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BIOCHEMICAL FUEL CELLS
Report No. 3
Contract No. DA 36-039 SC 90866
Task No. 3A 99-09-001-01
Third Quarterly Progress Report
1 January 1963 to 31 March 1963

U. S. ARMY ELECTRONICS RESEARCH
AND DEVELOPMENT LABORATORY
Ft. Monmouth, New Jersey

MAGNA CORPORATION

Research and
Development
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BIOCHEMICAL FUEL CELLS
Report No. 3

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Third Quarterly Progress Report

1 January 1963 to 31 March 1963

The Object of Research: The Development of Electrochemical Power Generators Using Biochemical Reactions.

This report prepared by:

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12. Current-Potential Curve for the *Clostridium butyricum*-glucose System Using the Compression Electrode Test Assembly.

1. PURPOSE

The concept of converting natural products into electrical energy is being studied under Contract No. DA-33-039 SC-90866. The object of this program is to study the feasibility of using a biochemical fuel for this purpose. A biochemical fuel cell is defined as a galvanic cell which uses a biochemical reaction as part of a process to convert natural materials into electricity. The approach has been to study simple biological systems using pure chemical substrates as models of practical systems to demonstrate feasibility, establish magnitude of energy yields, and develop promising approaches.

The experimental program has been divided into two tasks. Task I is concerned with establishing the biochemical and electrochemical properties of a selected system. Phase I, which is essentially complete, is a cultural and physiological study of the selected system. Phase 2 is a study of the electrode kinetics of the products of the biological reactions independent of the biological system. Phase 3 is a study of the electrode kinetics of the integrated biological and electrochemical system.

Task II is concerned with exploring various physical arrangements designed to optimize the performance of the biological electrode systems. This includes methods of confining the biological agent at or near the surface of the electron carrier.

2. ABSTRACT

Studies on the electrochemical behavior of two products, ammonia and hydrogen, of potentially useful biochemical reactions are reported.

The anodic behavior of hydrogen and ammonia under conditions compatible with biological systems are reported. Various catalysts were studied and the optimum catalyst and conditions for electro-oxidation compatible with the biological system selected.

Polarization characteristics of the B. pasteurii-urea and Cl. butyricum-glucose systems under conditions where the biological phase was physically confined at the electron carrier surface were obtained. Limiting current densities of 3 mA/cm^2 and open circuit potentials of -0.23 V vs SCE were obtained for the B. pasteurii-urea system. The performance of the Cl. butyricum-glucose electrode system was inhibited. Evidence is presented to indicate that the inhibition is probably due to carbon black adsorbing the hydrogen produced by the Cl. butyricum.

3. CONFERENCES

On 14 February 1963, Dr. H. P. Silverman of Magna Corp. visited the U. S. Army Electronic Research and Development Laboratory, Fort Monmouth, New Jersey, to discuss the progress of the present program and future work. It was suggested that some effort be devoted to studies of the oxygen electrode in neutral solutions and the glucose-glucose oxidase system be substituted for the *E. coli*-glucose system.

4. F A CTUAL DATA

4.1 Introduction

To understand a complex system it is first necessary to become knowledgeable about the component parts. Thus in the study of biochemical fuel cells the biochemistry and electrochemistry must be independently studied if their interaction is to be understood. The reports of the first and second quarters, during which Task I Phase 1 was essentially completed, described the biochemical properties of the five biological systems selected for study. Two of these systems produced hydrogen as a result of the biological processes; the other three produced ammonia. This third quarterly covering the period 1 January 1963 to 31 March 1963 is concerned with Phase 2, the electrochemical studies of hydrogen and ammonia oxidation, and Phase 3, the electrochemical studies of the integrated systems of Bacillus pasteurii-urea and Clostridium butyricum-glucose, of Task I. The electrochemical studies of hydrogen and ammonia were studied under conditions compatible with the biological systems. The integrated systems were studied both with dispersed suspensions of the bacteria and with the biological phase confined to the electrode surface by a compression electrode, described previously.[1]

4.2 Experimental

4.2.1 Compression Electrode

The compression electrode was modified during this quarter to minimize gas-leakage from the anode assembly. A schematic diagram of this improved lucite cell assembly is presented in Figure 1. The electrode consists of a suitable carbon mixture (6) placed in the anode compartment (5) and compressed against the current collector (7) by tightening the nylon nuts in back of the O-ring compression plate (9). Assembly of the cell in this manner assures good contact between the electrodes and the ion-exchange membrane (4) used to separate the anode from the cathode. The type of membrane used in the cell assembly is dictated by the product of the biological reaction (i.e. anion-exchange for ammonia and cation-exchange for hydrogen).

The carbon mixture utilized in this cell varies with the biological system being tested, but it is normally a carbon-water slurry (Vulcan XC-72-R Carbon Black prepared by Cabot Corp.) catalyzed with black platinum.* A suitable oxygen cathode (black platinum catalyzed with silver) completes the cell. The oxygen (or air) pressure in the cathode compartment is maintained at 6 inches of water and the gas is saturated with water vapor to prevent drying of the ion-exchange membrane** in the cell. Temperature is controlled by placing the entire cell assembly in a drying oven.

The anode potential is measured by means of a Luggin capillary arrangement in the anode compartment. The capillary assembly is filled with a 1% agar gel saturated with potassium chloride and this agar bridge is connected to a saturated calomel reference electrode. The anode potential (vs SCE) is measured by means of a high impedance voltmeter (Keithley Model 600 A Electrometer). The cathode potential vs SCE is obtained by algebraically subtracting the anode potential vs SCE from the measured cell voltage. Current-potential data with this cell were obtained in a manner described previously.[1]

4.2.2 Nonbiological Electrode Studies

The nonbiological electrode studies were performed using the cell assembly and procedures described in a previous report.[1] The black palladium catalyst was prepared

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* Platinum Black prepared by Engelhard Industries, Lot 7383.

