ALUMINUM-OXYGEN BATTERIES FOR SPACE APPLICATIONS

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Summary

An aluminum-oxygen fuel cell is under development at ELTECH Systems Corporation. Several highly efficient cell designs have been constructed and tested. Air cathodes catalyzed with cobalt tetramethoxyporphyrin have demonstrated more than 2000 cycles in intermittent use conditions. Aluminum alloys have operated at 4.2 kW h kg⁻¹ at 200 mA cm⁻². A novel separator device, an impeller fluidizer, has been coupled with the battery to remove the solid hydrargillite discharge product. A 60 kW, 720 kW h battery system is projected to weigh about 2200 lb for an energy density of 327 W h lb⁻¹.

Introduction

Existing secondary batteries suffer from high life cycle costs, short range, and acceleration, as well as long recharge times. ELTECH Systems Corporation has operated research programs on aluminum-air or -oxygen batteries and components since 1980. The ultimate goal of this endeavor is the development of a battery for electric vehicles which will overcome these limitations. The high specific energy density of aluminum-air (300+ W h lb^{-1} Al) and power density (26 - 30 W lb^{-1} peak), as well as the feature of mechanical rechargeability, have made its application to an electric automobile viable and attractive. The battery is returned to its fully charged state by replacement of aluminum into the cell stack, replenishment of the oxygen supply (if necessary), addition of water, and removal of the aluminate discharge product.

The aluminum-oxygen battery releases electric energy by the dissolution of aluminum at the anode and reduction of oxygen at the cathode:

Cathode: $3/4 O_2 + 3/2 H_2O + 3 e^- \longrightarrow 3 OH^-$

Anode: Al + KOH + 3 OH⁻ \longrightarrow KAl (OH)₄ + 3 e⁻

The electrolyte can be either saline or alkaline, such as potassium or sodium hydroxide. The use of saline electrolyte dramatically limits the power output of the battery due to its low electrical conductivity and the tendency of the electrolyte to become gelatinous with cell discharge. The ELTECH system uses an aqueous 5 - 10 M solution of potassium or sodium hydroxide. As the

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aluminum discharges it dissolves until a level of saturation is reached. The aluminum then precipitates as hydrargillite:

 $\begin{array}{l} \text{KAl}(\text{OH})_4 \longrightarrow \text{KOH} + \text{Al}(\text{OH})_3 \\ \text{Al}(\text{OH})_3 \longrightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \text{ (hydrargillite)} \end{array}$

With a properly designed electrolyte management system, electrolyte conductivity can be maintained at a high level and the power output of the battery system is not compromised. The reaction product (granular hydrargillite) is then continually discharged or stored and removed periodically.

Oxygen cathodes

The heart of the aluminum-air battery is the air cathode. Cathode research at ELTECH has resulted in dramatic improvement in lifetime and performance (Fig. 1). This is due to improvements in structure, catalyst, and catalyst support. A major break-through in catalyst stability and life under intermittent use conditions was the development of cobalt tetramethoxyporphyrin (CoTMPP) as a replacement for platinum. Extension of cathode life is also due to the development of a two-layer electrode structure. A strong, hydrophobic, conductive wetproof layer of carbon is pressed into a



Fig. 1. Air cathode improvements: 1981:⊠, First c/PTFE wetproof layer RBDA. 1982/ 1983: Pure PTFE backing:ℤ, Pt/RBDA;Ⅲ, uncatalyzed RBDA;⊠, CoTMPP/RBDA; ℤ, CoPC + spinel RBDA. 1984 - 1985:Ⅲ, Improved c/PTFE wetproof layer CoTMPP/ RBDA.

screen current collector. Next, a catalyzed active carbon layer is added. This structure has virtually eliminated loss of mechanical integrity and flooding as modes of electrode failure. In addition to the two-layer structure, air cathodes have been custom fabricated to meet specific performance targets.

