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ELECTROCHEMICAL PERFORMANCE INVESTIGATIONS
ON THE
HYDROGEN DEPOLARIZED CO₂ CONCENTRATOR
FINAL REPORT

BY

DR. JOHN R. AYLWARD

PREPARED UNDER ADDENDUM TO CONTRACT NAS 9-13679
ON THE
ONE MAN ELECTROCHEMICAL AIR REVITALIZATION SYSTEM

BY

HAMILTON STANDARD
DIVISION OF UNITED TECHNOLOGIES CORPORATION
WINDSOR LOCKS, CONNECTICUT

FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LYNDON B. JOHNSON SPACE CENTER
HOUSTON, TEXAS   77058

JULY, 1976

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ABSTRACT

Electrochemical Performance Investigations
on the
Hydrogen Depolarized CO_2 Concentrator

by

Dr. John R. Aylward

Addendum to Contract NAS 9-13679

June, 1976

This report describes the work done under an extension of Contract NAS 9-13679. The original contract was to fabricate and test an integrated WVE/HDC system for a One Man Electrochemical Air Revitalization System. The purpose of the extension was to determine the causes of abnormal voltage performance experienced with the HDC cells and to recommend solutions to this problem.

FOREWORD

This report was prepared by Hamilton Standard, Division of United Technologies Corporation for the National Aeronautics and Space Administration, Johnson Space Center in accordance with the extention to Contract NAS 9-13679. This report describes the work accomplished during the period of June, 1975 through June, 1976 in investigating the cause for the abnormal HDC voltage performance experienced with the One Man Electrochemical Air Revitalization System. This effort consisted mainly of a detailed investigation of the anodic and cathodic electrochemical reaction kinetics in complete cells and in "half" cells.

Personnel responsible for the conduct of this program were Mr. H. Brose, Program Manager; Dr. J. R. Aylward, Program Scientist; Dr. J. Giner, Consultant for Hamilton Standard; and Mr. N. Lance, Technical Monitor for the NASA Johnson Space Center.

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SUMMARY

The objective of this program was to determine the causes for abnormal HDC voltage performance and to formulate methods to achieve improved voltage performance characteristics.

An extensive investigation of anode and cathode polarization in complete cells and "half cells" was conducted to determine the factors affecting HDC electrode polarization and the nature of this polarization. Matrix-electrolyte-electrode interactions and cell electrolyte composition were also investigated.

The electrodes were found to have normal performance capabilities, and electrode polarization in the HDC cell is a combination of activation and mass transport polarization with the anions taking a direct part in the electrochemical reaction. The anode electrochemical reaction has an inherent limiting current density in the outer regions of the practical HDC operating current range. The HDC anode polarization characteristics were correlated with a theoretical kinetic analysis; and, except for some quantitative details, a rather complete understanding of the causes for HDC electrode polarization was formulated. One of the important findings, from a fundamental standpoint, resulting from the kinetic analysis was that platinum appears to catalyze the decomposition of carbonic acid to carbon dioxide and water.

It was found that anode poisoning by "reduced CO_2"* becomes significant only under, what one may call, abnormal operating conditions; and this poisoning process is reversible.

No unusual matrix-electrolyte-electrode interactions were found.

From this investigation, it was concluded that the abnormal voltage performance of the One Man ARS HDC cells was caused by insufficient cell electrolyte volume under normal operating conditions due to deficiencies in the reservoir to cell interfacing.

The major recommendations for improved HDC voltage performance are:

1. Modify the cell-reservoir configuration to insure adequate reservoir-cell electrolyte transfer rates.

2. Increase electrode catalyst loading to reduce electrode polarization and CO_2 poisoning and increase cell tolerance to electrolyte volume changes.

*See Appendix

INTRODUCTION

The work described in this report was done under an extension of Contract NAS 9-13679. The original contract was to fabricate and test an integrated WVE/HDC system for a One Man Electrochemical Air Revitalization System. The purpose of the extension was to determine the causes of abnormal voltage performance experienced with the HDC cells and to recommend solutions to this problem.

The HDC cells fabricated for the One Man ARS showed lower than normal cell voltage which was non-reproducible between cell buildups, and there was excessive short term cell voltage decay with time.

The general approach taken to determine the causes of the abnormal HDC voltage performance was to carry out a detailed study of electrode performance and measure pertinent electrolyte properties including electrolyte-matrix interactions. The electrode performance was measured in both the complete cells and in the floating electrode configuration* under a variety of conditions. The data obtained on the anode performance was correlatated with a theoretical kinetic analysis of anode polarization.

*J. C. Huddleston and J. R. Aylward, Hydrogen Depolarized Carbon Dioxide Concentrator Performance Improvements and Cell Pair Structural Tests, Contract No. NAS 9-12920, September, 1973.

CONCLUSIONS

The main reason for the abnormal HDC cell voltage performance was insufficient electrolyte volume in the cells which occurred because of the very slow rate of electrolyte transfer between the cell and the external reservoir. This effect was more pronounced than in previous cells because of the excessive compression required in the seal area with the neoprene-asbestos matrix to withstand a five psi hydrogen to air pressure differential. The practice of conditioning the cell electrolyte at a high relative humidity, where exact RH control is difficult, resulted in each cell having a different electrolyte volume; and subsequent operation at lower relative humidities gave different cell output voltages due to the different degrees of mass transport polarization caused by the insufficient cell electrolyte volume condition. This shortage of cell electrolyte gave excessive anode mass transport polarization which is conducive to "reduced CO_2" poisoning, and this effect was responsible for the observed short term voltage decay.

Other conclusions resulting from this work are as follows:

- The inherent electrochemical performance capability of the electrodes is completely normal.

- The electrode polarization in the HDC cell is a combination of activation and electrolyte mass transport polarization, and only the anode process has an inherent limiting current density in the practical HDC operating range.

- Reduced CO_2 poisoning is reversible and becomes significant only at low anolyte pH which occurs when operating near the anodic limiting current density and/or when the concentration of carbonic acid (H_2CO_3) in the anolyte becomes too high because of insufficient anolyte volume.

- There are no unusual matrix effects provided the matrix has the proper uniformity, chemical resistance, and a sufficiently high bubble point.

- Platinum appears to catalyze the conversion of carbonic acid to carbon dioxide and water.

- Carbonate and bicarbonate ions are directly involved in the electrochemical charge transfer reactions.

RECOMMENDATIONS

Based on the findings of this investigation, the following steps should be taken to improve HDC cell performance.

1. Modify cell-reservoir configuration to insure an adequate reservoir-cell electrolyte transfer rate.

2. The cell and reservoir should be filled with electrolyte via capillarity to achieve optimum electrolyte volume at the maximum operating relative humidity.

3. The electrode catalyst loading should be increased to give more reaction surface area and volume. This will also improve the cell tolerance to electrolyte volume changes and increase tolerance to "reduced CO_2" poisoning.

4. The matrix thickness should be minimized (consistent with good CO_2 transfer) to increase the anolyte concentration in order to avoid operation near the limiting anodic current density.

HDC CELL POLARIZATION BEHAVIOR

The complete anodic and cathodic polarization curves were measured on cells 029, 030, 031, and 032 to obtain a general idea of the anode and cathode polarization processes that might be responsible for poor voltage performance. Each cell was held at open circuit for three days prior to the run in order to achieve steady state conditions in the electrolyte. The "standard conditions" were: air temperature 21.1°C (70°F), air dew point 15.6°C (60°F), hydrogen back pressure 104.7 kPa (15.2 psia), air CO_2 partial pressure 400 Pa (3 mmHg). The measurements were made at controlled current in intervals of 1.0, 1.6, 2.5, 4, 6.3, 10 for each decade over the range 10^{-2} to 40A, and potential readings were taken after two hours at constant current except where it was necessary to run overnight (16 hours). The anode and cathode potential was initially measured with respect to an external air electrode which was checked against a saturated calomel electrode (SCE). Later, potential measurements were made directly against the SCE to avoid drift and pH corrections. Upon completion of the polarization curve measurement (to 40A), the current was set to 20A for overnight or longer to determine voltage decay. The results, corrected for IR drop, are shown in Figures 1 through 4.

Cathode

Examination of the cathode polarization curves shows normal Tafel behavior up to currents of one amp followed by an increase in slope indicative of the onset of mass transport polarization. With cell 029 (Figure 1), a second Tafel region appears at currents above 10 amps. The same behavior is shown by the cell 030 cathode (Figure 2), but an additional mass transport limitation is evident. On cells 031 and 032 (Figures 3 and 4) this second mass transport process combines with the first to mask the second Tafel region. A second run on cell 029 three weeks after the first run (Figure 1) reveals the onset of the second mass transport limitation in this cell at both the cathode and anode.

