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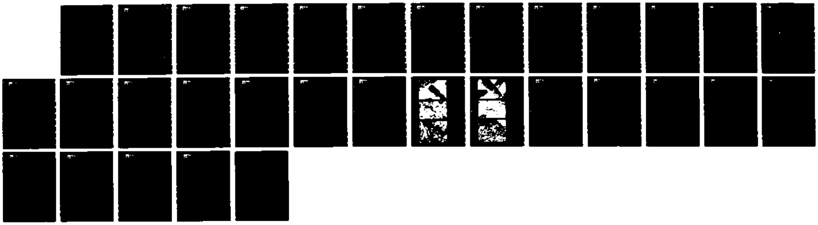

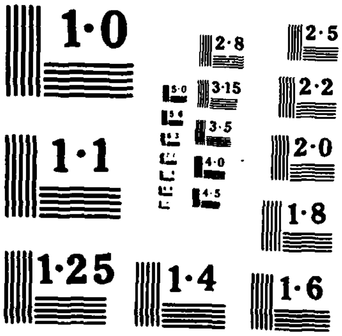
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UNITED TECHNOLOGIES
HAMILTON STANDARD

ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE

N00014-82-C-2182
CONTRACT NO. ~~N000~~-82-C-2182

MODIFICATION NO. 1

FINAL REPORT

MAY 1986

FOR

NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVENUE
WASHINGTON, D.C. 20375

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1.0 SUMMARY

Many researchers have studied the electrochemical reduction of carbon dioxide and related organic species to form concentrated liquid/gaseous products in laboratory scale hardware. Hamilton Standard has developed a high pressure SPE® electrolysis cell capable of reducing carbon dioxide streams to form pure, concentrated alcohols, carboxylic acids, and other hydrocarbons. The process is unique in that the byproducts of reaction include oxygen and, under some test conditions water. In addition, a relatively simple test system was designed and constructed permitting both batch and semibatch type electrochemical reduction studies.

In this study, cathode materials were developed which (1) had a characteristic high hydrogen overvoltage, and (2) posessed the intrinsic affinity for electrochemical reduction of the carbon dioxide species. In addition, suitable anode electrocatalyst materials were identified.

Studies involving the electrochemical reduction of carbon dioxide required the ability to identify and quantify reaction products obtained during cell evaluation. Gas chromatographic techniques were developed along with the establishment of ion chromatographic methods permitting the analysis of organic reaction products.

Hamilton Standard has evaluated electrochemical carbon dioxide reduction cells under a variety of test conditions. Much of the development work has focused on the evaluation of SPE® electrolysis cell conversion efficiency versus cathode feedstock employed including carbon dioxide dissolved in both nonaqueous and aqueous solvents of varying concentration, gaseous carbon dioxide, two phase (gaseous in conjunction with liquid) carbon dioxide, and high pressure liquid carbon dioxide streams. Coupled with the catholyte evaluation was a study involving the effect of carbon dioxide pressure on electroreduction efficiency. Cells were evaluated over varying current density and test duration.

High electrochemical conversion efficiency of carbon dioxide to liquid organic products may be obtained via proper selection of electrode materials and SPE® electrolysis cell operating conditions. Test results indicate that indium electroplated stainless steel cathode structures promote the electroreduction of carbon dioxide while inhibiting the hydrogen evolution reaction. High efficiency reduction of the carbon dioxide reactant requires a high concentration of the carbon dioxide species at the cathode/catholyte interface. High pressure liquid carbon dioxide catholyte feedstocks (1000-1200 psig) significantly enhance the carbon dioxide reduction reaction. In addition, electrolysis cells operated at low current densities (< 200 ASF) tended to exhibit higher electrochemical reduction efficiencies than did cells operating with the higher power input. SPE® electrolysis cells configured with proper electrode materials and operating under test conditions conducive to carbon dioxide electroreduction have demonstrated conversion efficiencies in excess of 70% in short term tests (less than eight hours duration).

® SPE is a registered trademark of Hamilton Standard Division of United Technologies Corporation

2.0 INTRODUCTION

The goal of this contract was the development of an improved process for the management of respired carbon dioxide. A reliable electrochemical conversion system would increase system reliability while reducing safety/health hazards. This electrochemical conversion system is based on a solid polymer electrolyte, a perfluorocarbon sulfonated membrane to which catalytic electrodes are physically bonded. Electrolyzer products are generated in a pure, concentrated state that does not require subsequent separation from the supporting electrolyte.

The electrochemical reduction of carbon dioxide to organic liquids has received considerable attention in recent years. The following reactions of carbon dioxide have been found to take place on the cathode:

$$(1)\quad CO_2\,(g) + 2H^+ + 2e^- = HCOOH\,(aq) \qquad E^o = -0.20V$$

$$(2)\quad CO_2\,(g) + 4H^+ + 4e^- = HCHO\,(aq) + H_2O \qquad E^o = -0.10V$$

$$(3)\quad CO_2\,(g) + 6H^+ + 6e^- = CH_3OH\,(aq) + H_2O \qquad E^o = -0.01V$$

Possible subsequent reactions are as follows:

$$(4)\quad HCOOH\,(aq) + 2H^+ + 2e^- = HCHO\,(aq) + H_2O \qquad E^o = 0.06V$$

$$(5)\quad HCOOH\,(aq) + 4H^+ + 4e^- = CH_3OH\,(aq) + H_2O \qquad E^o = 0.12V$$

$$(6)\quad HCHO\,(aq) + 2H^+ + 2e^- = CH_3OH\,(aq) + H_2O \qquad E^o = 0.24V$$

$$(7)\quad CH_3OH\,(aq) + 2H^+ + 2e^- = CH_4 + H_2O \qquad E^o = 0.58V$$

Figure 1 shows an example of the desirable reactions for this process. Other reactions may also occur in the SPE^R electrolysis system. Formation of more complex hydrocarbons such as carboxylic acids or esters may result from direct chemical reaction of electrolysis products either in the bulk solution or at the catholyte/catalyst interface. Additional possibilities include subsequent electrochemical reactions of simple organic products with carbon dioxide molecules.

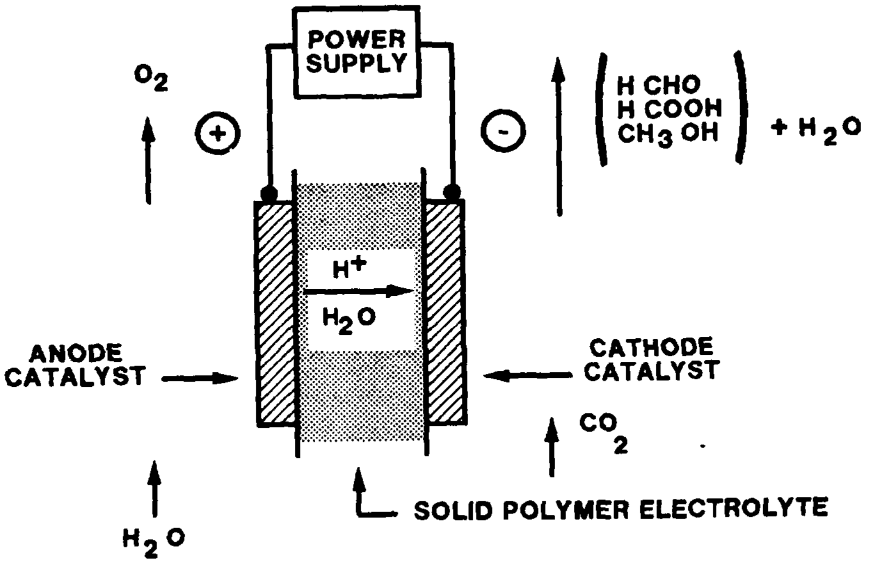
Two undesirable reactions may take place on the cathode. One such reaction is the combination of protons and electrons to form molecular hydrogen.

$$2H^+ + 2e^- = H_2\,(g) \qquad E^o = 0.00V$$

In addition, an undesirable reaction involving carbon monoxide and water.

$$CO_{2\,(g)} + 2H^+ + 2e^- = CO_{(g)} + H_2O\,(l) \qquad E^o = -0.06V$$

Proper selection of electrode materials and cell operating conditions can lead to the supression of both undesirable reactions.



