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UCID- 17426-77-8, 9, 10, 11

Lawrence Livermore Laboratory

Lithium-Water-Air Battery Project:
Progress During the Months of August-November

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December 20, 1977

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Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

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Abstract

This report summarizes work done on the Lithium-Water-Air Battery Research Program in the work period, August through November, 1977.

A prototype single-cell fuel cell has been developed. The single galvanic cell consists of two, 30-cm square aluminum plates separated by a two-faced air cathode mockup. The purposes of the model are to determine (1) ease and cost of electrode servicing and (2) weight and manufacturing cost of the hardware.

Projections of fuel cell performance and cost were made, based on the prototype cell and the performance of cells of similar anode-cathode spacing produced by Lockheed Missiles and Space Company. Performance is a strong function of the weight of water carried in the fuel cell, as water is the limiting reactant when sufficient aluminum is carried for a vehicle range of 1600 km.

Research concerning the electrochemistry of calcium in aqueous chloride-hydroxide electrolytes is summarized with reference to a recent presentation of the work at the Fall Meeting of the Electrochemical Society.

Polarization curves were obtained for the aluminum alloy used by Lockheed in fuel cell research. The experimental data agrees closely with Lockheed's published results.

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Introduction

During the work period reported here (August - November), Lawrence Livermore Laboratory has undertaken the design and construction of a full-scale, single-cell model of an aluminum-air fuel-cell. Parallel with this effort is a systems study of fuel cell performance characteristics based on the weights of components and reactants and the performance of similar cells tested at Lockheed Missiles and Space Company.

Earlier work in the electrochemistry of calcium has been completed, and results were presented at the Fall Meeting of the Electrochemical Society. Work was continued in the areas of: (1) effects of electrolyte additives and (2) effects of impurities and metallurgical pretreatment of the calcium anodes.

Experimental studies of selected aluminum alloys were begun.

Development of Fuel Cell Prototype Hardware: the Unit Galvanic Cell

The Lawrence Livermore Laboratory has primary responsibility for determining the economic feasibility of the metal-air fuel cell transportation systems. In a review published earlier this year, it was estimated that the servicing of the electric vehicle (introduction of plates and withdrawal and collection of reaction product slurries) should contribute significantly (ca. 10%) to the total cost of ownership and operation of the vehicle.^{1,2} Consequently it is of paramount importance to accurately determine, with the use of a model cell, the ease of anode and cathode replacement and electrolyte removal, and hence the cost of these services to the consumer. The Laboratory has undertaken the task of developing and demonstrating a full-scale unit galvanic cell. The model is shown in Figures 1-4.

The cell stack consists of alternating anode- and cathode chambers, which are constructed to allow the rapid entry of anode fuel plates (dimensions 30 x 30 x 0.25 cm) and air cathode modules (dimensions 32 x 36 x 0.63 cm). The unit cell (i.e., unit electrical element of the power source) consists of air cathode chamber and one-half of each of the two adjoining anode chambers. In each unit cell, the anode plates are shorted together, as are the two surfaces of the air cathode module. During operation, electrolyte is forced through grooves cut in the air cathode module, the anodes being held in contact to the cathode module by the air-pressurized polyethylene bellows. The bellows also serve to seal the gap between the anode and anode-chamber walls.

The dimensions of the unit cell were chosen such that each cell provides 5.0 kWh at 400 W. Fifty such cells connected in series produces a 75 V, 250 kWh, 20 kW fuel cell system. The unit cell energy content and power are based on the following operating characteristics: current density = 0.15 A/cm^2 ; cell voltage = 1.5 V; Faradaic efficiency of anode reaction = 0.95; internal power requirements for electrolyte and air pumping = 3% of total power. These data correspond to an energy utilization of aluminum of 4.1 kWh/kg, or 51% thermodynamic efficiency.

The experimental model was constructed from Lucite, using standard machine shop milling techniques. However, mass-produced cells would be constructed of cast polypropylene of roughly the same dimensions, with small variations in shape and with ribbed construction as appropriate.

The fuel cell case consists of 100 identical molded parts, two of which are joined together to form the unit cell. The parts may be produced by transfer molding of dense polypropylene. Each unit cell weighs 400 ± 40 g. The cost of the unit cell has been computed from the cost of the polymer (\$0.27/cell) and the manufacturing cost of polypropylene and polyethylene parts of similar size, tolerances, and complexity (roughly \$0.25-\$0.75/unit).

