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MIXED-FEED METHANOL-OXYGEN FUEL CELLS

by

Stephen R. Schulze

Submitted to the Department of Chemical
Engineering in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy
at the
Massachusetts Institute of Technology

Thesis Supervisor: Professor H. P. Meissner

August, 1966

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B.S., Harvey Mudd College
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Signature of Author: Stephen R. Schulze
Department of Chemical Engineering,
August 31, 1966

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H. P. Meissner, Thesis Supervisor

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Chairman, Departmental Committee on
Graduate Theses

ABSTRACT

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Mixed-feed fuel cells are fed with a single stream containing fuel, oxidant, and electrolyte. Since both fuel and oxidant come into contact with each electrode, the performance of such a cell depends upon how successfully the fuel reacts selectively at the anode, and the oxidant at the cathode. The mixed-feed performance and selectivity of several electrodes, with methanol and oxygen as reactants, was studied in order to gain an understanding of mixed-feed electrode behavior, and to determine the practicality of a cell of this type.

Silver metal was found to be a perfectly selective oxygen cathode: Methanol did not react at the silver cathode. However, platinum anodes did not perform in such an ideal manner. A porous diffusion type platinum electrode was very inefficient since a large non-current-producing reaction occurred between methanol and oxygen. A platinum metal gauze electrode was more efficient, due to a "physical" selectivity for methanol: The gauze was wetted with methanol and electrolyte, which excluded the gaseous oxygen from the platinum surface. When this electrode was used in conjunction with a silver cathode to form a complete cell, the fuel utilization efficiency for current production was 95%.

The mixed-feed current output of the platinum electrodes could be quantitatively related to the polarization curves for the single reactants. The non-current-producing reaction was found to occur by both a catalytic and electrochemical mechanism. The effect of temperature and methanol concentration on the mixed-feed behavior was also investigated.

Thesis Supervisor: H. P. Meissner
Professor of Chemical Engineering

Department of Chemical Engineering
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August 31, 1966

Professor William C. Greene
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dear Professor Greene:

In accordance with the regulations of the Faculty, I herewith submit a thesis, entitled "Mixed-Feed Methanol-Oxygen Fuel Cells," in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Stephen R. Schulze

Stephen R. Schulze

ACKNOWLEDGEMENTS

The general subject of this thesis, namely, mixed-feed fuel cells, was originally proposed by Professor H. P. Meissner. The author is indebted to Professor Meissner and Professor M. C. Deibert for their helpful suggestions and penetrating insights throughout the conduct of this investigation.

The financial support by the National Aeronautics and Space Administration (under grant number NsG-496) is gratefully acknowledged.

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I. SUMMARY

A. Objectives and Background

The concept of the mixed-feed fuel cell has been introduced by previous investigators[20,37,17]. The mixed-feed cell is different from the conventional cell in that both fuel and oxidant are mixed with the electrolyte solution. The mixture is fed to a series of alternating anodes and cathodes where the corresponding electrochemical reactions can take place. Since fuel and oxidant are in continuous contact with each other, the homogeneous reaction rate between them must be negligibly small in order to maintain a high electrochemical fuel efficiency. Furthermore, since both reactants come into contact with each electrode, the anode and cathode materials must be highly "selective" catalysts. In the ideal mixed-feed cell, only the fuel will react at the anode and only the oxidant at the cathode. If the electrodes are not perfectly selective, then an inefficient, or "direct," reaction can occur between the fuel and oxidant at each electrode which does not produce a useful current.

Even though the mixed-feed feature creates problems in fuel efficiency, it permits use of a very simple cell design. The layers of separating compartments which characterize the conventional cell can be eliminated and only one feed stream is required.

A few mixed-feed systems have been studied by previous investigators. They include hydrogen-oxygen[37], hydrazine-hydrogen peroxide[37,17], and methanol-hydrogen peroxide[20]. In each case, a silver cathode was found to be selective for the oxidant reduction. However, the platinum or rhodium anodes were very non-selective because they permitted direct reaction between the fuel and oxidant. Only about 50% of the fuel was utilized for current production.

Further work on mixed-feed systems was desirable in order to achieve a higher power efficiency, and to gain a basic understanding of mixed-feed electrode behavior. Methanol and oxygen were chosen as fuel and oxidant for this study because they are relatively inexpensive reactants and would therefore produce an economical cell. In addition, methanol and oxygen are known to be very inert towards each other in the absence of catalysts at aqueous fuel cell temperatures.

The objectives of this work may be specifically stated as follows:

(1) To develop and test selective electrodes for the methanol-oxygen system

The preparation of a slective oxygen cathode did not appear to be difficult because results in the literature indicated that both carbon[3,29,41] and silver[31] could be used as selective oxygen electrode catalysts. Therefore, both of these materials were to be tested in this study.

The development of a selective methanol electrode appeared to require particular study. The results in the literature indicated that platinum and the other platinum group metals are the only known catalysts for the electrochemical oxidation of methanol. This complicates the design of a selective anode because these platinum group metals are also excellent oxygen catalysts. In this work, several platinum anode designs were to be developed and tested with the aim of achieving a high anodic current efficiency.

(2) To design electrodes which deliver a high current density at low polarization

This presented a special problem in the case of the oxygen cathode. Preliminary calculations showed that the solubility of oxygen in electrolytes was too low to give high cathodic current densities in a cell system operating on dissolved oxygen. It was anticipated that this problem could be overcome by feeding gaseous oxygen bubbles with the electrolyte to the mixed-feed electrodes. The presence of gaseous oxygen bubbles near the cathode was expected to produce high cathodic current densities because the diffusion path of oxygen through the electrolyte would be reduced to short distances. It was realized that the presence of oxygen bubbles in the electrolyte could cause "gas binding"; that is, the gas could build up in the space between the electrodes, which would make ion flow impossible. This problem had to be faced up to in the design of the electrode.

(3) To develop an alkaline electrolyte which will reject carbon dioxide

In a practical methanol cell, the electrolyte must reject the carbon dioxide produced by methanol oxidation, and it must also be alkaline in order to be compatible with silver cathodes. An electrolyte which has been shown to meet these qualifications is aqueous cesium carbonate at 130°C.[12] However, this electrolyte is expensive and cannot be used at lower temperatures. An alternative to cesium carbonate was to be found if possible.

(4) To gain theoretical insight into the behavior of mixed-feed electrodes

The performance of mixed-feed electrodes can best be understood by comparing their behavior with a general theoretical model. A general theory was to be tested in this work by analysis of the data obtained with the platinum anodes.

B. Theoretical

1. Mixed-Feed Theory

A theoretical model is necessary to understand the behavior of mixed-feed electrodes. This theory attempts to predict the mixed-feed behavior from customary "single-feed" current-voltage curves. ("Single-feed" refers to electrode operation in the presence of only one reactant.) The electrochemical reaction of methanol and oxygen on platinum may be taken as an example. Methanol oxidation is the anodic reaction which produces electrons. The reduction of oxygen is the cathodic reaction which consumes electrons.

Anodic Reaction —— Production of Electrons

$$CH_3OH(aq) + 6\,OH^- = CO_2(g) + 5\,H_2O + 6\,e^- \qquad \text{(S-1)}$$

Cathodic Reaction —— Consumption of Electrons

$$\frac{3}{2}\,O_2 + 6\,e^- + 3\,H_2O = 6\,OH^- \qquad \text{(S-2)}$$

Both of these reactions can occur simultaneously at the same platinum electrode. If one of the reactions occurs in excess of the other, the net consumption or production of electrons must be drawn from the external circuit through the electrode as current. The basic assumption of this theory is that the rate of each electrochemical reaction during mixed-feed operation is equal to the rate during single-feed. If this is assumed, then the output current and the direct reaction for the mixed-feed electrode can be predicted from the single-feed data. Figure S-1 presents the polarization curves which might be obtained for the single-feed reaction of methanol and oxygen on a platinum electrode.

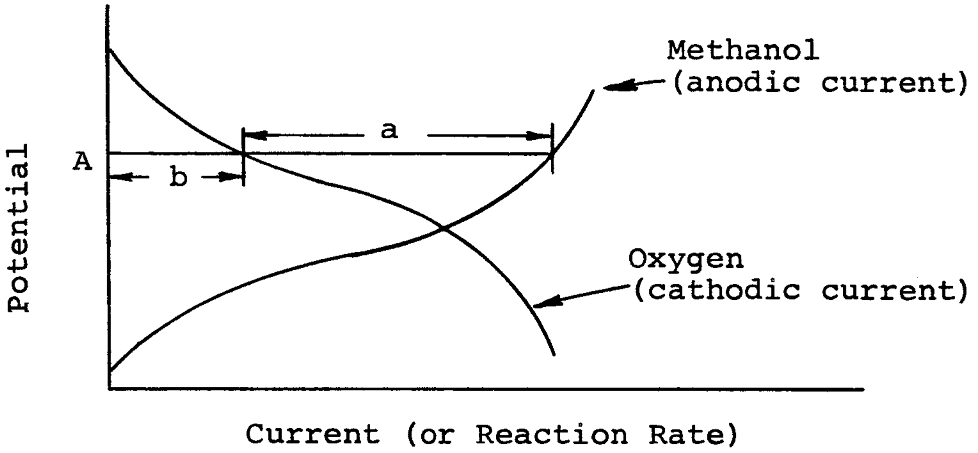
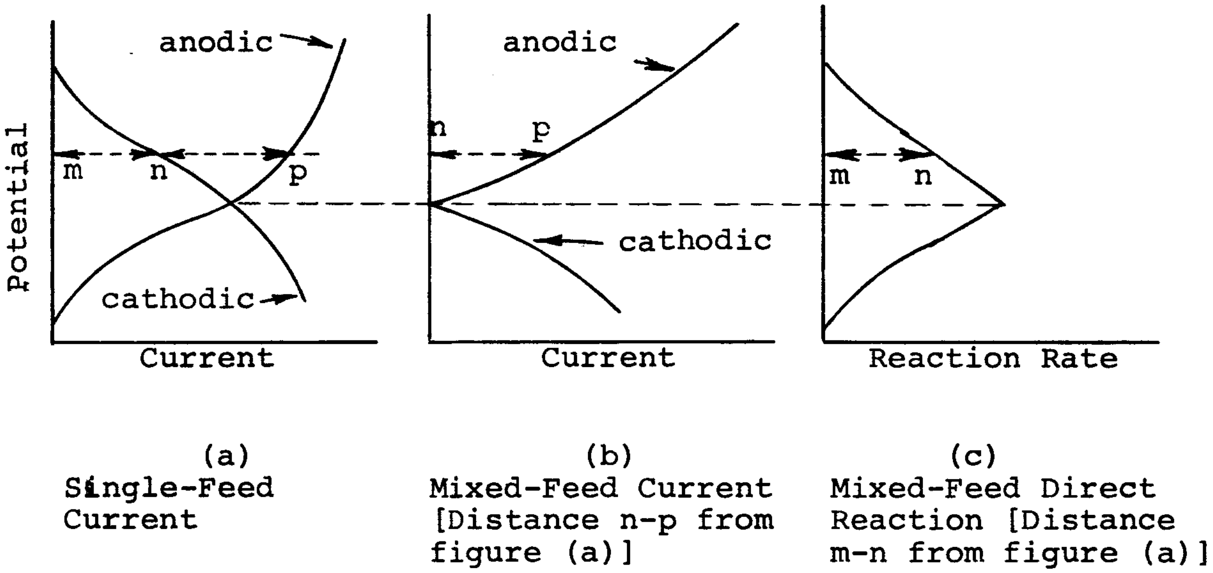


Figure S-1. Single-Feed Polarization

At any given potential, the rate of each electrochemical reaction is determined by these curves. The current output for the mixed-feed electrode can then be calculated from this knowledge of the rate of electron production and consumption. For instance, if the mixed-feed electrode were at potential "A" (Figure S-1), then the external current would be an anodic current of magnitude "a". That is, the excess of electrons produced by the methanol reaction, over the electrons consumed by the oxygen reaction, are drawn from the electrode as the current. The magnitude "b" represents the wasted, or "direct electrochemical" reaction. For a mixed-feed electrode of high efficiency, "b" should be as small as possible.

By relating the single-feed current curves in a similar manner at all potentials, mixed-feed curves may be predicted as in Figure S-2.



(a)
Single-Feed
Current

(b)
Mixed-Feed Current
[Distance n-p from
figure (a)]

(c)
Mixed-Feed Direct
Reaction [Distance
m-n from figure (a)]

Figure S-2. Prediction of Mixed-Feed Curves

The curve in Figure S-2(b) is the mixed-feed external current predicted from the single-feed curves of Figure

S-2(a). The open circuit potential for the mixed electrode occurs at the cross-over point for the single-feed curves. This is the potential for which the anodic and cathodic reactions exactly cancel each other. The oxygen reactivity causes the open circuit potential to be significantly polarized from the open circuit for single-feed methanol. The upper branch of the curve represents a net anodic current since the methanol reaction is largest in this region, and the lower branch represents a net cathodic current.

The predicted mixed-feed direct electrochemical reaction is plotted in Figure S-2(c). This curve is formed by each single-feed curve up to the cross-over point. The maximum direct reaction occurs at the open circuit potential.

The direct reaction plotted in Figure S-2(c) is entirely electrochemical in nature; it consists of two independent half cell reactions. The anodic and cathodic reaction species are linked only by electron flow through the electrode and ion flow through the electrolyte. However, an ordinary catalytic reaction between methanol and oxygen may also be expected to occur on the platinum surface. Unlike the electrochemical reaction, the catalytic reaction can occur only when both reactants are present, and, thus, the rate of the catalytic reaction cannot be predicted by single-feed electrochemical measurements. If a catalytic reaction occurs in conjunction with the electrochemical, then the total direct reaction will be greater than that predicted in Figure S-2(c). If the catalytic reaction is assumed to be constant over the entire potential region, then the total direct reaction would appear as in Figure S-3.

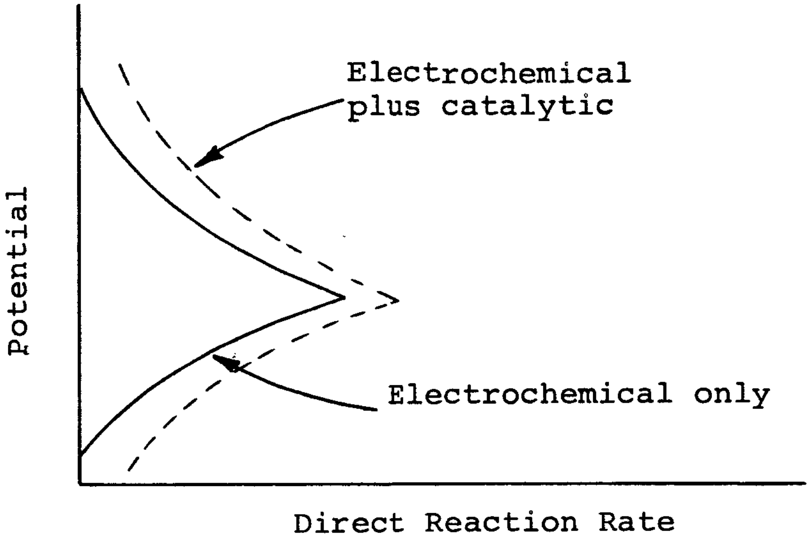


Figure S-3. Catalytic Reaction

There are several reasons why the foregoing hypothesis may be oversimplified. The rate of each electrochemical reaction might be changed during mixed-feed operation. The reactants must share the same surface area that they each have full use of during single-feed operation. Blocking of catalyst surface by the reactants could cause one (or both) of the reaction rates to be reduced. Moreover, the catalytic reaction could interfere with the electrochemical reaction rates. A rapid catalytic rate might well consume fuel or oxidant which would otherwise react electrochemically to produce current. A comparison of the experimental results with the predictions of this theory should indicate which, if any, of the complications are present.

2. Alkaline CO_2-Rejecting Electrolyte

In a practical methanol cell, the electrolyte must reject carbon dioxide so that the cell will operate at "steady-state" without continual electrolyte replacement; and the electrolyte must also be alkaline in order to be compatible with silver cathodes. In order for an alkaline electrolyte to operate at steady-state, the carbon dioxide vapor pressure of the electrolyte must be equal to the carbon dioxide partial pressure in the gas phase of the mixed-feed cell. The equilibrium between CO_2 and the alkaline electrolyte can be presented as follows:

$$CO_2(g) + CO_3^{=} = 2\ HCO_3^{-}$$

High operating temperatures are desirable in order to push this equilibrium to the left, which increases the alkalinity and improves the performance of the cell.

Operating cell current densities are usually greatest when very concentrated electrolyte solutions are used. Therefore, the alkali metal carbonate and bicarbonate which are used for this electrolyte should be very soluble. Cesium has been used by Cairns[12] because of its high solubility, but it is very expensive. Of the two common anions, potassium and sodium, potassium has the most soluble carbonate and was selected for this work.

Equilibrium data[43] for the potassium carbonate-bicarbonate system can be used to calculate the composition of a CO_2-rejecting electrolyte for operation at 70°C. For a CO_2 vapor pressure estimated at 0.08 atm, the resulting composition is:

20 (wt)% potassium carbonate
21 (wt)% potassium bicarbonate
59 (wt)% water

The potassium carbonate and bicarbonate are soluble above 65°C. Throughout the report, this electrolyte is referred to as "the potassium carbonate-bicarbonate mixture electrolyte."

Besides this CO_2-rejecting electrolyte, two other electrolytes were also tested in this work: 50(wt)% potassium carbonate, and 20 (wt)% potassium hydroxide. The pure potassium carbonate electrolyte was used for most of the measurements because it was more convenient than the mixture electrolyte: the potassium carbonate is completely soluble at room temperatures. It was anticipated that the findings with the hydroxide and carbonate electrolytes could be related to the performance in the mixture electrolyte.

C. Equipment and Procedure

Testing

Each electrode consisted of a thin circular disk with a polyethylene frame (Figure S-4).

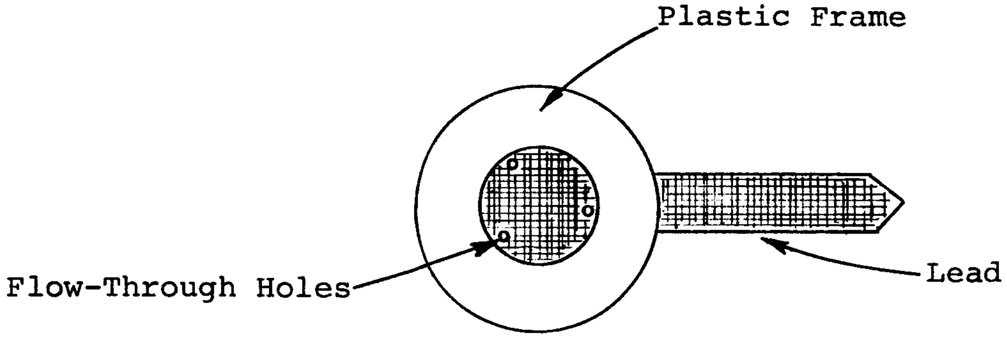


Figure S-4. Test Electrode

The active face area of each electrode was 2 cm^2. For testing, the electrolyte and oxygen gas bubbles were flowed upward through the horizontally placed electrodes (Figure S-5). The electrodes were held in a glass flow chamber

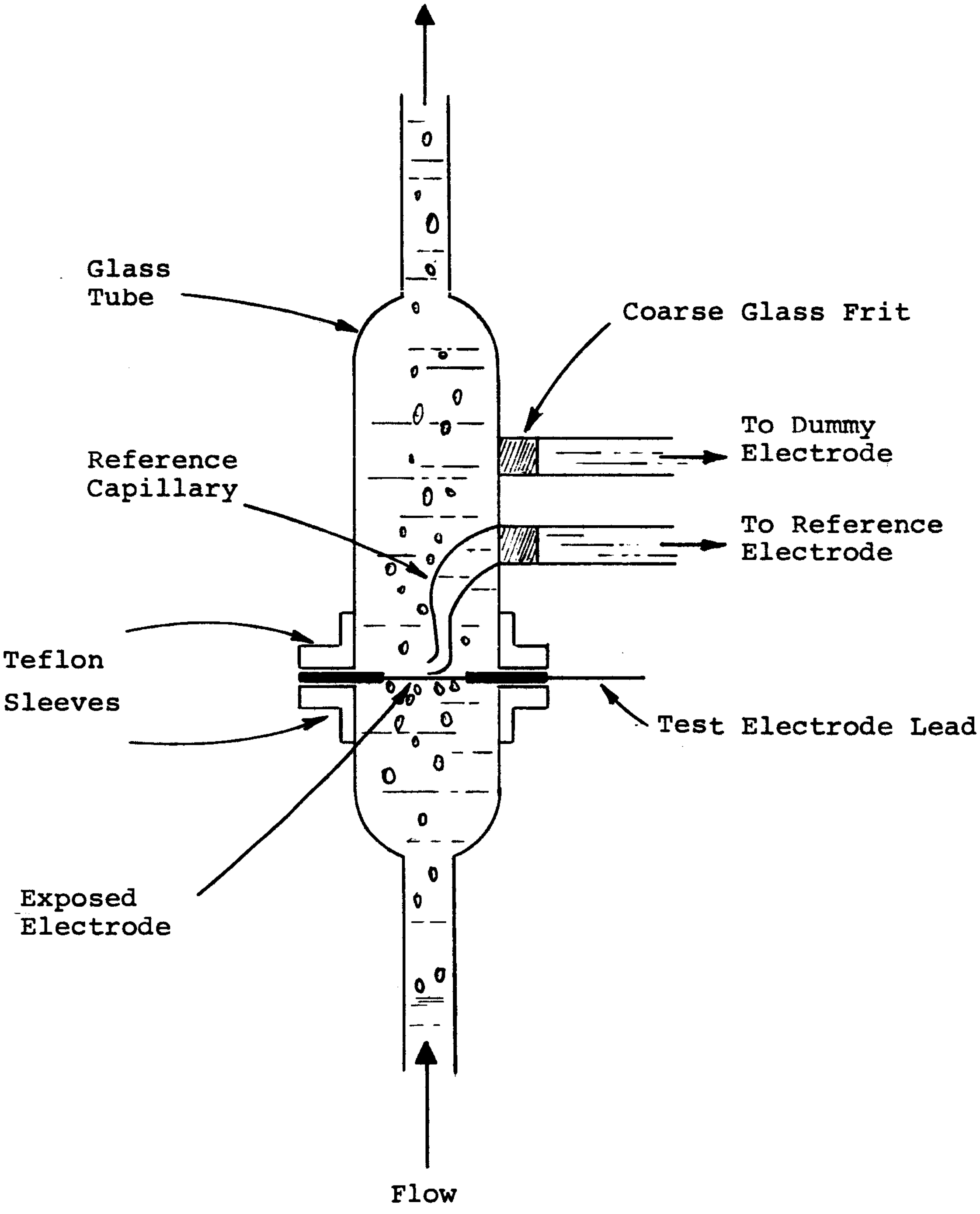


Figure [illegible]-5. Test Electrode Chamber which had electrolyte connections with a dummy electrode and reference electrode. A dummy electrode was used to make a complete circuit when only one electrode was being tested in the flow chamber, and a reference electrode was used to measure the potential of the test electrode. The reference electrode was a mercury-mercuric oxide (red) electrode with 50 (wt)% potassium carbonate electrolyte. The electrical system is diagramed in Figure S-6.

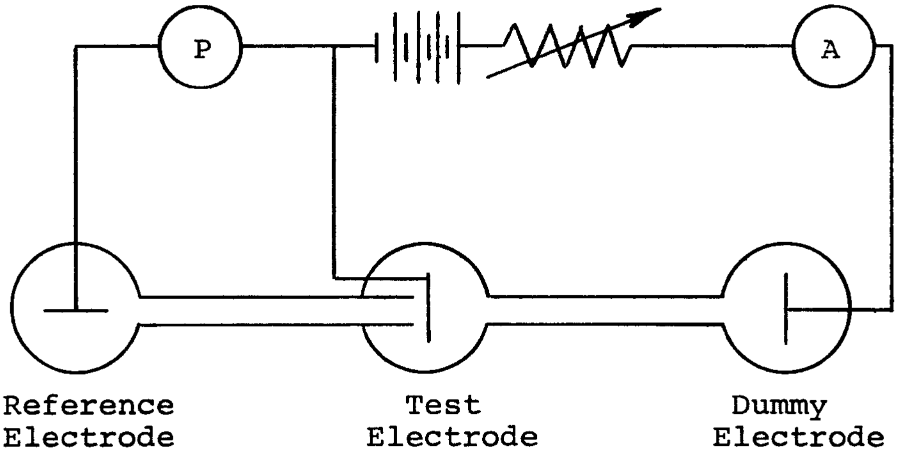


Figure S-6. Single Electrode Test Circuitry

A recording potentiometer, P, was used to measure the electrode potential. The current flow was controlled by the battery-rheostat combination and was measured by the ammeter, A. When an anode and cathode were tested simultaneously, the dummy electrode was not used.

The glass electrode chamber was connected to a flow system which continuously recirculated the fluids. The flow rate of each phase (electrode and gas) could be independently controlled by means of small gas and liquid pumps. The liquid flow rate through the 2 cm^2 electrode was usually 50 ml/min and the gas was 33 ml/min. The total liquid volume of the system was 120 ml and the gas volume was about 75 ml. A temperature bath was placed around most of the system. The temperature of the electrolyte at the test electrode was 70°C for most measurements.

Of course, the direct reaction rate between methanol and oxygen at the test electrode could not be measured with an ammeter. Instead, the methanol consumption was measured by chemical analysis of the electrolyte after running the system for about two hours. During this period, the electrolyte was continuously circulated, and the consumption of methanol gradually increased to between 5 or 10 percent of the total.

Since the product of methanol oxidation can be formaldehyde, formate, or carbon dioxide, it was very important for the analysis procedure to measure the consumption rate of "oxidizable equivalents" and not the consumption rate of "methanol molecules." A titration procedure was used which involved the complete oxidation of the methanol (and possibly formaldehyde and formate) in a small electrolyte sample to carbon dioxide. The sample was oxidized with an excess of potassium dichromate, which was then back-titrated with a ferrous ammonium sulfate solution. The formation of formaldehyde and formate in the electrolyte was also measured by chemical analysis. The formate was analyzed by first evaporating the methanol and formaldehyde from the electrolyte sample. The formate equivalents were then oxidized, and the excess dichromate was titrated. Formaldehyde was analyzed by a colorimetric method. An electrolyte sample was added to an acid solution of chromotropic acid. The depth of violet color which appeared upon heating was proportional to the concentration of formaldehyde.

Electrodes

Two basic types of electrodes were constructed and tested. The first was an electrolytically platinized fine mesh screen which was used as an anode. The screens were 150 mesh nickel or 80 mesh platinum. A group of two to four of these screens were used for each electrode (designated as "2-ply" or "4-ply" electrodes). A high area platinum coating was electrochemically deposited on these screens from a solution of chloroplatinic acid. Some of these screen electrodes were designed with two or three 1 mm holes in their faces (Figure S-4). These electrodes are designated "with holes" or "holed electrodes." For a 4-ply platinized nickel electrode, the geometric wire area was 9.8 $cm^2/(cm^2$ face area) and the platinum loading was about 19 mg/$(cm^2$ face area).

The other basic type of electrodes was Teflon bonded electrodes[15,36]. These electrodes were used primarily as cathodes. They were prepared by mixing and mulling a desired catalyst mix powder with a Teflon dispersion and water. The mixture formed a rubbery dough which was rolled out to form a thin membrane and then pressed onto one side of a metal gauze for support and current collection. After it was dried and heated to 300°C, the porous electrode was very non-wetting. This allowed the electrode to perform very well with gaseous reactants. The gas reacted on the underneath, "membrane," side of the electrode. Two or three holes were drilled through the face for electrolyte and gas flow, since the pores of the electrode were too small for bulk flow.

Three catalyst powder mixes were used to construct the Teflon electrodes:

(a) Platinum powder

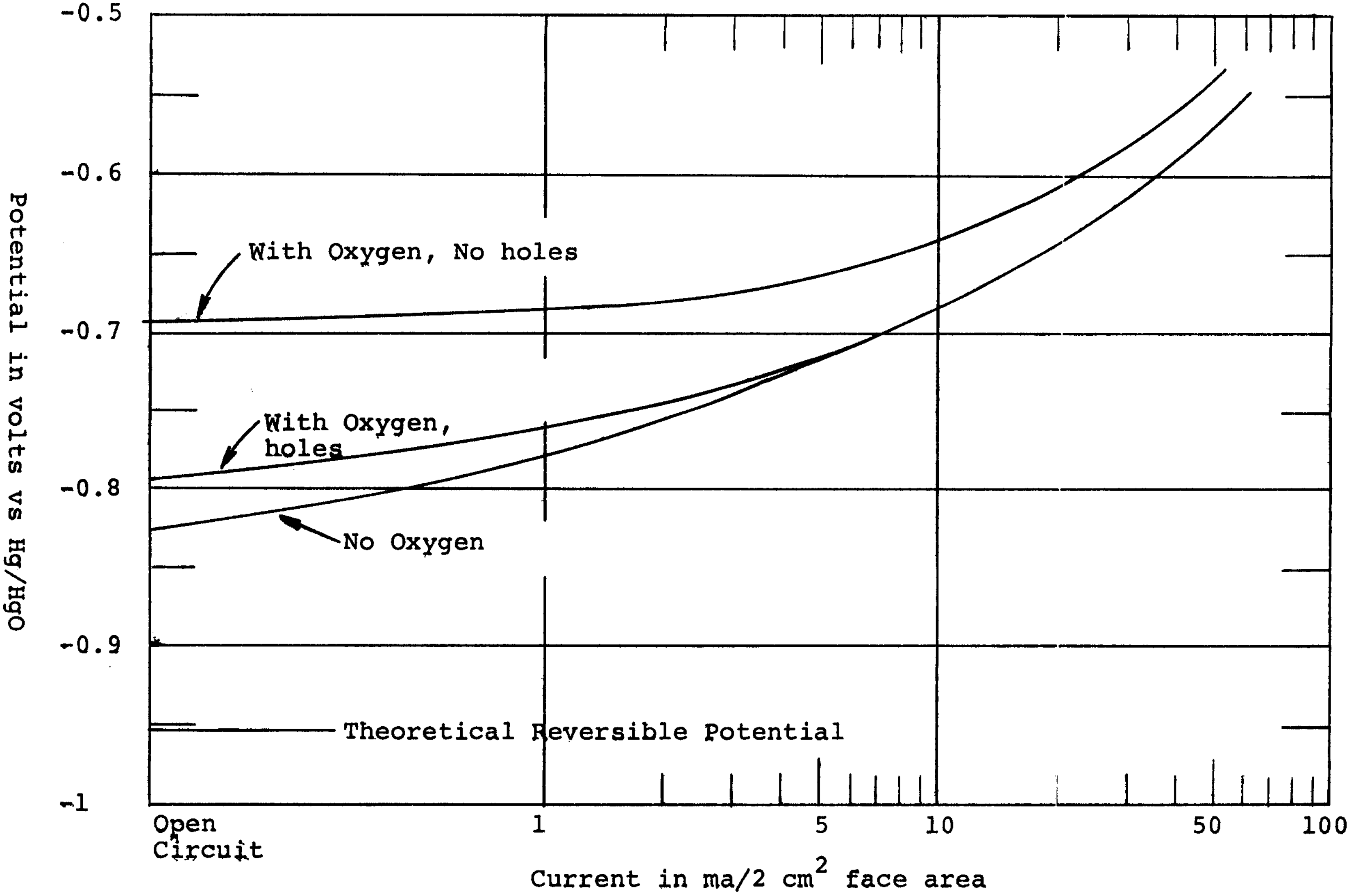
(b) Silver powder

(c) 85 (vol)% carbon and 15 (vol)% silver

D. Results and Discussion

Electrode and Cell Current Polarization

The holed platinized screen was the most successful anode found in this work. The good selectivity of this electrode was made possible by the low contact between the oxygen and the platinum surface. The 1 mm electrode holes played an important part in creating this selectivity because the oxygen bubbles could pass through these holes instead of going through the fine mesh screen. The effect of oxygen on the anodic performance of the holed and non-holed screen is demonstrated on Graph S-1 which contains polarization curves for a 4-ply platinized screen electrode. The methanol concentration was 0.04 M in potassium carbonate electrolyte at 70°C. The electrode was run with oxygen flow (mixed-feed) and without oxygen (single-feed, methanol). The single-feed polarization curve was not affected by the electrode holes. However, there was a large difference between the holed and non-holed electrodes during mixed-feed operation. The open-circuit polarization caused by the oxygen was only 0.03 v for the holed electrode, but was 0.13 v for the non-holed electrode. The difference between the single and mixed-feed curves also depended on the methanol concentration. At concentrations above 0.1 M, there was essentially no difference for the holed electrode.

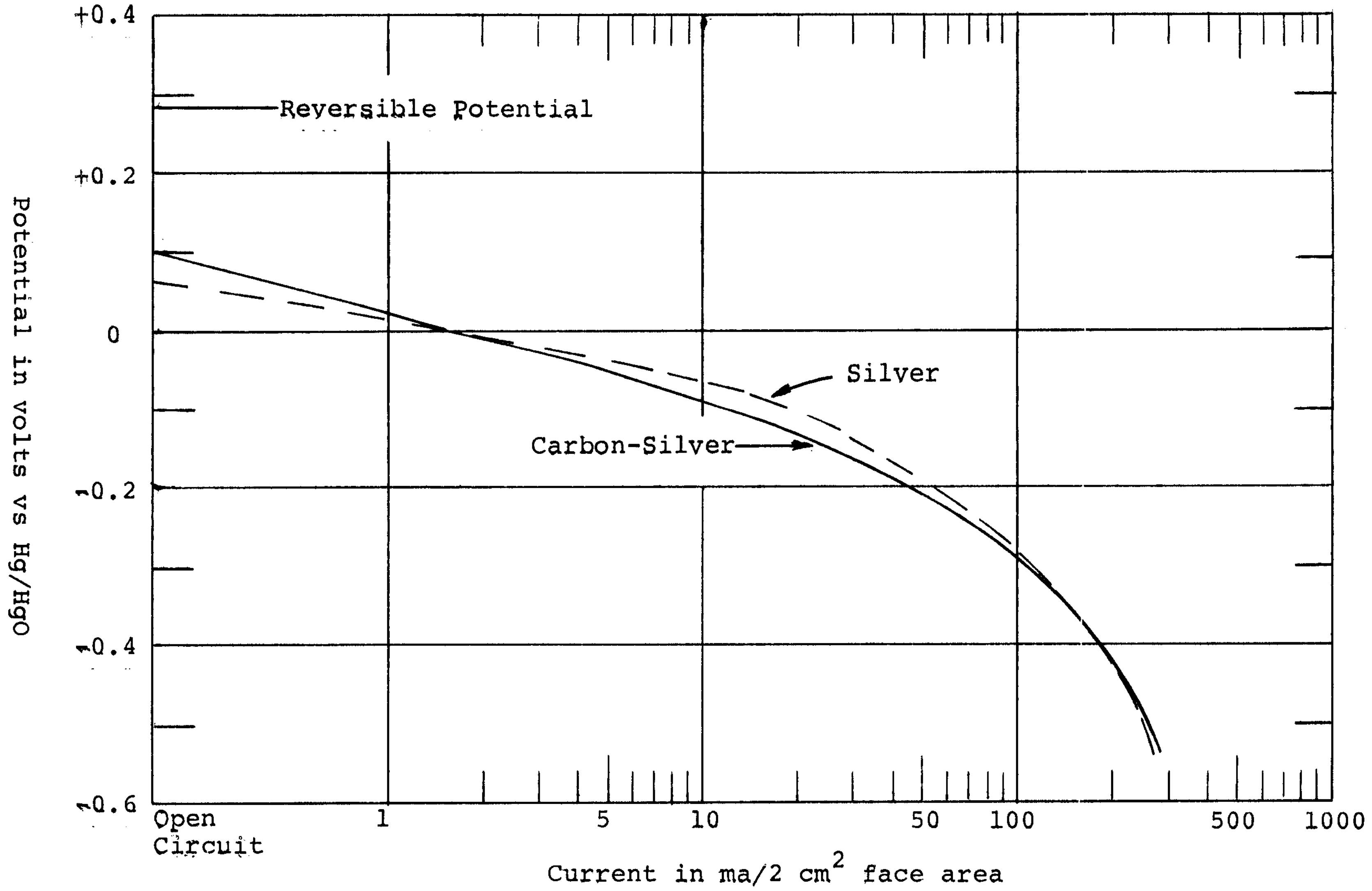


Graph S-1 Effect of Oxygen on Platinized Screen Anode; Platinized Nickel (4-ply); 70°C; 0.04 M methanol; K_2CO_3 electrolyte.

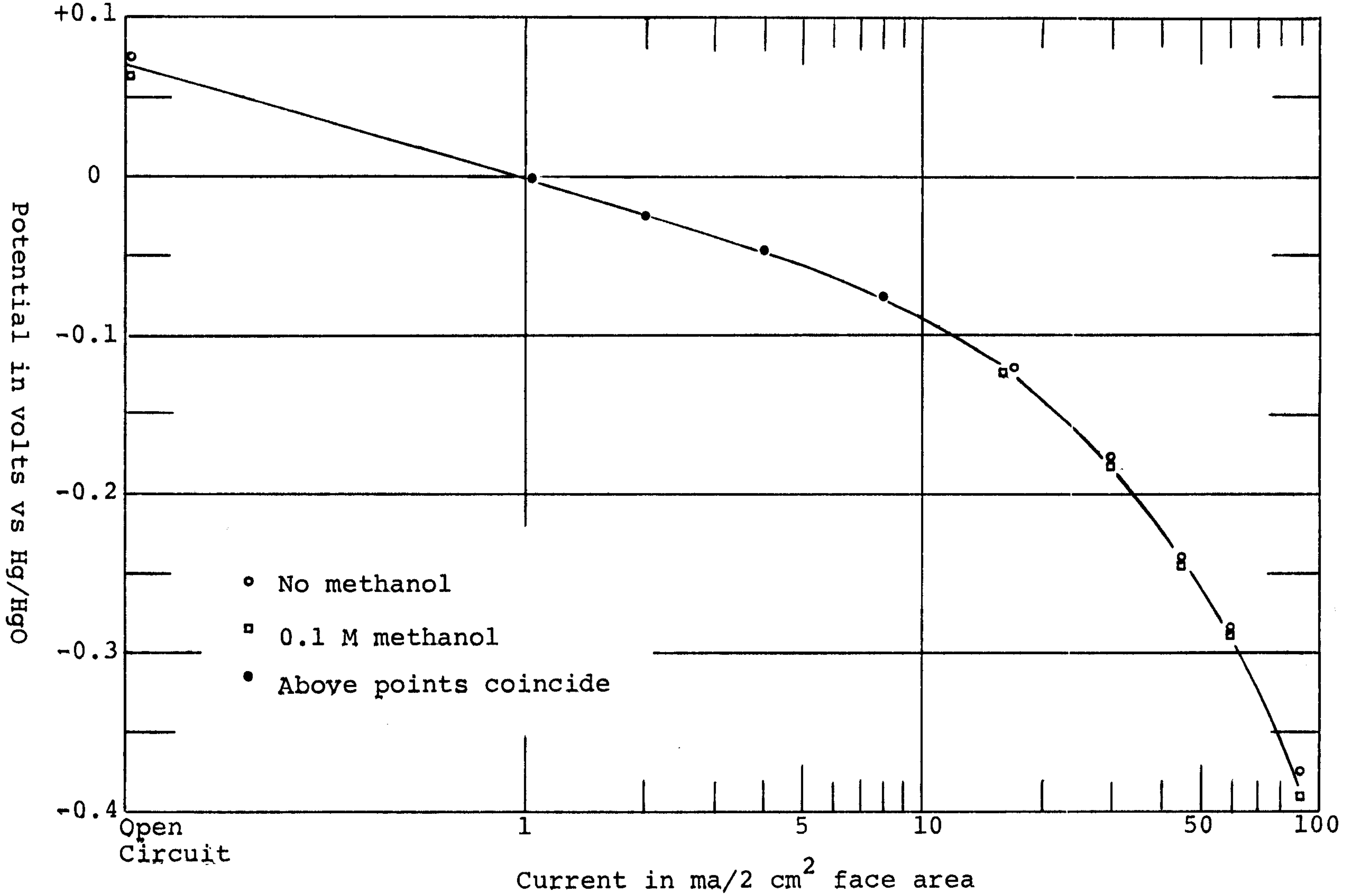
The thermodynamic reversible potential is -0.954 v for methanol oxidation under these conditions. The open circuit polarization for the single-feed curve of 0.13 v from the theoretical value, is not unusual.

Two Teflon bonded electrodes performed well as oxygen electrodes: silver, and carbon-silver. The polarization curves for these electrodes are presented on Graph S-2. The electrodes were newly prepared, so that their activity was at a maximum. These curves were measured with single-feed oxygen (no methanol was in the electrolyte). The most striking feature is the similarity between the polarization of the electrodes. The same sized particles were used to construct both electrodes, and the pore and diffusion characteristics of the electrodes were probably very similar. The agreement in the current-potential curves indicates that diffusion of oxygen may have been the main factor controlling polarization.

Graph S-3 compares the performance of the silver-Teflon electrode with single and mixed-feed. As is indicated, the methanol had no effect on the polarization curve. The thermodynamic reversible potential is +0.285 v. The open circuit polarization was 0.21 v, although the open circuit potential was not very reproducible for this electrode. Since the oxygen polarization curve was not affected by methanol, silver appears to be a very selective electrode.



Graph S-2. Comparison of Silver and Carbon-Silver Teflon Cathodes; Single-Feed Oxygen; 70°C; K_2CO_3 electrolyte.