ANODE REACTION: $2H_2O \longrightarrow 4\,H^+ + O_2 + 4E^-$

CATHODE REACTION: $4\,H^+ + 2\,CO_2 + 4E^- \longrightarrow 2\,HCOOH$

OVERALL REACTION: $2\,H_2O + 2\,CO_2 \longrightarrow O_2 + 2\,HCOOH$

FIGURE 1. CARBON DIOXIDE REDUCTION (WITHOUT SUPPORTING ELECTROLYTE)

3.0 LITERATURE STUDY

A literature study was conducted targeted at obtaining useful information pertaining to the electrochemical reduction of carbon dioxide along with related technologies. Pertinent reprints have been collected with information taken from the literature being used as a basis for SPE^R cell design.

In recent years, several researchers have investigated the electrochemical reduction of carbon dioxide on both metal and nonmetallic electrodes. Ulman, Aurian - Blajeni, and Halmann[1] present an overview of the topic, along with some of the historical apects of carbon dioxide reduction studies. Much of the research to date has focused on the electrochemical reduction of carbon dioxide dissolved in aqueous solvents. Ito et. al.[2] present the results of carbon dioxide reduction studies involving supporting aqueous catholyte solutions of $LiCO_3^-$, $(C_2H_5)_4$ $NClO_4$, and $(n - C_4H_9)_4$ NBr on solid state electrodes including In, Sn, Pb, and Pb (Hg). The primary reaction products obtained in this case were formic acid, propionic acid, oxalic acid, and n-butyric acid. Other researchers have also conducted studies of electrochemical carbon dioxide reduction on metallic electrode structures. Vassiliev et. al.[3] have conducted comprehensive carbon dioxide reduction studies on a variety of metallic electrodes including Sn, In, Bi, Sb, Cd, Zn, Cu, Pb, Ga, Ag, Au, Ni, Fe, W, Mo, and glassy carbon. Haggin[4] reports on the formation of methane using ruthenium catalyst materials.

Other researchers have investigated the electroreduction of carbon dioxide on nonmetallic cathodes. Kapusta and Hackerman[5] have evaluated the electrochemical reduction of carbon dioxide on metal pthalocyanine catalyzed carbon electrodes. Aurian - Blajeni et. al.[6] investigated the necessity of metallic electrode materials by implementing polyaniline-coated silicon electrodes.

In addition, investigations have been conducted into the utility of nonaqueous supporting catholyte solutions for electrochemical carbon dioxide reduction. Ito et.al.[7] have studied the effects of utilizing aprotic solvents and tetraalkylammonium salts in conjunction with various metallic electrode structures on carbon dioxide reduction efficiency. The principle reaction product obtained while employing lead electrodes as the cathode was oxalic acid. When indium, zinc or tin electrode materials were utilized, the prevalent reaction product was found to be carbon monoxide, however, low production efficiencies of oxalic, malonic, glycolic and formic acids were also noted.

Along with carbon dioxide reduction studies, related technologies were also researched. Hori, et.al.[8] and Stadler et.al.[9] investigated the feasibility of electroreducing the bicarbonate ion thus producing the formate ion. Ogura and Watanabe[10] studied the electrochemical reduction of carbon monoxide. Kang and Winnick[11] reported on the concentration of carbon dioxide by a membrane cell. Some recent studies by Frese et. al[12, 13, 14] have investigated the reduction of carbon dioxide to form methane, carbon monoxide, and methanol using Ga As, Mo, Cr, Ru, Ag, C, and Os electrodes. Reaction products depend on electrode material, temperature, and working electrode cell voltage.

4.0 EXPERIMENTAL

4.1 Optimization of the SPE Electrolysis Cell

An SPE® electrolysis cell has been developed at Hamilton Standard and is based on a solid polymer electrolyte membrane, Nafion®, produced by DuPont. It is a cation exchange membrane in the proton form. On one side of the membrane is placed a catalytic electrode structure, E-50, a proprietary material, which provides reaction sites for the anode half reaction:

$$2H_2O \rightleftharpoons 4H^+ + 4e^- + O_2\ (g)$$

This electrode material also provides electrical conductivity for the passage of electrons to the external circuit. The protons then migrate across the perfluorocarbon membrane for subsequent participation in the cathode half reaction.

On the cathode, two scenarios are possible. One is an undesireable reaction in which electrolysis of water molecules from the anode is completed on the cathode with carbon dioxide molecules taking no part in th reaction. This hydrogen evoloution reaction is what normally occurs in typical water electrolysis cells.

$$2H^+ + 2e^- \rightleftharpoons H_2\ (g)$$

The targeted reaction is the electreochemical reduction of the carbon dioxide molecule itself. Laboratory test results have shown excellent conversion to liquid organics such as methanol, formic acid, formaldehyde, and other organic species under some test conditions.

In the cathode compartment of the electrochemical cell, reduction of the carbon dioxide molecules necessitates that the carbon dioxide molecules reach an acitve electrode surface along with the migrated protons. These active sites are provided by a package of 40 mesh stainless steel screens tack welded to a titanium base. For good electrochemical carbon dioxide reduction efficiency it is necessary that the active area fulfill two requirements. The first is that it be a characteristically high hydrogen overvoltage material thus suppressing the hydrogen evolution reaction. The second is that it have a high affinity for electrochemical reduction of the carbon dioxide species. In the Hamilton Standard SPE® electrolyzer, this is achieved by depositing pure indium metal on an array of 316 stainless steel screens.

® Nafion is a registered trademark of E.I. DuPont

4.2 Laboratory Size Test Cell

The laboratory test cell assembly is shown in Figure 2, with a corresponding parts list. The membrane and electrode assembly, (MEA), Part 6, was centered in the test cell assembly. On the anode side was pressed a 0.05 $(ft)^2$ square shaped active area loaded to 6 $mg/(cm)^2$ with a proprietary E-50 catalyst mixture. Pressed against the membrane material on the cathode side was a 2.5 mil Zitex® porous teflon shim. This material separates the cathode screen from the membrane while providing a porous gateway for the passage of protons and carbon dioxide molecules.

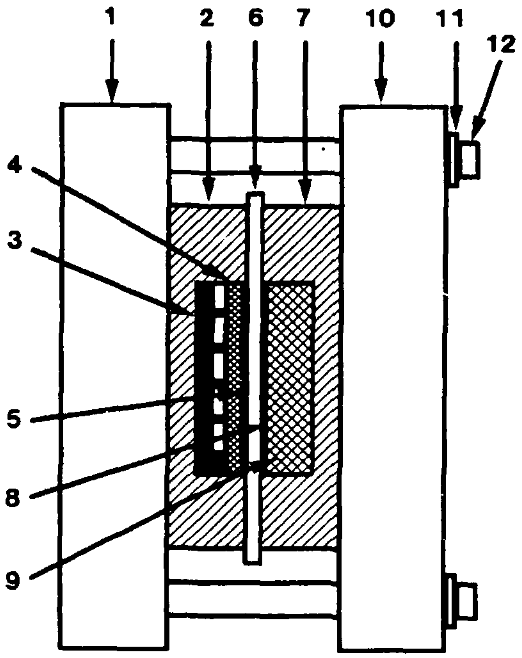
The anode compartment is composed of a fluid plate/current collector in which manifold grooves for the passage of anolyte fluids have been cut. Centered in the anode cavitiy are an array of platinized screens to provide electrical conductivity for the passage of electrons. These screens are held in intimate contact with the anode electrocatalyst.

