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

Progress Report
For the Period Feb. 1, 1979 to April 30, 1979

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CONTENTS

SECTION	PAGE
1 ABSTRACT	1
2 INTRODUCTION	2
3 ADVISORY MEETINGS AND CONSULTATIONS	3
3.1 Meetings	3
3.1.1 Hydrogen Depolarized Anodes for the Electro-winning of Zinc	3
3.1.2 Air Electrodes for Metal-Water-Air Batteries	6
3.1.3 Metal-Air Battery Project Meeting	6
4 TECHNICAL DISCUSSION: AIR CATHODES IN CAUSTIC HALF CELLS	14
4.1 Life Test Cathode	14
4.1.1 Summary of Segment Three-Life Test Cathode	14
4.1.2 Reference Measurements-Fourth Segment Life Test	16
4.2 Cathode Polarization(Reference) as a function of Platinum Loading	18
4.2.1 Preparation of Catalyst and Electrodes	18
4.2.2 Experimental Data, Cathode Pt Loading vs. Reference Potential	18
4.2.2.1 Cathode Performance(Reference) vs. Time	20
4.2.2.2 Cathode Pt Loading 0.00 to 0.55 mg/cm ² vs. Reference Potential	20
4.3 Current Collector-Carbon Cloth Electrode Assembly	24
4.3.1 Background Information	24
4.3.2 Data with Cathodes Incorporating a Current	26

CONTENTS

SECTION	PAGE
4.3.2.1 Air Cathode Performance vs. Time	26
4.3.2.2 Cathode-Current Collector Potential at 300 ASF vs. Cell Temperature	31
4.3.2.3 Cathode-Current Collector Potential at 300 ASF and 75°C vs. %CO ₂ Free Air Efficiency	35
5 TECHNICAL DISCUSSION: ZINC ELECTROWINNING PURE HYDROGEN FUEL	37
5.1 Background	
5.1.1 Current Status of Program	
5.2 Effect of Current Density of Ampere Efficiency and Power Consumption	38
5.2.1 Preliminary Considerations	38
5.2.2 Experimental Data - Current Density vs. Power Consumption	41
5.3 Effect of Electrolyte Temperature above 55°C	41
5.3.1 Background Information	41
5.3.2 Current Efficiency Data - Temperature Range 55-80°C	43
5.4 Effect of Impurities	43
5.4.1 Introduciton	43
5.4.2 60 ppm Fe ⁺⁺ Impurity	45
5.4.3 10 ppm Co ⁺⁺ Impurity	47
5.4.4 1 ppm Cu ⁺⁺ Impurity	47
5.4.5 Ge ⁺⁺⁺⁺ Impurity	47
5.4.6 Platinum Impurity	51
5.5 Future Investigation	55
5.5.1 Synthetic Electrolytes	55
5.5.2 Plant Liquor	
6 TECHNICAL DISCUSSION: METAL-WATER-AIR BATTERIES	56
6.1 Aluminum - Air Batteries	56

FIGURES

FIGURE NO.		PAGE
1	Platinum Particle Size ($\text{\AA}$) vs. Surface Area (m^2/gm)	7
2	Volts vs. Hg/HgO vs. Cathode Platinum Loading Zero Time Data	8
3	Cathode Performance vs. Time-Standard Prototech Co. 0.33 mg/cm^2 DC Electrode	9
4	Current Density Data: New Electrode vs. 10,500 Hour old Electrode, 0.33 mg/cm^2 Pt	10
5	Volts vs. Hg/HgO vs. Cell Temperature $^{\circ}\text{C}$ 0.33 mg/cm^2 Platinum	11
6	Volts vs. Hg/HgO vs. Cathode Air Efficiency 0.33 mg/cm^2 Pt Electrode	12
7	Current Density Data: Effect of Conductivity of Substrate, Standard Cell Conditions- 0.33 mg/cm^2 Pt	13
8	Life Test: Prototech Co. RA19 Type Cathode Segment 3	15
9	Current Density: New Electrode vs. 10,500 Hour Old Electrode, 0.33 mg/cm^2 Pt	17
10	Performance vs. Time: RA19 Type Cathode, Life Test Electrode, Segment 4	19
11	Cathode Performance vs. Time, Standard Prototech Co. 0.33 mg/cm^2 Pt Electrode	21
12	Cathode Depolarization on N_2 -Air- O_2 vs. Cathode Pt Loading	22
13	Volts vs. Hg/HgO vs. Cathode Platinum Loading Zero Time Data	23
14	Variation of Platinum Cathode Loading Performance vs. Time	25
15	Effect of Cathode Current Collector on Cell Voltage (A-C)	28
16	Current Density Data: Effect of Conductivity of Substrate, Standard Cell Conditions	29
17	Cathode Performance vs. Time, 0.33 mg/cm^2 Pt Electrode with R-6 Current Collector	30

SECTION 1

ABSTRACT

Data are presented in this Quarterly Report for investigations involving air cathodes in caustic half cells and hydrogen depolarized anodes for metal electrowinning (acid electrolytes).