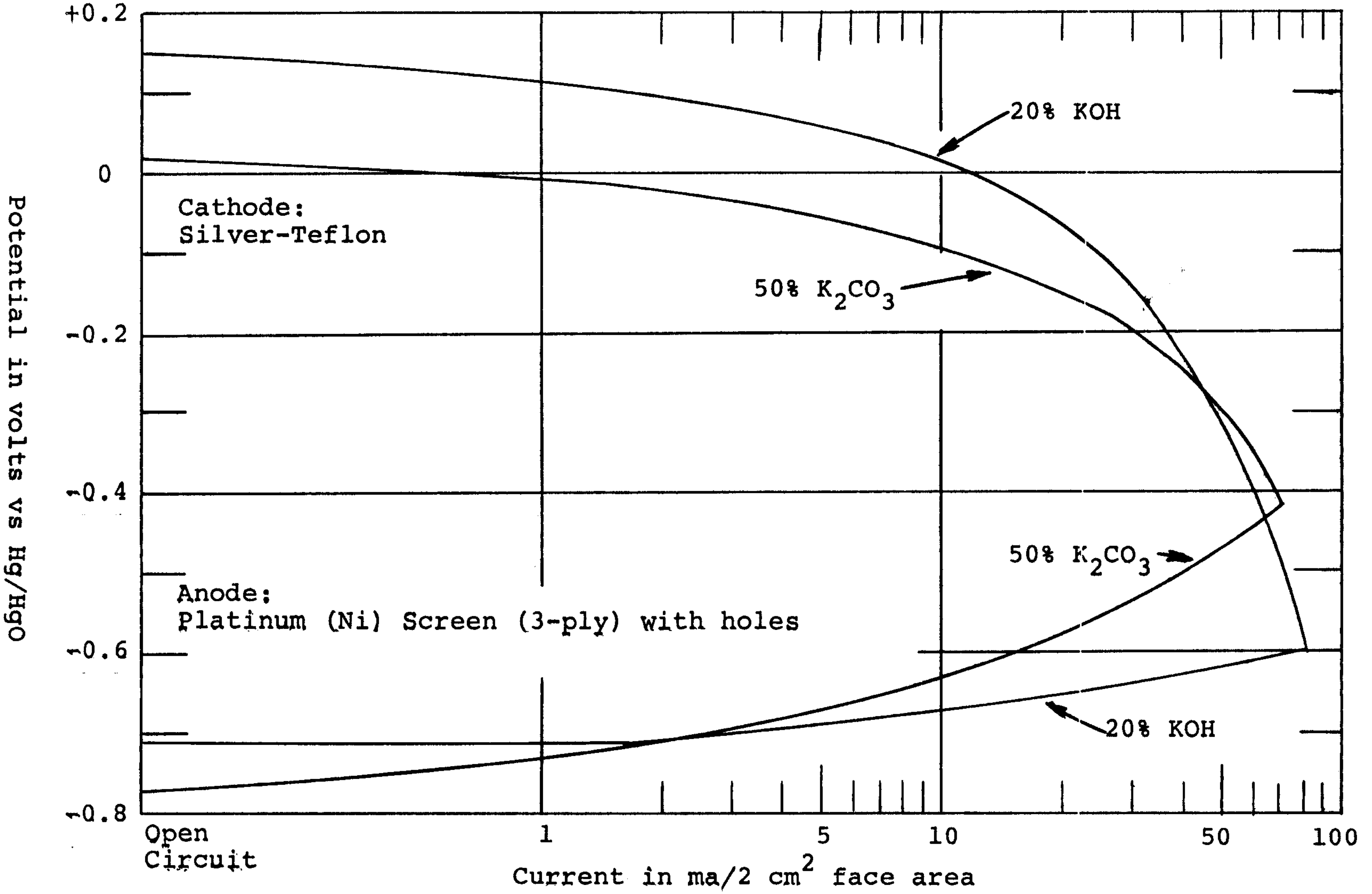


Graph S-3. Effect of Methanol on Silver-Teflon Oxygen Cathode; 70°C; K_2CO_3 electrolyte.

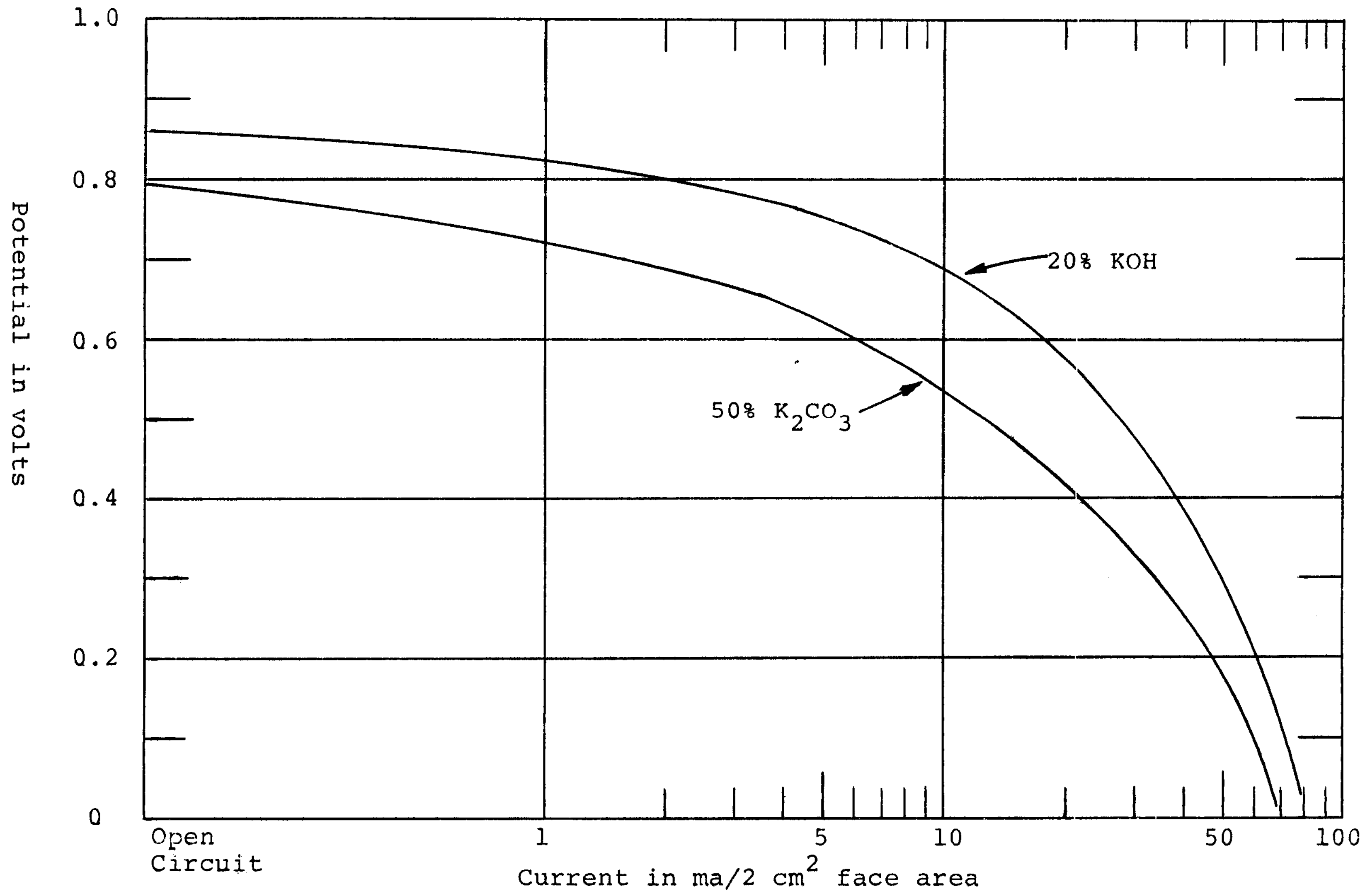
No current could be drawn when the silver was run with single-feed methanol. Similar results were obtained for carbon.

The silver-Teflon electrode was also operated with air instead of oxygen. The current output was reduced by exactly 50% at all potentials.

The mixed-feed polarization curves for an anode and cathode combination are shown in Graph S-4. A 3-ply platinized nickel screen electrode was placed about 1 mm above a silver-Teflon electrode. With carbonate electrolyte, the anode and cathode contributed about equally to the total cell current polarization. However, in hydroxide electrolyte, the anode was far superior and almost all of the current polarization was caused by the cathode. The silver electrode potentials were much better in hydroxide at low current densities. Graph S-5 shows the net potential difference between the half cells of Graph S-4. Although the hydroxide cell potentials were better by about 0.1 v, this does not seem to be caused by the more favorable thermodynamic potential for hydroxide. The thermodynamic advantage is due to the reaction of the CO_2 product to form carbonate. The cell voltage loss due to the resistance of the electrolyte was 0.008 v in carbonate and 0.004 v in hydroxide at 70 ma.



Graph S-4. Half-Cell Potentials for Anode-Cathode Combination; Mixed-Feed; 70°C; 0.5 M methanol.



Graph S-5. Net Cell Potentials for Hydroxide and Carbonate Electrolytes; same conditions as in graph 13.

The most important aspect of these results is that the polarization of each electrode during mixed-feed was no greater than with single-feed. For the cathode, this excellent performance was achieved by using a selective catalyst material. However, the anode's selectivity was due to a special electrode design which minimized the platinum-oxygen contact.

The cell polarization for these electrodes was also measured in the potassium bicarbonate mixture electrolyte. The output voltage with this mixture electrolyte was about 20% less than with the carbonate, due to greater polarization at both the anode and cathode. The high bicarbonate concentration of the mixture electrolyte appears to be responsible for lowering the performance. Higher operating temperatures would improve the voltage output of the CO_2-rejecting electrolyte, because the equilibrium amount of bicarbonate in the rejecting electrolyte would then be smaller.

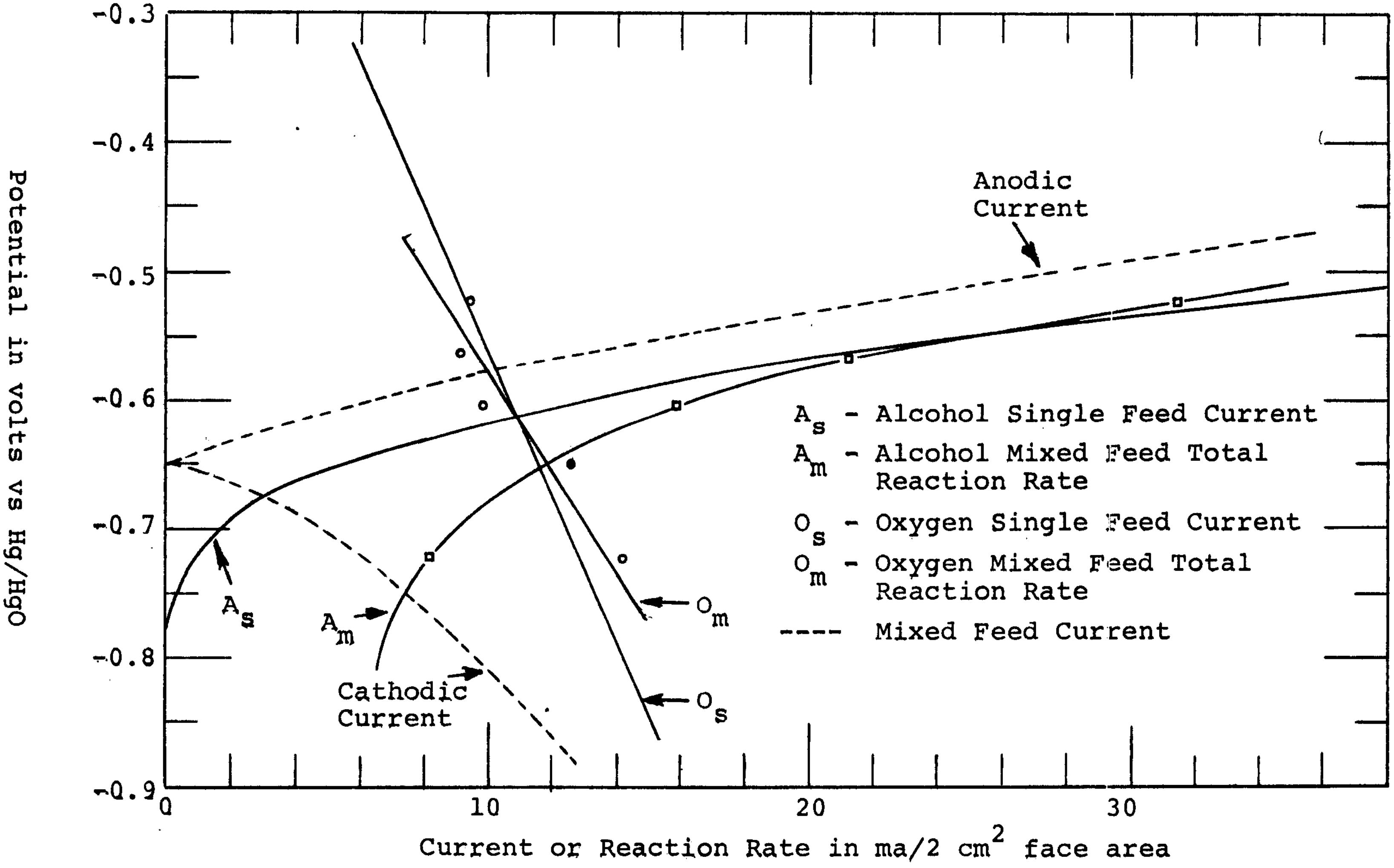
Mixed-Feed Theory and Direct Reaction

The potential-current curves for the silver-Teflon electrode indicated that methanol did not react electrochemically on silver, but left the possibility of a catalytic methanol-oxygen reaction during mixed-feed operation. Therefore, tests were performed at two methanol concentrations (0.01 M and 0.04 M) to determine if there was any direct reaction occurring on the silver-Teflon electrode. Methanol was allowed to come into contact with the electrode at open circuit, as well as while a cathodic current was drawn. In all cases, no methanol reacted (within the experimental error of about 1 ma). In other words, the silver electrode was completely selective for the reaction of oxygen only.

The direct reaction rate was measured on three platinum anodes:

i) Platinized nickel screen (4-ply) without holes
ii) Platinized nickel screen (4-ply) with holes
iii) Platinum-Teflon electrode

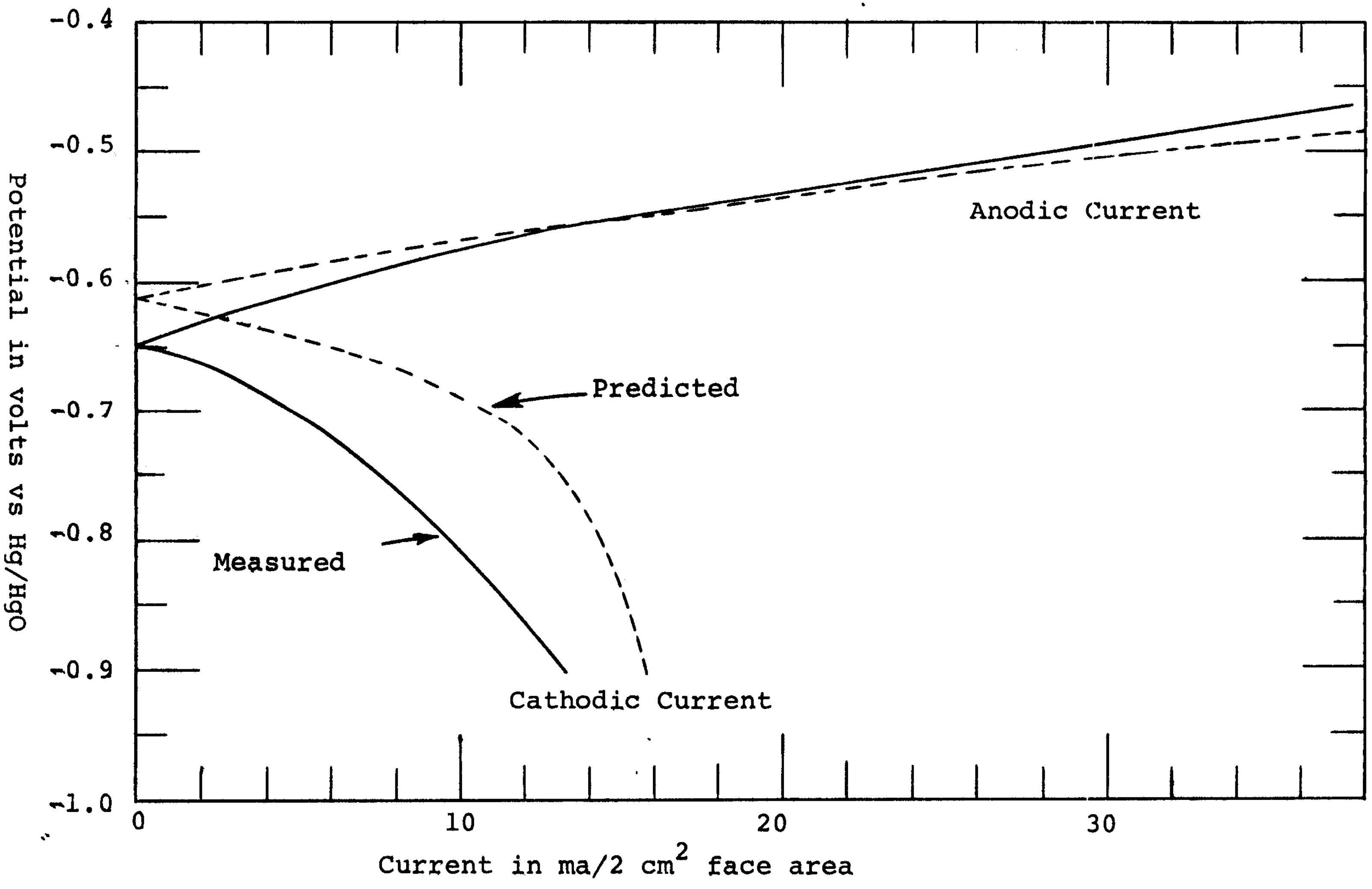
The behavior of each electrode was studied at two methanol concentrations (0.01 M and 0.04 M). The platinum-Teflon electrode was expected to be a very non-selective electrode and would not be considered as a practical electrode for a mixed-feed cell. This electrode was nevertheless studied, however, for comparison with the screen electrodes, and for evaluations of the theory of mixed electrodes. All the results were obtained at 70°C in a 50 (wt)% potassium carbonate electrolyte. The data for each electrode and methanol concentration was of the type presented in Graph S-6 for the non-holed, platinized screen with 0.01 M methanol. A single-feed current curve is shown for each reactant: Methanol produced the anodic current



Graph S-6. Data for Non-holed Screen; 0.01 M Methanol; Platinized (Ni) Screen (4-ply); 70°C; K_2CO_3 electrolyte.

curve, A_s (single-feed alcohol), and oxygen produced the cathodic current curve, O_s (single-feed oxygen). The measured mixed-feed current curve is denoted by a dotted line. The upper branch of the dotted curve (i.e., in the higher potential region) is an anodic current and the lower branch is cathodic. In addition to the above current curves, there are also two reaction rate curves for mixed-feed operation. These curves represent the total consumption rate of the reactants at the electrode. The reaction rate curves for oxygen (O_m) and methanol (A_m) were drawn through the data points shown. These data points were measured by the chemical analysis of the depletion of methanol equivalents during mixed-feed operation. The reaction rates were expressed in units of milliamperes for easy comparison with the current curves.

These basic data can best be understood by simplifications and comparisons as suggested by the theory presented in section B. The mixed-feed current can be predicted from the single-feed current curves as in Figure S-2. The predicted curve for the non-holed platinized electrode in 0.01 M methanol is compared with the measured mixed-feed curve in Graph S-7. The anodic branch of the mixed-feed current curve agrees very well with the curve predicted from the single-feed current curves. However, there is a small deviation between the cathodic branches: the actual cathodic

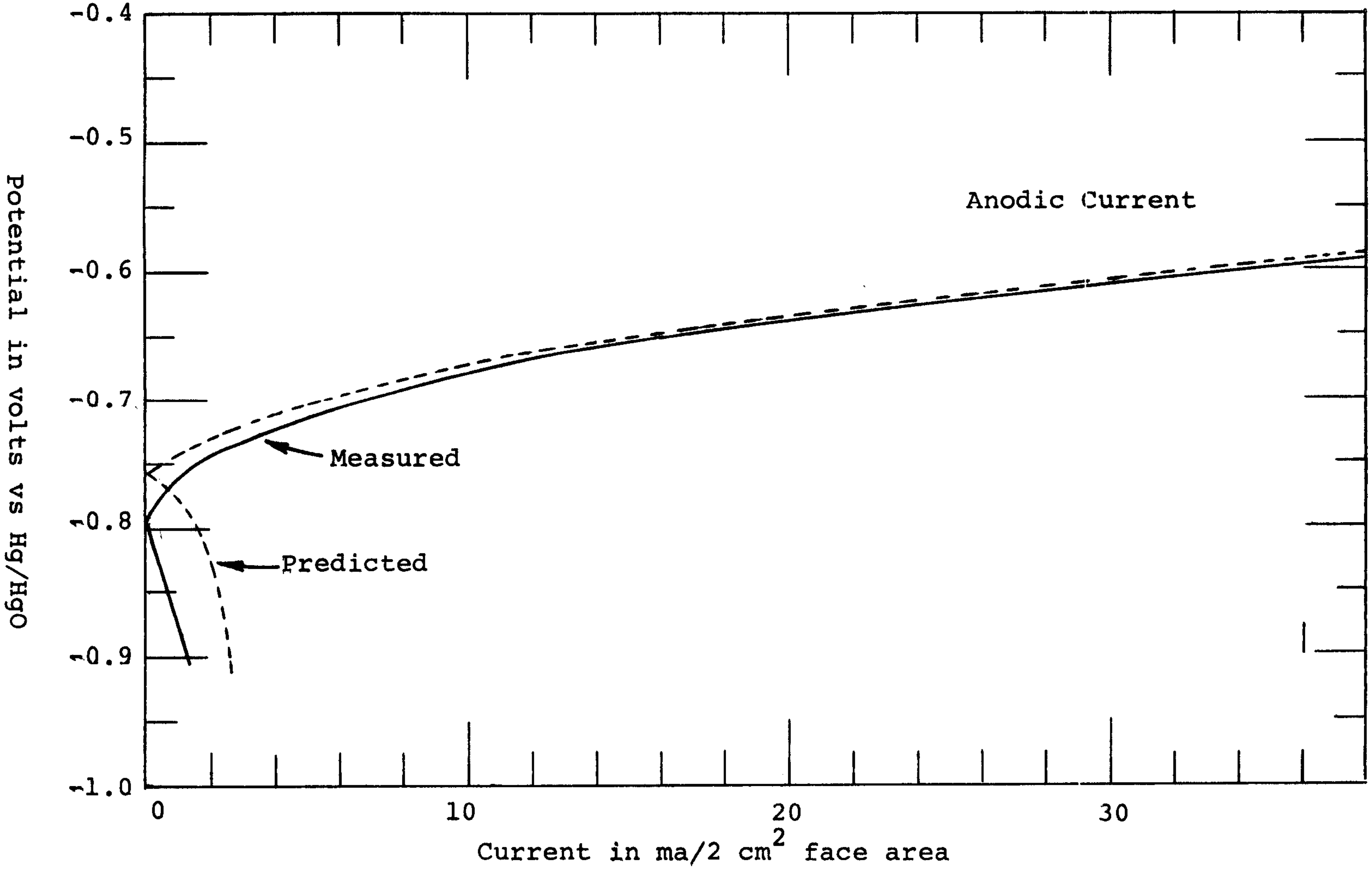


Graph S-7. Mixed-Feed Current for Non-holed Screen; 0.01 M methanol; 70°C; K_2CO_3 electrolyte current was lower than expected. With 0.04 M methanol, the relation between the measured and predicted curves was the same. In this case, however, the curves were shifted down in potential by about 0.05 v due to the increased methanol activity.

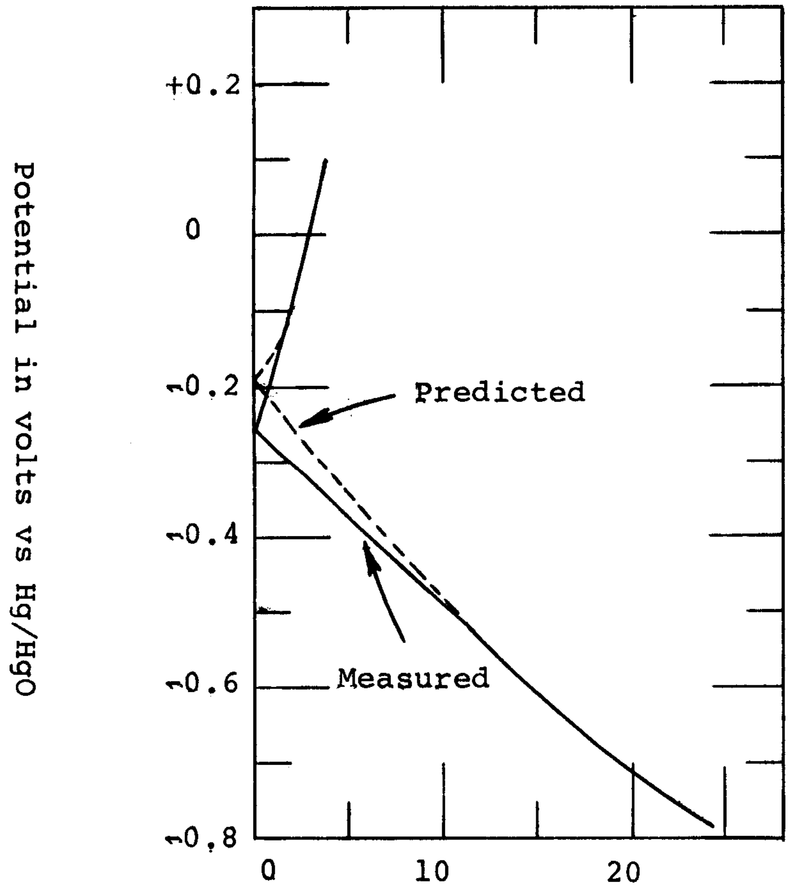
Graph S-8 contains the results for the holed screen electrode, operated with 0.04 M methanol. The cathodic current branch was much smaller for this electrode—an indication of the decreased oxygen reaction rate. Also, the open circuit potential was improved (lowered) by 0.11 v as a result of the holes.

This is in sharp contrast to the current curves obtained for the platinum-Teflon electrode at 0.01 M methanol (Graph S-9). This electrode had a higher oxygen reaction rate than the screens because the oxygen diffusion rate to the catalyst surface was much greater. Since the Teflon electrode was non-wettable, the oxygen gas contact was excellent. This electrode also showed good agreement between the experimental and predicted current curves. When the methanol concentration was increased to 0.04 M, the open circuit potential was sharply lowered to -0.5 v.

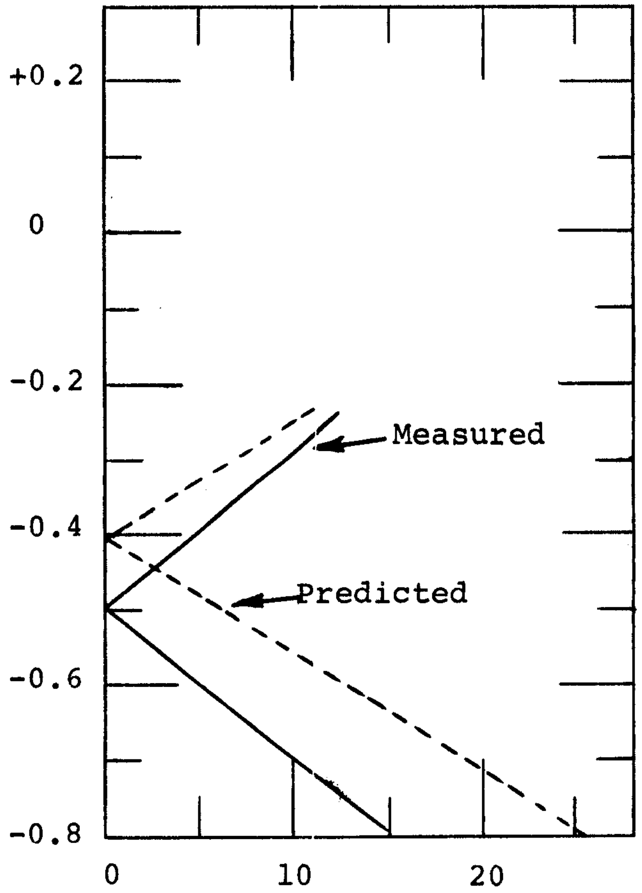
The direct (or non-current-producing) reaction between methanol and oxygen that occurs by an electrochemical mechanism can also be predicted from the single-feed curves (as was done in Figure S-2). The predicted and experimental



Graph S-8. Mixed-Feed Current for Screens with Holes; 0.04 M methanol; 70°C; K_2CO_3 electrolyte



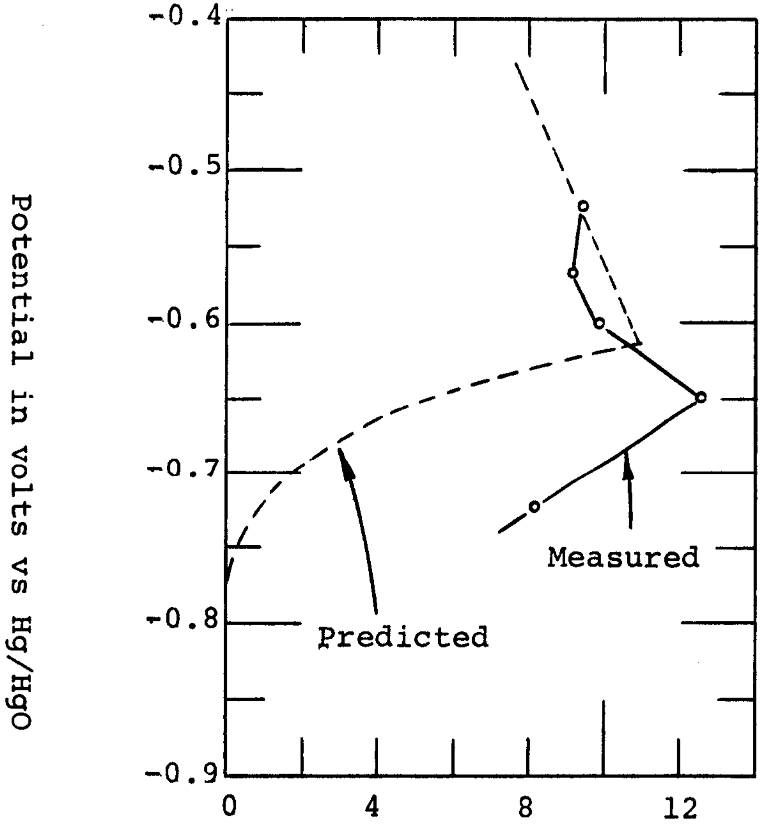
Graph S-9. Mixed-Feed Current for Platinum-Teflon Electrode; 0.01 M methanol; 70°C; K_2CO_3



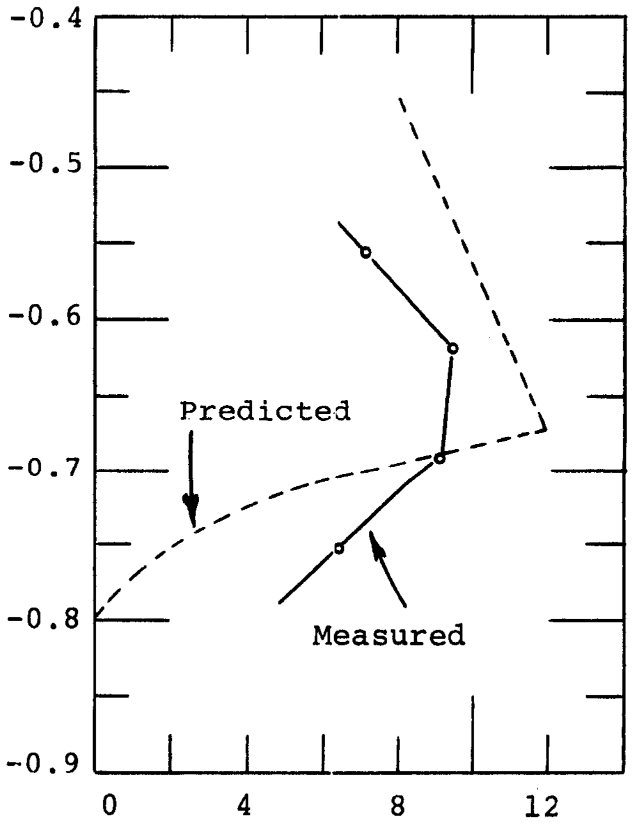
Graph S-10. Mixed-Feed Current for Platinum-Teflon Electrode; 0.04 M methanol; 70°C; K_2CO_3

rates for the non-holed platinized screen with 0.01 M methanol have been plotted on Graph S-11. At potentials above the open circuit value (-0.65 v), there is excellent agreement between the predicted and experimental direct reaction rate. However, in the lower region, the direct reaction rate was about 7 ma greater than predicted. This indicates that a catalytic (non-electrochemical) reaction between methanol and oxygen is occurring, in conjunction with the predicted electrochemical reaction. The catalytic reaction consumed some of the oxygen which otherwise would have reacted electrochemically to produce the cathodic current. And therefore, this catalytic reaction was responsible for the slightly low cathodic current density which was measured for this electrode in this potential region (Graph S-7). Similar curves were obtained when the methanol concentration was increased to 0.04 M (Graph S-12). The increase in methanol concentration did not cause a corresponding increase in the direct reaction because the direct reaction rate was limited by the oxygen supply.

As would be expected, the direct reaction rate for the holed screen was much smaller. At open circuit, the rate was about $2\frac{1}{2}$ ma at both methanol concentrations. At a polarized potential of -0.55 v, the rate was reduced to about 1 ma.



Graph S-11. Direct Reaction Rate for Non-holed Screen; 0.01 M methanol; 70°C; K_2CO_3

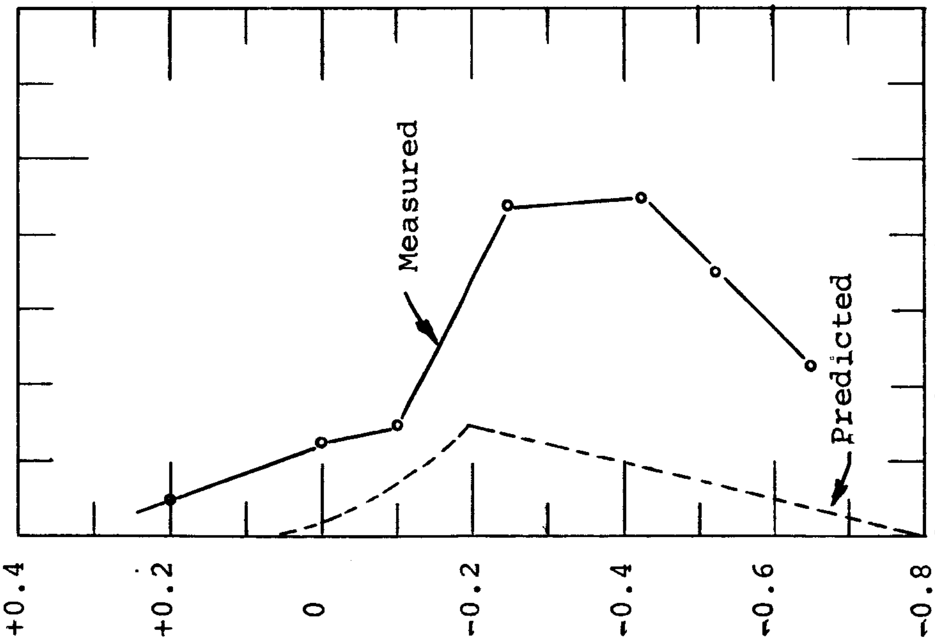


Graph S-12. Direct Reaction Rate for Non-holed Screen; 0.04 M methanol; 70°C; K_2CO_3

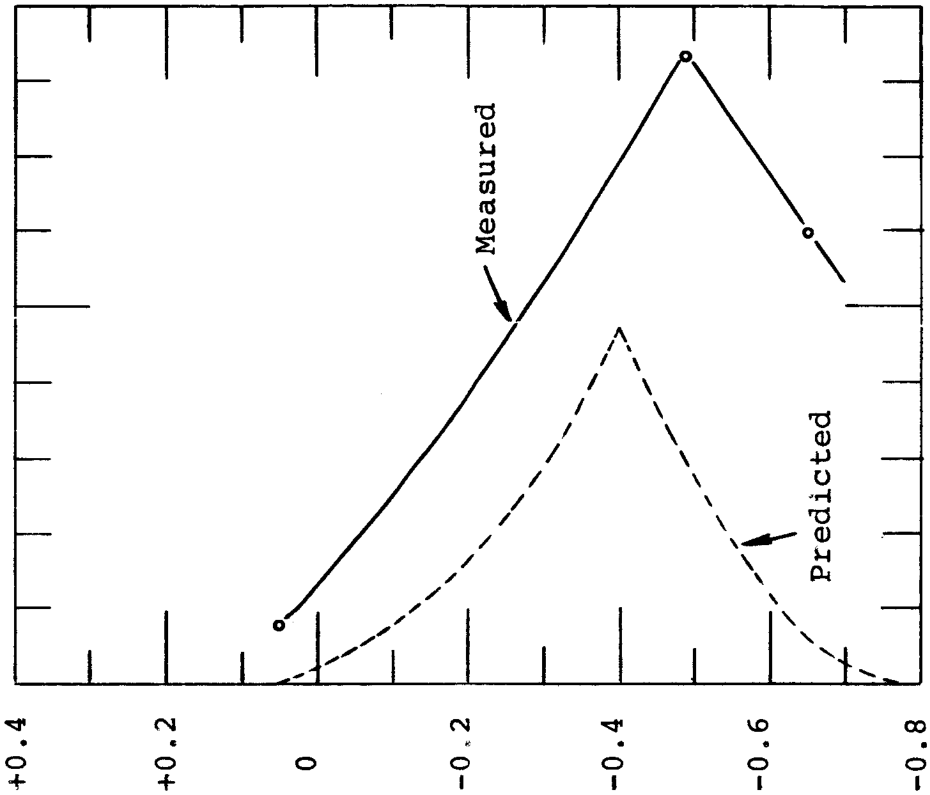
The platinum-Teflon electrode gave a much larger direct reaction rate since the oxygen availability was not as limited (Graphs S-13, and S-14). As shown on the graphs, the measured rates were appreciably larger than predicted. Since oxygen diffusion was not rate limiting for this electrode, the catalytic reaction was free to occur. Unlike the screen electrode, the direct reaction rate was found to increase markedly when the methanol concentration was increased to 0.04 M.

To summarize, the mixed-feed current curves can be approximately predicted from single-feed curves for all of the platinum electrodes. The good agreement is consistent with the basic assumption of the mixed-feed theory: The electrochemical reaction rate of each reactant during mixed-feed operation is about the same as during single-feed. In general, however, the direct reaction cannot be predicted from the single-feed curves because of the possibility of the catalytic reaction. Only when the oxygen rate was severely limited by mass transfer, was the actual direct rate close to the predicted values.

In order to determine the effect of temperature on the mixed-feed platinum screen electrode (non-holed), current and reaction rate measurements were made at temperatures from 49°C to 78°C. Mixed-feed, open circuit reaction rates and potentials were compared with values



Graph S-13. Direct Reaction for Platinum-Teflon Electrode; 0.01 M methanol; 70°C; K_2CO_3



Graph S-14. Direct Reaction for Platinum-Teflon Electrode; 0.04 M methanol; 70°C; K_2CO_3

Reaction Rate in ma/2 cm^2 face area

Potential in volts vs Hg/HgO

predicted from single-feed current curves. The open circuit potential was improved from -0.59 v at 49°C to -0.69 v at 78°C. Since the methanol reaction had a higher activation energy than the oxygen reaction, the methanol activity was increased more than the oxygen by increasing the temperature. The activation energy for the oxygen reaction was very low (4.5 kcal), because it was diffusion limited. Of course, the open circuit direct reaction rate increased with the temperature. However, this inefficient reaction rate at 78°C (8 ma) was only twice the rate at 49°C. The experimental reaction rates averaged about 1 ma higher than the predicted rates.

The most practical platinum electrode design to use in a mixed-feed cell is the platinized holed screen. The current efficiency for this electrode can be determined by dividing the anodic current by the consumption rate of methanol equivalents (expressed in ma). Thus, at -0.57 v for 0.01 M methanol, the anodic current was 11 ma/cm^2 and the efficiency was 95%. Using 0.04 M methanol at -0.59 v, the efficiency was also 95% at a current of 20 ma/cm^2. These values also represent the efficiency for a complete cell, if the selective silver electrode is used as cathode.

Products of Methanol Oxidation

In any methanol fuel cell, the methanol should be completely oxidized to carbon dioxide in order to obtain full use of the fuel. Therefore, the products of oxidation were analyzed for the system of this study. The platinized screen electrode was operated with 0.01 M methanol for several hours and then the concentration of oxidation products in the electrolyte was determined. At open circuit with mixed-feed, the major product was formate with a small amount of formaldehyde (6%). At an anodic current of 25 ma, the products were 83% formate and 17% carbon dioxide (as bicarbonate). The build-up of formaldehyde and formate in the electrolyte shows that these compounds are definitely intermediates in the oxidation of methanol. The formaldehyde formed only because the oxidizing conditions are not very strong at open circuit. The formaldehyde and formate could still be oxidized completely to carbon dioxide. To show that formate could subsequently be oxidized to carbon dioxide, polarization curves were measured for pure formate in potassium carbonate electrolyte. Formate was found to be just as reactive towards electrochemical oxidation as methanol. Therefore, the only reason why formate formed in the electrolyte during the methanol runs, was because its concentration was much lower than the methanol concentration. During long term cell operation, with continuous electrolyte and fuel recycling, the formate would reach a steady-state concentration, where it would react as rapidly as it was formed.

E. Conclusions

(1) Mixed feed electrode selectivity:

Silver has been shown to be a perfectly selective oxygen catalyst.

As was expected, no perfectly selective mixed-feed platinum anode could be found. Of the three platinum anode designs, the electrode which minimized the catalyst contact with the gaseous oxygen phase resulted in the greatest selectivity. Thus, a holed, screen electrode performed well because the oxygen reaction rate was severely mass transfer limited. When this electrode was used in conjunction with a silver-Teflon electrode in an experimental cell, current efficiencies as high as 95% could be obtained.

(2) Electrode current densities:

High cathodic current densities were found to be more difficult to obtain than high anodic current densities. Although the use of oxygen bubbles in conjunction with a newly prepared silver-Teflon cathode produced very good current densities, the performance of the electrode was found to deteriorate with use.

The anticipated problems with "gas binding" were overcome by the use of electrode holes: The holes prevented the gas from being trapped between the electrodes.

(3) Alkaline CO_2-rejecting electrolyte:

An alkaline electrolyte has been found which will reject the CO_2 produced by methanol oxidation at a cell operating temperature of 70°C. However, at this temperature the high bicarbonate concentration of the electrolyte had a harmful effect on the cell output voltage. Better operating voltages could be obtained with this electrolyte by cell operation at higher temperatures, because the equilibrium concentration of bicarbonate in the rejecting electrolyte would then be smaller.

(4) Theoretical understanding of mixed-feed electrode behavior:

The mixed-feed theory was applied to the performance of the platinum anodes. These studies shows that the mixed-feed current output could be approximately predicted from single-feed polarization curves for any given electrode. In general, however, the direct (non-current-producing) reaction rate at the platinum electrodes could not be predicted due to the possibility of a catalytic reaction between methanol and oxygen. The effect of temperature and methanol concentration on the behavior of mixed-feed electrodes could be predicted from single-feed measurements under corresponding conditions.