** Ionics Inc., Anion-Exchange Membrane AR-111-A.

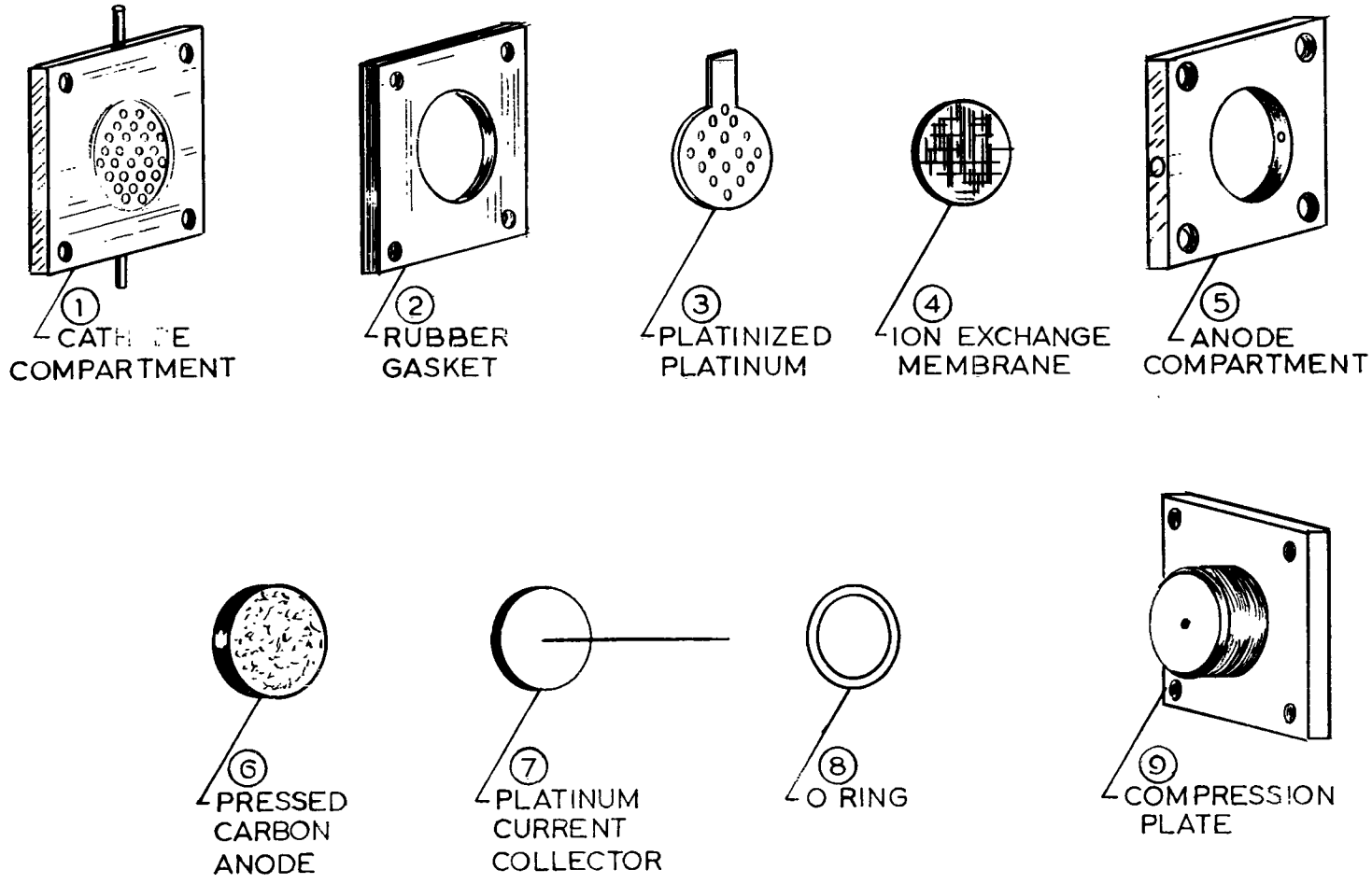

FIGURE 1. SCHEMATIC DIAGRAM OF THE COMPRESSION ELECTRODE CELL ASSEMBLY

by the method described by Ives and Janz [2] using a 5% palladium chloride, 0.1 molar hydrochloric acid plating bath.

4.2.3 Biological Electrode Studies

Current-potential curves were determined as described previously [1], using the new compression cell (see 4.2.1). The anode paste used with the B. pasteurii-urea system had the following composition: 2.5 g of carbon black, 200 mg of platinum black, 3.0 g of urea, and 300 mg of B. pasteurii cells (wet weight), moistened with 0.1 M Tris buffer, pH 8.0 to make a paste. The paste used with the Cl. butyricum-glucose system contained 1.5 g of carbon, 0.5 g of platinum black, 50 mg of Cl. butyricum cells (wet weight), and sufficient 0.1 M phosphate -0.1 M glucose, pH 7.0 to make a paste. In one experiment, 0.5 g of palladium black was substituted for the platinum black.

The effect of carbon, platinum, and palladium black on the activity of Cl. butyricum was determined in the Warburg apparatus. Because hydrogen absorption by the carbon, platinum, or palladium black would interfere with the measurement of hydrogen produced by the organism, these materials were saturated with hydrogen prior to the addition of the bacteria. This was done by gassing the Warburg flasks containing the inorganic materials with hydrogen until no further uptake of gas was noted. The main compartment of the flasks contained 3.0 ml of 0.1 M glucose -0.1 M phosphate, pH 7.0 plus carbon, platinum, or palladium black. One-half ml of a suspension of Cl. butyricum in 0.1 M phosphate, pH 7.0 was placed in the side arm.

The effect of carbon and platinum black on the potential of the Cl. butyricum-glucose system was investigated in the H-cell assembly described previously.[1] Fifteen ml of an actively gassing culture of Cl. butyricum in AC broth buffered with 0.1 M phosphate, pH 7.0 was placed in the anode compartment, and the cathode compartment was filled with 0.1 M phosphate, pH 7.0. Weighed amounts of carbon or platinum black were added to the anode compartment. The cell was purged with nitrogen to remove dissolved oxygen.

4.3 Results and Discussion

4.3.1 Nonbiological Electrode Studies

4.3.1.1 Ammonia Electrode Studies

The study of the electrochemical oxidation of ammonia under conditions compatible with the biological systems was continued during this quarter. Ammonium carbonate was used as the ammonia source.

Decreasing the ionic strength of the anolyte and increasing the ammonium carbonate concentration [1] caused an improvement in anode performance, but the electrode was still unable to support current densities in excess of 1 mA/cm^2.

Increasing the temperature, as illustrated in Figure 2, did not appreciably change the open-circuit potential of the ammonia anode. However, the anodic limiting current density doubled from 1 mA/cm^2 to 2 mA/cm^2. A temperature increase is compatible with improved biochemical performance because the biological hydrolysis of urea proceeds more rapidly at elevated temperatures.[1]

The compression electrode [1] (see Figure 1) was used to study the ammonium carbonate electrode under conditions comparable to the study of the biological electrode. An ion-exchange membrane is used to separate the anode and cathode compartments.

The initial test with this cell was performed using an ammonium carbonate-oxygen system. The cell, which was expected to develop an O.C.V. of 0.55 V [3] and exhibit little polarization up to a current density of 1 mA/cm^2, performed poorly as shown in Figure 3. Polarization of the ammonia anode occurred at lower current levels than previously observed. This was probably a result of (1) incomplete wetting of the carbon powder prior to assembling the cell (2) insufficient catalyst, i.e. black platinum (3) loss of ammonia through the ion-exchange membrane and (4) absorption of the ammonia by the carbon powder. The cathode potential was also approximately 0.2 V more anodic than expected and the cathode polarized at low current densities (i.e. 0.1 V at 200 $\mu A/cm^2$), probably as a result of diffusion of the ammonia through the membrane to the cathode. A new cell designed to correct these faults is being considered.

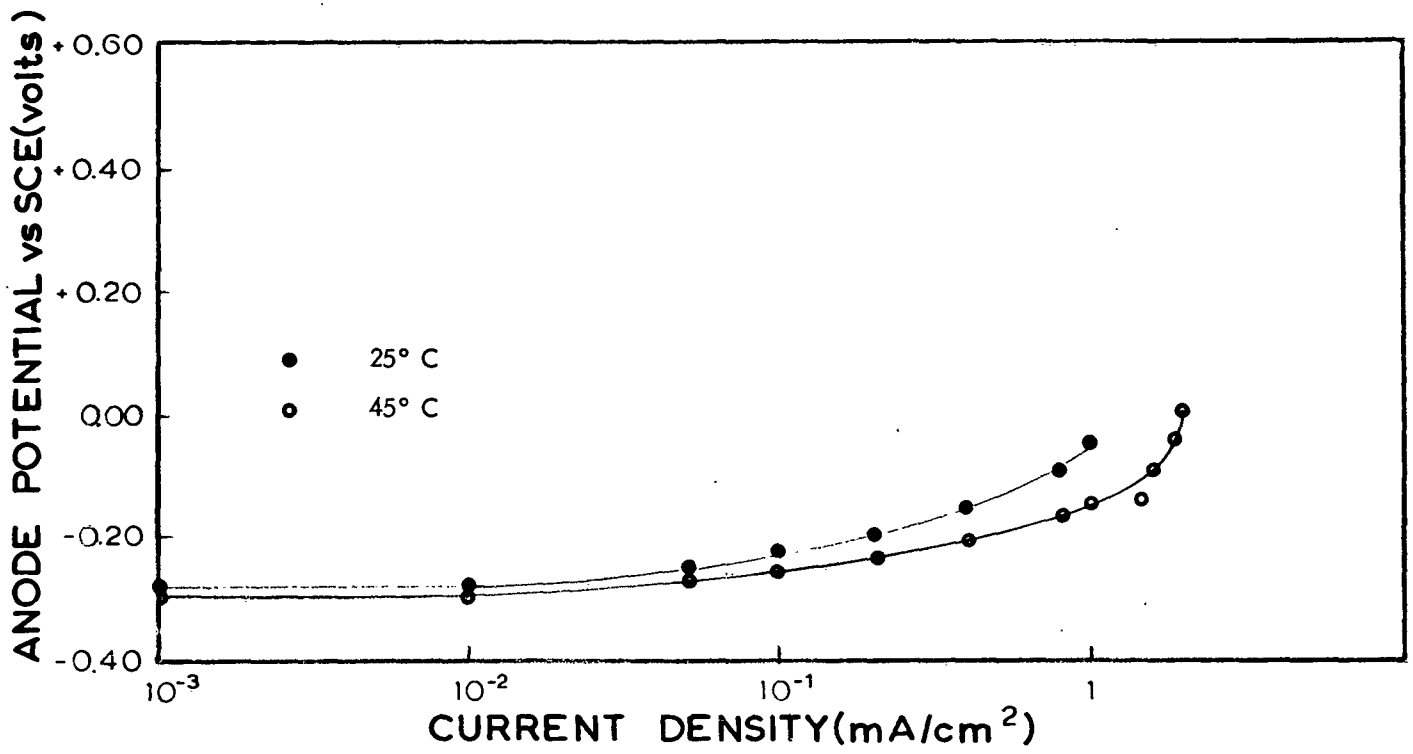

FIGURE 2. EFFECT OF TEMPERATURE ON THE ANODIC CURRENT-POTENTIAL CHARACTERISTICS OF A BLACK PLATINUM ELECTRODE IMMERSED IN 0.5 MOLAR AMMONIUM CARBONATE