Studies with air depolarized Pt cathodes in caustic hardware include:

- a) Progress of the RA19 type air diffusion electrode.
Reference data has been obtained with this 10,500 hour old electrode.
- b) Cathode performance (Reference) vs. time for a standard 0.33 mg/cm^2 cathode.
- c) Electrode-current collector evaluation.
- d) Electrode-current collector data as a function of cell temperature.
- e) Electrode-current collector data as a function of CO_2 free air efficiency.

Zinc electrowinning data have been obtained for tests involving

- a) Current Density vs. Power Consumption.
- b) Current efficiency over the temperature range of $55-80^\circ\text{C}$.
- c) The presence of Cobalt, Iron, Copper, Germanium and Platinum impurities in the electrolyte.

SECTION 2

INTRODUCTION

During the second half of DOE Contract #ET-78-C-02-4881 data for air depolarized cathodes in caustic half cells are being obtained with reference electrodes and in some cases with electrode-current collector assemblies. These refinements in experimental technique and mode of assembly were made so that the best possible electrode and the best set of cell parameters could be chosen for the caustic-chlorine (membrane) cell which is scheduled to be run during the last month of the program.

Studies involving a hydrogen depolarized anode for the electrowinning of zinc in synthetic electrolytes continue to demonstrate a large energy savings over the industrial process. Test results have been excellent and an actual plant electrolyte will be run before the completion of the contract.

SECTION 3

ADVISORY MEETINGS AND CONSULTATIONS

3.1 During the month of March, 1979, Dr. Walter Juda of Prototech Company participated in advisory meetings and consultations in the areas of hydrogen depolarized anodes for the electrowinning of zinc and air depolarized cathodes for metal-water-air batteries.

In April, 1979, Dr. Henry Petrow and Mr. Robert Allen attended the Metal-Air Battery Project Meeting held in Washington D.C. which was sponsored by DOE.

3.1.1 Hydrogen Depolarized Anodes for the Electrowinning of Zinc

On March 1, 1979, a morning meeting involving only non-confidential information, was held at the Research Laboratories of Tosco Corporation, 18200 W. Highway 72, Golden, Colorado, attended by Dr. B. Shulman, Director of Research of Tosco, Messrs. T. McNulty and W. Stern of Anaconda Company, Dr. H. Shalit of Atlantic-Richfield Company and Dr. W. Juda of Prototech Company. The subject of the meeting was Tosco's petroleum coke gasification process for pure hydrogen. The process involves catalytic steam reforming-partial oxidation of the coke, followed by the shift reaction and final methanation (to eliminate residual CO). With respect to economics, Shulman stated that the original

figures (see Quarterly report 11/1/78-1/31/79--page 58) may have been too low because they were based on gasifying 250-1000 T coke/day producing 17.5-70 million cu ft H_2 /day, whereas a zinc electrowinning plant, depending on size, could require only some 2-5 million cu ft/day. But, in view of the fact that the Tosco process can be carried out in ordinary steel equipment, there should not be too serious a cost penalty. A reasonable figure to be used for the zinc project at this time should be 0.2¢/SCF H_2 with coke at \$20/ton, and 0.23¢/SCF H_2 with coke at \$40/ton. The H_2 produced has ca. 60% of the BTU content of the coke. It was generally agreed that petroleum coke is likely to remain in a readily available source of hydrogen in contrast to natural gas.

Dr. Shulman then gave us a conducted tour of the Tosco pilot plant which gasifies routinely $\frac{1}{2}$ -2 tons/day of coke to H_2 -CO mixture (the 1st step of the process). Tosco's next step will be to scale-up to a level of about 20 T/day. (The eventual large scale production of H_2 --up to 70 million cu ft/day-- is intended for Tosco's Avon refinery). Should Tosco's process turn out to be the most economical, Tosco would consider selling hydrogen over the fence or licensing the technology for use in a zinc electrowinning plant.

On March 1, 1979 an afternoon follow-up meeting was held at the Anaconda Headquarters, 17th Ave. & Glenarm Place, Denver, Colorado, attended by the above representatives of Anaconda, Atlantic-Richfield and Prototech.

First, Dr. Shalit thought it possible that his process involving one-step production of pure hydrogen by reacting steam with carbon (a carbonaceous fuel including petroleum coke) in the presence of molten caustic may be low in cost and that he would initiate cost calculations based on his experiments and the known recycle step of liming the sodium carbonate produced and evaporating water from the aqueous caustic to re-produce molten caustic.

Second, the possible participation of Anaconda in the zinc electrowinning project was explored. It is intended that Prototech's program beginning on/or about August 1, 1979 (the end of Prototech's present DOE contract) will involve a scale-up to about a 6" x 6" H_2 anode-cell.