Calculation of Fuel Cell Weight and Performance Characteristics

Performance characteristics of the aluminum-air fuel cell have been calculated for a range of cell discharge curves, using the fuel cell component weights shown in Table I together with the weights of electrolyte and reactants.

The net cell reaction is taken as:

The electrolyte is 6N KOH. In this design, the fuel cell is initially stocked with 62.5 kg of aluminum (sufficient for a range of 1000 miles given the state of art utilization of 4 kWh/kg-Al) plus an additional 16 kg. The additional quantity constitutes a "residual" or minimum inventory which remains in the cell to facilitate the addition of new plates.

With so large a stock of aluminum, the energy storage capacity is determined by the weight of water. The end of the cycle is determined by the condition that the aluminum hydroxide constitute 50%-vol of the reaction product slurry.

The time average weight of the fuel system is given by:

$$\bar{W}_{fc} = W_{fh} + \bar{W}_{Al} + \bar{W}_{O_2} + W_{H_2O} + W_{el} = 137 + 2.94 W_{H_2O} \quad (2)$$

where,

W_{fh} = fixed hardware weights = 90 kg

$\bar{W}_{Al}$ = average weight of aluminum = 47.25 kg

$\bar{W}_{O_2}$ = average weight of oxygen consumed = $0.444 W_{H_2O}$

W_{H_2O} = weight of water for reaction

W_{el} = weight of electrolyte = $1.50 W_{H_2O}$

Specific energy, specific power, and specific gravity are given by the following equations:

$$\hat{E} = e_F e_a \frac{(V^O - i r) (F/3.6) W_{H_2O}}{W_{eq} W_{fc}} \quad (\text{Wh/kg}) \quad (3)$$

$$\hat{P} = e_a \frac{(V^O - i r) i A}{W_{fc}} \quad (\text{W/kg}) \quad (4)$$

$$D = W_{fc} / (220 + 3.41 W_{H_2O}) \quad (\text{kg/dm}^3) \quad (5)$$

where

e_F = Faradaic efficiency of the anodic reaction

e_a = fraction of fuel cell output available for propulsion
(a measure of auxiliary power requirements)

V^O = zero current voltage intercept of linearized cell
discharge curve

i = current density

r = internal resistance of cell, including current
collector resistance, taken as 1.33 ohm-cm

F = Faraday's constant

W_{cq} = equivalent weight of aluminum

A = total area of anode plated = 9 m^2

Figures 5-9 show fuel cell performance based on a specific cell design consisting of 50 unit cells. In Figure 5, the total fuel cell weight is fixed at 250 kg, which allows a store of water of 38 kg. Power vs. energy curves are given for three different galvanic cell characteristic curves. In Figure 6, cell voltage and current is fixed (and hence total power is fixed), and energy density, power density, and energy storage capacity are given as functions of total fuel cell weight. In Figure 7, the energy and power densities are expressed as volume densities. Figure 9 shows the performance of the aluminum-air system on a double-logarithmic chart along with those of other electric storage batteries and fuel cells.³ It should be kept in mind that the left hand curve of Figure 5 (and 9) ($V^0 = 1.5V$) approximately represents the "state of art" of the galvanic cell performance, while the right hand curve (labeled 1.9 V) is the best an aluminum-air system is likely to achieve without innovations in air-cathode technology.

Calcium Electrochemistry

A paper presented at the Fall Meeting of the Electrochemical Society summarizes and analyses the results of our initial study of the electro-chemistry of calcium electrode in alkaline electrolytes.⁴

The calcium samples used in these studies were of the highest purity commercially obtainable, but this was insufficiently pure for controlled studies of effects of minor constituents on surface film composition and electrode resistance. Electrodes will be prepared from higher purity

stock obtained from Y-12 with the controlled addition of trivalent impurities. In addition, samples of calcium subjected to various heat treatments and coldworking have been prepared to determine the effects of these parameters.

The influence of electrolyte additives (Li^+ or NH_3) on calcium anode behavior has been investigated. Additions of Li^+ to alkaline electrolytes had little effect, but NH_3 additions produced a marked improvement in voltage efficiency through a reduction of anode polarization.