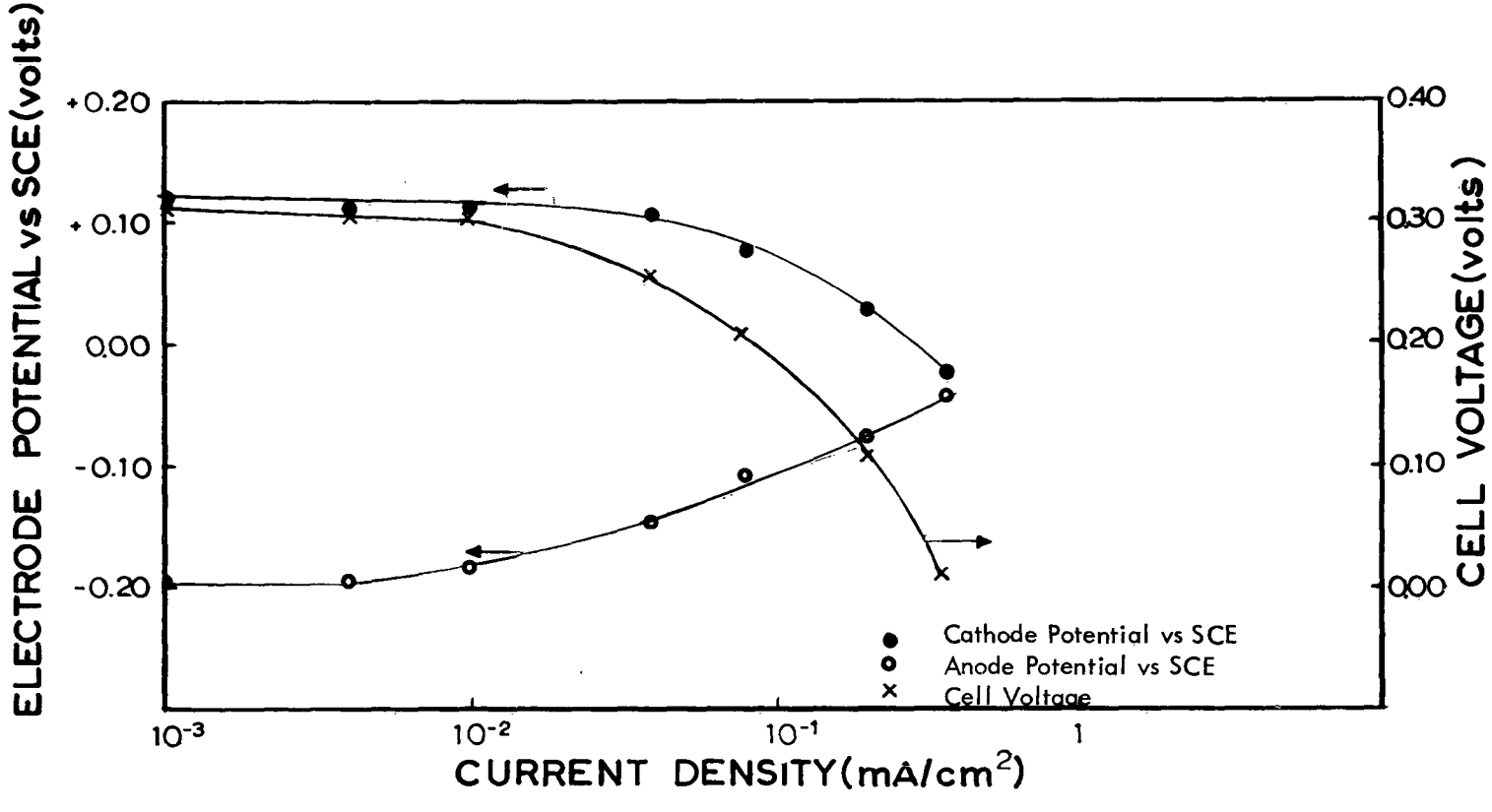

FIGURE 3. ELECTROCHEMICAL PERFORMANCE OF AN AMMONIUM CARBONATE-OXYGEN CELL UTILIZING THE COMPRESSION ELECTRODE TEST ASSEMBLY

Black palladium was reported [4] to be a better electrode catalyst for ammonia oxidation in neutral or basic electrolytes than any of the other metals of the platinum series. The effectiveness of the black palladium electrode was tested in a simple cell by immersing it in 0.5 molar ammonium carbonate. An open-circuit potential of -0.700 V vs SCE and an anodic limiting current density near 10 mA/cm^2 was observed. Although the current-potential data obtained agreed well with that reported in the literature,[4] it was suspected that this electrode was not oxidizing ammonia because the observed electrode potential was more anodic than would be expected for this reaction at a pH of 9.5. Palladium is a well-known "hydrogen-scavenger," capable of absorbing up to 0.7 of an atom of hydrogen per atom of palladium.[5] Therefore, the improved electrochemical performance noted above was probably due to hydrogen absorbed during the plating procedure.[2] This hypothesis was confirmed when the increased electrochemical activity noted with this anode was eliminated by anodically polarizing the electrode (10 mA/cm^2 for 2 hours) prior to immersion in the ammonium carbonate anolyte. Anodically polarized black palladium proved ineffective as a catalyst for ammonia oxidation (limiting current density less than 50 $\mu A/cm^2$).

Impure urease was observed to inhibit the electrochemical activity of the ammonia anode, as shown in Figure 4. Although the limiting current density was not measureably affected by this addition, the electrode potentials were shifted to less anodic values at any given current density. This shift seems to be due to the adsorption of protein material onto the surface of the electrode. Purification of the enzyme or containment of the enzyme in a dialysis bag is being investigated to see if this will reduce, or eliminate, this effect.

The organism, Bacillus pasteurii, also caused this "poisoning" but to a lesser extent.

In summary, the following operational parameters have given the best performance, to date, for the ammonia anode.