Finally, the immediate experimental program, according to W. Stern, should emphasize the effect of impurities on the cell operation, with Sb, As, Co, Ni and Ge being the most serious potential offenders. At first, experiments with 1 ppm Ge + 10 ppm Co should be run, as this combination will most seriously affect the conventional process. The presence, in the electrolyte, of $CaSO_4$ (saturated) needs also to be evaluated as a deposit of $CaSO_4$, if it occurs, on the anode would be harmful. Further, W. Stern will see to it that a 55 gallon drum of plant electrolyte be shipped to Prototech to ascertain operation with the actual electrowinning electrolyte composition.

3.1.2 Air Electrodes for Metal-Water-Air Batteries

On March 5, 1979, Dr. Walter Juda of Prototech Company visited Dr. J. Cooper and Mr. E. Behrin of Lawrence Livermore Laboratory at Livermore, California to discuss a variety of topics concerning air electrodes for metal-water-air batteries.

On the same date, Dr. Juda visited Mssrs. E. Littauer, F. Bauman and J. Lee Morris Jr. of Lockheed Missles and Space Company at Palo Alto, California. Discussions centered around Lockheed's test results employing a standard Prototech Company RA19 type air cathode in an Aluminum-air battery.

3.1.3 Metal-Air Battery Project Meeting (Sponsored by DOE)

From April 10-11, 1979, Dr. Henry Petrow and Mr. Robert Allen of Prototech Company attended the Metal-air Battery Project Meeting held in Washington, D.C. which was sponsored by DOE. During the meeting, Dr. Henry Petrow presented a paper outlining Prototech Company's progress and developments in the area of air depolarized cathodes in caustic half cells.

The data presented at this meeting are shown in figures 1 through 7.

PLATINUM PARTICLE SIZE ($\text{\AA}$)

vs.

SURFACE AREA (m^2/gm)

Figure 1

VOLTS VS Hg/HgO
VS
CATHODE PLATINUM LOADINGS
ZERO TIME DATA

Figure 2

CELL TEMPERATURE = 75°C
ELECTROLYTE CONCENTRATION = 23% NaOH
AIR (CO₂ FREE) EFFICIENCY = 33%
CURRENT DENSITY = 390 ASF
ELECTRODE AREA = 4 SQ IN

CATHODE PERFORMANCE VS. TIME
STANDARD PROTDTECH CO. 0.33 mg/cm² PC ELECTRODE

Figure 3

CURRENT DENSITY DATA
NEW ELECTRODE VS. 10,500 HOUR OLD ELECTRODE
0.33 mg/cm² Pt

Figure 9

VOLTS vs. H_2/HgO
vs.
CELL TEMPERATURE °C
0.33 mg/cm² PLATINUM
Figure 5

VOLTS VS. Hg/HgO

VS.

CATHODE AIR EFFICIENCY

0.33 mg/cm² Pt ELECTRODE

Figure 6

CURRENT DENSITY DATA
0.33 mg/cm² PT ELECTRODES
EFFECT OF CONDUCTIVITY OF SUBSTRATE
STANDARD CELL CONDITIONS

Figure 7

SECTION 4

TECHNICAL DISCUSSION

AIR CATHODES IN CAUSTIC HALF CELLS

4.1 Life Test Cathode

During this report period, the cathode life test initially described in the August 1 to August 31, 1978 Progress Report (page 9) continued on stream until March 23. This third segment of testing reached 5289 hours of continuous operation (total of 10,500 hours of operation for the RA19 type electrode under study) before the test was voluntarily stopped to insert a Hg/HgO reference electrode in the circuit.

4.1.1 Summary of Segment Three-Life Test Cathode

Prior to the start of DOE contract #ET-78-C-02-4881, Protech Company was in the process of life testing an RA19 type-carbon cloth based air cathode. This electrode had been run for approximately 5200 hours during two segments of testing and the performance data and method of evaluation were reported in Quarterly Report August 1, 1978-October 31, 1978.

Simultaneous with the initiation of the present contract, a third segment of testing was started with this electrode. During this new segment of operation, the Δ volts Air vs. N_2 method of evaluation continued to be used. Figure 8 documents the progress of this electrode over a 5289 hour time period from August 8, 1978

Figure 8

Life Test
ProtoTech Co. RA 19 Type Cathode
Segment 3

to March 23, 1979. The total accumulated hours on the electrode reached 10,500 before the test was voluntarily stopped to insert a Hg/HgO reference electrode in the circuit.

Important milestones achieved during this third segment of testing are as follows: (Refer to figure 8).

- A) Cathode evaluation by the Δ volts-Air vs. N_2 method showed only 20 to 30 mv of decay over the 5289 hour time period.
- B) The electrode has surpassed one year of operation (non-continuous) and continues to operate at 300 ASF and 33% air efficiency in excellent fashion. (23% NaOH electrolyte and 75°C cell temperature).
- C) Over one-half year of continuous operation has been logged on this air depolarized cathode and no evidence of catalyst failure and/or deterioration of electrode structure is evident.

