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AN ELECTROCHEMICAL CARBON DIOXIDE REDUCTION - OXYGEN GENERATION SYSTEM HAVING ONLY LIQUID WASTE PRODUCTS

Final Report - Phase II

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FOREWORD

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Prinicpal Investigator for Ionics was Mr. Floyd H. Meller, Senior Engineer in Ionics' Research Division, assisted by Dr. Kathleen Brummer, Consultant in Electrochemistry, and Mr. Richard Shields, Project Chemist. The work was carried out under the supervision of Mr. Daniel L. Brown, Manager of Contract Research for Ionics. The research sponsored by this contract was performed between May, 1967 and March 1968.

ABSTRACT

The electrochemical reduction of carbon dioxide has been investigated as a means of simplifying the disposal of carbon dioxide and hydrogen from a submarine atmospheric regeneration unit. Ejection of these materials as organic liquid wastes is preferable to the compression and gas phase discharge systems in current use.

This investigation comprises phase II of the problem of developing an electrochemical cell to accomplish the desired reduction reactions. Conceptually, the cell consists of an anode at which water is electrolyzed to oxygen, a cathode at which carbon dioxide is reduced, and an electrolyte path between the two. A two stage reduction is required to balance the system metabolically consisting of the following general progression:

$$CO_2 \rightarrow HCOOH \rightarrow HCHO \text{ or } CH_3OH.$$

Four cathode materials were found to catalyze the CO_2 reduction. They are mercury, gallium, indium and the quaternary alloy Cerrolow 136. The latter material is most effective when used in the liquid phase. The reduction of HCOOH is accomplished to a limited degree on tin or Cerrolow 136.

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SECTION I

INTRODUCTION

One of the important changes desired in the design of nuclear submarines is the elimination of the requirement for overboard discharge of waste gases from the atmospheric control system. At present, carbon dioxide is concentrated at pressures slightly above ambient and then compressed to much higher pressures in order to discharge the gas from the confines of the submarine at various submergence depths. On the other hand, hydrogen, which is formed at the cathodes of the water electrolysis unit, is generated at pressures of about 3,000 psi in order to eliminate the need for a hydrogen compressor. The dangers inherent in the generation of hydrogen (and oxygen) at this pressure is obvious. Moreover, as submarines are built which have deeper diving capabilities, the problems associated with carbon dioxide compression and hydrogen evolution at even higher pressures will become more severe.

With regard to these problems, Ionics has investigated an electrochemical process which could completely eliminate the need for overboard discharge of gases from submarines. The process generates all the oxygen required by the crew and converts all the respired carbon dioxide into simple liquid organic compounds. This report represents the conclusions of Phase II of that investigation; the purpose of which was to determine the engineering feasibility of this concept. Can the desired reactions be made to occur at rates sufficient for the design of practical units?

The electrochemical reduction of carbon dioxide has been reported by a variety of investigators. Like many organic reactions, the reaction is not rapid and the overvoltage is significant. This can cause significant differences in results reported. Allen (1) quotes eight references (2-9) dating from 1870 to 1931 as reporting the nearly quantitative reduction to formic acid on certain cathodes. More recently, Van Rysselberghe (10,11) has demonstrated that, on mercury, dissolved CO_2 rather than bicarbonate ion is the reducible species, and that the reduction proceeds principally to formic acid. There is disputed evidence concerning the further reduction of formic acid (12,13). Leitz and Viklund investigated the technical feasibility of the reduction of carbon dioxide and the further reduction of formic acid in electrochemical systems in Phase I of this program (14).

Ionics' proposed process can be described in broad terms as follows. Carbon dioxide, obtained highly concentrated from a scrubbing unit, is dissolved in an electrolyte and fed to cathode compartments of an electrolytic cell. Here, cathodic reduction of the carbon dioxide solution occurs at the surface of the catalytic electrodes. Concurrently, water is fed to anode compartments where it is electrolyzed to form gaseous oxygen and hydrogen ions. The hydrogen ions migrate to the cathode where they react with carbon dioxide.

Anode construction is not a problem since the oxygen reaction is catalyzed by a number of precious metals, including platinum. The problem lies in selection of the cathode material. This occurs because the reversible potential for CO_2 reduction is approximately the same as the reversible potential for hydrogen evolution, which is a competing reaction. It is the necessity for encouraging the former reaction while suppressing the latter that requires careful selection of catalyst and operating conditions.

CO_2 reduction catalysts produced principally formic acid (HCOOH). This is not a sufficient reduction to balance the desired respiration coefficient. Consequently, some of the formic acid formed in the first stage, must be further reduced to methanol in a second stage. From an overall system consideration water and carbon dioxide are fed to the electrolytic cell and oxygen, formic acid and methanol or formaldehyde are produced.

SECTION II

INITIAL PROGRAM

Preliminary Considerations

Overall system considerations and operational goals for a practical air purification unit are reviewed in Appendix A. Current densities of the order of 40 amperes per square foot (ASF) at 100% cathode efficiencies will result in a two stage unit of approximately eight cubic feet weighing 800 pounds. This unit is designed to handle a crew of 120 men.

Reduction reactions for the two stages were investigated in phase I of this program (14). The cathode reactions are as follows:

Stage 1. $CO_2(g) + 2H^+ + 2e^- \rightarrow HCOOH(aq) \quad E^o = -0.196V$

Stage 2. $HCOOH + 4H^+ + 4e^- \rightarrow CH_3OH + H_2O \quad E^o = +0.123$

Cathodes demonstrating high efficiencies for these reactions as determined in Phase I studies are summarized in Table I.

TABLE I

PERFORMANCE OF REDUCTION CATALYSTS (14)

Reduction	Metal	Potential Volts	Current Density ma/cm^2	Current Efficiency Range %
Stage I	Mercury		1.0	100
	Indium	-1.2 to -1.4	0.04 to 0.56	14 to 69
	Silver	-1.34	0.157	39
Stage 2	Tin	-0.7 to -1.0	0.02	96 to 100

Although significant current efficiencies were obtained, the operating current densities were, in most cases, far below the design level. Then too, in the case of the best CO_2 reduction cathode, mercury, a toxicity problem could exist in the confined environment of a submarine making this material undesirable. The considerations requiring immediate study prior to engineering design were:

- Investigate additional electrode materials for better performance.
- Increase cathode current density several orders of magnitude.

Electrode Material Studies

Several electrode material - electrolyte systems were studied as possible alternates to the mercury-bicarbonate system for carbon dioxide reduction and the tin-bicarbonate system for formic acid reduction. The techniques used for evaluation were polarographic determinations using the potential sweep and step methods developed for Phase I studies (14).

Electrodes were prepared by encapsulating the electrode material in an epoxy casting compound and subsequently exposing a fixed area, usually 0.25 sq.cm, by metallographic polishing techniques.

Electrode and electrolyte combinations tested are summarized in Table 2.

TABLE 2

SUMMARY OF TESTS *

Electrode	Electrolyte				
	$NaHCO_3$ (0.1N)	Me_4NOH (0.1N)	Eth_4NI (0.1N)	H_2SO_4 (0.1N)	0.1N H_2SO_4 +0.1N Na_2SO_4
Bismuth	X	XX	X	X	
Cadmium	XX	XX	X		
Cadmium Amalgam	XX	XX	X		
Carbon - Filament	XX	XX	X	X	X
Copper Amalgam	XX	XX	X	X	
Indium	XX	XX	X	X	X
Lead Amalgam	XX	XX	X	X	X
Niobium	XX		X	X	
Platinum Screen	XX	XX	X	X	X
Platinized Pt.Screen	XX	XX	X	X	X
Silver	XX	XX	X	X	X
Tin	XX	XX	X	X	X

* Each combination indicated (X) was tested for CO_2 and HCOOH reactants separately. Combinations indicated (XX) were also checked using both reactants simultaneously to observe additive effects.

A number of useful electrode-electrolyte combinations were predicted by the polarographic data. Confirmatory tests in larger cells using product analysis for evaluation were, to a high degree, disappointing. A closer investigation showed that although the polarographic method for measuring a reaction at an electrode is a very useful tool, there are many pitfalls associated with it. The maximum current available from the test apparatus used is 1 ma, therefore a very small electrode must be used. Impurities in the test solution can give rise to excessive background current and perhaps surface effects by adsorption on the electrode.

Impurity sources of significance can include the following:

- Organics in commercial distilled water
- Leachants from the epoxy encapsulating material
- Dissolved oxygen
- Organics in inert gas streams

All of these impurities can give an apparent positive reaction in this study. Adsorption on the electrode surface on the other hand may inhibit the reaction giving a false negative result.