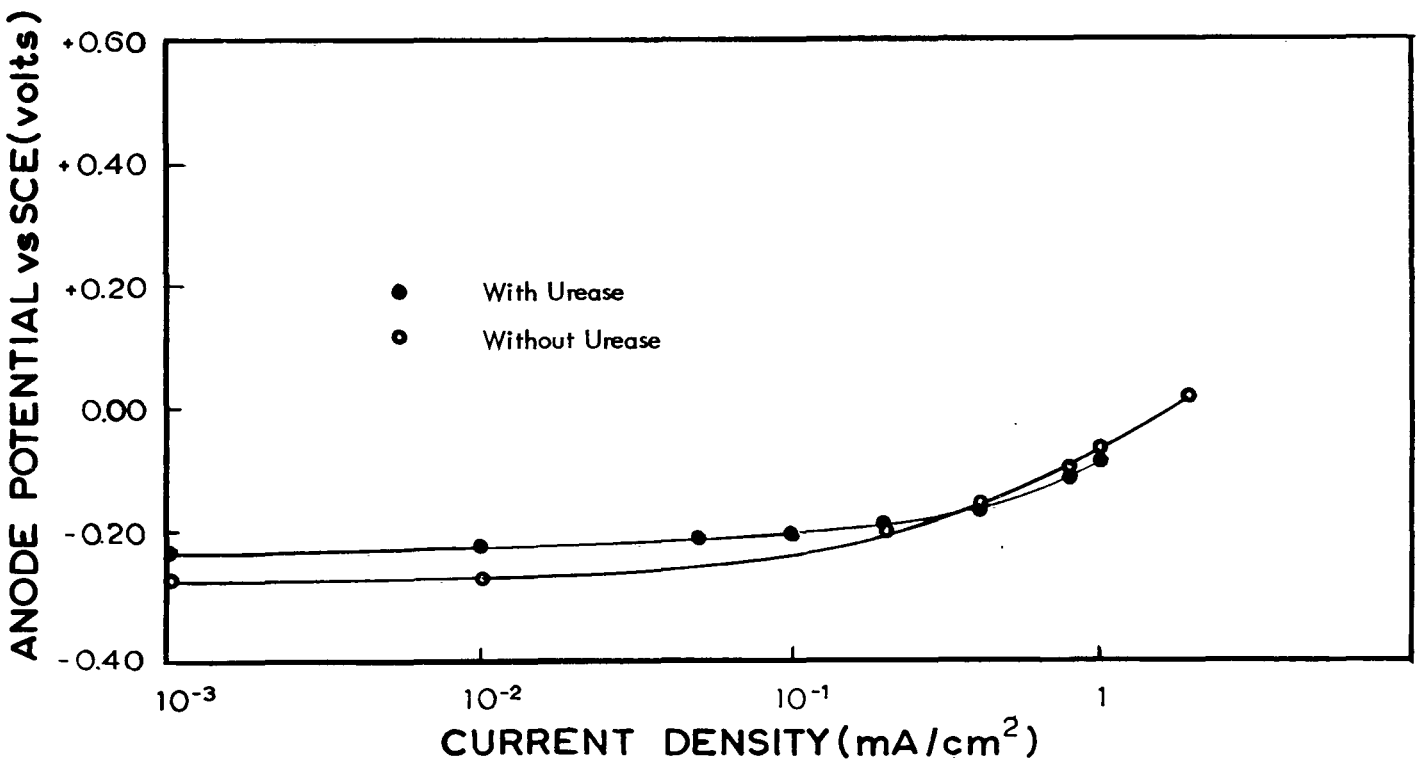

FIGURE 4. "POISONING" OF THE AMMONIUM CARBONATE ANODE AS A RESULT OF IMPURE UREASE ADDITION TO THE ELECTROLYTE

1. Black platinun as the electrode catalyst
2. pH of 9.5
3. Temperature of 45°C
4. Ammonia concentration of 0.5 molar (or greater)
5. Low ionic strength of the anolyte

4.3.1.2 Hydrogen Electrode Studies

The study of the electrochemical oxidation of hydrogen under conditions compatible with the biological production of hydrogen was started. Initially, only limited success in the electrochemical oxidation of hydrogen was realized (see Figure 5). The black platinum anode had an open-circuit potential of -0.605 V vs SCE and an anodic limiting current density of only 800 $\mu A/cm^2$. An increase in temperature of 10°C had little effect on the anode performance, as shown in Figure 6. Analysis of the data suggests that the hydrogen anode performance was limited by the slight solubility [6] of hydrogen in the electrolyte. Since palladium has the ability to absorb large volumes of hydrogen into the bulk of the metal [5] in addition to the normal surface adsorption of hydrogen which takes place with most metals of the platinum series, a palladized palladium anode should serve as a hydrogen sink and considerably improve the performance of the hydrogen anode. A black palladium anode was allowed to stand 20 minutes immersed in 0.1 molar phosphate buffer at pH 7.0 with hydrogen bubbling into the anolyte. (See Figure 7) An open-circuit potential of -0.55 V and anodic limiting current density of 4 mA/cm^2 were observed with this hydrogen-charged electrode. The high internal resistance of the test cell prevented investigation of the palladium anode at higher current levels than 4 mA/cm^2 because of limitations of the electronic equipment; however, it was evident from the shape of the current-potential curve that there was essentially no polarization (other than ohmic) up to this current density.

The effectiveness of black palladium compared to black platinum as the electrode catalyst for hydrogen oxidation in hydrogen-saturated phosphate solutions is illustrated in Figure 8. In both cases the electrodes were charged with hydrogen prior to the start of the experiment. The open-circuit potential of the black palladium electrode was 0.05 V less anodic than the black platinum (-0.555 V vs SCE as compared to -0.605 V vs

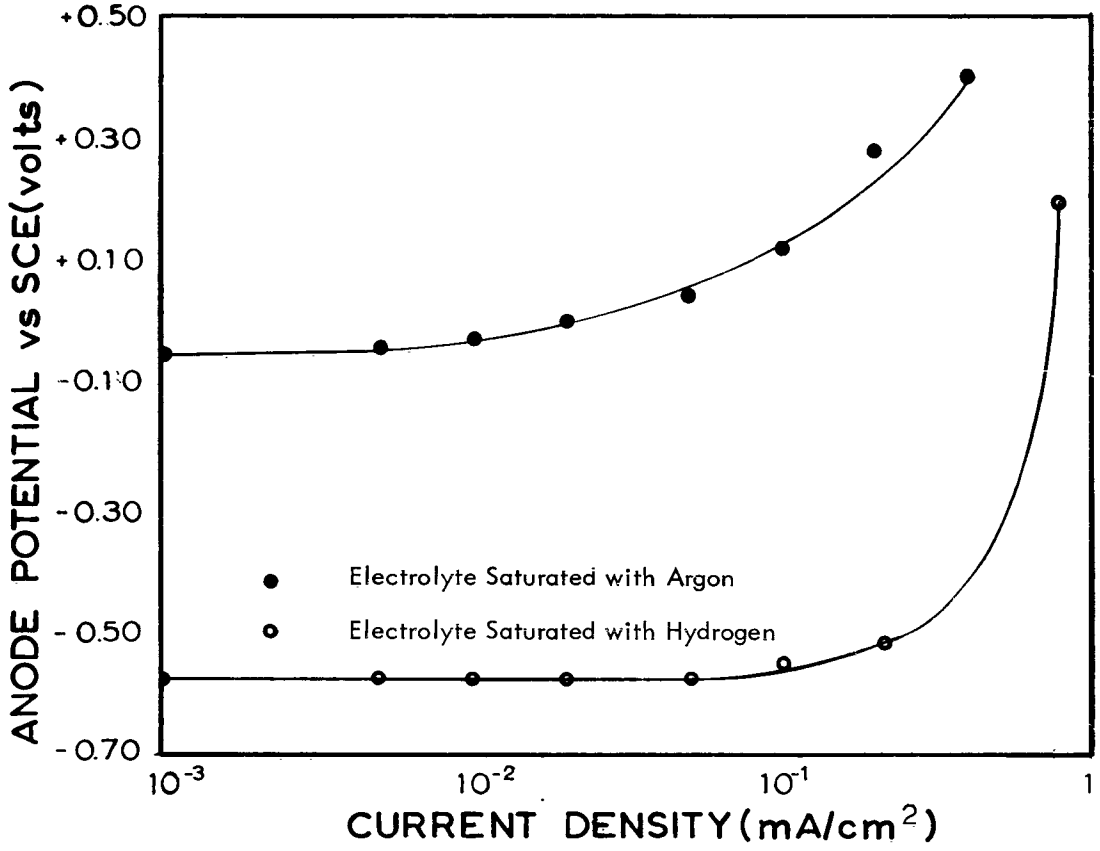

FIGURE 5. EFFECT OF HYDROGEN GAS ON THE ANODIC CURRENT-POTENTIAL CHARACTERISTICS OF A BLACK PLATINUM ELECTRODE IMMERSED IN 0.1 MOLAR PHOSPHATE BUFFER AT pH 7.0