4.1.2 Reference Measurements-Fourth Segment-Life Test

With a Hg/HgO reference electrode in the circuit, the life test cathode resumed operation in the standard hardware. After the electrode achieved steady state (one day of operation) a discharge curve was taken and the data compared to a new RA19 type electrode. The curves, figure 9 , show that the performance of the 10,500 hour old cathode was only 50-60 mv inferior, at 300 ASF (33% CO_2 free air efficiency), to a new cathode whose life time of operation was one hour.

Thus far, the fourth segment of operation, as evaluated

CURRENT DENSITY DATA
NEW ELECTRODE VS. 10,500 HOUR OLD ELECTRODE
0.33 mg/cm² Pt

Figure 9

with a Hg/HgO reference electrode, has demonstrated the same type of performance profile as obtained with similar cathodes (refer section 4.2.2.1 of this report). Performance vs. time data are plotted in figure 10 . It is observed that after an initial period of decay, the cathode to reference voltage stabilized and performance has been steady for almost one month of operation.

4.2 Cathode Polarization (Reference) as a function of Platinum Loading

4.2.1 Preparation of Catalyst and Electrodes

Catalysts ranging from 1-15% Pt were prepared on a high surface area carbon support according to Prototech Company's U.S. Patent No. 3,044,193. By maintaining the same weight and thickness of the catalyst layer, the electrode loading was varied in direct proportion to the %Pt catalyst employed.

Since carbon itself is catalytic for air reduction in a caustic media, electrodes were also fabricated without platinum.

4.2.2 Experimental Data, Cathode Pt Loading vs. Reference Potential

Previous screening data, obtained without the benefit of a Hg/HgO reference, have been reported in Quarterly Reports August 1, 1978 to October 31, 1978 (page 37) and November 1, 1978 to January 31, 1979 (page 9). These data indicate that:

- A) An electrode Pt loading of at least 0.20 mg/cm^2 was necessary to obtain maximum initial cathode performance at 300 ASF, utilizing the particular high

Figure 10

Performance vs Time

RA 19 Type Cathode - Life Test Electrode

Segment 4

Hg/HgO Reference Data

Cell Temperature = 152
Electrolyte Concentration = 23% NaOH
Air (CO₂ free) Efficiency = 33%
Current Density = 300 ASF
Electrode Area = 4.54 inches

surface area carbon carrier.

- B) Electrodes fabricated with lower platinum loadings than those mentioned in A) yielded erratic performance and weeping problems are prevalent.

Data being presented in this report, except for standard loaded electrodes which serve as the yardstick for evaluating others are essentially zero time values. Most runs were up to two weeks in duration.

4.2.2.1 Cathode Performance (Reference) vs. Time

Standard Prototech Company 0.33 mg/cm² Pt Electrode

Performance data (Reference) vs. time on stream has been plotted in figure 11 for a standard 0.33 mg/cm² Pt air cathode which was run for slightly over one month. The Hg/HgO data increased (more negative) over the initial 6-7 days of operation but then assumed a steady state mode of operation for the remainder of the test.

4.2.2.2 Cathode Pt Loading 0.00 to 0.55 mg/cm² vs. Reference Potential

Figure 12 shows the performance on air and oxygen depolarization and H₂ evolution of electrodes whose Pt content has been varied from 0.00 to 0.55 mg/cm². Since performance on air depolarization is the criteria of evaluation of air cathodes, figure 13 has been plotted on an expanded scale for this mode of cathode operation. It will be observed that as the Pt content of the electrode is raised from 0.00 to approximately 0.20 mg/cm²,

Figure 11

Cathode Performance vs. Time

Standard Prototech Co. 0.55 mg/cm² Pd Electrode
RA-19 Type

Cell Temperature = 75°C
Electrolyte Concentration = 23% NaOH
Air (CO₂ free) Efficiency = 33%
Current Density = 300 A/SF
Electrode Area = 1.50 IN

the gain in performance (vs. a Hg/HgO Reference) is in the order of 0.20 volts. Above 0.2 mg/cm^2 , little effect is noted.

The performance vs. time curves, obtained over several hundred hours of operation for a variety of electrode Pt loadings are shown on figure 14. The profile of the curves indicate that the initial performance loss (vs. a reference) is independent of Pt loading. However, it is reiterated that the lower loaded electrodes present somewhat of a problem in attaining steady state. (Weeping is difficult to clear).

4.3 Current Collector-Carbon Cloth Electrode Assembly

4.3.1 Background Information

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 the material of choice (SPWB-3).

Carbon (graphite) cloth was selected for many reasons but paramount were the weight, cost, corrosion properties and ease by which electrodes could be manufactured with large areas and in large volumes. Except for electrical resistance, this material should be equal to or better than other substrates.

Figure 19

Variation of Platinum Cathode Loading
Performance vs time

4.3.2 Data with Cathodes Incorporating a Current Collector

When a series of current collectors were incorporated into the cathode assembly, the cell voltage of caustic half cells decreased, illustrating the effect of this parameter. Refer Table 1 and figure 15 . These initial data were obtained without the use of a reference electrode, but all subsequent data obtained in this study utilized the Hg/HgO reference as a measure of cathode performance.

