Energy Savings by Means of Fuel Cell Electrodes
In Electro-Chemical Industries

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CONTENTS

Section	Page
1 ABSTRACT	1
2 INTRODUCTION	2
3 CONSULTATION AND ADVISORY MEETINGS	3
3.1 Electrowinning of Zinc with Hydrogen Anodes	3
3.1.1 Meeting at Anaconda Co.	3
3.1.2 Meeting at Tosco Corporation	5
3.2 Air Electrodes for Metal-Water-Air Batteries	7
3.2.1 Meeting at Lockheed	7
4 TECHNICAL DISCUSSION: Air Cathodes in Caustic Half Cells	11
4.1 Design of Experimental Caustic Half Cells	11
4.1.1 Cell Reaction	11
4.1.2 Baseline Cell	12
4.2 Air-Cathode Development	18
4.2.1 Background	18
4.2.2 Initial Design of Electrodes	18
4.2.3 Parameters for Evaluating Electrodes	19
4.3 Life Test Cathode	23
4.3.1 General	23
4.3.2 Life Test Data	23
4.3.3 Summary-Life Test Data	26
4.3.4 Rejuvenation Process	26
4.4 Effect of Half Cell Temperature on Air Depolarization of RA19 Type Cathodes	28
4.4.1 Design of Test	28
4.4.2 Experimental Data	28
4.5 Reproducibility of RA19 Type Cathodes	28
4.5.1 Performance and Air Efficiency Data	28
4.6 Half Cell Data at Current Densities Higher than 300 ASF	30
4.6.1 Preliminary Data	30
4.6.2 Limiting Current Density of RA19 Type Standard Air Cathode	32

Section	Page
4.7 Additional Tests With a 1" x 1" Cell	35
4.7.1 Air Efficiency Data for a 1" x 1" RA19 Type Cathode	35
4.7.2 Effect of Electrode Size-Air Plenum Design	
4.8 Cathode Polarization as a Function of Platinum Loading	37
4.8.1 Preparation of Catalyst	37
4.8.2 Experimental Performance Data:	
Δ Air-N ₂ Voltage at 300 ASF	37
4.8.3 Air Efficiency as a Function of Electrode Platinum Loading	41
4.9 Effect of Thin Porous Conducting Substrate on Performance of Air Cathodes	41
4.9.1 Background Information	41
4.9.2 Reproducibility of Standard Cloth	43
4.9.3 Evaluation of Other Substrates	45
5 TECHNICAL DISCUSSION: The Hydrogen Anode in Electrowinning of ZINC	50
5.1 Technical Considerations	50
5.1.1 Cell Reactions	50
5.1.2 Parasitic Electrode Reactions	51
5.1.3 Half Cell Evaluation of Anodes in Sulfuric Acid Electrolytes	52
5.2 Cell Design	52
5.2.1 Zinc Electrolysis Cell Design	52
5.3 Test Data	57
5.3.1 Experimental Zinc Electrowinning Data	57
5.3.2 Summary	59
6 TECHNICAL DISCUSSION: Metal-Water-Air Batteries	61
6.1.1 Air Cathode Half Cell Data-Sodium Aluminate Electrolyte	61
6.1.2 Evaluation of Prototech Company Air Cathode in an Aluminum-Air Battery	61
6.1.3 Materials Sent to Lockheed Space and Missile Corporation	63

FIGURES

Figure		Page
1	Top view, Caustic Cell	13
2	Right side view, Caustic Cell	14
3	Left side view, Caustic Cell	15
4	Front cross-section, Caustic Cell	17
5	Variations from Average Voltage on a Discharge Curve: 1000 Hour Test, 50 and 1000 Hour Test	22
6	Life Test: Prototech Company RA19 Air Cathode	25
7	Air Depolarization of RA19 Type Cathode as a Function of Half Cell Temperature °C	29
8	Δ Air-N ₂ Voltage Vs. %Air Efficiency Average Data for RA19 Type Cathode	31
9	Limiting Current Density of Prototech Co. RA19 Type Air Cathode	33
10	Δ Voltages: 1 Square Inch Electrode Area 0-1000 Amps/Square foot Current Density	34
11	Effect of Air Efficiency on Δ Voltage Air-N ₂ 1 Square Inch Electrode Area Current Density Equal to 288 Amps/ft ²	36
12	Effect of Electrode Size: Air Plenum Design Δ Voltage Air-N ₂ vs. % Air Efficiency	38
13	Air Efficiency as a Function of Electrode Platinum Content	42
14	Air Diffusion Characteristics of SKFB and SPWB6 Substrates	48
15	Prototech Company Hydrogen Anode Half Cell Data	53
16	Top View of Zinc Electrowinning Cell	55
17	Front Cross Section: Zinc Electrowinning Cell	56
18	Discharge Curve: Prototech Company Air Cathode - NaOH/NaAlO ₂ Electrolyte	62

TABLES

Table	Page
1 Discharge Data: Life Test Cathode	27
2 Effect of Cathode Platinum Loading on Air Depolarized Electrode Performance	39
3 Half Cell Data: Electrodes Fabricated on Inner and Outer Portions of Carbon Cloth Bolt	44
4 Evaluation of Electrode Substrates	46
5 Discharge Curve Data for SKFB and SPWB6 Substrates	47
6 Electrolysis of ZnSO_4 Solution	60

Photograph

1 Test Stand for H_2 Depolarized Electro-winning of Zinc	58
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Section 1

ABSTRACT

Caustic half cells are described and data reported for tests run to evaluate the technology involved in the operation of air cathodes for the Caustic-Chlorine Industry. The majority of tests were run at 300 ASF in a 23% NaOH electrolyte at 75°C with a CO₂ free air efficiency of 33%. Data is presented for a 7200 hour life test which is in operation and represents the state of the art. Runs have been made to identify the limiting current density and air efficiency for the standard RA19 type air cathode.

Also presented are tests involving cell temperature, electrode platinum variation and evaluation of several thin, porous, conducting substrates on which the catalyst layer is deposited during electrode fabrication.

Technical data on advisory meetings and experimental cell design for hydrogen anode evaluation in the electrowinning of zinc were reported. Preliminary results demonstrate a savings of over 0.6KWH/lb of zinc for 3 to 4 hours runs employing pure hydrogen as fuel and a 0.33 mg/cm² Pt anode.

In the area of metal-water-air batteries a consultatory meeting was held and the initial data obtained at Lawrence Livermore Laboratory for a standard Prototech Company air cathode in an Aluminum-Air Battery has been reported to be most encouraging.

Section 2

INTRODUCTION

During the past eight years, Prototech Company has developed durable and efficient fuel and air electrodes utilizing a new platinum electrocatalyst. This electrocatalyst, when supported on a high surface area carbon provides platinum particles of from 15 to 25 angstroms (110 to 170 m²/g) and gas diffusion electrodes fabricated with the catalyst have demonstrated excellent performance in several applications with only 0.05 to 0.50 grams of electrocatalyst per square foot of electrode area.¹

Utilizing this technology, the present program has been undertaken. Emphasis is being placed on anode and cathode development for the Electrochemical Industry, as well as consultation on and provision of air electrodes for metal-water air batteries research. In addition, a previously developed catalyst is being investigated for the selective oxidation of carbon monoxide in reformer streams, which development is important to hydrogen depolarized anodes which operate at relatively low (55°C) temperatures.