II. INTRODUCTION

A. Object of Study

Fuel Cell Geometry and Performance

A large part of the current research on fuel cells utilizes the porous gas diffusion electrode. The cell electrolyte is contained between two flat porous catalytic electrodes, and the gas reactants are supplied to the outer side of the electrodes (Figure 1). An electrolyte-gas interface is maintained within the electrode structure (Figure 2).

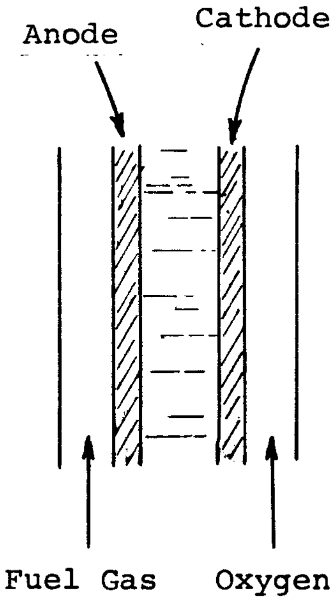


Figure 1

Cell Cross-section

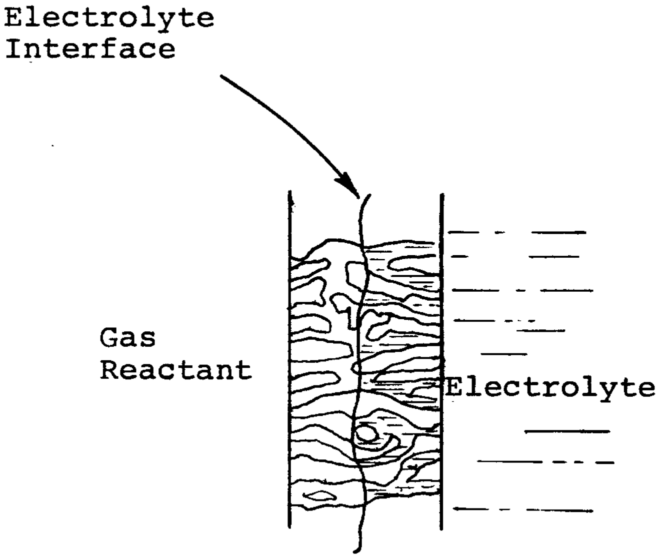


Figure 2

Electrode Cross-section

This system is used because the porous electrodes present a large surface area for catalytic reaction, and because the system can be used with reactants which have low solubility in the electrolyte.

Davyton[40] first used this cell design with aqueous electrolyte. Bacon[2] has obtained 470 ma/(cm^2 face area) current density at 0.68 volts output, using hydrogen and oxygen as reactants. He operated at 400 psi and at 200°C, and used porous nickel electrodes with concentrated potassium hydroxide solution as electrolyte.

Although this is exceptional performance, there are several problems with this system. Extensive pressure control gear are needed to maintain a stationary gas-electrolyte interface. "Wetting" or "flooding" of the electrodes with electrolyte is a constant problem and is the main cause of cell break-down. Also, gas seeps into the electrolyte space between electrodes and must be removed.

General Electric Company has varied the Bacon cell to accommodate hydrocarbon fuels. Porous platinum electrodes are used with an electrolyte of 90 (wt)% phosphoric acid.[21] This cell is operated with hydrocarbon paraffins such as propane and octane at around 150°C and at atmospheric pressure. Using air as oxidant, General Electric reports attaining 20 ma/cm^2 at 0.58v. Since an acid electrolyte is used, the carbon dioxide product is expelled and does not consume the electrolyte. The use of platinum makes possible a reasonable hydrocarbon reaction rate. Of course, the problem of maintaining the gas-liquid interface is not solved. Also, the hot acid has caused problems of corrosion.

General Electric has also used 80% solutions of cesium carbonate at 130°C as electrolyte[12], which presents only mild corrosion problems. This electrolyte may be regarded as a pre-carbonated caustic solution; the carbon dioxide product is discharged into the anode gas stream. Using methanol and oxygen they obtained 20 ma/cm^2 at 0.56 volts. However, reasonable reaction rates could not be obtained with paraffin hydrocarbons.

Bacon[2] first used the porous gas-diffusion electrode because he could not obtain satisfactory reaction rates when the reactants were pre-dissolved in the electrolyte. In this case, the electrolyte was flowed parallel to the electrode plate. Evidently the performance was poor because the diffusion path for the reactants was too long. Despite the improvement made by the gas-liquid interface design, recent investigations by Reti[41], Weber[47], Meissner, and Hartner[22] show that an important rate-limiting step at these electrodes is the diffusion of the reactant from the gas-liquid interface to the immersed pore wall. Consequently, these authors believe that most of the reaction takes place on a small fraction of the catalyst surface near the gas-liquid interface.

In order to use the catalyst surface more efficiently, "flooded-flow" electrodes have been employed[1,41]. In this system, the reactant is pre-dissolved in the electrolyte which is then flowed through the porous structured (or screen) electrodes. Besides increasing the effectiveness of the catalyst, this system eliminates the bothersome gas-liquid interface.

Mixed-Feed Design Proposal

A simplification in fuel cell design can be achieved if the fuel and oxidant can be mixed together in the electrolyte without appreciable direct reaction between them. The electrolyte can then be passed through a series of catalytic anodes and cathodes (Figure 3).

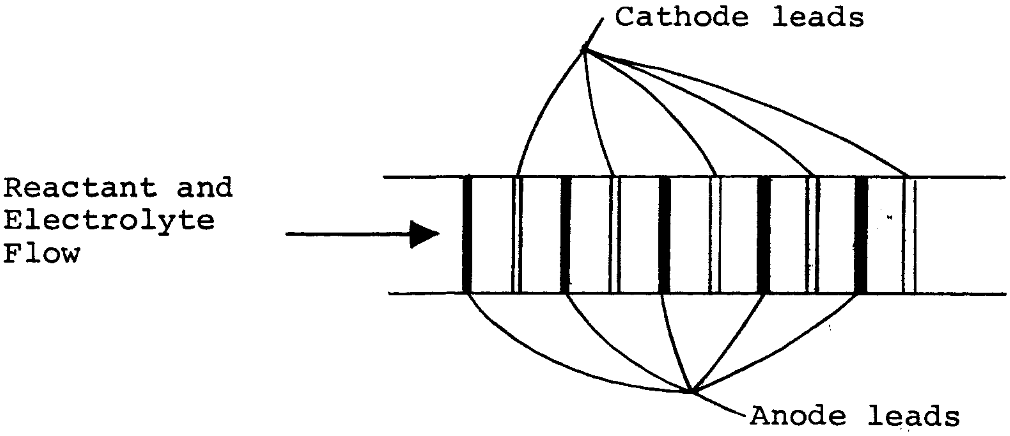


Figure 3. Mixed-feed, flow cell

These electrodes must be of such a nature that only the methanol will react at the anode, and only the oxygen will react at the cathode.

This mixed-feed design requires less controls than are needed for the gas-diffusion electrode, and also makes a closer packing of cells possible. Since the ion flow can take place in two directions from each electrode, the ohmic polarization is cut in half.

The primary problem associated with this design is the reactant "selectivity" at the electrodes. Since both the fuel and oxidant are in contact with each type of electrode, the anode and cathode materials must be highly specific catalysts. In this way, only the desired reactant will be electrochemically active at each electrode. In general, however, a small amount of the oxidant might be expected to react at the fuel electrode, for example. These oxidant equivalents will consume an equal amount of fuel equivalents. This "direct reaction" on the fuel electrode does not contribute any electrons to the external circuit and, thus, fuel is wasted and the efficiency of the cell is reduced. Therefore, the "current efficiency" (the fraction of the fuel equivalents consumed which produce useful current) for a mixed-reactant cell becomes an important parameter. The current efficiency for a conventional cell is always 100% because there is no opportunity for the oxidant to react at the fuel electrode nor for the fuel to react at the oxidant electrode; the direct reaction cannot occur.

The direct reaction is also likely to increase the polarization of each electrode. Thus, a mixed electrode may also have a lower voltage efficiency than the conventional electrode.

The Objectives of this Study

The primary goals for the early stages of research on mixed-feed fuel cells should be to demonstrate that high power efficiencies can be obtained, and to gain a basic understanding of mixed-feed electrode behavior. Methanol and oxygen were chosen as the fuel and oxidant for this study because they are relatively inexpensive reactants and would therefore produce an economical cell. In addition, methanol and oxygen are known to be very inert towards each other in the absence of catalysts at aqueous fuel cell temperatures.

The objectives of this work may be specifically stated as follows:

(1) To develop and test selective electrodes for the methanol-oxygen system

The preparation of a selective oxygen cathode did not appear to be difficult because results in the literature indicated that both carbon[3,29,41] and silver[31] could be used as selective oxygen electrode catalysts. Therefore, both of these materials were to be tested in this study.

The development of a selective methanol electrode appeared to require particular study. The results in the literature indicated that platinum and the other platinum group metals are the only known catalysts for the electrochemical oxidation of methanol. This complicates the design of a selective anode because these platinum group metals are also excellent oxygen catalysts. In this work, several platinum anode designs were to be developed and tested with the aim of achieving a high anodic current efficiency.

(2) To design electrodes which deliver a high current density at low polarization

This presented a special problem in the case of the oxygen cathode. Preliminary calculations showed that the solubility of oxygen in electrolytes was too low to give high cathodic current densities in a cell system operating on dissolved oxygen. It was anticipated that this problem could be overcome by feeding gaseous oxygen bubbles with the electrolyte to the mixed-feed electrodes. The presence of gaseous oxygen bubbles near the cathode was expected to produce high cathodic current densities because the diffusion path of oxygen through the electrolyte would be reduced to short distances. It was realized that the presence of oxygen bubbles in the electrolyte could cause "gas binding"; that is, the gas could build up in the space between the electrodes, which would make ion flow impossible. This problem had to be faced up to in the design of the electrodes.

(3) To develop an alkaline electrolyte which will reject carbon dioxide

In a practical methanol cell, the electrolyte must reject the carbon dioxide produced by methanol oxidation, and it must also be alkaline in order to be compatible with silver cathodes. An electrolyte which has been shown to meet these qualifications is aqueous cesium carbonate at 130°C. [12] However, this electrolyte is expensive and cannot be used at lower temperatures. An alternative to cesium carbonate was to be found if possible.

(4) To gain theoretical insight into the behavior of mixed-feed electrodes

The performance of mixed-feed electrodes can best be understood by comparing their behavior with a general theoretical model. A general theory was to be tested in this work by analysis of the data obtained with the platinum anodes.

B. A Theory for Mixed-Feed Electrodes

Electrochemical Reaction

In order to have a basis for predicting mixed-feed electrode behavior, a theoretical model is required. Such a theory has been described by Paradis[37] and is similar to the model often used in corrosion studies. This theory is based on the fact that an anodic and a cathodic reaction can occur simultaneously on the same electrode. This type of electrode is often referred to as a "bi-electrode".[32] The anodic reaction produces electrons which are discharged to the body of the electrode, and the cathodic reaction consumes electrons from the body of the same electrode. If there is no net current flowing from this electrode into the external circuit (i.e., the electrode is at "open-circuit") then the rate of the anodic electron production at this electrode must be equal to the cathodic electron consumption. If, however, there is a net flow of electrons from the electrode (anodic current), then the anodic production of electrons must be greater than the cathodic consumption at this electrode, by an equivalent amount. Naturally, a bi-electrode which is to function as a cell anode must have an anodic reaction rate which is significantly greater than the cathodic reaction rate. Just the opposite is true for a bi-electrode to be used as a cell cathode.

The initial assumption of this theory is that the anodic and cathodic reactions occur independently of each other. Therefore, for example, at a given potential, the anodic reaction rate is unaffected by the presence or absence of the cathodic reaction. When the anodic and cathodic reactions occur simultaneously, their individual rates will be the same as when each of the reactions is allowed to occur alone. The main requirement for this assumption to hold, is that no surface blocking occurs by either of the reactants.

If this assumption is valid, then the net external current for a mixed-feed electrode can be predicted from

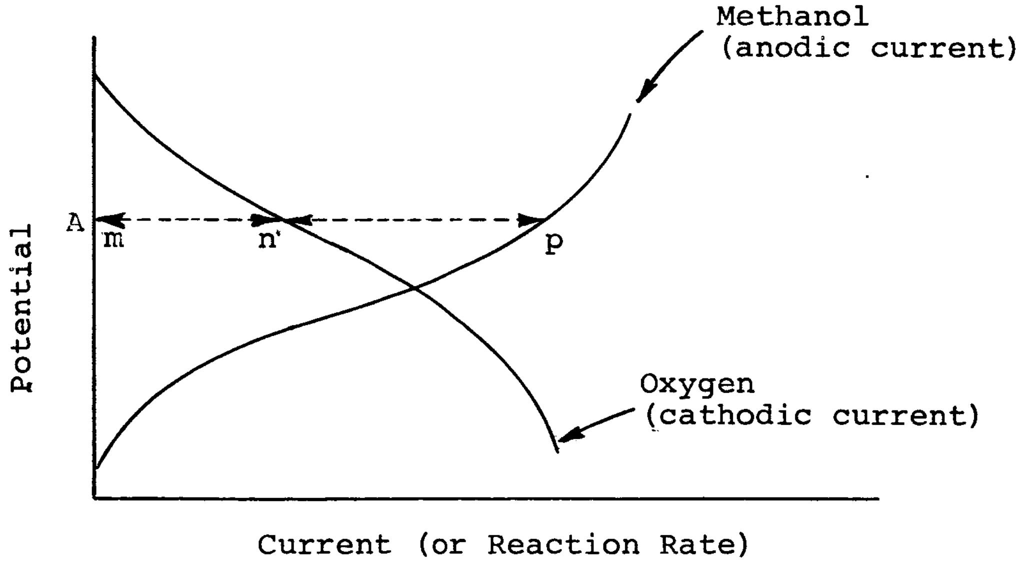


Figure 4. Single-Feed Polarization

the single-feed electrode currents (or reaction rates). Figure 4 presents the qualitative polarization curves which might be expected for the single-feed reaction of methanol and oxygen on a platinum electrode.

The "current" axis may also be considered to be "reaction rate" since the reaction rate is proportional to the external current for a single-feed electrode. Since these single electrode reaction rate curves are assumed to be valid when both reactions occur simultaneously, the external current from the mixed-feed electrode can be predicted from the excess of one reaction rate over the other.

For instance, if the mixed-feed electrode were at potential "A" (Figure 4), then the external current would be an anodic current of magnitude "n-p". The magnitude "m-n" represents the anodic reaction which is canceled by the oxygen cathodic reaction. This is the wasted, or non-current-producing reaction. Throughout this paper, this reaction will be referred to as "direct electrochemical" reaction.

Therefore, two mixed-feed electrode curves may be predicted from these single-feed curves (Figure 5a).

The predicted mixed-feed external current is shown as a function of potential (Figure 5b). This curve was obtained as the difference of the two single-feed curves.

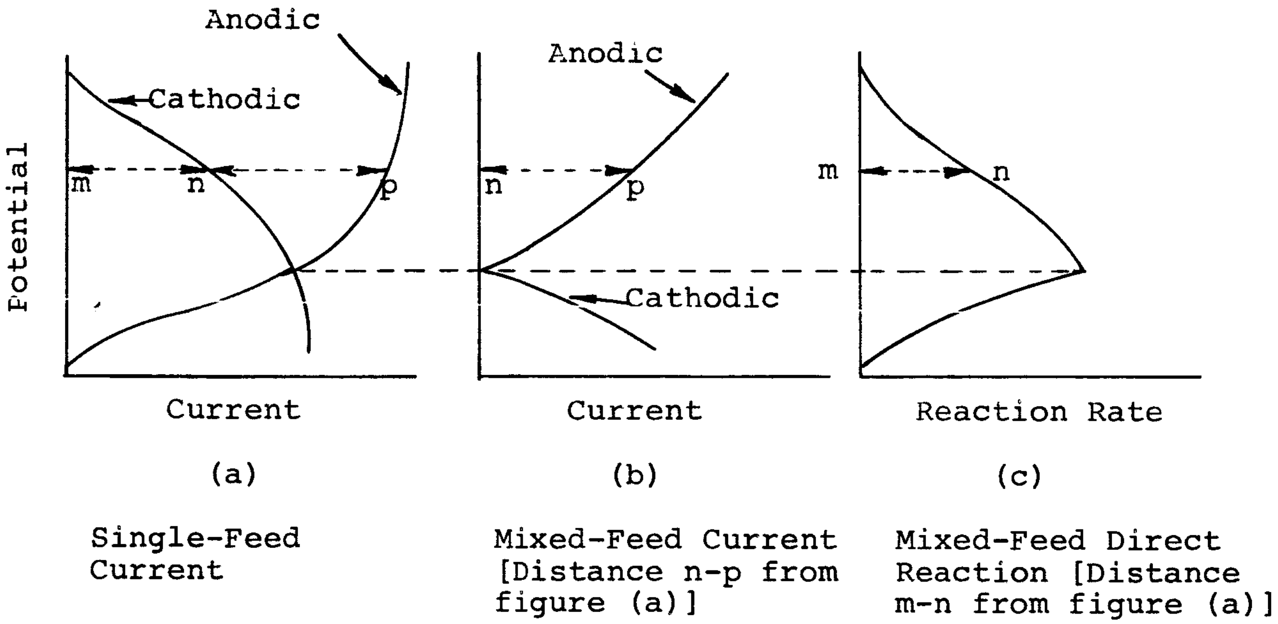


Figure 5. Prediction of Mixed-Feed Curves

The open-circuit potential for the mixed electrode occurs at the crossover point for the single-feed curves. This is the potential for which the anodic and cathodic reactions exactly cancel each other. The upper branch of the curve represents a net anodic current, and the lower represents a cathodic current. Throughout this report, the upper branch will always be the anodic current.

The predicted mixed-feed direct electrochemical reaction has also been plotted (Figure 5c). The maximum direct reaction occurs at the open circuit potential for the mixed electrode.

Catalytic Reaction

The direct reaction plotted in Figure 5c is entirely electrochemical in nature [i.e., the anodic and cathodic reactions which cancel each other, occur independently and with complete electron discharge to (and from) the electrode catalyst body.]. The anodic and cathodic reaction species are linked only by electron flow through the electrode, and ion flow through the electrolyte. However, in conjunction with this direct electrochemical reaction, a common catalytic reaction may occur between the anodic and cathodic reactants on the surface of the electrode. Unlike the electrochemical reactions, the direct catalytic reaction can occur only when both reactants are present. This reaction would occur between adsorbed species on adjoining catalytic sites, or between one adsorbed species and a reactant in the solution which comes into contact. Complete electron discharge to the electrode body does not need to occur during the mechanistic steps of this catalytic reaction.

If a direct catalytic reaction occurs, then the total direct reaction (electrochemical plus catalytic) will be greater than the direct electrochemical reaction predicted in Figure 5c. If the catalytic reaction rate is assumed to be constant over the entire potential region, then the total direct reaction rate would appear as in Figure 6.

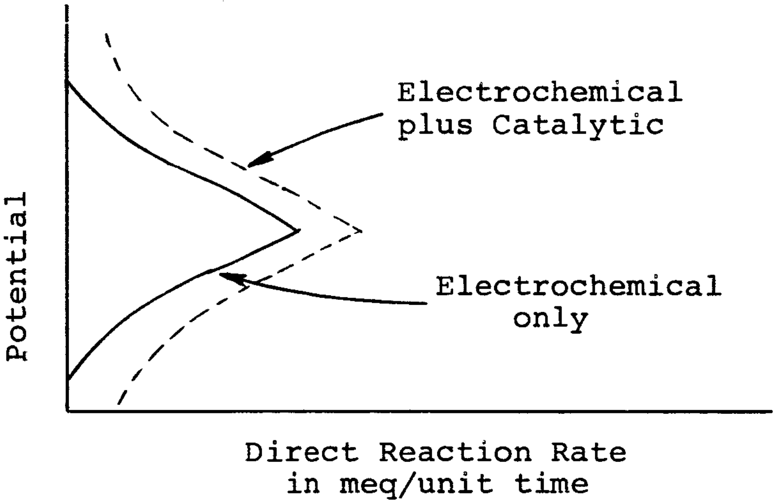
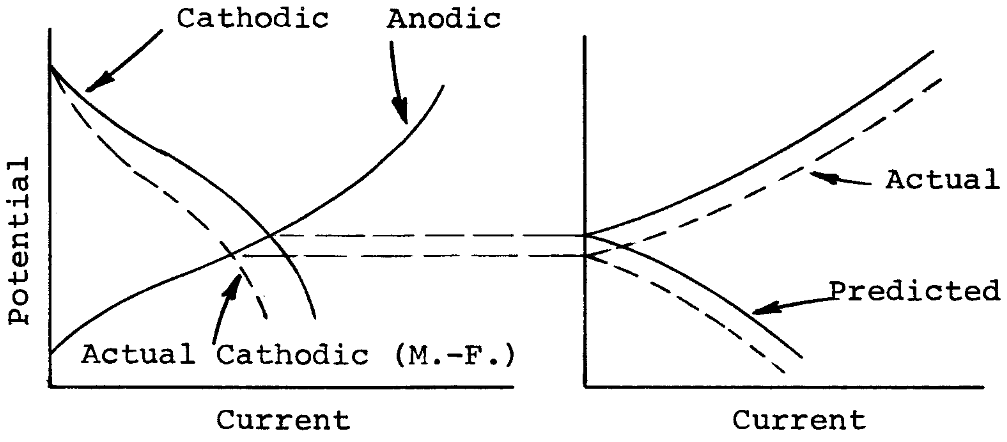


Figure 6. Catalytic Reaction

(The catalytic reaction rate would be expected to vary with electrode potential only if electron discharge to the solid catalyst took place, and only if this was an important rate limiting step.) Of course, only the total of both direct reactions can be experimentally measured. If the experimental total direct reaction is greater than the predicted direct electrochemical reaction, then the difference would be assumed to be catalytic.

Diffusion Limiting Effects

In general, the catalytic reaction would have no direct effect on the electrochemical reaction rates. In this case, the mixed-feed external currents would still be as predicted in Figure 5b. However, if diffusion (or adsorption) is an important rate limiting step for one of the two reactants, then the catalytic reaction may compound this problem. The catalytic reaction would reduce the amount of reactant available for the electrochemical reaction. A lower electrochemical reaction rate would then have an effect on the mixed electrode's current output. This is illustrated in Figure 7.



(a)
Single-Feed Current

(b)
Mixed-Feed Current

Figure 7. Current Prediction with Catalytic Reaction and Diffusion Limitations

In this case it is assumed that the cathodic reaction is mass transport limited. The catalytic reaction causes the electrochemical cathodic reaction to be reduced during mixed-feed operation (dotted line, Figure 7a). Two sets of mixed-feed currents are shown in Figure 7b. The "predicted" curves are the same as in Figure 5b. The "actual" curves (dotted line) represent the external current obtained due to the reduction in the cathodic reaction rate. The "actual" curve of Figure 7b is the difference between the "Anodic" and "Actual Cathodic" curve of Figure 7a. This shows that the external current curve is shifted to lower potential. Therefore, if this electrode were being used as an anode, the open circuit potential and current would actually become more favorable as a result of the catalytic reaction.

As before, the total direct reaction will be the sum of the catalytic and electrochemical direct reactions. However, if the cathodic reaction rate is almost completely diffusion controlled, a limit is placed on the total oxidant reaction rate. In this case, the sum of the catalytic and electrochemical oxidant reaction rates cannot be greater than the oxidant supply rate. This means that in the potential region positive to the open circuit potential, the total direct reaction rate will match the amount "predicted" (as in Figure 5c)——despite the occurrence of the catalytic reaction. Of course, in the lower potential region, the catalytic reaction will cause an increase in the total direct reaction. This is illustrated in Figure 8.

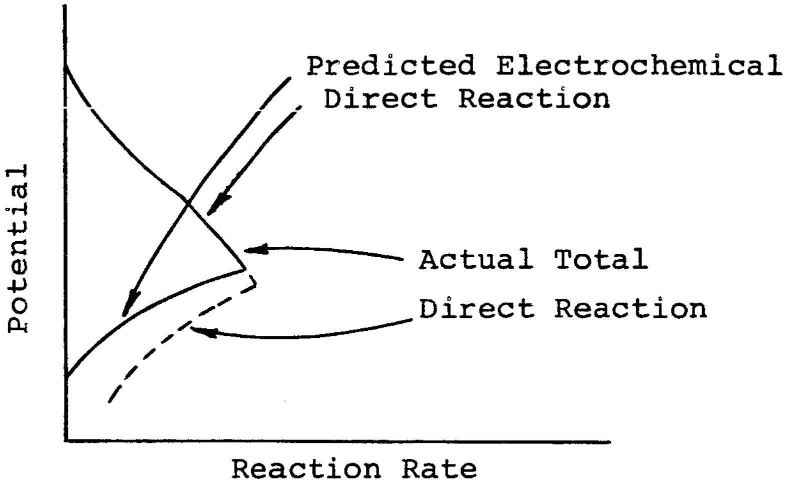


Figure 8. Reaction Rate Prediction with Cathodic Diffusion Control and Catalytic Reaction

Blocking Effects

Another possible complication in mixed electrode behavior is the blocking of the catalyst surface by one of the reactants. During mixed-feed operation, the reactants must share the same surface area that they had full use of during single-feed operation. This could reduce one (or both) of the reaction rates during mixed operation. If this happened, then the external current and direct electrochemical reaction could not be predicted from single feed current rate.

C. Alkaline CO_2-Rejecting Electrolyte

In a methanol-air cell, the electrolyte will come into contact with carbon dioxide from two sources: the carbon dioxide produced by methanol oxidation at the anode, and the carbon dioxide in the air which is delivered to the cell. In a practical methanol cell, the electrolyte must reject carbon dioxide so that the cell will operate at "steady-state" without continual electrolyte replacement; and the electrolyte must also be alkaline in order to be compatible with silver cathodes. In order for an alkaline electrolyte to operate at steady-state, the carbon dioxide vapor pressure of the electrolyte must be equal to the carbon dioxide partial pressure in the gas phase of the mixed-feed cell. The equilibrium between CO_2 and the alkaline electrolyte can be presented as follows:

$$CO_2(g) + CO_3^{=} = 2\ HCO_3^{-}$$

High operating temperatures are desirable in order to push this equilibrium to the left, which increases the alkalinity and improves the performance of the cell.

Operating cell current densities are usually greatest when very concentrated electrolyte solutions are used. Therefore, the alkali metal carbonate and bicarbonate which are used for this electrolyte should be very soluble.

Cesium has been used by Cairns[12] because of its high solubility, but it is very expensive. Of the two common anions, potassium and sodium, potassium has the most soluble carbonate and was selected for this work.

The concentration of potassium carbonate and potassium bicarbonate in a CO_2-rejecting electrolyte for operation at 70°C can be calculated from equilibrium and solubility data available in the literature. (See the complete calculation in Appendix B.) The maximum vapor pressure of CO_2 in the gas phase of a mixed-feed cell has been calculated as 0.08 atm. This vapor pressure can be combined with the equilibrium data of Sieverts and Fritzsche[43] to give an expression for the relation between the concentrations of potassium carbonate and potassium bicarbonate. The concentration of these salts which satisfies this expression, and are soluble at temperatures above 65°C, are as follows:

20(wt)% potassium carbonate
21(wt)% potassium bicarbonate

Throughout the report, this electrolyte is referred to as "the potassium carbonate-bicarbonate mixture electrolyte."

Besides this CO_2-rejecting electrolyte, two other electrolytes were also tested in this work: 50 (wt)% potassium carbonate, and 20 (wt)% potassium hydroxide. The pure potassium carbonate electrolyte was used for most of the measurements because it was more convenient than the mixture electrolyte: the potassium carbonate is completely soluble at room temperatures. It was anticipated that the findings with the hydroxide and carbonate electrolytes could be related to the performance in the mixture electrolyte.

D. Previous Studies on Methanol and Oxygen Electrodes

Reversible Electrode Potentials

Throughout this report, the European convention regarding the sign of half cell potentials will be used. That is, a positive value for the standard electrode potential, E^o, will mean that the half cell reaction has a larger reducing tendency than the hydrogen half cell in acid of unit activity.

$$H_2 = 2\ H^+ + 2\ e^- \qquad E^o = 0.0\ v$$

The standard half cell potential for the complete oxidation of aqueous methanol to carbon dioxide is very close to the standard hydrogen half cell potential. In one normal acid electrolyte, the potential is +0.030 v.

$$CH_3OH(aq) + H_2O = CO_2(g) + 6\ H^+ + 6\ e^- \qquad E^o = 0.030\ v$$

The standard oxygen half cell potential is 1.229 v in one normal acid electrolyte.

$4\ H^+ + O_2 + 4\ e^- = 2\ H_2O \qquad E^o = 1.229\ v$

The combination of the methanol and oxygen half cells yields a complete cell with a total potential of 1.20 v.

$CH_3OH(aq) + \frac{3}{2}\ O_2 = CO_2 + 2\ H_2O \qquad E^o = 1.20\ v$

For a hydrogen-oxygen cell the complete cell standard potential would be 1.23 v. This would be the net cell potential for an electrolyte of any pH since each half cell is affected equally by a change in pH. However, for methanol oxidation, the potential varies with pH since carbon dioxide is a product of oxidation. As long as the equilibrium carbon dioxide vapor pressure over the electrolyte is one atmosphere, then the methanol half cell potential will always be 0.03 v more positive than the hydrogen electrode in an electrolyte of the same pH. This will be the case in all acid electrolytes, or in an "equilibrium" bicarbonate-carbonate electrolyte in which carbon dioxide is expelled at a vapor pressure of one atmosphere. However, if a more basic "non-equilibrium" electrolyte is used, the conversion of carbon dioxide to carbonate, or bicarbonate, will decrease the methanol half cell potential.

Therefore, in a one normal hydroxide electrolyte, the half cell reaction,

$CH_3OH + 8\ OH^- = CO_3^= + 6\ H_2O + 6\ e^- \qquad E^o = -0.895$

gives a standard potential of -0.895 v compared to -0.828 v for the hydrogen half cell (see Appendix A). The potential decrease due to carbonate production is 0.097 v.

For the 50 (wt)% potassium carbonate electrolyte used for most of this work, the carbon dioxide is converted to potassium bicarbonate. The reversible half cell potential is -0.814 v at 70°C.

$$CH_3OH + CO_3^{=} + 6\ OH^- = 2\ HCO_3^- + 4\ H_2O + 6\ e^- \qquad E_{rev} = -0.814\ v$$

(This potential was calculated from the Nernst equation by using the actual electrolyte concentrations—not the standard states of unit activity. See Appendix A.) The total reversible methanol-oxygen cell potential in this electrolyte is 1.239 v compared to 1.229 v for the hydrogen-oxygen cell.

$$CH_3OH + \frac{3}{2}\ O_2 + CO_3^{=} = 2\ HCO_3^- + H_2O \qquad E_{rev} = 1.239\ v$$

In basic electrolyte, several investigators have reported that methanol is only oxidized to formate[11,38]. In this study, there is evidence that formate is an important intermediate, but that it is subsequently oxidized to carbon dioxide. The reversible half cell potential for the oxidation of methanol to formate in 50 (wt)% potassium carbonate electrolyte is -0.806 v.

$$CH_3OH + 5\ OH^- = HCOO^- + 4\ H_2O + 4\ e^- \qquad E_{rev} = -0.806\ v$$

This reaction is not as thermodynamically favorable as the complete oxidation and therefore would cause a lower open circuit cell potential of 1.231 v.

The oxidation of formate has a much more favorable reversible potential.

$$HCOO^- + CO_3^= + OH^- = 2\ HCO_3^- + 2\ e^- \qquad E_{rev} = -0.831\ v$$

A complete list of the half (and whole) cell potentials for hydroxide, carbonate, and bicarbonate electrolytes are contained in Appendix A.

Of course, the potentials which are experimentally measured are actually the difference between the half cell test electrode potential and the potential of another half cell reference electrode.

Two reference electrodes are used in this work. Some measurements were made with the saturated calomel electrode which has a potential of +0.242 v.[27] The other reference electrode used was mercury-mercuric oxide couple in 50 (wt)% potassium carbonate at 25°C. The potential of this electrode is 0.140 v. The presence of a liquid junction in some cases will affect the net reference potential (See Appendix A for details).

Electro-oxidation of Methanol

The first extensive work on methanol electro-oxidation was done by Mueller and co-workers in the 1920's. Pavela[38] in 1954, repeated and extended Mueller's work. These investigators found that the methanol half cell open circuit potential was usually 0.2 to 0.3 v more positive than the standard electrode potential when a platinized platinum electrode was used at 25° - 50°C. When the potential was increased, the resulting current followed the Tafel equation until an unstable region was reached (about 0.8 v more positive than the reversible potential). There was a range of about 0.5 v in which the potential could not be held constant, but instead drifted to higher values. Oscillations in potential and current were also observed in this region. Subsequent investigators[18] found that when potentiostatic equipment was used to maintain the electrode potential in this region, the current was very low (Figure 9).

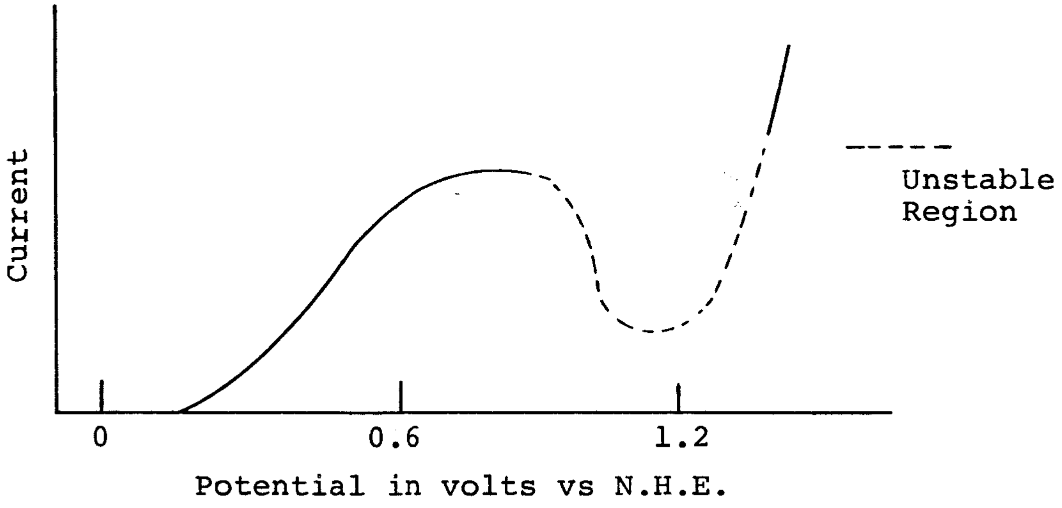


Figure 9. Current-Voltage Curve for Methanol on Platinum

Recently, a great deal of work has been done to elucidate the mechanism of methanol oxidation on platinum. Most investigators agree that formaldehyde and formate are intermediates in the oxidation of methanol to carbon dioxide because these compounds have often been observed in the anolyte[11,38]. Also stirring of the electrolyte often causes[38] a small reduction in current—presumably due to the removal of these reaction intermediates from the electrode surface. In acid electrolyte, the reaction of methanol always proceeds to carbon dioxide, but in base the product is either formate or carbonate, depending on the activity of the catalyst.

The decrease in current at potentials above 0.8 v is due to the formation of a non-catalytic oxide film on the platinum surface in this potential region[16,18,34]. Eustis[16] and Liung[34] believe that there is also a "lower" catalytic oxide film present on the surface at lower potentials, and that this oxide plays a role in the oxidation mechanism. However, Gilman and Breiter's[18,8,9] work led them to conclude that methanol oxidation takes place on a plain metal surface, and that adsorption and electron discharge are both important rate determining steps in methanol oxidation.

The observed oscillations are evidently caused by some electrode processes occurring in unison[38]. Slott believes that the platinum-oxide layer plays an important role in causing this abnormal electrode behavior[44].

The performance obtained with methanol electrodes varies greatly for different investigators.

Several investigators have studied the performance of platinum-impregnated carbon electrodes. With these electrodes, the rate of reaction is usually no greater than about 10 ma/cm^2. This poor performance may be attributed to the small amount of platinum used, and to its poor distribution on the carbon. Apparently, the carbon contributes nothing to the catalysis of methanol oxidation except to provide a large area base for the platinum. In general, the oxidation of methanol only proceeds to formate with these catalysts when used in basic electrolyte.

Wynn[49] fed aqueous solutions of methanol and potassium hydroxide into the center of a porous carbon tube provided with 1 mg/cm^2 platinum black on the outside of the carbon tube. A similar Ag_2O - CoO - Al_2O_3 impregnated carbon tube was used for the air electrode. The two tubes were placed next to each other in 40% KOH electrolyte. At 25°C, the open circuit voltage was 0.77 v and a current density of 8 ma/cm^2 at 0.35 v was obtained.

Buck and Griffith[10] used a similar system except that the cathode was platinum impregnated. At 24°C, the open circuit cell potential was 0.86 v in 5 N NaOH, and it was 0.61 v in 5 N H_2SO_4. The difference was due to the methanol electrode, which showed larger open circuit polarization in acid electrolyte. The cell potential fell by 0.3 v when currents of $1\frac{1}{2}$ ma/cm^2 were drawn in both acid and base electrolytes.

Hunger[26] used two porous metal disks separated by an anion exchange membrane. The disks were provided with a dehydrogenation catalyst (probably platinum) on the membrane side of the disk. Liquid methanol was allowed to remain stagnant on one side, while oxygen was passed by the other. The open circuit voltage was 0.83 v and only 1 ma/cm^2 could be drawn at 0.5 v.

Pavela's methanol half cell studies were made with an electrolytically platinized platinum electrode. In both acid and base electrolytes, he obtained 50 ma/cm^2 at polarizations of about 0.6 v from the reversible potential.

Several investigators have achieved excellent results using porous platinum metal electrodes, although these electrodes undoubtedly contain more of the expensive metal. The results of General Electric Co. have already been discussed in section II.A. Boies[7] constructed a methanol cell using sodium chlorite as the oxidant. The anode was platinized, flame-sprayed Raney nickel, and the cathode was flame-sprayed nickel-silver. The electrolyte was 5 N KOH. Methanol (5 M) and $NaClO_2$ (4 M) were used in the anolyte and catholyte compartments, respectively. The compartments were separated by a dialysis membrane, and the fuel and oxidant circulated through them. At 55°C, the open circuit voltage was 0.93 v. and 100 ma/cm^2 were obtained at 0.7 v.

Austin[1], using porous platinum-black electrodes, obtained 100 ma/cm^2 with 0.4 v polarization for the methanol half cell. Electrolyte (0.05 M CH_3OH in 4 M KOH) was flowed through the disk at 1 cm/min. There was 230 mg of platinum per cm^2 electrode area.

The most extensive work with porous metal catalysts has been reported by Krupp[31] and Binder[5]. Performance measurements were made using porous Raney metal disks of copper, cobalt, nickel, platinum, palladium and rhodium in 5 N KOH and 5 N H_2SO_4. The performance was independent of whether the metal disks were operated as porous gas-diffusion electrodes, or whether they were completely immersed in electrolyte containing dissolved methanol. In both acid and base, the methanol reacted completely to carbon dioxide (or carbonate). With platinum at 80°C, the methanol half cell showed 0.4 v polarization in 5 N KOH at 100 ma/cm^2 and 0.5 v polarization in 5 N H_2SO_4 at the same current density. In 5 N KOH, palladium had 0.06 v less polarization than platinum, but was much inferior in acid. Rhodium had less activity than palladium and platinum; copper, cobalt, and nickel were completely ineffective.

In 5 N K_2CO_3 at 80°C, a limiting current density of only 10 ma/cm^2 was obtained with palladium. General Electric probably obtained better results with cesium carbonate electrolyte because higher concentrations and temperatures were used.

Krupp constructed a fuel cell using a palladium fuel electrode and a silver oxygen electrode. Methanol (1 M) was dissolved in the 5 N KOH electrolyte. The silver electrode was operated as a porous gas-diffusion electrode. The open circuit voltage was 1.0 v at 80°C; 50 ma/cm^2 was obtained at a potential of 0.6 v. This represents the best performance found by this reviewer for a methanol-oxygen, low temperature fuel cell.

In conclusion it may be said that although excellent methanol oxidation rates have been demonstrated on the platinum group metals, there are no reports in the literature of effective catalysis by less expensive materials.

Electro-Reduction of Oxygen

The reversible potential for complete oxygen electroreduction (1.23 v) is rarely obtained in practice—a potential of around 1.0 v is much more common. In 1943, Berl[3] showed that one reason for this was the presence of hydrogen peroxide in the electrolyte. He found that when an activated carbon electrode was used in basic electrolyte, the reduction of oxygen proceeded only to hydrogen peroxide. Therefore, the electrode potential was determined by the reaction:

$$O_2 + H_2O + 2\ e^- = HO_2^- + OH^-$$

The standard electrode potential for this reaction is +0.68 v. Weisz and Jaffe[48] showed that the oxygen polarization on carbon was even larger in acid than in base electrolyte.

Using an ultrapure system, Bockris and Huq[6] obtained the reversible oxygen potential of 1.23 v on a platinum electrode in sulfuric acid electrolyte. Hoare[23,24] found that not only did the system have to be absolutely free of hydrogen peroxide, but that the platinum electrode had to have a well oxidized coating in order to suppress the half cell reaction:

$$PtO + 2\ H^+ + 2\ e^- = Pt + H_2O$$

Hoare believes that the standard electrode potential for this reaction is 0.88 v, and that if the platinum does not have a complete coating of oxide, then a mixed electrode potential between 0.88 and 1.23 v is obtained. His mixed potential was 1.06 v.

The most common oxygen electrode catalysts are platinum and silver. Silver appears to be just as effective as platinum, although silver cannot be used in an acid electrolyte since the silver is oxidized. These catalysts reduce oxygen completely to hydroxide. These metals also catalyze the decomposition of hydrogen peroxide:

$$HO_2^- = OH^- + \frac{1}{2} O_2$$

Since the reduction of oxygen to peroxide is rapid on carbon, Kordesh[29,30] has prepared excellent oxygen electrodes by impregnating porous carbon with catalysts which will decompose hydrogen peroxide. He has used such catalysts as Co - Al, Ag, Fe - Mn - Ag. Open circuit potentials were about 1.1 v. Using this cathode, Kordesh reports that 200 ma/cm^2 was obtained from a porous gas diffusion hydrogen-oxygen cell at 0.9 v. The electrolyte was 6 N KOH and the temperature was 60°C.