The cathode compartment is also composed of a fluid plate/current collector containing manifold gooves which allow for the passage of catholyte. Spot welded to this plate is a grooved flow field configured from pure indium foil. These grooves promote turbulence within the catholyte stream allowing the carbon dioxide molecules to reach the active screen assembly. Spot welded to this flow field are 6- 40 mesh 316 stainless steel screens plated with indium to form the cathode active area. These, in turn, were compressed against the Zitex® material on the cathode side of the membrane.

The fluid plates were sandwiched between two end plates, parts 1 and 10, then compressed by tightening the end plate bolts. Endplate compression promotes intimate contact between electrolyzer components thus reducing resistive losses in the test cell assembly.

Current flow was afforded by attaching cabled leads from each current collector/fluid plate to the power supply. Voltage measurement was made possible by affixing small gold-plated pins to the surface of each current collector.

® Zitex is a registered trademark of Chemplast, Inc.



F/N	DESCRIPTION
1	END PLATE
2	CURRENT COLLECTOR
3	FLOW FIELD
4	INDIUM PLATED SCREENS
5	ZITEX® SHIM
6	MEMBRANE
7	CURRENT COLLECTOR
8	E-50 CATALYST
9	PLATINIZED SCREENS
10	END PLATE
11	WASHER
12	BOLT

FIGURE 2. LABORATORY CARBON DIOXIDE REDUCTION TEST CELL ASSEMBLY

4.3 *Laboratory Test System*

The Hamilton Standard SPE® electrolyzer is conveniently operated with a very simple test system capable of pressures approaching 1500 psig. A representative fluid schematic for the electrochemical carbon dioxide reduction test system is represented by Figure 3.

Liquid/gaseous carbon dioxide is metered into the system through valve V1. It is then circulated through a high pressure centrifugal pump and passes into the test cell cathode compartment via 1/4" 316 stainless steel tubing. After reaction, the catholyte stream exits the test cell assembly, passes through a series of separators, then back through the recirculating pump. Separated gasses pass from the separators, through a pressure regulator, a flow controller, then out of the test system. Argon for system overpressurization passes through valve V2 and into the test system.

The anode separator is filled with either distilled water or some type of supporting electrolyte solution to decrease cell resistance. The resulting anolyte is circulated with a piston pump through the anode portion of the test cell assembly. The anode chamber of the test system is pressurized through valve V3 with nitrogen.

The test system electrical schematic can be seen in Figure 4. The electrical system is designed so that critical operational parameters such as temperature, pressure, current and cell voltage may be continuously monitored, however, no provision is made for automatic operation.

Power is supplied to the electrolysis cell by a Hewlett Packard 2022 B power supply. Operational hardware such as resistance heaters and power supplies may be shut down via an emergency switch connected in line with a system relay shutdown.