The use of hydrogen depolarized electrodes and air depolarized cathodes anticipates savings of the order of 1.0 volts in caustic-chlorine cells and 1.4 volts in the electrowinning of zinc.

1. U.S. Patent No. 4,044,193

Section 3

CONSULTATION AND ADVISORY MEETINGS

3.1 ELECTROWINNING OF ZINC WITH HYDROGEN ANODES

3.1.1 Meeting at Anaconda Co., Denver, Colorado on Operating Condition of Zinc Electrolysis Cell

Trip Report by W. Juda

Subject: Electrowinning of Zinc with Hydrogen Anodes

DOE-Prototech Contract No. ET-78-C-02-4881, Task 1)

Date of Meeting: September 22, 1978

Attendees: T. McNulty (Anaconda), W. Juda (Prototech Co.)

The discussion centered on initial operating conditions of an experimental zinc electrowinning cell using Prototech's hydrogen anode with emphasis on obtaining data suitable for an economic evaluation and comparison with the standard process using lead anodes.

Preliminary experiments in sulfuric acid had shown that hydrogen anode functioning is concentration dependent and that about 100 g/l of acid is needed for satisfactory anode performance (refer Section 5.1.3). Should this acid concentration result in an excessive loss of current efficiency at the cathode, an anion exchange (IE) membrane should be used to maintain low acid concentration in the zinc-bearing catholyte and high acid concentration in the acid anolyte.

After consultation, by phone, with Mr. W. Stern of Anaconda (in Anaconda's Tucson laboratories), the following was concluded.

Typical conventional cells (other than the rarely practiced "high acid" Tainton process--see 1936 AME volume on Zinc) operate at 35-45°C, with relatively expensive cooling required, using up to 120-130 g/l Zn, as AnSO_4 , and free acid between 10 g/l and 120 g/l. The temperature is kept low to minimize lead contamination of the cathode as well as avoiding a lowering of hydrogen overvoltage. For further details, refer to "Electrolysis of Zinc Sulphate Solution", Handbook of Non-ferrous Metallurgy, Vol. 2, Chapter XIV.

The hydrogen anode process may lead to different operating conditions. One major result of the process comparison is to be expressed as energy per pound of zinc, i.e. kw hrs/lb. While higher temperature operation and high acid may decrease cathodic current efficiency (C.E.), the lower voltage reduction may offset this effect, and hydrogen efficiency would be unaffected since cathodic hydrogen can be recycled to the anode. Lead poisoning is eliminated. Hence, operation at approximately 60°C, with about 100 g/l of free acid and 120 g/l Zn as AnSO_4 is a worthwhile first set of experiments, particularly since successful operation at the higher temperature would also result in important savings due to a lower cooling requirement. If reasonable

energy savings per lb. are obtainable with the above relatively high acid concentration for good H_2 -anode performance, no IE membrane would be necessary. Current densities should be in the range of 20-40 A/sq. ft. with the anode slightly smaller than the cathode to avoid "treeing" at the cathode edges (see above reference, p. 412). Anode-cathode spacing should be kept the same as in the conventional process, i.e., at first, at the upper practical limit of 2", for a deposition period of up one day. Pure aluminum sheets should be used as starting cathodes. The acid Zn sulfate electrolyte should be pure, except that 1-2 g/l of $MnSO_4$ and some sodium, potassium and calcium shall be added later. Zn depletion should be kept low (i.e. Zn can remain above 100 g/l) as ZnO is commonly added to the depleted electrolyte prior to further electrolysis.

3.1.2 Meeting at Tosco Corporation, Rocky Flats Research Laboratories, Golden, Colorado on Source of Impure Hydrogen

Trip Report by W. Juda

Date of Meeting: September 21, 1978

Attendees: Mark T. Atwood (Manager of Laboratories) and J.H. Barney (Manager, Engineering and Pilot Plants).

I outlined to Atwood, and again to Barney who joined the meeting later, the tasks of our DOE contract which relate to the application of our hydrogen anode to zinc (and copper and other metal) electrowinning. I stressed the importance of

locating an economic source of crude hydrogen substantially free from anode poisons such as CO. Our own work under the contract involved the experimental determination of energy savings in zinc electrowinning, first with CO-free hydrogen and then with crude hydrogen, containing initially about 0.75-1% CO, (as is present in hydrogen obtained by reforming hydrocarbons and shifting) purified by catalytic CO-oxidation. Atwood pointed out that hydrogen-rich streams (ca. 70% H₂) are available in copious quantities in refineries, but that they contain saturated and unsaturated hydrocarbons. To evaluate the potential use of such refinery streams in electrowinning, it is necessary to have information on the following.

- (1) The composition of the H₂-rich streams, including in addition to the H₂-content especially the nature and concentration of unsaturated hydrocarbons (and sulfur compounds if present);
- (2) quantitative information of the availability of crude refinery hydrogen; and
- (3) cost information, including costs at the refinery and delivered costs at electrowinning (mining or other) sites, the latter to enable us to evaluate the logistics problem.

Depending upon the above data, it may be worthwhile to experiment with such refinery hydrogen, including elimination or conversion of anode poisons, to establish their usefulness in metal electrowinning with fuel cell anodes. Atwood promised

to send me as much data on the above as is available at Tosco.

3.2 AIR ELECTRODES FOR METAL-WATER-AIR BATTERIES

3.2.1 Meeting at Lockheed Palo Alto Research Laboratory,
Palo Alto, California on Reactive Metal-Water-Air Batteries
for Automotive Propulsion
Trip Report by W. Juda

Subject: Reactive Metal-water-air Batteries for Automotive
Propulsion - (DOE-Prototech Contract No. ET-78-C-02-4881
Task 4)

Date of Meeting: September 18, 1978

Attendees: E. L. Littauer, K.C. Tsai, F. Bauman (LPARL)
J. Cooper, R. Homsy (Lawrence Livermore Laboratory)
W. Juda (Prototech Company)

The contractual and technical situation was reviewed for my benefit. The Continental Group (owners of Continental Can Co.) had acquired Lithium-air battery patents and had co-sponsored with DOE commercial development work for the above purpose at Lockheed over the past few years. Lithium air batteries have the advantage of forming a thin ionically-conducting solid film between the anode and the cathode (without short-circuiting), thereby realizing a very low internal resistance battery, especially under moderate pressure. Lockheed has built and operated Lithium batteries, essentially as described, for example, in their report to DOE No. COO/1262-1 of October, 1977 (under Contract No. EY-76-C-03-1262).

At the time of the meeting, no experimental work on Li-air batteries was in progress as the anticipated DOE cost-sharing had still not been signed. Littauer and Cooper anticipated that two contracts, one for FY-78 (agreed to, in principle, but not yet funded) and the other for FY-79 would be signed "promptly". It was further explained that the FY-78 contract would be between Lockheed and DOE, in parallel with a contract between Lawrence Livermore Laboratory (LLL) and DOE, whereas the FY-79 Lockheed contract would be a subcontract from LLL, the latter becoming prime contractor in FY-79 and thereafter. This contractual change would, however, not affect the budget at Lockheed, as above.