Subsequent evaluations of electrode materials were made in the larger cells described below. Evaluation of electrode performance was made by analysis of the reduction products generated.

Current Density Studies

A test series was outlined to evaluate the effects of the following variables:

- Electrode Surface Preparation
- Catholyte Agitation Methods
- Catholyte Temperature

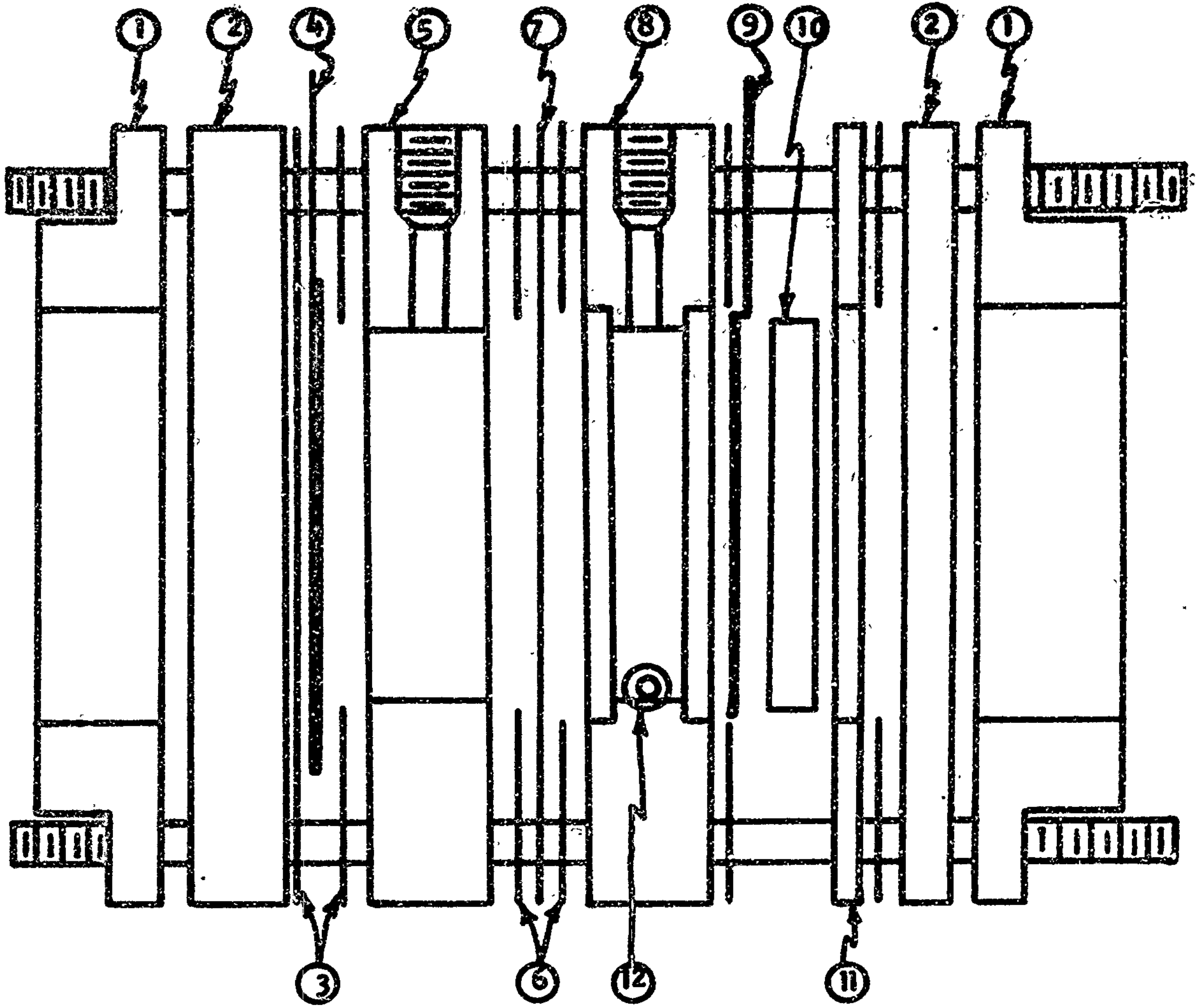
A group of cells having plane surface cathodes of 25 cm^2 and a catholyte chamber of approximately 60 cm^3 were constructed for the tests. An expanded side view of the cell is shown in Figure 1.

Initial tests were performed on the formic acid reduction using the tin electrode.

Electrode surface preparations were directed to the increase of surface area over the smooth surfaces tested in Phase I of this program. Techniques used included:

- Macro Etching
- Electrodeposition
- Vapor Blasting
- Wire Wound "Flow Through" Electrode

Experimental results on significant tests for the various preparation techniques are summarized in Table 3.



1. End Plate
2. End Block
3. Electrode (Anode) Gaskets
4. Anode
5. Anode Compartment
6. Membrane Gaskets
7. Membrane
8. Cathode Compartment
9. Cathode
10. Pressure Plate
11. Spacer Lock
12. Sample Port & Pump Inlet

FIGURE 1

MACRO CELL

TABLE 3

CURRENT DENSITY VARIATIONS WITH SURFACE PREPARATION

Electrode	Potential Volts	Current Density ma/cm^2	Current Efficiency Range %
Smooth Tin	-0.9	0.017	2.1-14.1
Macro Etched Tin	-0.9	0.066	1.4-13.4
Electro Deposited Tin	-0.9	0.50	6.8-36.8

Significant tests* on the wire wound and vapor blasted electrodes were not achieved.

Catholyte agitation was accomplished by solution pumping or inert gas bubbling techniques. Current density values were increased about 15X when pumping was employed. Inert gas flow was less effective.

The current density studies were evaluated by means of product analysis based on a three stage oxidation of the organic species generated (see Appendix B for the analytical method). The results obtained from multiple runs of the cell under identical conditions were inconsistent. System factors were ruled out through a lengthy investigation, leaving the analytical method in question. Subsequent investigation showed that the analytical method imposed severe limitations on earlier data. It can be safely concluded, however, that electrodeposition is a valid and useful method of increasing surface area and hence current density for reduction of organic species. Additional work is necessary to correlate the deposition conditions with organic reduction rates, but increases of one to two orders of magnitude seem realistic.

Analytical Procedure Investigation

A series of tests were performed to evaluate the analytical procedure used for product determination. The tests were of two basic types: 1) Verification of the standard (stock) solutions; 2) Analytical runs on "unknowns" made from the stock solutions. Three investigators were involved in the Group 1 verification tests. Although the same three investigators participated in the Group 2 "unknown" runs, the statistical data was compiled largely from the work of two of these men and verified by the work of the third.

The analysis of the analytical error was performed in two ways: 1) simple probability analysis, and 2) linear regression. The population distribution is shown in Figure 2. The distribution indicates an increasing variation from a normal probability sample as one proceeds from the formaldehyde to the methanol determinations. This situation prompted the selection of the results of the linear regression analysis as the best evaluation tool for establishing confidence limits for the analytical method for formic acid and methanol.