To determine the effectiveness of one type of carbon cloth current collector assembly, comparative tests were run on this electrode and others fabricated on raw cloth and on a 100 mesh gold plated tantalum metal screen. This latter, rather expensive, electrode obviously possesses efficient current collecting capabilities.

Results, as shown in figure 16 , for essentially zero time data, demonstrates the major performance improvement of a carbon cloth electrode when a current collector is incorporated into the cathode assembly. With the particular current collector under test, this improvement fell short of equalizing the cloth to the above 100 mesh metal screen electrode.

4.3.2.1 Air Cathode Performance vs. Time

Carbon cloth with current collector and Noble Metal Plated Screen

Performance data obtained as a function of time on stream has been plotted in figure 17 for an electrode/current collector

TABLE 1

EFFECT OF CATHODE CURRENT COLLECTION

ON

CELL VOLTAGE (AC)

Cell Temperature = 75°C
Cathode = 0.33 mg/cm² Pt

Electrolyte Concentration = 23% NaOH

Test	Current Collector	Current Collector Identification	Anode to Cathode Cell Voltage						
			350 ASF	300 ASF	250 ASF	200 ASF	150 ASF	100 ASF	50 ASF
1	No	None	2.80	2.51	2.23	1.97	1.69	1.41	1.09
2	Yes	R-1	2.63	2.37	2.12	1.88	1.65	1.38	1.10
3	Yes	R-2	2.61	2.35	2.10	1.87	1.63	1.36	1.10
4	Yes	R-4	2.54	2.30	2.07	1.84	1.61	1.36	1.09
5	Yes	R-6	2.54	2.30	2.07	1.85	1.62	1.38	1.09
6	Yes	R-10	2.52	2.28	2.04	1.82	1.61	1.36	1.09

Figure 1.5

Effect of Cathode Current Collector
ON
Cell Voltage (A-C)

CURRENT DENSITY DATA
0.33 mg/cm² PT ELECTRODES
EFFECT OF CONDUCTIVITY OF SUBSTRATE
STANDARD CELL CONDITIONS

Figure 16

Figure 17

Cathode Performance vs Time

0.53 mg/cm² Pt Electrode with R-6 Current Collector

assembly. These data include both air and oxygen values. Performance vs/ a Hg/HgO reference decreased over the initial 7 to 10 days of operation but then assumed at a steady state mode of operation for the remainder of the test (720 hours). The decrease in performance was somewhat greater on air than on oxygen.

Figure 18 is a plot of the discharge curves obtained at approximately 1 and 720 hours of operation. It is of interest to note that the performance below 100 ASF actually improved during this time period.

For comparative purposes, an electrode fabricated on a noble metal plated screen was allowed to run for 1700 hours. The performance vs. time curve is shown in figure 18. The only distinct difference between the cloth-current collector data (figure 17) and figure 19 is that the performance loss of the metal screen electrode was about double that of the cloth electrode over the initial 7 to 10 days of operation. Beyond this point, the performance was steady for 1200 hours.

4.3.2.2 Cathode-Current Collector Potential at 300 ASF vs. Cell Temperature

Cathode (with current collector) to reference voltages at 300 ASF are plotted in figure 20 for a cell in which the cell temperature was raised from approximately 40 to 90°C.

It will be observed that cathode performance (vs. reference) improved with increasing temperature. The effect is pronounced from 40 to 60°C but is rather negligible as the temperature is raised above 75°C. (75°C is the normal operating temperature of Prototech Company hardware).

Figure 20

Volts vs Hg/HgO

vs

Cell Temperature °C

0.33 mg/cm² PLATINUM

4.3.2.3 Cathode-Current Collector Potential at 300 ASF and 75°C vs. %CO₂ Free Air Efficiency

One criterion used to evaluate air cathodes is the ability of that electrode to operate at high air efficiencies. Data obtained for a standard cathode (with current collector) in a cell that had reached steady state vs. %CO₂ free air efficiency are presented in figure 21 .

It was found that air efficiencies of up to 50% had relatively little effect on cathode performance. Above this value, increasing polarization losses are observed. It is mentioned that these values were obtained without the use of an effective gas distribution system. Thus, this performance is subject to improvement.

VOLTS VS. Hg/HgO
VS.
CATHODE AIR EFFECIENCY
0.33 mg/cm² Pt ELECTRODE

Figure 21

SECTION 5

TECHNICAL DISCUSSION

ZINC ELECTROWINNING PURE HYDROGEN FUEL

5.1 Background

5.1.1 Current Status of Program

Data presented for hydrogen depolarized anodes in Quarterly Reports August 1, 1978 to October 31, 1978 and November 1, 1978 to January 31, 1979, have demonstrated an energy savings of approximately 0.70 KWH/lb of zinc, that is a savings of more than one-half the power consumed in today's industrial processes which utilize a Pb (Ca) anode. These results were obtained with a Prototech Company gas diffusion anode which contained 0.33 mg/cm² Pt and operated on a pure hydrogen fuel in a cell run at 55°C with a synthetic electrolyte containing 120 g/l zinc and 98 g/l H₂SO₄. The current density was 36 ASF and the spacing was 2 inches between electrodes (4 hour runs).