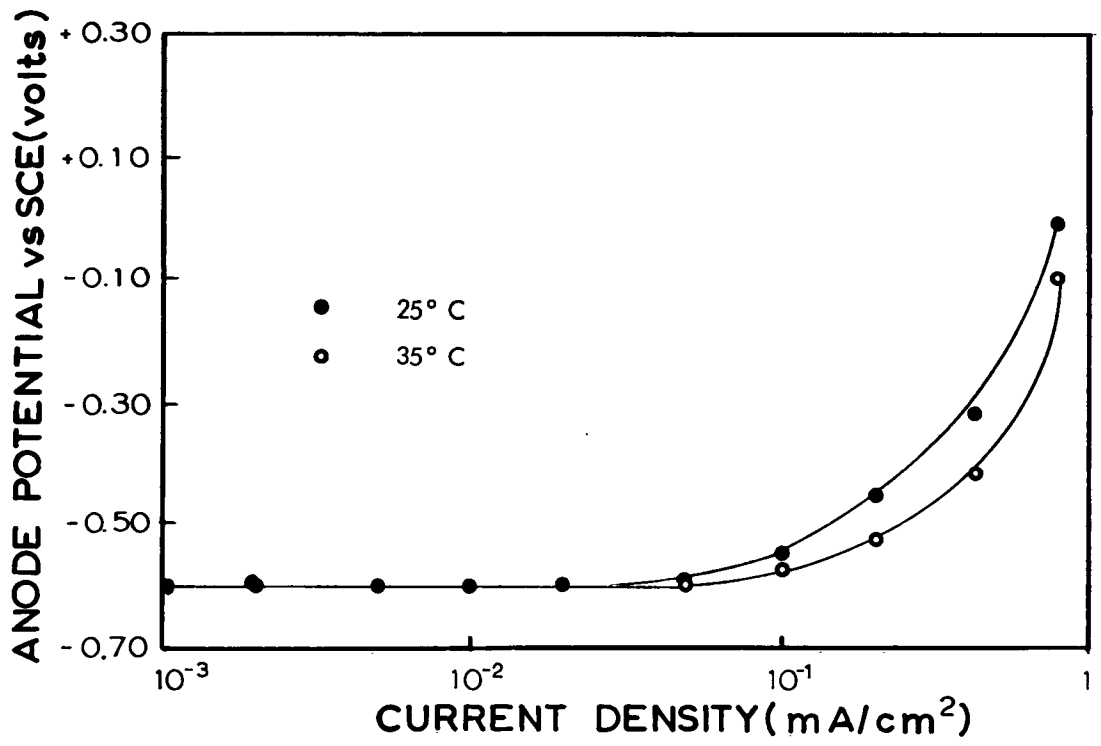

FIGURE 6. EFFECT OF TEMPERATURE ON THE ANODIC CURRENT-POTENTIAL CHARACTERISTICS OF A BLACK PLATINUM ELECTRODE IMMERSED IN HYDROGEN-SATURATED 0.1 MOLAR PHOSPHATE BUFFER AT pH 7.0

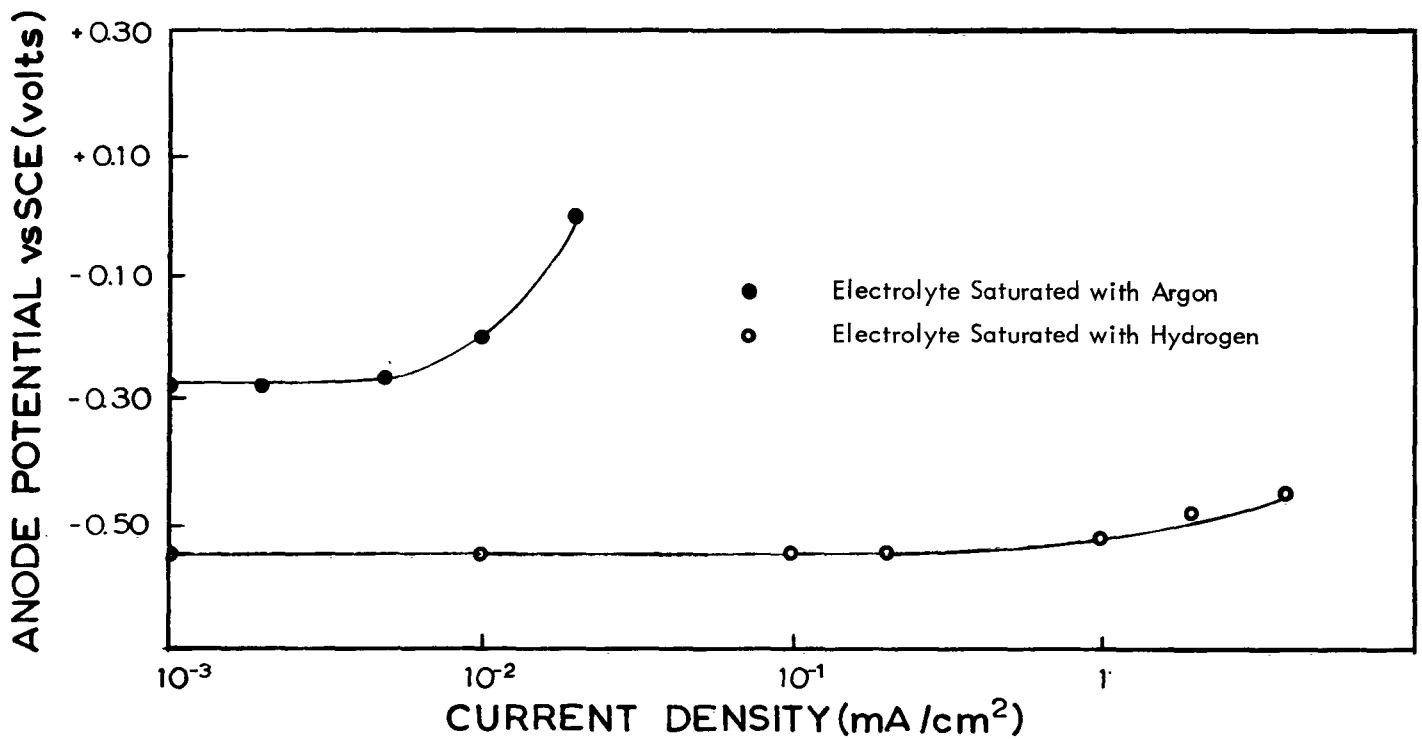

FIGURE 7. EFFECT OF HYDROGEN GAS ON THE ANODIC CURRENT-POTENTIAL CHARACTERISTICS OF A BLACK PALLADIUM ELECTRODE IMMERSED IN 0.1 MOLAR PHOSPHATE BUFFER AT pH 7.0

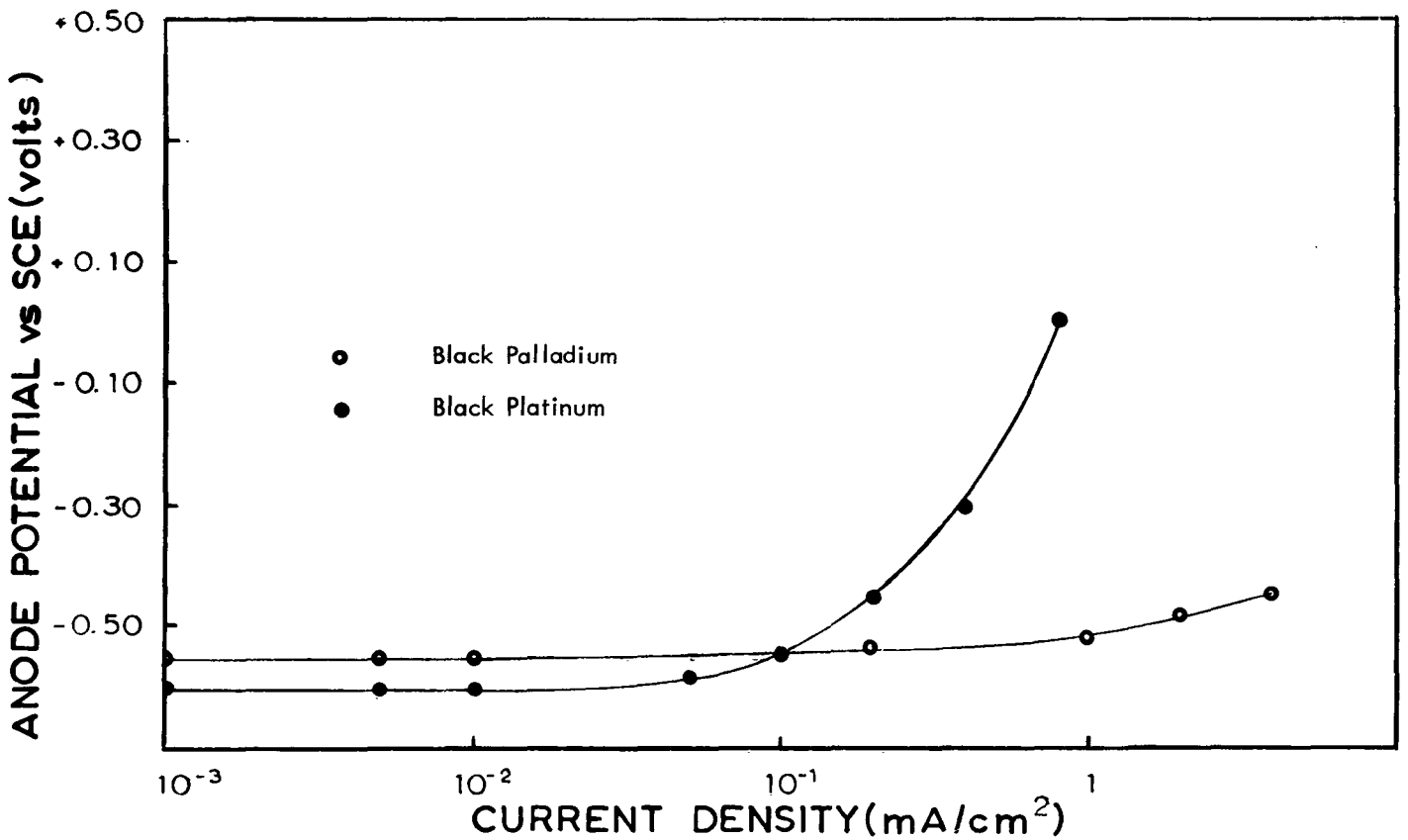

FIGURE 8. COMPARISON OF BLACK PALLADIUM TO BLACK PLATINUM AS THE ELECTRODE CATALYST FOR HYDROGEN OXIDATION IN HYDROGEN-SATURATED 0.1 MOLAR PHOSPHATE BUFFER AT pH 7.0

SCE), which is consistent with the potentials reported for these electrodes in the literature.[7] The black palladium, however, performed considerably better under load with a limiting current density of 4 mA/cm^2 to only 800 $\mu A/cm^2$ for the black platinum.