Cooper summarized his and his associates view that the aluminum air battery has so much superior a potential for automotive propulsion that future development work should almost entirely be directed to it rather than to further developing the Lithium air battery. While Littauer agreed to this view (see also the paper by Cooper and Littauer entitled "Mechanically Rechargeable, Metal-Air Batteries for Automotive Propulsion" presented at the 13th Intersociety Energy Conversion Engineering Conference, August 20-25, 1978), he stated that Lockheed would have to develop comparative experimental evidence between Li-air and Al-air batteries to justify abandoning the Li-air program in favor of Al-air work, in view of the Continental Group's ownership of Lithium-air patents.

I stated that Prototech's air electrodes have been tested extensively in half cells in sodium hydroxide solution, and recently also in mixed sodium hydroxide-aluminate electrolyte, with very encouraging results. (Refer section 6.1.1) With regard to the latter a discharge curve had been sent to Cooper and Littauer prior to the meeting. One very cursory test in Lithium hydroxide, at Prototech, was however, unsatisfactory indicating that further work in LiOH was indicated. After some discussion, it was agreed that such experimentation would best be carried out at Lockheed. In order to give Lockheed's staff the benefit of Prototech's experience with its air cathodes, it is necessary to make available to Lockheed Prototech's proprietary know-how under a confidentiality agreement. I have sent such a proposed agreement to Dr. Littauer.

Cooper expressed interest in testing a Prototech air cathode in his laboratory in an Al-air battery or in a half-cell with a sodium hydroxide-aluminate electrolyte. Cooper is running such cells with electrode areas of about one square inch and is anxious to assess Prototech's air cathode performance promptly. In view of Prototech's confidentiality requirement preventing disclosure of proprietary know-how to a secrecy agreement, Cooper's start-up and other procedures were described to R. Allen of Prototech, by phone. R. Allen and W. Juda anticipated that these techniques are likely to be adequate to insure reasonable, though perhaps not optimum performance with Prototech's air cathode, (based on Prototech's experience with half-cells.) W. Juda then gave

Cooper a 3" x 3" air-cathode for this preliminary evaluation.

After lunch, Littauer took me through the Chemistry Laboratory and gave me an overview of Lockheed's activities.

Air electrodes as described in the above reprint to DOE (No. COO/1262-1) were exhibited.

Upon completion of the Lockheed-Prototech confidentiality agreement we plan to make available to Lockheed air-cathodes and know-how relating to their use for their experimentation with Li-air as well as Al-air batteries, as soon as their program is reactivated under the above contracts.

Section 4

TECHNICAL DISCUSSION

Air Cathodes in Caustic Half Cells

4.1 DESIGN OF EXPERIMENTAL CAUSTIC HALF CELLS

4.1.1 Cell Reactions

The evaluation of air breathing cathodes, as an energy saving device for the caustic chlorine industry, can be expedited by utilizing half cell apparatus rather than the more complex ion exchange membrane - DSA Anode - Chlorine producing hardware. In a half cell apparatus, the overall effect is to consume oxygen (from air) at the cathode and generate oxygen at the anode, while the caustic electrolyte remains unchanged. The anode and cathode reactions are as follows.

The cathode can also be operated on oxygen or nitrogen. In the case of oxygen, Equation 2 describes the reaction. When employing nitrogen, hydrogen is liberated at the cathode according to the following reaction:

If equation 3 is operative, the electrolyte is not invariant but increases in caustic concentration because of the consumption of water in the electrolysis reaction.

4.1.2 Baseline Cell

The caustic half cell hardware described in Figures 1, 2, 3 and 4 has been developed over several years. It provides electrode areas of 2" x 2" (25.8 cm^2) separated by a distance of approximately $1\frac{1}{4}$ ". The caustic is continuously pumped from a reservoir through the electrolyte cavity which is somewhat larger in dimension than the working area of the electrodes so that gas bubbles rising to the top of the cavity do not reduce available electrode area. Both the gas and electrolyte exit from the top of the plenum, with the electrolyte returning to the reservoir and the gas vented to the atmosphere.

Figure 1, which is a top view of the cell, depicts the modular construction of the cell and the arrangement of inlet and outlet lines. Also shown is the position of the thermocouple well and electrolyte back pressure tube.

Figure 2 and 3 are the right side (anode side) and left side views (cathode side) of the hardware. A small heater pad mounted on the graphite end plate (right side) provides the means for operating the cell at temperatures between 50 and 100°C . The left side view outlines the 6 mil nickel foil window frame cathode current collector. This frame has a 2" x 2" opening and together with a gasket and thin Lucite plate of similar dimensions defines the cathode working area.

FIGURE 1, TOP VIEW

-14-

NICKEL ANODE AND
CURRENT COLLECTORS

FIGURE 2 , RIGHT SIDE VIEW

FIGURE 3, LEFT SIDE VIEW

When the bolts are tightened during cell assembly, the foil current collector and cathode are pressed together to provide a reproducible means of distributing current to the electrode.

The front cross section, as shown in figure 4, displays the air plenum and electrolyte cavity. A Lucite window allows observation of the entire air chamber and gas side of the cathode. Visual inspection of the gas side of the cathode is highly desirable because gas diffusion electrodes tend to "weep", especially when utilized as air cathodes in caustic electrodes and the effectiveness of means to prevent or minimize this phenomenon is most readily ascertained visually. It will be observed that the air plenum is void of any gas distribution system. To this point in our investigation no attempt has been made to optimize this variable; such optimization is likely to become necessary when the cells are scaled-up. This cell design, especially the electrolyte cavity has several desirable features. Because of the modular construction, an ion exchange membrane can easily be placed between the anode and cathode and sufficient space is available to insert a Luggin capillary against the cathode and connect a reference electrode into the circuit.

While figure 4 clearly shows the gas space above the working area of the electrodes, it does not show the electrolyte and gas vent which is located in the rear of the cell, directly behind the electrolyte back pressure tube.

FIGURE 4., FRONT CROSS-SECTION

4.2 AIR-CATHODE DEVELOPMENT

4.2.1 Background

Prototech Company has been involved in an internally sponsored research project directed at adapting its proprietary depolarized cathode to typical caustic-chlorine cell conditions for about two years prior to August 1, 1978. When this project was initiated, proprietary processes in the fields of Pt catalysis and electrode fabrication had already been developed at Prototech during several preceeding years. These developments had produced low loaded carbon supported Pt air cathodes which have now been proven to be efficient and stable in a caustic half cell application for the production of hydroxyl ions. The electrodes were also evaluated, for short term performance, in caustic chlorine hardware containing an ion exchange membrane (nafion) and found to provide a saving of from 0.9 to 1.0 volts over the traditional iron grid cathodes employed in today's industrial processes.

4.2.2 Initial Design of Electrodes

Early experimentation with thin (10-30 mils) Pt catalyzed air electrodes (0.33 mg Pt/cm^2 of electrode area) which had performed well in acid media, revealed several problems when tested in the caustic electrolyte.

1. The electrodes were prone to uncontrollable weeping of electrolyte through the catalyzed substrate to the gas side.

2. Air efficiency was very low at 300 Amps per square foot. (ASF)
3. Flooding problems reduced the ability of the electrode to function under air depolarization at 300 ASF for more than a few days.