Current studies, reported herein, involve:

1. Effect of current density on ampere efficiency and power consumption
2. Tests with cell temperatures above 55°C
3. Effect of impurities on the efficiency of zinc deposition.

5.2 Effect of Current Density on Ampere Efficiency and Power Consumption

5.2.1 Preliminary Considerations

It has been found that the slope of the discharge curves (9 to 72 ASF) of a Pb(Ca) and hydrogen depolarized anode in a zinc electrowinning cell containing a synthetic electrolyte (120 g/l zinc and 98 g/l H₂SO₄ at 55°C) are essentially identical. Refer to figure 22 . The effect of hydrogen depolarization is to decrease the cell voltage by approximately 1.85 volts at all current densities.

Ampere efficiency, as calculated by equation 1, is independent of cell voltage:

$$(1) \quad \frac{\text{grams zinc deposited} \times 100}{1.219 \times \text{amps} \times \text{hours}} = \% \text{ ampere efficiency}$$

but cell voltage, is a most important consideration when calculating the power consumption for zinc deposition by equation 2,

$$(2) \quad \frac{\text{amps} \times \text{cell voltage} \times \text{hours} \times 454}{1000 \times \text{grams zinc deposited}} = \text{KWH/lb zinc.}$$

With an assumed 90% current efficiency (see figure 22), these data can be translated into KWH/lb zinc vs. current density, as shown in figure 23. To confirm these calculated values, tests were run at varied current densities.

FIGURE 22
CURRENT DENSITY - VOLTAGE CURVES

5.2.2 Experimental Data - Current Density vs. Power Consumption

Data obtained for a hydrogen depolarized anodes operating at varied current densities in zinc electrowinning cells are shown in figure 24 . These data indicate that the ampere efficiency increases with current density and consequently since these values rise above 90%, the power consumption is somewhat lower than the calculated values presented in figure 23.

5.3 Effect of Electrolyte Temperature above 55°C

5.3.1 Background Information

Previous data (page 43 of Quarterly Report November 1, 1978 to January 31, 1979) for hydrogen depolarized zinc electrowinning cells operated over a temperature range of ambient to 55°C showed that the major effect was a reduction in cell voltage. However, this reduction in voltage was reasonably level in the vicinity of 55°C.

The present study involved the temperature range 55-80°C. Since it was already known that the effect on cell voltage would be minimal, the main interest was to determine at what temperature the parasitic cathode and/or anode reactions would decrease ampere efficiency (and thus increase power consumption) to an unacceptable level.

Figure 29
Effect of Current Density
on
Current Efficiency and Power Consumption

5.3.2 Current Efficiency Data - Temperature Range 55-80°C

Figure 25 shows the current efficiency and power consumption curves for hydrogen depolarized zinc electrowinning cells operating between 55-80°C. The desired cell reactions still predominate at 80°C but a significantly reduced ampere efficiency and rapidly increasing power consumption is demonstrated above 70°C, thus, the normal cell temperature of 55°C is well under any value that will lead to a noticeable decrease in efficiency.

5.4 Effect of Impurities

5.4.1 Introduction

It is stated on page 423 of "Electrolysis of Zinc Sulfate Solution", Handbook of Non-Ferrous Metallurgy, Vol. 2, Chapter XIV that "Cathodic impurities have the greatest effect upon the efficiency of zinc deposition, and their control is one of the major problems in electrowinning". If any impurity which lowers the hydrogen overvoltage on zinc to the point where hydrogen can be evolved, comes into contact with a zinc surface during electrolysis, hydrogen will be evolved on the surface of the impurity and zinc will be dissolved.

Those metals whose hydrogen overvoltage is below that of zinc but whose decomposition voltage is above that of sulfuric acid, including iron, nickel and cobalt, are injurious to electrolysis but do not ordinarily contaminate the deposited zinc.

Figure 25
Effect of Electrolyte Temperature
ON
Current Efficiency and Power Consumption
55 - 80°C

They are soluble and consume power by being alternately deposited on the zinc surface and redissolved in the acid electrolyte. They are particularly detrimental to electrolysis when present with certain other impurities.

Metals such as copper, arsenic, germanium and antimony are deposited with zinc and form points of low hydrogen overvoltage where hydrogen is evolved at the expense of zinc. Another metal which falls into this class is platinum. Platinum is particularly deleterious to zinc plating because hydrogen overvoltage is so low on this metal that if present in sufficient concentration, no zinc is plated at all.

In order to establish the utility of the hydrogen depolarized anode, tests were run with known impurity levels in the electrolyte. These data are reported in the following sections.

