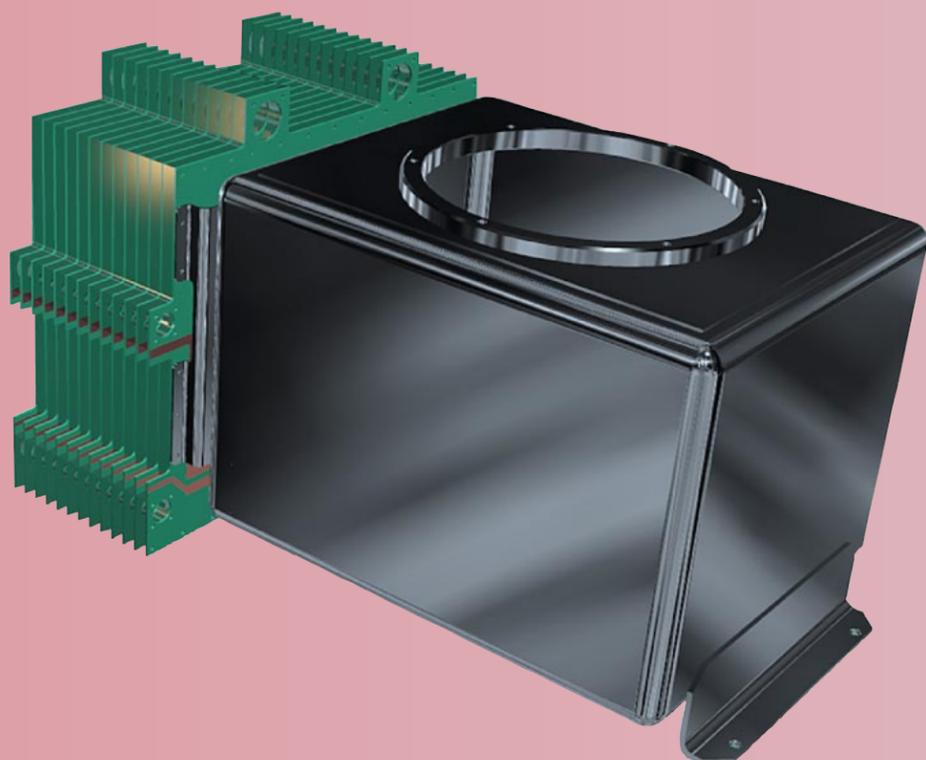


Powering Future Vehicles with the Refuelable Zinc/Air Battery



A recent road test at LLNL underscored the zinc/air battery's capacity to give electric vehicles some of the attractive features of gas-driven cars: a 400-km range between refueling, 10-minute refueling, and highway-safe acceleration.



Figure 1. Santa Barbara Municipal Transit District bus at Lawrence Livermore National Laboratory.

LABORATORY employees may have done a double take one day last February when they saw a blue-and-white bus emblazoned with the words "Downtown Waterfront Electric Shuttle" coursing around the site. The bus (Figure 1), on loan from the Santa Barbara Municipal Transit District, was being powered in part by a revolutionary new type of battery called the refuelable zinc/air battery. The battery was operated as part of the bus's power train to verify the road-worthiness of a fully engineered prototype.

Developed at Lawrence Livermore National Laboratory, the battery weighs only one-sixth as much as standard lead/acid batteries and occupies one-third the space, yet costs less per mile to operate. What's more, because the battery is easily refuelable, it promises trouble-free, nearly 24-hour-a-day operation for numerous kinds of electric vehicles, from forklifts to delivery vans and possibly, one day, personal automobiles.

The battery's inventor, LLNL electrochemical engineer John Cooper, was one of a handful of bus riders that day, monitoring the battery's performance and occasionally driving the remarkably powerful vehicle. The road test underscored the potential of the battery to give electric vehicles some of the attractive features of gas-driven cars: a 400-km range (250 miles) between refueling, rapid refueling (10 minutes), and highway-safe acceleration. The positive test results also cleared the way for discussions with a host of interested commercial partners about further development.