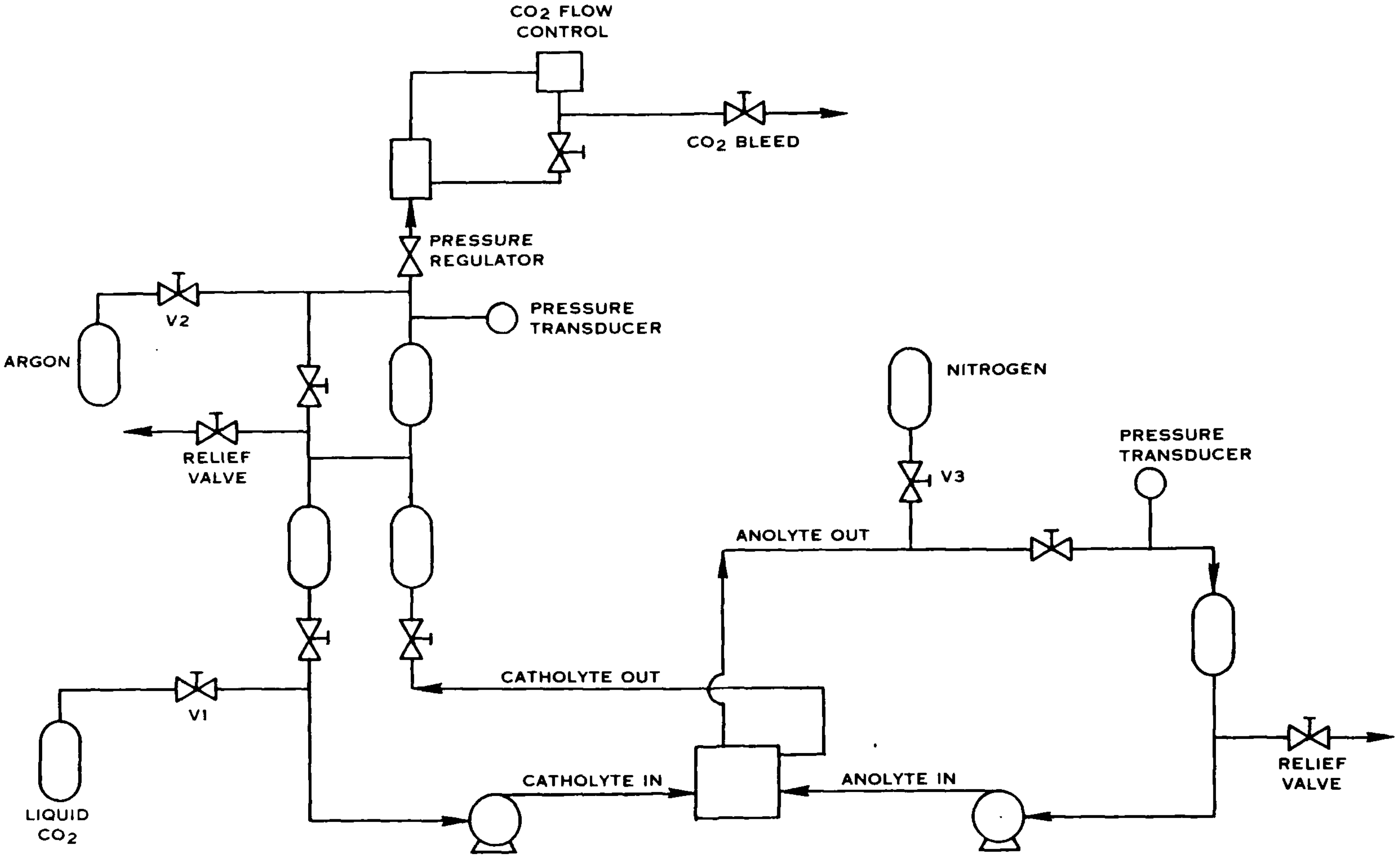


FIGURE 3. CARBON DIOXIDE REDUCTION FLUID SCHEMATIC

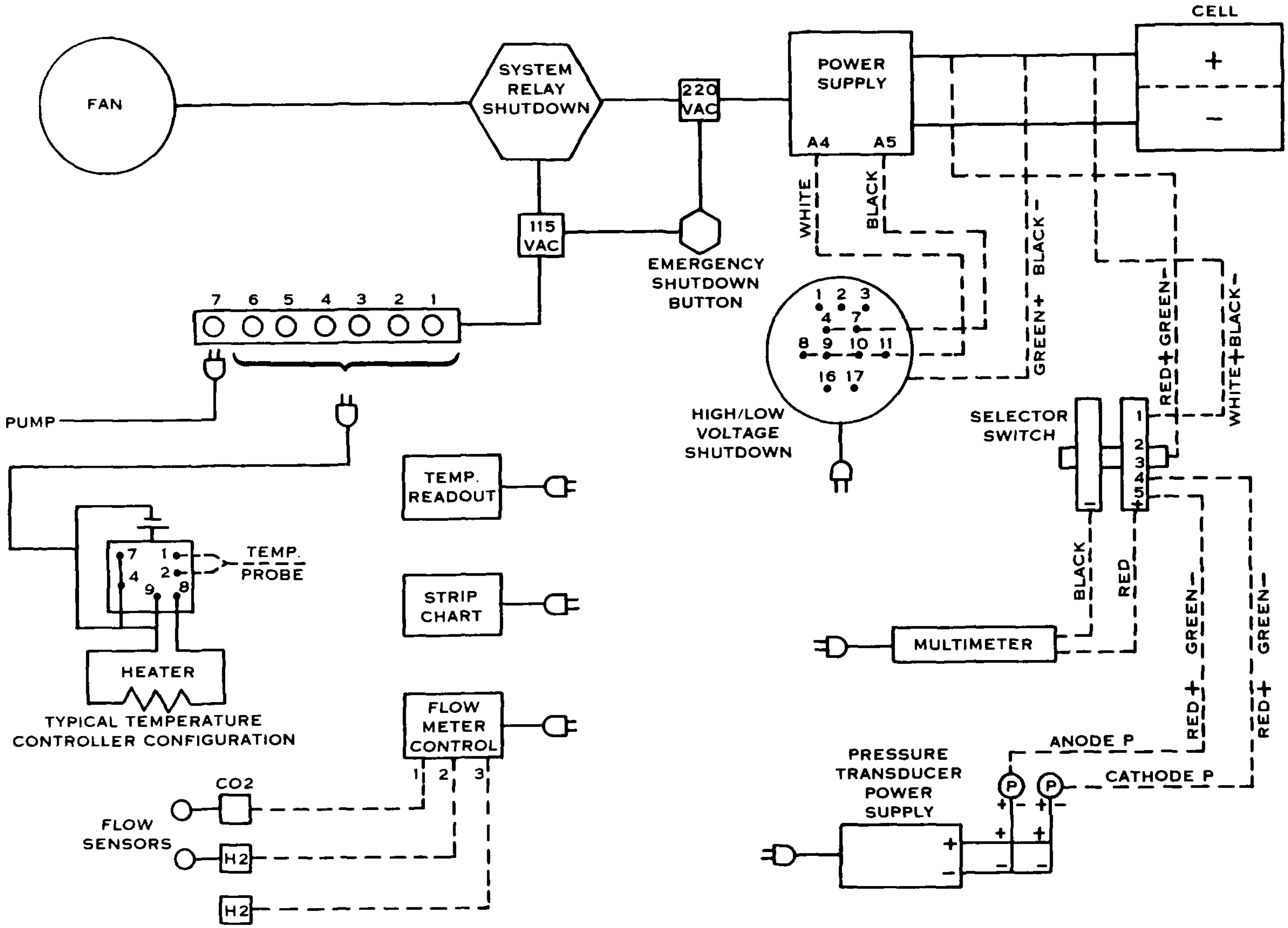


FIGURE 4. CARBON DIOXIDE REDUCTION ELECTRICAL SCHEMATIC

5.0 RESULTS

5.1 *Analysis of Reaction Products*

Quantification of organic liquids produced during carbon dioxide electroreduction studies is based on a batch type test run where all products are washed from the active surface with a one liter charge of process fluid. The concentration of a liquid organic species present in the test system can be determined via gas or ion chromatography. The entire quantity of organic component produced during a test run may then be back calculated using a mass balance.

Reaction products were analyzed with a Shimadzu 3BF gas chromatograph modified for liquid phase analysis. This gas chromatograph utilizes a 1/8" stainless steel column and operates at 125°C. The gas chromatograph was coupled with a Shimadzu RAF-1A reaction furnace operating at 650°C enabling detection of products such as methanol, formic acid, and formaldehyde. This addition, seen in Figure 5, provides a means of detecting reaction products after separation by conversion to methane.

A Dionex 2110 ion chromatograph was also used for reaction product analysis. This device was fitted with a HPICE separator column and AFS-2 supressor column. In this case, the eluent was 0.75mm octane sulfonic acid flowing at 1.2 ml/min. The regenerant was 5.0mm tetrabutylammonium hydroxide. The ion chromatography results supported the gas chromatograph analysis data.

The theoretical quantity of product obtained during a carbon dioxide electroreduction test run may be calculated from Faraday's law as follows:

$$g = I\ e\ t\ /\ 96500$$

Where g represents the theoretical mass of organic product, I represents the cell operating current in amperes, e is the chemical equivalent weight of the organic product, and t is the duration of the test run in seconds.

The efficiency (percent) of conversion to a particular reaction product may be calculated as follows:

$$\text{Efficiency} = 100\ (g\ \text{actual}/g\ \text{theretical})$$

Where g, actual, represents the total quantity of the reaction product obtained via gas or ion chromatography and g, theoretical, is the theoretical mass of a reaction product obtained for given test conditions.

The total efficiency of conversion to organic products for a test run may be determined by summing the conversion efficiencies of each reaction product detected from a cathode wash after each test run. This relationship may be expressed as:

$$\text{Total Efficiency} = E_a + E_b + E_c + \ldots\ldots$$

Where E_a, E_b, and E_c represent the efficiency of conversion to organic products a, b, and c, respectively.

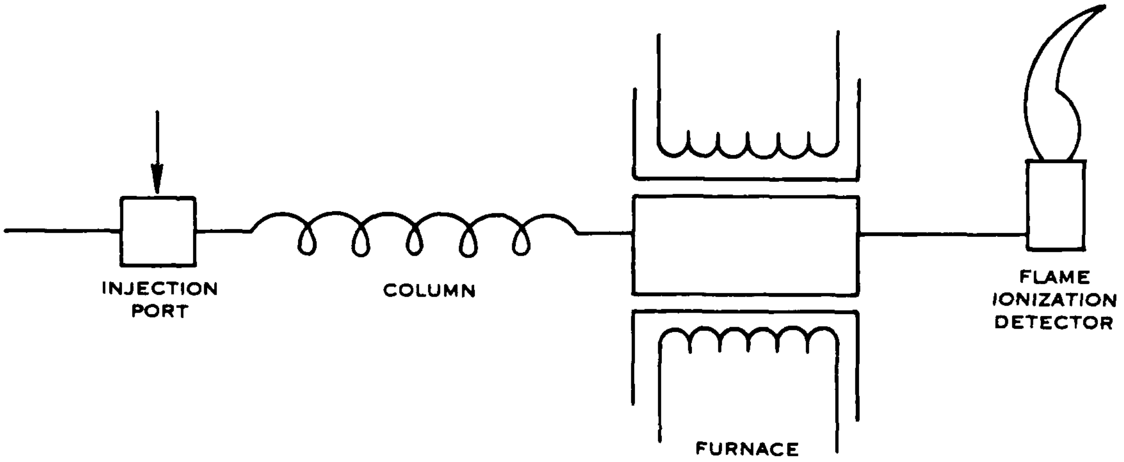


FIGURE 5. SCHEMATIC OF REDUCTIVE REACTION GAS CHROMATOGRAPH

5.2 Optimization of the Catalyst/Electrode System

The structure and composition of the cathode electrocatalyst is the key to efficient electrochemical reduction of carbon dioxide. Various catalyst materials were screened for their activity to the electroreduction of the carbon dioxide molecule. The approach here was to evaluate (1) noble metal oxide/blends and (2) high hydrogen overvoltage metals such as indium. The materials included oxides of Pt-Ir, Ru-Ir-Ta, Pd-Rh, Ru, Pd-Ru-Rh, and Rh. Each of these materials favored the hydrogen evolution reaction over carbon dioxide reduction. It was found, however, that indium metal (1) does have activity for the electrochemical reduction of carbon dioxide and (2) retards the hydrogen evolution reaction.