From this information it appears that there are two different cathodic electrochemical reactions corresponding to the two Tafel regions. The first reaction, which predominates at low currents, becomes mass transport limited above one amp, and the second electrochemical reaction eventually takes over as the current is increased. The second electrochemical reaction also becomes mass transport controlled under some conditions. The fact that the anode polarization also appears to be affected under the same
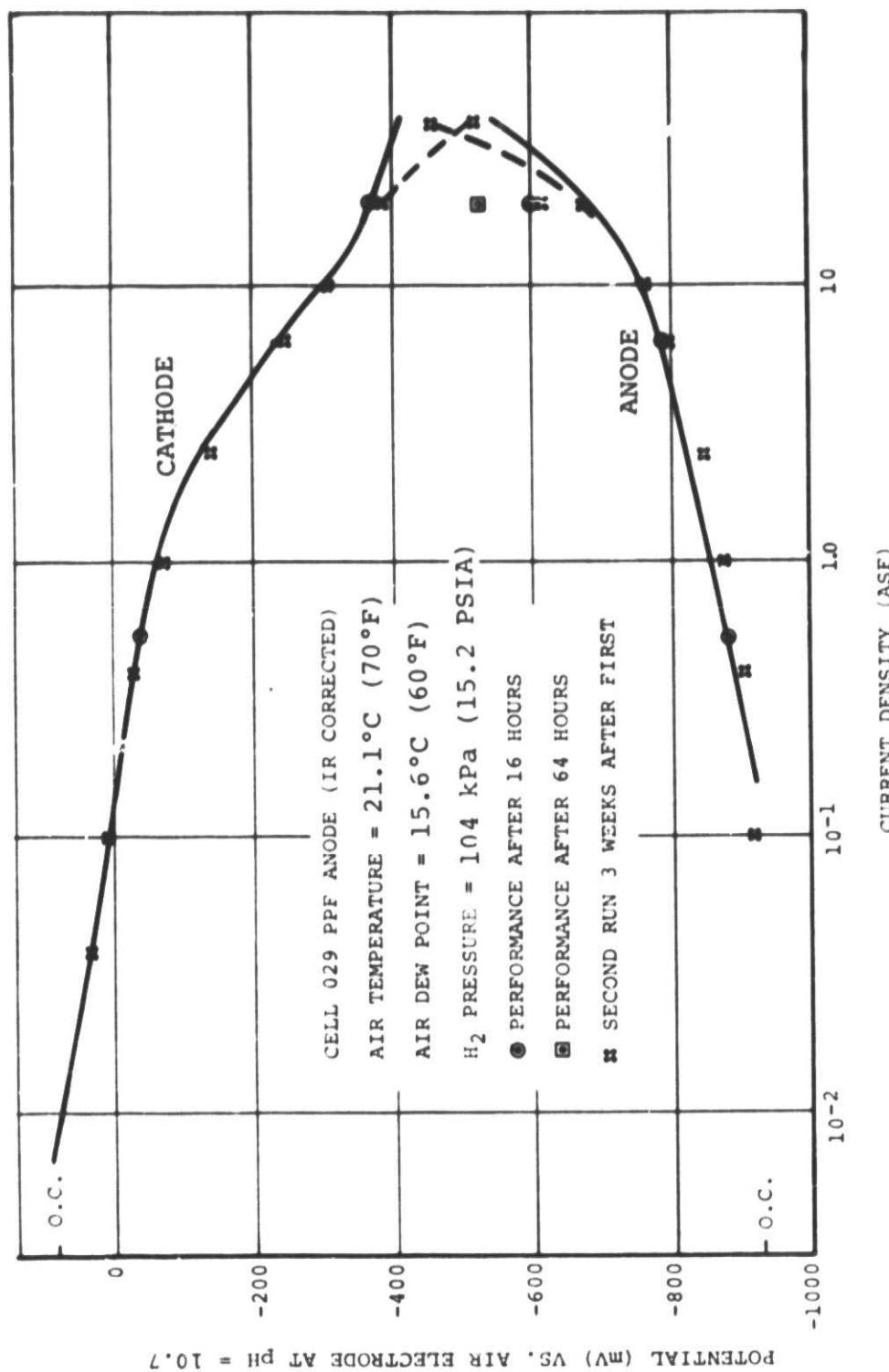
FIGURE 1 - POLARIZATION CHARACTERISTICS OF CELL 029 ELECTRODES
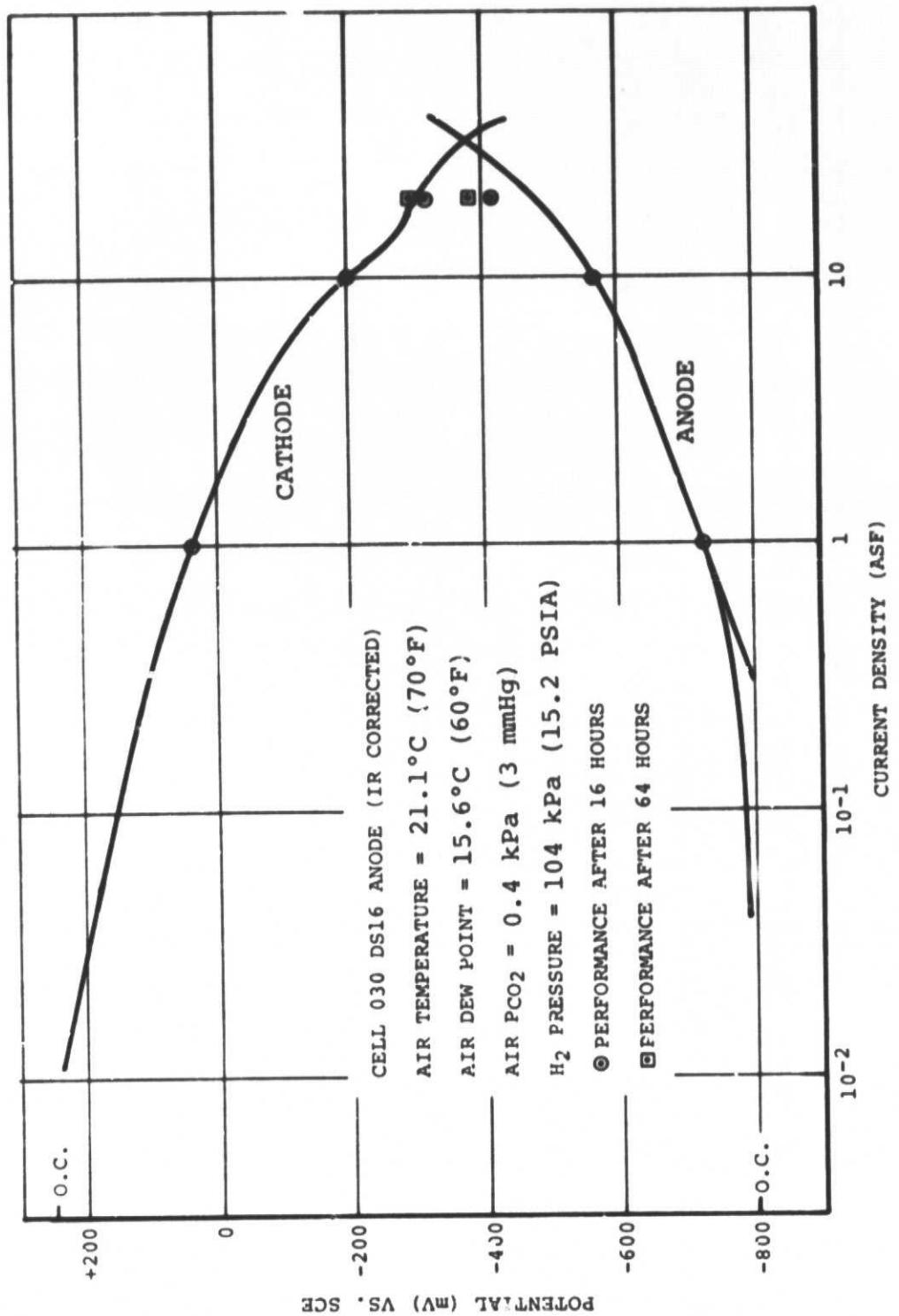
FIGURE 2 - POLARIZATION CHARACTERISTICS OF CELL 030 ELECTRODES

CELL 030 DS16 ANODE (IR CORRECTED)

AIR TEMPERATURE = 21.1°C (70°F)

AIR DEW POINT = 15.6°C (60°F)

AIR P_{CO_2} = 0.4 kPa (3 mmHg)

H_2 PRESSURE = 104 kPa (15.2 PSIA)

⊙ PERFORMANCE AFTER 16 HOURS

⊡ PERFORMANCE AFTER 64 HOURS

CURRENT DENSITY (ASF)

POTENTIAL (mV) VS. SCE
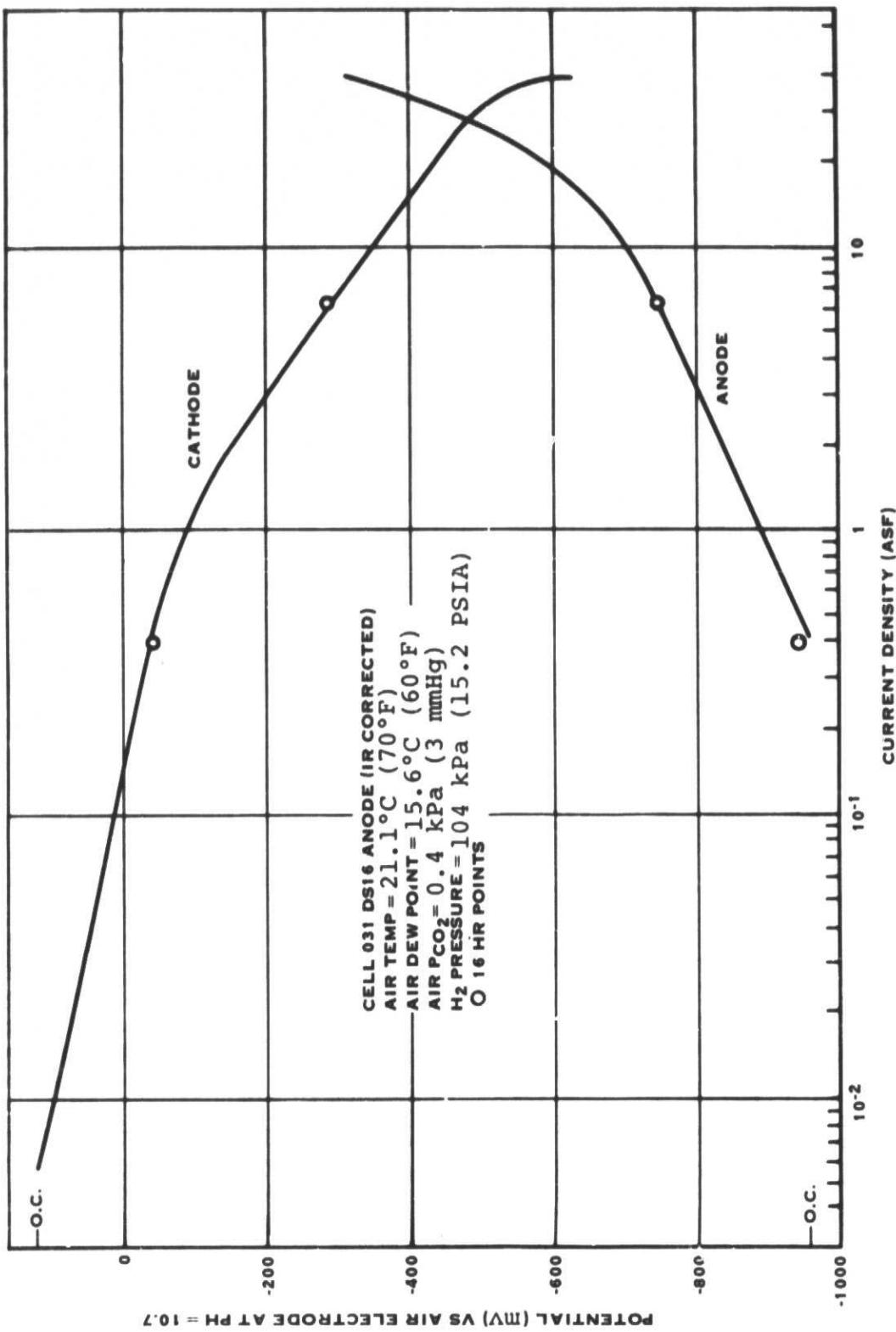
FIGURE 3. POLARIZATION CHARACTERISTICS OF CELL 031 ELECTRODES

conditions (Figure 1) would indicate that the second mass transport limitation at the cathode is not caused by inherent deficiencies in electrode characteristics or reaction kinetics. The most obvious cause of this second cathodic mass transport process is out-of-tolerance electrolyte, i.e., insufficient or excess electrolyte volume. Insufficient electrolyte volume would result in very high local current densities which would be conducive to mass transport polarization. Excess electrolyte volume would inhibit the mass transport of gaseous reactants to the catalyst surface making this step rate-determining.