The effect of temperature on the anodic current-potential characteristics of a black palladium electrode immersed in hydrogen-saturated phosphate buffer is summarized in Figure 9. The temperature dependence of the saturated calomel reference electrode, $E_t = E_{25} + 0.00076\ (t - 25)$,[8] accounted for the approximately 8 millivolt more anodic open-circuit potential observed for the hydrogen anode at the higher temperature.

The effect of ionic strength of the electrolyte on the anodic current-potential characteristics of a black palladium electrode immersed in hydrogen-saturated phosphate buffer is illustrated in Figure 10. The electrochemical performance of the anode was not markedly affected by increasing the concentration of the phosphate buffer from 0.1 to 0.2 molar; considering that this increase in ionic strength again reduced the ohmic polarization component.

The results of these experiments indicate that palladium anodes operated near ambient temperature in low ionic strength, neutral electrolytes should yield open-circuit potentials vs SCE near -0.570 V and support current densities up to 6 mA/cm^2 for periods of several hours.

An equally important facet of the performance of palladium anodes is the rate at which the palladium can absorb hydrogen. Although palladium anodes have suitable short-term (several hours) discharge characteristics when charged with hydrogen and operated under conditions compatible with biological hydrogen-production, these anodes were unable to support current densities in excess of 1.5 mA/cm^2 for extended periods of time. Thus, the rate of hydrogen-absorption into the palladium appears to be the limiting step in the electrode process. Methods to enhance this absorption are currently being investigated. For example, an increase in current was obtained [9] by only partially rather than fully immersing a platinum electrode into hydrogen-saturated electrolytes. This increase in current was attributed to a considerably higher rate of hydrogen transport at the gas-solid-liquid interface than at the solid-liquid interface. Thus, it may be possible to increase the rate of hydrogen absorption of the palladium by a similar procedure.

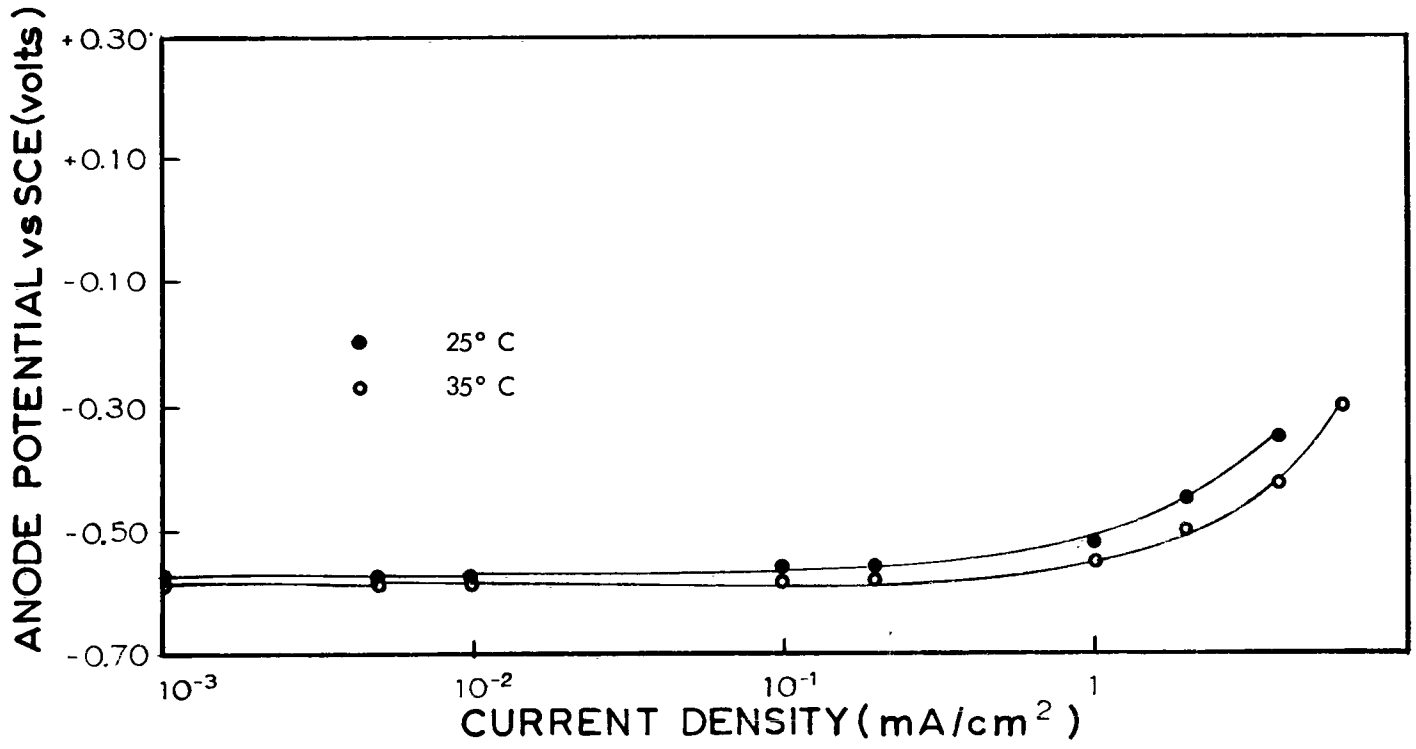

FIGURE 9 . EFFECT OF TEMPERATURE ON THE ANODIC CURRENT-POTENTIAL CHARACTERISTICS OF A BLACK PALLADIUM ELECTRODE IMMERSED IN HYDROGEN-SATURATED 0.2 MOLAR PHOSPHATE BUFFER AT pH 7.0