Proper structuring of the cathode electrocatalyst, indium, leads to highly efficient electrochemical conversion of carbon dioxide to liquid organic products. Indium electrodes pressed against/onto the cathode side of the ion exchange membrane tends to favor the hydrogen evolution reaction. Deposited indium metal on 316 stainless steel screens placed in intimate contact with an inert Zitex® film/membrane produces a viable catalyst structure for efficient electrochemical reduction of carbon dioxide.

The methodology involved in activating the 316 stainless steel screens with pure indium metal had a significant effect on the electrochemical reduction of carbon dioxide to form organic liquid products. Preparation included electroplating 40 mesh stainless steel screens to a thickness of 0.05 mils after flashing with a thin coating of nickel plate. The coating process was taken one step further in one experiment by heating the material to 350°F (above the melting point of pure indium metal) allowing the coating to flow, followed by cooling at room temperature. A performance comparison of the two electrode configurations can be seen in Figure 6. Metallographic studies of the heat treated indium plate versus the electroplated indium deposit show similarities in the metal structure. The indium metal tended to "ball up" when heated due to the high surface tension, leaving spots of the stainless steel screen uncovered. These bare stainless steel areas may have inhibited the carbon dioxide reduction reaction allowing some hydrogen evolution to occur.
Photomicrographs showing the indium configuration on the screens can be seen in Figures 7 and 8.

Low pressure evaluation of the optimized cathode structure (0-100 psig carbon dioxide), resulted primarily in the production of formic acid using various testing parameters. High pressure evaluation of the same electrode structure (800-1500 psig carbon dioxide) tended to shift the reaction to the formation of methanol, formaldehyde and formic acid (mostly).

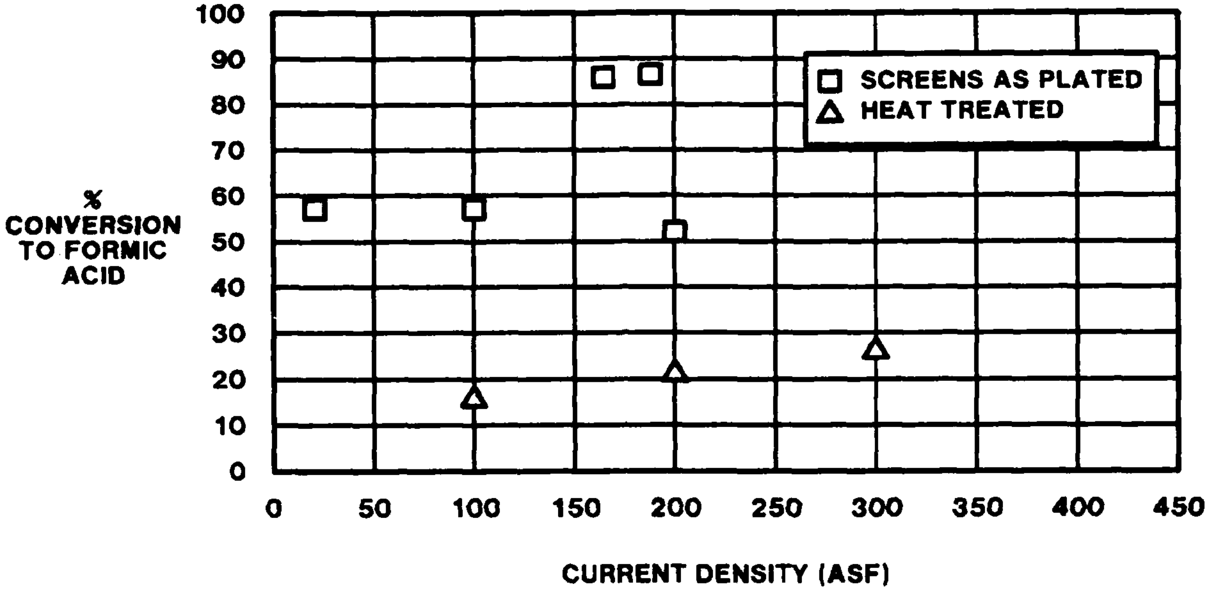
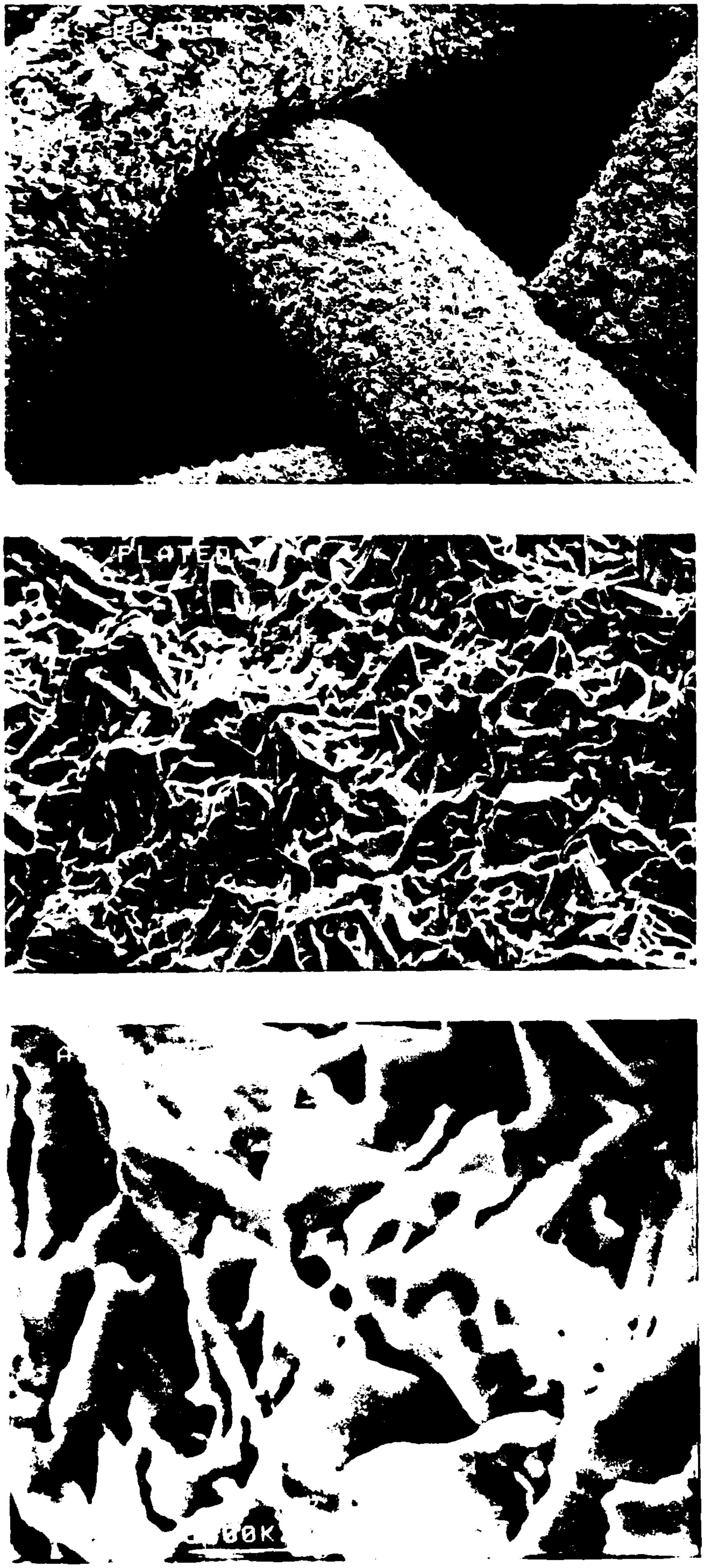