A modification in the technique of catalyzation and a choice of a better substrate resulted in an electrode which performed very satisfactorily in the catalyst range of 0.30 to 0.50 mg/cm² Pt.

Employing such electrodes, a number of tests were run for many hundreds of hours which proved the feasibility of an air depolarized cathode as an energy saving device in the production of hydroxyl ions. The electrode reaction appeared to be in accordance with equation 2 as no H₂ gas was produced. (An iron cathode reacts according to equation 3.)

4.2.3 Parameters for Evaluating Electrodes

The performance of an air depolarized cathode in a caustic half cell was initially evaluated as follows:

- a) Difference in Voltage (ΔV N₂ - Air: Cathodic H₂
Evolution vs. Cathodic Air Operation

When the cell operates in the absence of air, hydrogen is evolved at the cathode during electrolysis. As the cathode is platinized, the hydrogen overvoltage is low and increases slightly with increasing

current density. Thus, introducing pure nitrogen to the cathode yields a hydrogen-evolving cathode which is, in effect, merely a reference electrode requiring a correction for the hydrogen overvoltage. This overvoltage is estimated to be of the order of 50-100 mv at 200-300 ASF. When the gas feed to the cathode is switched from nitrogen to air, air cathode operation sets in, and the drop in cell voltage ($\Delta V_{N_2 - \text{air}}$) is then a measure of the air cathode performance, with only the H_2 overvoltage being a relatively minor correction. At least every 168 hours of running (1 week) a discharge curve is taken over the range of 50 to at least 300 ASF on air and nitrogen. The difference in cell voltage values between air and nitrogen at 300 ASF have been arbitrarily used as criteria of cathode performance. This difference ranges from 0.78 to 0.82 volts for acceptable initial performance, and progression to a lower level has been viewed as some sign of cathode weakening.¹

b) Δ Voltage O_2 - Air

Similar to a), comparison of voltage difference

1. The hydrogen overvoltage on platinized carbon is at least 0.2 volts lower than on an iron grid. Thus, the overall voltage reduction for air depolarization of an air diffusion cathode is the Δ value of the air and nitrogen readings plus at least 0.2 volts minus the hydrogen overvoltage correction.

between cathode operation on air and oxygen, under electrolysis at various current densities, provides data on diffusion, flooding and catalyst poisoning problems. In theory $\Delta V_{O_2 - \text{air}}$ should be merely the Nernst difference estimated at 27 mv at 33% air utilization. Invariably, $\Delta V_{O_2 - \text{air}}$ is larger than a Nernst loss and as the $\Delta V_{\text{air-nitrogen}}$ decreases the $\Delta V_{O_2 - \text{air}}$ increases. Typical values between air and oxygen at 300 ASF and 33% efficiency are 0.10 to 0.13 volts, demonstrating losses other than Nernst losses. These losses are attributed to diffusion losses perhaps resulting from electrode structure involving accessibility of platinum particles.

c) Cathode Stability as Determined by Cell Voltage

Change in cell voltage can be less than a) and b) (less than 0.1 volts) with a stabilized cathode and includes anode polarization and IR fluctuations. However, experience with this type of hardware has proven that an abrupt variation from a stabilized cell voltage is usually indicative of changes in cathode performance, and conversely, when the cell voltage remains relatively constant the cathode is functioning in a stable manner. Figure 5 is a plot of the variation of the 50 hour and 1000 hour discharge curves from the average of seven curves taken during the course of a 1000 hour run. It is observed that a line drawn

Figure 5

Variation From Average Voltage
on a Discharge Curve
1000 Hour Test
50 and 1000 Hour Points

through the original and final points would pivot around a current density of 250 ASF along the average line with the lower current densities showing a somewhat decreased cell voltage and the higher, an increased voltage. No explanation can be afforded at this time for this phenomenon. Since the variation is small (<0.1 volt), the use of cell voltage as a rough monitoring device for cathode stability is acceptable.

4.3 LIFE TEST CATHODE

4.3.1 General

Early in December, 1977, Prototech Company started a life test on an air breathing cathode with a platinum loading of 0.43 mg/cm^2 , the platinum being supported on a high surface area carbon. (See U.S. Patent No. 4,044,193.) This electrode is still in operation and represents the state of the art at Prototech as of October 31, 1978.

4.3.2 Life Test Data

The life test has been conducted at 75°C with 23% NaOH at an overpressure of air of 15 inches of water. This electrode, as well as all others run at Prototech Company, is being evaluated employing compressed air generated by an on site compressor which is scrubbed free of CO_2 prior to entering the cell. Data presented in figure 6 is a plot of the Δ air vs.

nitrogen voltage for the life test cathode that has accumulated over 7000 hours of operation, over three periods. An important goal of the life test has been, and continues to be, to determine whether the performance decay of Run 1 was reversible in that initial performance could be restored and then maintained by a simple rejuvenation process. Prior to run 2 and run 3, the electrode was restored by a simple washing and sintering procedure and was repositioned in the proper alignment in the same cell before initiating run 2 and run 3. The duration of run 2 was 2370 hours with a discernible voltage decay (see fig. 6). To this point in time, October 31, 1978, an additional 2113 hours of running time at 300 ASF (33% air efficiency) has been logged on the life test cathode during the third run. Thus far, the electrode has performed in a remarkable manner and the latest data is clearly equivalent to the initial 700 hours of electrode operation. It is of interest to note that the life test cell now contains Hypalon gaskets, which is a change from the previously employed neoprene rubber gaskets.

This new run (3) confirms that at least one form of electrode decay is reversible and good performance can be restored by a simple rejuvenation process. Also, continuation of the life test still underway is expected to give an indication of the length of time of maintaining the restored performance level.

4.3.3 Summary - Life Test Data

Prototech Company's air cathode has been run in a caustic half cell for over 7200 hours. During this time period the electrode has decayed to unacceptable performance (twice) and has been restored to its original zero time performance level. Data presented in table 1 shows the actual cell voltage (including IR) of discharge curves taken during periods of stable operation for all three runs with this electrode. It is concluded that the platinum catalyst employed to fabricate the cathode has not deteriorated and the structure of the electrode has not been irreversibly damaged.

4.3.4 Rejuvenation Process

The simple process employed to rejuvenate the life test cathode has been tested on other electrodes. In all cases, the process has been capable of restoring initial performance but except for the life test cathode no electrode has been tested long enough after rejuvenation to yield additional information on the duration of this restored performance level.