5.4.2 60ppm Fe⁺⁺ Impurity

Current efficiency data obtained for a hydrogen depolarized and a Pb (Ca) anode in the presence of 60 ppm of Fe⁺⁺ ions are tabulated in Table 2. While each cell shows effects from this level of iron impurity, the hydrogen anode cell is much more tolerant than the currently utilized industrial cell as the acid concentration is increased above 1 molar H₂SO₄.¹

1. The hydrogen depolarized anode eliminates the anodic oxidation of Fe⁺⁺ to Fe⁺⁺⁺ thus, ampere efficiency is not lowered by iron being alternately reduced at the cathode and re-oxidized at the anode.

TABLE 2

Effect of Iron Impurity
on
Current Efficiency and Power Consumption

H₂ Depolarized vs. Industrial Pb(Ca) Anode

<u>H₂ Depolarized Anode</u>					
Test	ppm Fe ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	-----	98	1.23	92.3	.500
2	60 ppm	101	1.23	87.6	.523
3	60 ppm	105	1.22	85.3	.530
4	60 ppm	108	1.23	83.7	.550
5	60 ppm	111	1.21	81.5	.550

<u>Pb(Ca) Anode</u>					
Test	ppm Fe ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	-----	98	3.11	90.0	1.30
2	60 ppm	101	3.10	86.8	1.33
3	60 ppm	105	3.10	77.5	1.49
4	60 ppm	108	3.10	60.3	1.91
5	60 ppm	111	3.10	54.6	2.10

5.4.3 10ppm Co^{++} Impurity

Current efficiency data obtained for a hydrogen depolarized and a lead (calcium) anode in the presence of 10 ppm of Co^{++} ions are tabulated in table 3. The impurity effect was essentially equal for both anodes at 55°C. However, as the temperature of the electrode was lowered, the current efficiency of the Pb anode cell improved at a somewhat faster rate than the hydrogen depolarized cell.

5.4.4 1ppm Cu^{++} Impurity

The presence of 1 ppm Cu^{++} impurity in the electrolyte had little effect on ampere efficiency for either a Pb (Ca) or a hydrogen depolarized anode. Data are presented in table 4.

5.4.5 Ge^{++++} Impurity

Germanium is by far the most troublesome impurity tested to date. This ion lowers the hydrogen overvoltage on zinc to such an extent that the presence of 1 ppm in the electrolyte (55°C) is sufficient to prevent the deposition of a continuous zinc plate. The cathode product is essentially H_2 gas. This effect is independent of the anode employed.

In order to determine a tolerable Ge^{++++} concentration range (current efficiency > 85%), the impurity level was decreased by orders of magnitude until substantially typical zinc plating was achieved. These data, which are presented in table 5 show that it is necessary to avoid germanium concentration above 0.05 ppm in the zinc electrowinning solution in order

TABLE 3
EFFECT OF COBALT IMPURITY
ON
CURRENT EFFICIENCY AND POWER CONSUMPTION
H₂ Depolarized vs. Industrial Pb(Ca) Anode

<u>H₂ Depolarized Anode</u>					
Test	ppm Cobalt Impurity	Cell Temperature	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	10 ppm	35°C	1.38	91.5	0.562
2	10 ppm	45°C	1.30	89.5	0.545
3	10 ppm	50°C	1.26	86.8	0.542
4	10 ppm	55°C	1.27	85.7	0.552

<u>Pb(Ca) Anode</u>					
Test	ppm Cobalt Impurity	Cell Temperature	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	10 ppm	35°C	3.22	94.1%	1.27
2	10 ppm	45°C	3.12	92.5%	1.25
3	10 ppm	50°C	3.07	92.5%	1.24
4	10 ppm	55°C	3.03	84.5%	1.33

TABLE 4

Effect of Copper Impurity
on
Current Efficiency and Power Consumption
H₂ Depolarized vs. Industrial Pb(Ca) Anode

<u>H₂ Depolarized Anode</u>					
Test	ppm Cu ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	1 ppm	98.0	1.24	93.1	.50
2	1 ppm	101.4	1.25	92.5	.51
3	1 ppm	104.7	1.25	90.0	.52

<u>Pb(Ca) Anode</u>					
Test	ppm Cu ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	1 ppm	98.0	3.11	93.1	1.24
2	1 ppm	101.4	3.10	91.1	1.26
3	1 ppm	104.7	3.11	92.2	1.25

TABLE 5
EFFECT OF GERMANIUM IMPURITY
ON
CURRENT EFFICIENCY AND POWER CONSUMPTION
OF
HYDROGEN DEPOLARIZED ANODE

55°C Cell Temperature

33% H₂ Efficiency

Test	g/l H ₂ SO ₄	g/l Zinc	ppm Ge +++++	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	98	120	0.000	1.24	93.0%	0.500
2	98	120	0.001	1.24	91.0%	0.510
3	98	120	0.010	1.25	87.0%	0.535
4	98	120	0.050	1.24	87.1%	0.530
5	98	120	0.100	1.25	79.4%	0.587
6	98	120	1.000	1.26	00.0%	0.000

to maintain good ampere efficiency.

