Conf-940812--23

UCRL-JC-117946
PREPRINT

Demonstration of a Zinc/Air Fuel Battery to Enhance the Range and Mission of Fleet Electric Vehicles:

Preliminary Results in the Refueling of a Multicell Module

John F. Cooper, Dennis Fleming, Larry Keene, Arturo Maimoni, Keith Peterman, Ronald Koopman

Lawrence Livermore National Laboratory
Livermore, California

This paper was prepared for submittal to
The 29th Intersociety Energy Conversion Engineering Conference
Monterey, CA
August 7 – 12, 1994
Paper No. AIAA - 94 - 3841

August 8, 1994

Demonstration of a Zinc/Air Fuel Battery to Enhance the Range and Mission of Fleet Electric Vehicles:

Preliminary Results in the Refueling of a Multicell Module

by

John F. Cooper, Dennis Fleming, Larry Keene, Arturo Maimoni,
Keith Peterman and Ronald Koopman
Lawrence Livermore National Laboratory, Livermore CA 94550

Paper No. AIAA - 94- 3841
29th Intersociety Energy Conversion Engineering Conference
Monterey, CA August 7-12, 1994

Demonstration of a Zinc/Air Fuel Battery to Enhance the Range and Mission of Fleet Electric Vehicles: Preliminary Results in the Refueling of a Multicell Module

John F. Cooper, Dennis Fleming, Larry Keene, Arturo Maimoni,
Keith Peterman and Ronald Koopman
Lawrence Livermore National Laboratory, Livermore CA 94550

Abstract

We report progress in an effort to develop and demonstrate a refuelable zinc/air battery for fleet electric vehicle applications. A refuelable module consisting of twelve bipolar cells with internal flow system has been refueled at rates of nearly 4 cells per minute, indicating a refueling time of 10 minutes for a 15 kW, 55 kWh battery. The module is refueled by entrainment of 0.5-mm particles in rapidly flowing electrolyte, which delivers the particles into hoppers above each cell in a parallel-flow hydraulic circuit. The concept of user-recovery is presented as an alternative to centralized service infrastructure during market entry.

Introduction

There has been a renewed interest in zinc/air batteries in electric vehicle propulsion because of the unique combination of high-energy density and low hardware cost. If the zinc/air battery can be made mechanically rechargeable by a simple and rapid technique, the battery can provide an electric vehicle with unlimited range extension, without resorting to slow electrical recharge, battery exchange or heat engines. The option of mechanical recharge is important in fleet electric vehicles such as shuttle busses and delivery vans and other industrial or enclosure-operated vehicles, which often must operate over 8 hours each day to effectively return the high cost of the vehicle. Battery exchange essentially doubles the battery investment, while range extension using heat engines defeats the primary purpose of emissionless power sources.

It is possible to divide mechanically-rechargeable battery concepts into two groups: (1) reconstructable cell and (2) refuelable cell batteries. *Reconstructable cell batteries* are characterized by the physical removal and refurbishing of battery components such as anode plates or cassettes, or even unit cells. Reconstructable cell batteries have been developed by Electric Fuel, Ltd. (Israel) and have demonstrated ranges of over 260 miles in delivery vans in Germany and Italy [1]. Anode cassettes are removed (along with unconsumed zinc and zinc-oxide products) by robotics and reconstructed at an industrial plant. Advantages of simplicity must be balanced against the cost of industrial infrastructure. Moreover, anode consumption is incomplete and the cells are incapable of partial recharge.

Refuelable batteries employ a homogeneous electrochemical fuel, which is pumped into the battery in a manner which is similar to refueling an automobile. All cell hardware remains on the vehicle and is undisturbed by the refueling operation. The purpose of seeking a refueling technology is to eliminate the requirements for centralized industrial infrastructure to support vehicle operation. Unlike cell reconstruction, the recovery of zinc from battery reaction products as a fuel can be accomplished using small-scale electrolysis equipment which is owned and operated by the fleet and conveniently located at the fleets' home base. Examples of refuelable batteries are the CGE zinc/air slurry battery [3] and the concepts proposed by Evans [2] or Alcazar [4]. Our approach provides for the transfer of 0.5-1.5 mm zinc particles entrained in a high velocity (~ 0.5 m/s) flow of electrolyte to hoppers above each cell. The hoppers gravity feed to the cells on discharge. The self-feeding cell, fuel cycle, and discharge characteristics (on scales of 80- to 1000 cm^2) have been reported earlier [5-7]. This communication reports progress in an on-going effort to demonstrate a 12-cell module in laboratory and on-vehicle tests, and presents results of refueling experiments.