Table 1
Discharge Data
Life Test Cathode

Run 1
Hour of Run 238
Total Hours on Electrode 238

ASF	Air Volts	N ₂ Volts	O ₂ Volts
50	0.89	1.80	0.87
100	1.19	2.07	1.15
150	1.48	2.33	1.42
200	1.74	2.59	1.66
250	2.00	2.84	1.90
300	2.25	3.05	2.14

Run 2
Hour of Run 70
Total Hours on Electrode 2965

ASF	Air Volts	N ₂ Volts	O ₂ Volts
50	0.92	1.83	0.90
100	1.20	2.09	1.16
150	1.47	2.33	1.40
200	1.72	2.55	1.63
250	1.99	2.78	1.87
300	2.22	2.99	2.08

Run 3
Hour of Run 70
Total Hours on Electrode 5290

ASF	Air Volts	N ₂ Volts	O ₂ Volts
50	0.89	1.75	0.87
100	1.15	2.01	1.12
150	1.42	2.27	1.37
200	1.69	2.52	1.62
250	1.95	2.78	1.87
300	2.22	3.02	2.12

Run 3
Hour of Run 2113
Total Hours on Electrode 7234

ASF	Air Volts	N ₂ Volts	O ₂ Volts
50	.88	1.73	.86
100	1.15	2.01	1.11
150	1.42	2.27	1.37
200	1.68	2.54	1.62
250	1.98	2.80	1.88
300	2.24	3.04	2.12

4.4 EFFECT OF HALF CELL TEMPERATURE ON AIR DEPOLARIZATION OF RA19 TYPE CATHODES

4.4.1 Design of Test

One of the cell variables under investigation during the current contract is cathode air depolarization as a function of cell temperature.

Employing an air cathode containing 0.33 mg/cm^2 Pt, half cells were run at 53°C , 75°C and 85°C . These temperature levels are sufficiently different to provide data regarding short term effect of temperature on air cathode performance.

4.4.2 Experimental Data

Data presented in figure 7 shows that, at least on a short term basis, cell temperature within the above range is of little consequence to the ability of Prototech Company air cathodes to perform in an acceptable manner at 33% air efficiency and at a current density of 300 ASF.

4.5 REPRODUCIBILITY OF RA 19 TYPE CATHODES

4.5.1 Performance and Air Efficiency Data

It has been found that RA19 type air cathodes are extremely reproducible. Since most caustic half cells have been run at 75°C with 23% NaOH electrolyte and at an air efficiency of 33%, which are the operating conditions of air depolarized cathode life test discussed in section 4.3, the data

Figure 7
 Air Depolarization of RA-19 Type Cathode
 as a function of
 Half Cell Temperature °C

2.5% NaOH electrolyte
 33% air efficiency (CO₂ free air)
 0.33 mg/cm² Pt cathode

○ = 85°C Cell Temperature
 △ = 75°C Cell Temperature
 Z = 55°C Cell Temperature

presented in table 1, for the life tests, are considered to be typical discharge data for standard electrodes. Because the IR drop across cells may vary slightly from test to test, the slope of all discharge curves are not identical but the vast majority of standard electrode data can be normalized to the life test performance.

Also, in addition to discharge curves, another area of importance is the performance of an electrode at increased air efficiency. Figure 8 is a plot of the average 300 ASF Δ air-N₂ values obtained from cells over an air efficiency range of 16 to 74.7%. This plot is considered to be the present state of the art for 2" x 2" electrodes run in the hardware described in section 4.1.2 and it will be used to evaluate other substrates as well as the low loaded air cathode discussed in section 4.8.

4.6 HALF CELL DATA AT CURRENT DENSITIES HIGHER THAN 300 ASF

4.6.1 Preliminary Data

Several tests have been run at current densities (340-350 ASF) above the customary 300 ASF. At 33% air efficiency it was found that stable performance was easily achieved but that the Δ air-N₂ voltage had decreased by 20-40 mv.

The presently utilized hardware was ruled unacceptable for studying current densities higher than 350 ASF due to the increased evolution of O₂ at the anode (half cell reaction) which interfered with the normal exit of the flowing electrolyte from the cell.

Figure 8

Δ Air-N₂ Voltage vs % Air Efficiency
Average Data for RA-14 Type Cathodes

One test was performed at 400 ASF by masking off 25% of the electrode and running the cell at the same amperage (8.30 amps for 4.0 square inches of electrode area) as is employed for 300 ASF tests. This run demonstrated the need to determine the limiting current density of an air breathing cathode because it appears that the Δ air-N₂ voltage data lie on the straight line discharge curve even at 400 ASF.

4.6.2 Limiting Current Density of RA19 Type Standard Air Cathode

By decreasing the cathode area to 1 square inch it has been possible to obtain air depolarized cathode data up to 1000 amps per square foot. These data, figure 9, were obtained at an air efficiency of 20% for all of the current densities tested and it was found that an RA19 type cathode does not attain a limiting current density out to 1000 ASF.

When these data, which include IR, were plotted, figure 10, using Δ O₂-N₂, Δ air-N₂ and Δ O₂-air voltages several striking features were observed. First, the air data has a pronounced break at around 500 ASF. (Not readily seen in figure 9.) For both Δ air-N₂ and Δ O₂-air points, the curves show two straight line segments with a dramatic change in slope occurring approximately at the 500 ASF point. One possible explanation for the phenomenon is that hydrogen evolution commences on the air depolarized cathode around 500 ASF and the change in slope reflects competition between two reactions. Second, the Δ O₂-N₂ curve shows that the hydrogen overvoltage on the cathode increases with current density. And third, the RA19

Figure 9

Limiting Current Density
of
Proto Tech Co. RQ-19 Type Air Cathode

Cell Temp °C = 75
NaOH Conc = 25%
Electrode Area = 1 square inch
Overpressure = 15" H₂O
Air Efficiency = 20%
mg/cm² PE = 0.33

Figure 10

Δ Voltages

1 Square Inch Electrode Area

0 - 1000 Amps/Square foot C.D.

cathode performs extremely well on oxygen over the current density range of zero to 1000 ASF.

4.7 ADDITIONAL TESTS WITH A 1" x 1" CELL

4.7.1 Air Efficiency Data for a 1" x 1" RA19 Type Cathode

As stated in section 4.1.2 of this report, no attempt has been made to optimize air distribution on the gas side of the cathode in the standard half cell. Since the construction of the air plenum for the 1" x 1" and 2" x 2" cells is similar except that the standard cell has a void volume four times that of the 1" x 1" experimental cell, air efficiency data was obtained in this piece of hardware to more closely identify the diffusion characteristics of the RA19 cathode.

Data obtained at 288 ASF and air efficiencies of from 16 to 80% are plotted in figure 11. Less than 0.10 volts were lost in electrode performance over this range of air efficiencies. These data were obtained fairly rapidly, thus, the possibility existed that the electrode had not reached equilibrium after each increase in air efficiency. This theory was tested by running the cell at approximately 80% air efficiency for 24 hours. During this period no detectable decrease in cathode performance was observed. Thus, for at least this period of time, the cathode is capable of stable performance at a very high air efficiency. A fact which is not negligible since one has to remove CO_2 from the air.

Figure 11

Effect of Air Efficiency

ON

Δ Voltage Air + N₂

1 Square Inch Electrode Area

Current Density = 238 amps/ft²

4.7.2 Effect of Electrode Size - Air Plenum Design

The air efficiency data obtained at 288 ASF in a 1" x 1" cell was compared with that obtained at 300 ASF in the standard 2" x 2" hardware. A plot of these data, figure 12, clearly demonstrates the superiority of the data collected in the smaller cell. Undoubtedly, air distribution is an important consideration even in cells having only a 2" x 2" electrode area.