For all of its advancements, the chemistry of the zinc/air battery is relatively simple (Figure 2). The device combines atmospheric oxygen and pellets of zinc metal in a liquid alkaline electrolyte to generate electricity with byproducts of zinc oxide and potassium zincate. In operation, the battery consumes all of the zinc. Refueling is easily

accomplished by replacing spent electrolyte with fresh electrolyte containing recycled zinc pellets.

Such a refuelable battery has clear advantages over rechargeable and reconstructible batteries. For example, it can be "topped off" and even refueled on the roadway in an emergency. Except for the alkaline electrolyte (which contains the same hydroxide found in popular liquid drain cleaners), all of the materials making up the battery are relatively safe and do not pose the environmental dangers found in other battery types containing lead, concentrated acids, flammable metals, and other toxic or hazardous materials.

Because new zinc fuel can be generated from spent zinc oxide in the electrolyte by using relatively small and simple equipment designed by Laboratory researchers, the battery needs only a modest investment to support it. Refueling would be done at a company's home base using existing maintenance personnel. Quick, easy

refueling is a particular advantage for companies needing rapid refueling or extended use throughout the day for their fleets of shuttle buses, taxis, delivery vans, passenger vans, forklifts, or aircraft support vehicles.

Fast Development

The successful bus test capped a remarkably short development period for the battery. It started in 1991, when Cooper

noticed a Lab energy program poster display of a proposed oil shale retort. One display pictured crushed shale rock falling by gravity through a narrow channel before it was heated for oil extraction.

“The rock formed an open matrix by bridging small gaps, which slowed the feed rate,” Cooper recalls. “I reasoned that the

Figure 2. Nearly continuous use of fleet vehicles is possible with 10-minute refueling at 4- to 6-hour intervals using the process illustrated here.