Anode

The anode polarization curves for the four cells show an initial Tafel region followed by behavior typical of mass transport polarization with an approach toward a limiting current density. One interesting feature is the difference in Tafel slope between the PPF anodes (Figures 1 and 4) and the DS16 anodes (Figures 2 and 3). The major difference between the two electrode types is in catalyst loading which would affect the exchange current but not the Tafel slope if the reaction involved only a simple charge-transfer step. Thus, it appears that the anodic reaction is more complex than one would ordinarily assume.

When the current was held at 20 amp for periods up to 64 hours (Figures 1 and 2), there was a slow increase in anode polarization, but no significant change in cathode polarization. This loss in anode performance could be recovered completely by a short nitrogen purge of the anode gas chamber (anode oxidation); and is, therefore, attributed to "reduced CO_2"* poisoning. There was no evidence of "reduced CO_2" poisoning at currents corresponding to the anodic Tafel region. It was also observed that a poisoned anode would gradually return to the original performance line when the current was reduced to a value in the Tafel region. From these results it can be concluded that "reduced CO_2" poisoning is a reversible process, and that the onset of "reduced CO_2" poisoning is brought about by conditions associated with the deviation of the anodic polarization from Tafel behavior.

Special Cell Experiments

A number of experiments were conducted on the complete cells in an attempt to learn more about the nature of the mass transport problems in the high current range. Figure 5 shows the effect of changes in air dew point on the electrode performance of cell 029 at 20 amps. It can be seen that increasing the dew point, which

*See Appendix for a more detailed discussion on "reduced CO_2."

AIR TEMP = 21.1°C (70°F)
PCO_2 = 0.4 kPa (3 mmHg)
C.D. = 20 ASF
PH_2 = 104 kPa (15.2 PSIA)

CELL VOLTAGE (mV)

POTENTIAL VS AIR ELECTRODE (mV)

ANODE

CATHODE

TIME (HOURS)
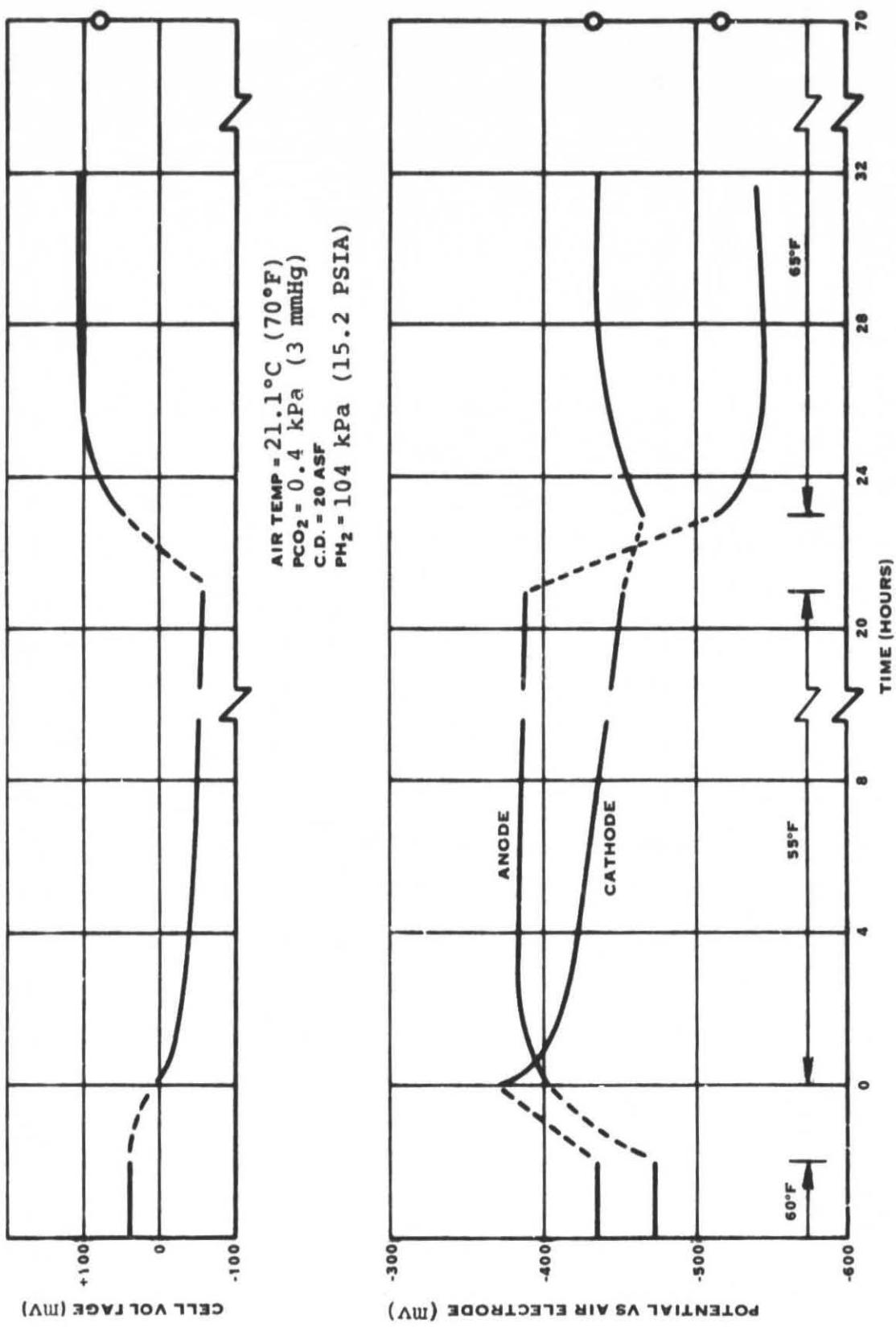
FIGURE 5. EFFECT OF AIR DEW POINT ON CELL 029 PERFORMANCE

11

...
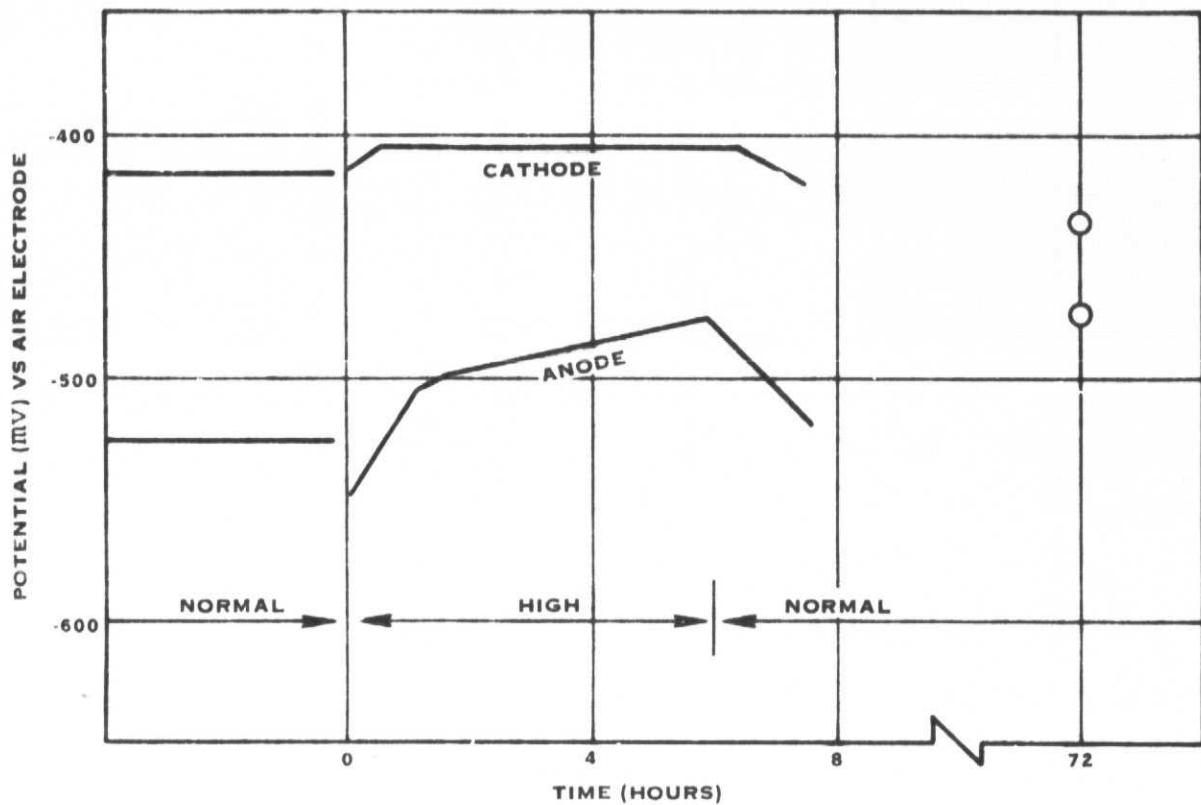
FIGURE 6. EFFECT OF HYDROGEN FLOW RATE ON CELL 029
PERFORMANCE AT 20 ASF
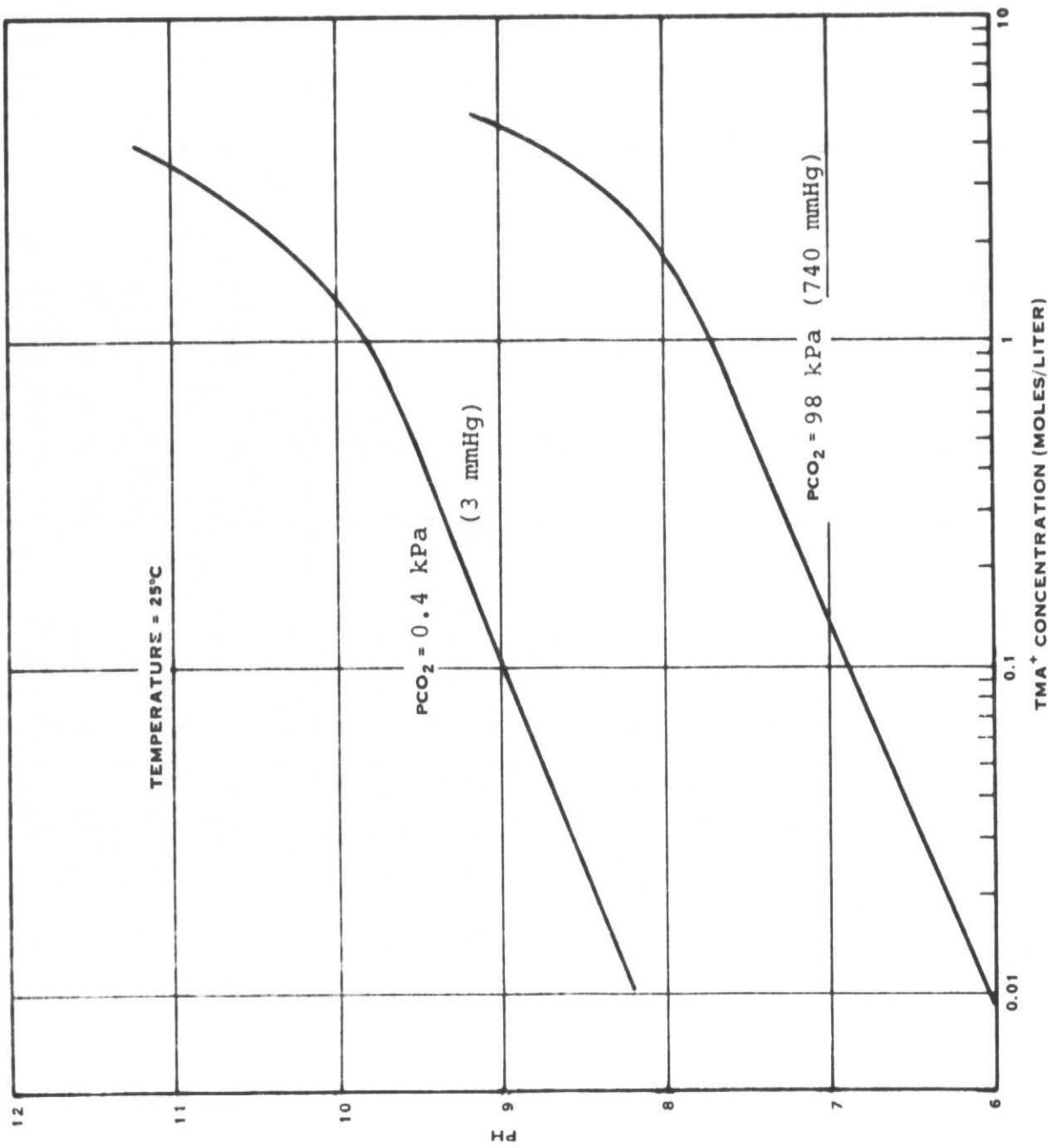
FIGURE 7. PH OF TMA⁺ SOLUTIONS IN EQUILIBRIUM WITH CARBON DIOXIDE