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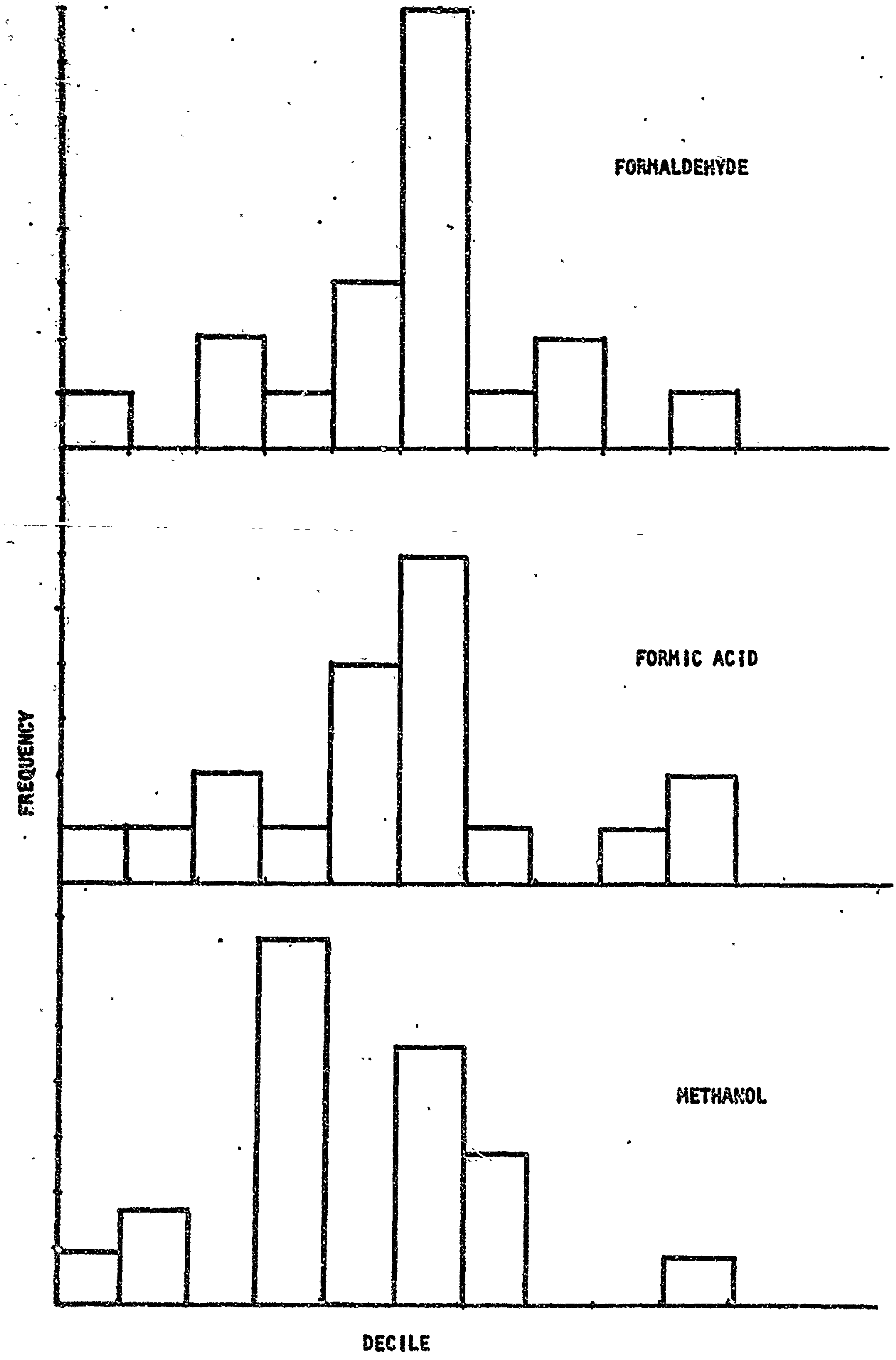
* Test significance is discussed in "Analytical Procedure Investigation" below.

FIGURE 2
POPULATION - FREQUENCY DISTRIBUTION



The linear regression technique takes into account the variation in slope from 1.00 in the relationship:

$$\tilde{Y}_o = aX + b \quad (1)$$

where $\tilde{Y}_o$ = the most probable amount of reactant detected in the titrating flask.

X = the amount of reactant in the titrating flask.

The standard deviation (s) used to calculate confidence limits is larger by this method.

A summary of the results of the statistical analysis is presented in Table 4. Minimum titration volumes for two confidence levels are reported. The variance and standard deviation from the mean were developed for the linear relationship noted above using the student "t" distribution and 95% confidence limits. Although this data is of some significance in determining the reliability of the mean it has no real value in predicting the validity of a given titration. In the interest of clarity this data is not presented. The use of (s) to designate the standard deviation is Bennett and Franklin's (15) term to indicate that the information is from a small finite sample and not a statistical population in which case the σ term would be used.

TABLE 4

SUMMARY - STATISTICAL DATA

Reactant	Slope	Intercept	Standard Deviation	Minimum Titration (V) Confidence Limits (%)	
	(a)	(b)	(s)	67%	95%
Formaldehyde -	1.00	-0.047	-0.129	0.055	0.20
Formic Acid	1.00	0.1536	0.720	0.38	0.69
by Linear Regression	1.0096	0.1688	0.772	0.41	0.74
Methanol	1.00	0.0258	0.095	0.23	0.40
by Linear Regression	1.037	0.0133	0.109	0.23	0.43

Calculation of minimum titration values (ml):

$$V_{67\%} = (b + s)/c \quad (2)$$

$$V_{95\%} = (b + 2s)/c \quad (3)$$

where: $V_{67\%}$ and $V_{95\%}$ = volume of titre in ml @ 67% and 95% confidence levels respectively.

b = best intercept in mg.

s = standard deviation of mean in mg.

c = conversion constant in mg/ml

= 1.5 mg/ml titre for formaldehyde

= 2.3 mg/ml titre for formic acid

= 0.533 mg/ml titre for methanol

Test Evaluation Techniques

A simple comparison of the minimum titration values at a given confidence level noted in Table 4 with previous test results provides a yes-no classification of product verification. Tests with titres exceeding the minimums can be considered to positively identify the existence of product. Some question as to the reliability of early test data will still remain however since the test procedure has undergone a series of technique refinements with the statistical data representing the best possible method.

Although the titration comparison is a useful tool for quickly examining the credibility of earlier tests, it does not give a convenient method for determining the probable range of values for a given test or a method of evaluating the test design. The latter point is particularly important when considering the design of future tests.

With the need for a more usable form of the function in mind, the following relation was derived for the current efficiency at the 95% confidence level:

$$\epsilon = \frac{n(y - b)}{akitA} \pm \frac{2sn}{akitA} \qquad (4)$$

where ϵ = cathode efficiency (as decimal)
y = product detected by analysis (mg)
n = equivalents/mole
a = best slope of X_o, Y_o line from statistical analysis
b = best intercept of X_o, Y_o line from statistical analysis
s = standard deviation
i = current (ma)
t = time (hrs.)
A = aliquot fraction (dimensionless)
k = conversion constant (mg meq/ma hr. m-moles)

Five reactions are possible as determined by tests:

1) $CO_2 + 2H^+ \rightarrow HCOOH$
2) $CO_2 + 4H^+ \rightarrow HCHO + H_2O$
3) $CO_2 + 6H^+ \rightarrow CH_3OH + H_2O$
4) $HCOOH + 2H^+ \rightarrow HCHO + H_2O$
5) $HCOOH + 4H^+ \rightarrow CH_3OH + H_2O$

From these reactions and statistical results the following simplification of the cathode efficiency relation (equation 4) can be made: Table 5 summarizes input data.

TABLE 5

INPUT DATA - CURRENT EFFICIENCY RELATION

Reaction	n	a	b	s	A	k
1 $CO_2 \rightarrow HCOOH$	2	1.0096	0.1688	0.772	0.167	1.72
2 $CO_2 \rightarrow HCHO$	4	1.00	-0.047	0.129	"	1.12
3 $CO_2 \rightarrow CH_3OH$	6	1.037	0.0133	0.109	"	1.19
4 $HCOOH \rightarrow HCHO$	2	1.00	-0.047	0.129	"	1.12
5 $HCOOH \rightarrow CH_3OH$	4	1.037	0.0133	0.109	"	1.19

Substituting in Equation 4: (subscript here denotes reaction)

$$\epsilon_1 = \frac{2(Y-0.1688)}{1.0096 \times 1.72 \times It \times 0.167} \pm \frac{2 \times 0.772 \times 2}{1.0096 \times 1.72 \times It \times 0.167}$$

$$= \frac{6.90Y - 1.16}{It} \pm \frac{10.6}{It}$$

in like manner.

$$\epsilon_2 = \frac{21.39Y + 1.00}{It} \pm \frac{5.52}{It}$$

$$\epsilon_3 = \frac{29.13Y - 0.39}{It} \pm \frac{6.34}{It}$$

$$\epsilon_4 = \frac{10.70Y + 0.50}{It} \pm \frac{2.76}{It}$$

$$\epsilon_5 = \frac{19.41Y - 0.26}{It} \pm \frac{4.23}{It}$$

From this relationship a cathode efficiency range can be determined which is defined by the second term of the equation.

The efficiency range term is also defined by a second set of limits - that is:

$$0 \leq \epsilon \leq 1.0 \quad (5)$$

This second constraint puts logical and useful limits on the function which allows some comment to be made about results in the questionable region at the extremes of the overall range.

If we let δ_ϵ equal the range term of equation (4) we have:

$$\delta_\epsilon = \frac{2sn}{akAIt}$$

$$= \frac{K}{It}$$

where K = constant for a given reaction
It = ma-hrs.

or

$$\delta'_\epsilon = K'/It$$

where $K' = K/26.8$

It = meq.