Kordesh's data indicates that high current densities can be obtained at porous gas diffusion oxygen cathodes—even at low fuel cell temperatures. Reti[41] used a similar silver impregnated porous carbon electrode. He compared the performance when it was operated as a gas-diffusion electrode to when it was used as a "flooded-flow" electrode. He found that more than twice as much current could be drawn when operated as a flooded-flow electrode.

Deibert has reported excellent results with polytetrafluoroethylene bonded platinum gas-diffusion electrodes[15]. With a 40% KOH electrolyte at 90°C, he obtained an open circuit potential that was 0.17 v below the standard oxygen electrode potential. The polarization only increased by 0.21 v when 500 ma/cm^2 was drawn.

E. Previous Studies on Mixed-Feed Electrodes

Methanol Systems

The performance of Krupp's methanol-oxygen cell is discussed in section C (Electro-Oxidation of Methanol). This was a "mixed-feed" cell in the sense that the methanol was dissolved in the electrolyte and came into contact with both anode and cathode. Tests were run which showed that there was negligible activity of the methanol at the oxygen silver electrode. This was not a mixed-feed cell with respect to the oxidant, because oxygen did not come into contact with the anode.

Grimes[20] constructed a mixed-feed cell of methanol and hydrogen peroxide. The electrodes were platinum and silver plated on nickel sheets. These electrodes were put into potassium hydroxide electrolyte, with 5 (vol)% methanol and 0.1 (wt)% hydrogen peroxide. A current density of about 55 ma/cm^2 at 0.37 v was obtained at about 90°C. The methanol was oxidized only to formate. Approximately 50% of the methanol was consumed by direct reaction with peroxide. The bulk of this direct reaction probably occurred at the platinum electrode. The peroxide exhibited considerable activity at the platinum anode, and this was responsible for the low open circuit cell voltage of 0.4 v. When peroxide was isolated from the anode, the cell potential was 0.8 v. The methanol was not reactive at the silver cathode.

Hydrogen-Oxygen Systems

Bianchi and Mazza[4] have studied the simultaneous reaction of hydrogen and oxygen at annealed platinum electrodes. Their results indicated that platinum cannot function as a selective anode nor as a selective cathode for these reactants. The electrode was highly polarized from both reversible electrode potentials at open circuit. The direct reaction rate was not measured.

The reaction of hydrogen and oxygen on platinum electrodes has been examined in more detail by Paradis[37]. Paradis obtained results for the mixed electrode at open circuit only. He showed that favorable anodic potentials could be obtained by using a high hydrogen to oxygen gas ratio. At high hydrogen to oxygen ratios, his results were in accordance with the theory described in section B. The open circuit potential for the mixed electrode was equal to the potential predicted from the single-feed polarization curves. The direct reaction rate was greater than predicted from the polarization curves—indicating that a direct catalytic reaction was occurring. At hydrogen to oxygen mole ratios below two, the platinum surface was "blocked" by an oxide coating which raised the potential far above the predicted values. Also, the oxide coating reduced the direct reaction rate below the predicted value. Evidently, the oxide coating hindered the electrochemical oxidation of hydrogen.

Hydrazine-Hydrogen Peroxide System

Paradis also reports on some work done with hydrazine and hydrogen peroxide mixed electrodes[37]. These results show that silver is a fairly selective hydrogen peroxide electrode. This is consistent with Krupp's observation of oxidant selectivity at a silver electrode with methanol and oxygen mixed-feed. The mixed potential-current curves for hydrazine and peroxide on silver were in approximate agreement with the predicted curves.

A rhodium electrode was used as anode. As with the platinum-hydrogen-oxygen system, the electrode potential varied with the reactant ratio. At high hydrazine to peroxide concentration ratios, the electrode produced excellent anode potentials. However, fifty percent or more of the hydrazine consumption was by the wasted direct reaction.

III. APPARATUS AND PROCEDURE

A. Summary of Measurements

Six different electrodes were used in this work. The potential versus current curves (polarization curves) were obtained for the reaction of methanol and/or oxygen at these electrodes. Both single and mixed-feed measurements were made. The electrodes include two carbon types, three platinum types, and a silver electrode. Also, polarization curves were measured for the reaction of air on the silver electrode, and for formate reaction at a platinum electrode.

Total direct reaction rate measurements were made with three electrodes: the silver and two platinum electrodes. The effect of methanol concentration and temperature was studied. Chemical analysis was utilized to determine the total methanol reaction rate. The electrode formation of formate and formaldehyde was also studied by chemical analysis.

Most of the measurements were made with an aqueous 50 (wt)% potassium carbonate electrolyte at 70°C. However, some data was obtained with a 20 (wt)% potassium hydroxide electrolyte, and with the potassium carbonate-bicarbonate mixture electrolyte.

B. Electrode Fabrication

Porous Carbon Disk Electrode

A few measurements were made with a porous carbon disk electrode. The carbon was Pure Carbon Company's fuel cell grade FC-19. This carbon was used unmodified, and also with silver impregnation by the method described by Reti[41]. However, no data is presented in this work for the silver impregnated carbon disks because the results were the same as for the unmodified carbon.

The carbon disk (diameter: 20 mm, thickness: 3 mm) was sealed across the end of a glass tube with epoxy resin. Silver leads made contact with the carbon between the disk and inner glass tube wall (Figure 10).

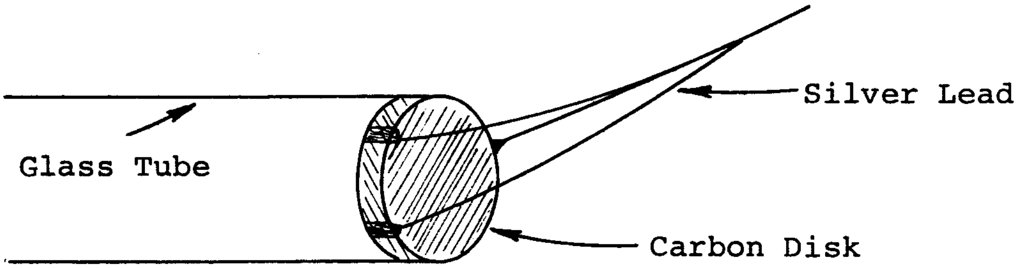


Figure 10. Carbon Electrode

Platinized Wire Gauze Electrodes

Two types of electrolytically platinized fine mesh screen were used: 150 mesh nickel screen and 80 mesh platinum—10% rhodium screen. The high area platinum coating was prepared by electrolytic reduction of chloroplatinic acid. (For details, see Appendix C.) In most cases, a group of four screens (designated, 4-ply) were used as an electrode. These screens were sealed together with a polyethylene frame (Figure 11).

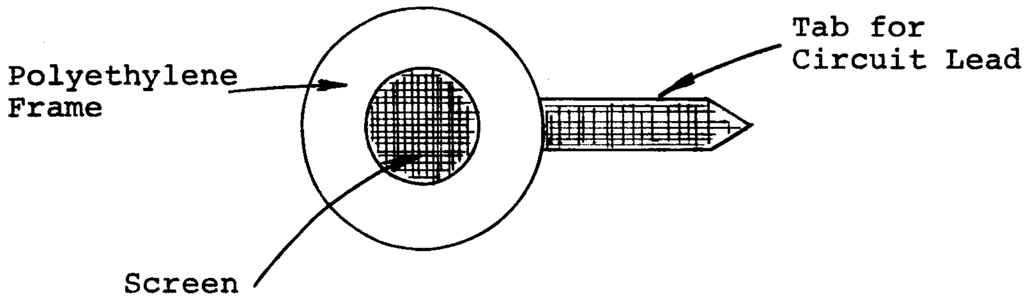


Figure 11. Screen Test Electrode

The face area of the electrode was 2 cm^2. The electrolytic platinum loading for such a group of four screens was 19 mg/(cm^2 face area).

The nickel substrate screens performed better than the platinum substrate screens. In part, this was due to the high nickel geometric wire area. The nickel had a geometric area of 2.45 $cm^2/(cm^2$ face area) versus 1.51 $cm^2/(cm^2$ face area) for the platinum screen. The platinized coating appeared to be blacker on the nickel than on the platinum. This may indicate that the nickel's coating was more porous and had a higher surface area. This would cause the nickel to give better kinetic rates for a given geometric area.

For some measurements, three or four small holes (1 mm in diameter) were drilled in the screens.

Teflon Containing Electrodes

Three Teflon bonded porous gas diffusion electrodes were used in this work. The electrodes were of the type described by Deibert[15] and the details of fabrication are in Appendix C. In general, the desired catalyst powder is mixed and mulled with an aqueous dispersion of finely divided Teflon particles. The resulting rubbery dough is rolled out to form a pancake (approximately 0.01 in. thick) which is pressed onto one side of a screen for support and current collection. Upon heating in an oven at 300°C, the electrode has a high porosity and is very non-wetting. These features allow the electrode to perform very well with gaseous reactants. For cell operation, the screen side of the electrode makes contact with the electrolyte.

The catalyst powders used were platinum, silver, and a carbon-silver mix. The catalyst loadings were as follows:

a) Platinum: 25 mg/cm^2
b) Silver: 12 mg/cm^2
c) Carbon: 5 mg/cm^2
Silver: 3 mg/cm^2

The carbon-silver and silver electrodes were expected to be selective oxygen electrodes. The platinum electrode was tested for comparison with the platinum screen electrodes.

Since bulk flow of electrolyte or reactant cannot take place through the very fine pores of these electrodes, three or four small holes (diameter: 1 mm) were drilled through the screens around the periphery. These electrodes were placed in a polyethylene frame as were the gauze electrodes. The exposed electrode face area was 2 cm^2.

Reference Electrodes

A Beckman fiber-junction saturated calomel electrode was used for a few measurements. However, this electrode gave erratic readings after immersion in potassium carbonate electrolyte for several hours. For this reason, a mercury-mercuric oxide reference electrode was prepared and used for most of the work. Aqueous potassium carbonate was used as the reference electrolyte, thereby eliminating liquid junction potentials when this electrolyte was also used for the test electrode.

The method of preparation for the Hg/HgO electrode was similar to the procedure of Ives and Janz[27]. Reagent grade mercuric oxide (red) was washed in boiling distilled water about six times. About two grams of the oxide was placed on a small pool of mercury. The electrode was connected to the test system with a potassium carbonate electrolyte bridge, and to the external circuit with a platinum lead from the mercury (Figure 12).

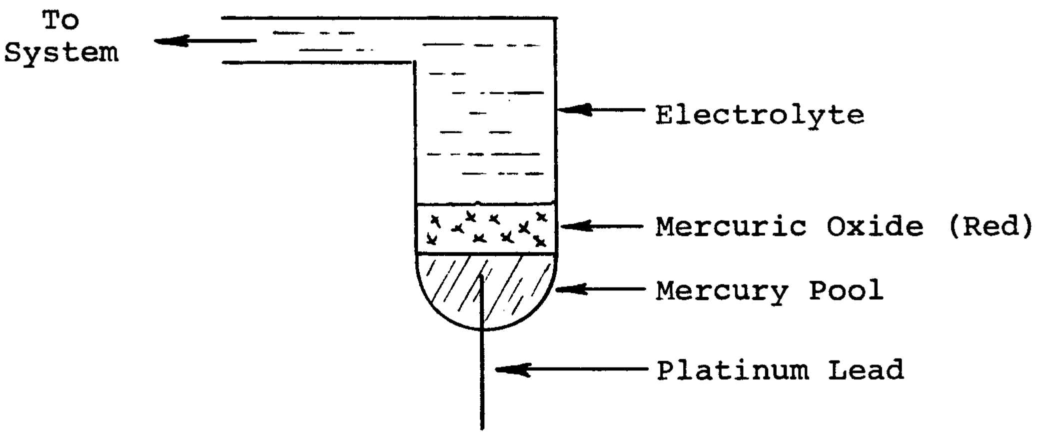


Figure 12. Hg/HgO Reference Electrode

C. Flow System

The flow system was designed for continuous flow of liquid and gas phases through the electrodes. The liquid phase was a solution of electrolyte and methanol. The gas phase was usually oxygen. Figure 13 (next page) is a diagram of the test electrode chamber. The two phases

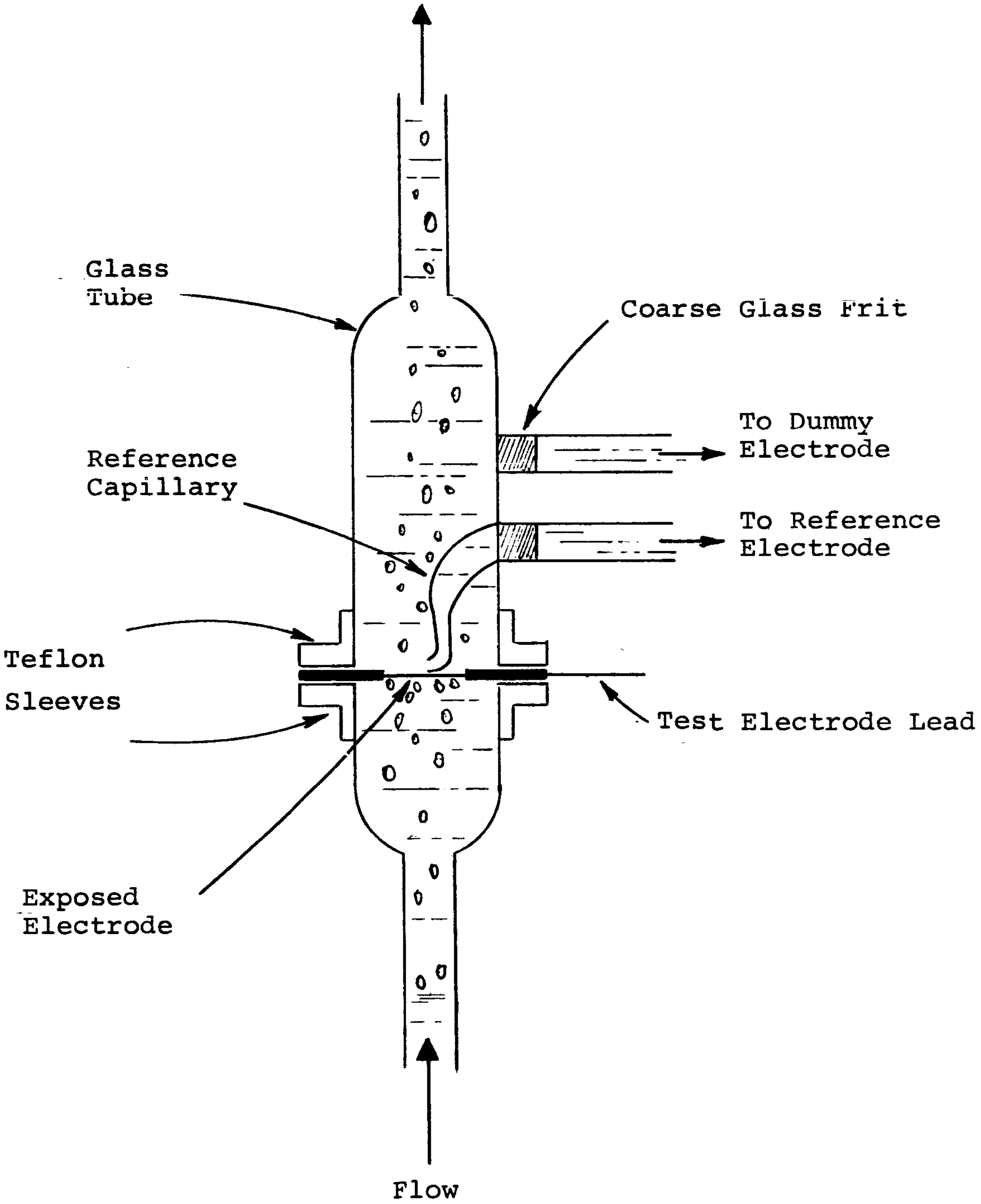


Figure 13. Test Electrode Chamber

were flowed up through the horizontally placed electrode (or electrodes). The glass chamber was constructed in two halves and had a diameter of 2 cm. Teflon sleeves were fitted over each half and the electrode was clamped between them. The electrodes had a polyethylene frame so that a tight seal could be formed between the Teflon and electrode. The exposed electrode area was 2 cm^2. A reference electrode capillary tube came to within about one millimeter of the electrode in order to eliminate electrolyte IR voltage drop from the potential measurements. The side tubes which lead to the dummy and reference electrode compartments contained a glass fritted disk to reduce diffusion from the flow system to these side compartments.

When operating with screen electrodes, the gas and liquid flowed through the fine mesh screen. When larger holes (1 mm diameter) were drilled in the screens, the gas flowed through these large holes. The purpose for these holes was to reduce the oxygen-platinum contact. For the Teflon-type electrodes, the fluids passed through three or four holes near the periphery of the electrode. The oxygen made good contact with these non-wettable Teflon electrodes because oxygen bubbles would accumulate below the electrode. The active, membrane side of the electrode was faced downward.

Figure 14 is a schematic diagram of the flow system. It consists of a flow loop and pump for each phase. The flow rate of each phase could be controlled independently. After the mixed phases passed through the test electrodes, they were allowed to separate in the settling reservoir. The gas was initially passed through a condenser to keep water and methanol from condensing in the flow loop. The gas was pumped back down where it again joined the liquid phase a few inches below the electrode chamber.

The system was constructed of glass; the connecting tubes were one-fourth inch in diameter. The total liquid volume of the system was 120 ml and the gas volume was about 75 ml. The system had appropriate drains and sampling ports fitted with no-air stoppers. A temperature bath was drawn up around most of the flow system. The pumps were located above the bath. The gas pump was a Will's Neptune Dyna-Pump. The liquid metering pump was a Micro-Bellows Pump made by Research Appliance Company. The separating reservoir was located at the bottom of the temperature bath, so that it could be stirred from beneath the bath by means of a magnetic stirrer. The dummy electrode was located within the temperature bath but the reference electrode was not. The electrolyte was cooled somewhat when it passed out of the hot bath to be pumped. The actual electrolyte temperature at the point

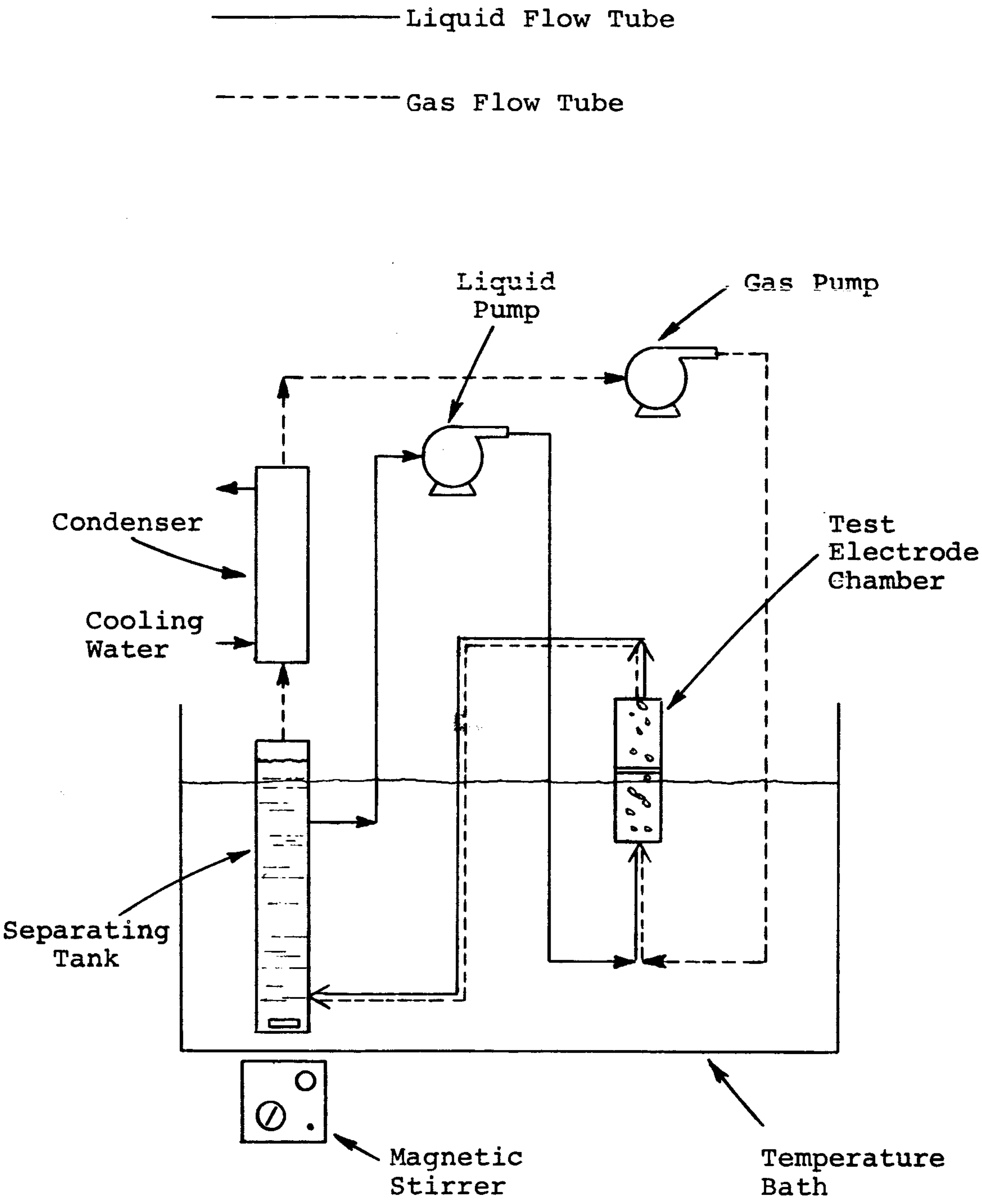


Figure 14. Flow System

of the test electrode was measured for various hot bath temperatures.

Unless otherwise noted the data was obtained at a test temperature of 70°C. The liquid flow rate was 50 ml/min, or a flow velocity of 25 cm/min at the electrode. The gas flow rate was 33 ml/min, or a flow velocity of 17 cm/min at the electrode.

D. Current Measurements

Figure 15 shows the circuitry used when a single electrode was being tested.

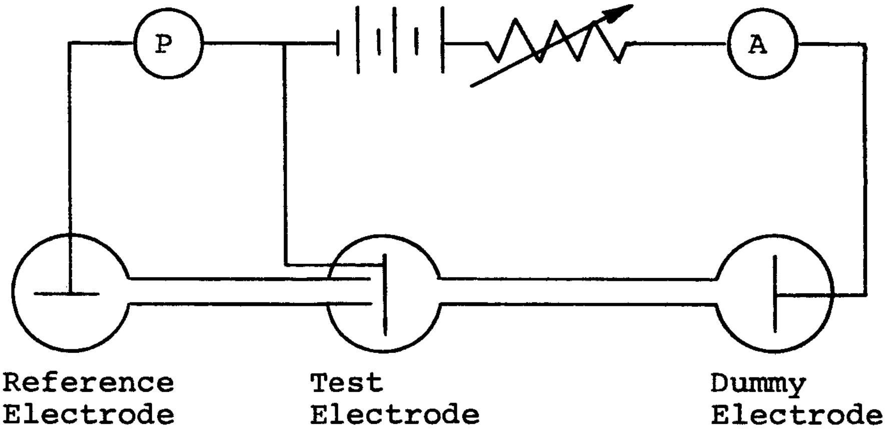


Figure 15. Single Test Electrode Circuitry

The measurements were made by applying a constant current to the test electrode. This current (which also passed through the dummy electrode) was controlled by a battery and rheostat. The current was measured with a

Weston Model 91 multirange ammeter accurate to $\frac{1}{2}$ % of full scale. A reference electrode was connected to the test electrode by means of a Luggin capillary. The potential difference between the test electrode and the reference electrode was measured by means of a Sargent recording potentiometer. Of course, virtually no current flowed through the reference electrode.

Either hydrogen or oxygen gas is produced in the dummy compartment—depending on whether a cathodic or anodic current is passing through it. This gas was removed after a couple of milliliters had accumulated; it was withdrawn with a syringe which was inserted through a "No-Air" stopper located at the top of the dummy compartment. Similarly, the oxygen gas pressure in the flow system was maintained to within 5% of one atmosphere by periodic addition of oxygen via a syringe. The electrode performance was found to be insensitive to pressure variations of this magnitude. No carbon dioxide gas was produced since it reacted with the electrolyte to produce bicarbonate. However, the amount of reaction was so small that the electrolyte composition could be considered to be invariant. At the most, 0.005 molar bicarbonate was formed—compared to 5.6 molar carbonate.

Figure 16 shows the circuitry used when an anode and cathode were tested simultaneously. In this case, the anode and cathode were placed next to each other in the flow path. The distance between the electrodes was one millimeter.

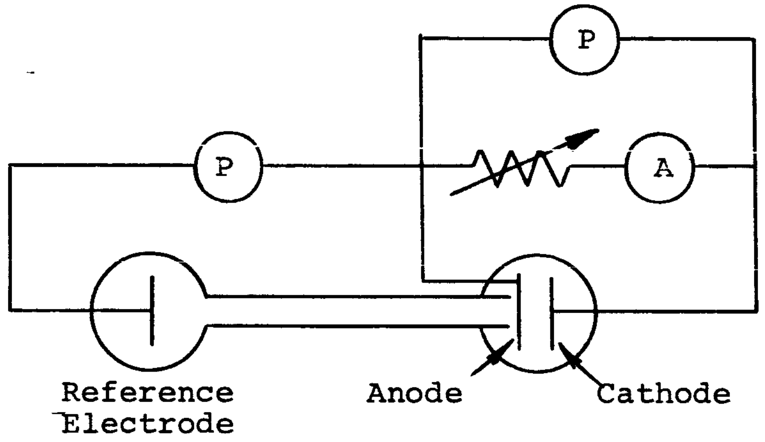


Figure 16. Cell Test Circuitry

With this complete cell, no outside power supply was needed to pass current through the electrodes. The potential was measured between the two test electrodes, as well as between the reference electrode and the test electrode which was nearest to the Luggin capillary.

When a given current was applied to the test electrode, the potential usually approached a steady value in an asymptotic manner. This steady potential was usually obtained within two minutes. Presumably, this delay was the time needed for the adsorbed reactant to achieve a new "steady state" coverage on the catalyst surface.

In general, the performance of the electrodes tended to deteriorate with use. In the case of the platinized screen electrodes, the reduction in performance appeared to be proportional to the coulombs passed through the electrode. The most likely explanation is that carbon monoxide slowly formed to adsorb and block catalyst sites. The electrode could be almost completely reactivated by either of two methods. However, there was still a general deterioration over a period of several days, since the reactivation was only approximately 95% effective. The rate of deterioration became rather small after several days use. Comparative measurements were usually made during this period when reproducibility was reasonable. The two methods for reactivation were (1) to evolve oxygen by drawing a large anodic current or (2) to expose the electrode to air for a couple of hours. Either process would be expected to oxidize adsorbed carbon monoxide.

The Teflon electrodes' deterioration was greater since no method was found for their reactivation. However, these electrodes did achieve reasonable stability after an initial sharp drop in activity. These oxygen electrodes deteriorated in a manner different from that of the screen electrodes. The decreasing activity occurred only at the higher current densities; this indicates that increasing diffusional resistance was the cause. The electrode membrane became more wettable with use. This would reduce the oxygen contact and cause diffusional polarization. Another possibility is that the electrode's pores gradually filled with electrolyte or water——thereby decreasing the diffusion rate of the gas. Measurements were made during the initial highly activated period, as well as during the later stable period. Of course, all comparative data was taken during the more stable period.

E. Reaction Rate Measurements

In order to determine the direct reaction rate between methanol and oxygen, the methanol consumption was measured by chemical analysis. Generally, the test electrode was operated under steady conditions for about two hours. During this period, the electrolyte was recirculated, and the net consumption of methanol equivalents (usually less than 10%) was measured by a titration procedure. Therefore, the electrode was not actually run under steady-state conditions. However, a 10% change in methanol concentration would not produce any noticeable change in electrode current or reaction rate.

The methanol concentration in the electrolyte was measured before and after the run. The consumption of methanol equivalents was determined as the product of the change in concentration and the liquid volume of the system. At operating temperatures, the vaporization of methanol into the gas phase was significant. Therefore, the system was cooled before the methanol analysis was made. Also, the vaporized methanol was redissolved by mixing and circulation for one-half hour at room temperature before each analysis.

The complete procedure may be stated as follows. The liquid loop of the system was filled with about 122 ml of aqueous 50 (wt)% potassium carbonate electrolyte. As the electrolyte was stirred and circulated, a syringe was used to add 2 ml potassium carbonate containing an analytic quantity of methanol. The gas portion of the system was filled with oxygen and the system was closed. The electrolyte was stirred and recirculated for one-half hour to mix it well. The oxygen gas was then recirculated through the liquid for one-half hour before a pair of analysis samples (2 ml each) were removed. The temperature bath was then heated to the desired temperature. The run was begun by circulating the oxygen gas and by drawing the desired current. During the run, oxygen gas was resupplied to the flow system as described in section III.D. At the end of a measured time interval, the gas flow and current were stopped, and the temperature bath was removed. After the electrolyte cooled to room temperature, the oxygen was again circulated for one-half hour before a final pair of analysis samples were removed.

The first analysis was used to calculate the initial concentration, as well as the volume of electrolyte. The volume could be calculated since a known amount of methanol was added to the system. A correction was made for the small amount of methanol consumed during the circulation of oxygen at room temperature. This correction also had to be applied to the final analysis. The amount of the correction was determined by separately measuring the methanol consumption during room temperature circulation. Appendix E contains a sample calculation of the methanol equivalents consumed per unit time. This reaction rate was expressed in milliamperes (1 milliampere = 1.037×10^{-8} equivalents per sec). In this way, the total methanol reaction rate could be directly compared to the measured current.

The homogeneous reaction rate between methanol and oxygen was measured by circulating the electrolyte (with methanol) and oxygen for two hours with the electrode removed from the system. The reaction rate was measured for 0.01 molar and 0.04 molar methanol. In both cases there was no methanol consumption. Therefore, under these conditions the homogeneous reaction rate between methanol and oxygen was found to be zero (within experimental error).

There was a small methanol "leak" through the rubber of the gas pump diaphragm. With 0.04 molar methanol, the methanol leaked out at the rate of 3.7 ma. No leak could be detected with 0.01 molar methanol. Therefore, all reaction rate measurements which were made with 0.04 molar methanol had to be corrected for the 3.7 ma leak rate. The leak rate was measured by circulating nitrogen instead of oxygen.

Diffusion of methanol to (and from) the dummy and reference side compartments was a problem. When the methanol concentration in the side compartment was equal to the initial methanol concentration in the main flow system, the measured values for the methanol reaction rate were found to be up to 10% too low. This was due to methanol diffusion into the flow system. By using a methanol concentration in the side compartment which was approximately equal to the expected final concentration in the flow system, this error was considerably reduced. The largest errors were then in the analysis procedure. (See Appendix F for a more detailed discussion of the errors.)

F. Chemical Analysis

Methanol

The methanol concentration of the electrolyte was measured by a titration procedure[28]. This involved the methanol oxidation by an excess of potassium dichromate. The excess was then back-titrated with a standard ferrous solution. The methanol is oxidized to carbon dioxide. Therefore, this analysis actually measures the total oxidizable equivalents in the electrolyte. For a complete reaction rate run, the difference between the initial and final analysis actually gives the number of equivalents consumed, regardless of the methanol oxidation product.

A 2 ml electrolyte sample was used for each analysis. This was added to a flask containing a pipetted sample at dichromate solution. After careful addition of concentrated sulfuric acid through a condenser, the solution was refluxed over a boiling water bath for 30 to 45 minutes to completely oxidize the methanol. The solution was then cooled and phenylanthranilic acid was added as indicator before the titration with ferrous sulfate. The details of this procedure are in Appendix D.

This analysis gave an error in the reaction rate of about 8%, or a minimum error of 1 ma (See Appendix F).

Formate

The amount of formate formed in the electrolytic and catalytic oxidation of methanol was measured for the platinized screen electrode. A 2 ml sample of the electrolyte was diluted with water and then boiled for 45 minutes to evaporate off all methanol and formaldehyde. Dichromate was then added and the solution treated as for methanol analysis. Tests showed that no formate was lost during evaporation.

Formaldehyde

The electrolyte solutions were analyzed for formaldehyde content by the chromotropic acid colorimetric method[45]. A deep violet color is produced by a reaction of formaldehyde with chromotropic acid (11:8-dihydroxynaphthalene-3:6-sulfonic acid) in sulfuric acid. A small portion of electrolyte was added to a solution of sulfuric acid and chromotropic acid. The mixture was heated for 30 minutes to develop full color. The depth of color was then compared by eye to several known samples. The amount of formaldehyde in the electrolyte was very small, so that measurement by a light adsorption instrument was not necessary. This method will detect traces of formaldehyde down to 5×10^{-7} gm/ml. For the details of this analysis, see Appendix D.

G. Porous Carbon Measurements

The current measurements for the porous carbon electrode were not made with the flow system described in section C. Figure 17 shows the apparatus used. The carbon electrode (placed at the end of a glass tube) was immersed in a solution of electrolyte and methanol. Oxygen gas was flowed through the carbon disk and into the electrolyte. A platinized platinum screen anode was placed about 0.5 cm from the carbon disk. The solution was heated with a hot plate.

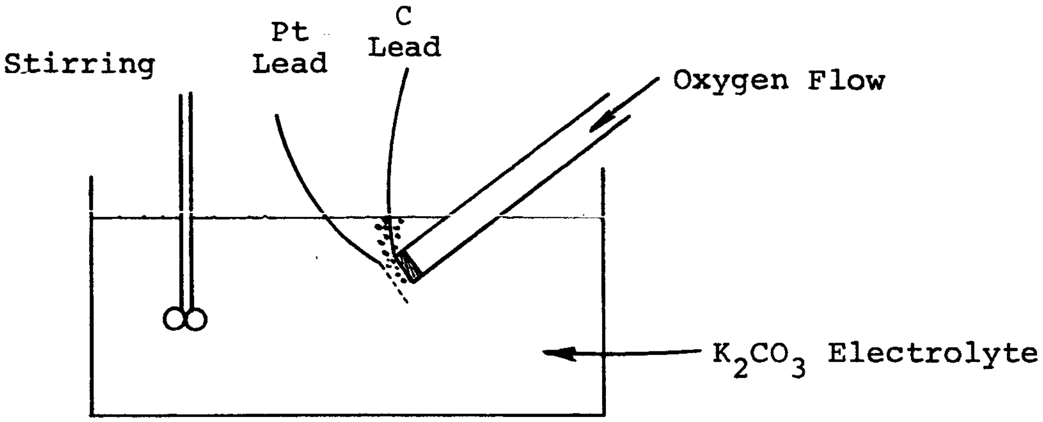


Figure 17. Carbon Electrode Test Apparatus

IV. RESULTS AND DISCUSSION OF RESULTS

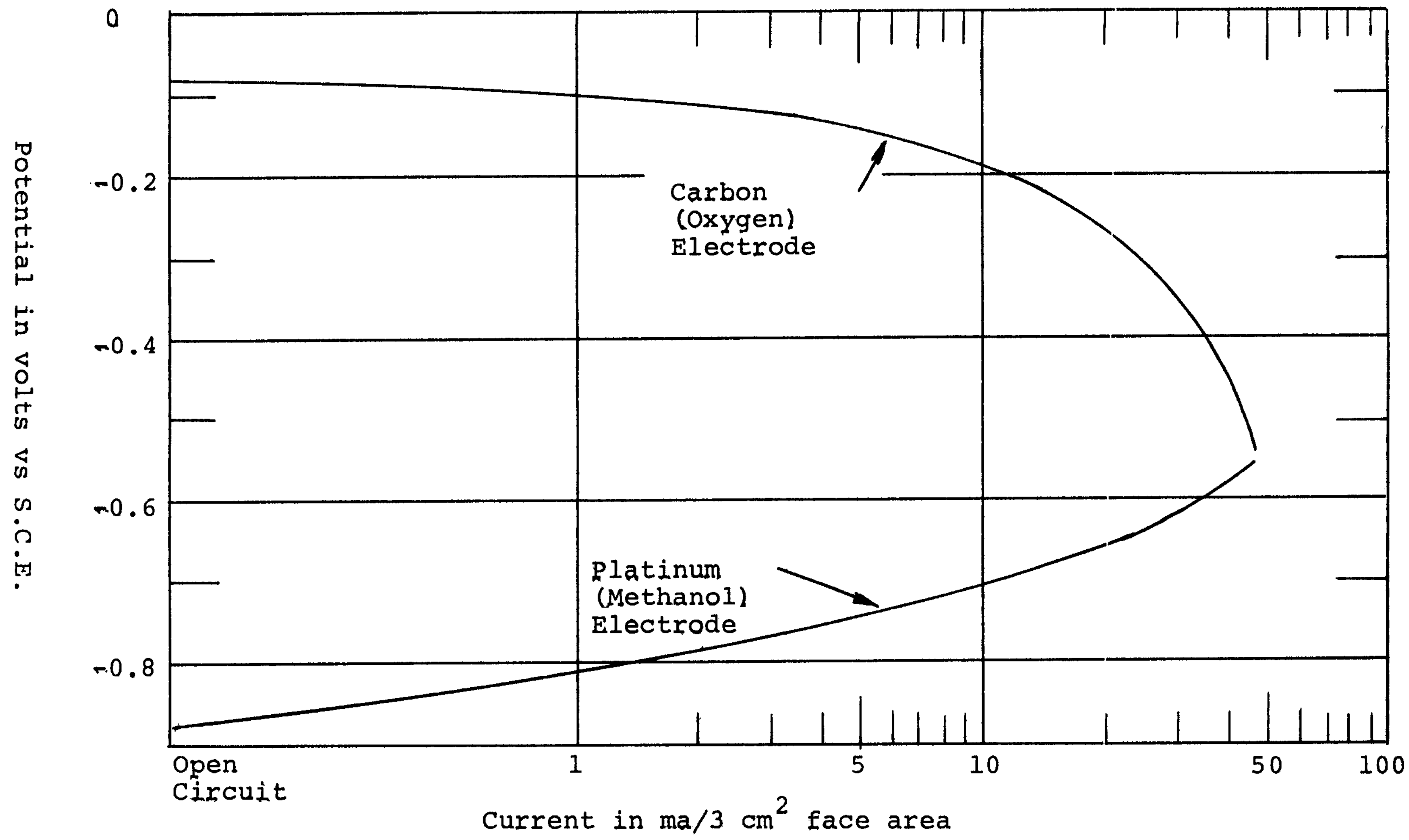
A. Polarization Curves

1. Porous Carbon Cathode

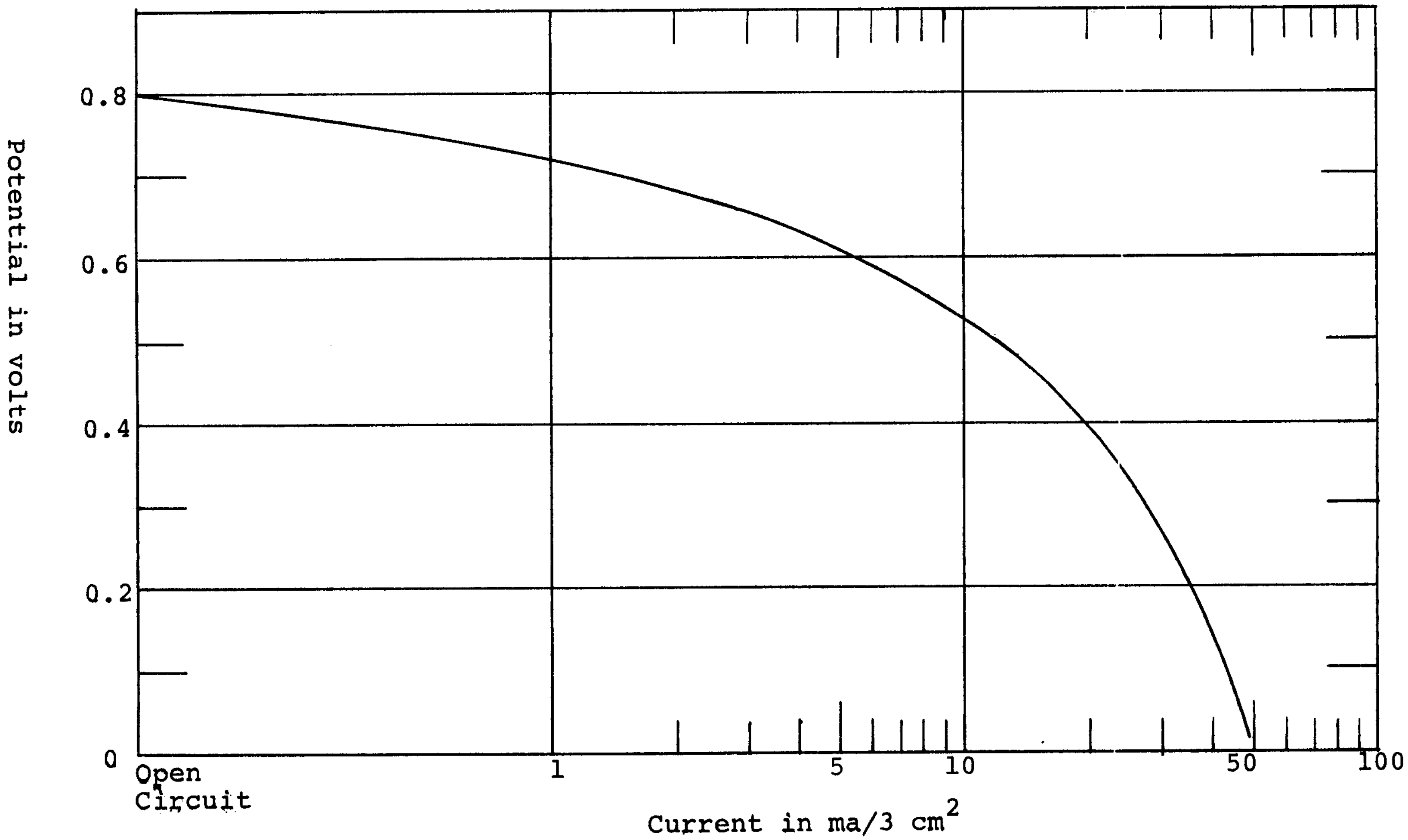
A porous carbon cathode was operated with a platinum screen anode in 50% potassium carbonate at 87°C. The carbon cathode was operated by bubbling oxygen gas through the electrode into the electrolyte. (See description in section III.G.) The methanol concentration in the electrolyte was 0.1 M. The half cell polarization curves for the reaction of methanol on the platinum, and oxygen on the carbon, are shown on Graph 1. Graph 2 shows the net cell potential difference between these two half cells.