Technical Approach and status

Self feeding cells. Each self-feeding cell contains a hopper positioned above a narrow, wedge-shaped interelectrode gap (Figure 1). The gap at its largest dimension is only a few times larger then the particles of zinc. Particles entering the gap do not close-pack, but form an open structure through which electrolyte may flow with negligible hydraulic resistance [7]. The open structure is the result of particle bridging which results in a quasi-stationary packed bed containing numerous open voids, which continually form and collapse as the bed discharges. Beds are typically 40% solid zinc. Hydraulic power dissipation in beds in single and bipolar stacks is 0.3-0.7 W/m^2, as measured in 80, 600, and 1000 cm^2 cells [7]. In 600 cm^2 cells, essentially all of the zinc fed to the cell was converted to electricity (i.e., fully utilized) and no metal is removed from the cell during recharge operations [5]. Power yields from 80 cm^2 cells are 5 kW/m^2 [6,7]. The structure of the current 250 cm^2 cells used in the current multicell stack essentially replicates (triples) the 80 cm^2 cell structure, to yield a unit with the appropriate ratio of power to energy for bus applications.

Bipolar stack design. The battery is constructed in modular form. It consists of a cell stack (comprised of cells, hoppers and refueling ports), and an electrolyte storage tank (which contains electrolyte and discharge products). Each cell is bounded by a bipolar transfer plate (with internal connections to the adjacent cell), and a polymer frame (which supports electrodes, hopper and internal flow channels for electrolyte circulation and refueling.) There are no external busses except at the terminal ends of the stack. The unit (except for air supply), is self-contained. Heat rejection is accomplished by forced air convection across serrated heat fins on the exterior of the stack (Aavid Engineering, Nassau, NH). The battery is modular in design, and scales roughly as 125 W/cell and 300 Wh/liter of tank volume. The battery (including prorated auxiliaries for air treatment and transfer and excluding test-related auxiliaries and sensors) weighs about 45 kg. It was designed in the size and shape to occupy the space provided for two commercial 6-V lead-acid batteries now being used in electric busses.

Refilling results . The stack is refueled by (1) draining spent electrolyte containing zincates and suspended zinc oxide particles from the storage vessel and (2) by entrainment of zinc particles into the hoppers in a fast-moving flow of zinc-depleted electrolyte. (Figure 2). As the particles flow over ports in a refueling tube, a fraction of the particles fall into each hopper. Cells attain full capacity sequentially from inlet to exit. Using proprietary flow interrupters and by breaking inter-module connections before refill, shorting of the cells is prevented. Stacks of 12-full size cells have been refilled completely in only 4.3 minutes, and improved control over the zinc particle injection into the flow should reduce this further to 2-3 minutes. Figure 3 shows the time at which each of twelve cells reaches full capacity, indicating a fill rate of 2.4 and 3.9 cells per minute (i.e., the inverse slopes of the time/cell plots) for two different injection techniques. At the higher rate, and EV battery pack consisting of three parallel branches (each with three modules) will be filled in less than 10 minutes. Since the batteries of any vehicle would be filled in parallel (not sequentially) from a common flow, the vehicle refueling target of 10 minutes is a reasonable goal for any combination of 3x3 battery packs.

Development Problems and Discussion

The key technical issues in this and other zinc/air refuelable battery development efforts are (1) life under duty of the air electrode, (2) integrity of the air/electrolyte seals under fatigue, (3) capacity of the electrolyte to hold zinc products in a form that can be readily removed as liquids, (4) the mutual compatibility of each step of the fuel cycle consisting of zinc electrowinning, particle fabrication, refueling and discharge; and (5) high polarization of the air electrode, which limits geometric power-density of the cell overall battery power.

While air electrodes have not been tested in flowing caustic/zincate electrolytes under bus or van duty cycles, air electrodes were tested in caustic/aluminate electrolyte as part of an effort to develop aluminum/air batteries. Under conditions of fixed discharge at 60 °C, air electrodes were operated at 2 kA/m^2 without failure for 12,000 h in flowing 7.5M KOH + 1.0 M aluminate [8]. Higher temperatures (80 °C) and rates (4.5 kA/m^2), or on/off cycles (3 hours on; 3 hours of cold standby in filled cell) reduced life to 4000 h and 6000 h, respectively. Fortunately the natural markets for refuelable zinc/air (busses, vans, industrial vehicles) tend to operate for long periods of time per shut down, which produces the conditions more favorable to long electrode life.