The δ_ϵ term can now be used to evaluate earlier tests or used to determine test parameters for future tests. Evaluations of earlier tests are shown in examples 1 and 2.

Example 1: Test No. 25 - Platinum catalyst
Potential = 0.3v
Reaction 5: $HCOOH \rightarrow CH_3OH$
Cathode Efficiency = 36.5%
Aliquot = 0.167
Titre = 0.35 ml
Current Passed = 0.382 meq

At a 95% confidence limit a minimum titre of 0.43 ml would be required to confirm the existence of product and therefore the value of this test and/or catalyst is questioned.

It is now useful to determine the validity of the test design so that a better evaluation of the reason for the test result can be made. To do this the $\delta_\epsilon = 0.157/It = 0.157/0.382$

$$= 0.41$$

$$\therefore \epsilon = 0.365 \pm 0.41$$

Considering the constraint on ϵ by the relation

$$0 \leq \epsilon \leq 1.0$$

the range for the cathode efficiency in this case is:

$$\epsilon_{\%} = 0 \rightarrow 77.5\%$$

With a range this broad, specific conclusions about the catalyst cannot be made and therefore the test design is considered inadequate and the test not very informative.

It is interesting to note that even in the case where no product is found ($y = 0$) the δ_ϵ function will allow a judgement of the test design.

Example 2: Test 32 - Tin catalyst
Potential = 1.3v
Reaction 5: $HCOOH \rightarrow CH_3OH$
Current Passed = 18.1 meq.
Cathode Effic. = 0
Aliquot = 0.167
Titre = 0

$$\delta'_{\epsilon} = 0.157/It = 0.157/18.1 = 0.0087$$

$$\therefore \epsilon = 0 \pm 0.0087$$

$$\text{or} \quad \epsilon_{\%} = 0 \rightarrow 0.87\%$$

The range in this case is significantly small and therefore the test design is considered to be adequate and the test highly informative. The catalyst however is considered inactive under the conditions of this test.

Future Test Design

The design of a new test now becomes simplified.

With the δ'_{ϵ} relationship established, one can use this function to establish the required value of the (It) parameter for any given efficiency range. Thus, to establish a meaningful test at say, a ±5% cathode efficiency range and under the conditions of Example 1, the following calculation would be made:

Example 3: $\delta'_{\epsilon} = 0.157/It$

$$It = 0.157/\delta'_{\epsilon} = 0.157/0.05 = 3.15 \text{ meq.}$$

Under the conditions of this test, elapsed time would be approximately 380 hours instead of the 46 hours actually run.

A narrower efficiency range would of course increase this elapsed time requirement, while a broader range would shorten it at the expense of test significance. The actual value of the range selected will ultimately rest on the purpose of the test being performed.

The elapsed time for the test in Example 3 can be cut in half by doubling the aliquot taken for analysis and eliminating the "duplicate run" technique now used in the analytical procedure.

Conclusions

The polarographic method of evaluating electrode activity for the required organic reductions, and the three stage oxidation technique used for product analysis have been found to have serious limitations in this program. Work performed in Phase I and the "Initial Program" of Phase II of this study are subject to these limitations.

Analysis of the tests run to this point show many results based on inconsistent data. Confirmed "significant" data show the following best results:

Stage 1: CO_2 reduction - Mercury electrode 100% current efficiency
Indium electrode 5-10% " "

State 2: Formic Acid reduction - tin electrode 7-13% " "

Significant analytical results can now be assured by utilizing the test design method determined in the statistical study of the analytical method. Carbon dioxide and formic acid reduction tests reported in Sections III and IV of this report utilize this test design technique. Electrodes that showed promise in the "Initial Program" were rerun.

SECTION III

REDUCTION OF CARBON DIOXIDE

Preliminary Considerations

A large number of electrode materials have been tested for the reduction of CO_2, and of these the most effective is mercury (11,14). The reactive species appears to be dissolved CO_2 rather than bicarbonate ion. This may be a serious limitation in the eventual practical application of an electrochemical reduction system since at high current densities, the limited solubility of CO_2 in water can give rise to extreme concentration polarization problems.

Two properties which the more successful CO_2 reduction electrodes seem to possess are:

- High hydrogen overvoltage
- They do not adsorb CO_2 or CO

The latter condition for CO_2 seems to be an anomaly. Normally one would expect it necessary for the CO_2 to be adsorbed on the electrode surface to be reduced. However, it is generally true that, where CO_2 is adsorbed, CO is adsorbed more strongly. CO or some similar species, is probably an intermediate in CO_2 reduction and is normally difficult to reduce further, thus blocking the electrode surface for additional CO_2 adsorption. It may therefore be a disadvantage to use an electrode which adsorbs CO_2. If non-adsorption is a criteria it will be necessary to force the reaction by means of a large potential difference. An electrode which has a high hydrogen overpotential is therefore required, hence the success of mercury and indium. Other elements which do not adsorb CO_2, although some may adsorb CO, are Rh, Pd, Pt, Al, Mn, Cu, Au, K, Mg, Ag, Zn, Cd, Hg, In, Ga, Si, Ge, Sn, Pb, As, Sb, Bi, Te and Se. Many of these materials have been investigated as reduction electrodes with varying degrees of success. Not all elements in the group fulfill the requirement of high hydrogen overpotential. Of the group that show promise, films are observed to form which coat the surface of the electrode perhaps making it less active.

Two approaches to the discovery of successful CO_2 reduction electrodes can be considered:

- Find an electrode that is kinetically more favorable to the reduction of CO_2, and is not poisoned by reaction products.
- Find an electrode that has high initial reaction rates which can be maintained by simple continuous regeneration.

Possibilities for the initial case include nickel or cobalt oxides and ruthenium (16). Other proprietary mixed oxides are additional possibilities.

Conditions to satisfy the latter requirement include cells with electrode wipers or liquid metal electrodes.

Experimental

Several materials were run in the large cells (figure 1) in an attempt to find an electrode favorable to the desired reaction. Test design and analysis for product followed the program developed by the statistical analysis of the analytical chemical procedure. Table 6 summarizes typical results. Current efficiencies attained did not approach a useful range.

TABLE 6

CATHODIC EFFICIENCY FOR CO_2 REDUCTION OF VARIOUS ELECTRODES

Electrode	Preparation	Current Efficiency
Platinum Black	Sintered in PTFE on Titanium	3.9%
Ruthenium	Sintered in PTFE in Pt Screen	3.6
Nickel		0.0-3.1
Lead Amalgam		1.8
Platinum	Bright Platinized	0.0
Lead		0.0
Iron		0.0
Esso #100	Sintered in PTFE in Pt Screen	0.0

The two approaches to electrode surface renewal were investigated.

Rotary mechanical wipers were used in a cell with an indium cathode. Galling of the metal surface rapidly occurred even with low pressure smooth teflon wipers. Mechanical and tensioning problems were a constant companion during these tests. Materials of greater physical integrity are required for success with this approach.

Liquid metal tests were run in a flat horizontal cell using the general system shown in Figure 3. A three compartment cell with a serpentine flow path was constructed. Solutions were pumped through the various compartments with the catholyte having the additional facility of being heated or cooled to maintain the cathode in the liquid or solid state depending on the design of the test. Constant pump agitation was maintained at a level just below which the liquid metal cathode would be forced from the system. Direct observation of the cathode surface was not possible in the cell. However, the gradual buildup of suspended solids in the catholyte gave a qualitative measure of the purging of the cathode surface film.