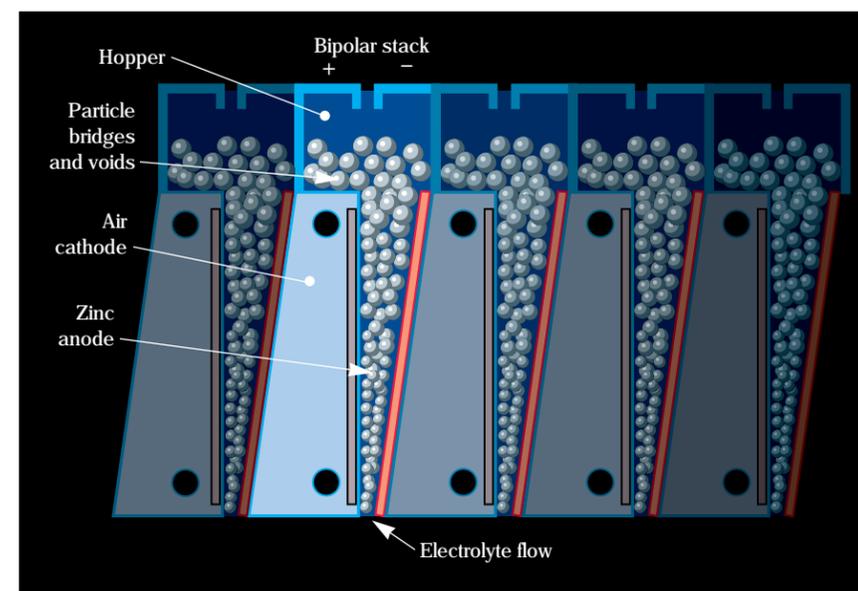
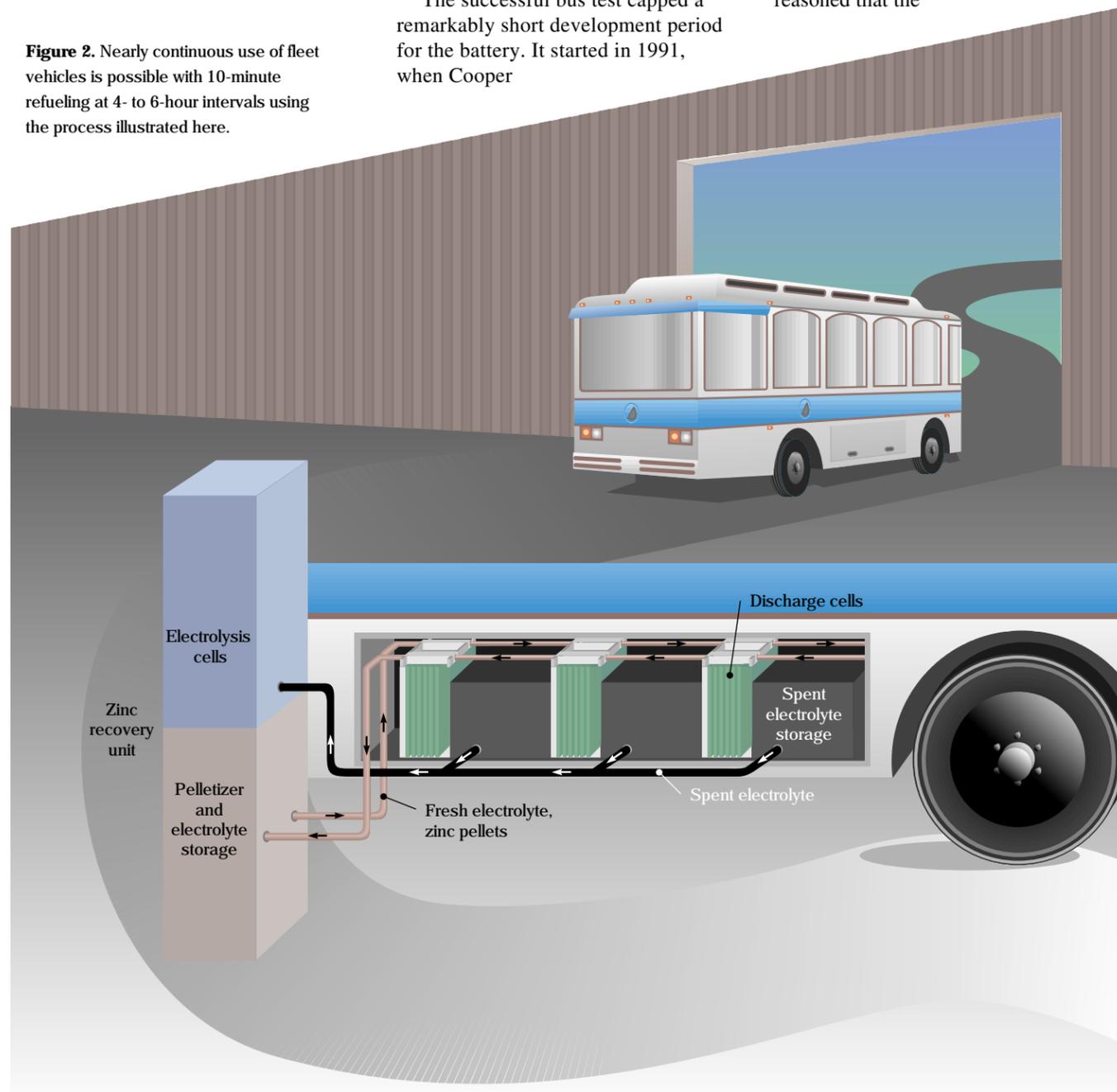


Figure 3. Zinc pellets are gravity fed from hoppers to cells.

same principle could be used to advantage in designing a particle electrode in a small gap, where we want an open matrix, allowing electrolyte to flow through freely.”

Some months later, he had successfully tested a self-feeding design for a zinc/air battery, with a hopper from which zinc particles fell through a restricted opening into a reaction cell (Figure 3). This novel design, the basis for Cooper’s 1993 patent on the battery (see box p. 10), solved a persistent problem with previous zinc/air battery designs, in which the zinc particles and reaction products would eventually clog the cell, preventing complete oxidation and reducing power generation.

Cooper is no stranger to battery design. In the early 1980s, he was the Department of Energy’s national program leader for an aluminum/air battery development effort headquartered at the Laboratory and conducted in cooperation with five corporate partners. That program advanced to the stage where it was transferred to industry, but the battery

did not see commercial development in autos because of ample and relatively cheap worldwide petroleum supplies and the battery’s chief drawback—aluminum corrosion. The technology instead evolved into batteries for emergency power reserve units, submarine propulsion, and forklift trucks.