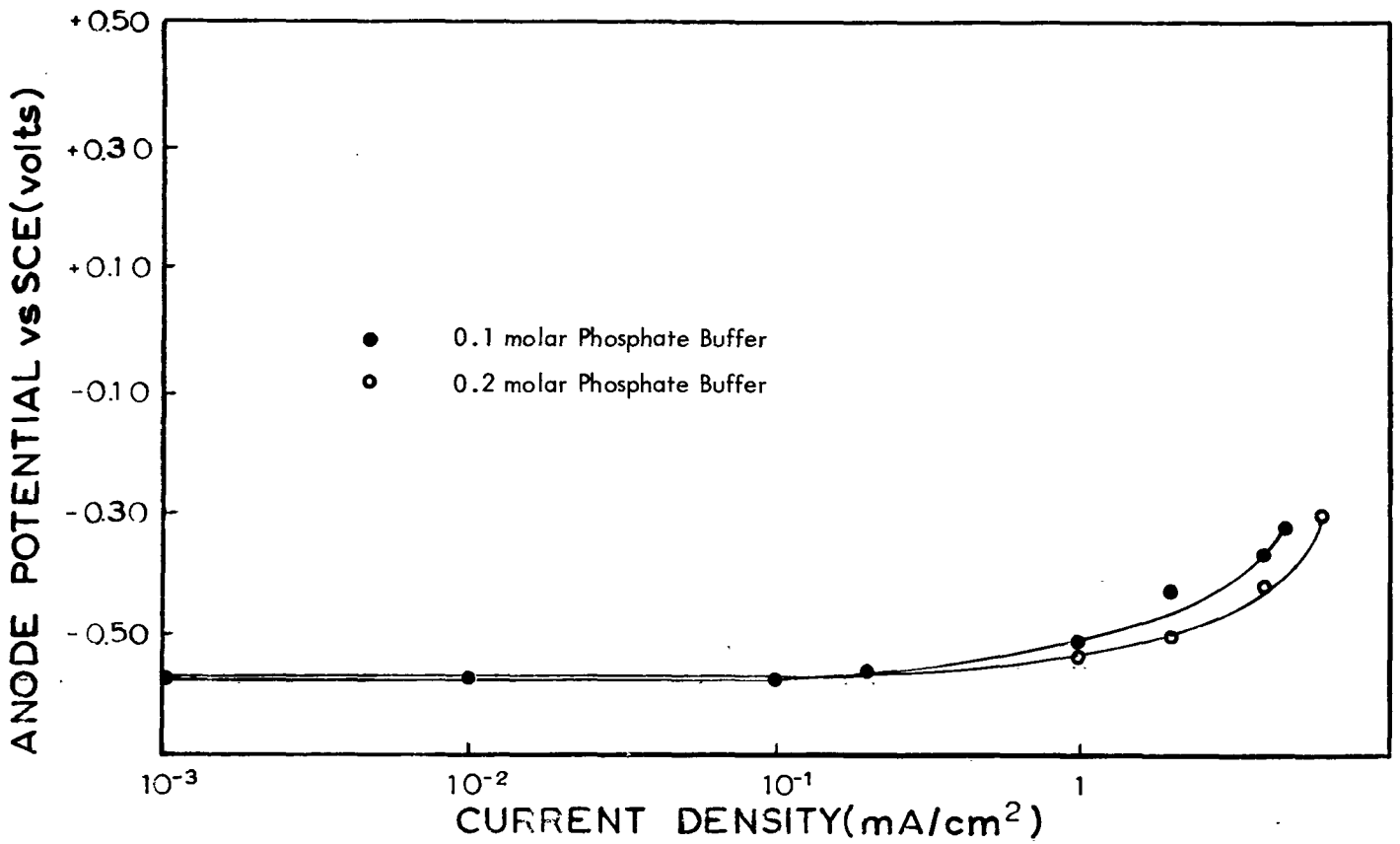

FIGURE 10. EFFECT OF IONIC STRENGTH OF THE ELECTROLYTE ON THE ANODIC CURRENT-POTENTIAL CHARACTERISTICS OF A BLACK PALLADIUM ELECTRODE IMMERSED IN HYDROGEN-SATURATED PHOSPHATE BUFFER AT pH 7.0

4.3.2 Biological Electrode Studies

4.3.2.1 Bacillus pasteurii

The B. pasteurii-urea system was tested with the newly designed compression electrode assembly (see 4.2.1). The results of current-potential measurements are shown in Fig. 11. Theopen circuit potential was -0.23 volts vs SCE, in good agreement with the potential observed earlier in the H-cell.[1] A limiting current density of 3 mA/cm^2 was obtained with the compression electrode. This is somewhat higher than the 1.1 mA/cm^2 observed in the previous style compression electrode.[1]

4.3.2.2 Clostridium butyricum

The Cl. butyricum-glucose system was also tested with the new compression electrode. Using the same ratio of carbon to platinum black as with the B. pasteurii, it was not possible to obtain an open circuit potential more anodic than -0.11 volts vs SCE. However, when the carbon to platinum black ratio was reduced to about 1:1, an open circuit potential of -0.56 volts was obtained. (Fig. 12). This potential is close to that found in experiments performed with the H-cell.[1] However, the limiting current was only 0.1 mA/cm^2, which is about 10% of the current observed in the H-cell. Further experiments were performed to try to determine the cause of this effect. A possible reason for the low potential observed with the compression electrode is an inhibition of the activity of the organism. This was tested by measuring hydrogen production by Cl. butyricum in the presence of carbon (Table I). A slight inhibition of activity was observed, but not enough to account for the poor performance with the compression electrode. Platinum black and palladium black did not inhibit the organism.

To see if the poor performance of the Cl. butyricum-glucose compression anode was due to adsorption of hydrogen by the carbon, the following experiment was performed. An actively gassing culture of Cl. butyricum was placed in the anode compartment of an H-cell. A potential of -0.64 volts vs SCE was observed with a sand-blasted platinum electrode. Then 67 mg/ml of carbon black was added. The potential shifted to a more cathodic potential of -0.25 volts vs SCE. Upon adding platinum black (3 mg/ml) the potential again became more anodic and was -0.53 volts vs SCE. This process was repeated several times with similar results. Apparently an equilibrium exists between hydrogen