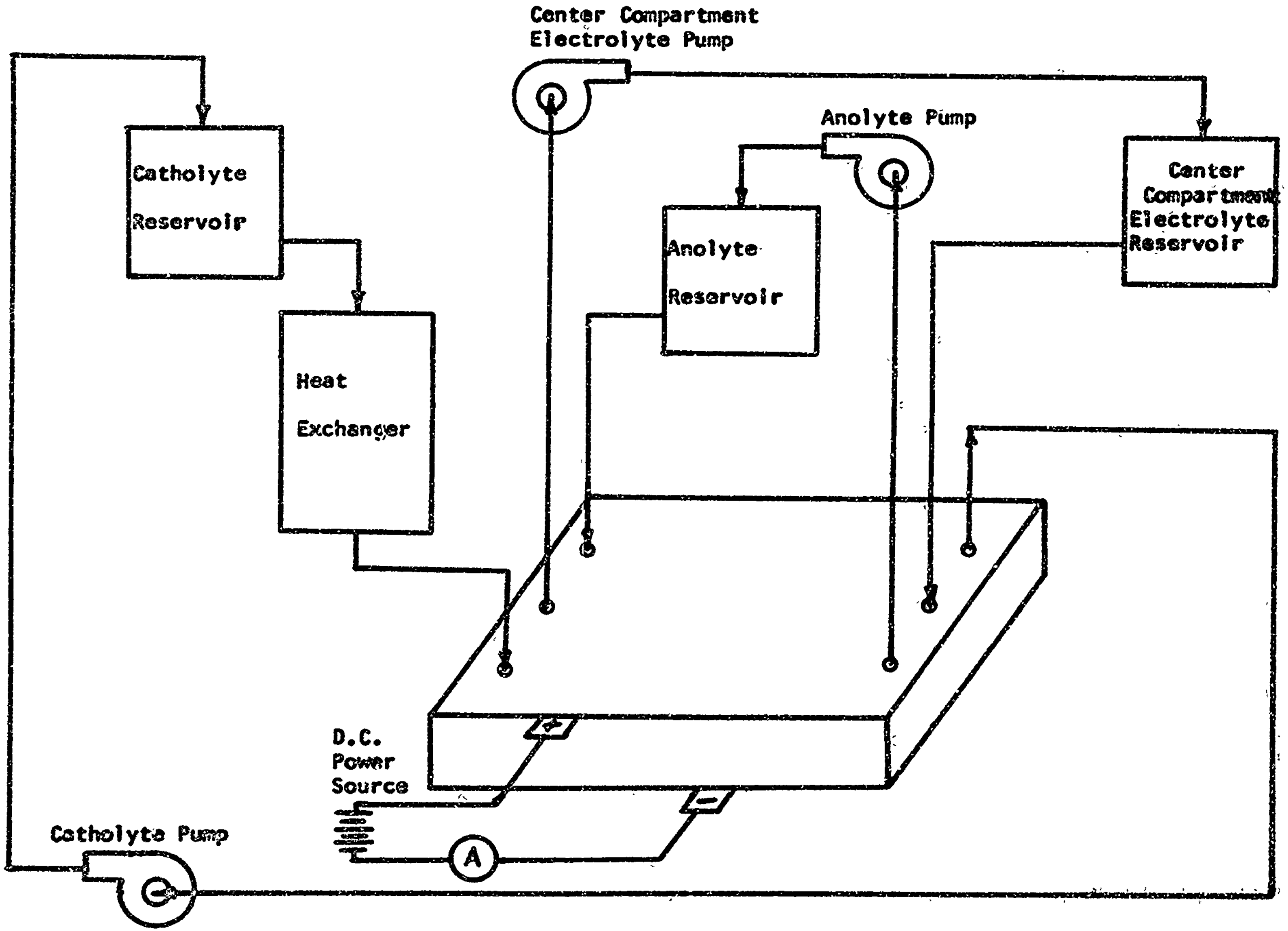


FIGURE 3: Liquid Metal Electrode Test System

Table 7 summarizes the data on significant tests in this series. The Cerrolow Alloy 136* was chosen for its favorable melting point, 136°F, and the presence of indium in the alloy which had given favorable results on CO_2 reduction. In all cases 0.5N $NaHCO_3$ catholyte was used.

TABLE 7

COMPARISON OF CATHODIC EFFICIENCY FOR CO_2 REDUCTION ON ELECTRODES IN SOLID AND LIQUID PHASE

Electrode	Phase	Current Efficiency %	Current Density ma/cm^2
Mercury	Liquid	93-100	1.0
Gallium	Liquid	34.9	16.4
Gallium	Solid	34.0	16.4
Cerrolow 136	Liquid	36	1.1
Cerrolow 136	Solid	24.3	0.9
Indium	Solid	20.5	2.9

Comparing the gallium tests in Table 7, it would appear that no significant improvement is realized by operating in the liquid state. Gallium with a melting point of 29.8°C is a near ideal material to evaluate the phase parameter since other considerations i.e. the reduction in solubility of CO_2 at elevated temperatures is minimized.

The results with the Cerrolow 136, however even with the decreasing solubility factor for CO_2 (liquid phase tests were run at 65°C) showed a marked improvement in the liquid phase. Products obtained from the Cerrolow 136 tests showed partial reductions beyond the formic acid stage. Typically, 5-10% of the reduction products were formaldehyde indicating a partial second stage reaction of the progression:

$$CO_2 \xrightarrow{\text{stage 1}} HCOOH \xrightarrow{\text{stage 2}} HCHO$$

This can no doubt be attributed to the presence of tin in the alloy which has been found to catalyze the second stage step.

It is interesting to note that the group of metals presented in Table 7 were by far the superior materials tested for the CO_2 reduction reaction. No suitable theory beyond the high overvoltage characteristics of the pure metals has evolved to explain this behavior.

The variation of current efficiency with current density for mercury and Cerrolow 136 is shown in Table 8. The effective current density term, defined as the product of current efficiency and current density best expresses the design parameter required for a practical cell.

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*Manufactured by Cerro dePasco, composition: 21% In, 12% Sn, 18% Pb, Bal. Bi.

TABLE 8

EFFECT OF CURRENT DENSITY ON CURRENT EFFICIENCY

Electrode	Current Density ma/cm^2	Current Efficiency %	Effective Current Density ma/cm^2
Mercury	1.0	100	1.0
	2.0	45.1	0.9
	10.0	62.5	6.25
	25	52.8	13.2
	50	41	20.5
Cerrolow 136 (Liquid Phase)	0.12	11.3	0.014
	0.9	36	0.32
	11.1	51.6	5.7
	44.4	74.2	32.9

Tests above the 50 ma/cm^2 range were beyond the capabilities of the laboratory equipment. The progression evolving for Cerrolow 136 in the liquid phase shows the unexpected result of increased efficiency with increasing current density. Additional testing is required to verify this trend.

Conclusions

Four electrode materials have been found that are capable of catalyzing the cathodic reduction of CO_2 to formic acid at a rate sufficient for test in a practical operating system. They are mercury, indium, gallium and the proprietary quaternary alloy, Cerrolow 136.

The mercury electrode, known prior to this study, is toxic and for that reason is a secondary choice for any practical systems.

The Cerrolow 136, an alloy of indium, bismuth, tin and lead with a melting point of 136°F, shows excellent promise for a working system. Use of this material in the liquid phase appears to be advantageous. The Cerrolow 136 alloy has further advantages: a) A partial reduction beyond formic acid to formaldehyde is automatically achieved, and b) the reduction reaction increases in efficiency with increasing current density over the range tested. If the latter unusual trend continues and can be verified by additional tests a very successful first stage reduction system is available.

SECTION IV

REDUCTION OF FORMIC ACID

Preliminary Considerations

The observation that a two stage reduction is necessary to balance the respiration coefficient was verified in Phase I of this program. Therefore, a study of the reduction of formic acid in the absence of CO_2 is required.

Cathodic reduction of formic acid was shown by Leitz and Viklund (14) to occur most efficiently at electrode potentials of approximately -0.9 volts. Slight increases in the potential difference resulted, on a tin electrode, in reaction rate reductions to essential zero. From this it was concluded that unlike the CO_2 reduction reaction that appears to be activation controlled and can be forced by increasing potential, the formic acid reduction is apparently controlled by the rate of adsorption of the reactive species on the surface of the electrode. It has been found very difficult to maintain high reaction efficiencies for this reduction on any fixed electrode surface.

It was observed in testing the solid tin electrode that high initial reaction efficiencies would occur with rapid reduction in efficiency resulting for longer term tests. This factor tends to verify the adsorption rate limitation proposed above. A second possibility is the masking or poisoning of the electrode surface with an adsorbed layer of the reduced species thus limiting the sites for additional formate adsorption. What appeared to be required to satisfy observed conditions was a self regenerating electrode that would preferentially adsorb formate ion.

The liquid metal electrode was investigated as a self regenerating means. A theoretical basis for the identification of electrode materials that would preferentially adsorb the formate species is unknown. Therefore, the Edisonian approach to electrode selection was used.

An alternate method to perform the desired reduction of formic acid involves the use of a two stage, or carrier, reaction. In this case, a redox couple between two positive ions would be used to perform the desired reduction of formic acid with the oxidized component of the couple then cathodically reduced at an inert cathode in the electrochemical cell, thus regenerating the reactant for the chemical step. A detailed discussion of this approach to formic acid reduction follows in the experimental section below.