TABLE I. WEIGHTS OF COMPONENTS OF ALUMINUM-AIR FUEL CELL

I. Fixed Hardware

A. Galvanic cell cases (50 cells @ 400 g/cell)	20 kg
B. Current collectors	
1. Anode collectors (Aluminum disks)	3.8
2. Copper feedthroughs (anode compartment)	1.4
3. Inter cell busses	1.3
4. Intra cell busses (anode compartment)	2.4
C. Air bellows (30 mil polyethylene)	7.7
D. Weight Air Cathode Module	8.4
E. Interconnecting polypropylene tubes	0.6
F. Water storage tank (spherical, 40 l, 0.2 cm thick polyethylene)	1.1
G. Electrolyte storage and settling tank (100 l) dimensions: 30 cm x 50 cm x 66 cm, constructed of 30 mil steel lined with 30 mil polyethylene)	9.3
H. Flow suppressor (100 perforated sheets of polyethylene, 30 x 26 x 0.025 cm)	2.0
I. Supporting framework for flow suppressor	0.5
J. Motor (1 hp)	2.5
K. Gear reduction	3.0
L. Electrolyte pump (positive displacement, oscillating piston pump; polyethylene) 50 pumps, 90 g.	4.5
M. Air filter (removal of CO ₂)	2.0
N. Fiberglass shield	3.0
O. Air compressor (30 psi)	4.0
P. Aluminum frame for support of cell stack (dimensions: 65 x 75 x 40 cm; constructed of 2.5 cm angle aluminum stock, 0.25 inch stock)	6.3
Q. Shield and drip pan.	2.8
R. Heat dissipation channels (10m ² , 5-mil aluminum honeycomb.)	3.4
Total fixed hardware weight	90 kg

II. Fuels and Electrolyte

A. Aluminum

1. Average weight of aluminum, consumable
(1/2 of 62.5 kg required for 1000 mile range) 31.3 kg
2. Residual aluminum (minimum inventory during
restock) 16.0

B. Water (variable) (quantity determines cycle length) W_{H_2O}

- C. Weight of oxygen taken onboard during fuel cell
operation (average over cycle) $0.44 W_{H_2O}$

- D. Weight of electrolyte sufficient for 50%-vol
slurry at end of cycle (6N KOH) $1.51 W_{H_2O}$

Total weight of fuels and electrolyte $47.3 + 2.95 W_{H_2O}$ (kg)

Total weight of fuel cell system $137 + 2.95 W_{H_2O}$ (kg)

Figure 1. Fuel Cell Stack (Side View). A unit cell contains two anode plates and one two-faced air-cathode module, as shown at the top of the diagram. The unit cell case consists of two identical polypropylene castings joined along the cell's median vertical plane of symmetry.

Figure 2. Detail of Electrolyte Entrance Section of Unit Cell. A 30-mill thick polyethylene bellows, which is pressurized to 0.5 psi, provides dual functions of sealing the anode compartment and maintaining anode-cathode contact.

Figure 3. End View of Unit Fuel Cell. Electrolyte entrance section is shown, with positions of vertical flow tubes and anode sheets indicated.

Figure 4. Experimental unit cell model. In the right hand photograph, inflatable air bag, aluminum plate, and air-cathode mockup are shown. Electrical contact between feed throughs (shown) and the aluminum anode will be made with the use of current collectors between the aluminum and the air bag (current collectors are not shown).

Figure 5. Dependence of power-energy density characteristics on cell-voltage intercept and current density, for a fixed hardware design and water inventory. Fuel cell hardware weight = 90 kg; aluminum inventory = 47.25 kg average; water inventory = 38 kg; total fuel cell system weight = 250 kg; cell voltage = $V^0 - 1.33 i$. Data point corresponds to the most probable state of development and is the basis for the curves of Figure 6.

Figure 6. Effect of increasing the inventory of water on the performance of a 20 kW fuel cell. Fixed parameters: current density = 0.15 A/cm^2 ; cell voltage (operating) = 1.5 V; total anode area = 9 m^2 ; Faradaic efficiency = 0.95; auxiliary power requirements = 3% of nominal power.

Figure 7. Dependence of fuel cell performance characteristics on weight of water inventory. Fixed parameters: zero-current voltage intercept = 1.7 V; internal cell resistance = 1.33 ohm-cm²; weight of water inventory and total fuel cell system weight, as shown.

Figure 8. Energy and power density based on volume. Same parameters as in Figure 7.

Figure 9. Power and energy density for secondary batteries and mechanically rechargeable fuel cells. Lower energy density limit: near term or state of art; upper limit: 1990 projection.³ Curves for the Al/air system are those of Figure 5 and were derived from the weights of hardware components and reactants in Table I.

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We gratefully acknowledge the contribution of Earl Kelly to the design and fabrication of the fuel cell model.

"Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48."

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