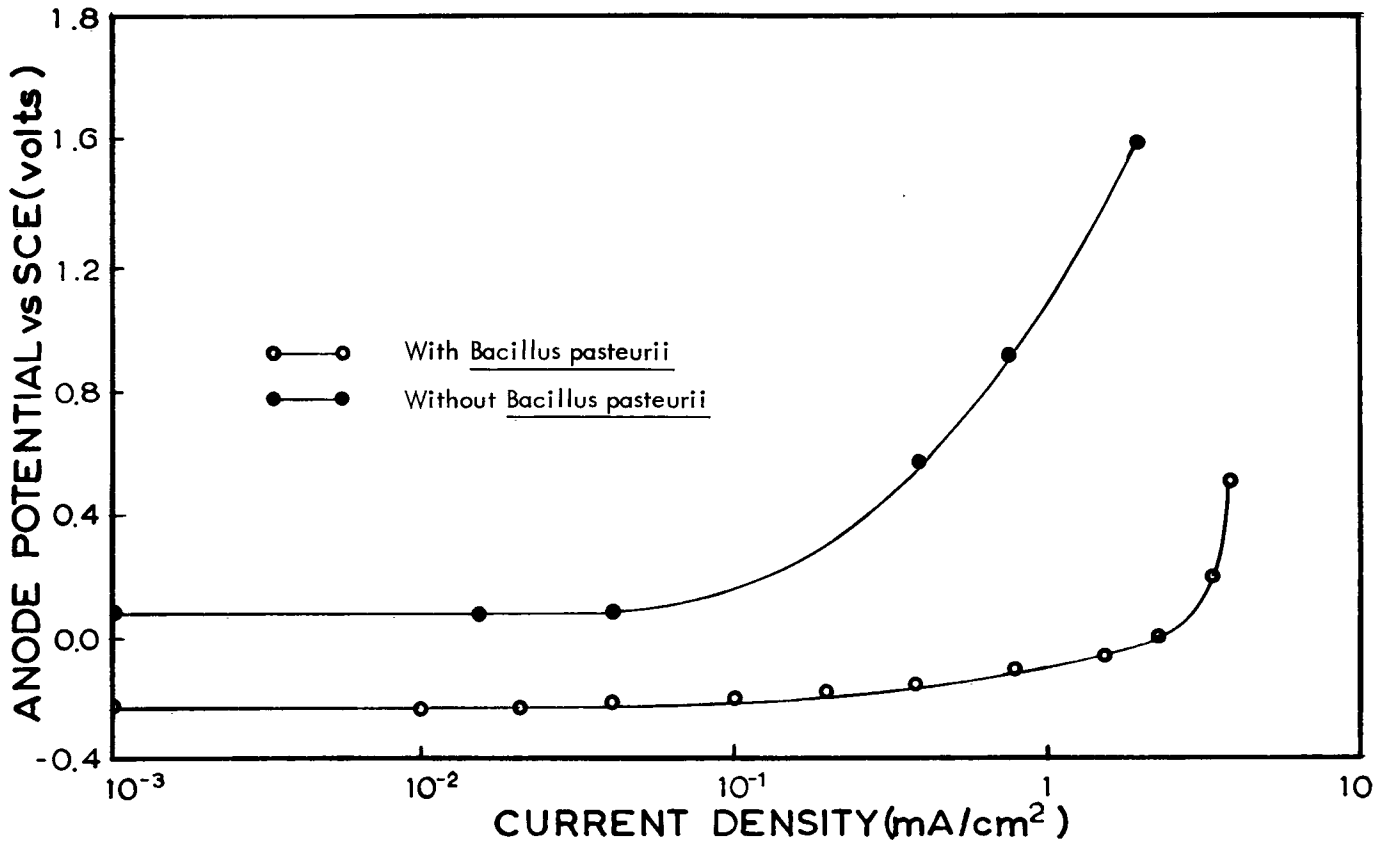

FIGURE 11. CURRENT-POTENTIAL CURVE FOR THE BACILLUS PASTEURII-UREA SYSTEM USING THE COMPRESSION ELECTRODE TEST ASSEMBLY

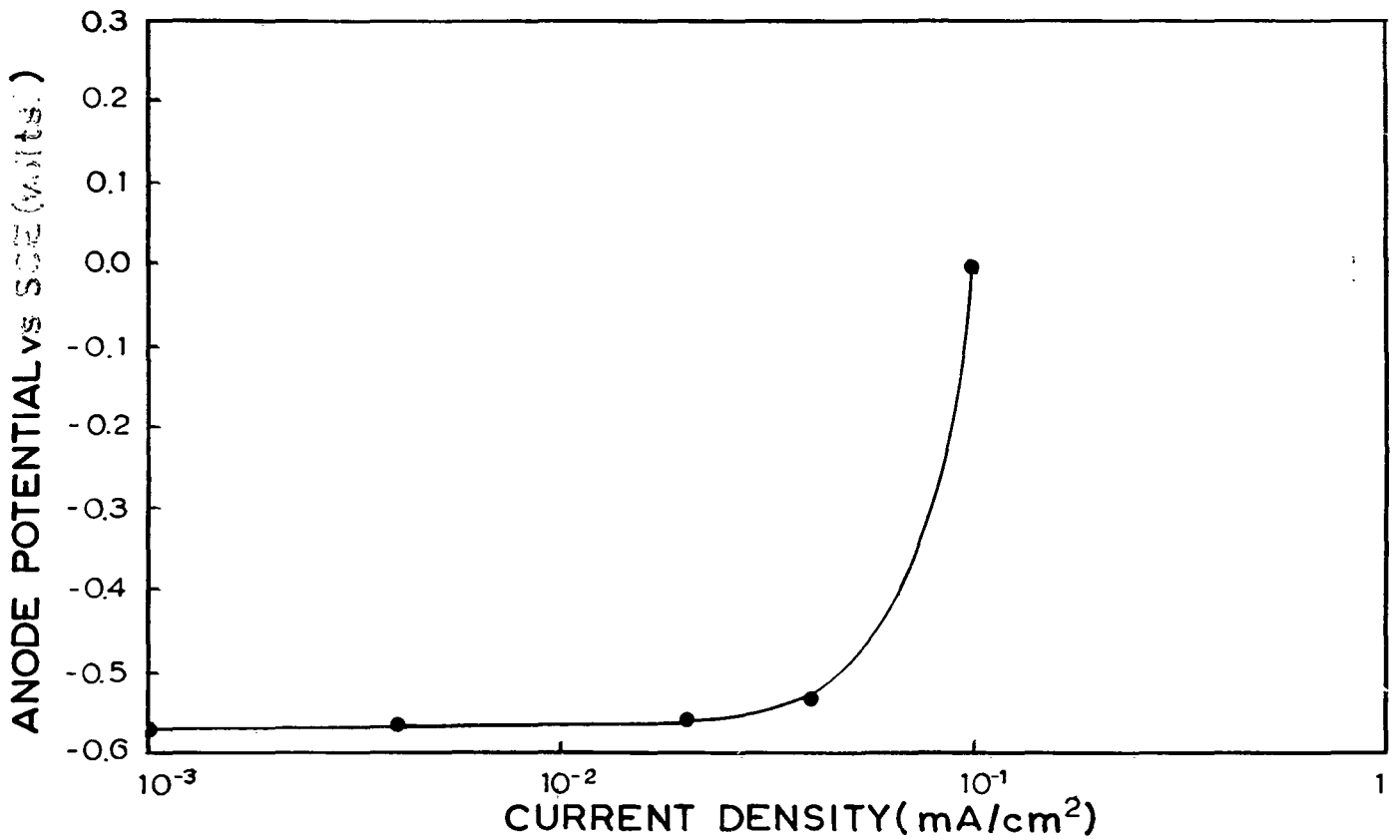

FIGURE 12. CURRENT-POTENTIAL CURVE FOR THE CLOSTRIDIUM BUTYRICUM-GLUCOSE SYSTEM USING THE COMPRESSION ELECTRODE TEST ASSEMBLY

absorbed on carbon and hydrogen absorbed on platinum black. When carbon black is present in excess most of the hydrogen is adsorbed by it and the observed potential is that for the oxidation of hydrogen on a carbon surface and vice-versa. Since there is a higher overvoltage for the oxidation of hydrogen on a carbon surface than on a platinum surface, the electrode potential becomes more positive as the carbon to platinum ratio increases.

Table I

Effect of Carbon, Platinum, and Palladium Black on the Rate of Hydrogen Production by *Cl. butyricum.*

Test Substance	Concentration (mg/ml)	Rate of H_2 Evolution (l/hr)
none	-	50
carbon	15 mg/ml	41
platinum black	3 mg/ml	55
palladium black	8 mg/ml	55

5. CONCLUSIONS

5.1 The maximum current density (3 mA/cm^2) achieved thus far was with the B. pasteurii-urea system in a new type of compression cell.

5.2 Ammonia Anode

5.2.1 The limiting current density of the nonbiological ammonia anode was increased from 1 mA/cm^2 to 2 mA/cm^2 by increasing the anolyte temperature from 25°C to 45°C.

5.2.2 The oxidation of ammonia is inhibited by the presence of impure urease or Bacillus pasteurii.

5.2.3 Black palladium is ineffective as the electrode catalyst for the oxidation of ammonia under conditions compatible with biological ammonia-production.

5.3 Hydrogen Anode

5.3.1 Black palladium is more effective than black platinum as the electrode catalyst for the oxidation of hydrogen under conditions compatible with biological hydrogen-production.

5.3.2 The nonbiological hydrogen anode will support 4 mA/cm^2 at a polarization of 0.1 V using black palladium as the electrode catalyst.

5.3.3 The limiting current density of the nonbiological hydrogen anode was not appreciably affected by increasing the ionic strength or temperature of the anolyte.

5.4 The Cl. butyricum system does not function as well in the compression cell as it does in an H-cell because of the adsorption of hydrogen by the carbon used in the compression cell.

6. PROGRAM FOR NEXT INTERVAL

6.1 Investigate the performance of the nonbiological hydrogen anode as a function of pH.

6.2 Investigate methods of increasing the rate of hydrogen absorption by black palladium.

6.3 Investigate the performance of the Bacillus pasteurii-urea electrode as a function of temperature.

6.4 Investigate the performance of the Clostridium butyricum-glucose electrode as a function of temperature.

6.5 Seek to determine the rate limiting step in the performance of biological electrodes by varying the concentration of the biological catalyst and substrate.

6.6 Substitute graphite for carbon black in the Cl. butyricum-glucose electrode in the compression cell.

7. REFERENCES

1. Magna Corporation, Biochemical Fuel Cells, Second Quarterly Progress Report, Contract No. DA-36-039-SC-90866.
2. Reference Electrodes, D. Ives and G. Janz, p 111.
3. Fuel Cell, Vol. 2 - Edited by G. J. Young, p 153 - Preliminary Appraisal of the Ammonia Fuel Cell System - R. A. Wynveen.
4. Monsanto Chemical Co., Fuel Cells, Final Report, Contract No. DA-44-009-ENG-4154 (1960).
5. Solid Surfaces and the Gas-Solid Interface, Advances in Chemistry, Series 33, p 86 - Effect of Hydrogen Adsorption on the Magnetic Susceptibility of Palladium Dispersed on Silica Gel, L. Royerson and A. Solbakken.
6. Manometric Techniques, Third Edition, Umbreit, Burris, and Stauffer, p 61.
7. J. Chem. Physics, 28, 16 (1958) - Electrochemical Behavior of the Palladium - Hydrogen System, Schuldiner, Castellan, Hoare.
8. Introduction to Electrochemistry, S. Glasstone, p 232.
9. J. Electrochemical Soc., Vol. 110, No. 2, Feb. (1963) p 145 - Electrochemical Oxidation of Hydrogen on Partially Immersed Platinum Electrodes, F. G. Will.

8. IDENTIFICATION OF PERSONNEL

The distribution of hours of the key personnel assigned to this program for the third quarter is as follows:

	Hours
H. P. Silverman, Project Manager	34
J. Brake, Biochemist	488
W. Momyer, Electrochemist	268
S. Miranda, Technician	176
E. Nichols, Technician	50
Misc. Personnel	88-3/4
TOTAL	1104-3/4

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