Experimental

Electrode Investigation

A comparison of solid and liquid metal electrodes was made using gallium and Cerrolow 136. The gallium electrode did not catalyze the formate reduction in either the solid or liquid state. Cerrolow 136 tests showed an 85% increase in reaction efficiency for the liquid metal electrode over the solid electrode at current densities of 1 ma/cm^2. The effective current density for the liquid Cerrolow 136 is 0.14 ma/cm^2.

Electrode tests were designed by criteria developed in the statistical analysis of the analytical chemical method. Product analysis was used to evaluate the results of each run with the Feigl spot tests (17) for formaldehyde and methanol used to verify findings for certain runs. The most effective material found as a catalytic cathode for formate reduction was tin or its use as a component in Cerrolow 136. Table 9 summarizes the results.

TABLE 9

CATHODIC EFFICIENCY FOR FORMATE REDUCTION OF VARIOUS ELECTRODES

Electrode	Preparation	Current Efficiency
Cerrolow 136	Liquid phase	13.7%
Cerrolow 136	Solid phase	7.4
Tin	Polished	7
Tin	Electro plated	13
Esso 377-87-8	sintered in PTFE on Pt. screen	3.4
Esso 100	" " " " " "	2.0
Esso 377-87-12	" " " " " "	1.1
Iron	wrapped wire	1.1
Gallium	solid and liquid phases	1.0
Rhenium, Ruthenium, Lead Platinum (Black & Bright), 3 Proprietary Materials		>1.0

Redox Couple Investigation

The reduction potentials of formic acid to formaldehyde and methanol are:

$$HCOOH + 2H^+ + 2e^- \rightarrow HCHO + H_2O \qquad E^o = +0.056V$$

$$HCOOH + 4H^+ + 4e^- \rightarrow CH_3OH + H_2O \qquad E^o = +0.123V$$

These potentials refer to the standard hydrogen potential. It should therefore be very easy to carry out these two reductions electrochemically; that is thermodynamically the reductions are easy. Actually, it is very difficult to reduce formic acid either to formaldehyde or to methanol.

If the reacting species is to formate ion, it may not react at a cathode surface, because of the repulsion between two negative charges. To overcome this problem reduction has been attempted by means of a positively charged reducing couple. A number of couples have been investigated, which have a suitable redox potential and some which have the added advantage of complexing with the formate ion.

The possibility of carrying out the reduction in a very strong acid medium, where the formic acid is protonated and therefore positively charged, has also been considered.

A large number of suitable redox couples exists; it is necessary only that they should have a negative value of E^o and that the ions involved in the couple should have a positive charge. Typical examples are:

$Mo^{5+} \sim Mo^{6+} + e \qquad E^o = -0.34V$

$Cr^{++} \sim Cr^{+++} + e \qquad E^o = -0.41V$

$Cr \sim Cr^{++} + 2e \qquad E^o = -0.91V$

$Ti^{++} \sim Ti^{+++} + e \qquad E^o = -0.37V$

$Eu^{++} \sim Eu^{+++} + e \qquad E^o = -0.30V$

$In^o \sim In^{+++} + 3e \qquad E^o = -0.34V$

$V^{++} \sim V^{+++} + e \qquad E^o = -0.255V$

The two couples investigated were Cr^{++}/Cr^{+++} and V^{++}/V^{+++}. The reactions were carried out under the following conditions:

1. Two values of pH were investigated a) pH = 1, where the hydrogen ion concentration is high and formic acid is not dissociated, b) pH = 4, where the hydrogen ion concentration is not so high and formic acid is dissociated. The low pH measurements were made in sulphuric acid and the high pH measurements in an equi-molar solution of formic acid and sodium formate; each constituent was 0.5M.
2. The temperature was 80°C.
3. Chromium or vanadium sulphate was added and reduced, in situ, with zinc. Oxygen was excluded throughout the experiment by bubbling nitrogen through the solution.
4. The concentration of the reduced state of the redox couple was very high compared with the concentration of the oxidized state, to ensure that the redox potential was as low as possible (that is more negative than E^o).
5. The experiments were run for 24 hours.
6. The analysis for formaldehyde and methanol were conducted by first distilling the solution to remove chromium and vanadium and then analyzing the distillate.

The results of these experiments are shown in Table 10.

The results showed a higher yield of methanol than formaldehyde. This probably indicates that formaldehyde is reduced to methanol relatively easily and that the difficult step is the first one, from formic acid to formaldehyde. The percentage conversion to methanol in these four experiments is summarized in Table 11.

TABLE 10

REDOX REACTIONS - PRODUCT DETECTED BY ANALYSIS

Component	Distillate	Cold Trap	Total
(Exp. #1. Vandium Couple, pH = 1, T = 80°C)			
HCHO	1.8 milli moles	0.0 milli moles	1.8 milli moles
HCOOH	302.	21.0	323.
CH_3OH	9.2	0.5	9.7
Total detected	80%	5.5%	85.5%
(Exp. #2 Vanadium Couple, pH = 4, T = 80°C)			
HCHO	2.3	0.0	2.3
HCOOH	147	0.4	147.4
CH_3OH	24.8	2.2	27.0
Total detected	19.3%	0.26%	19.56%
(Exp. #3 Chromium Couple, pH = 1, T = 80°C)			
HCHO	0.3	0.0	0.3
HCOOH	56.8	0.8	57.6
CH_3OH	3.9	0.8	4.7
Total detected	93.6%	1.3%	94.9%
(Exp. #4 Chromium Couple, pH = 4, T = 80°C)			
HCHO	3.0	0.0	3.0
HCOOH	145	11.8	156.8
CH_3OH	22.9	0.2	23.1
Total detected	19.2%	1.2%	20.4%

TABLE 11

SUMMARY OF REDOX RESULTS

Experiment	% Conversion to Methanol	pH	Redox Couple
1	2.6%	1	Vanadium
2	5.0%	4	Vanadium
3	6.1%	1	Chromium
4	4.6%	4	Chromium

The reduction proceeds only to a slight extent and is apparently unrelated to the pH of the solution. It must be noted however that extremely low recovery of the initial reactants was reported in experiments 2 and 4.

The total moles of initial reactant detected in these tests is approximately 20%. Normal recoveries are in the range of 80 to 90%. Speculation as to the composition of the 80% of reactant undetected can range from extreme optimism to extreme pessimism on the value of this reduction approach at pH4. Additional laboratory work is required to identify the value of this reaction. Results at pH 1 are of little value due to the low yields.

Conclusions

The best results attained for the reduction of formic acid to formaldehyde or methanol have been accomplished in short term runs on electro deposited tin, and for longer run tests on molten Cerrolow 136. The active component in the Cerrolow alloy is presumed to be tin. Maximum effective current densities recorded of 0.14 ma/cm^2 are well below the desired design minimums for practical unit design. However, a continuous reaction at this rate does appear to be possible using the liquid metal electrode.

The redox couple approach requires further study. Rapid quantitative reductions of formic acid to formaldehyde are known. One such method is used in the chemical spot tests performed in this study. This particular system, however, is not regenerable. The chromium and vanadium reactions at pH4 require further study.

SECTION V

RECOMMENDED PROGRAM FOR FUTURE RESEARCH

The concept of the electrochemical conversion of carbon dioxide to liquid organic wastes is technically feasible and, with additional study, should become practical. Work on this program has resulted in the development of some useful new approaches to the problems involved and the pinpointing of areas for future effort.

Future research should be directed into the following areas:

Improvement In The Product Analysis Method

This is perhaps the most important single area of preliminary work that needs to be done. Instrumental methods of analysis that are fast and capable of identifying the specific products in very low concentrations with dependable accuracy need to be developed prior to any meaningful reaction rate studies. The present analytical system does not allow the measurement of the low concentrations needed to measure reaction rates. Test evaluation suffers as a consequence. Work on chromatography techniques, perhaps utilizing new digital readouts and computerized programming methods, would be most useful in this effort.

Improvement In Second Stage Reduction System (HCOOH Reduction)

In the case of electrochemical reductions a program should be instituted to study the electrode reactions, determine the rate limiting step and devise theories and systems to improve the rate function. Reduction products their conditions of formation, and their "poisoning" effect on catalytic electrode systems should be investigated.

The development of the "carrier reaction" approach using a redox couple can be a valuable parallel investigation. Reaction products, chemical rate steps, and driving force studies should be performed on chemical systems. The main consideration for a practical system using this approach is the necessary second step of regenerating the redox couple, perhaps electrochemically.