The half cell polarization curve for carbon shown on Graph 1 was obtained during mixed-feed operation, since methanol was dissolved in the electrolyte. However, exactly the same half cell curve was obtained when no methanol was in the electrolyte. This indicates that methanol is not active at carbon, and that carbon is a very selective oxygen catalyst.

Unfortunately, the current density for this carbon electrode was rather low (a maximum of 17 ma/cm^2 was drawn. This was undoubtedly due to severe channeling of the oxygen gas through the larger carbon pores. The oxygen diffusion into the liquid filled pores was evidently much too low to



Graph 1. Half cell Potentials for Carbon Disk Cathode and Platinum Screen Anode; 87°C; 1 M Methanol, K_2CO_3 electrolyte.



Graph 2. Cell Potential for Carbon Disk Cathode and Platinum Screen Anode; 87°C; 1 M methanol; K_2CO_3 electrolyte.

keep all of the carbon surface supplied with reactant. Changes in the oxygen flow paths through the porous structure caused a variation in the current density, which hurt the reproducibility of the electrode. As a result of these difficulties, no detailed study of this electrode was made.

Reti[41] and Kordish[29] report that the performance of carbon cathodes in potassium hydroxide electrolyte is improved by impregnating the carbon with a silver-aluminum catalyst. This improvement is attributed to the action of the silver in decomposing the hydrogen peroxide formed from the oxygen by carbon catalysis, resulting in a more favorable potential.

$$H_2O + O_2 + 2e^- \underset{\text{catalysis}}{\underset{\text{carbon}}{=\!=\!=\!=}} HO_2^- + OH^-$$

$$HO_2^- \underset{\text{catalysis}}{\underset{\text{silver}}{=\!=\!=\!=}} OH^- + \frac{1}{2} O_2$$

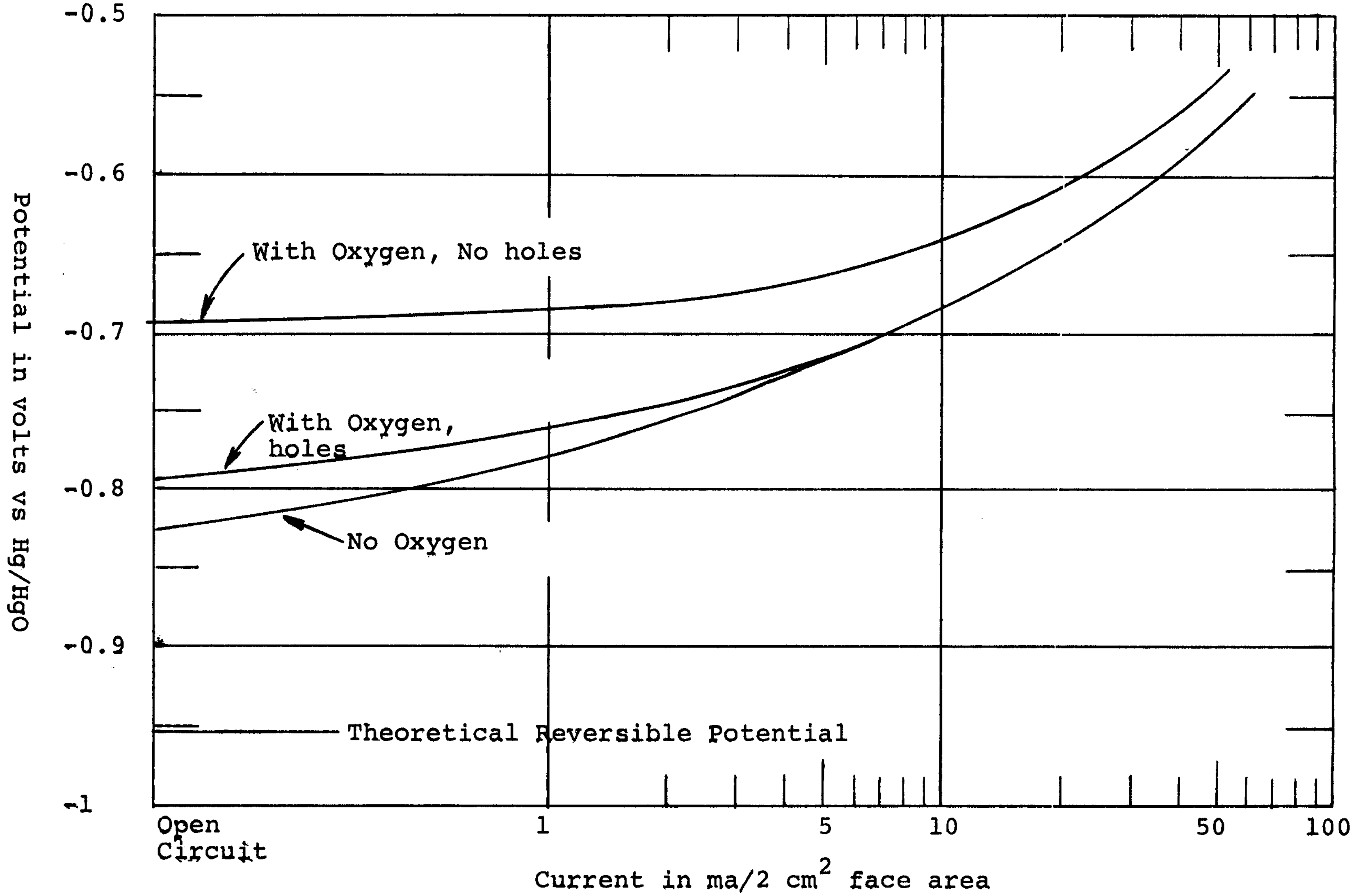
The possibility of effecting a similar improvement here was explored. Carbon-silver electrodes were made by the procedure of Reti and tested in potassium carbonate electrolyte without methanol. No potential improvement resulted, presumably because hydrogen peroxide is very unstable in hot potassium carbonate electrolyte, and decomposes without requiring silver catalysis. Hydrogen peroxide was found to be unstable in potassium carbonate by observing that oxygen was vigorously evolved when small amounts of a solution of HO_2^- were added to this electrolyte.

2. Platinized Screen Anodes

Effect of Oxygen and Holes

The holed platinized screen was the most successful anode found in this work. Although this electrode was not completely selective for methanol oxidation, its mixed-feed performance was very good in comparison with single-feed operation. The performance of the platinized screen was found to be greatly improved by designing the electrodes with two or three 1 mm holes through their faces. Extensive tests were made for the screen electrode with, and without, the holes.

Half cell polarization curves for the platinized screens are shown in Graph 3. The current is expressed in ma/(2 cm^2 face area). Curves are presented for single-feed methanol operation with the holed screen, and mixed-feed operation with the non-holed screen. The methanol concentration was 0.04 M and the electrolyte was 50 (wt)% potassium carbonate at 70°C. The single-feed (methanol) polarization curve was not affected by the presence of holes. However, there was a large difference between the holed and non-holed electrode during mixed-feed operation



Graph 3. Effect of Oxygen on Platinized Screen Anode; Platinized Nickel (4-ply); 70°C; 0.04 M methanol; K_2CO_3 electrolyte.

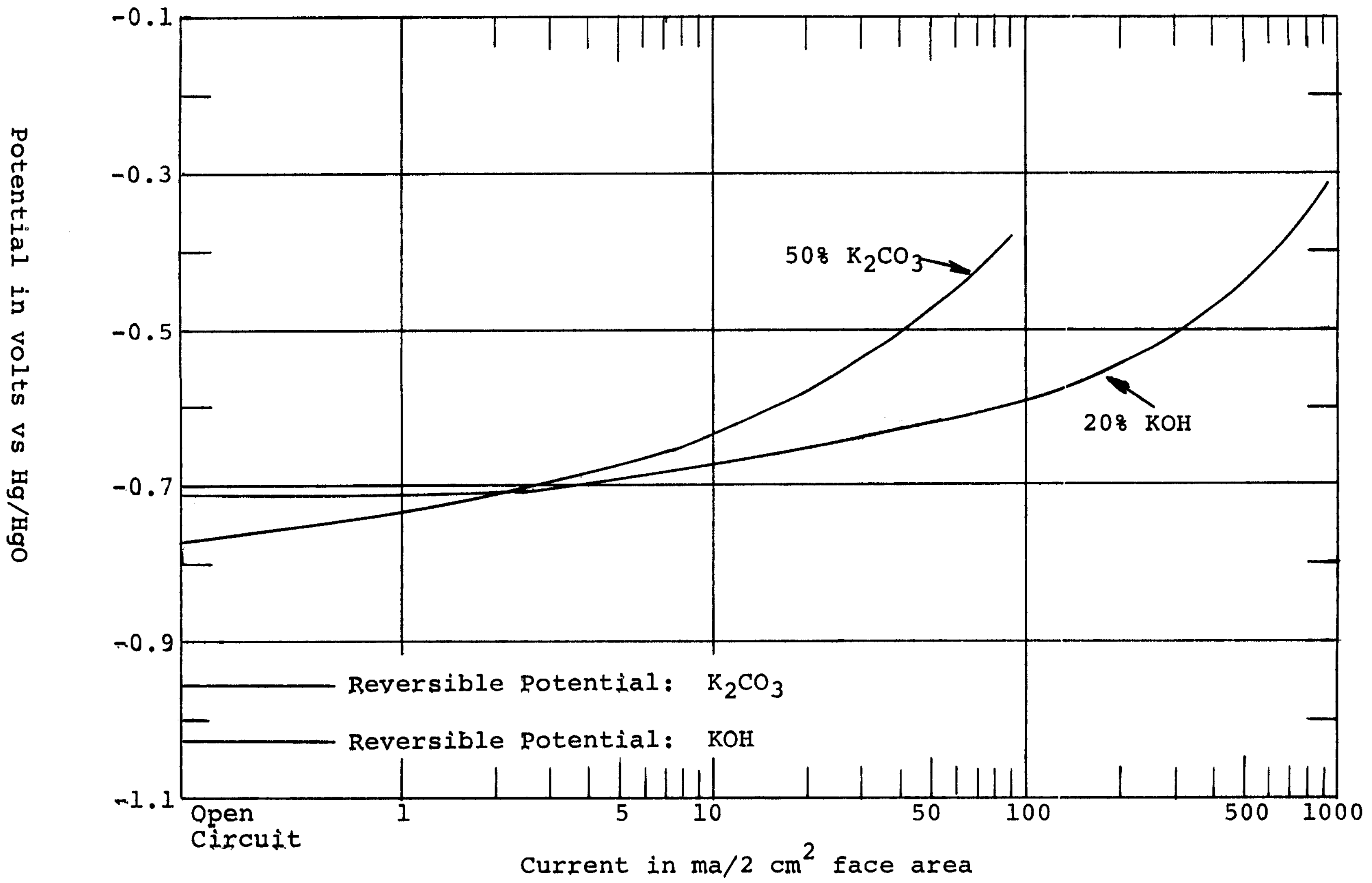
(curves labeled "with oxygen" in Graph 3). Compared to single-feed operation, the open circuit polarization caused by the oxygen was only 0.03 v for the holed electrode, but was 0.13 v for the non-holed electrode. Above 4 ma, there was no difference between the single and mixed-feed polarization curves for the holed electrode. The holes improved the mixed-feed performance of the electrode because the oxygen bubbles flowed through the large holes instead of through the fine mesh screen, reducing the oxygen mass transfer rate to the screen surface.

These electrodes, and the relation between single and mixed-feed operation, are studied in more detail in section IV.B.

Effect of Electrolyte

The performance of a platinized nickel electrode (with holes) in potassium carbonate electrolyte is compared with potassium hydroxide electrolyte in Graph 4. Both curves were obtained under mixed-feed operation, but the effect of the oxygen on the electrode polarization was negligible.

Both of these curves were measured with a Hg/HgO reference electrode containing potassium carbonate electrolyte. When the carbonate reference was used with the hydroxide test electrolyte, an error was brought into the potential readings due to the difference in pH and the



Graph 4. Mixed-Feed Screen Anode Comparison of Hydroxide and Carbonate Electrolytes; Platinized Nickel (3-ply) Screen with hole; 70°C; 0.5 M methanol.

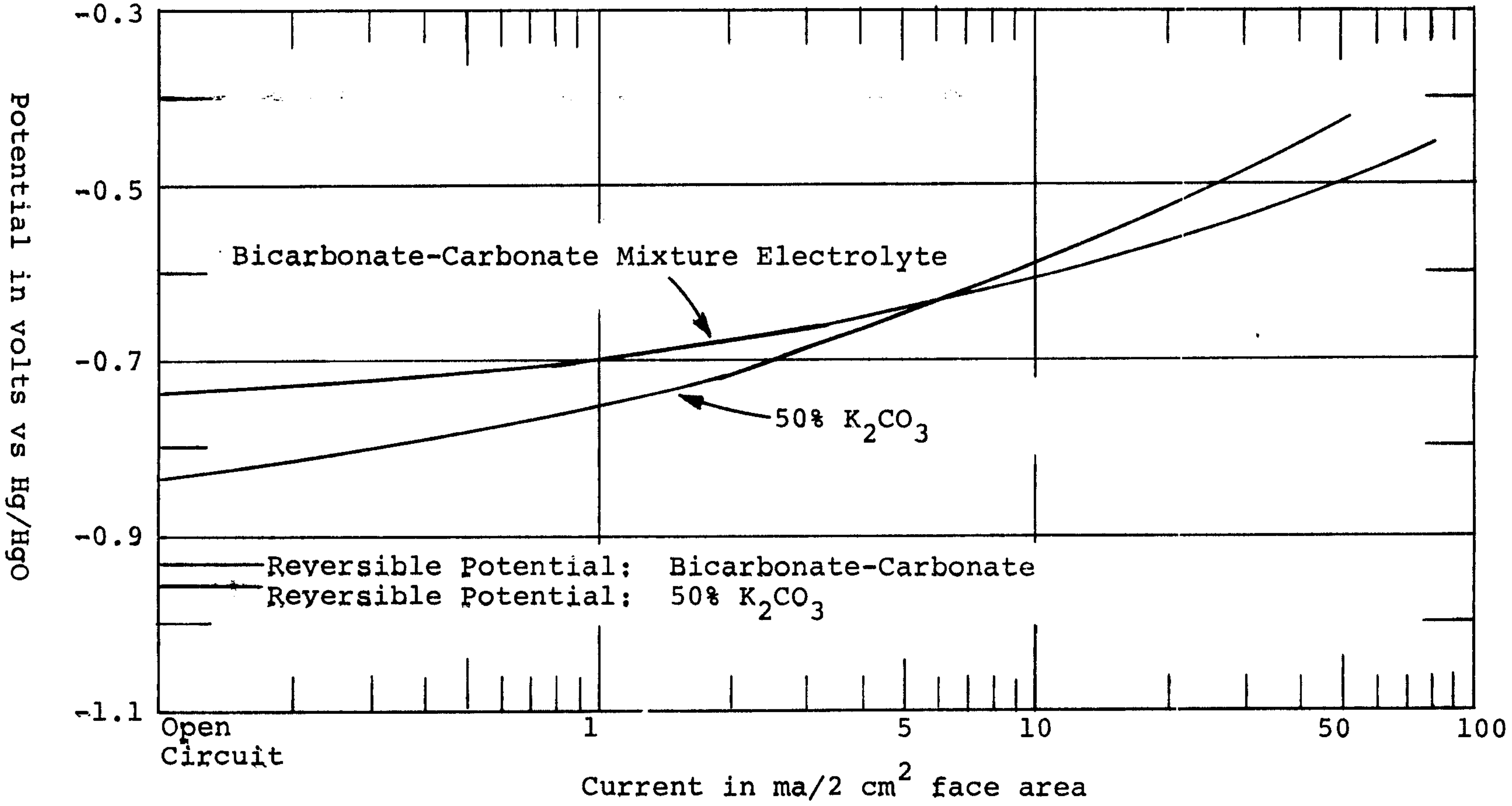
liquid junction potential. In order to correct for this error, all potentials with hydroxide electrolyte have been made less negative by 0.10 v (see Appendix A).

The thermodynamic reversible potential is more favorable in potassium hydroxide than in potassium carbonate because of the subsequent reaction of the carbon dioxide product with these electrolytes: The free energy gain in potassium hydroxide is much greater than in potassium carbonate. Nevertheless, the experimental potential was better in the case of the carbonate electrolyte. The open circuit polarization from the reversible potential was 0.31 v in hydroxide, but was only 0.18 v in carbonate.

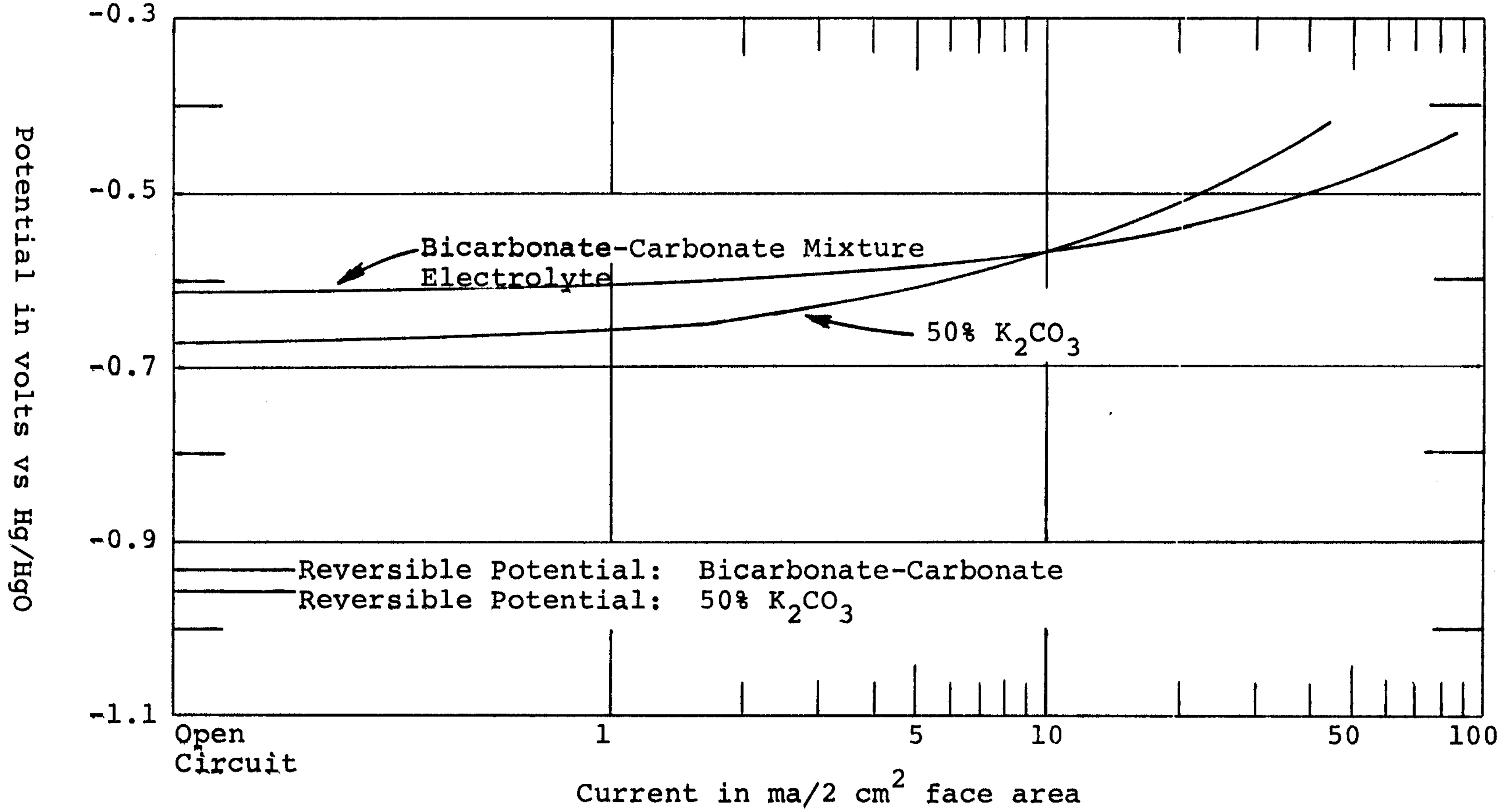
Despite the poor open circuit potential in hydroxide, the performance of this electrolyte was excellent when current was drawn: The maximum current in hydroxide was almost ten times the maximum current in carbonate. This indicates that the polarization in carbonate was not due to a diffusion limiting step at this methanol concentration, since the diffusion rate of methanol in hydroxide would not be expected to be ten times the rate in carbonate.

The platinized screen electrode was also tested in the carbonate-bicarbonate "mixture" electrolyte (see section II.C. and Appendix B). The equilibrium carbon dioxide vapor pressure of this electrolyte at 70°C is 0.08 atmospheres. This electrolyte was purposely designed to reject carbon dioxide at 0.08 atmospheres because this was the estimated maximum pressure of CO_2 in the gas phase of a methanol-air cell.

Since this electrolyte was acidic enough to attack nickel, platinized platinum screens were used instead of platinized nickel. The performance of a non-holed electrode in this electrolyte is compared with the carbonate electrolyte during both methanol single-feed (Graph 5), and mixed-feed (Graph 6). The complete polarization curve in the mixture electrolyte behaved somewhat like that in the hydroxide electrolyte. That is, at low current densities the polarization in the mixture electrolyte was greater than in carbonate, but as the current was increased the polarization became less than in the carbonate. For a given potential at high polarizations, the mixture electrolyte allowed almost twice as much current as the carbonate. The results on Graph 6 indicate that the effect of oxygen on the electrode polarization was about the same in both electrolytes. This would indicate that most of the qualitative conclusions in section B. for this mixed-feed electrode in carbonate electrolyte, are probably also valid in the carbonate-bicarbonate mixture electrolyte.



Graph 5. Single-Feed Screen Anode Comparison of Carbonate and Mixture Electrolytes; Platinized Platinum (2-ply) Screen with no holes; 70°C; 0.1 M methanol.

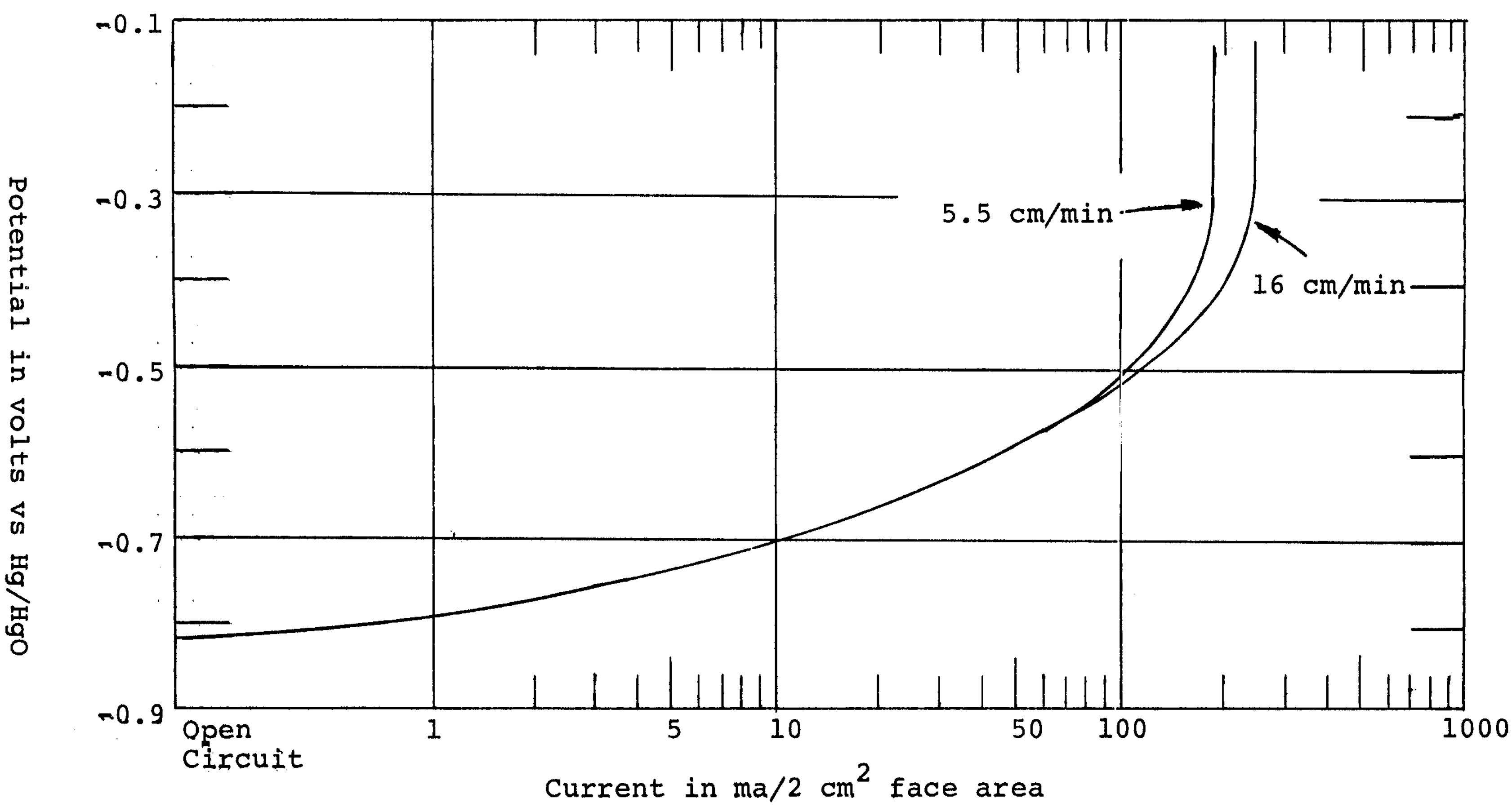


Graph 6. Mixed-Feed Screen Anode Comparison of Carbonate and Mixture Electrolytes: Platinized Platinum (2-ply) screen with no holes; 70°C; 0.1 M methanol.

Effect of Flow Rate and Diffusion Limitations

Polarization curves for the screen electrode were measured at two electrolyte flow velocities: 5.5 cm/min and 16 cm/min. This data was expected to indicate whether or not diffusion of methanol to the screen electrode was an important rate limiting step. The polarization curves, shown on Graph 7, were obtained with a methanol concentration of 0.01 M in carbonate electrolyte. At currents less than 100 ma, the polarization was identical for the two flow rates, and was probably caused by a chemical kinetics rate limiting step called "activation polarization." The slope of the curve at these low currents was 0.09 v per decade, which roughly corresponds to the slope expected from the Tafel equation[40].

At high currents, the flow rate did have an effect on the polarization, which is the behavior to be expected if the final polarization was caused by a diffusion rate limiting step. The limiting current approaches 190 ma for the flow rate of 5.5 cm/min and about 250 ma for 16 cm/min. In order to judge whether these maximum currents are really diffusion limiting currents, some approximate calculations of the rate of methanol mass transfer to the screens have been made in Appendix G. At 5.5 cm/min and 16 cm/min, the calculated limiting currents are 143 ma and 216 ma, respectively. The ratio of



Graph 7. Effect of Flow Rate on Screen Anode; Platinized nickel (4 ply) screen; Single Feed; 70°C; 0.01 M methanol; K_2CO_3 electrolyte.

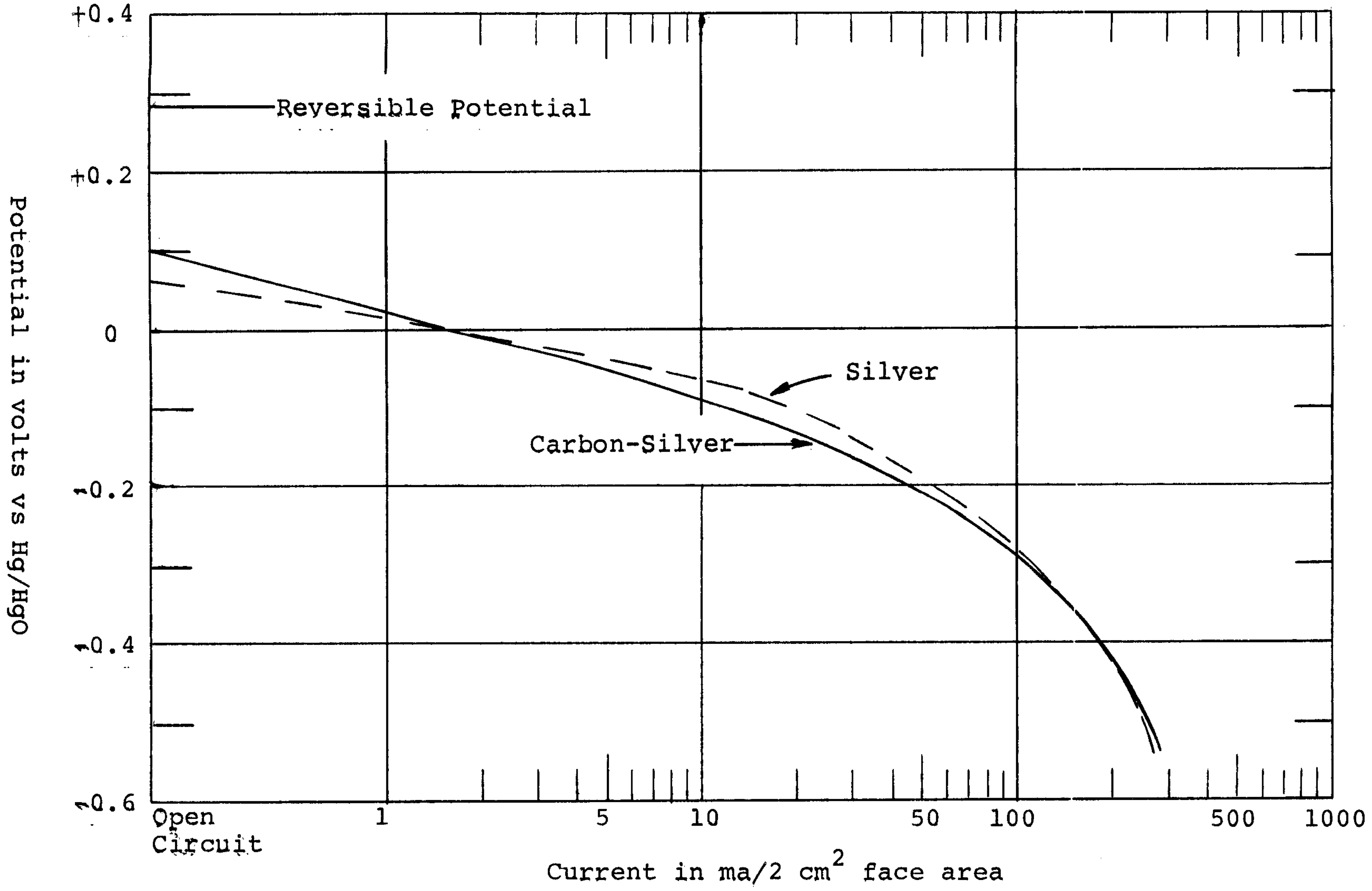
the calculated currents is 0.66 compared with an experimental ratio of 0.75. This rough agreement is a strong indication that these maximum currents are indeed diffusion limiting currents.

The diffusion limiting current was found to be directly proportional to the reactant concentration at low concentrations. This is indicated by the limiting currents for formate and methanol oxidation in Graph 39. The diffusion limiting current was tripled by a three-fold increase in the formate concentration. The limiting currents were about 100 ma and 300 ma versus calculated values of 85 ma and 255 ma, respectively. Furthermore, the methanol limiting current (also Graph 39) was three times the formate limiting current for equal molar concentrations (about 300 ma and 100 ma, respectively). This would be expected for a diffusion limiting current, since there are six equivalents per molecule of methanol, versus only two for formate.

Despite the results of the preceding paragraphs, the polarization of the screen electrodes was found to not be caused by diffusion limitations when very high methanol concentrations were used. The polarization curve in Graph 4 for the carbonate electrolyte with a methanol concentration of 0.5 M can be taken as an example; the calculated limiting current is 8,700 ma, compared with the experimental value of about 100 ma. In this case other factors are undoubtedly causing the polarization, such as an adsorption rate limiting step. Since this electrode was not as freshly prepared as the electrode of Graph 7, the surface could be partially blocked by carbon monoxide adsorption.

3. Silver and Carbon Teflon Cathodes Polarization and Selectivity

Two Teflon bonded electrodes performed well as oxygen electrodes: silver, and carbon-silver catalyst electrodes. The oxygen single-feed polarization curves for these electrodes in carbonate electrolyte are presented on Graph 8. The electrodes were newly prepared, so their activity was at a maximum. The most striking feature is the similarity between the polarization of the two electrodes. This similarity indicates that "diffusion," rather than "activation," polarization was controlling the performance of the electrode, since the electrochemical activity of the two catalyst systems would not be expected to be identical. The diffusion of oxygen through the pores of the membrane is probably rate controlling because the pore characteristics of the two electrodes are likely to be very similar. Both electrodes have the same volume ratio of catalyst particles to Teflon particles, and both silver and carbon particles are about 100 to 200 Å in size. Within the membrane, the small catalyst particles probably surround the Teflon particles (1000 Å) to form a catalyst "ball."



Graph 8. Comparison of Silver and Carbon-Silver Teflon Cathodes; Single-Feed Oxygen; 70°C; K_2CO_3 electrolyte.

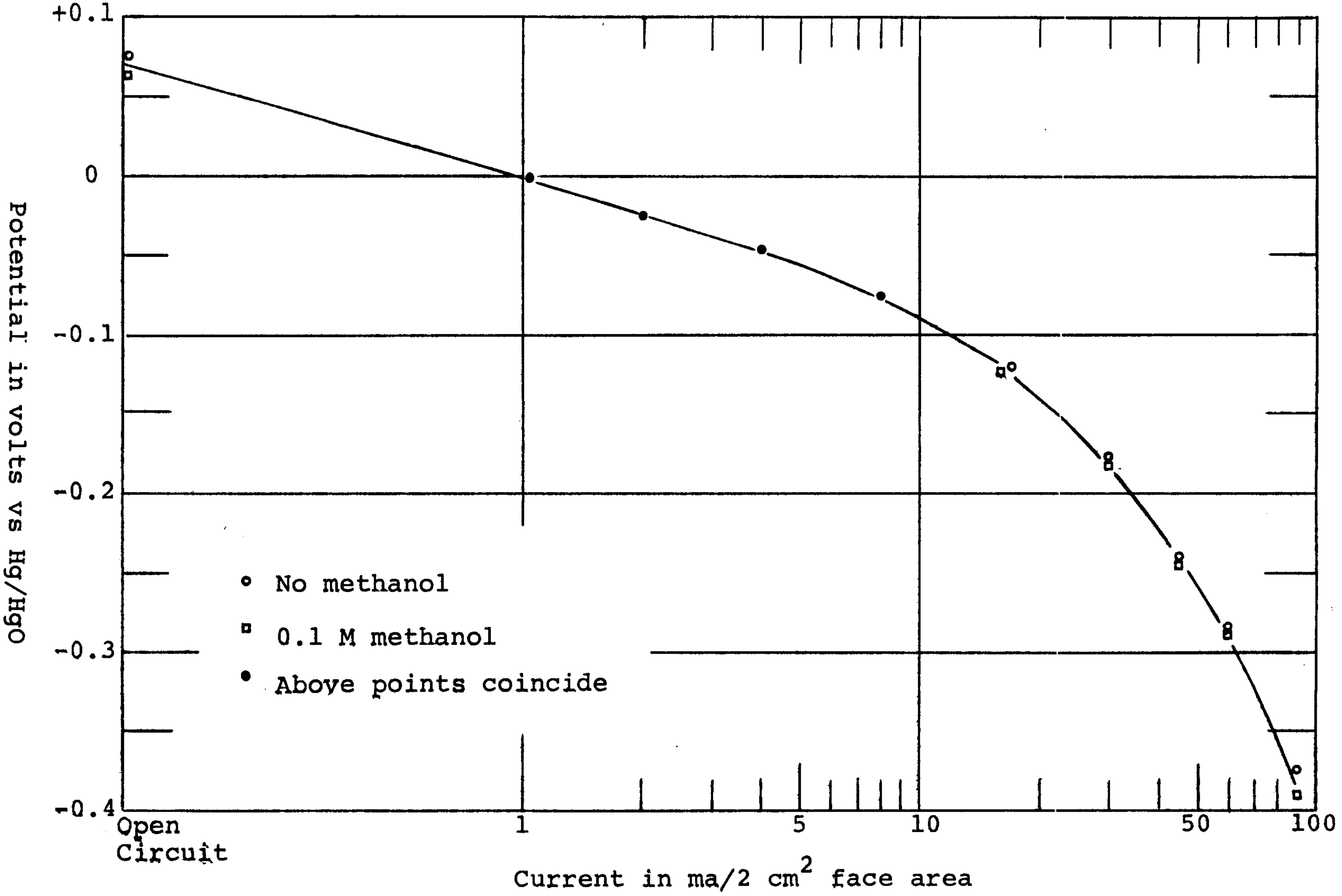
Contact between these balls permits the membrane to be conducting and the voids created between the balls form the porous structure for diffusion. Then, the nature and size of the pores would be about the same for both carbon and silver electrodes.

As discussed in section III.D., the polarization of these electrodes increased with use. This added polarization was most likely due to a decrease in the pore diffusion rate. The pores may "collapse," or possibly fill with liquid as the electrode is used. An attempt to reactivate these electrodes by heating them at 300°C for an hour was unsuccessful.

Graph 9 shows the performance of the silver-Teflon oxygen electrode after the initial deactivation period. At a given potential, the current was reduced to about two-thirds of the current obtained when the electrode was first used. This graph also shows that the methanol had no effect on the oxygen polarization curve: Measurement points taken when no methanol was in the electrolyte coincide with the points obtained in 0.1 M methanol.

Attempts were made to operate the silver electrode as a single-feed methanol anode, however, no methanol anodic current could be drawn.

Therefore, silver appears to be an extremely selective oxygen electrode. The methanol does not react electrochemically at the silver, nor does it interfere with the

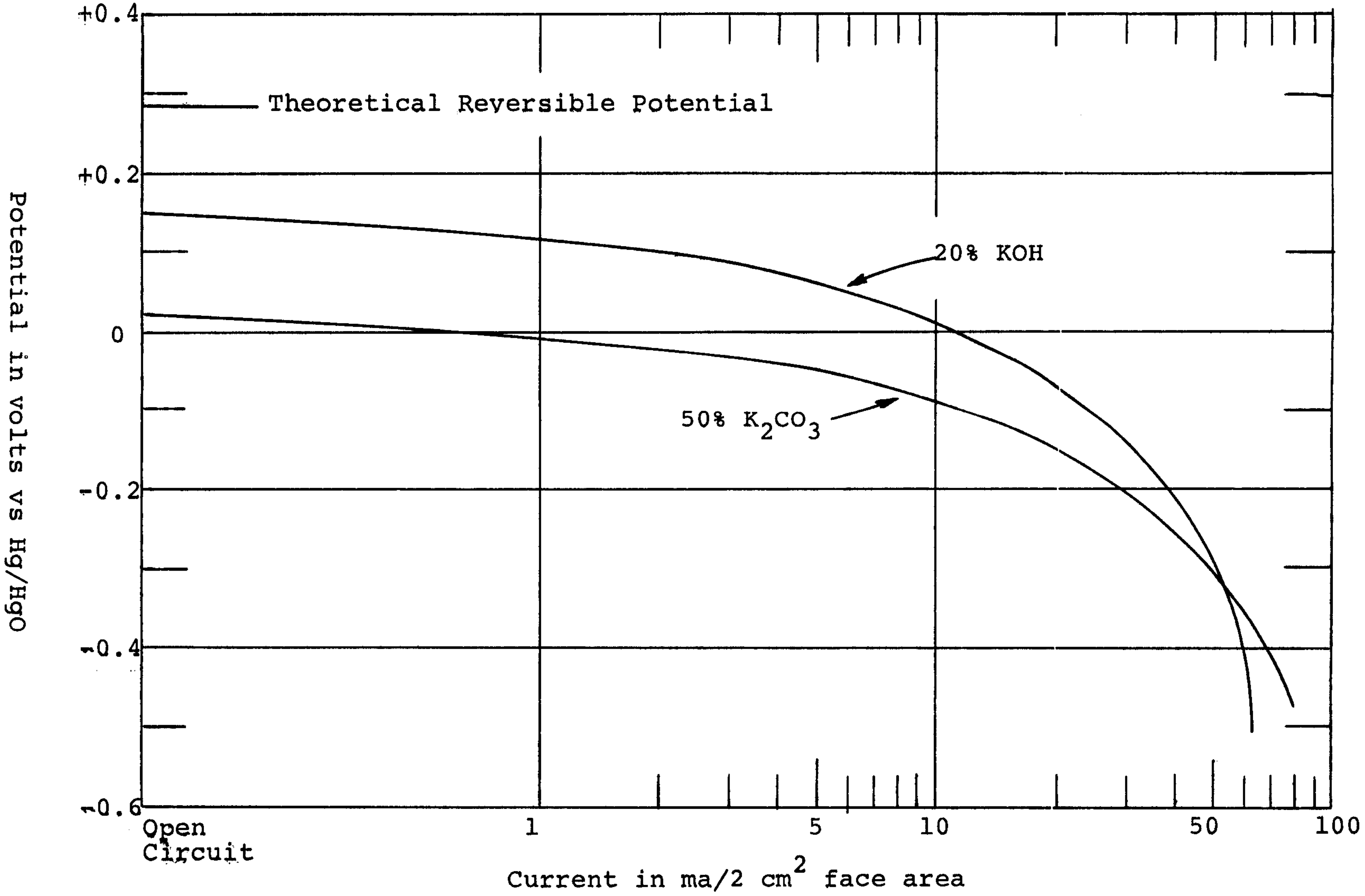


Graph 9. Effect of Methanol on Silver-Teflon Oxygen Cathode; 70°C; K_2CO_3 electrolyte.