is retained in the electrolyte for long periods at open circuit
means that the discharge of CO_2 from the electrolyte is a slow
process. Under normal HDC operating conditions the equivalent
CO_2 pressure (H_2CO_3 concentration) at the anode must be quite
high giving a lower than equilibrium anode pH which in turn en-
hances "reduced CO_2" poisoning.

It can also be seen from the data in Figure 7 that the electro-
lyte pH changes rapidly over the cation concentration range
associated with normal HDC operation ($>$1M). Any factors which
reduce the anolyte TMA^+ concentration, such as high current
densities, air relative humidities, and effective electrode
spacing, will give a significant lowering of anolyte pH making
the anode more susceptible to "reduced CO_2" poisoning.

Matrix Electrolyte Pumping

Previous experience with HDC operation indicated a tendency for
the electrolyte to be pumped from anode to cathode which would
result in decreased anode performance. The mechanism for this
pumping was attributed to electrokinetic effects. To determine
the magnitude of electroosmotic pumping within the HDC matrix, an
experiment was conducted to measure the streaming potential as a
function of electrolyte pressure across the matrix.* A neoprene
asbestos-Tissuquartz composite and a fuel cell asbestos (P&W)
were tested with 1M TMA^+ electrolyte of pH 9. A platinum screen
on each side of the matrix was used to measure the potential
across the matrix before and after applying a solution pressure
difference. For both matrix materials it was found that the
potential difference decayed to zero ($\pm$2 mV) within 13 minutes
indicating that the steady state electrokinetic effects (electro-
osmotic pumping) in the matrix are very small at the high elec-
trolyte concentrations in the HDC cell. The reason for the
potential decay with time is not known, but since the magnitude
of the potential difference and the decay rate were independent
of pressure difference, up to 6.9 kPa (10 psi), it is felt that
the measured potential difference was not related to electro-
kinetic phenomena.

CATHODE POLARIZATION

An investigation of cathode polarization was made with floating
electrodes to elucidate the electrochemical reactions and mass
transport processes inherent in the HDC CO_2 removal process. The
floating electrode test allows the evaluation of the performance
of a single electrode under ideal electrolyte take-up conditions
and independent of other cell components.

*The streaming potential should be directly proportional to the
 pressure difference.

Since the electrolyte mass transport conditions in the floating electrode cell are quite different than in a complete cell due to the difference in cell geometry, there is not necessarily a one to one performance correlation between the two in the regions where mass transport phenomena are predominant. However, the same general polarization characteristics and response of these characteristics to pertinent variables will be present in both cases.

Cathode polarization studies in the complete cell indicated that two distinct electrochemical reactions occur, and that the first reaction, which predominates in the low current region, becomes mass transport limited at currents above one amp. The second electrochemical reaction also becomes mass transport limited but to different degrees in the four cells. This second mass transport process, as discussed previously, was attributed to conditions brought about by insufficient cell electrolyte volume. The purpose of these cathode studies with the floating electrode was to identify the two electrochemical reactions and their associated mass transport limitations. Another objective was to determine if the matrix had any anomalous effect on electrode performance.

The cathode floating electrode tests were made on a one cm^2 DS16 electrode under potentiostatic conditions at a sweep rate of 10 mV/min starting at open circuit. The potential sweep was reversed after the current had reached 100 mA/cm^2. In some cases, potential readings were measured after 30 minutes at selected constant currents to provide an indication of the degree to which steady state conditions had been approached during the potential sweep runs. In general, the 10 mV/min sweeps gave a close approximation to steady state performance, except in regions where mass transport was rate controlling.

Figure 8 gives the cathodic potential sweep curves in 2.5M TMA^+ of pH 9.4 with and without a matrix (neopreme asbestos). Without the matrix, there is a small hysterisis in the mass transport controlled region, and the second Tafel slope shows no evidence of mass transport polarization up to current densities of 100 mA/cm^2. With the matrix present, the first electrochemical reaction becomes mass transport limited at lower current densities as one would expect, and some IR drop becomes noticeable at high current densities. Also, there is a large hysteresis on the back sweep. The true steady state line would be somewhere between the down and up sweeps, and the transition from one electrochemical reaction to the other would be more gradual as seen in the cathodic polarization curves for the complete cell (Figures 1 and 2).

2.5M TMA$^+$
PH = 9.4
SWEEP RATE = 10 mv/MIN

NO MATRIX

WITH MATRIX

CURRENT DENSITY (MA/CM^2)

POTENTIAL (VOLTS) VS S.C.E.
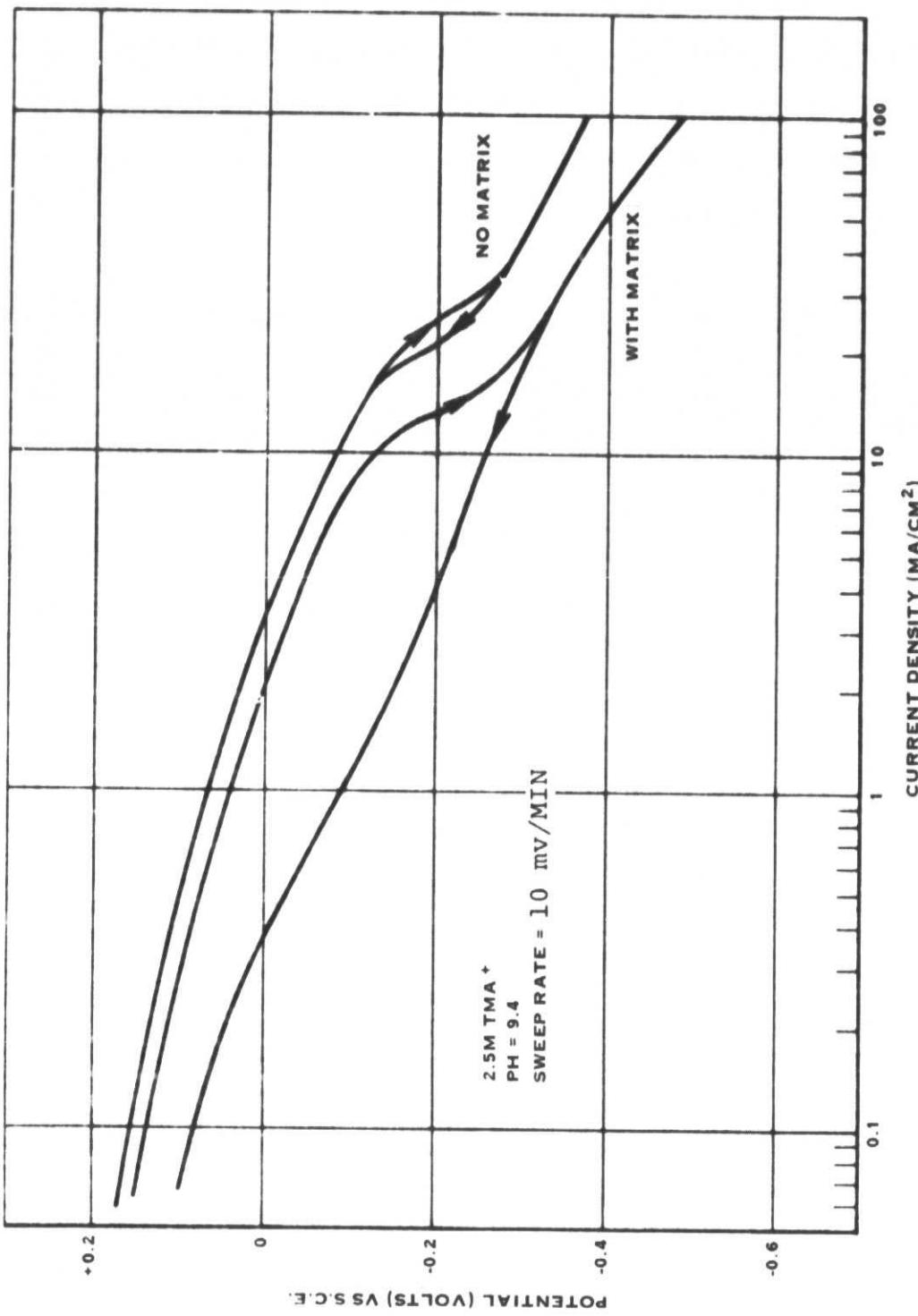
FIGURE 8. EFFECT OF MATRIX ON FET WITH DS16 CATHODE IN AIR

In order to identify the two electrochemical reactions, potential sweeps were run at various solution pH's (8.4 to 15) corresponding to various ratios of the anions HCO_3^-, $CO_3^=$, and OH^- at a constant TMA^+ concentration of 3M. Selected results are given in Figure 9. At a pH of 15 (3M TMAOH) it is well established that the electrochemical oxygen reduction reaction involves the reaction of water, as proton donor, with the oxygen species adsorbed on the electrode surface to produce, ultimately, hydroxide ions. At any pH above approximately four, water is the proton donor in the oxygen reduction reaction unless there is a stronger proton donor (acid) present in sufficient amounts. As long as water is the proton donor, the oxygen reduction reaction is independent of pH except for second order effects. These second order effects can be seen in Figure 9 upon comparison of the pH 15 and pH 13 Tafel lines. There is a tendency for the Tafel slope to decrease as the pH is increased. The reasons for this behavior are much too involved to be discussed here, and the reader is referred to a recent paper by J. P. Hoare* for full details on oxygen reduction kinetics.