Develop Liquid Metal Cells and Specific System Alloys

The liquid metal cells show great promise in this area of organic electrode reactions. Specific study of cell mechanisms should be undertaken on the systems discussed on a scientific program basis as contrasted with the current engineering orientation. Optimization of the liquid metal electrode along with alloy optimization may go a long way towards making the current technical system a practical reality. When active species, i.e. tin for formic acid reduction, are identified, their incorporation as a major constituent in a low melting alloy becomes a metallurgical problem worthy of study.

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APPENDIX A

OVERALL SYSTEM CONSIDERATIONS

During normal activity, the human respiratory process consumes approximately 1 SCFH of oxygen, at the same time releasing 0.85 SCFH of carbon dioxide. In submarines, the required oxygen is supplied by a high pressure electrolytic oxygen generator which also produces 2 SCFH of hydrogen as a by-product with each SCFH of oxygen. Thus, a 120-man submarine must handle approximately 240 SCFH of waste hydrogen and 102 SCFH of waste carbon dioxide. Both the hydrogen and the carbon dioxide must be collected and eliminated to avoid contamination of the submarine atmosphere. This is currently done by absorption and/or compression followed by ejection overboard. That is, 2 SCFH of hydrogen and 0.85 SCFH of carbon dioxide a volumetric H_2/CO_2 ratio of 2.35, must be eliminated for every SCFH of oxygen consumed. Ionics proposes to do this in an electrochemical device in which carbon dioxide and hydrogen react to form liquid organic products which can be disposed of easily. In addition, the same device generates breathing oxygen by the electrolysis of water.

Formic acid (HCOOH), formaldehyde (HCHO) and methanol (CH_3OH) are the most likely reaction products at the cathodes. Methane (CH_4) is not expected since organic electroreduction rarely proceeds all the way to the hydrocarbon.

A reaction such as the following is envisioned:

$$(x+y+z)CO_2 + (x+2y+3z)H_2 = xHCOOH + yHCHO + zCH_3OH + (y+z)H_2O$$

These reactions could proceed spontaneously under the right conditions, but high temperatures and pressures are required. However, in a two compartment electrochemical cell, the reaction can be split into two half reactions

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad \text{(anode reaction)}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow \text{organics}, \qquad \text{(cathode reaction)}$$

which can be made to proceed by application of sufficiently large electrical potentials to the cell. In this case an electric rather than a pressure driving force supplies the necessary energy for activation. Under the same conditions, a competing reaction which generates hydrogen can occur at the cathode. Any energy associated with this reaction is totally wasted.

$$2H^+ + 2e^- \rightarrow H_2$$

The primary aim of this feasibility study was to find a cathode material which causes the desired cathode reaction to proceed at a reasonable rate while suppressing the unwanted cathode reaction. The term "catalyst" refers specifically to that aspect of electrode material or structure which directly affects the kinetics of the electrode reaction. The ratio of current carried by the CO_2 reduction reaction to total current applied is called current efficiency.

The reduction to formic acid reported by earlier investigators indicated that the best catalyst for reduction of CO_2 to formic acid was not necessarily good for further reduction. Consequently, a two-unit system was envisioned, where CO_2 would be reduced to formic acid in the first unit and formic acid further reduced to formaldehyde and/or methanol in the second unit.

The average required degree of reduction of the CO_2 depends on the desired respiration coefficient (ratio of CO_2 removed to O_2 generated). Since generation of 1 mole of oxygen requires 4 equivalents, operation at 0.85 respiration coefficient produces an average reduction of 4.7 equivalents per mole of CO_2. The degree of reduction of the probable organic products is 2 equivalents/mole for formic acid, 4 for formaldehyde and 6 for methanol. Therefore, the composition of the organic product stream is given by a solution to the equations:

$$2x + 4y + 6z = \frac{4}{RQ}$$

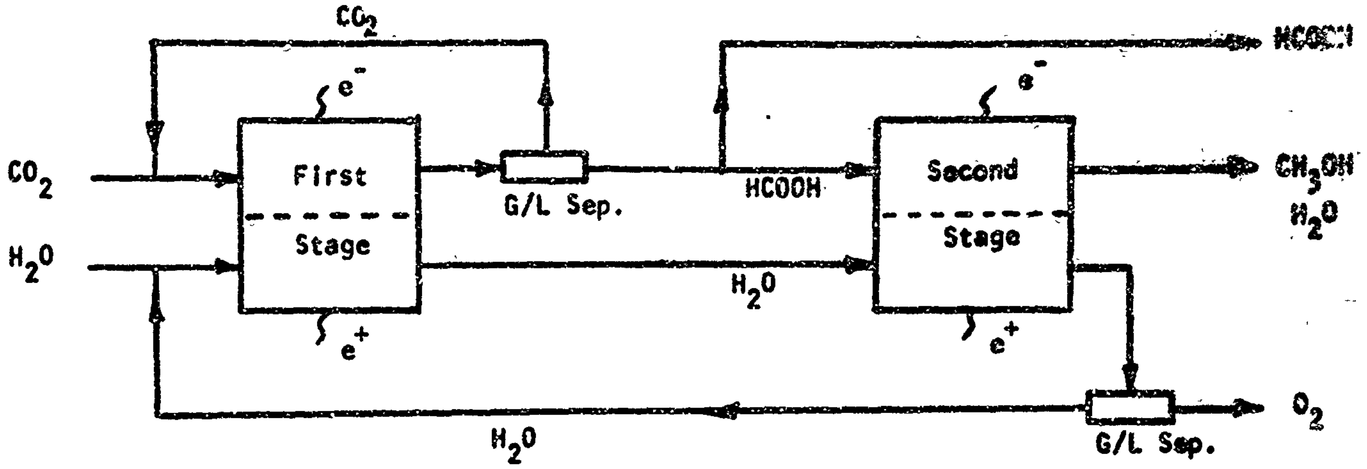
$$x + y + z = 1$$

where RQ is the respiration coefficient, and x, y and z are mole fraction of organics of formic acid, formaldehyde and methanol respectively. Possible solutions range over a wide variety of three component mixtures. Since the concentration of formaldehyde will probably be low, i.e., $y = 0$, a likely solution is 67.5 mole % CH_3OH, 32.5 mole % $HCOOH$.

Based on the results of this feasibility study, one can speculate on the design characteristics of a 120-man system. One possible system design is presented in Figure 1-A. The following assumptions have been made in the preparation of this schematic flow diagram:

- The feed gas is essentially pure CO_2.
- Two separate modules comprise the electrochemical unit although the anode streams of each are hydraulically connected.
- The operating characteristics of the two modules are optimized so that only formic acid and methanol represent the organic products of reaction in their respective modules.

FIGURE 1-A



Schematic Drawing of CO_2 Reduction - O_2 Generation Unit

The subscripts 1 and 2 refer to the first and second stage respectively. Other parameters are defined as follows with assumed values supplied for some until the technical developments have been made which will provide more accurate values.

i_1	current density (1st stage) - 40 ASF
i_2	current density (2nd stage) - 40 ASF
E_1	voltage per cell (1st stage) - 5.0 volts
E_2	voltage per cell (2nd stage) - 5.0 volts
η_1	current efficiency (1st stage) - 1.00 (100%)
η_2	current efficiency (2nd stage) - 1.00 (100%)
W	total power - watts
t	cell thickness - 0.0119 ft.
V	total volume - $ft.^3$
F	ratio of active area to total area - 0.60 (60%)
L	total weight - lbs.
ρ	average unit density - 100 $lbs./ft.^3$

On a basis of 102 SCFH pure CO_2 feed, the total power is given by:

$$W = W_1 + W_2$$

$$W = E_1 i_1 A_1 + E_2 i_2 A_2$$

$$i_1 A_1 = \frac{128 \text{gm moles}}{\text{hr}} \times \frac{2 \text{eq}}{\text{gm mole}} \times \frac{26.8 \text{ amp hr}}{\text{eq}} \times \frac{1}{\eta_1} = \frac{6860}{\eta_1}$$

$$i_2 A_2 = \frac{86.5 \text{gm moles}}{\text{hr}} \times \frac{4 \text{eq}}{\text{gm mole}} \times \frac{26.8 \text{ amp hr}}{\text{eq}} \times \frac{1}{\eta_2} = \frac{9250}{\eta_2}$$

This is calaculated on the basis of a second stage reduction only to CH_3OH but the results do not depend on this assumption.

$$W = \frac{6860 E_1}{\eta_1} + \frac{9250 E_2}{\eta_2}$$

= 80,550 watts = 80.5 KW (using estimated values)

The stack volume is given by:

$$V = V_1 + V_2 = \frac{A_1 t}{F} + \frac{A_2 t}{F}$$

$$= \frac{6860 t}{i_1 \eta_1 F} + \frac{9250 t}{i_2 \eta_2 F}$$

= 3.40 + 4.55 = 7.95 ft^3 (estimated value)

Finally, the stack weight is estimated from:

$$L = V\rho$$

= 795 lbs (estimated value)

Both volume and weight factors should be increased to include end plates. This cannot be calculated until the cell shape has been determined but it will be roughly a 10% increase.