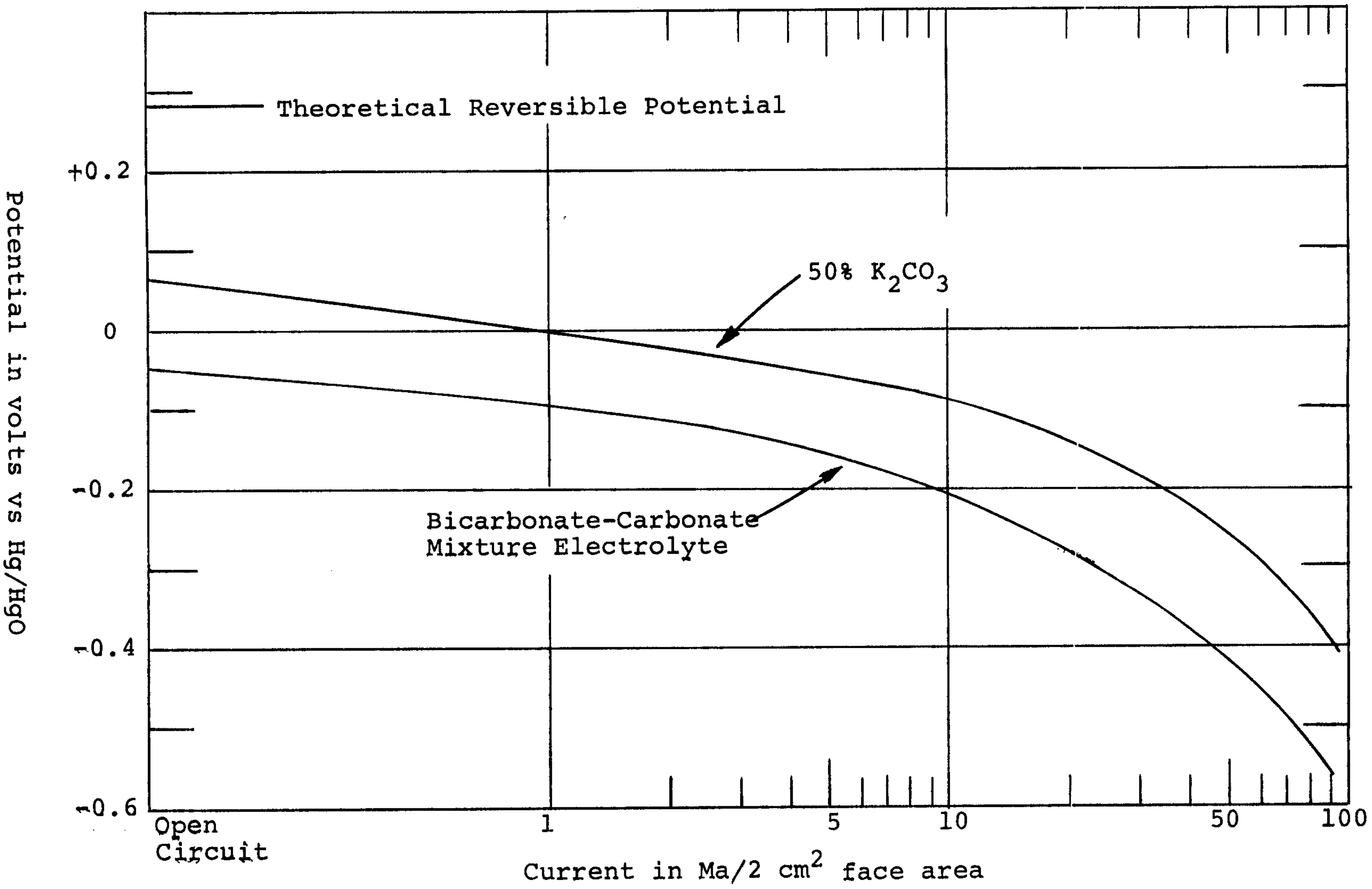
oxygen reactivity. However, it is still conceivable that the methanol can be reacting in a catalytic manner during mixed-feed operation. This possibility was tested and the results are discussed in section IV.B.1.

Effect of Electrolyte

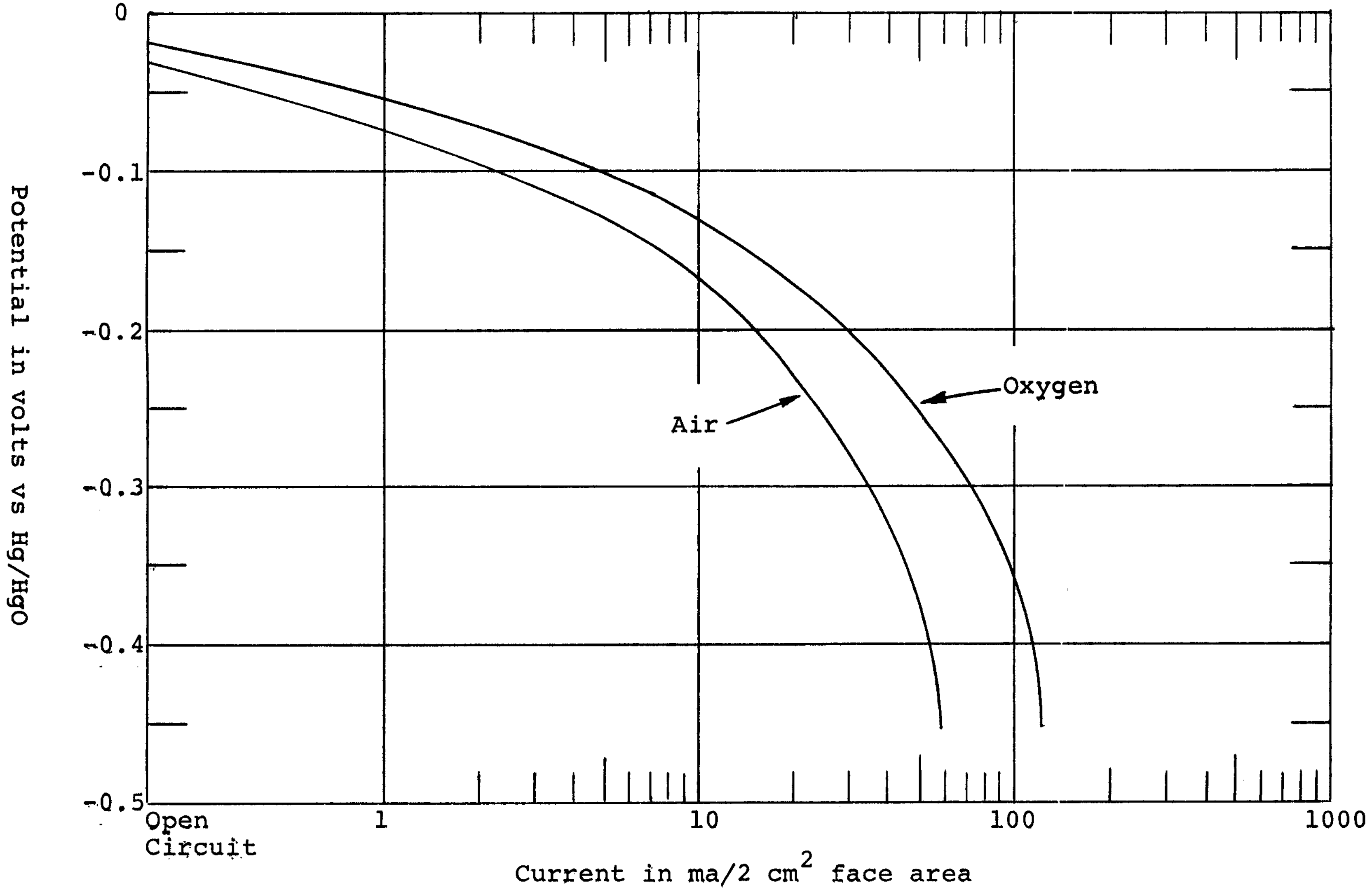
The silver cathode performed better in potassium hydroxide than in the carbonate electrolyte (Graph 10). The greatest difference between the polarization curves in these electrolytes occurred at low current densities. The open circuit polarizations from the thermodynamic reversible potential for the hydroxide and carbonate electrolytes were 0.13 v and 0.26 v, respectively. (The open circuit polarization shown in Graphs 8 and 9 for carbonate is only 0.21 v, which demonstrates the difficulty in obtaining reproducible open circuit potentials.) The superior performance in hydroxide was to be expected, since oxygen electrodes usually perform best in strongly basic electrolytes. The silver electrode performance in the bicarbonate-carbonate mixture electrolyte is compared with the performance in carbonate electrolyte in Graph 11. The polarization curve with the carbonate is about 0.10 v to 0.15 v more favorable than with the mixture electrolyte. This is a part of the general trend towards poorer performance in less basic electrolytes: The pH of the mixture electrolyte is 9.4, compared to 12.2 for the carbonate.



Graph 10. Mixed-Feed Silver Teflon Cathode Comparison of Hydroxide and Carbonate Electrolytes; 0.5 M methanol; 70°C.



Graph 11. Single-Feed Silver-Teflon Cathode Comparison of Carbonate and Mixture Electrolytes; 70°C.



Graph 12. Reaction of Air at Silver-Teflon Electrode; Single-Feed; 70°C; K_2CO_3 electrolyte.

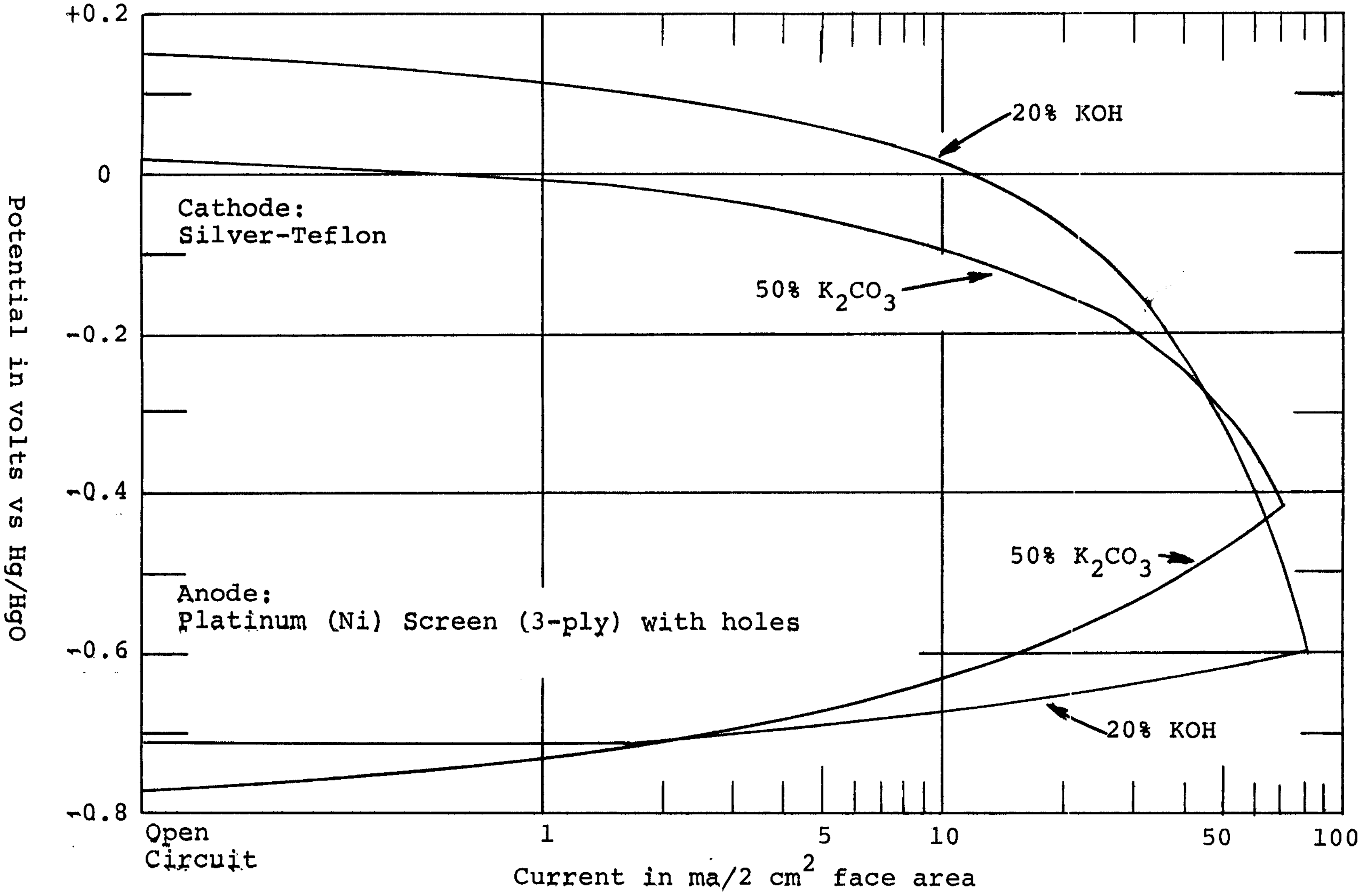
Air Versus Oxygen

Graph 12 shows the comparative results for the use of air and oxygen on the silver-Teflon electrode in 50 (wt)% potassium carbonate electrolyte without methanol. The current density obtained with air was very close to one-half the current obtained with pure oxygen at any given potential. This could be of some importance in the design of a methanol-air cell.

4. Complete Fuel Cell Polarization Curves

The half-cell, mixed-feed polarization curves for an anode and cathode combination are shown in Graph 13. The anode was a 3-ply nickel screen with holes, and the cathode was a silver-Teflon electrode. These electrodes were operated simultaneously with a separation of about one millimeter. The reference electrode capillary was next to the platinum screen, so that the cathode potentials include the electrolyte IR loss. However, at 70 ma/(2 cm^2) the IR potential loss is only about 0.008 v at an electrode separation of 1 mm for the potassium carbonate electrolyte at 70°C (see Appendix H). The corresponding electrolyte IR loss for the hydroxide electrolyte is only 0.004 v.

In the carbonate electrolyte the anode and cathode contributed about equally to the total cell current polarization. However, in hydroxide electrolyte, the



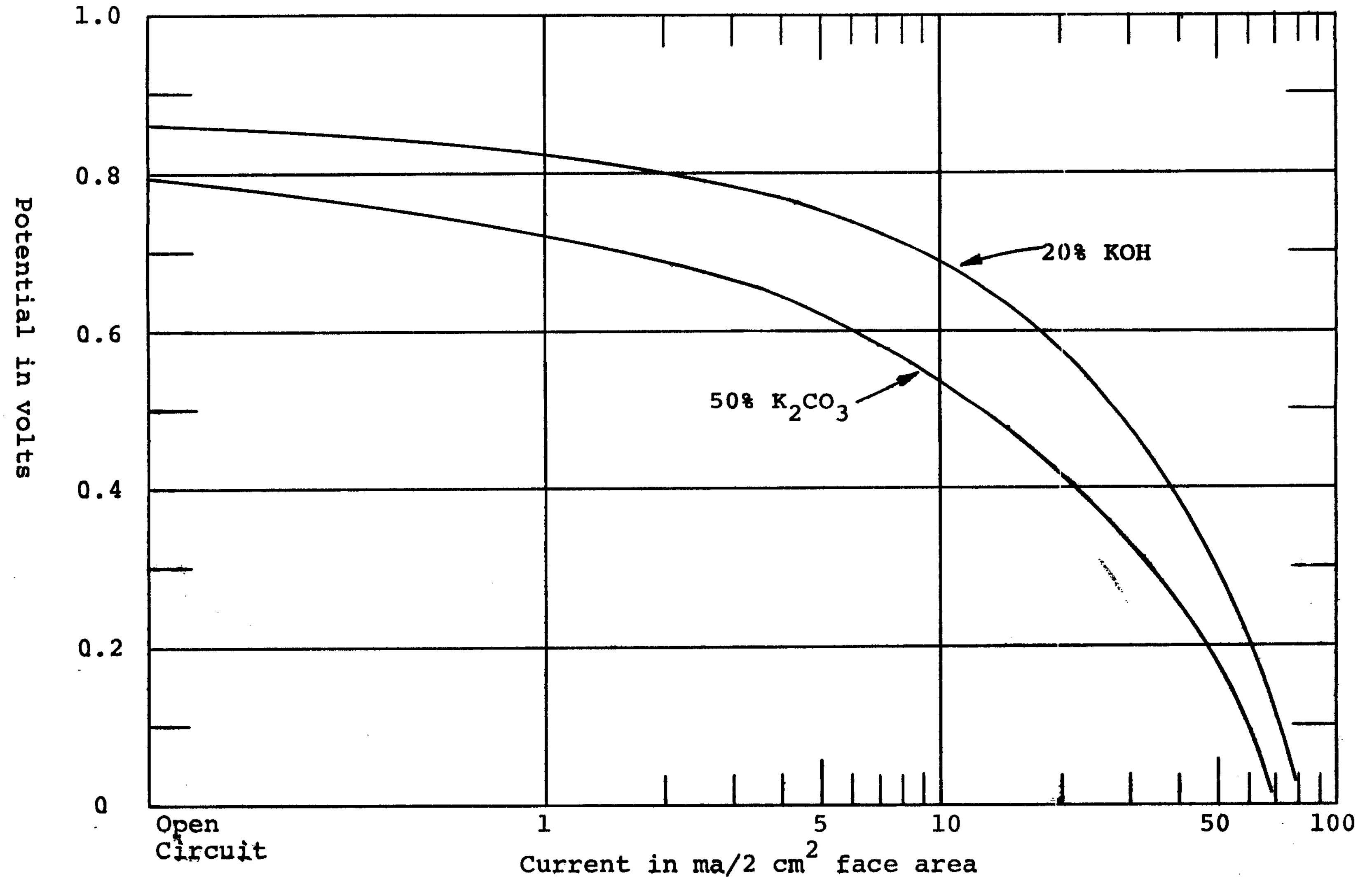
Graph 13. Half-Cell Potentials for Anode-Cathode Combination; Mixed-Feed; 70°C; 0.5 M methanol.

anode was far superior and almost all of the current polarization was caused by the cathode.

Graph 14 shows the net cell potentials for these two electrolytes. These potentials are the difference between the half cell curves of Graph 13. The cell potentials were about 0.1 v better at all current densities in the hydroxide. The electrode which caused the superior cell performance in hydroxide was the cathode at low current densities, and anode at high current densities. The more favorable thermodynamic reversible potential in hydroxide electrolyte does not appear to be a direct factor.

The results for this mixed-feed, potassium carbonate electrolyte cell can be compared with Cairns'[12] porous gas diffusion cell operating with 90 (wt)% cesium carbonate. His cell provided 20 ma/cm^2 at 0.56 v when operated at 130°C. The potassium carbonate cell gives 4 ma/cm^2 at 0.56 v and 70°C. The performances for the two cells are similar, if compensation is made for the difference in temperature. However, it is doubtful that the performance of the mixed-feed cell at 130°C would match Cairns' cell, since the low solubility of methanol at 130°C might severely polarize the anode.

The most important aspect of these results is that the polarization of each electrode during mixed-feed was no greater than with single-feed. For the cathode, this

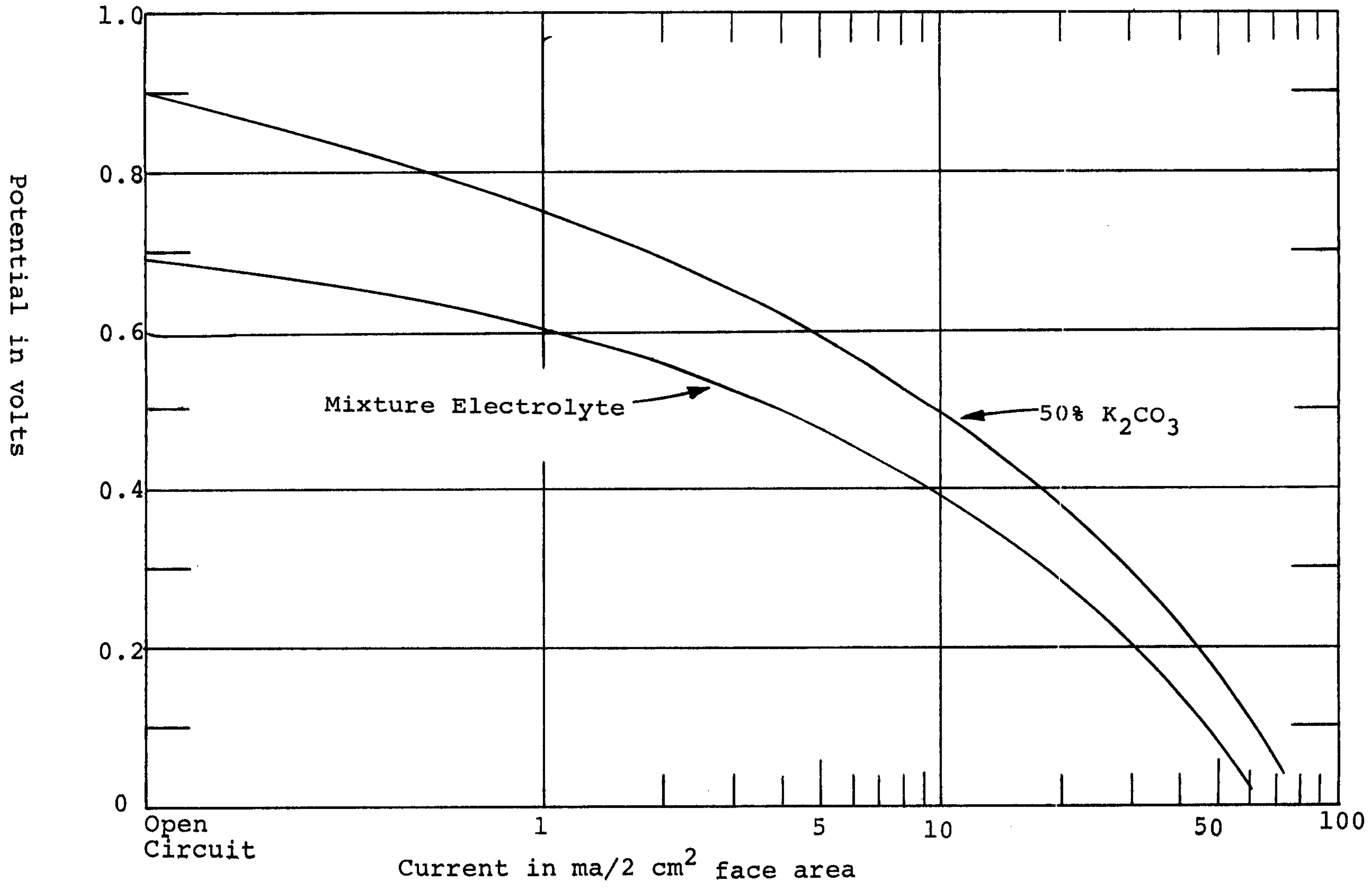


Graph 14. Net Cell Potentials for Hydroxide and Carbonate Electrolytes; same conditions as in graph 13.

excellent performance was achieved by using a selective catalyst material. However, the anode's selectivity was due to a special electrode design which minimized the platinum-oxygen contact.

The net cell polarization with the bicarbonate-carbonate mixture electrolyte is shown on Graph 15. These curves were obtained by taking the difference between the half-cell electrode curves in Graphs 5 and 11. Although these half-cell curves were measured during single-feed instead of mixed-feed, the results in mixed-feed would have been identical (providing a <u>holed</u> platinized screen were used). Graph 15 shows that the output voltage with the mixture electrolyte was about 20% less than with the carbonate. At low currents, the greater polarization in the mixture electrolyte was caused by both the anode and cathode, but at high currents, it was caused only by the cathode.

It becomes evident that the large bicarbonate concentration of the CO_2-rejecting electrolyte at 70°C reduces the cell performance. However, if the cell were operated at higher temperatures, then the equilibrium concentration of bicarbonate in the rejecting electrolyte would be smaller and the performance correspondingly improved. Despite this advantage of high temperatures, operating at over 100°C could create problems of excessive anode polarization, since



Graph 15. Single-Feed Cell Potentials for Carbonate and Mixture Electrolytes; Silver-Teflon Cathode; Platinized (Pt) Screen Anode (2-ply); 0.1 M methanol; 70°C.

the solubility of methanol in the electrolyte would be reduced. A high operating pressure would not be a satisfactory way to increase the methanol solubility because this would also increase the equilibrium bicarbonate content of the electrolyte.

B. Direct Reaction Rate Measurements and Mixed-Feed Theory

1. Silver-Teflon Cathode

The potential-current curves for the silver-Teflon electrode indicated that methanol did not react electrochemically on silver, but left the possibility of a catalytic methanol-oxygen reaction during mixed-feed operation. Therefore, tests were performed at two methanol concentrations (0.01 M and 0.04 M) to determine if there was any direct reaction occurring on the silver-Teflon electrode. Methanol was allowed to come into contact with the electrode at open circuit, as well as while a cathodic current was drawn. In all cases, no methanol reacted, within experimental error (about 1 ma). In other words, the silver electrode was completely selective for the reaction of oxygen only.

This gives a current efficiency for the silver cathode of 100%, since no methanol is wasted by reaction at the cathode. In order to determine the current efficiency of a complete mixed-feed cell, the anode must also be considered. Since the efficiency of the cathode is 100%, the total cell efficiency will equal the efficiency of the anode. The anodic efficiency is studied in detail in the next section.

2. Platinum Anodes

Data

The direct reaction rate between methanol and oxygen was studied on three different platinum electrodes.

i) Platinized nickel screen (4-ply) without holes
ii) Platinized nickel screen (4-ply) with holes
iii) Platinum-Teflon electrode

The behavior of each electrode was studied at two methanol concentrations—0.01 M and 0.04 M. All the data was obtained at 70°C with the 50 (wt)% potassium carbonate electrolyte. These data are presented in Graphs 16 through 21. Each graph contains the results for a given electrode and methanol concentration. There are several curves on each graph, which are labeled as follows, where:

A refers to Alcohol
O refers to Oxygen
s refers to Single-feed
m refers to Mixed-feed

Current Curves—measured with a milliammeter

A_s Single-feed Methanol (Alcohol) Current Curve-anodic current

Only methanol reactant was contacted with the electrode and the anodic current delivery from the electrode was measured.

O_s Single-feed Oxygen Current Curve—cathodic current

Only oxygen reactant was contacted with the electrode and the cathodic current delivery from the electrode was measured.

----- Mixed-feed Current Curve—anodic and cathodic branches

The dotted curve in each of the graphs represents the current delivery from the electrode during mixed-feed operation. Both methanol and oxygen were contacted with the electrode. The upper branch of the curves (in the higher potential region) is the anodic current, and the lower branch is the cathodic current.

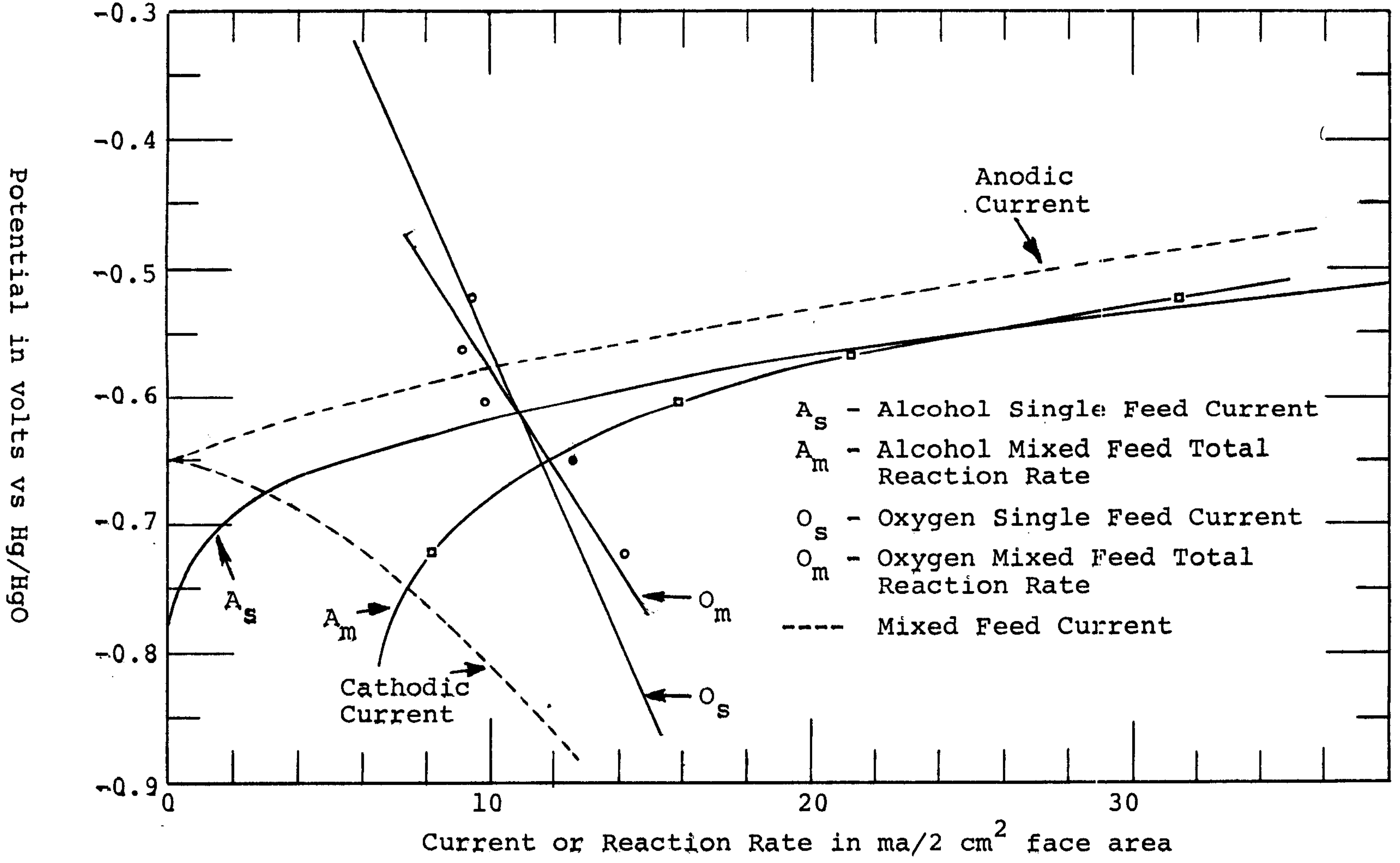
Reaction Rate Curves—measured by chemical analysis of methanol depletion

A_m Alcohol, Mixed-Feed Total Reaction Rate

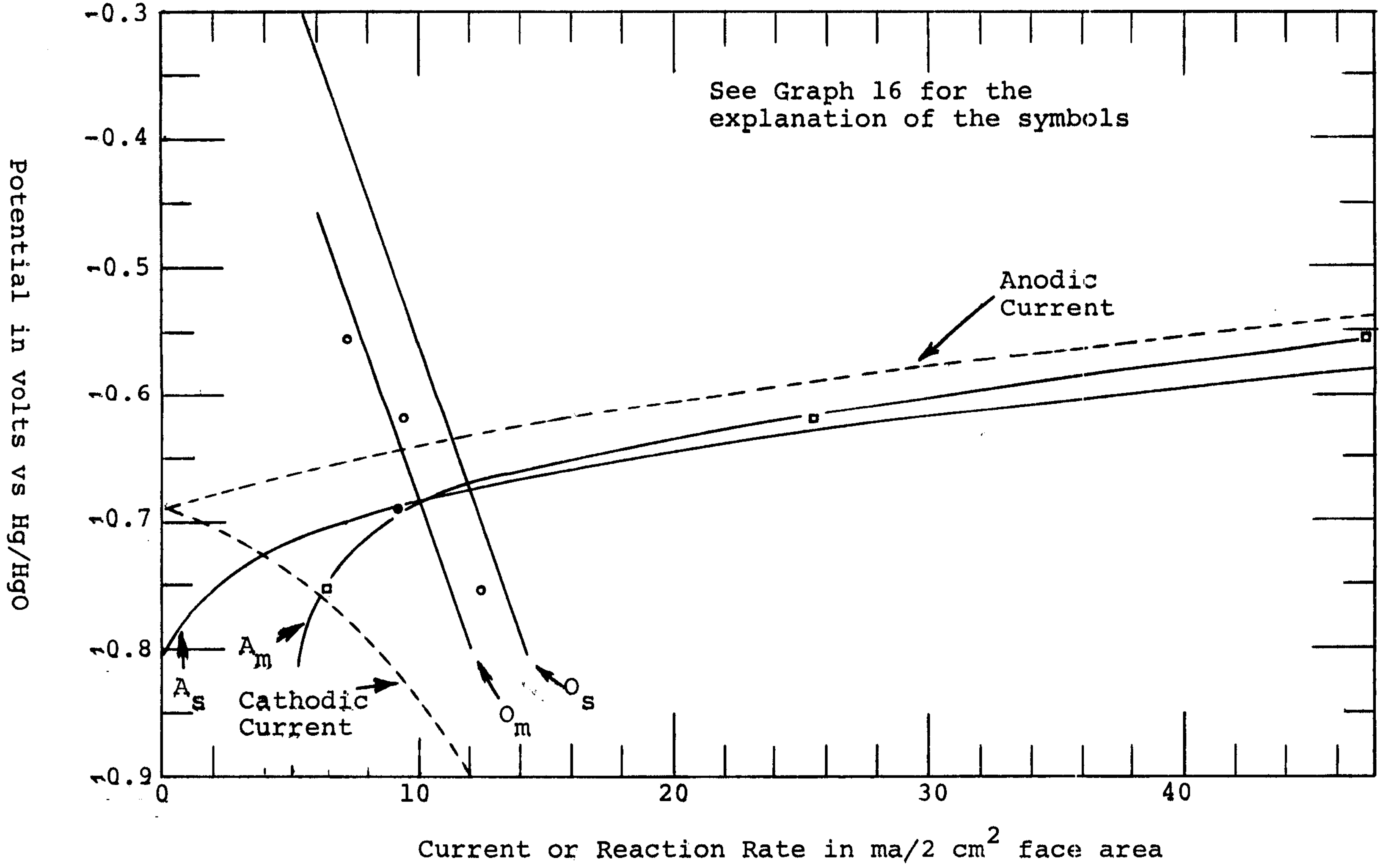
This is the total reaction rate of methanol equivalents during mixed-feed operation. Even though this is a "reaction rate," it is expressed in units of milliamperes for easy comparison with the currents. The total methanol reaction rate is equal to the sum of the methanol which reacts to produce a current and the methanol which reacts directly with oxygen (no current observable).

O_m Oxygen, Mixed-Feed Total Reaction Rate

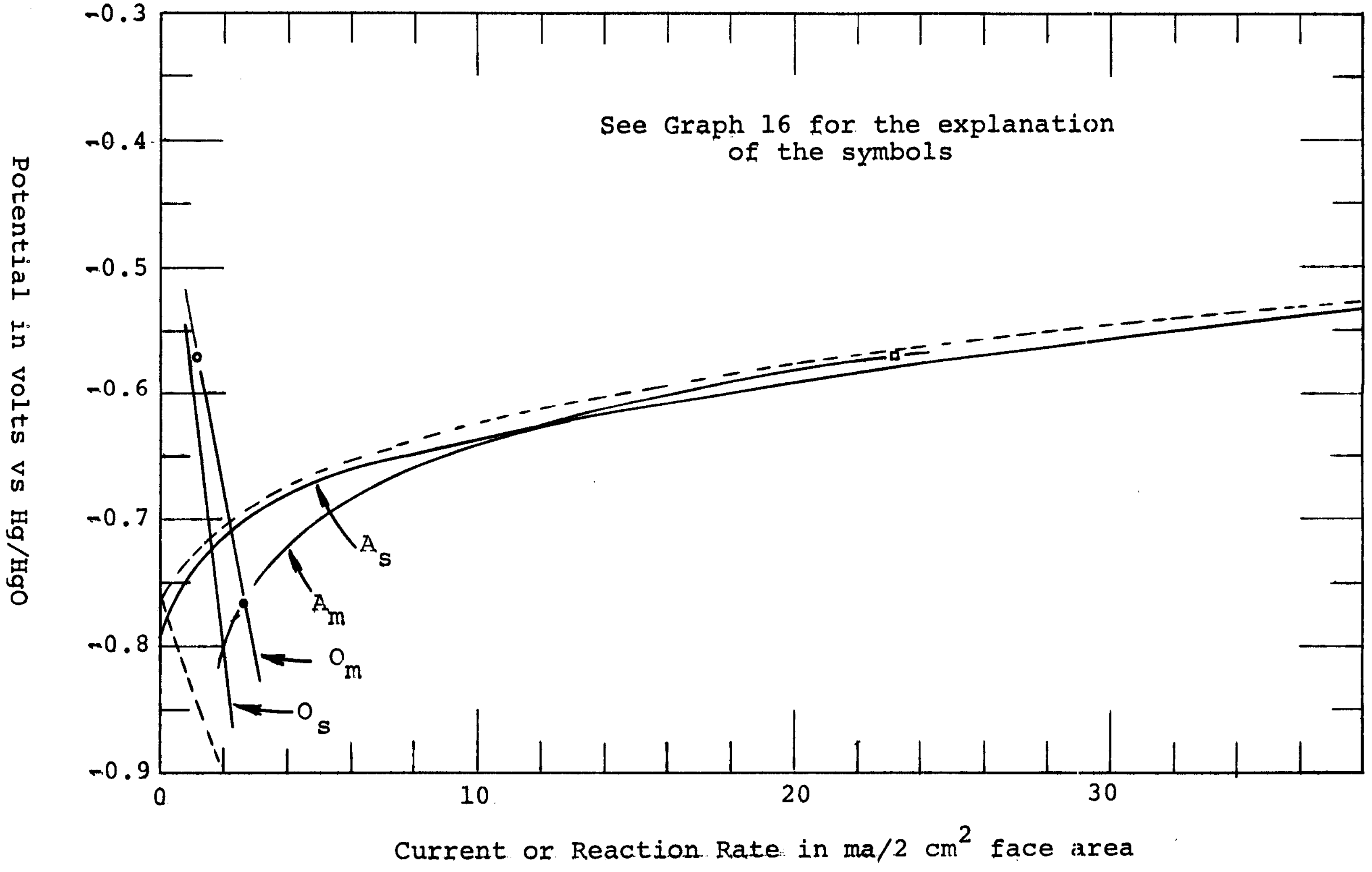
This is the total reaction rate of oxygen during mixed-feed operation. This oxygen reaction rate is expressed in milliamperes and is determined by a material balance: If there is an anodic current flowing, the oxygen rate is equal to the total methanol reaction rate (in ma) minus the anodic (methanol) current; if there is a cathodic current flowing, the total oxygen rate is equal to the cathodic current plus the methanol reaction rate (in ma).



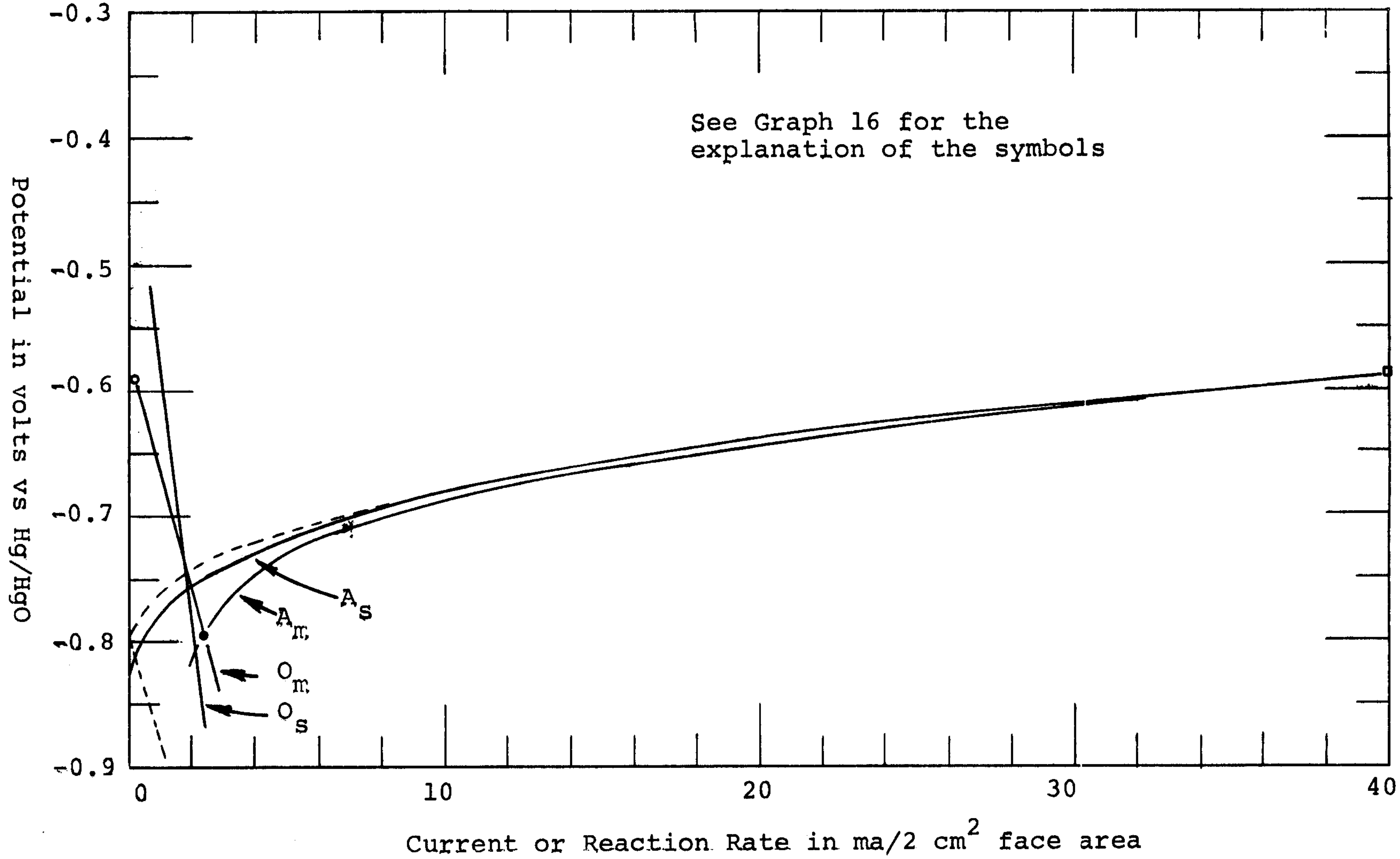
Graph 16. Data for Non-holed Screen; 0.01 M Methanol; Platinized (Ni) Screen (4-ply); 70°C; K_2CO_3 electrolyte.