Table 1. Experimental parameters in the refilling of a 12 cell zinc/air module.

Parameter	Value
Module specifications:	
Voltage	13.8 V at 50 A; 12.0 V at 100 A
Capacity	440 AH, independent of rate
Peak sustained power	1.6 kW
Flow rate	4.5 liters/minute
Pressure drop across injection tubes	2 kPa
Peak hydrostatic pressure	6 kPa
Zinc concentration in fuel	200 g/liter (3 %-vol.)
Rate of cell fill-up (slope Figure 3, #2)	15.25 s/cell, average

Table 2 Calculated parameters in the refilling of a battery consisting of nine modules in a 3-series, 3-parallel hydraulic configuration

Parameter	Value
Battery specifications: 9 series modules	
Voltage	120 V @ 50 A; 104 V @ 100 A
Energy yield at rate	53 kWh @ 50 A (8.8 h) ; 46 kWh @ 100 A (4.4 h)
Time to transfer fuel	<10 minutes
Pressure drop across assembled battery	6-10 kPa
Pump rate	13.5 liters/minute (3.5 gpm)

The weak link in zinc/air batteries (as in all metal/air batteries) is the integrity of the electrolyte/air seal. Fatigue of this barrier under flow- and road-induced vibrations may determine battery life.

Although our cell design is compatible with power densities well over 100 W/kg, we have chosen to design for high energy density, rapid refuelability without complex infrastructure, and tolerance of road shocks. In our view, zinc/air is most effectively used in a power-leveled, essentially parallel hybrid, where a high rate battery, supercapacitor or flywheel provide for peak short duration power and draw energy substantially from regenerative braking. This approach maximizes power density of the system. It greatly increases battery electrical efficiency and life, reduces vehicle weight and recovers part of considerable braking energy of heavy vans and busses used in stop-and-go duty cycles.

While low energy efficiency has long been a disadvantage of secondary and mechanically rechargeable zinc/air, a higher energy efficiency is expected for this system for two reasons. The use of very large particles (0.5-1.5 mm) with low specific surface areas limits zinc corrosion rates to low levels compared with slurries of zinc dendrites. (Measured coulomb efficiencies approach 100% over 16 hour runs in our 600 cm^2 cells [5]). Secondly, the separation of the discharge and zinc recovery processes into separate hardware allows each process to be separately optimized for optimum efficiency. The zinc recovery process may operate *continuously* at a lower current than the discharge current; hence recovery hardware is proportionately smaller and cheaper at the same current density. We expect that a fuel cycle will have an DC/DC energy efficiency of 57-61% when the characteristics of our cell are combined with advanced catalyzed oxygen evolution electrodes (e.g., from Electrolyser, Ltd., Toronto). This is a significant improvement over the ~40-45% efficiencies obtained with slurry batteries with internal recharge capability [3].

Conclusions

The use of the hopper as a physical buffer between the cell and high-velocity stream of electrolyte protects the cells from possible abrasion and puncture during refill, and allows filling rates compatible with an objective for 10 minute refueling of a bus, van or truck battery. The hoppers provide a means of cell-to-cell capacity equalization, partial recharge ("topping off") and emergency refueling on the roadway using simple, portable equipment (pumps and tanks). The fixed electrodes, membranes and current collectors within each cell are not disturbed by the refueling process. The hoppers store 85% of the zinc mass external to the cell, and therefore lessen cell inertia and the effect of road shocks.

We have begun module tests in the laboratory, which will be followed by on-vehicle tests to verify particle flow under vehicular conditions of impulse and vibration. Following this, the modules will be integrated into progressively larger battery systems and tested. In a subsequent communication, we will describe a process for zinc recovery by means of user-owned and operated equipment.

Acknowledgments

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. We gratefully acknowledge the support of Lawrence Livermore National Laboratory internal research, and support of the U.S. Department of Transportation through CALSTART, Inc.