The depolarization of the oxygen reduction reaction observed in Figure 9 at pH 12 and lower is obviously due to the reaction of the adsorbed oxygen species with a proton donor which is a stronger acid than water, i.e., the bicarbonate ion. The degree of depolarization increases with increasing bicarbonate ion concentration. The overall electrochemical reactions corresponding to the two Tafel regions are, therefore:

1. $(0) + 2HCO_3^- + 2e \longrightarrow 2CO_3^= + H_2O$

2. $(0) + H_2O + 2e \longrightarrow 2OH^-$

where (0) represents the adsorbed oxygen. These reactions occur simultaneously; the total current being the sum of the two individual currents. The rate of the first reaction depends on the concentration of the bicarbonate ion at the catalyst surface. When the bicarbonate ion concentration approaches zero, the first reaction becomes totally mass transport controlled (limiting current density), and higher current densities are carried by the water discharge reaction.

It can also be seen from Figure 9 that there is no evidence of any mass transport limitation in the water discharge reaction up to current densities of 100 mA/cm^2. Indeed, from the nature of the reaction, one would certainly not expect any mass transport problem in this current density range provided the electrode has sufficient electrolyte without being flooded.

*J. P. Hoare, Electrochim. Acta. <u>20</u> 267 (1975).
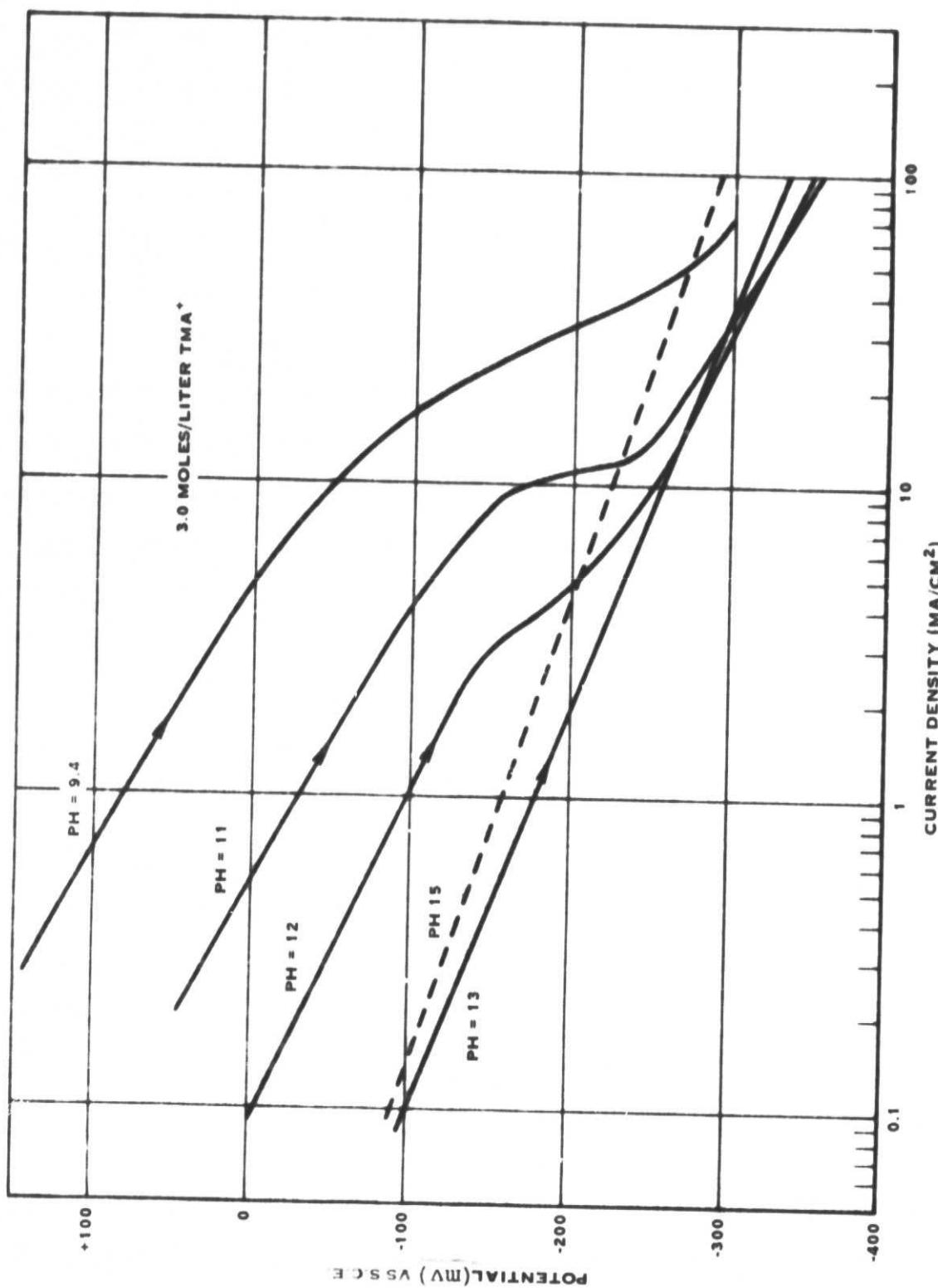
FIGURE 9. FET OF DS16 CATHODE VERSUS PH

In the overall cathodic reaction there is the following sequence of chemical reactions in addition to the electrochemical reactions discussed above.

1. $CO_2 \text{ (g)} \rightleftharpoons CO_2 \text{ (aq)}$

2. $CO_2 \text{ (aq)} + OH^- \longrightarrow HCO_3^-$

3. $HCO_3^- + OH^- \rightleftharpoons CO_3^= + H_2O$

Reaction 2 is normally the rate determining step for CO_2 transfer, and its rate is controlled by a combination of mass transport and slow reaction kinetics. Reaction 2 also limits the current density for depolarization of the cathodic electrochemical reaction. Thus, it would be necessary to increase the rate of reaction 2 in order to improve cathode performance in terms of increased voltage and CO_2 transfer rate. The most obvious way of accomplishing this is to increase the catalyst-Teflon loading so as to give an effective increase in cathode surface area and catholyte volume. Also, an electrode structure which facilitates the mass transport of dissolved CO_2 and hydroxide ions in the catholyte is need to obtain increased CO_2 transfer rates. The type of structure necessary to enhance the catholyte mass transfer rate cannot be presently defined, but it has been found empirically that a cathode with a lose catalyst-Teflon structure generally gives higher CO_2 transfer rates than one with a tight catalyst structure, other factors being equal.

ANODE POLARIZATION

From the anode polarization curves of the complete cell, the following conclusions were made:

1.   The anode process suffers from mass transport polarization, and eventually a limiting current density is approached.

2.   The anode electrochemical reaction involves more than a single charge transfer reaction.

3.   The phenomena of "reduced CO_2" poisoning becomes evident only in the mass transport controlled region.

The purpose of the anodic studies with the floating electrode technique was to identify the anodic electrochemical reactions and determine the cause for the anodic mass transport polarization and its influence on "reduced CO_2" poisoning.

Experimental Evaluation

To obtain an overall view of the anodic electrochemical process, potential sweeps were first made in a mixed carbonate-bicarbonate electrolyte at two cation concentrations (3 and 1M TMA$^+$). The results are given in Figures 10 and 11. The potential sweep starting at the initial open circuit (I.O.C.) potential was first increased in the positive direction followed by a reversal to the negative direction and reversed again to the positive direction as indicated by the arrow heads in Figures 10 and 11. At potentials more positive than the appropriate open circuit, the current is anodic, and at potentials more negative than the open circuit, the current is cathodic. Comparing first the overall data in Figures 10 and 11, it can be seen that the anodic current density, at a given potential, is dependent on the electrolyte concentration. This implies that the anion is directly involved in the overall anodic electrochemical reaction. If this is the case, the two anodic limiting currents, observed on the first positive potential sweep, would correspond in turn to the mass transport controlled discharge of the two anions $CO_3^=$ and HCO_3^-. On the anodic back sweep the carbonate ion concentration in the anolyte is negligible due to depletion by the electrode reaction; and the first limiting current, attributed to carbonate ion discharge on the up sweep, is not observed. Also, the new open circuit potential is more positive than the initial open circuit because of the decrease in anolyte pH caused by the anodic reaction. Continuing on the down sweep the current becomes cathodic, eventually reaching a limiting value. The cathodic reaction in this region is

$$HCO_3^- + e \longrightarrow CO_3^= + (H)$$

and the limiting current occurs upon depletion of the bicarbonate ion next to the electrode surface. The subsequent cathodic current involves the normal water discharge reaction

$$H_2O + e \longrightarrow OH^- + (H)$$

and upon reversing the potential sweep (positive), the new open circuit occurs at a more negative value than the original due to the increase in pH caused by the above reaction. This effect is more pronounced for the run in Figure 10 than in Figure 11 because the maximum cathodic current and, therefore, the total number of coulombs was higher for the run in Figure 10.