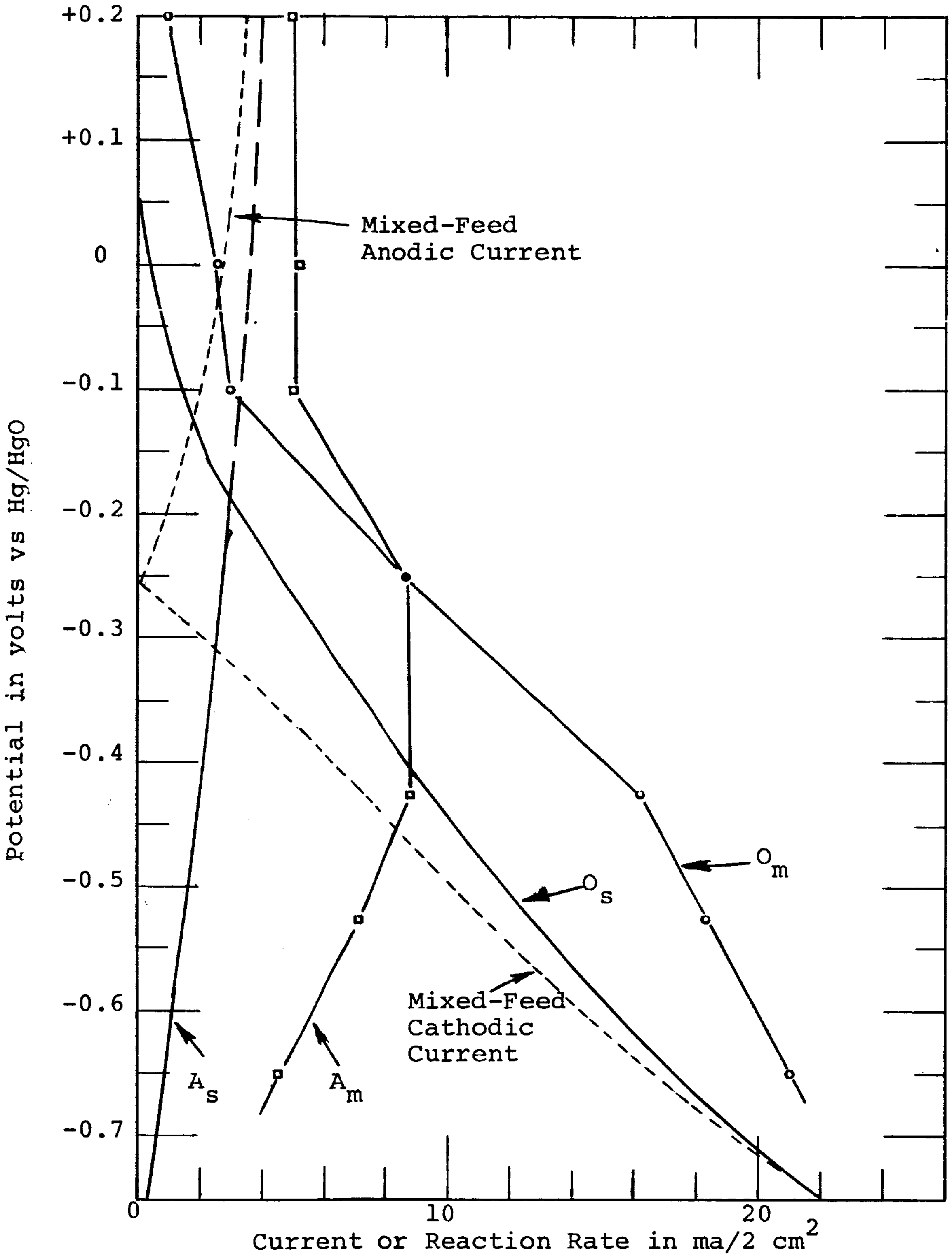
Graph 17. Data for Non-Holed Screen; 0.04 M methanol; Platinized (Ni) Screen (4-ply); 70°C; K_2CO_3 electrolyte.



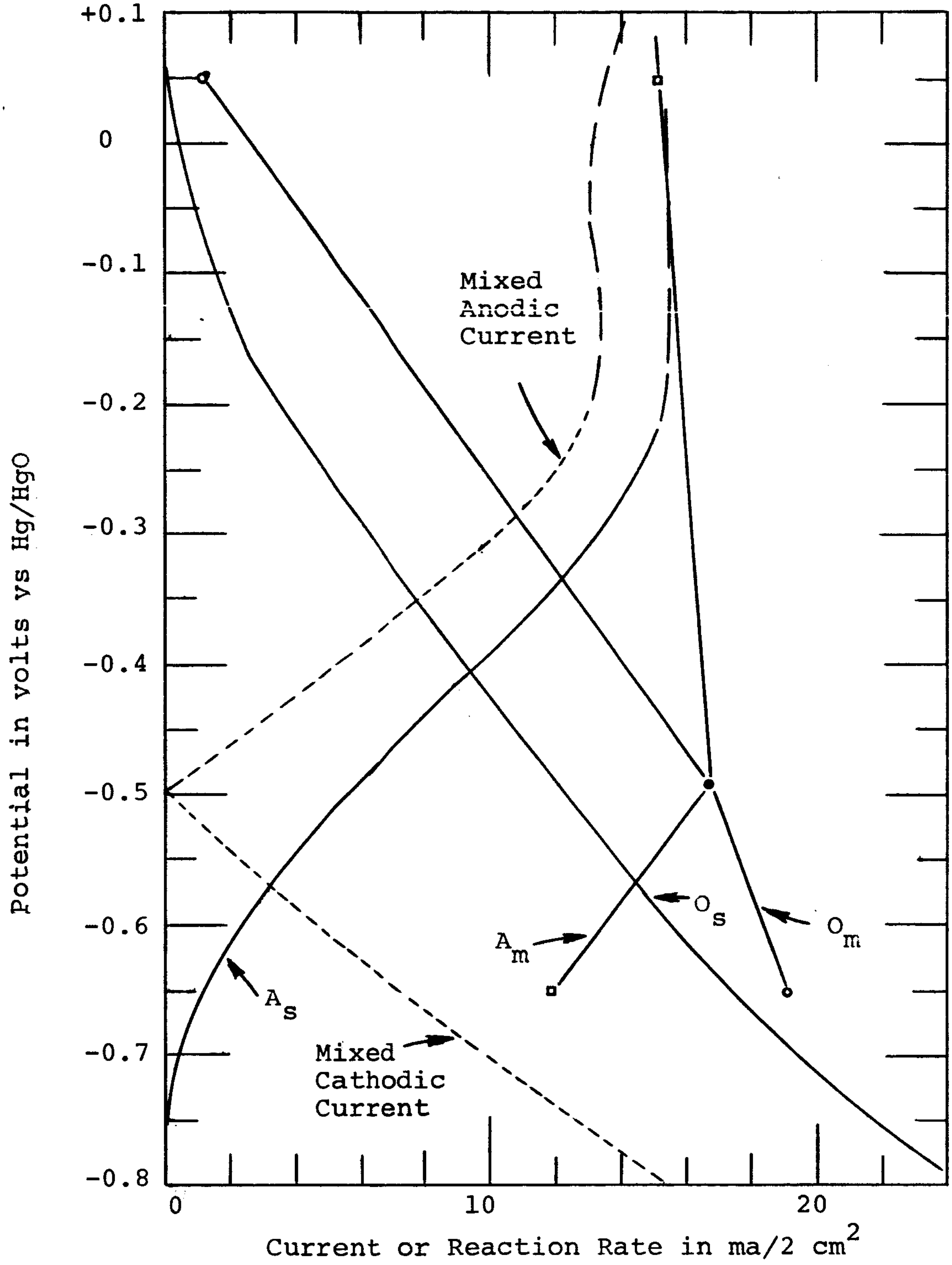
Graph 18. Data for Screen with Holes; 0.01 M methanol; Platinized (Ni) Screen (4-ply); 70°C; K_2CO_3 electrolyte.



Graph 19. Data for Screen with Holes; 0.04 M methanol; Platinized (Ni) Screen (4-ply); 70°C; K_2CO_3 electrolyte.



Graph 20. Data for Platinum-Teflon Electrode; 0.01 M methanol; 70°C; K_2CO_3 electrolyte.



Graph 21. Data for Platinum-Teflon Electrode; 0.04 M methanol; 70°C; K_2CO_3 electrolyte.

The square data points shown on the graphs represent the measured total methanol reaction rate, and the curves marked A_m are drawn through these points. In some cases, the points shown are averages of more than one value. The duplicate values differed by an amount corresponding to the average error as discussed in Appendix F. The curves, O_m, have been drawn through the round points which correspond to the total oxygen reaction rate. The data points for the other curves are not shown because they were measured with an ammeter and yielded very smooth curves.

The dashed lines in Graphs 20 and 21 represent the anodic current in the potential region for which an oxide coating completely covers the platinum surface. (See section II.D. for a discussion of this phenomenon.) Since potentiostatic equipment was not used, the potential could not be held constant in this area: The current varied over a 1 ma range and the potential varied over a 0.05 v range.

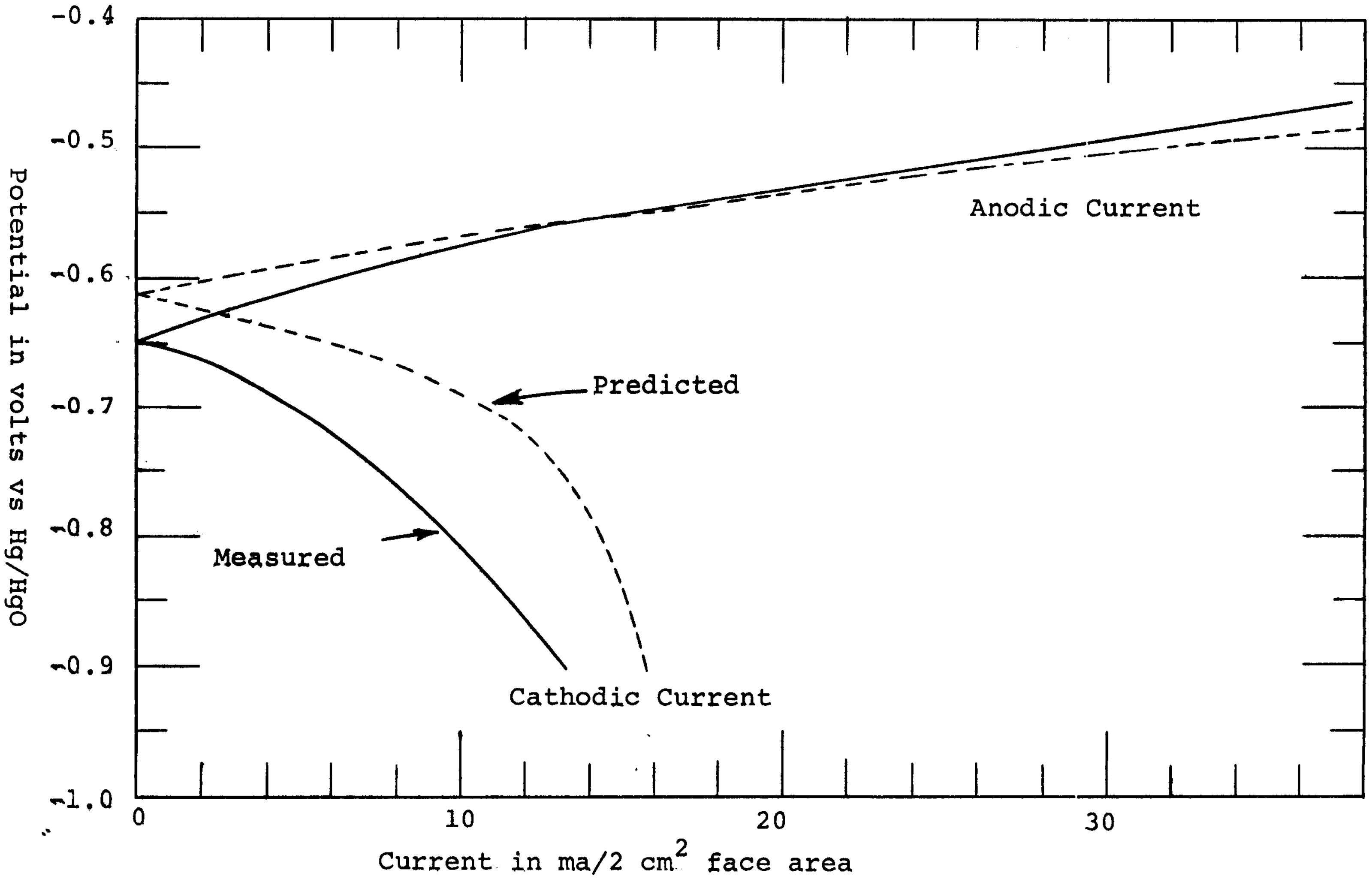
The significance of the data in each of these graphs can best be observed by simplifications and comparisons as suggested by the theory in section II.B.

Mixed-Feed Current Densities

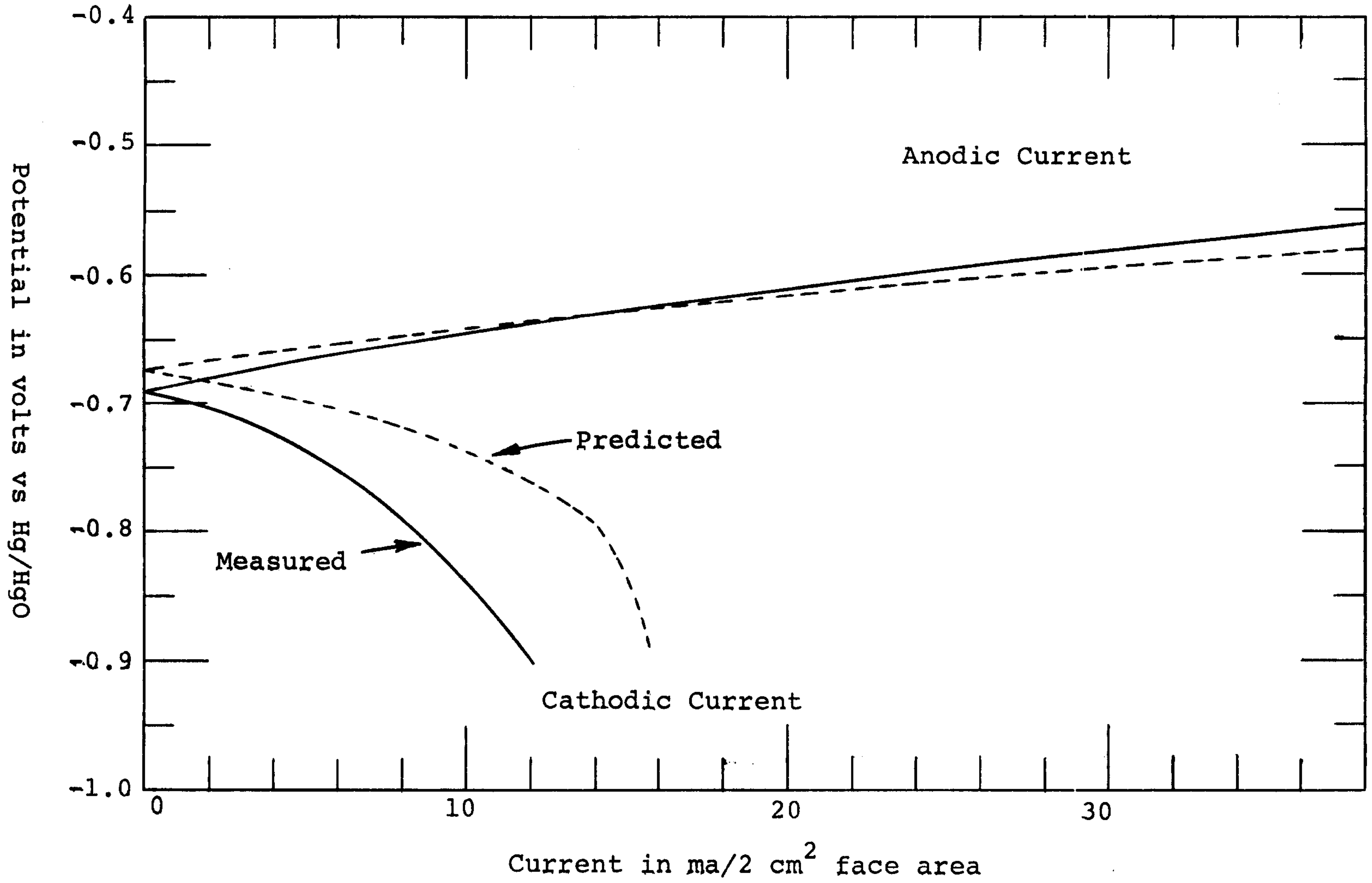
The theory of mixed-feed electrodes suggests that mixed-feed current densities can be predicted by calculating the difference between the single-feed currents for methanol and oxygen at any given potential. The predicted current will be in the anodic direction if the methanol single-feed current is greater than the oxygen single-feed current, and vice versa. When this calculation is done at all potentials, a "Predicted" mixed-feed current curve is obtained. Graphs 22 through 27 compare such predicted curves with the current curves which have actually been measured. In all cases, the branch of the current curve located in the lower region of the potential scale is a cathodic current and the upper branch is an anodic current.

The results for the non-holed platinized screen with 0.01 M methanol are shown in Graph 22. The anodic branch of the mixed-feed current curve agrees very well with the curve predicted from the single-feed current curves, and the measured open circuit potential was only slightly more negative than the predicted value. However, there was more deviation between the cathodic branches; the actual cathodic current was lower than expected. When the methanol concentration was increased four-fold to 0.04 M, the relative positions of the actual and predicted curves remained the same (Graph 23). In this case, however, both curves were shifted down in potential and the anodic branches had a lower slope. This was a direct consequence of the higher methanol activity.

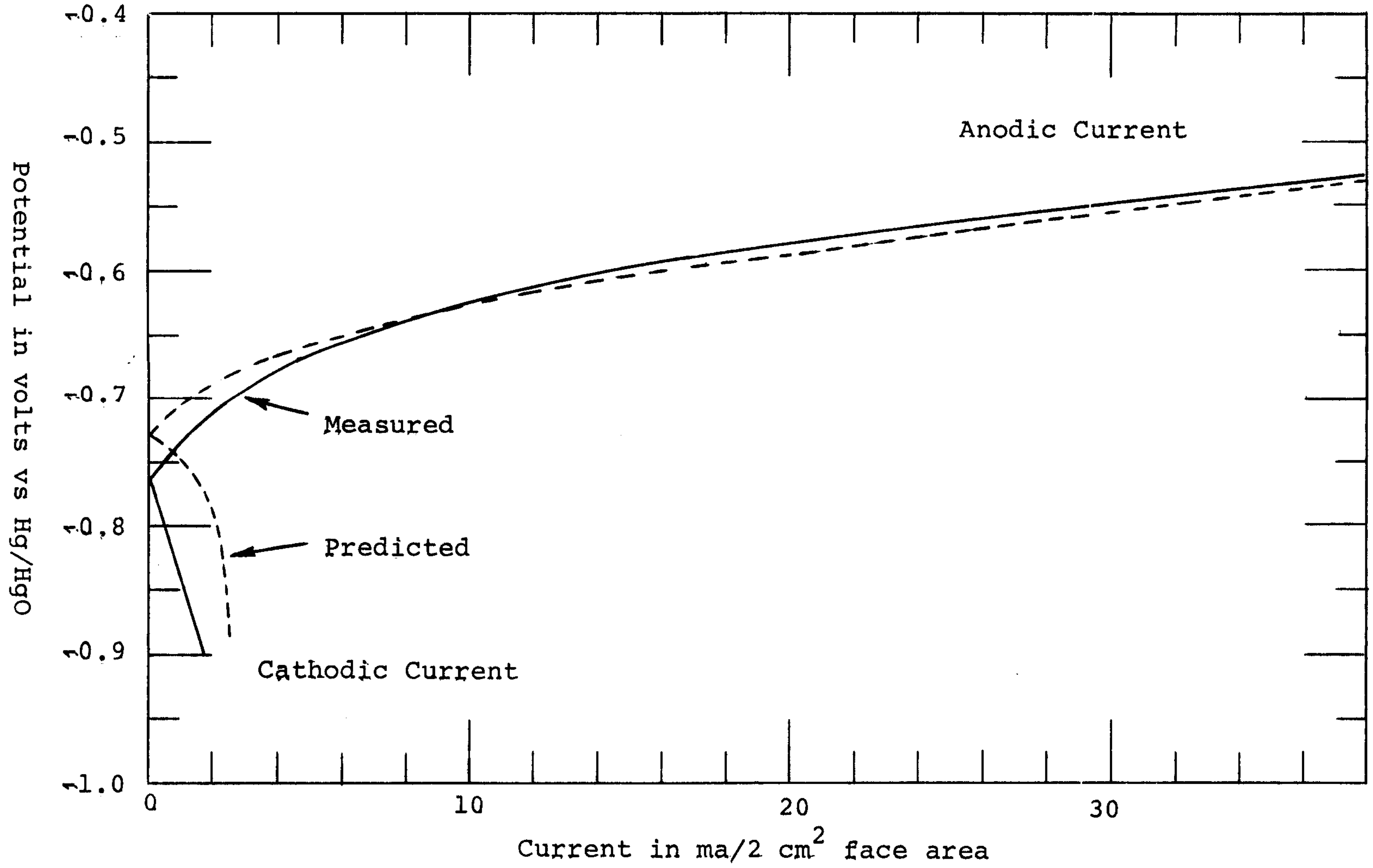
Graphs 24 and 25 contain the results for the holed platinized screen at 0.01 M and 0.04 M methanol, respectively.



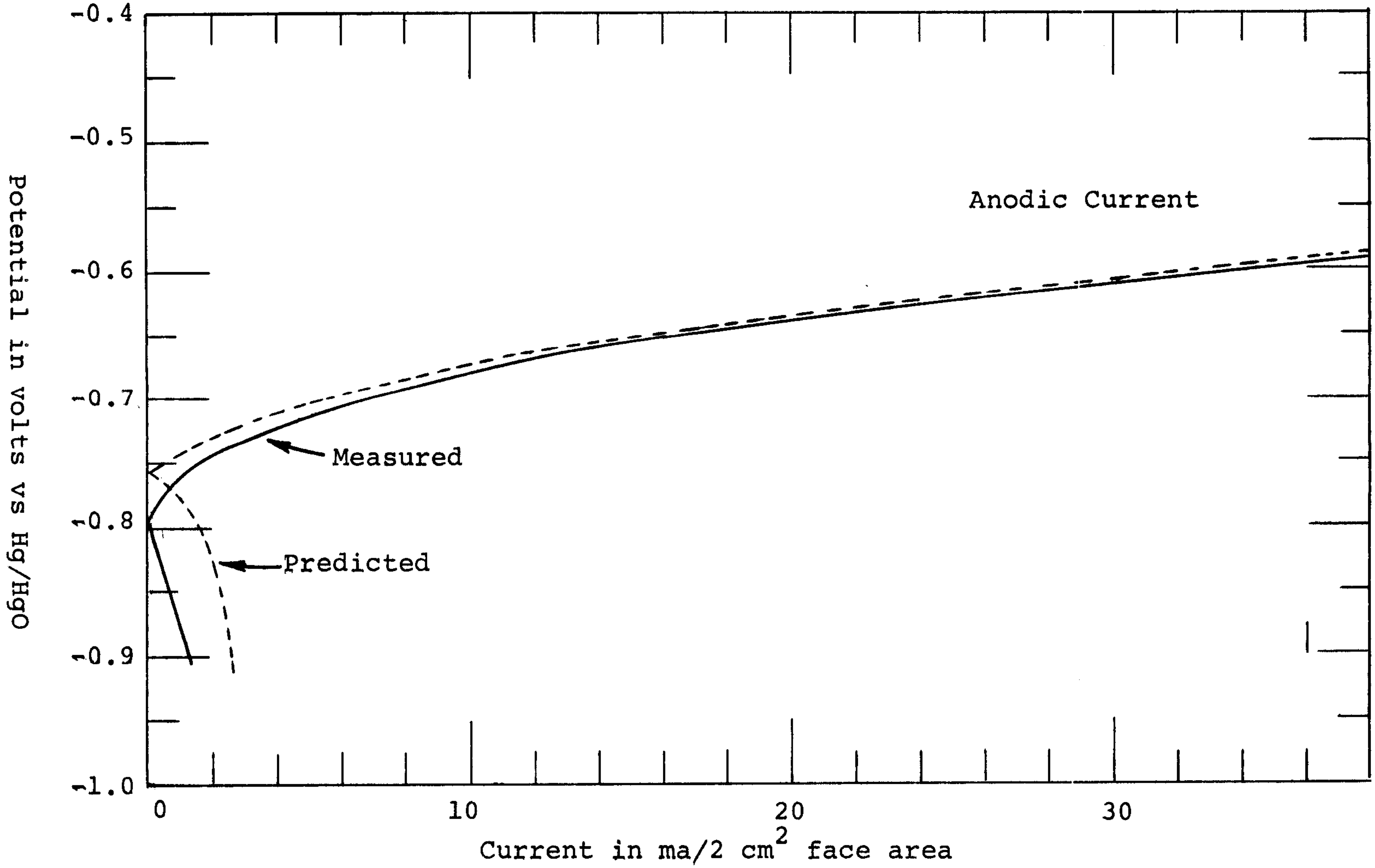
Graph 22. Mixed-Feed Current for Non-holed Screen; 0.01 M methanol; 70°C; K_2CO_3 electrolyte



Graph 23. Mixed-Feed Current for Non-holed Screen; 0.04 M methanol; 70°C; K_2CO_3 electrolyte.



Graph 24. Mixed-Feed Current for Screen with holes; 0.01 M methanol; 70°C; K_2CO_3 electrolyte.



Graph 25. Mixed-Feed Current for Screens with Holes; 0.04 M methanol; 70°C; K_2CO_3 electrolyte

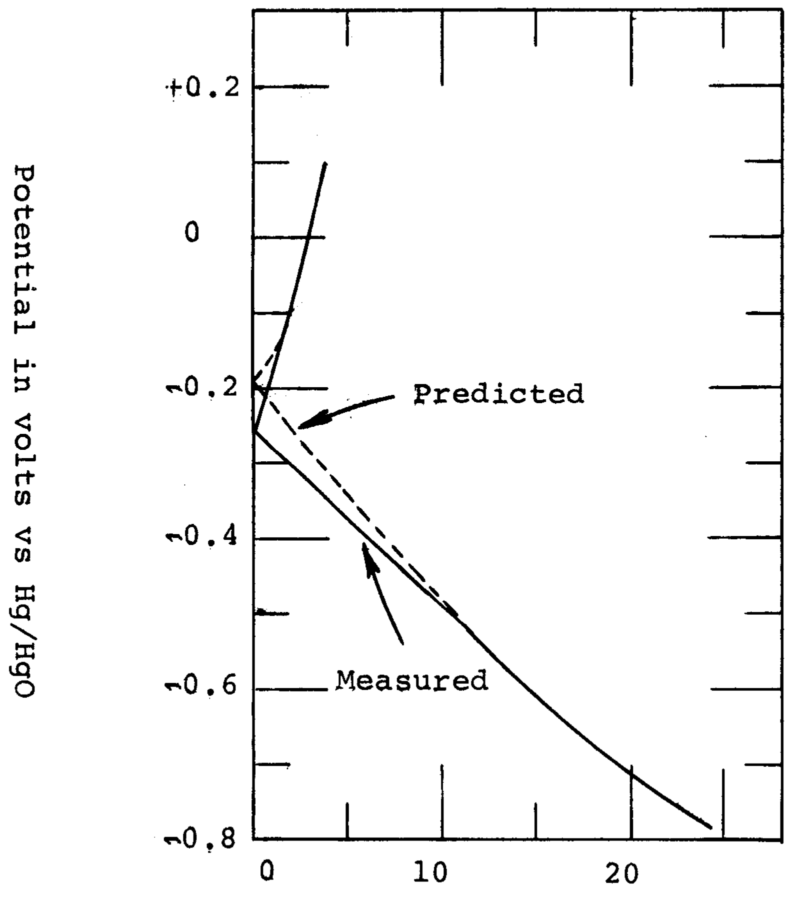
Compared to the non-holed screen electrode, the cathodic current was very much smaller, which is an indication of the decreased oxygen reaction rate caused by designing the screen electrode with holes. The holes improved (lowered) the screen's open circuit potential by 0.11 v for both methanol concentrations. In general, the predicted and experimental current curves agree very well for both concentrations. However, the small deviations mentioned for the non-holed screen also occur with the holed screen: the open circuit potential was slightly more negative than predicted and the cathodic current was lower than predicted.

The reason for these deviations can be determined from the data on Graphs 16 through 19. In all cases, the methanol total reaction rate (A_m) in the low potential regions was larger than the single-feed methanol current (A_s). This high methanol reaction rate during mixed-feed consumed more oxygen by direct reaction than was expected. Since the oxygen supply was limited by mass transfer, this direct reaction reduced the amount of oxygen available for the production of the cathodic current. There are several reasons why it is believed that the oxygen reaction rate was severely mass transfer limited. The very steep slope of the single-feed oxygen polarization curve is very indicative of a low oxygen supply:

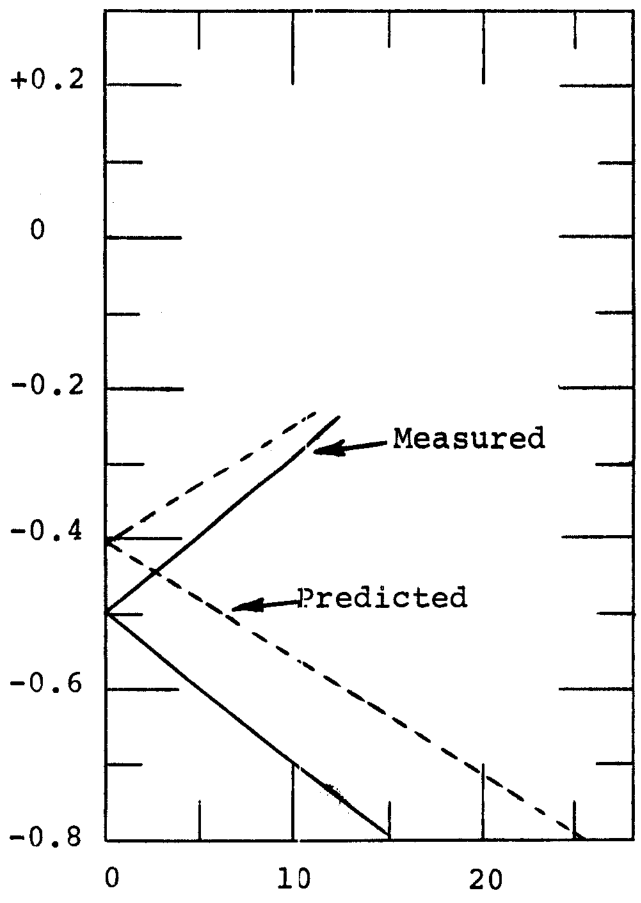
electrokinetic rate limiting steps always yield a curve with a much lower slope. Also, the results of section IV.B.3. show that the activation energy for the oxygen reaction was low (about 4.5 kcal), which is indicative of a diffusion limiting step. Finally, the large influence of the 1 mm electrode holes on the oxygen reaction rate can only be explained by assuming a mass transfer limiting step.

Graph 26 presents the current curves for the platinum-Teflon electrode operating with 0.01 M methanol. The relative reactivities of methanol and oxygen are reversed from that of the screen electrode: the maximum oxygen current (cathodic) was much larger than the maximum methanol current. Correspondingly, the experimental and predicted open circuit potentials were much higher (i.e., closer to the oxygen reversible potential). The high oxygen reactivity was made possible by the good oxygen gas contact with the non-wettable Teflon electrode. As in the case of the screen electrode, there was very good agreement between the predicted and experimental current curves. A great deal of support is given to the mixed-feed theory by the fact that agreement between the predicted and experimental current curves was obtained for both electrodes, despite their different nature.

A four-fold increase in the methanol concentration at the platinum-Teflon electrode caused a large shift of



Graph 26. Mixed-Feed Current for Platinum-Teflon Electrode; 0.01 M methanol; 70°C; K_2CO_3



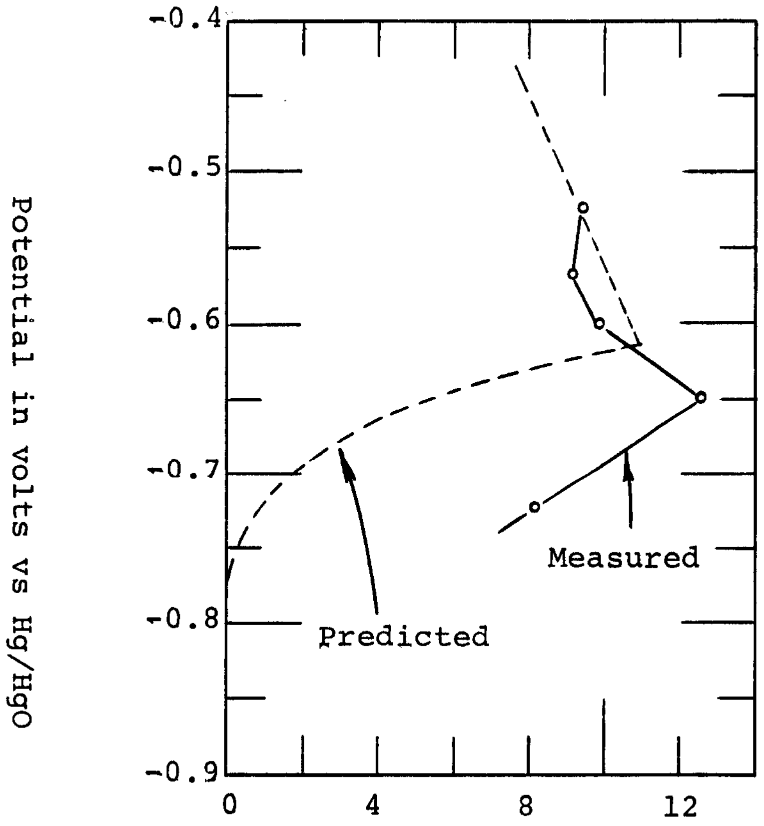
Graph 27. Mixed-Feed Current for Platinum-Teflon Electrode; 0.04 M methanol; 70°C; K_2CO_3

the current curves towards the methanol reversible potential (Graph 27). There is a slight difference between the predicted and actual curve at this methanol concentration.

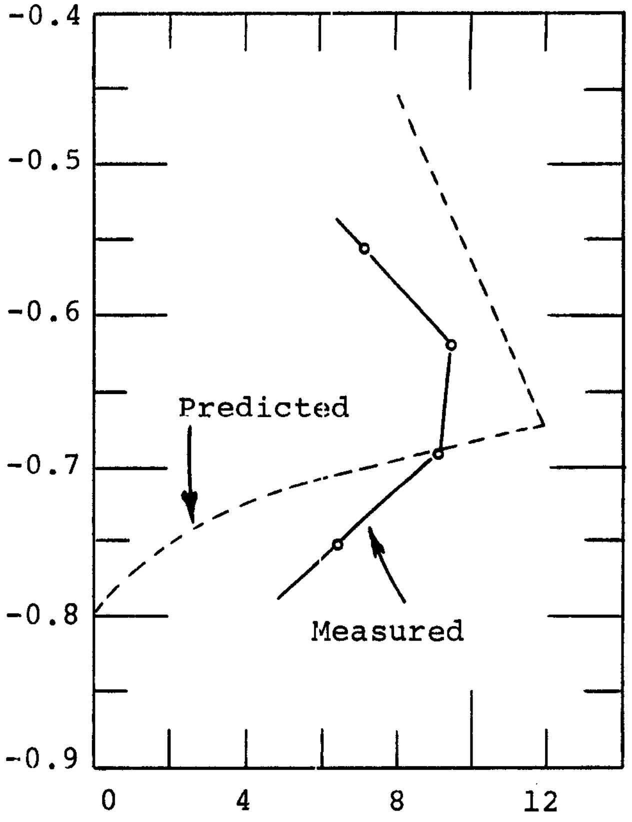
Direct Reaction Rates

The electrochemical direct reaction rate between methanol and oxygen can also be predicted from the single-feed current curves. This is the non-current-producing reaction between methanol and oxygen which occurs by an electrochemical mechanism. (See section II.B. for the explanation of how this is predicted.) If an ordinary catalytic direct reaction occurs in conjunction with the electrochemical, then the total direct reaction rate would be larger than the predicted rate.

The predicted and experimental direct reaction rates have been plotted on Graphs 28 through 33. The points shown on the graphs are the experimentally measured reaction rates. These points have been connected by straight lines: the smooth curves represent the predicted values. Graph 28 shows the results for the non-holed platinized screen with 0.01 M methanol. At potentials higher than the open circuit value (i.e., above -0.65 v), there is excellent agreement between the predicted and experimental direct reaction rate. However, in the potential region below -0.65 v, the direct reaction rate was about 7 ma greater than the predicted values.



Graph 28. Direct Reaction Rate for Non-holed Screen; 0.01 M methanol; 70°C; K_2CO_3



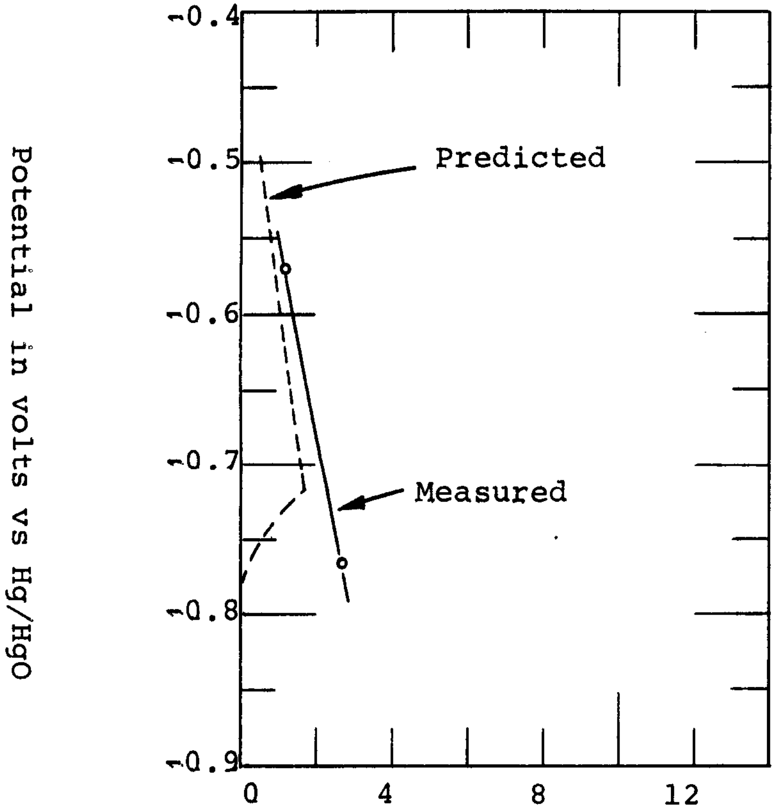
Graph 29. Direct Reaction Rate for Non-holed Screen; 0.04 M methanol; 70°C; K_2CO_3

The reason why the experimental direct reaction rate is greater than the predicted rate in the lower potential region is because a catalytic reaction is occurring in conjunction with the electrochemical reaction. There is a very good reason why the catalytic reaction did not cause the experimental direct reaction rate to be greater than the predicted rate in the upper potential region also. In order to understand this reason, it first must be realized that the "predicted" curve is equal to the single-feed oxygen reaction rate and the "measured" curve is equal to the mixed-feed oxygen reaction rate in the upper potential region. These two reaction rates were equal because they were both controlled by the mass transfer rate of oxygen, which was certainly the same in mixed-feed and single-feed. In other words, the oxygen mass transfer rate was limiting the rate of the total direct reaction, which kept the catalytic reaction from becoming excessive.

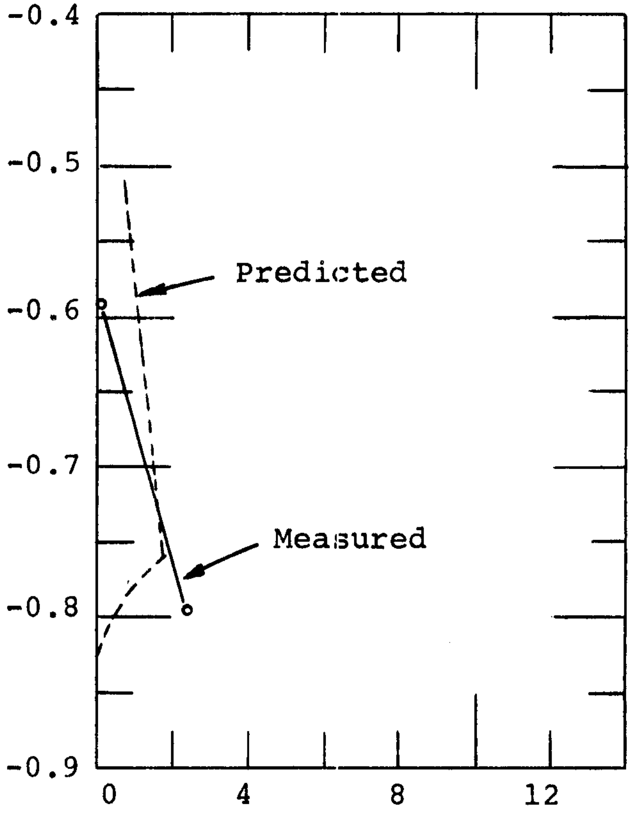
Similar curves were obtained when the methanol concentration was increased to 0.04 M (Graph 29). In the upper potential region, the direct reaction rate was actually slightly less than the predicted value. The most important aspect of the results at this concentration is that the direct reaction rate was not greater than the direct rate in 0.01 M methanol. This is further evidence that the direct reaction rate is entirely limited by oxygen diffusion.

The increased efficiency of the holed platinized screen is demonstrated in Graphs 30 and 31. Qualitatively, the relation between the experimental and predicted direct reaction rates are the same as for the non-holed electrode, but since the oxygen contact was so much smaller, the direct reaction rate was reduced to about one-fourth the rate for the non-holed electrode. The total direct reaction rate was found to be unaffected by the methanol concentration for this electrode also.

