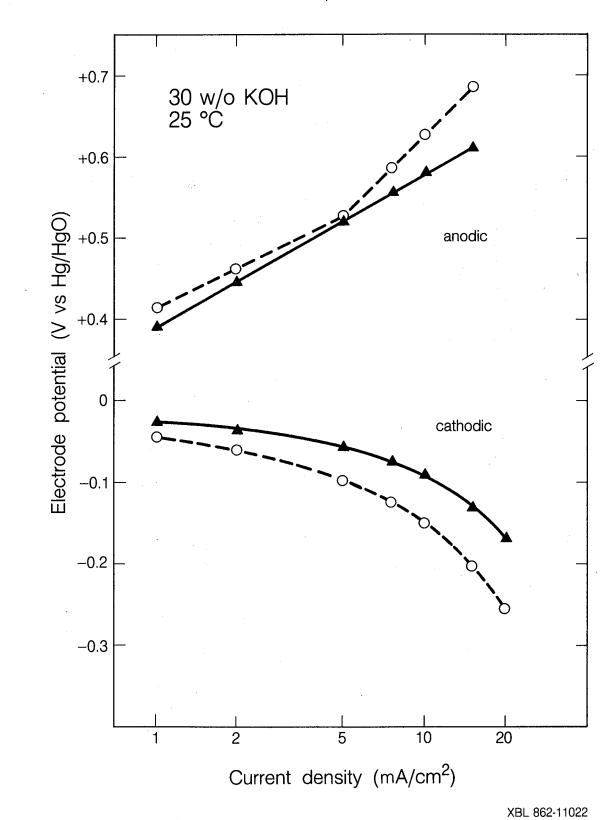
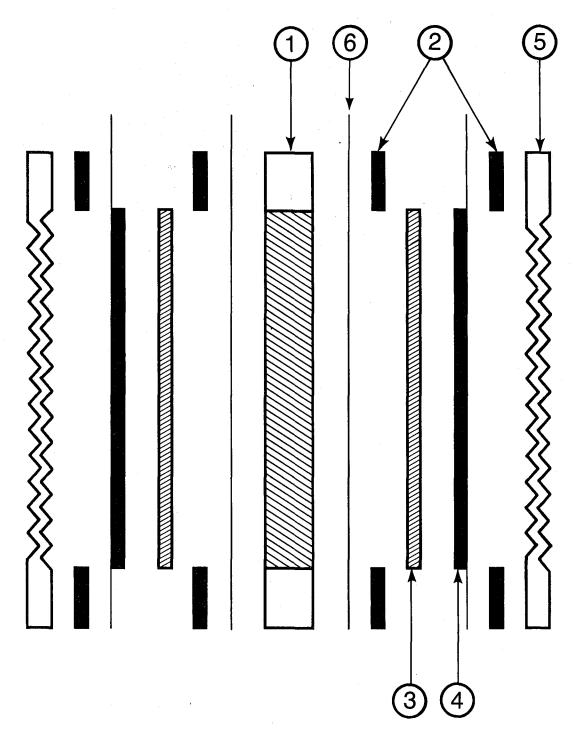


Fig. 2



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Fig. 3

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