These initial experiments indicate that two anodic electrochemical reactions, involving the simultaneous discharge of carbonate and bicarbonate ions, are characteristic of the HDC anode. Additional experiments were designed to obtain more quantitative information on the details of anodic polarization.
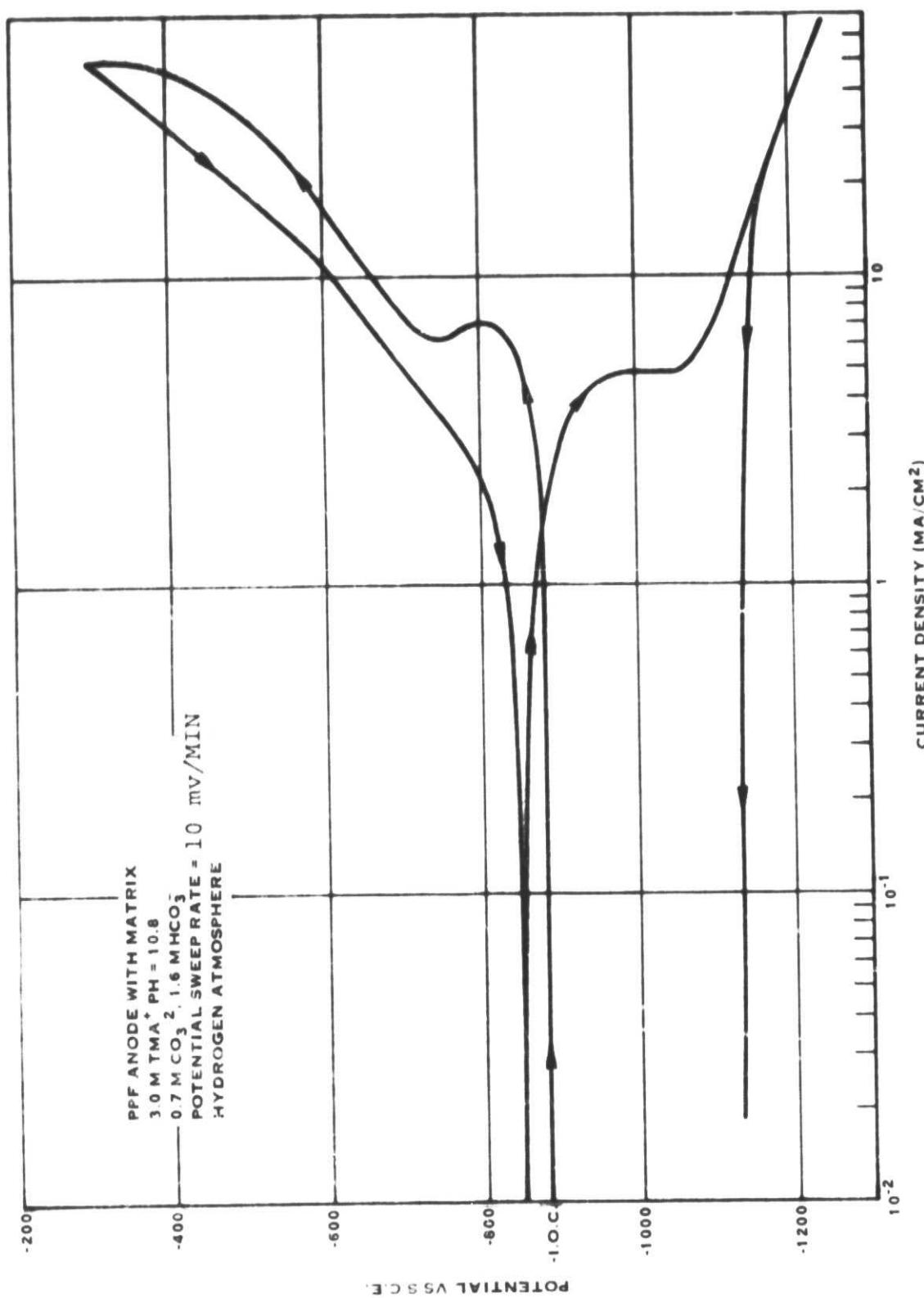
FIGURE 10. POTENTIAL SWEEP ON HYDROGEN ELECTRODE (FET) IN 3M TMA⁺ SOLUTION OF PH 10.8

PPF ANODE WITH MATRIX
3.0 M TMA⁺ PH = 10.8
0.7 M CO_3^2. 1.6 MHCO_3^-
POTENTIAL SWEEP RATE = 10 mv/MIN
HYDROGEN ATMOSPHERE

PPF ANODE WITH MATRIX
1.0 M TMA⁺, PH = 10.01
0.22 M CO₃⁼ .0.56 M HCO₃⁻
POTENTIAL SWEEP RATE = 10 mv/MIN
HYDROGEN ATMOSPHERE

I.O.C.

CURRENT DENSITY (MA/CM²)

POTENTIAL (MV) VS S.C E
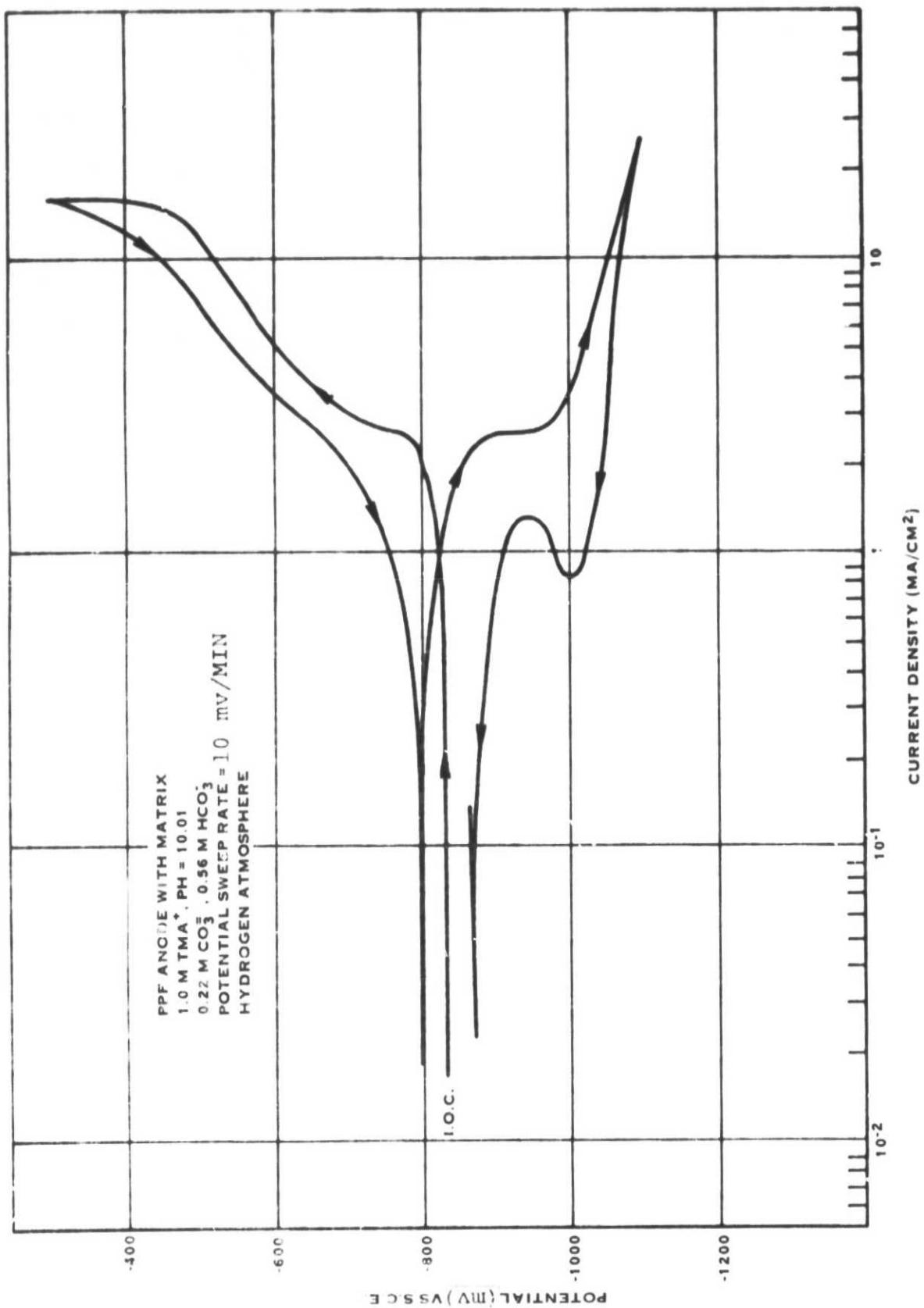
FIGURE 11. POTENTIAL SWEEP ON HYDROGEN ELECTRODE (FET)
IN 1M TMA⁺ SOLUTION OF PH 10.01

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Figure 12 shows the effect of solution (bicarbonate) concentration on anodic polarization when the carbonate ion concentration is negligible. It can be seen that the current density at a given potential is directly proportional to the bicarbonate ion concentration which proves that the bicarbonate ion takes a direct part in the anodic electrochemical reaction. The open circuit potential depends only on solution pH as would be expected from thermodynamics. It is also obvious that the exchange current for bicarbonate ion discharge is quite small compared to the normal HDC operating current density so that significant activation polarization is present in addition to mass transport polarization. The apparent Tafel slope is approximately 0.14 volts, whereas a normal Tafel slope of 0.12 volts would be expected for this type reaction in the absence of mass transport complications. The data in Figure 12 also shows that HDC operation at a current density of 20 ma/cm^2 requires that the anolyte concentration be greater than one mole per liter. This puts a limit on the maximum operating air relative humidity for any given effective electrode spacing and current density.

Figure 13 shows the effect of anion type on anode polarization. The open circuit potential in each case is directly proportional to solution pH. The pH 15 solution (3M TMAOH) has polarization characteristics typically associated with the hydrogen electrode in hydroxide solutions where the reaction is hydroxide ion discharge to form water, i.e.

$$(H) + OH^- \longrightarrow H_2O + e$$

With the pure bicarbonate electrolyte (pH 8.4) a Tafel region is obtained followed by a limiting current density as discussed above. By analogy with the hydroxide ion discharge reaction, the anodic reaction in bicarbonate solution must involve bicarbonate ion discharge to form carbonic acid, i.e.

$$(H) + HCO_3^- \longrightarrow H_2CO_3 + e$$

The limiting current occurs when the bicarbonate ion concentration at the anode catalyst surface becomes zero, and in this situation the mass transport of bicarbonate to the electrode surface is completely controlling the reaction rate, making the current independent of potential.

In pure carbonate solution (pH 12) the initial reaction must involve the discharge of carbonate ion to produce bicarbonate i.e.

