The performance of several alternative catalyst systems was also examined. In particular, cobalt tetramethoxyphenylporphyrin offers greatly improved voltages over platinum. Polymeric cobalt phthalocyanine plus spinel exhibits initial performance inferior to that of platinum but sustains its performance for over 100 cycles. In fact, uncatalyzed RB carbon offers a reasonably good performance-life-cost compromise.

Significant progress has been made in developing cathodes for this application. Improvements in cathode structure and the use of certain non-noble metal catalysts have resulted in an extension of cathode life from 100 cycles in 1981 to 1000 cycles at this date.

The specific objectives of the ELTECH cathode development program for 1983 are as follows:

- Develop a nonprecious metal catalyst for an air cathode with adequate performance to 1500 cycles;
- Identify the optimum structure and physical properties of a cyclically driven air cathode; and
- Determine the role of carbon corrosion in the failure of air cathodes.

CONTROL OF ELECTROLYTE COMPOSITION

Aluminum Company of America, Alcoa Laboratories

The objective of this research was to develop and demonstrate processes and components for the control of aluminum/air battery electrolyte composition through the precipitation of aluminum trihydroxide. The tasks under this contract included the following:

- Determine the physical properties of the circulating electrolyte as a function of its chemical composition and temperature;
- Establish conditions for hydrolysis of the electrolyte that will yield crystals of the desired particle size at rates sufficient to permit battery operation; and
- Develop engineering data for separation and washing of the aluminum hydroxide reaction product.

The contract was completed in April 1983 and a final report was published in May 1982. The following is a summary of the results of this work.

Determination of the physical properties of electrolytes

Physical property data on density, viscosity, and electrical conductivity were developed and reduced to correlation form for synthetic electrolytes containing nominally 7 g/l Sn and 0.02 g/l Ga in 3, 4, 5, and 6 M NaOH electrolytes. Concentrations of $Al(OH)_4^-$ were selected at six levels for each NaOH concentration. Measurements of each physical property were made at 25, 40, 60 and 80 °C.

Density correlation

$$d_e = 1078 + 20.74C_{Na} + 29.46C_{Al} + 1.199C_{Na}^2 - 0.7183T + 0.0028T^2$$

where d_e = electrolyte density (g/l), C_{Na} = NaOH (molar), C_{Al} = $Al(OH)_4^-$ (molar), T = temperature (°C).

Viscosity correlation

$$\begin{aligned}\log_{10}u = {} & 0.3507 - - 0.01467T + 1.032 \times 10^{-4}\, T^2 + C_{Na}(7.568 \times 10^2 + 6.191 \\ & \times 10^{-4}T - 1.201 \times 10^{-5}T^2) + C_{Al}(7.950 \times 10^{-2} + 1.855 \times 10^{-2}C_{Na} \\ & - 2.716 \times 10^{-3}T + 3.039 \times 10^{-5}T^2 - 1.855 \times 10^{-7}T^3)\end{aligned}$$

where u = electrolyte viscosity (centipoise).

Electrical conductivity correlation

$$K = a_0 + \exp(-E/RT)[a_1(3C_{Al} + C_{Na})^{1/2} + a_2C_{Na} + a_3C_{Na}^2 + a_4C_{Na}^3]$$

where K = conductivity (mho/cm), E = activation energy (cal/mol), R = universal gas constant ($E/R = 1857.62$), T = temperature (K), C_{Al} = $Al(OH)_4^-$ (molar), C_{Na} = NaOH (molar), $a_0 = 8.9081 \times 10^{-3}$, $a_1 = 80.3158$, $a_2 = 153.660$, $a_3 = 21.7830$, $a_4 = 1.12866$.

Nominal values for Sn and Ga impurities in the electrolytes were 7.05 g/l and 0.20 g/l, respectively. The correlations are valid over the temperature range 25 °C to 80 °C and for the following ranges of NaOH and $Al(OH)_4$ values:

NaOH (molar)	$Al(OH)_4$ (molar)
3	0.0 - 2.0
4	0.0 - 2.8
5	0.0 - 3.4
6	0.0 - 4.0

Determination of the hydrolysis reaction kinetics

A total of 69 isothermal batch experiments were performed to generate data from which a kinetic correlation for precipitation rate could be developed. Correlation of the individual rate constants derived using the integral method of analysis resulted in the following expression:

$$-\mathrm{d}c/\mathrm{d}t = K_0 \mathrm{e}^{-E/RT} A_t{}^{1.0} (C_t - C^*)^2/(C_{\text{Na-free}})^2$$

where $\mathrm{d}c/\mathrm{d}t$ = mol Al/min, $K_0 = 1.923 \times 10^5\ \mathrm{e}^{-8.735} C_{\text{Sn}}$, T = temperature (Kelvin), $E = 12.4 \pm 1.1$ Kcal/g mol, $R = 1.9872$ cal/g mol °C.

$$C_{\text{Na-free}} = C_{\text{Na-total}} - (C_{\text{Na}} \text{ equivalent of Al, Sn, and Ga in solution})$$

where C_{Sn} = molar Sn, $C_t - C^*$ = molar Al supersaturation, A_t = seed surface area m^2/l clear liquor (based on microtrac analysis).

The tin impurity adversely affects the precipitation rate with 0.06 M Sn resulting in a 41 percent decrease in the rate constant. Test results were insensitive to Ga concentration in the range studied (0 - 0.8 g/l). As part of the experiment, solubility data were developed and correlated.

$$\ln C^*_{\text{Al}} = -2.6964 + 0.01824(T) + 0.36185(C_{\text{Na}}) + 0.75575(C_{\text{Sn}}) + 14.811(C_{\text{Ga}})$$

where C_{Al} = molar Al at supersaturation, C_{Na} = molar NaOH, C_{Sn} = molar Sn, C_{Ga} = molar Ga, T = temperature °C.
The range of applicability of the above correlations is summarized in the following table.

Variables	Units	Range
Temperature	Kelvin	313 - 353 (or 40 - 80 °C)
NaOH	molar	3 - 5
Sn	molar	0 - 0.06
Ga	molar	0 - 0.00861
Seed surface area†	m^2/l clear liquor	10 - 70
Relative saturation	††	40 °C, R.S. = 3.0 max 60 °C, R.S. = 2.0 max 80 °C, R.S. = 1.0 max

†By microtrac analysis
††Relative saturation = $(C_{\text{Al}} - C^*_{\text{Al}} - C_{\text{Al}})/C^*_{\text{Al}}$

The rate equation form using total caustic in the denominator was also thoroughly evaluated. However, that equation is not believed to be as accurate as the equation using free-caustic squared in the denominator, especially at high relative saturations of aluminate.

Operation of continuous precipitator

A full-scale precipitator was designed, constructed, and operated in a continuous mode to assess production rate, population changes with time, and hardware aspects. A digester was used to perform the function of an aluminum/air battery, that is to drive $Al(OH)_4^-$ into solution. It was found that the required production of $Al(OH)_3$ could be attained at the high relative saturations indicated by computer simulations. The cyclone system for solid-liquid separation and classification did not function satisfactorily to provide a relatively solid-free electrolyte for recycle to the battery and a coarse fraction of the $Al(OH)_3$ as product leaving the mixed-suspension, classified product removal (MSCPR) precipitator. There is a need to test alternative designs for the precipitator hardware. These could include more effective methods for solid-liquid separation for mixed suspension type operation or alternatively, a fluidized bed operation.

Recent publications

1 T. G. Swansiger, Determination of the physical properties of the circulating electrolyte in the aluminum–air battery as a function of chemical composition and temperature, *Progress Report — Task 1*, Alcoa Laboratories, Alcoa Center, PA, April 20, 1981.

2 T. G. Swansiger, C. Misra, and F. S. Williams, Development and demonstration of process and components for the control of aluminum–air battery electrolyte composition through the precipitation of aluminum trihydroxide, *LLNL, UCRL-15503*, Alcoa Laboratories, Alcoa Center, PA, *Final Report of Subcontract No. 5724709*, May 1982.

ALUMINUM ANODE RESEARCH AND DEVELOPMENT

Reynolds Metals Company

This effort studied the feasibility of producing battery anodes directly from a Hall cell product, investigated the recycling of battery reaction products, and determined electrochemical properties of certain aluminum alloys.

The experimental program consisted of casting a series of alloys to simulated Hall cell metal and the use of these alloys in experiments to determine the effects of typical impurities on electrode efficiency. The addition of manganese to aluminum to minimize the deleterious effects of iron on coulombic efficiency was also examined.

The study of anode production from Hall cells indicated that aluminum anode plates containing 0.04 percent Ga and the minor impurities normally