4.8 CATHODE POLARIZATION AS A FUNCTION OF PLATINUM LOADING

4.8.1 Preparation of Catalyst

Catalysts have been prepared on a high surface area carbon support containing 1.0, 2.0, 3.0, 4.0, 5.0, 7.5 and 15% Pt. These materials were prepared according to Prototech Company's U.S. Patent No. 4,044,193. Employing the five lower catalyst preparations, tests have been run to demonstrate the effect of platinum loading in an air breathing cathode while maintaining the same weight and thickness of catalyst layer as is present in the standard RA19 type electrodes.

4.8.2 Experimental Performance Data : Δ Air-N₂ Voltage at 300 ASF

Cells run with electrodes prepared from the lower loaded catalysts, that is, 1.0, 2.0, 3.0, 4.0 and 5.0% Pt and a catalyst prepared with no platinum have yielded erratic and anomalous results. Experimental data, table 2, indicate the following:

Figure 12

Effect of Electrode Size - Air Plenum Design

Δ Voltage Air - N₂ vs % Air Efficiency

Table 2

Effect of Cathode Platinum Loading on Air Depolarized Electrode Performance

Cell Temp^oC = 75

Electrolyte Concentration = 23% NaOH

Air Efficiency = 33% at 300 ASF

Test	% Pt Catalyst	Cathode Loading mg/cm ² Pt	Initial Cathode Weeping	Total Hours Cell Run	Cathode Performance - ΔAir-N ₂ Volts						
					50 ASF	100 ASF	150 ASF	200 ASF	250 ASF	300 ASF	350 ASF
1	0.0%	0.000	Slight	191	1.23	1.25	1.27	1.29	1.26	1.24	1.19
2	1.0%	0.031	Moderate	19	.85	.85	.86	.84	.84	.79	.75
3	1.0%	0.035	Slight	116	.89	.91	.92	.93	.92	.90	.87
4	2.0%	Slight	201	201	.86	.85	.85	.82	.76	.71	.64
5	2.0%	0.066	Slight	92	.89	.90	.90	.89	.86	.83	.77
6	3.0%	0.099	Heavy	77	.87	.88	.87	.81	.74	.61	.41
7	3.0%	0.099	Moderate	70	.87	.89	.88	.86	.85	.80	.74
8	3.0%	0.105	Moderate	188	.89	.91	.91	.89	.84	.77	.70
9	4.0%	0.130	Heavy	142	.89	.88	.88	.88	.85	.82	.76
10	5.0%	0.180	Heavy	47	.85	.85	.85	.83	.81	.73	.60
11	5.0%	0.170	Moderate	71	.86	.87	.86	.85	.83	.79	.75

- A. Duplicate performance data for tests were erratic and stabilized performance was not achieved in the customary 24-48 hours of cell operation.
- B. Electrolyte weeping (Electrolyte flooding through or forming droplets on the air side of the cathode) was excessive for the majority of cases or difficult to alleviate by the customary process.
- C. Gas percolation through the electrodes was greater than normal, both in volume and duration.
- D. The performance of the electrode could not be evaluated by method A outlined in section 4.2.3 because the decreased level of Pt in the electrode caused the hydrogen overvoltage to be high and/or erratic and any determination based on $\Delta_{\text{air-N}_2}$ voltage was not valid.
- E. It will be necessary to incorporate a reference electrode into the circuit in order to obtain accurate performance data with low Pt loaded cathodes or electrodes containing no platinum.
- F. Short-term cell performance with an electrode containing no platinum was surprisingly good for the one test reported but several other similar electrodes failed within a few hours of operation apparently because of flooding.

4.8.3 Air Efficiency as a Function of Electrode Platinum Loading

During the course of Runs 1, 8 and 11 which are tabulated in table 2, air efficiency data was obtained over the range of 16 to 60%. These data, including similar data for a standard $0.33 \pm 10\%$ mg/cm^2 Pt cathode, are plotted in figure 13. Inspection of this plot shows that for 5% catalyst, and consequently an electrode loading of 0.170 mg/cm^2 , the air efficiency data was approximately equal to the standard. The 3% catalyst (0.105 mg/cm^2 Pt electrode) was clearly inferior and the electrode containing no platinum demonstrated a severe air diffusion problem beyond 50% air efficiency. It is noted that the very high $\Delta_{\text{air-N}_2}$ values for the non-platinum electrode are the result of the high hydrogen overvoltage on carbon.

4.9 EFFECT OF THIN POROUS CONDUCTING SUBSTRATE ON PERFORMANCE OF AIR CATHODES

4.9.1 Background Information

The choice of the thin, porous, conducting substrate that holds the catalyst layer is extremely important if an efficiently operating air cathode is to be produced. Over the past several years Prototech Company has examined some of the options that are available with respect to substrates and has selected a carbon cloth as its material of choice. This cloth, which will hereafter be referred to as the standard substrate, (RA19 type cathodes) has proven to be stable in a

Figure 13

Air Efficiency
As a function of
Electrode Platinum Content

caustic half cell environment and provides excellent utilization of the catalyst bearing layer.

There are, however, many types of carbon and graphite cloths and the question of whether a superior material is available is of prime importance.

4.9.2 Reproducibility of Standard Cloth

An unexpected characteristic of the standard cloth is that the thickness and texture can vary depending on whether the sample is taken from the "outer or inner" portion of the bolt. Tests run with both "outer and inner" samples of cloth, table 3, indicates that there may be a small but detectable variation in performance depending on the cloth sampled within a bolt.

In this particular case, the sample from the inner part of the bolt decreased approximately 25% in thickness and showed a slightly lower Δ air-N₂ performance than normal (.77 volts vs. .80 volts.)

Since the data obtained is borderline with respect to the accepted performance level, a series of tests should be run with cloth from various portions of the same bolt before a particular carbon (graphite) cloth is recommended for routine use.

Table 3
Half Cell Data - Electrodes Fabricated
on
Inner and Outer Portions of Carbon Cloth Bolt

Discharge Data

Electrode from Outer Portion 150 Hour Data			Electrode from Outer Portion 163 Hour Data		
ASF	Δ Air-N ₂ Voltage	Δ O ₂ -Air Voltage	ASF	Δ Air-N ₂ Voltage	Δ O ₂ -Air Voltage
50	.87	.01	50	.87	.01
100	.88	.01	100	.86	.02
150	.88	.02	150	.86	.04
200	.86	.04	200	.83	.08
250	.81	.08	250	.80	.11
300	.79	.10	300	.76	.15
350	.75	.14	300	.68	.23

Decay Data

300 ASF 33% Air Efficiency		300 ASF 33% Air Efficiency	
Hours	Δ Air-N ₂ Voltage	Hours	Δ Air-N ₂ Voltage
54	.79	67	.77
78	.78	163	.76
150	.79	235	.75

4.9.3 Evaluation of Other Substrates

In evaluating substrates, the ultimate criteria of acceptability is the performance of a platinum electrode fabricated on that material. More specifically, an electrode fabricated on that substrate and containing less than 0.50 mg/cm^2 Pt must yield a $\Delta_{\text{air-N}_2}$ voltage of $0.80 \pm .02$ volts at a current density of 300 ASF, 33% air efficiency at 75°C and in an electrolyte containing 23% NaOH. Some factors which can cause deviation from the above are:

- A. Air diffusion problems
- B. Electrode weeping
- C. Electrode flooding
- D. Excessive percolation of air through the electrode.