References

1. Jonathan R. Goldstein and Binyamin Koretz, Tests of a full-sized mechanically rechargeable zinc-air battery in an electric vehicle, *Proc. Intersociety Energy Conversion Engineering Conference,* Paper no. 93410, Atlanta Georgia, August 1993; see also proceedings of December 1,2 1993 Zinc/air Battery Workshop, Sandia National Laboratory, Albuquerque.
2. Evans, J. W. and Savaskan, A zinc-air cell employing a packed bed anode *J. Appl. Electrochem.,* **21**, 105-110 (1991)
3. Appleby, J. and M. Jacquier The C. G. E. Circulating Zinc/Air Battery, *J. Power Sources* vol. 1, pp. 17-34 (1976/77)
4. Sierra Alcazar H. B., Nguyen P. D. and Pinoli, A. A., *Technology Base Research on Zinc/Air Battery Systems,* LBL-Report No. 23960, September 1987.
5. J. Noring, S. Gordon, A. Maimoni, M. Spragge, and J. F. Cooper, Mechanically Refuelable Zinc/Air Electric Vehicle Cells, *Proc. 183rd Meeting of the Electrochemical Society*, Honolulu HI, May 1993; LLNL Report UCRL-JC-112422.
6. John F. Cooper, Larry Keene, Arturo Maimoni, Jon Noring, and Keith Peterman, A continuous feed zinc/air fuel battery for fleet electric vehicle applications, *Proc. 185th Meeting of the Electrochemical Society*, San Francisco, CA May 22-27, 1994.
7. John F. Cooper, Larry Keene, Jon Noring, Arturo Maimoni, and Keith Peterman, "Regenerative Zinc/Air and Zinc/Ferricyanide Batteries for Stationary Power Applications," Proc. 36 Power Sources Conference, Cherry Hill, NJ, June 6-9 1994.
8. Private communication: Eric Rudd (Eltech, Inc.) to J. F. Cooper, July 1993.

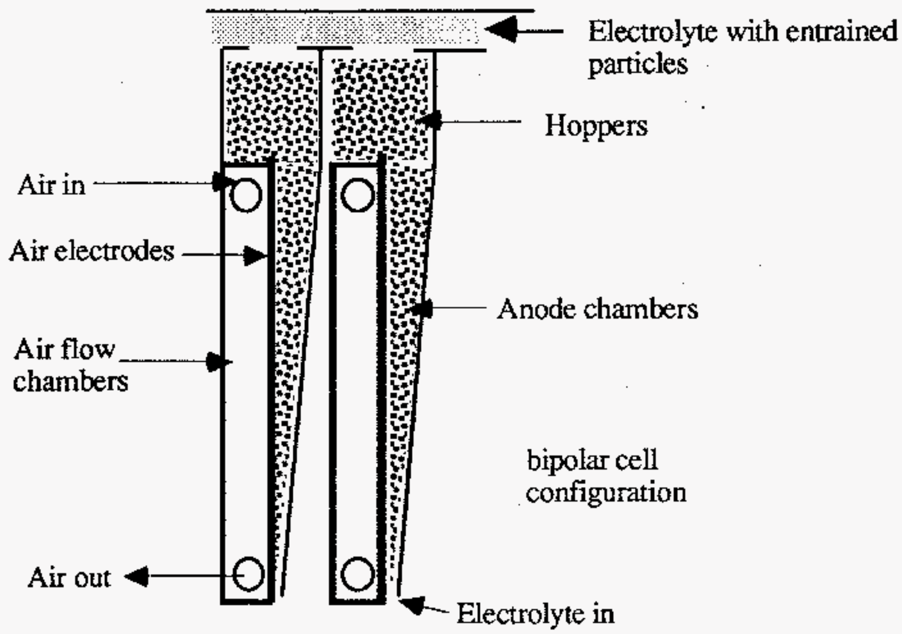

Figure 1. The cell is refueled by a transfer of zinc particles into hoppers, which in turn gravity feed into the cells during discharge. Particle bridging prevents close packing and maintains a low hydraulic resistance [7].