With Livermore’s Laboratory Directed Research and Development funding in hand, Cooper worked for two years beginning in mid-1992 with a small team of mechanical and chemical engineers and technicians as a part of the Laboratory’s Energy, Manufacturing, and Transportation Technologies (EMATT) program. The project’s goals were to develop an engineering zinc/air prototype battery based on Cooper’s design, optimize its energy storage and power characteristics, and show that the self-feeding cells could operate under realistic road vibrations and accelerations.

Finally, to be successful in the marketplace, the zinc/air battery had to be able to be refueled quickly, easily, and safely without the need for a new

infrastructure of expensive, complex equipment. Energy researchers have long recognized that if a way could be found to refuel a battery simply and rapidly, it could provide an electric vehicle acceptable to consumers. Quick and easy refueling is important in fleet electric vehicles such as shuttle buses and delivery vans, which often must operate more than 8 hours daily.

The alternatives to refueling pose significant disadvantages. For example, exchanging batteries doubles the investment in batteries and specialized equipment; adding a gasoline or diesel engine produces air emissions; and electrical recharging takes hours to complete. (The traditional lead/acid batteries used in Santa Barbara’s 12 electrically powered city buses require 4 to 8 hours of recharging after 4 or more hours of use.)

During the development phase, the battery was tested in various configurations of cells and air electrodes. Cells were tested with air electrodes of 80, 250, 600, and 1000 cm², with the 250-cm² size judged the most

Battery Design and Operation

The LLNL zinc/air battery is constructed in modular form of unit cells (see the drawing below), each of which is made up of a hopper, a self-feeding galvanic cell, and refueling ports. The cells are joined together in a battery module that is connected to an electrolyte storage tank containing electrolyte and discharge products. The hoppers in each cell act as buffers, helping to protect the fragile air electrodes from damage during refueling, handling, or road shocks.

Each cell contains a lightweight plastic frame, an electronic circuit board, and a paper-thin air electrode. The electrode is the most expensive component in the battery and accounts for half the battery cost. As many as 12 cell stacks can be combined with one electrolyte storage tank to form a battery, and Cooper envisions both a 6-cell and 12-cell basic unit, as with lead/acid batteries.

In operation, 1-mm zinc particles are pushed along the base of a horizontal fill tube by the flowing electrolyte. The zinc particles flow through slots leading into individual hoppers above the reaction cell. (Cooper likens the process to “hosing gravel down a driveway.”) The very narrow (less than 3-mm-wide) cell opening allows the particles to feed uniformly into the cell to form an open, loosely packed structure, which permits the oxidation of all of the zinc and easy flow of electrolyte. At the same time, electrolyte flows easily upward through the cell and hopper to remove heat and reaction products. Electric power to drive both air and electrolyte pumping is negligible, consuming less than 0.5% of the battery’s gross power output.

The battery’s unusual modular design permits the independent choice of the battery’s power (measured in kilowatts) and energy capacity (measured in kilowatt-hours). The very lightweight cells provide the power, and a storage tank holding the reserve of heavy electrolyte determines (along with the zinc) the total energy capacity of the battery and most of the weight. “Within broad limits, we can combine any number of cells with any amount of electrolyte and zinc, depending on the ratio of power to energy we need,” Cooper says.