Thus far, six substrates, obtained from three different companies have been tested. These data are summarized in table 4. Of these, the CLTCM material could not be evaluated in a half cell as it was not compatible with the electrode fabrication process currently being utilized. Only two substrates, SKFB and SPWB6, were considered worthy of further testing (table 4) and cells employing cathodes fabricated on these substrates were allowed to run for at least one week during which time decay data, discharge curves, (table 5) and air diffusion data were obtained.

Figure 14 is a plot of the air diffusion characteristic of the two substrates which yielded performance data that was deemed acceptable for further consideration. Included in the figure is the diffusion curve for the standard cloth. It can

Table 4

Evaluation of Electrode Substrates

Cell Temp°C = 75

Electrolyte Concentration = 23% NaOH

Substrate Identification	Electrode Thickness	Pt Loading mg/cm ²	Air Efficiency	Performance Data ΔAir-N ₂ Voltage at 300 ASF	Current Density at which cathode performance is equal to standard
UCWCA	20 mils	0.35	16%	0.41 volts	---
UCWCA	20 mils	0.36	16% 33%	0.38 volts 0.32 volts	100 ASF or less
SKFB*	36 mils	0.53	33%	0.78 volts	All values tested
SKFB*	36 mils	0.45	33%	0.80 volts	All values tested
SSWB8	20 mils	0.34	16% 33%	0.63 0.48	200 ASF or less
SPWB6	17 mils	0.34	16% 33%	0.77 0.72	250 ASF or less 200 ASF or less
CLTGM	22 mils	0.33	16% 33%	0.68 0.53	200 ASF or less
CLTCM	14 mils	COULD NOT FABRICATE ELECTRODE - SUBSTRATE NOT COMPATIBLE WITH PROCESS			

*Low bubble pressure at 15" H₂O ΔP

Table 5

Discharge Curve Data
for
SKFB and SPWB6 Substrates

Cell Temp^oC = 75

Electrolyte Concentration = 23% NaOH

Standard Substrate
Cathode
Pt Loading = 0.33

SKFB Substrate
Cathode
Pt Loading = 0.45

SPWB6 Substrate
Cathode
Pt Loading = 0.34

ASF Δ Air-N₂ Volts

ASF Δ Air-N₂ Volts

ASF Δ Air-N₂ Volts

50 .88

50 .86

50 .88

100 .88

100 .86

100 .89

150 .87

150 .87

150 .87

200 .86

200 .86

200 .85

250 .85

250 .84

250 .81

300 .81

300 .80

300 .72

350 .77

350 .75

350 .61

Figure 14
Air Diffusion Characteristics
of
SKFB and SPW36 Substrates

be seen that at least up to 50% air efficiency, the SKFB material is quite close to the standard but tails off rapidly beyond this point. The SPWB6 does not have a flat portion to its curve and is deviating rapidly from the standard as the air efficiency increases.

The following is a summary of the data obtained in the study.

1. Electrolyte "weeping" was not a problem as the proprietary process of Prototech Company for clearing weeping was successful in all cases.
2. Cathode stability was excellent irrespective of poor or good performance.
3. The only substrate which demonstrated excessive air percolation was the SKFB material. This condition, despite the fact that this substrate yielded essentially standard air depolarization performance.
4. In general, electrode flooding was the cause of low air performance.
5. Performance on oxygen was typical for all the materials tested.
6. Electrode thickness alone does not appear to be the cause of poor air performance.
7. The only substrate which approximates the standard is the 32 mil SKFB material.
8. Previous data, (precontract) have shown that the high loading of SKFB cannot account for the performance level observed.

Section 5

TECHNICAL DISCUSSION

The Hydrogen Anode in Electrowinning of Zinc

5.1 TECHNICAL CONSIDERATIONS

5.1.1 Cell Reactions

In the electrowinning of zinc the electrochemical reaction (1) $\text{Zn}^{++} + 2\text{e}^- \rightarrow \text{Zn}$ has a negative potential (-0.763 volt at room temperature),¹ with respect to the conventional zero voltage of the reaction (2) $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$. Therefore, zinc cannot be plated from zinc sulfate solution by means of a hydrogen electrode without an external power supply. In the case of zinc, the hydrogen anode contributes a part of the electricity directly through reaction (2) and, in addition, eliminates the oxygen overvoltage associated with the lead alloy anode now used in electrowinning of zinc from slightly acid zinc sulfate solutions.

In view of the fact that the zinc deposition potential is negative with respect to hydrogen, zinc ions cannot be reduced chemically to zinc metal by hydrogen. Thus, there is no a priori need for a membrane to protect the hydrogen anode from contact with zinc ions.

1. Oxidation Potentials, Second Edition, Wendell M. Latimer, p. 182.

Typical zinc plating electrolytes are carefully purified of contaminants and contain about 100 g/l of zinc as zinc sulfate and no more than 10 g/l of free sulfuric acid,* so long as the free acid is kept at this level, the current efficiency of conventional electrowinning is 92 to 94%, i.e. small amounts of hydrogen are evolved to account largely for the remaining 6 to 8%. The amount of acid produced anodically in the conventional electrolysis reaction

is the same as that produced by the hydrogen anode electrolysis reaction (4) $\text{Zn}^{++} + \text{SO}_4^{--} + \text{H}_2 \rightarrow \text{Zn} + \text{SO}_4^{--} + 2\text{H}^+$. Therefore, the current efficiency is expected to remain about the same in the latter case, except that here, in contrast to conventional electrolysis, the cathodic by-product hydrogen can be cycled back to the hydrogen anode to approach 100 percent hydrogen utilization.

5.1.2 Parasitic Electrode Reactions

One important question to be resolved is the performance of the electrodes as a function of free acid content in the range of 35 to 60°C. This consideration is important because parasitic anode and cathode reactions are possible in a hydrogen depolarized cell operating at high sulfuric acid concentrations (~ 100 g/l) and temperatures ($\sim 60^\circ\text{C}$.)

*Private communication, T.P. McNulty, The Anaconda Co.

Parasitic cathode reactions which will lower current efficiency (in both the conventional and the proposed hydrogen depolarized cell) are shown in equations 5 and 6:

Also, a parasitic anode, and indeed detrimental, reaction is possible by generating hydrogen sulfide according to equation 7:

5.1.3 Half Cell Evaluation of Anodes in Sulfuric Acid Electrolytes

With the understanding of the reactions recorded in sections 5.1.1 and 5.1.2, a series of tests were run in a half cell at 55°C in which the hydrogen depolarization of a standard Prototech Company anode (0.33 mg/cm² Pt) was measured as a function of sulfuric acid concentration. The data, figure 15, indicate that an acid concentration of at least 50 g/l H₂SO₄ is necessary for acceptable depolarization values.

5.2 CELL DESIGN

5.2.1 Zinc Electrolysis Cell Design

After consultation with Anaconda Co. and reference to "Electrolysis of Zinc Sulfate Solution", Handbook of Non-ferrous Metallurgy, Vol. 2, Chapter XIV, a set of initial operation parameters were chosen and a cell designed to evaluate hydrogen depolarized anode performance for the electrowinning of zinc.