$$(H) + CO_3^= \longrightarrow HCO_3^- + e$$
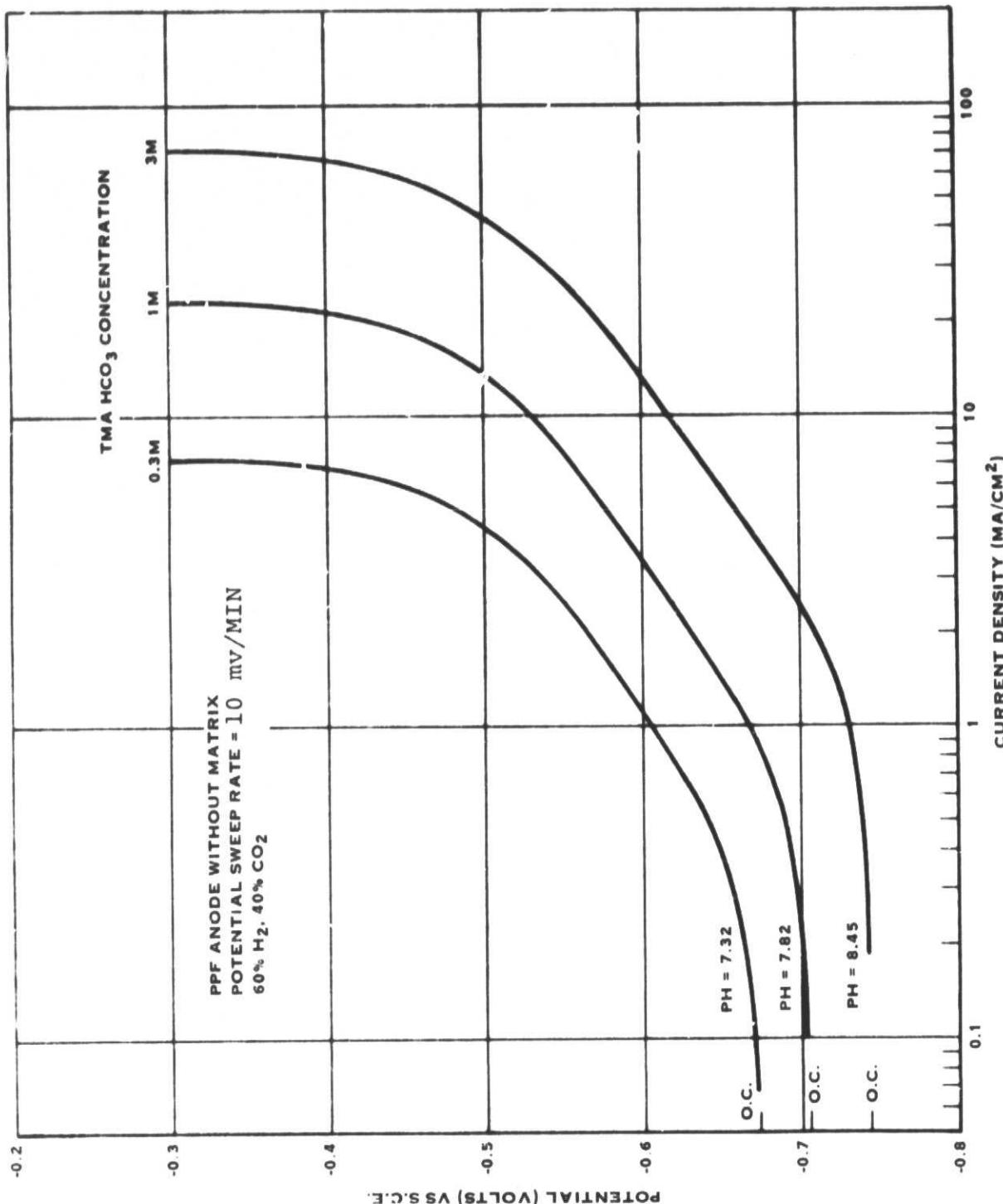
FIGURE 12. EFFECT OF BICARBONATE ION CONCENTRATION ON HDC ANODE POLARIZATION
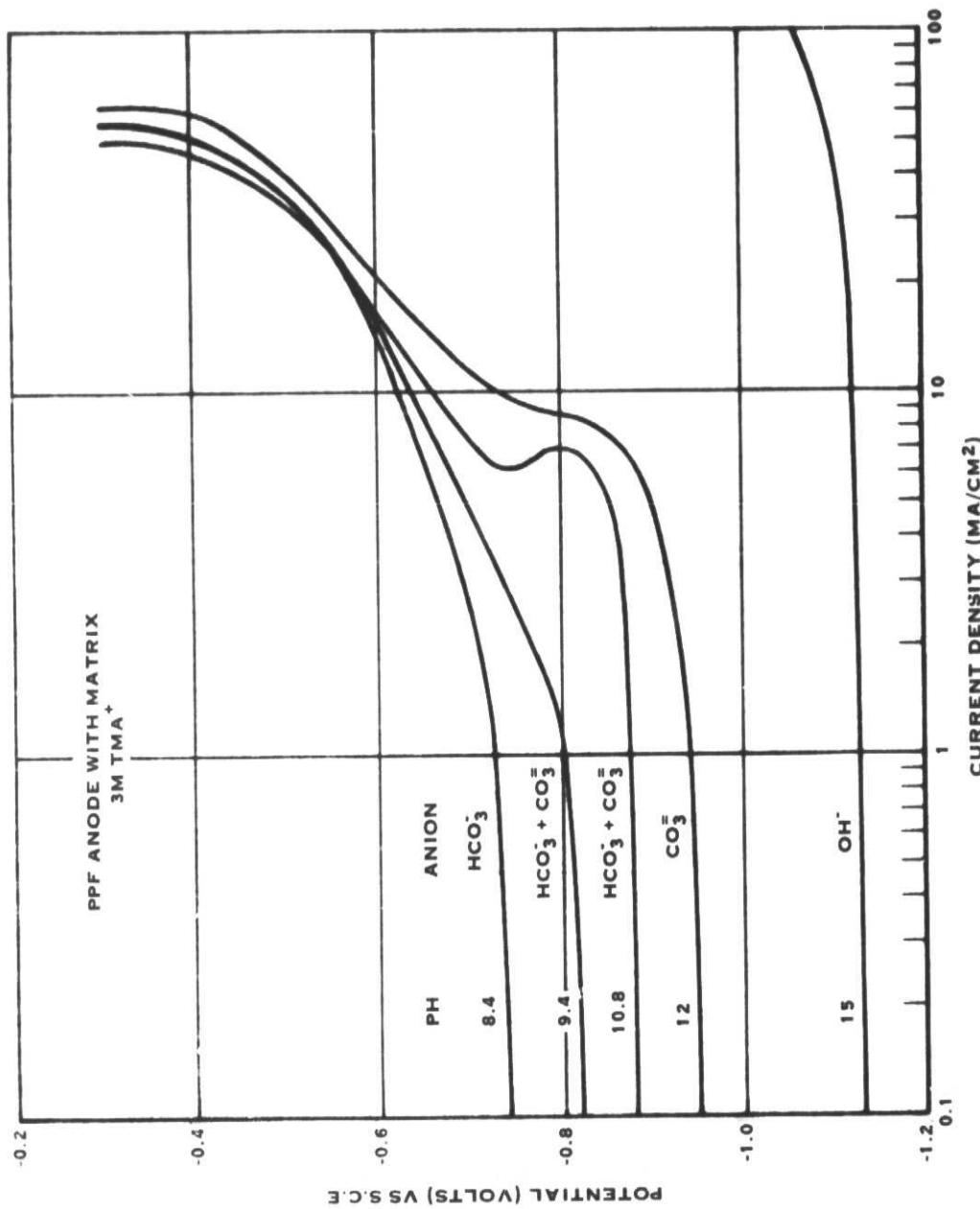
FIGURE 13. EFFECT OF ANION TYPE ON HDC ANODE POLARIZATION

The first limiting current is due to the depletion of the carbonate ion in the anolyte. At higher currents bicarbonate ion discharge takes over, and eventually the limiting current for bicarbonate discharge is reached.

When the electrolyte contains both carbonate and bicarbonate ions, the two anodic reactions occur simultaneously; the relative rate of each depending on their respective concentrations in the anolyte, which in turn is affected by their mass transport rates. It was shown from chemical analysis that the average HDC electrolyte composition after normal operation is predominantly bicarbonate with some carbonate, and the pH is between 9 and 10. Thus, upon increasing the cell current from open circuit, two electrochemical reactions, carbonate and bicarbonate ion discharge, occur in parallel. The relative rate of each reaction would depend on their respective exchange currents and mass transfer rates. In addition, the product of the carbonate discharge reaction (bicarbonate) is a reactant for the bicarbonate discharge reaction so that the two electrochemical reactions are coupled. As a consequence of this, the apparent cell Tafel slope is much steeper than the normal 0.12 volts associated with a simple charge transfer reaction. This effect is also evident from the data in Figure 13.

At normal HDC operating current levels the carbonate ion concentration in the anolyte is negligible because the back diffusion of carbonic acid (H_2CO_3) toward the cathode results in the conversion of any carbonate to bicarbonate before the carbonate can come near the anode surface. Stated another way, the anolyte pH at normal operating currents is too low for the existence of carbonate ion. As a result, bicarbonate ion discharge is the only significant electrochemical reaction under such conditions.

To determine the relative rates of the three possible anodic electrochemical reactions, measurements were made of the exchange current on a 1 cm^2, 20 mg/cm^2 PPF anode for each anion. The polarization was measured over the $\pm$ 5 mV range where the current is a linear function of potential, and the exchange current calculated from the slope in the usual manner. The results given in Table 2 show that the exchange current decreases in the order $OH^- > CO_3^= > HCO_3^-$ and is naturally a function of anion concentration.

Table 2
Relative Exchange Current Density (mA/cm^2)
Versus Concentration and Anion Type

Concentration	OH^-	$CO_3^=$	HCO_3^-
3M	34	10	1.6
1M	--	5	0.8
0.3M	--	--	0.43

In spite of the high exchange current for hydroxide ion discharge, the concentration of this ion in the HDC anolyte will always be less than $10^{-4}M$ so that the contribution of the hydroxide ion discharge reaction to the overall anodic electrochemical process will be negligible even near the open circuit potential. The carbonate ion exchange current (Table 2) is the same order of magnitude as the carbonate ion limiting current (Figure 13). Therefore, the carbonate ion discharge reaction should be mostly mass transport controlled, and this is evident from the pH 12 polarization curve in Figure 13. The low exchange current associated with bicarbonate ion discharge means that the HDC anode will have significant activation polarization in addition to the mass tranport polarization, and this is also evident from the overall polarization curves shown in Figures 12 and 13.

Kinetic Analysis

From the data and discussion presented above, it is concluded that the overall anodic polarization curve for the HDC consists of two parallel but coupled electrochemical reactions:

a. $M-H + CO_3^= \longrightarrow M + HCO_3^- + e$

b. $M-H + HCO_3^- \longrightarrow M + H_2CO_3 + e$

The total current is the sum of the currents from each electrochemical reaction

$$\dot{i} = \dot{i}_a + \dot{i}_b$$

and $\dot{i}_b = f(\dot{i}_a)$ due to the fact that the product from reaction (a) is a reactant in reaction (b). Near the open circuit potential, reaction (a) predominates over reaction (b), and as the current increases, the concentration of the carbonate ion in the anolyte decreases while the bicarbonate ion concentration increases until the two reaction rates are equal ($\dot{i}_a = \dot{i}_b$). At higher currents the bicarbonate ion discharge reaction (b) predominates, and the bicarbonate ion concentration in the anolyte decreases, eventually

reaching zero at the limiting current density. The back diffusion of carbonic acid (H_2CO_3), which is a product of reaction (b), also modifies the carbonate to bicarbonate ion concentration ratio in the vicinity of the anode via the fast chemical reaction

$$H_2CO_3 + CO_3^= \rightleftharpoons 2HCO_3^-$$

thereby favoring reaction (b).

The overall kinetics of the anode process were derived for the simple case where only one of the electrochemical reactions (b) takes place. These kinetics apply when the carbonate ion concentration in the anolyte is negligible compared to the bicarbonate ion concentrations, and steady state experimental data for these conditions is relatively easy to obtain. The kinetic treatment for the more general case would require a detailed knowledge of the carbonate ion mass transport rate to the anode and is beyond the scope of the present effort.