FIGURE 6. ELECTROREDUCTION EFFICIENCIES OF INDIUM ELECTRODE STRUCTURES

In on 316
As Plated



125x

1250x

5000x

FIGURE 7. SEM of Indium Electrode Structure As Plated

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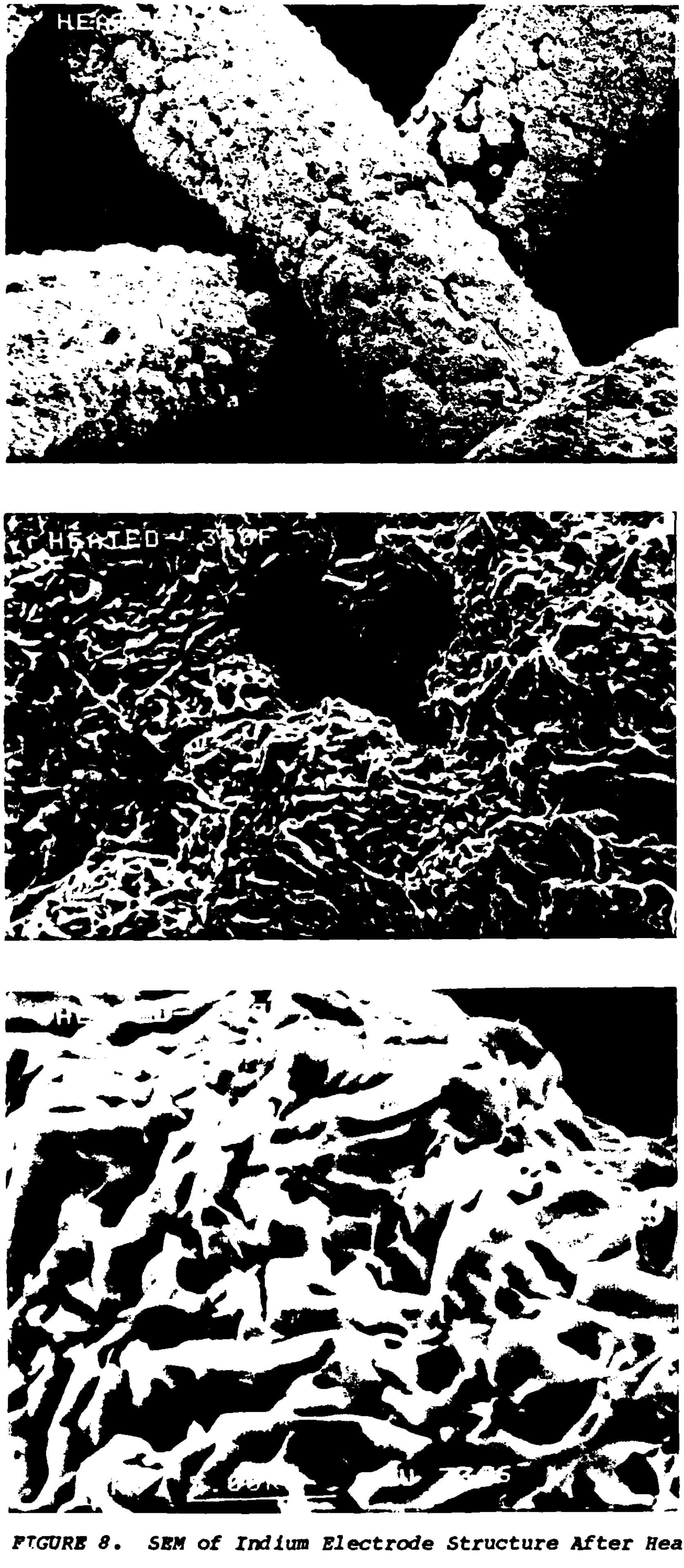

In on 316

Heated to 350°F

125x

1250x

5,000x

FIGURE 8. SEM of Indium Electrode Structure After Heat Treatment

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5.3 *Effect of Cathode Feedstock on Electroreduction Efficiency*

Monoethanolamine/Propylene Carbonate Solvents- Previous studies have indicated that the active species participating in the carbon dioxide reduction reaction is the dissolved carbon dioxide molecule. Both monoethanolamine and propylene carbonate were identified as fluids having a relatively high affinity for the carbon dioxide molecule. Studies indicate that the electroreduction efficiencies of test runs completed with carbon dioxide molecules dissolved in these solvents are poor; especially at high current densities where conversion efficiencies are essentially zero.

Two Phase Gas/Liquid Flow- An investigation of two phase flow at the cathode was conducted in the SPE® electrolyzer. A 0.1 molar lithium carbonate solution was recirculated at 150-300 cc/min with gaseous carbon dioxide passing over the cathode at 50 cc/min. Feeding gaseous carbon dioxide in two phase flow with the liquid catholyte allows the carbon dioxide molecules used up in reaction to be continuously replenished with gaseous supplies. Test results obtained from two phase studies are represented by Figure 9.

Gas/Liquid carbon dioxide- The effect of pure carbon dioxide catholyte on electrochemical conversion has also been investigated. Variations in pressure from 50 psig to 1200 psig including gaseous feeds, saturated gas/liquid feeds and liquid feeds have been examined. Results indicate that operation with gaseous carbon dioxide feeds produces similar conversion results to the saturated gas/liquid catholyte system. Test results are shown in Figure 10.

High pressure liquid carbon dioxide catholyte feeds have produced the best and most consistent electrochemical conversions to liquid organic products. Figure 11 shows test results of cells operated with high pressure catholyte fluid streams (1000-1200 psig). Conversions of 70% to 100% are consistently obtained at low current densities using indium plated stainless steel screens as the active area on the cathode. This liquid carbon dioxide remains liquid as it contacts these screens, crowding the reaction sites with carbon dioxide molecules thus eliminating the hydrogen evolution reaction.

Supporting Electrolyte- In a similar set of high pressure experiments, the effects on conversion of using lithium carbonate or sodium hydroxide as supporting electrolytes in varying concentration at the cathode were examined. Results of several test runs indicate that increasing the concentration of lithium carbonate in the cathode compartment led to an increased conversion to formic acid. Conversion efficiency was reduced, however, when the lithium carbonate was replaced by sodium hydroxide as a supporting electrolyte at a similar concentration. The results indicate that lithium ion helps augment electrochemical carbon dioxide conversion to liquid organics.