Anode development

Commercially available aluminum is not adequate for this application due to its very high corrosion rate in the alkaline electrolyte. Much work has been devoted to the optimization of aluminum alloys. ELTECH has developed and/or tested a variety of proprietary alloys which has demonstrated very high power densities and energy yields (Fig. 2). It can be seen that one alloy, BDW, has a specific energy of 4.2 kW h kg⁻¹ at 200 mA cm⁻² and a power density of 0.6 W cm⁻². In lieu of adding the alloying agents *in situ*, corrosion inhibitors and potential boosters are effective when added directly to the electrolyte. It was found that addition of small amounts of $In(OH)_3$ and Ga_2O_3 directly to the electrolyte reduced corrosion and polarization of a five-nines-pure aluminum anode.



Fig. 2. Energy yield vs. c.d. (all alloys).

Cell design and testing

With anode and cathode performance characteristics well within range of target values, the integration of these into a functioning aluminum-air prototype cell progressed rapidly. The first testing was done on the "wedge"





Fig. 3. Wedge cell, 5-cell stack.

type cell (Fig. 3). This prototype has operated routinely at a peak power of 440 W and 1.15 V per cell module. A 10 cell stack, or 4.4 kW unit, has recently been installed in a small vehicle and successfully operated as the main traction power source.

Several new battery designs are now in the prototype stage. Unlike the wedge cell these units are insensitive to changes in orientation, are sealed against electrolyte leakage, and can be manufactured by mass-production methods. Both designs are bipolar and have substantially reduced weight and volume. Multi-stack testing is expected to commence within several months.

System integration

The process system for the aluminum-air battery is shown in Fig. 4. Air or oxygen is provided to the cell in cryogenic or compressed form. The caustic electrolyte is recirculated to provide for optimum battery output and thermal management. Circulation and separation of the aluminate discharge product is provided by a novel device, an impeller fluidizer. This device (Fig. 5) separates, contacts, and pumps the solid/liquid electrolyte. A locally





Fig. 5. Helipump impeller fluidizer.

confined fluidized bed of fine particles is dynamically held within the vessel by the interaction of centrifugal force and convection, both produced by an impeller-driven swirling flow. Clear electrolyte stripped of solid discharge product is returned to the battery stack while a highly concentrated solidscontaining stream is stored for removal at a later date.

The importance of solids removal from the electrolyte, which is returned to the battery stack, is shown in Fig. 6. As solids build up in the stream, the electrolyte conductivity is compromised and the battery voltage is reduced.



Fig. 6. Electrolyte resistance vs. % solids.

Battery performance projections

Projections of cell performance can be made based on polarization and electrolyte conductivity generated at ELTECH. A high performance air cathode



Fig. 7. Current density vs. cell voltage for Al-air battery using RX808, 0.6 M sodium stannate, ELTECH air cathode, 5 M KOH, 60 °C, 1 mm gap.

coupled with an RX808 anode, using a stannate inhibitor in a 5 M KOH electrolyte at 60 °C is shown in Fig. 7. As can be seen, the cell voltage is in excess of 1 V even at current densities of 1.2 A cm^{-2} .

Projections of size and weight of a battery system can be made based on pilot cell testing. Table 1 gives an estimate of the size and weight of a 60 kW battery operated continuously for 12 h.

The power density of the aluminum-oxygen system is sensitive to the requisite power rating and larger battery systems have higher energy and power densities (Fig. 8).

Reactants	Weight (lb)	FT3	
Aluminum	600	3.6	
Oxygen	600	*	
H ₂ O	600	9.5	
Process equipment	400	10.0	
Total	2200	23.1*	
W h lb^{-1} :	327		

TABLE 1

*Oxygen form not specified.



Fig. 8. Aluminum-oxygen battery. Power density vs. rated power.

Conclusions

The aluminum-oxygen battery system is in the prototype stage at ELTECH Systems Corporation. Cell performance projections indicate that cell voltages in excess of one volt can be obtained at a current density of $1.2 \text{ A} \text{ cm}^{-2}$.