The complete anodic reaction is

$$H_2 + 2M \rightleftharpoons 2M\text{-}H$$

$$2(M\text{-}H + HCO_3^- \longrightarrow M + H_2CO_3 + e)$$

$$H_2CO_3 \longrightarrow H_2O + CO_2(aq)$$

$$CO_2(aq) \rightleftharpoons CO_2(g)$$
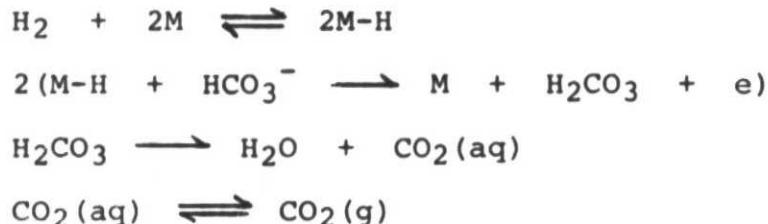
where M is a catalyst site, and M-H represents adsorbed atomic hydrogen. It is assumed that the first and last steps are at equilibrium for all practical current densities, and that the amount of adsorbed atomic hydrogen (M-H) is independent of current density. Under steady state conditions the current density ($\imath$) is given by:

$$\imath = nF \left[\vec{k}(HCO_3^-) \exp \frac{F\mathcal{E}}{2RT} - \overleftarrow{k}(H_2CO_3) \exp \frac{-F\mathcal{E}}{2RT} \right]$$

where $\mathcal{E}$ is the metal-solution potential difference, the k's are the rate constants including the H_2, M and M-H terms, and the other terms have their usual significance. By definition the exchange current density ($\imath_o$) is

$$\imath_o = nF \vec{k}(HCO_3^-)_o \exp \frac{F}{2RT}\mathcal{E}_o = nF \overleftarrow{k}(H_2CO_3)_o \exp \frac{-F}{2RT}\mathcal{E}_o$$

where X_o are the appropriate terms when $\dot{\imath} = 0$. Dividing $\dot{\imath}$ by $\dot{\imath}_o$ gives

$$\dot{\imath} = \dot{\imath}_o \left[\frac{(HCO_3^-)}{(HCO_3^-)_o} \exp \frac{F\eta}{2RT} - \frac{(H_2CO_3)}{(H_2CO_3)_o} \exp \frac{-F\eta}{2RT} \right]$$

where $\eta = \mathcal{E} - \mathcal{E}_o$ is the overvoltage. From simple mass transport theory, it can be shown that

$$\frac{(HCO_3^-)}{(HCO_3^-)_o} = \frac{\dot{\imath}_\ell - \dot{\imath}}{\dot{\imath}_\ell}$$

where $\dot{\imath}_\ell$ is the limiting current density for bicarbonate ion. The ratio $(H_2CO_3)/(H_2CO_3)_o$ can be calculated as a function of the current density from the carbonic acid dehydration rate constant, anolyte volume, and a knowledge of the carbonic acid mass transport rate out of the anolyte. Since the $(H_2CO_3)/(H_2CO_3)_o$ term is important only at low overvoltages where the negative exponential terms is of significant magnitude, the mass transport rate of carbonic acid away from the anolyte can be neglected. The ratio is then

$$\frac{(H_2CO_3)}{(H_2CO_3)_o} = \frac{K'\,\dot{\imath}}{nFd\,\vec{k}'(CO_2)_o} + \frac{(CO_2)}{(CO_2)_o}$$

where

K' = equilibrium constant for $H_2CO_3 \quad CO_2 + H_2O$
$\vec{k}'$ = forward rate constant for carbonic acid dehydration
d = anolyte volume per unit electrode area

Since it was assumed initially that the conversion of $CO_2(aq)$ to $CO_2(g)$ was at equilibrium, the ratio $(CO_2)/(CO_2)_o = 1$. With $K = 667$, $\vec{k}' = 20$/sec and $d = 3 \times 10^{-3}$ cm^3/cm^2 for a 20 mg/cm^2 PPF electrode, the above equation reduces to

$$\frac{(H_2CO_3)}{(H_2CO_3)_o} = 8.5 \times 10^3\,\dot{\imath} + 1$$

for $P_{CO_2} = 0.4$ atm where $(CO_2)_o = 0.0135$ moles/liter.

From this it is apparent that at current densities above $\sim 10^{-5}$ amp/cm^2 the carbonic acid concentration will be significantly greater than the equilibrium value. In this case the calculated polarization curves were grossly different than the experimental data. In order to match the experimental data, it was necessary to assume that the rate constant ($\vec{k}'$) is at least a factor of 40 greater than the literature value for aqueous solutions. The only

explanation for this discrepancy which can be offered at this time is the possibility that the electrode acts as catalyst for carbonic acid dehydration. When it is considered that the carbonic acid is formed directly on the catalyst surface, the above conclusion seems reasonable.

With the assumption that $(H_2CO_3)/(H_2CO_3)_O \approx 1$ at low values of the overvoltage,* the rate equation simplifies to

$$i = \frac{2\, i_1\, i_O\, \text{Sinh } 19.3\, \eta}{i_1 + i_O \exp 19.3\, \eta}$$

which gives an excellent fit to the anode floating electrode polarization curves run in bicarbonate solution with a 60% H_2, 40% CO_2 gas.

From the definition of the exchange current density, it can be shown that

$$i_O = nF \left(\frac{\vec{k}\, \overleftarrow{k}}{K} \right)^{1/2} (H+)_O^{1/2}\ (HCO_3^-)_O$$

where K is the equilibrium constant for the reaction $HCO_3^- + H+ \rightleftharpoons H_2CO_3$. Thus, the exchange current density for bicarbonate ion discharge should be proportional to the square root of the hydrogen ion activity times the activity of the bicarbonate ion, i.e.

$$i_O = k\, \gamma\, (HCO_3^-)_O\ 10^{-pH/2}$$

where k is a constant, γ the activity coefficient, and $(HCO_3^-)_O$ the bicarbonate ion concentration. Table 3 shows the value of k calculated from the measured exchange current density and solution pH for various bicarbonate ion concentrations where it can be seen that the above theoretical relationship holds.

Table 3
Correlation of Exchange Current Density
with pH and Bicarbonate Ion Activity

$(HCO_3^-)_O$	pH			k
3	8.43	1.33	1.6×10^{-3}	6.58
1	7.82	1	8×10^{-4}	6.50
.3	7.32	1	4.3×10^{-4}	6.55
.1	6.87	1	2.4×10^{-4}	6.53

*This is equivalent, numerically, to assuming that $\vec{k}' \gg 20/sec$.

APPENDIX

"REDUCED CO₂" POISONING

The cathodic reduction of carbon dioxide to formate ion (or formic acid) in aqueous solution has been investigated by many authors/1-13/. Giner/14,15/was the first to report that carbon dioxide reacts with adsorbed atomic hydrogen on a platinum surface in acid solution to form a strongly adsorbed species which he called "reduced CO_2." The "reduced CO_2 species acts as a poison for the electrochemical hydrogen dissolution-evolution reaction because it is strongly adsorbed on the catalyst (platinum) site, thereby, decreasing the surface area available for hydrogen adsorption. Subsequent investigations by others/16,17/in acid solution confirmed the finds of Giner. At Hamilton Standard we have shown that the same "reduced CO_2" species is formed in basic electrolyte if free CO_2 (as opposed to HCO_3^- or $CO_3^=$) is allowed to come in contact with a hydrogen electrode.

Van Rysselberghe and co-workers/6,18/also demonstrated that HCO_3^- and $CO_3^=$ ions are not reduced but that CO_2 must be present. Smith and Jordan/13/confirmed these results and also showed that the electroreductive species is dissolved free CO_2 rather than H_2CO_3.

Ryu, Andersen, and Eyring/19/have studied the reaction mechanism for the electrochemical reduction of carbon dioxide on a mercury cathode in sodium bicarbonate solution saturated with CO_2. The reduction of CO_2 to formate was found to occur in two consecutive steps:

I. $CO_2 + H_2O + e \longrightarrow HCO_2(ads) + OH^-$

II. $HCO_2(ads) + e \longrightarrow HCO_2^-$

with the second step rate controlling at low cathodic overvoltages. On platinum, near the potential of the hydrogen electrode, the surface is covered with adsorbed atomic hydrogen* so that Step I above occurs via two steps, i.e.:

Ia. $H_2O + e \longrightarrow H(ads) + OH^-$

Ib. $CO_2 + H(ads) \longrightarrow HCO_2(ads)$

*Mercury does not adsorb hydrogen so that water is the direct proton doner for CO_2 reduction on a mercury electrode as indicated in Step I.

From this, it is apparent that the reaction observed by Giner and others corresponds to Step Ib, and the "reduced CO_2" species is actually an adsorbed formate radical (HCO_2 ads). Further reduction of CO_2 to formate (Step II) requires very high cathodic overvoltages, whereas the formation of the adsorbed formate radical (Step I) is relatively a very rapid reaction (equilibrium). This explains why the adsorbed formate radical (reduced CO_2) is a poison for the hydrogen reaction.

The oxidation of the formate radical (reduced CO_2) back to CO_2 (reverse of Reaction I) occurs readily at potentials above +0.6 volts versus a hydrogen reference electrode in the same solution. A closed circuit nitrogen purge of the HDC cell (hydrogen starvation) affectively accomplishes this oxidation of the adsorbed formate radical, thereby restoring original anode performance.

REFERENCES

1. M. E. Royer, C.R. Acad, Sci., 70, 73 (1870).

2. A. Cohen and S. Jahn, Ber. Deut. Chem. Ges., 37, 2836 (1904).

3. R. Ehrenfeld, ibid., 38, 4138 (1905).

4. F. Fisher and P. Prziza, ibid., 47, 256 (1914).

5. M. Rabinowitsch and A. Maschowetz, Z. Elektrochem., 36, 845 (1930).

6. T. E. Teeter and P. Van Rysselberghe, J. Chem. Phys., 22, 789 (1954).

7. Proceedings of the Sixth Meeting of the International Committee on Electrochemical Thermodynamics and Kinetics, Butterworth London, 1955, pp. 538.

8. T. E. Teeter, Ph.D. dissertation, University of Oregon, Eugene, Oregon, June, 1954.

9. M. Hong, Ph.D. dissertation, University of Utah, Salt Lake City, August, 1969.

10. W. Paik, T. N. Andersen, and H. Eyring, Electrochim. Ack. 14, 1217 (1969); W. Paik, Ph.D. dissertation, University of Utah, Salt Lake City, Utah, August, 1968.

11. L. V. Haynes and D. T. Sawyer, Anal. Chem., 39, 332 (1967).

12. J. L. Roberts, Jr., and D. T. Sawyer, J. Electroanal. Chem., 9, 1 (1965).

13. J. Jordan and P. T. Smith, Proc. Chem. Soc., 246 (1960); P. T. Smith and J. Jordan, "Polarography 1964, Proceedings of the Third International Congress," (T. J. Hills, Ed., Maemillan, London, 1966, pp. 407-418).

14. J. Giner, Electrochim. Acta, 8, 857 (1963).

15. J. Giner, Electrochim, Acta, 9, 63 (1964).

16. S. Schuldiner, et al, NRL Report 6388, U.S. Naval Research Laboratory, Washington D.C., April, 1966.

17. S. B. Brummer and K. Cahill, J. Electroanal. Chem., 21, 463 (1969).

18. P. Van Rysselberghe, J. Amer. Chem. Soc. 68, 2050 (1946).

19   J. Ryu. T. N. Andersen and H. Eyring, J. Phy. Chem. 76, 3278 (1972).