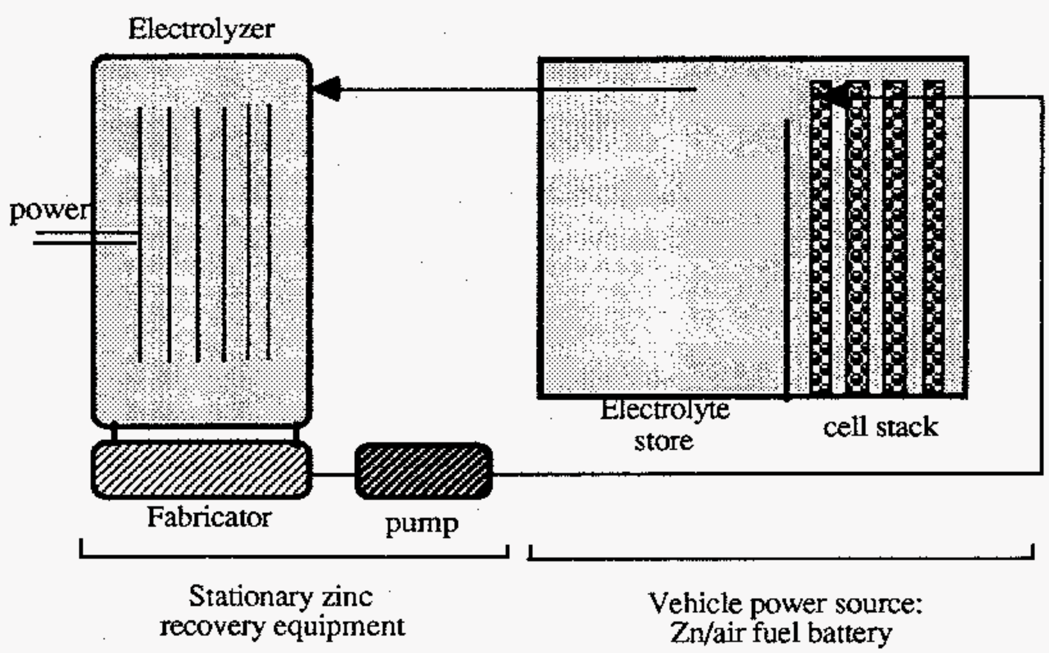

Figure 2. A zinc/air battery is refueled by rapid exchange of spent electrolyte for a fresh electrolyte with entrained zinc particles. User recovery at fleet facilities eliminates the need for merchant service infrastructure during market entry.

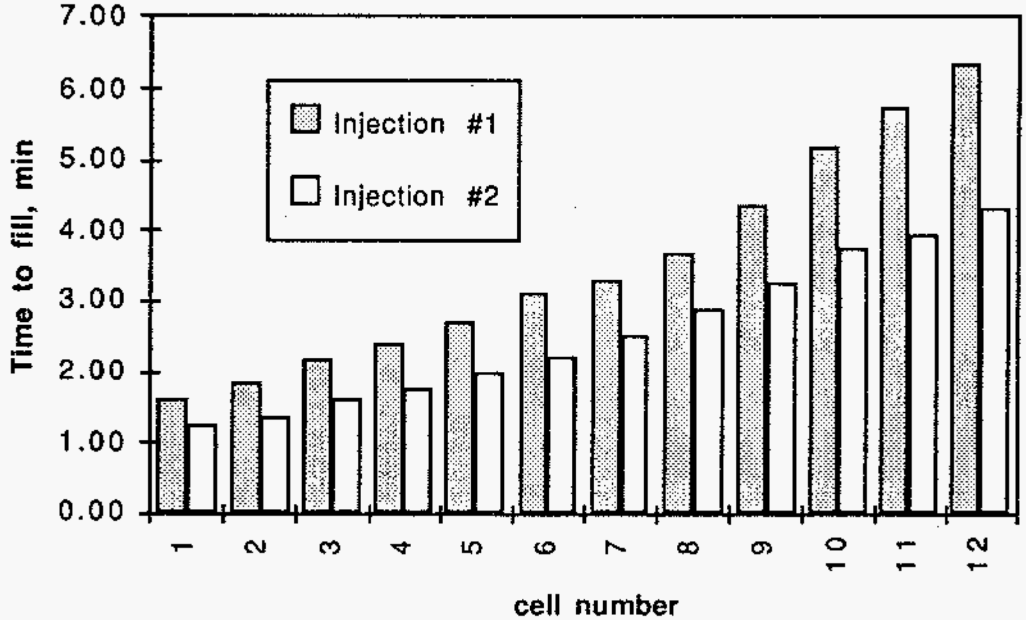

Figure 3. Using an improved injection technique (#2), the filling of a 12-cell stack (440 Ah) is accomplished in 4.3 minutes, at an average rate of 15 s/cell, (4 cells/min.). The filling of nine modules (3 parallel sets of 3 series hydraulically-connected modules) should take ~ 9 minutes.