Given this unique characteristic, each kilowatt of

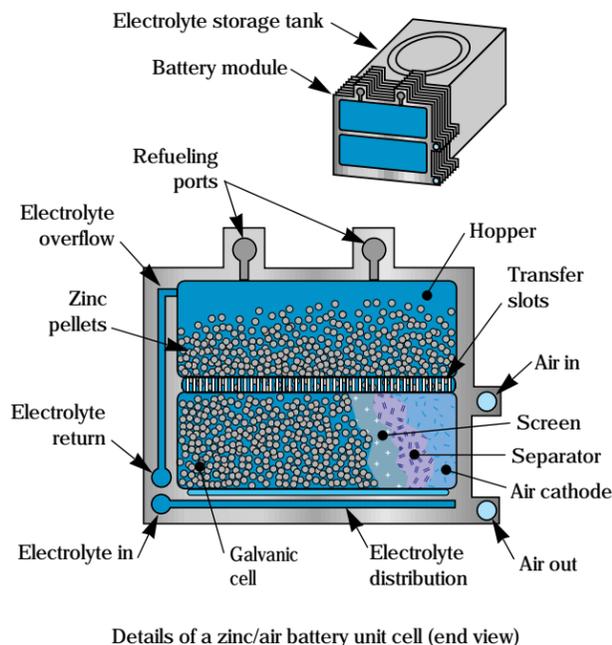
power contributes weight of 2.8 kg and volume of 3 L to the battery, while each kilowatt-hour of energy contributes 6.5 kg and 4 L. Thus, a battery with 30 kW of power and 60 kWh of energy weighs 474 kg (1040 lb) and occupies 330 L (12 ft³). Because power and energy are independent, the traditional terms of “specific power” and “energy density” have no unique meaning in this case. Still, Cooper speaks loosely of the battery yielding 140 Wh/kg in vehicle sizes, or about five times greater than that delivered by lead/acid batteries.

During refueling, spent electrolyte containing oxidized zinc particles is drained and fresh electrolyte is added. Stacks of 12 full-size cells are refilled at a rate of 15 seconds per cell in the laboratory. A battery pack consisting of three parallel branches, each with three modules of 12 cells—108 cells in all—would be filled in parallel from a common flow in about 10 minutes. Because the batteries of any vehicle would be filled in parallel, the refueling target of 10 minutes is a reasonable goal for any combination of three-by-three battery packs.

Existing bus or delivery van maintenance facilities would operate as ready-made refueling and recycling stations. Crews would replenish the electrolyte mixture with fresh material they had recycled on site. Exhausted electrolyte (an alkaline liquid containing zinc compounds) removed at the time of refueling would be recycled to produce new zinc fuel entrained in fresh

electrolyte. Recycling would be done with small-scale electrolysis equipment the size of a vending machine, which Livermore researchers designed.

The recovery equipment would be operated by the fleet’s vehicle maintenance crew and located at the fleet’s home base. The recovery unit’s cost would be about one-fifth that of a typical zinc/air battery because it would operate continuously (hence, be smaller) and would not require an expensive air electrode or heavy, expensive high-amperage power sources. The electrodeposited zinc plate would be shredded into small particles and then pressed into uniform, 1-mm pellets by a small machine.



Details of a zinc/air battery unit cell (end view)

appropriate for bus-size vehicles. Cells were operated for as long as 16 hours, with intermittent refueling. Stacks of 12 cell modules were refueled in only 4 minutes. Batteries were discharged in units of 1, 3, and 6 cells. To simulate road conditions, the research team used a vibration table for some tests.

Road Testing the Prototype

With laboratory tests complete by the end of 1994, the team prepared for a vehicle test sponsored by the U.S. Department of Transportation’s Federal Transit Administration. Early this year the Santa Barbara Metropolitan Transit District provided the Laboratory with a 6.6-m (22-ft), 5.7-metric-ton electric shuttle bus.

For the bus test, one six-cell, 7-V engineering prototype zinc/air battery was cabled in electrical parallel with a three-cell, 6-V lead/acid battery. This hybrid unit then was placed in series with the standard 216-V lead/acid battery power plant of the bus, using diodes to prevent reverse polarization of the zinc battery (Figure 4).

The bus was driven on a 1.2-km loop around the Lab for about 5 hours for a total of 120 km (75 miles), at which point the lead/acid batteries were 80% discharged. The road test validated the design of the self-feeding zinc/air cells under typical driving vibrations from starts, stops, turns, and accelerations. The self-feeding cells functioned correctly without becoming clogged with zinc particles or starved for fuel, and they operated well in the hybrid configuration. In addition, the test validated the integrity of the electrolytic air seal, the weak link in all metal/air batteries. Fatigue of this crucial seal caused by variations in full particle flow and stresses from the road surface could limit a battery’s lifespan; long-term

tests will be necessary before commercialization of the battery.