APPENDIX B

ANALYTICAL PROCEDURES

Analytical procedures for the identification of organic products of reaction were qualified as the investigation proceeded. A number of techniques were found to be unsuitable. The presence of organics was indicated by UV but no peak was obtained within the range of the instrument, 360 to 700 mμ, so this technique was incapable of quantitative development. Considerable effort was spend on analysis by vapor phase chromatography, to little avail. With a thermal conductivity detector, and a variety of column lengths and packing materials, the water peak consistently overwhelmed the other components due to the great preponderance of water in the solutions analyzed. Consideration was also given to use of a flame-ionization detector which is blind to the presence of water and consequently commonly used for analysis of dilute organic solutions. However, the detector is also relatively insensitive to small organic compounds, i.e. those having no carbon-carbon bonds, which includes all of the compounds being sought.

Three tests which proved successful consisted of a three-titration scheme for organic product analysis, spot tests with chromotropic acid, and measurement of evolved gas for determination of current inefficiency. The organic analysis is based on selective oxidation of the three anticipated products under successively stronger oxidizing conditions. Formaldehyde is oxidized to formic acid with sodium hypoiodite. Formic acid and methanol are oxidized to carbon dioxide respectively with warm basic permanganate and boiling acidic dichromate with reflux. A complete statistical evaluation of this method is discussed in section II of this report.

In contrast to the titration procedure, where the experiment must be run for a considerable length of time to develop an analyzable quantity of product, hydrogen evolution measurement can be used to determine spot or transient current efficiencies. While the CO_2 must be removed from the evolved gas when solutions are saturated with CO_2, the procedure is simple with formic acid solutions. Results from the hydrogen evolution measurements agreed within 5 percentage points to those obtained by titration when both measurements were performed simultaneously.

Chromotropic acid spot tests were useful in verifying the existence of product in some of the later tests. Early results with this spot test method were negative.

LIQUID PRODUCT ANALYSIS FOR FORMIC ACID, FORMALDEHYDE AND METHANOL

1. <u>Reagents Required</u>

0.1N Sodium Thiosulfate ($Na_2S_2O_3$)
0.1N Potassium Permanganate ($KMnO_4$)
0.1N Iodine Solution
0.1N Potassium Dichromate ($K_2Cr_2O_7$)
20% Potassium Iodide Solution (KI)
9N Sulfuric Acid (H_2SO_4)
2N Sulfuric Acid
5N Sodium Hydroxide (NaOH)
Stable Starch Solution
Sodium Carbonate Crystals (Na_2CO_3)

2. Procedure

Formaldehyde

Take 10 ml aliquot. Add 30 ml 0.1N Iodine plus 5 ml 2N H_2SO_4. After 2 minutes add 10 ml 5N NaOH, and let sit for 30 minutes. Dilute with 50 ml H_2O. Add 10 ml 20% KI. Add 10 ml 9N H_2SO_4. Titrate excess iodine with 0.1N $Na_2S_2O_3$.

Formic Acid plus Formaldehyde

Take 10 ml aliquot. Add 0.25 grams Na_2CO_3. Add 50 ml 0.1N $KMnO_4$ and heat to 70°C. Add 5 ml 9N H_2SO_4. Add 10 ml 20% KI. Add 2-3 ml starch solution. Titrate excess iodine with 0.1N $Na_2S_2O_3$.

Methanol, Formic Acid, plus Formaldehyde

Take 10 ml aliquot. Add 50 ml 0.1N $K_2Cr_2O_7$. Add 100 ml 9N H_2SO_4 and reflux for 60 minutes. Dilute to 500 ml. Add 10 ml 20% KI. Titrate excess iodine with 0.1N $Na_2S_2O_3$.

3. Calculations

X = Iodine Titre = 30ml - ml $Na_2S_2O_3$ used in first titration.

Y = Permanganate Titre = 50ml - ml $Na_2S_2O_3$ used in second titration.

Z = Dichromate Titre = 50ml - ml $Na_2S_2O_3$ used in third titration.

A = gms formaldehyde per liter

B = gms formic acid per liter

C = gms methanol per liter

$$A = \frac{30}{2}\,\frac{X}{100} = 0.15X$$

$$B = \frac{46}{2}\,\frac{Y-2X}{100} = 0.23\,(Y-2X)$$

$$C = \frac{32}{6}\,\frac{Z-Y}{100} = 0.0533\,(Z-Y)$$

SPECIFIC SPOT TESTS FOR FORMIC ACID, FORMALDEHYDE AND METHANOL

Procedures for the confirmation of the presence of formaldehyde, formic acid, and methanol in aqueous solution are given by Feigl (19). Positive tests are contingent upon the reaction of formaldehyde with 4,5 dihydroxy - 2,7 naphthalene - disulfonic acid, disodium salt (chromotropic acid) in the presence of concentrated sulphuric acid. Tests for formic acid and methanol first require that the former be reduced to formaldehyde with magnesium and hydrochloric acid, and that the latter be oxidized to formaldehyde by the action of potassium permanganate in phosphoric acid and subsequently discolored by the addition of sodium bisulphite. The resulting formaldehyde may then be treated with chromotropic acid and sulphuric acid. Gentle heating initiates the reaction, and upon cooling, a positive test is characterized by the appearance of a violet color. A negative test is characteristically tan to light brown, a color which darkens considerably upon aging.

These analyses display a fair degree of quantitative character. A rough attempt at quantitative testing was accomplished by visually comparing both known and unknown samples with known standards. The results of this attempt were reasonably accurate under the conditions and methods employed.

Reagents: Only reagent grade materials should be employed.

1.	Sulphuric Acid	Conc.
2.	Chromotropic Acid	
3.	Phosphoric Acid	5%
4.	Sodium Bisulphite	powder
5.	Potassium Permanganate	1.5N - 0.1N
6.	Hydrochloric Acid	2N - 12N
7.	Magnesium Metal	powder

Formaldehyde

1. Add sample, about 1 drop to a small test tube, about 1 cm x 5 cm.
2. Add a few milligrams of chromotropic acid.
3. Add 3 ml. H_2SO_4
4. Mix well
5. Heat in water bath at 60°C for 10 minutes.

Formic Acid

1. Repeat step 1. under formaldehyde
2. Add a few milligrams of Mg powder.
3. Add about 1 drop HCl - Allow to react.
4. Some Mg must remain (if not repeat step 2.)
5. Repeat steps 2. through 5. under formaldehyde.

Methanol

1. Repeat step 1. under formaldehyde
2. Add a drop of $KMnO_4$ solution.
3. Add a drop of H_3PO_4 solution - wait 1 minute.
4. Add a few milligrams of $Na_2S_2O_5$ - If, after shaking, solution is not colorless repeat this step until it is colorless.
5. Repeat steps 2. through 5. under formaldehyde.

A violet color, intensifying upon cooling, constitutes a positive test.

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13. ABSTRACT

The electrochemical reduction of carbon dioxide has been investigated as a means of simplifying the disposal of carbon dioxide and hydrogen from a submarine atmospheric regeneration unit. Ejection of these materials as organic liquid wastes is preferable to the compression and gas phase discharge systems in current use.

This investigation comprises phase II of the problem of developing an electrochemical cell to accomplish the desired reduction reactions. Conceptually, the cell consists of an anode at which water is electrolyzed to oxygen, a cathode at which carbon dioxide is reduced, and an electrolyte path between the two. A two stage reduction is required to balance the system metabolically consisting of the following general progression:

$$CO_2 \xrightarrow{yields} HCOOH \xrightarrow{yields} HCHO \text{ or } CH_3OH.$$

Four cathode materials were found to catalyze the CO_2 reduction. They are mercury, gallium, indium and the quaternary alloy Cerrolow 136. The latter material is most effective when used in the liquid phase. The reduction of HCOOH is accomplished to a limited degree on tin or Cerrolow 136.

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I. Contract Nonr N00014-66-C0139
II. Ionics Inc. Watertown, Mass.
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