Studies indicate that the effect of similar levels of Ge^{++++} in a Pb anode cell are equal to or worse than that described above for the hydrogen depolarized anode.

5.4.6 Platinum Impurity

It has recently been reported that the presence of traces of dissolved platinum in a sulfuric acid electrolyte causes the rapid dissolution of zinc metal.¹ Since the hydrogen depolarized anode currently being investigated by Prototech Company contains a highly dispersed (surface area 120-170 m^2/gram) platinum catalyst it is extremely important to establish that such an electrode does not introduce a highly injurious impurity into the system.

Employing the standard synthetic electrolyte (120 g/l zinc and 98 g/l H_2SO_4) a series of tests were run to establish a tolerable level of platinum impurity. These data, table 6, show the following:

- a) For the system under study, a dissolved platinum impurity level of 0.1 ppm appears to be a safe maximum. At this level, the ampere efficiency and power consumption (KWh/lb zinc) average 85% and 0.57 respectively.

1. Dr. Anthony F. Sammells, Institute of Gas Technology and Dr. John Appleby, Electric Power Research Institute, during presentations and discussions at the Metal-Air Battery Project Meeting held in Washington, D.C. on April 10-11, 1979 and sponsored by DOE.

TABLE 6

Zinc Electrowinning

Effect of Platinum Impurity on Current Efficiency and Power Consumption

 H_2 Depolarized Anode

Test	ppm Platinum Impurity	Cell Temperature	Current Density	Cell Voltage	% Current Efficiency	Power Consumption KWH/lb zinc
1*	5.0 ppm	55°C	36 ASF	<<1.00	-----	-----
2	1.0 ppm	55°C	36 ASF	1.25	83.1%	0.61
3	1.0 ppm	55°C	36 ASF	1.27	83.0%	0.57
4.	0.1 ppm	55°C	36 ASF	1.26	82.7%	0.57
5.	0.1 ppm	55°C	36 ASF	1.25	81.0%	0.58
6	0.1 ppm	55°C	36 ASF	1.25	86.1%	0.54
7	0.1 ppm	55°C	45 ASF	1.38	85.2%	0.60
8	0.1 ppm	55°C	54 ASF	1.51	86.4%	0.64

*Sufficient Platinum solution at start up to render the cathode comparable to a Pt Electrode.

- b) Ampere efficiency at 0.1 ppm platinum impurity, is independent of current density over the range of 36 to 54 ASF.
- c) Excessively high levels of dissolved platinum (5 ppm) result in a hydrogen concentration cell (H_2 depolarized anode and H_2 evolved at platinized cathode) as the cell voltage at 36 ASF is well below the decomposition potential of zinc.

About the only conceivable way that platinum could be introduced into the electrolyte (0.1 ppm) of a zinc electrowinning cell from a hydrogen depolarized electrode is if erosion results in fragmentation of the catalytic layer. An attempt was made to create such a situation by abrading the electrolyte surface of electrodes so that small catalytic particles were free to drop off the anode when it was placed in the electrolyte. Several tests were run with abraded anodes and results, as described in table 7 indicate that such treatment had no effect on zinc plating, indicating that the platinum particles were insoluble in the electrolyte.

TABLE 7

Current Efficiency and Power Consumption Data

New H₂ Depolarized Anodes

Surface Abraded

Test	Cell Temperature	Current Density	Cell Voltage	% Current Efficiency	Power Consumption KWH/lb zinc
1	55°C	36 ASF	1.25	91.0%	0.51
2	55°C	36 ASF	1.24	92.5%	0.50
3	55°C	36 ASF	1.32	94.3%	0.52

5.5 Future Investigation

5.5.1 Synthetic Electrolytes

Long term tests, that is greater than four (4) hours, will be run to determine any change in

- a) anode performance
- b) plating efficiency.

5.5.2 Plant Liquor

Hydrogen depolarized anodes will be evaluated in an actual zinc electrowinning plant liquor. A 55 gallon drum of liquor, complete with the appropriate analysis, has been shipped from Anaconda Company and testing should be complete by June, 1979.

SECTION 6

TECHNICAL DISCUSSION

METAL-WATER-AIR BATTERIES

6.1 Aluminum - Air Batteries

Samples of Prototech electrodes (Pt loading of $0.30 \pm 10\%$ mg/cm²) without a current collector assembly have been supplied to Lockheed, and samples with and without a current collector (same Pt loading) have been supplied to Lawrence Livermore Laboratory.

Dr. Littauer of Lockheed presented data at the Metal-Air project meeting in Washington, April 10-11, 1979 showing that the Prototech Company RA19 type cathode performed in accordance with the goals set for the battery up to a current density of about 300 ma/cm² at 60°C. Similarly, Dr. Cooper of Lawrence Livermore Laboratory presented data, at the same meeting, showing the improved performance of a Prototech Company electrode-current collector assembly over another commercially available electrode.