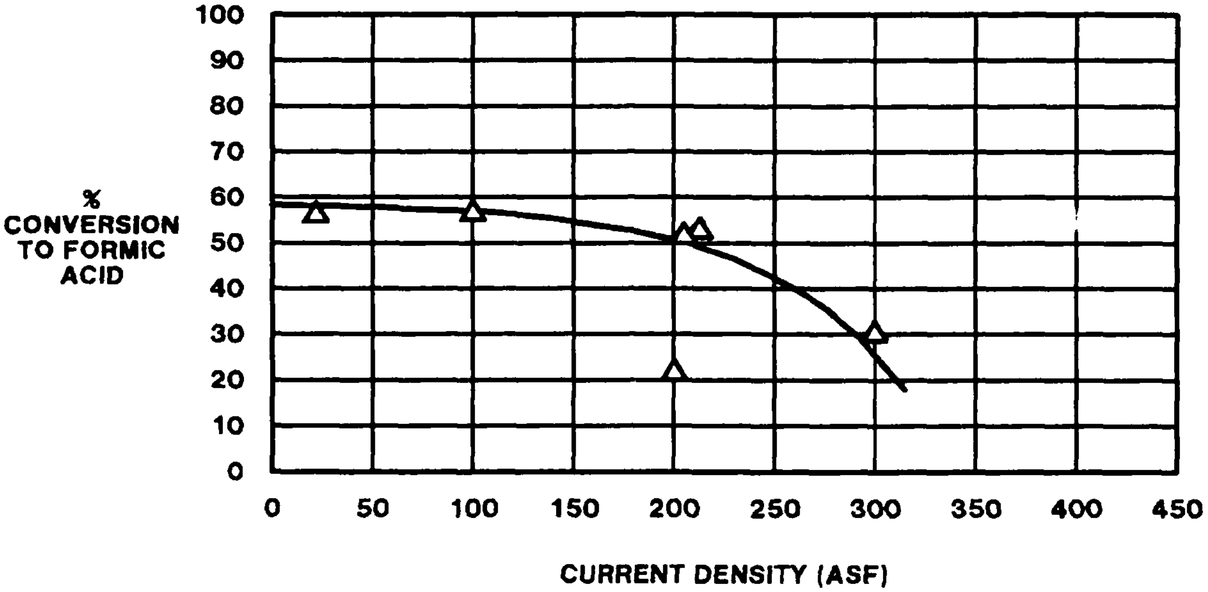

FIGURE 9. EFFECT OF TWO PHASE FLOW ON ELECTRO-REDUCTION EFFICIENCY

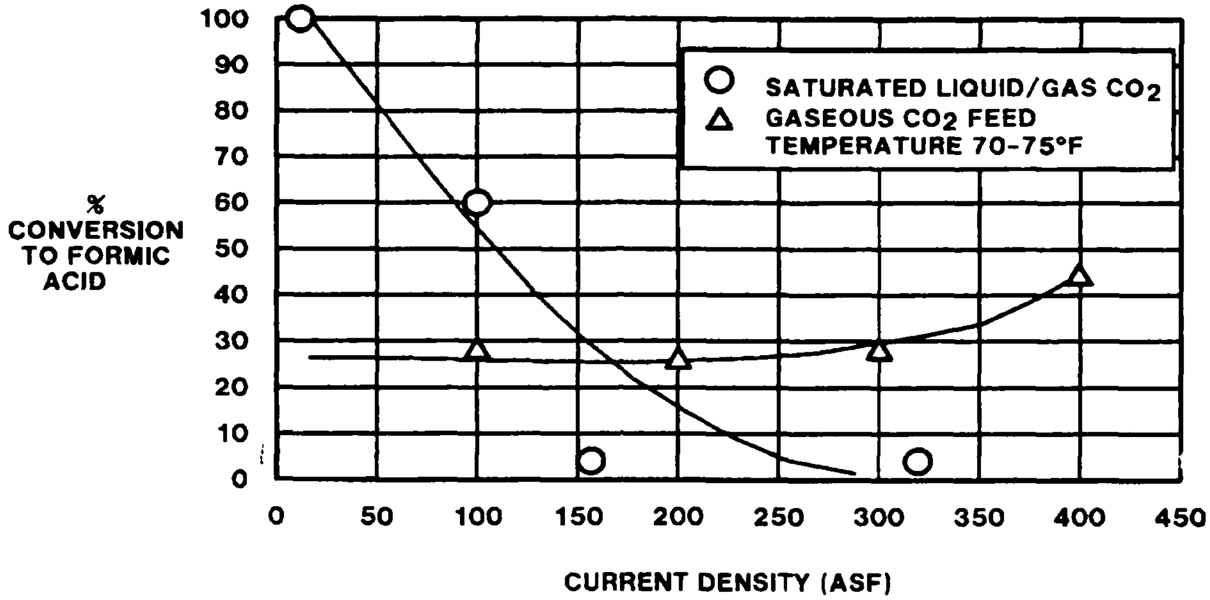

FIGURE 10. EFFICIENCY OF CONVERSION TO FORMIC ACID VERSUS CATHODE FEEDSTOCK

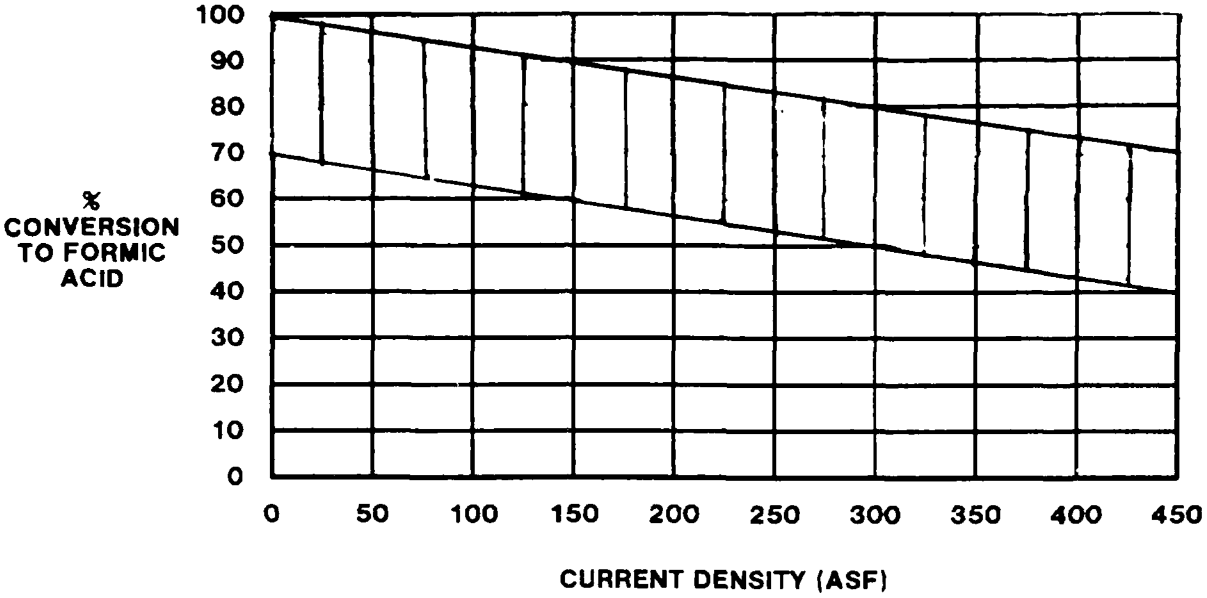

FIGURE 11. EFFECT OF LIQUID CARBON DIOXIDE FEED ON ELECTRO REDUCTION EFFICIENCY

5.4 Effect of Current Density on the Electrochemical Reduction of Carbon Dioxide

As can be seen in Figure 12, the effect of current density on the efficiency of conversion to liquid organics is great in most cases. We can easily rationalize this by carefully examining what happens at the catalyst/catholyte interface. Since the catholyte solution is well mixed upon entering the cathode compartment, the concentration of carbon dioxide molecules in the bulk catholyte, Cb, is relatively constant. Knowing that the active area in the cathode compartment is very large, the number of carbon dioxide molecules present at the catalyst/catholyte interface, Cs, at any instant is constant. The mole flux to the electrode surface is thus proportional to the difference between Cb and Cs, and should also be a constant.