Figure 15
ProTech Coal Hydrogen Anode
Half Cell DATA

H₂ Depolarization vs H₂SO₄ Electrolyte Concentration

The cell, figures 16 and 17 and photograph 1, is of modular construction and provides 2" x 2" electrode areas. Except for electrodes and current collectors there are no metal parts in the cell because trace metal contamination is to be avoided to achieve high current efficiency. The assembly consists of distinct anode and cathode sections with a 2.0 inch distance separating the electrodes. The void space between the electrodes is filled with electrolyte when the hardware, which is suspended on PVC holders, is lowered into a battery jar containing the test solution.

Figure 16, which is a top view of the cell depicts the anode and cathode sections of the assembly and clearly shows the Nylon spacers, nuts, bolts and rod used to isolate each section so that when the test is completed the zinc coated cathode can be removed without disturbing the anode compartment.

Figure 17 is a front cross section of the hardware. It displays the hydrogen plenum and anode assembly. As with all Prototech Company cells, a lucite window is provided to observe the gas side of the electrode under investigation. If it is necessary to employ an ion exchange membrane in the cell, this would be located approximately $\frac{1}{4}$ " in front of the anode, facing the cathode and the 2.0 inch spacing between the electrode would be maintained. The cathode section of the cell is solid, with the aluminum cathode rigidly held in place by lucite blocks and PVC frames. Current and voltage probes exit the cell at the top and are not in contact with the electrolyte. At the present time a 20 mil copper current collector is employed in the

FIGURE 16, TOP VIEW

FIGURE 17, FRONT CROSS-SECTION VIEW

anode section and a 15 mil aluminum sheet is used as the cathode.

The cell, suspended in the electrolyte in the battery jar, is shown in photograph 1. It will be noted that the electrolyte temperature is maintained by a mercury switch temperature controller connected to a glass coated heating rod. Also seen is stirring action of a Teflon coated magnetic stirrer. Auxiliary cell equipment includes a rectified power supply, a 0-2 amp amp meter, a volt meter and a soap bubble flow meter for monitoring the hydrogen gas flow.

5.3 TEST DATA

5.3.1 Experiemntal Zinc Electrowinning Data

Employing the cell described in section 5.2 and an electrolyte composition of 120 g/l $\text{Zn}^{++}(\text{SO}_4=)$ and 1.0 molar H_2SO_4 (98 g/l H_2SO_4), several tests were run with the conventional Lead (Calcium) anode and a Prototech Company, 0.33 mg/cm² Pt, H_2 depolarized anode. The data (table 6) which were obtained at a current density of 36 amps per square foot, demonstrated the striking energy savings of at least 0.60 KWH per lb of deposited zinc when a hydrogen depolarized anode was employed.

For short term tests, (3.5 hours), the energy consumption with a lead anode was at least 2.2 times greater than that required for the hydrogen depolarized anode. At a temperature of 55°C, (3.5 hours) the current efficiency was slightly

PHOTO 1

Test Stand for H_2 Depolarized Electrowinning of Zinc

lower for the hydrogen anode but these percentages still represented values in excess of 90%.

The test at the lower cell temperature with the lead anode yielded an excellent current efficiency level but since the voltage increased (higher IR), the overall power consumption was essentially identical to the 55°C test with the same anode.

Zinc deposits obtained from the tests described in table 6 were light gray and crystalline. Treeing, which was noticeable for the 4.5 hour runs was quite pronounced when the cell was run 23 hours.¹

Also, for this 23 hour test with a hydrogen depolarized anode, the current efficiency dropped to approximately 80%. Private communication disclosed that the impurities present in the reagent grade zinc sulfate, which was employed to prepare the electrolyte, were sufficient to lower the current efficiency of a 24 hour test.² Subsequent tests will have to be run with a purified electrolyte to establish a current efficiency for 24 hour tests.

5.3.2 Summary

Initial short term tests with hydrogen depolarized anodes for the electrowinning of zinc demonstrate the following:

1. A substantial savings in power consumption.
2. High current efficiency without the use of an ion exchange membrane.

1. The edges of the cathode present sharp surfaces that tend to become points of higher current density than the rest of the surface. This effect is conducive to the formation of deposited zinc trees.

2. Mr. William Stern, Anaconda Company

TABLE 6

Electrolysis of ZnSO_4 Solution (Zinc Deposition)Prototech Company H_2 Depolarized Anode and

Commercial Pb(Ca) Anode

Test #	Electrolyte Composition		Test Hours	Type of Anode	Cell Voltage	Current Density ASF	Fuel Efficiency*	Current Efficiency	Cell Temperature	Power Consumption KWH/lb Zinc
	Zn^{++}	H_2SO_4								
1	120 g/l	98 g/l	3.5	Prototech Company H_2 Depolarized Pt anode	1.36 Volts	36ASF	20%	90.3%	55°C	0.560
2	119 g/l	100 g/l	23.0	Prototech Company H_2 Depolarized Pt anode	1.30 Volts	36ASF	20%	79.8%	55°C	0.607
3	120 g/l	98 g/l	3.5	Commercial Pb(Ca) Anode	3.15 Volts	36ASF	---	94.1%	55°C	1.250
4	119 g/l	100 g/l	3.5	Commercial Pb(Ca) Anode	3.28 Volts	36ASF	---	98.4%	35°C	1.240
5	117 g/l	102 g/l	3.5	Prototech Company H_2 Depolarized Pt anode	1.36 Volts	36ASF	20%	91.9%	55°C	0.550

* The H_2 fuel efficiency was not optimized.

Section 6

TECHNICAL DISCUSSION

Metal - Water - Air Batteries

6.1 ALUMINUM - AIR BATTERIES

6.1.1 Air Cathode Half Cell Data-Sodium Aluminate Electrolyte

A series of tests were conducted with a half cell to obtain performance of a representative Prototech Company air cathode in the typical alumina-NaOH electrolyte of an aluminum-air battery. The cell, which was run with a flowing electrolyte and at a temperature of 75°C, showed no signs of performance decay at 100 ASF (33% air efficiency) for the 140 hours of the test.

A discharge curve obtained during the course of the run is shown in figure 18. The slopes of the curves for cathode operation on air, nitrogen and oxygen are similar to those obtained with the same type electrode in a 23% NaOH electrolyte.

In addition to operation at 100 ASF, the cell was run for several days at 300 ASF. Again, performance was quite stable.

6.1.2 Evaluation of Prototech Company Air Cathode in an Aluminum - Air Battery

A 3" x 3" Prototech Company RA19 type air cathode ($0.33 \pm 10\% \text{ mg/cm}^2 \text{ Pt}$) has been evaluated in an aluminum - air

Figure 1B
 Discharge Curve
 Prototech Co-Air Cathode - NaOH/NaAlO₂ Electrolyte

battery at Lawrence Livermore Laboratory. Performance data was reported to be excellent and, indeed, the discharge curve represented an advancement in the state of the art.¹

6.1.3 Materials Sent to Lockheed Space and Missile Corporation for testing.

Four 3½" x 3½" RA 19 type air cathodes have been submitted to Lockheed Space and Missile Corporation for evaluation in metal - water - air batteries. In addition to these electrodes, two experimental electrode-current collector assemblies have been included for evaluation.

1. Data reported to Prototech Company by communication with Dr. Cooper of Lawrence Livermore Laboratory.