The test run also indicated the zinc/air battery’s potential savings in vehicle weight, battery weight and volume, and cost to operate over a lead/acid battery. For example, replacing the lead/acid batteries in the Santa Barbara bus with zinc/air units would reduce vehicle weight from 5.7 to 4.0 metric tons, the battery weight from 2.0 to 0.35 metric tons, battery volume from 0.79 to 0.25 m³, and electricity cost from 5.6 cents per mile to 4.7 cents per mile (Figure 5).

Yet power remains the same.

The zinc/air battery is less efficient than the lead/acid battery (60% versus

70% conversion efficiency, respectively). Nevertheless, the lighter weight of the zinc/air battery cut a total of 1.7 metric tons from a 5.7-ton bus, so the total energy use is 17% less than that of a lead/acid-powered bus because of the lower vehicle mass. Additionally, the marked reduction in vehicle weight means reduced tire and brake wear, which are major cost factors in large vehicles.

The Savings Are Long-Term

When commercialized, zinc/air batteries will probably be the least expensive advanced battery on the market. Cooper estimates a unit sized



Figure 4. Developer John Cooper, left, and electronic technician Douglas Hargrove, inside the Santa Barbara bus during its test run at the Laboratory.

for a bus would cost around \$2000. The dominating cost is that of the air electrode, about \$120 per square meter in large quantities. Since the battery delivers more than 4 kW/m² of air electrode, the cost of this unit is only about \$30 per kilowatt. When all components are considered, the total production cost is about \$50 per kilowatt for peak-power production plus \$2 per kilowatt-hour capacity. Lead/acid units cost about \$75 per kilowatt-hour.

The cost of the recycling equipment depends on how much fuel is needed each day. For buses running 12 hours a day, the recycling unit would cost about 25% of the battery it serves. The recycling unit has no expensive components and uses metal sheets instead of the more expensive air electrode.

Although the zinc/air battery has sufficient power by itself to power large

electric vehicles, combining it with another power source (lead/acid battery, supercapacitor, or flywheel) is recommended. The hybrid power plant allows better acceleration and greater flexibility in selecting routes with varying grades. Finally, with few peaks in the current, the life of the electrodes in the battery is expected to be as great as 12,000 hours. Regenerative braking, in which the considerable braking energy turns magnets to recharge a flywheel or capacitor, will decrease total energy use by another 10%.

Cooper's interest in zinc/air batteries has been shared by many energy researchers. Zinc/air batteries have been developed for both mobile and stationary power applications because of their low cost and high energy density. The batteries have found other uses in hearing aids, military field electronics, and laptop computers. In these applications, however, zinc/air batteries are very expensive for the low power they provide, and they cannot be refueled.

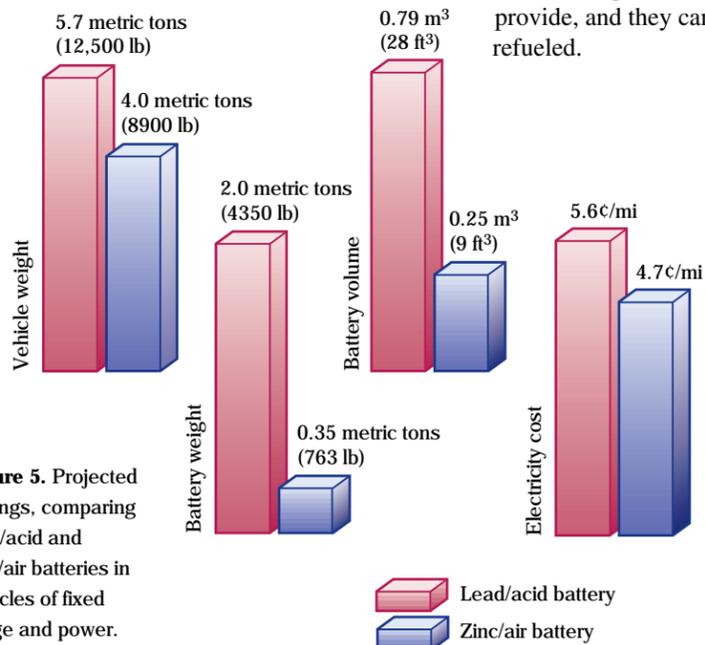


Figure 5. Projected savings, comparing lead/acid and zinc/air batteries in vehicles of fixed range and power.