As the current density of reaction is increased, the number of protons and electrons reaching the cathode surface are proportionally increased. Thus, the ratio of carbon dioxide molecules to protons is decreased. If the carbon dioxide pressure is increased so that carbon dioxide is present in the liquid form, then the concentration of carbon dioxide molecules at the electrode surface will also be proportionally increased. The ratio of carbon dioxide molecules to protons at the cathode surface will thus be increased. The dependence of current density on this ratio is shown in Figure 12.

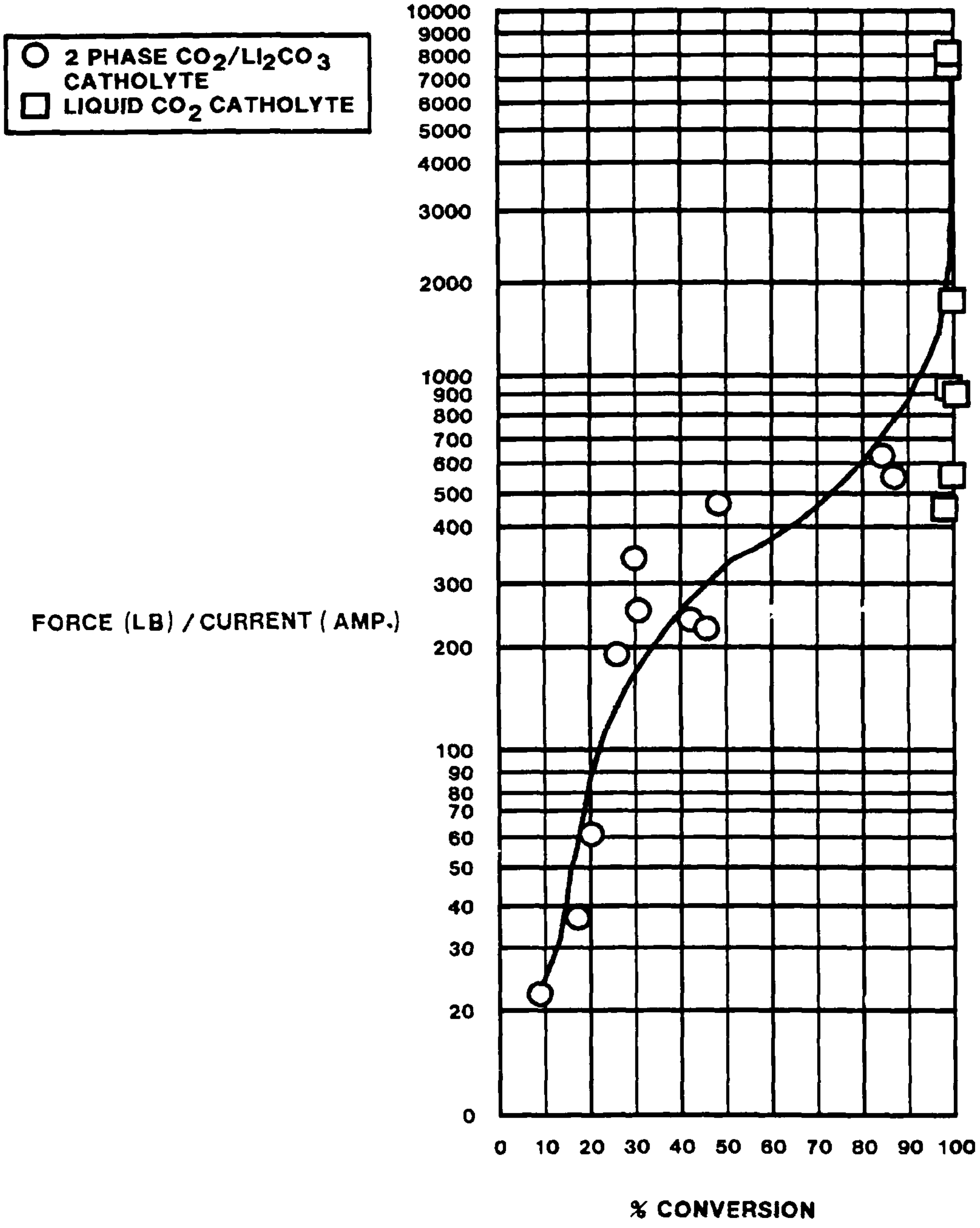

FIGURE 12. EFFECT OF CURRENT DENSITY AND CARBON DIOXIDE PRESSURE ON ELECTROREDUCTION EFFICIENCY ACTIVE AREA (0.05 FT^2)

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7.0 CONCLUSIONS

Hamilton Standard has developed a laboratory size, high pressure SPE® electrolysis cell capable of reducing carbon dioxide streams to form liquid organic products in addition to generating oxygen. With continued development, this electrochemical conversion system could provide a reliable method for carbon dioxide management.

The major accomplishments of the program include the following:

HARDWARE

- *A high pressure SPE® electrolysis cell was developed capable of high efficiency product conversion.*
- *Cathode materials having (1) high hydrogen overvoltages, and (2) high affinity for carbon dioxide reduction, were identified and evaluated.*
- *Electrocatalyst structuring studies were conducted. It was found that 316 stainless steel screens electroplated with indium augmented carbon dioxide reduction efficiencies while limiting the hydrogen evolution reaction.*

SYSTEM

- *A high pressure test system was designed and constructed of corrosion resistant materials. The test system was capable of high current (0-200 ASF), and high pressure (0-1500 psig) electrolysis operation.*

ANALYSIS

- *Analytical procedures were developed for reaction product monitoring. A Shimadzu 3 BF gas chromatograph was modified for liquid phase analysis. In addition, a Dionex 2110i chromatograph was used in reaction product identification and quantification.*

TEST RESULTS

- *High carbon dioxide reduction efficiencies may be obtained via operation with the proper cathode structure and test conditions.*
- *It is necessary to feed liquid carbon dioxide reactants at high pressure to maintain a high reactant flux to the cathode. Low pressure gaseous carbon dioxide feeds along with carbon dioxide dissolved in various solvents do not result in good reduction efficiencies. In general, as the concentration of the supporting electrolyte is increased, the suppression of the hydrogen evolution reaction is also increased. Lithium ion appears to augment the electrochemical reduction of carbon dioxide to liquid organics.*
- *It was found that an increase in the current density of electrolyzer cell operation hampered conversion efficiency to liquid organic products. An increase in reactant pressure at high current densities boosts carbon dioxide reduction efficiency.*

8.0 RECOMMENDATIONS

Further work should be conducted to:

- Continue to develop/optimize alternate cathode catalysts for more efficient electrochemical carbon dioxide reduction, especially at high current densities.
- Modify/optimize the Navy OGP hardware for use as a test cell for electrochemical carbon dioxide reduction.
- Develop a safe high pressure (up to 1200 psig) breadboard test facility for conduction of parametric testing.
- Design a single and multiple cell electrolysis preprototype stack.

END

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