Commercial interest in zinc/air batteries for powering electric vehicles has grown significantly during the 1990s. An Israeli company in 1994 demonstrated a zinc/air-battery-powered van that had a range of more than 420 km with highway acceleration and sustained speeds. However, unlike the LLNL design, that battery is not refuelable; the battery's spent electrodes must be delivered to a plant for reconstruction.

Commercial Development

The LLNL refuelable zinc/air battery is now ready for advanced development as part of a commercialization effort with one or more industrial partners. Cooper has received scores of requests for more information from battery manufacturers and potential users. Many inquiries have been in response to news articles about the battery that appeared earlier this year in the *London Times* newspaper and *Design News* magazine. "There is an enormous world market, with literally millions of units that could take advantage of the new battery," he says. "More than 90% of new battery concepts fail, so no one talks to you until you've demonstrated a prototype unit that works on the bench and in a vehicle."

Cooper cautions that before commercial units find their way into vehicles, more work needs to be done, particularly in determining the longevity of the air electrode under actual or simulated road use and how many times the zinc reaction products can be recycled. Cooper believes these challenges are not insurmountable and that full-scale production can begin as early as 2000. One strong selling point is that, because of its modular design,

the battery can easily be tailored to accommodate varying needs, from small forklifts to large urban buses to silent military vehicles.

Down the road, passenger cars might also be powered by zinc/air batteries. As the cars proliferated, they could be refueled at service stations. Cooper says some oil companies are interested in the idea because it is a potential new market for their stations. In the long run, commercial zinc recovery plants could take advantage of large-scale production using electrolysis cells combining electrical and hydrogen energy to reduce zinc oxide to zinc. This process would operate with a substantial savings over the purely electrical route to recovery and would give the zinc/air battery an almost unbeatable total energy efficiency. The zinc/air battery's total energy use would be comparable to a fuel cell at one-tenth the cost.

Another factor favoring electric vehicles is energy flexibility. The U.S. transportation sector depends almost exclusively on crude oil, most of it imported. Electricity, by contrast, can be produced by power plants using a wide variety of energy sources, including coal, natural gas, hydroelectric power, solar energy, and nuclear energy.

A final argument for electric vehicles is that they require less maintenance and are easier to repair because the vehicle's "power train" is simpler than that found in gasoline-powered vehicles. In a typical electric vehicle, an electric motor powered by batteries provides torque to the front wheels. An electronic motor controller regulates current through the motor and transforms the battery's dc voltage to ac.

The switch from gasoline power plants to zinc/air batteries for passenger cars would make the most economic and environmental sense in urban areas, where gasoline-powered cars burn excessive fuel and generate significant pollution in start-and-stop driving. Such a fundamental shift to electric propulsion is no longer just an environmentalist's dream. In 1990, the state of California enacted regulations requiring 2% of all cars sold in the state to run without any polluting emissions by the year 1998. The exact benefit to the environment, however, depends on the emissions generated by local power plants that produce the electricity to build, recharge, or refuel the batteries.

Cooper says that the new technology is likely to have its greatest impact on fleets of electric vehicles. "Buses, vans, and industrial vehicles have a unique combination of high daily usage, low power requirements, and in-place service infrastructure. This combination makes their owners and operators an ideal market for refuelable zinc/air batteries."

Key Words: alternative fuel; electric vehicle; refuelable; zinc/air battery

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About the Engineer



JOHN COOPER holds a Ph.D. in physical chemistry with special emphasis on electrochemical engineering. For 10 years at the Laboratory, he has worked on electrochemical batteries as power sources for alternative, environmentally clean vehicles. From 1978 to 1983, he was the national program leader for the Department of Energy's efforts to develop aluminum/air batteries. His professional career has focused on active research in

electrochemical process development for environmental remediation and waste processing, textile manufacturing, electroplating, and metals recovery. Other research interests include optical crystals and processes, transport phenomena in aqueous systems, and molten salt processes. Cooper is the author or coauthor of more than 80 publications in the area of electrochemical processes and devices.

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