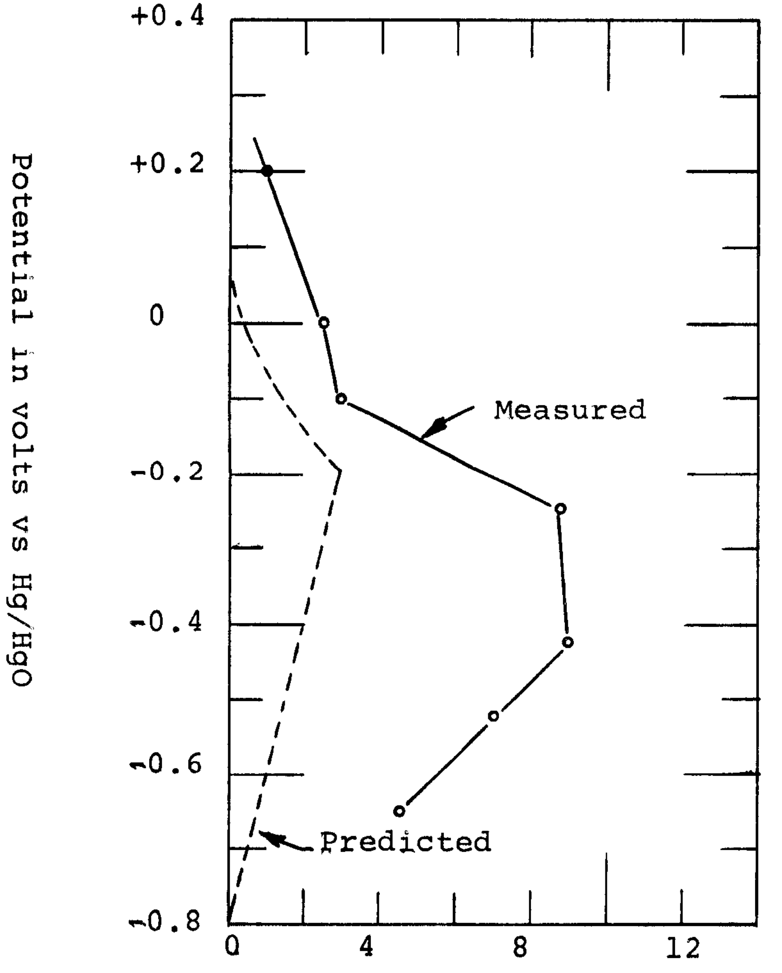
The total direct reaction rate measurements for the platinum-Teflon electrode are presented on Graphs 32 and 33. For this electrode, the experimental direct reaction rates were much greater than the predicted values. Also, a four-fold increase in methanol concentration produced almost a two-fold increase in the direct reaction rate at open circuit. This behavior is markedly different from that of the screen electrode. The absence of a dominating diffusion limiting step in the case of the Teflon electrode permitted the catalytic reaction to occur in conjunction with the electrochemical direct reaction. The minimum catalytic reaction rate which was occurring at this electrode is represented by the difference between the experimental and predicted reaction rate curves at any given potential. At potentials above -0.2 v, the catalytic reaction rate was very low——only 1 or 2 ma. This low catalytic rate was



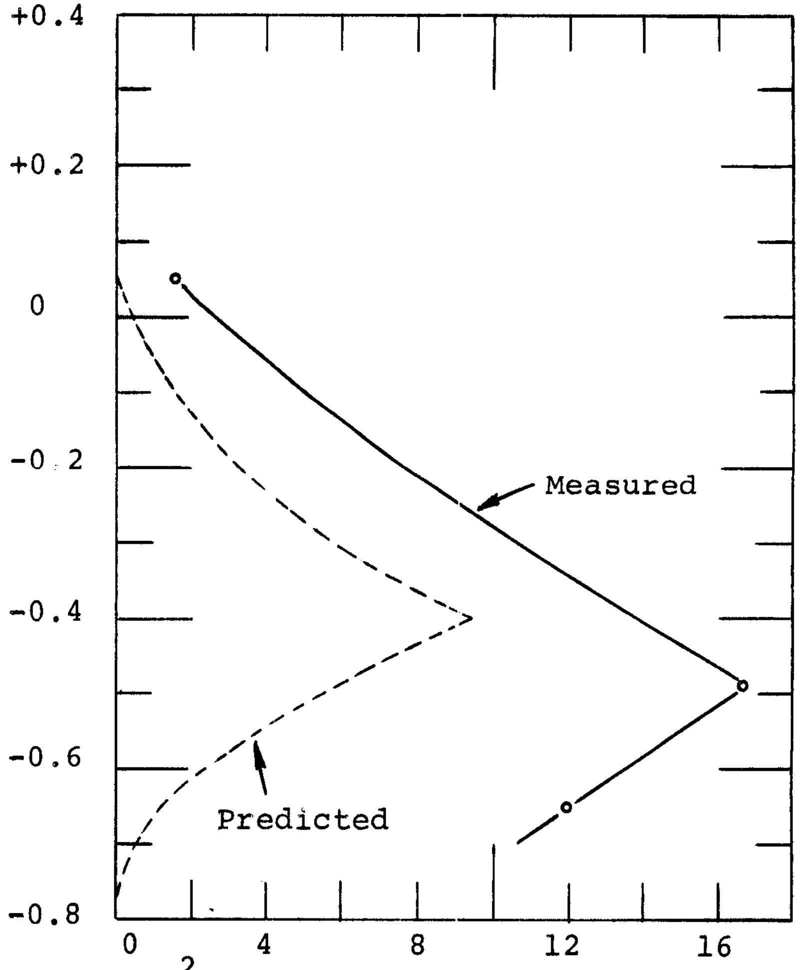
Graph 30. Direct Reaction Rate for Screen with Holes; 0.01 M methanol; 70°C; K_2CO_3



Graph 31. Direct Reaction Rate for Screen with Holes; 0.04 M methanol; 70°C; K_2CO_3



Graph 32. Direct Reaction for Platinum-Teflon Electrode; 0.01 M methanol; 70°C; K_2CO_3

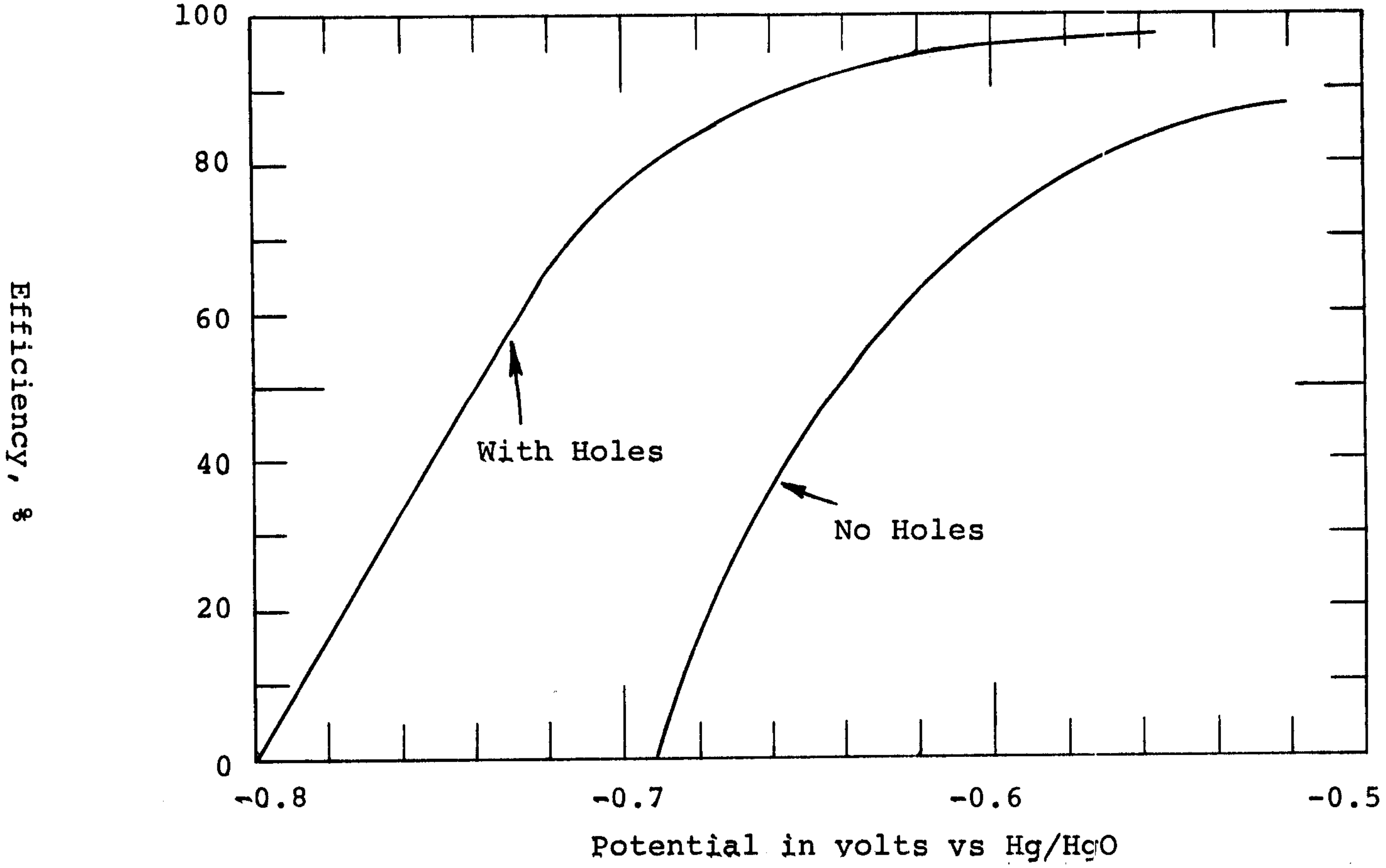


Graph 33. Direct Reaction for Platinum-Teflon Electrode; 0.04 M methanol; 70°C; K_2CO_3

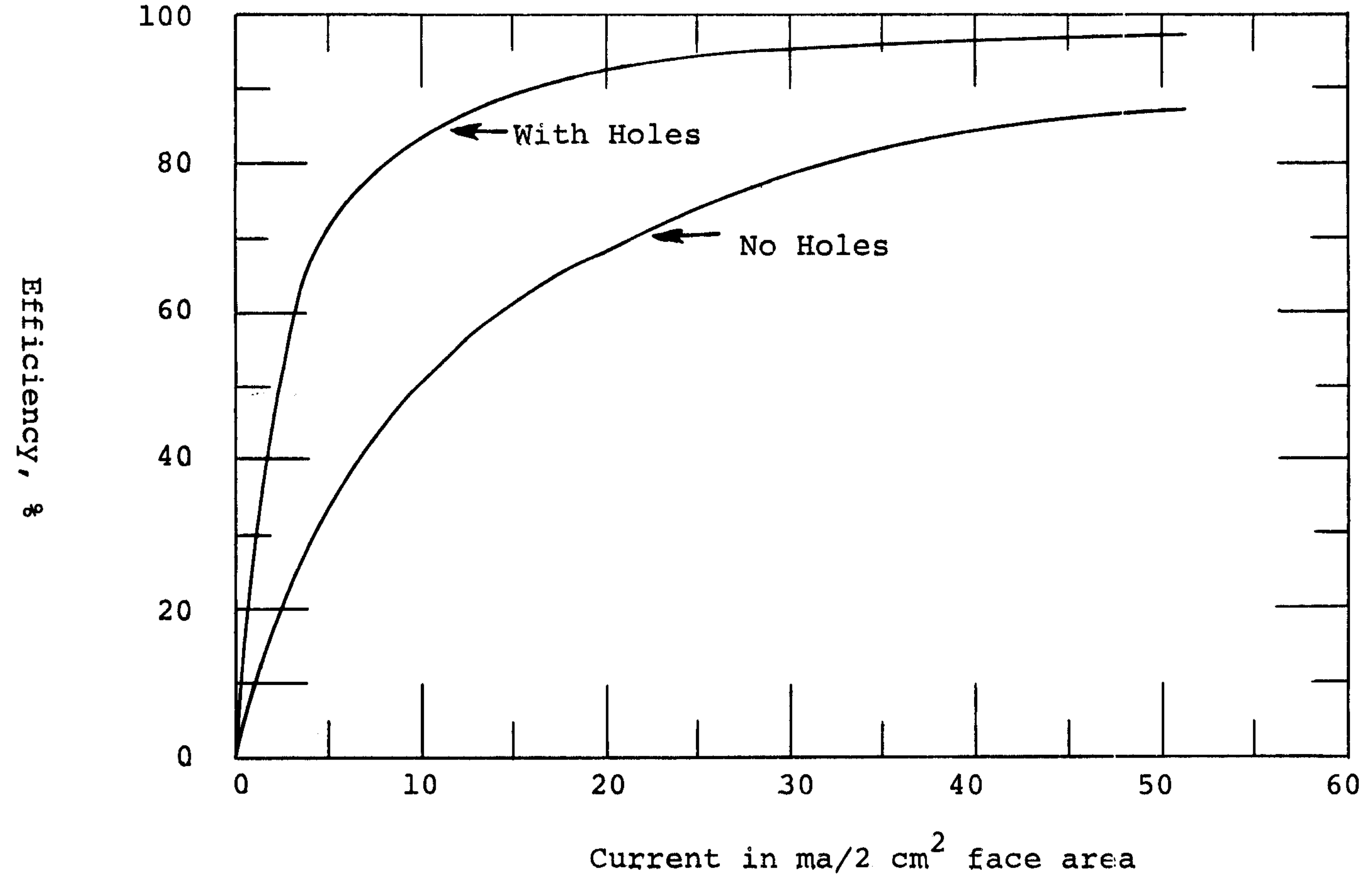
caused by the oxide film which coats the platinum surface at potentials above -0.2 v: Evidently, the rapid catalytic oxidation of methanol must involve adsorption of the methanol molecule on a clean platinum surface. When oxygen covers the platinum surface, it is very difficult for methanol to adsorb and react. As Gilman[18] showed with potentiostatic equipment, even the electrochemical oxidation of methanol is hindered by the oxide layer. (See section II.D.) Paradis[37] found a similar reduction in the direct reaction between hydrogen and oxygen on platinum electrodes when the platinum was covered with an oxide layer.

Current Efficiency

The "current efficiency" for a mixed-feed methanol anode is defined as:—100% times the methanol equivalents consumed to produce current, divided by the total methanol equivalents consumed. This definition can be applied to the data of Graphs 17 and 19 to calculate the current efficiency of the platinized screen anode (holed and non-holed) in 0.04 M methanol. These efficiencies are shown as a function of the anode potential in Graph 34, and as a function of the anode current in Graph 35. The efficiency was found to increase rapidly as the anodic current was increased. The beneficial effect of the electrode holes in improving the electrode efficiency is readily apparent.



Graph 34. Screen Anodic Current Efficiency vs Potential; Platinized (Ni) Screen (4-ply) Electrode; 0.04 M methanol; 70°C; K_2CO_3



Graph 35. Screen Anodic Current Efficiency vs Current; Platinized (Ni) Screen (4-ply) Electrode; 0.04 M methanol; 70°C; K_2CO_3

For example, at a current of 32 ma, the holed electrode had an efficiency of 95% compared to 80% for the non-holed electrode.

Summary

The direct reaction rate measurements on the platinum electrodes make certain conclusions possible regarding the simultaneous electrode reactions of methanol and oxygen.

(a) The mixed-feed current curves can be approximately predicted from the single-feed curves. The slight differences between the predicted and experimental current curves appear to be caused by the preferential consumption of the reactant in short supply (oxygen) by the catalytic reaction.

(b) In general, the inefficient reaction (or direct reaction) cannot be predicted from the single-feed curves due to the possibility of a catalytic reaction between methanol and oxygen. However, this catalytic reaction will not be very large if the electrode potential is in the region for which an oxide layer coats the platinum, or if the reaction rate of one of the reagents is diffusion limited. Therefore, a "selective" anode can be obtained by an electrode design which limits the electrode contact with oxygen.

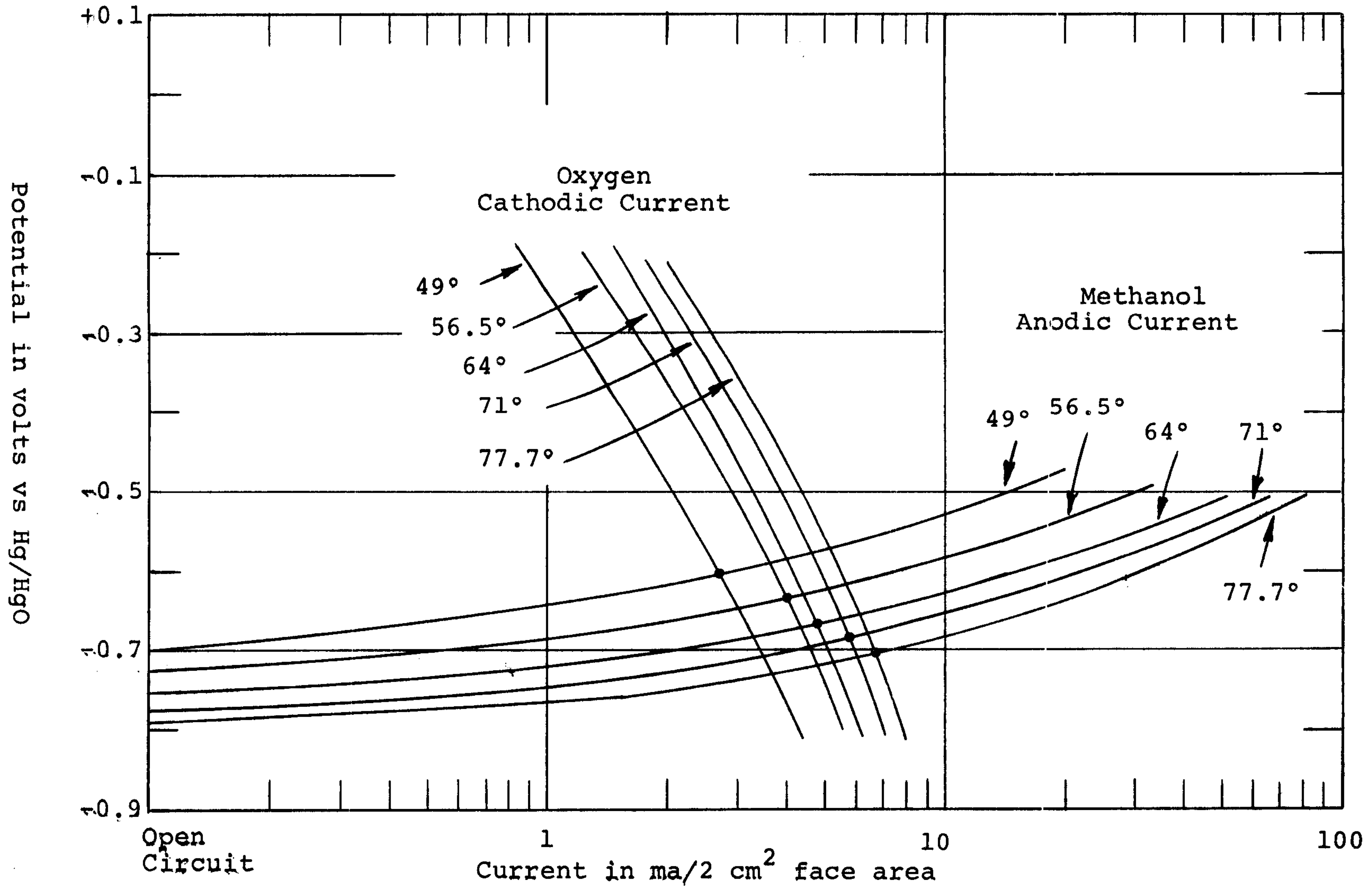
In this way, a platinum anode has been designed which gives a current efficiency of about 95%

3. Effect of Temperature on the Platinized Screen Electrode

In order to determine the effect of temperature on the operation of the platinum screen electrode, mixed-feed and single-feed measurements were made at temperatures from 49°C to 78°C. A non-holed, platinized nickel screen was used with a methanol concentration of 0.01 M.

The single-feed current curves for methanol and oxygen are presented on Graph 36. At any given potential, approximate activation energies for each of the electrochemical reactions can be calculated. For example, at a potential of -0.65 v, the activation energy for the methanol electro-oxidation was about 30 kcal. The activation energy was lowered as the current was increased, indicating that diffusion limitations became more important. The activation energy for the electro-reduction of oxygen at -0.75 v was only about 4.5 kcal due to the mass transfer limitations on the oxygen reaction rate.

The mixed-feed open circuit potential and direct reaction rate can easily be predicted from the single-feed curves. For each temperature, the cross-over point of the oxygen and methanol single-feed curves (Graph 36) determines the expected potential and reaction rate for mixed-feed at

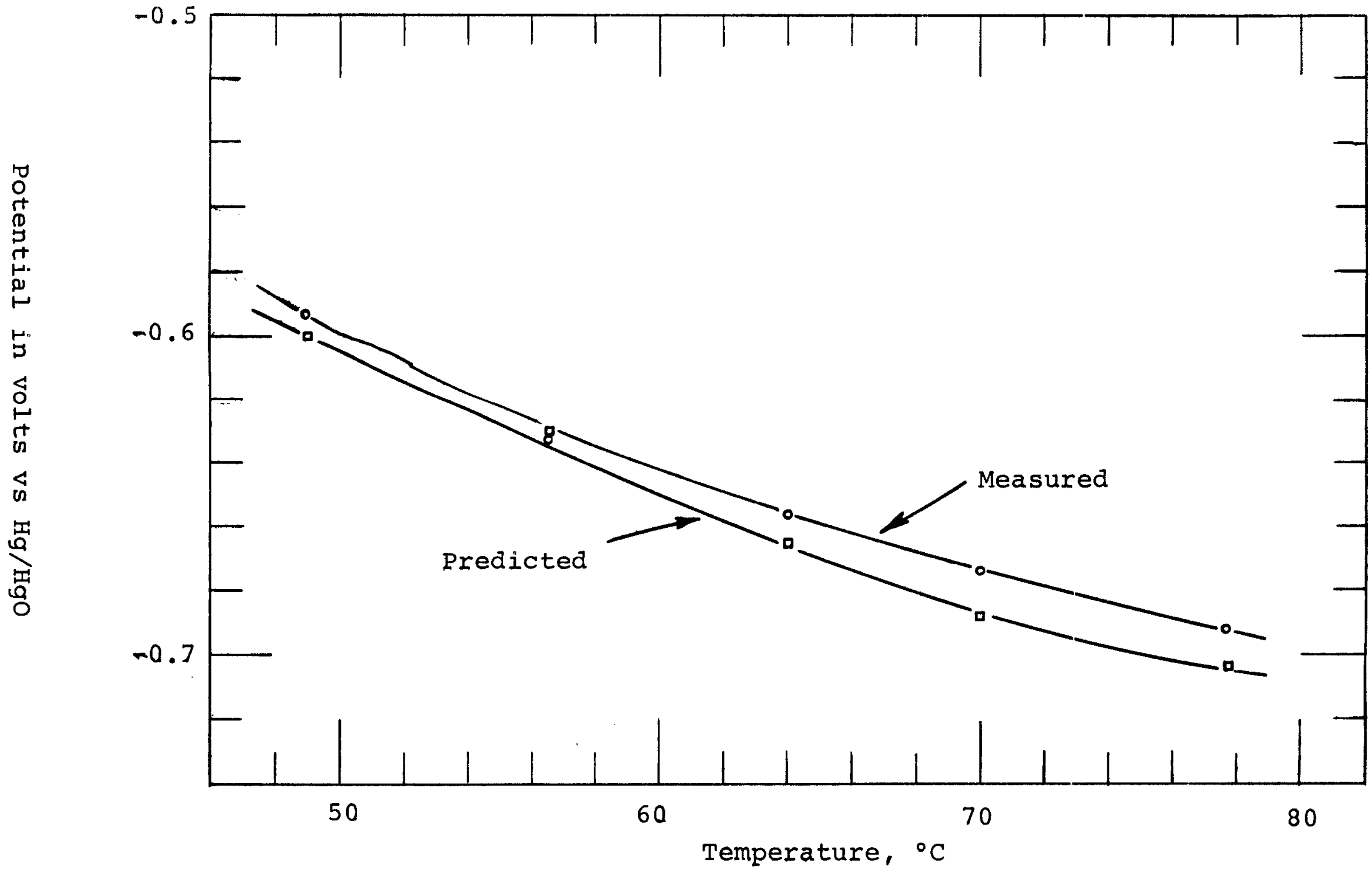


Graph 26. Single-Feed Currents for Screen Electrode at Various Temperatures; Non-holed Platinized (Ni) Screen (4-ply); 0.01 M methanol; K_2CO_3

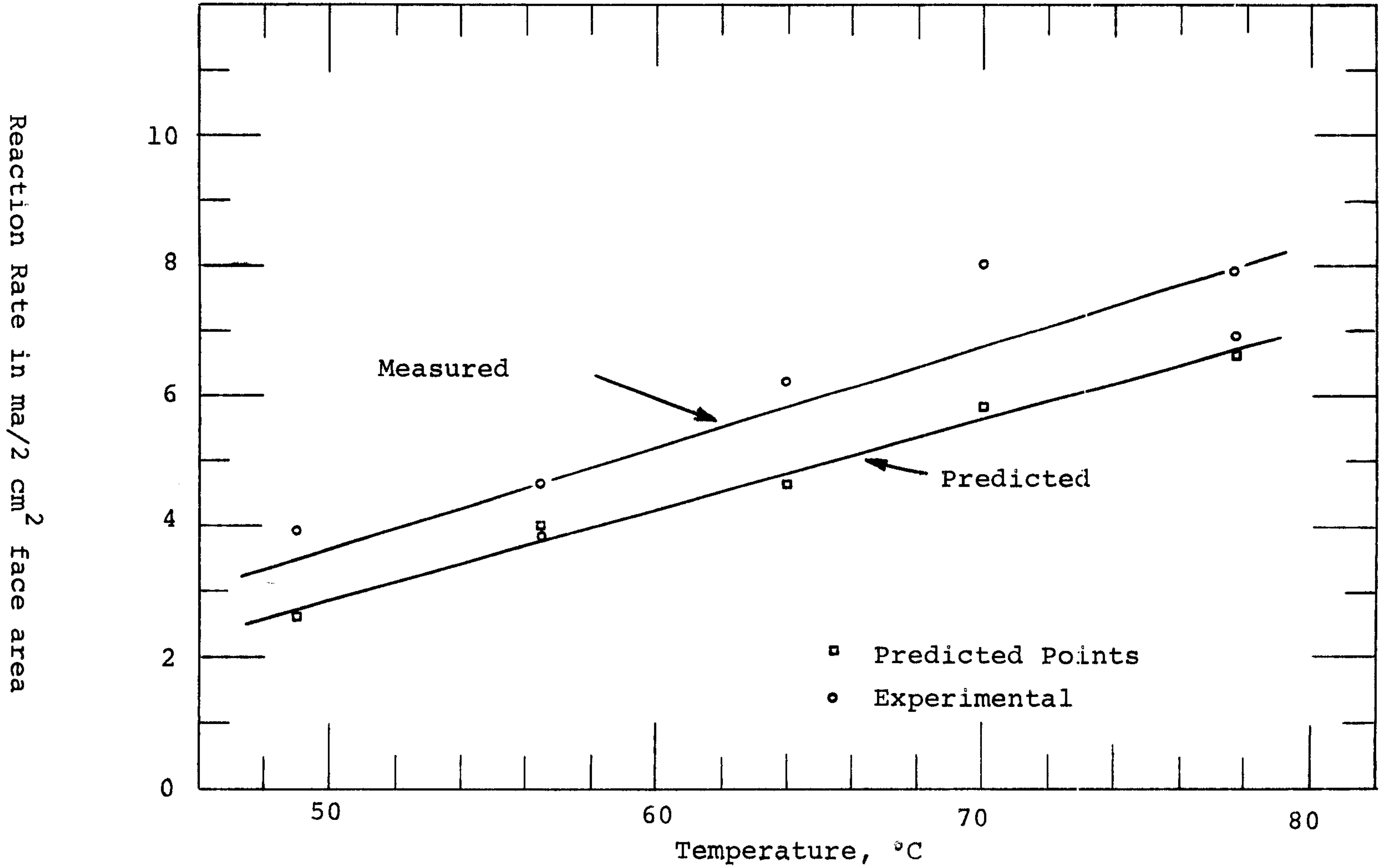
open circuit. These predicted open circuit potentials have been plotted on Graph 37, together with the experimental mixed-feed results. The experimental open circuit potentials were very close to the predicted values at all temperatures: The difference between the experimental and predicted potentials was only about 0.01 v. The open circuit polarization of the mixed-feed anode was found to be reduced as the temperature was increased. This indicates that high temperatures would be beneficial to the voltage output of a mixed-feed cell which utilized this anode.

The similar comparison between the open circuit reaction rate and the predicted rate is shown on Graph 38. As would be expected, the reaction rate was increased by an increase in the temperature. There was approximate agreement between the experimental rate and the predicted rate; the slight difference between the best straight lines for the predicted and experimental data is not significant, due to errors in analysis and electrode deactivation.

If these measurements had been made with the platinum-Teflon electrode, the agreement between the experimental and predicted reaction rate curves would probably not have been very good. This is because the large catalytic reaction would have caused the experimental and predicted reaction rate curves to diverge as the temperature was increased.



Graph 37. Mixed-Feed Open Circuit Potentials for Platinized Screen at Various Temperatures; Non-holed Platinized (Ni) Screen (4-ply); 0.01 M methanol; K_2CO_3 electrolyte.



Graph 38. Open Circuit Direct Reaction Rate for Platinized Screen at Various Temperatures; 0.01 M methanol; K_2CO_3 electrolyte.

C. Products of Methanol Oxidation

In any methanol fuel cell, the methanol should be completely oxidized to carbon dioxide in order to obtain full use of the fuel. If the methanol were only oxidized to formaldehyde or formate, then the total oxidizable equivalents of the fuel would not be utilized.

The products of oxidation were determined for the platinized screen electrode operating with 0.01 M methanol in the carbonate electrolyte at 70°C. This was done by operating the electrode for several hours and then analyzing the concentration of products in the electrolyte. The analytical methods are described in section III.F. and Appendix D. The electrode was operated in two different ways:

(1) at an anodic current of 25 ma with single-feed methanol

(2) at open circuit with mixed-feed.

The analyses showed that both formaldehyde and formate were formed by the oxidation of methanol. The following table gives the moles of each product as a percentage of the total methanol molecules reacted.

Moles Formed of Each Product

(percentage of total)

Run / Product	(1) Single-Feed Methanol; 25 ma	(2) Mixed-Feed Open Circuit
Formaldehyde	—	6%
Formate	83%	94%
Carbon Dioxide (as Bicarbonate)	17%	—

The number of equivalents consumed to form each product can also be calculated. This is expressed as a percentage of the total consumed equivalents in the following table.

Equivalents Consumed to Produce Each Product

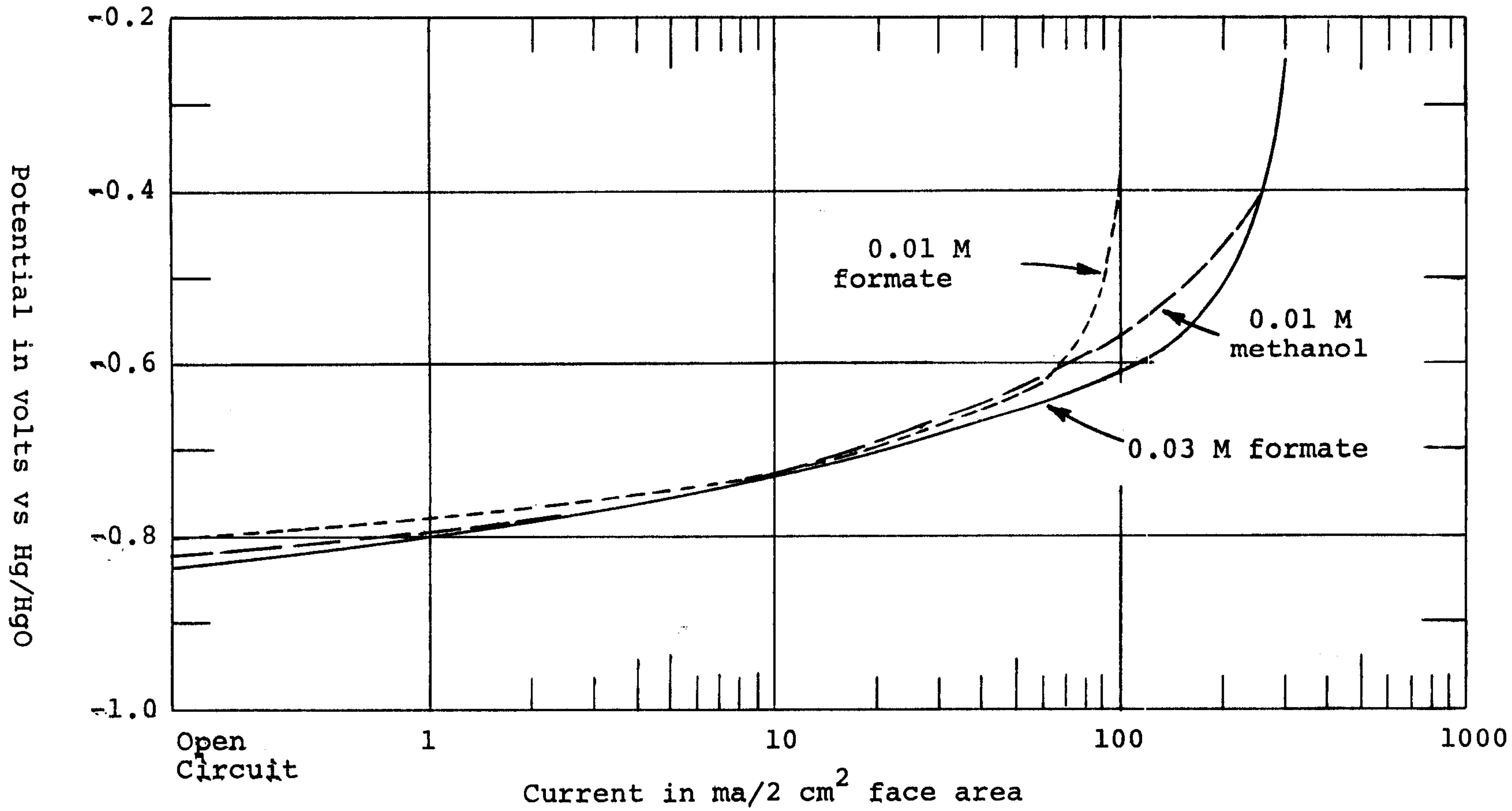
(percentage of total

Run / Product	(1) Single-Feed Methanol; 25 ma	(2) Mixed-Feed Open Circuit
Formaldehyde	—	3%
Formate	77%	97%
Carbon Dioxide (as Bicarbonate)	23%	—

In run (1), no formaldehyde was found in the electrolyte. The analysis would have detected as little as a 0.5% formation of formaldehyde (on the molar basis). In run (2), the major product was formate, with only a small amount of formaldehyde.

Taken by themselves, these data would indicate that formate would be an important product of methanol oxidation in a methanol fuel cell. However, other measurements were made which show that the formate would be only an intermediate product, and that it would subsequently be oxidized to carbon dioxide. These measurements were the potential-current curves for pure potassium formate reacting on the platinized screen electrode. Graph 39 compares the polarization curves for single-feed 0.01 M formate, 0.03 M formate, and 0.01 M methanol in carbonate electrolyte at 70°C. The 0.01 M formate curve is almost identical with the 0.01 M methanol curve until diffusion polarization becomes important at high currents. The methanol limiting current was about three times the 0.01 M formate limiting current, because methanol has three times as many oxidizable equivalents per mole as formate does. The 0.03 M formate curve has the same limiting current as the 0.01 M methanol, as would be expected.

These curves show that formate is just as reactive as methanol for electrochemical oxidation, and that the reason



Graph 39. Formate vs Methanol Current on Screen Anode; Single-Feed; Platinized (Ni) Screen (4-ply); 70°C; K_2CO_3 electrolyte.

why the formate was formed during the methanol oxidation runs was because the methanol concentration was much greater than the formate concentration. During long term cell operation with continuous electrolyte and fuel recycling, the formate would reach a steady-state concentration, where it would be consumed as rapidly as it was formed. Thus, the methanol would ultimately be completely oxidized to carbon dioxide.

V. CONCLUSIONS

A. Conclusions Regarding the Mixed-Feed Design for a Methanol-Oxygen Fuel Cell

1. Cathode

Silver is a very selective cathode material for a mixed-feed, methanol-oxygen fuel cell. An oxygen current efficiency of 100% was obtained for the Teflon-bonded silver electrode, because methanol was neither catalytically nor electrochemically reactive on silver. The silver-Teflon electrode can also be used with air as the oxidant. However, the current output with air was only one-half the output with pure oxygen at a given potential.

A disadvantage with a silver cathode is that it must be used in a basic electrolyte. Carbon also appears to be a very selective cathode, however, it also should be used only in a basic electrolyte since it polarizes excessively in acid.

2. Anode

Several platinum anodes were prepared and tested in this work. A holed-platinized screen electrode was found to be very selective for methanol and to deliver reasonable anodic current densities. This electrode performs in a selective manner because the physical form of the electrode favors the reaction of methanol (in liquid phase) instead of oxygen (gaseous phase): The oxygen reaction rate at this electrode was severely mass transfer limited. The resulting current efficiency for this electrode was about 95% at fuel cell operating conditions. High operating temperatures and high methanol concentrations were found to be beneficial to the operating mixed-feed potentials of this electrode.

Formate and formaldehyde were found to be intermediates in the oxidation of methanol to carbon dioxide. However, in a cell with continuous recycling of electrolyte, the final product of oxidation would be carbon dioxide.

3. Electrolyte

An alkaline electrolyte was found which rejects the carbon dioxide produced by methanol oxidation at a temperature of 70°C. This steady-state electrolyte is an aqueous mixture of potassium carbonate and bicarbonate which has a carbon dioxide vapor pressure of about 0.08 atmospheres at 70°C. One disadvantage of this electrolyte is that the cell output voltage was not as high as when pure potassium carbonate or hydroxide electrolytes were used. Better operating voltages could be obtained with the steady-state electrolyte by cell operation at higher temperatures, because the equilibrium concentration of bicarbonate in the rejecting electrolyte would then be smaller.

4. Cell Geometry

The mixed-feed cell design is much simpler than the conventional gas diffusion cell. However, part of the advantage of the mixed-feed cell is lost if a gaseous reactant is used, since the cell must then be designed for two-phase flow. A cheap, soluble oxidant that gives high current efficiencies when used in conjunction with methanol would be highly desirable.

B. Conclusions Regarding the Simultaneous Reaction of Methanol and Oxygen at Platinum Anodes

1. Current-Potential Curves

When the mixed-feed theory was applied to three platinum anodes, it was found that the mixed-feed current output for these platinum anodes could be approximately predicted from single-feed measurements. The good agreement between the predicted and experimental results tends to support the basic assumption of the mixed-feed theory: The electrochemical reaction rate of each reactant during mixed-feed operation is about the same as during single-feed.

The mixed-feed anodic performance of the platinum electrodes was best at high temperatures and high methanol concentrations, since both of these factors increased the methanol reaction rate relative to the oxygen reaction rate. The concentration and temperature effects could be predicted from the single-feed current curves obtained under corresponding conditions.

2. Direct Reaction Rates

Methanol and oxygen can react on platinum with an electrochemical, as well as catalytic mechanism. Therefore, the direct reaction rates predicted by single-feed current curves may be low, due to the possible occurrence of the catalytic reaction. However, if the electrode is designed to minimize oxygen-platinum contact, then the direct reaction rate will be approximately equal to the predicted values and the catalytic reaction will not seriously hinder the electrodes' efficiency.

An increase in methanol concentration did not increase the direct reaction rate for the screen electrode since the oxygen supply was diffusion limited. However, in the case of the platinum-Teflon electrode, both the catalytic and electrochemical direct reaction rates were increased by an increase in the methanol concentration.

The direct reaction rate was found to be very low in the potential region where the platinum surface is covered by an oxide layer, indicating that the adsorption of methanol on a clean platinum surface plays an important part in the catalytic reaction between methanol and oxygen.

VI. RECOMMENDATIONS

Before the operation of a methanol-air, mixed-feed cell becomes practical, several problems must be overcome.

The silver-Teflon cathode produced an acceptable current density when freshly prepared. However, the electrode performance gradually deteriorated with use. A silver cathode must be designed which maintains high activity for long periods of time.

The platinum screen electrodes appeared to become poisoned by carbon monoxide adsorption after operation for several hours. Methods for oxidizing the carbon monoxide during cell operation should be devised so that the electrode will continue to perform well for periods longer than a few hours.

Further work should be done to determine the optimum temperature for operation with the potassium carbonate-bicarbonate, carbon dioxide-rejecting electrolyte. A high temperature is desirable in order to minimize the bicarbonate concentration in the electrolyte because the cell voltage is reduced by the presence of bicarbonate. However, the temperature should not be increased to the point where the low methanol solubility in the electrolyte causes excessive anode polarization.

The problems associated with two phase flow in the methanol-air cell must also be overcome. In a large scale-up of this type of cell, it would be difficult to obtain an even supply and distribution of air over the entire cathode surface.

APPENDIX A

Thermodynamic Potentials

1. Cell Potentials

The following standard cell potentials have been calculated by the use of the thermodynamic equation:

$$\Delta F^o = -n\mathcal{F}E^o$$

where n = equivalents per mole

$\mathcal{F}$ = Faraday's constant, 23,100 cal/volt-equiv

F^o = Free Energy for the reaction, cal/mole

The values for the standard free energy of formation were obtained in W. M. Latimer's Oxidation States[33].

Complete Oxidation of Methanol		E^o
a.	$CH_3OH + \frac{3}{2} O_2 = CO_2 + 2H_2O$	1.199
b.	$CH_3OH + \frac{3}{2} O_2 + 2OH^- = CO_3^= + 3H_2O$	1.296
c.	$CH_3OH + \frac{3}{2} O_2 + CO_3^= = 2HCO_3^- + H_2O$	1.224
Oxidation of Methanol to Formic Acid or Formate		
d.	$CH_3OH + O_2 = HCOOH + H_2O$	1.085
e.	$CH_3OH + O_2 + OH^- = HCOO^- + 2H_2O$	1.237
Oxidation of Formate and Formic Acid		
f.	$HCOOH + \frac{1}{2} O_2 = CO_2 + H_2O$	1.427
g.	$HCOO^- + \frac{1}{2} O_2 + OH^- = CO_3^= + H_2O$	1.415
h.	$HCOO^- + \frac{1}{2} O_2 + CO_3^= + H_2O = 2HCO_3^- + OH^-$	1.199

The large difference between the potentials for the partial and complete oxidation of methanol in acid electrolyte explains why the complete oxidation reaction always occurs. In basic electrolyte, this difference is smaller. The formate ion is much more stable than formic acid. Equations (c), (e), and (h), correspond to the reactions occurring in a 50 (wt)% potassium carbonate electrolyte. However, the standard cell potentials have been calculated on the basis of an activity of unity for all of the electrolyte ions. This is of course not the case. The concentration of carbonate is 5.6 Molar. At 70°C (the usual operating temperature), the hydroxide ion concentration was measured to be 0.393 M. (See section 4 on Reference Electrodes.) By the reaction,

$$CO_3^{=} + H_2O = OH^- + HCO_3^-$$

the bicarbonate concentration must also be 0.393 M. (This concentration would increase slightly by the oxidation of methanol, but never more than 1% in this work. The activities of carbonate, bicarbonate, and hydroxide are assumed to be equal to their molarities and the deviation in the activity of water from unity is neglected. The activity of methanol or formate was taken as unity. The Nernst equation can then be used to correct equation (c) for the actual ion concentrations.

$$E_{rev} = E^{o} - \frac{0.05915}{n} \log \frac{\left(A_{HCO_3^-}\right)^2 \left(A_{H_2O}\right)}{\left(A_{CO_3^=}\right)\left(P_{O_2}\right)^{3/2}\left(A_{CH_3OH}\right)}$$

$$= 1.224 - \frac{0.05915}{6} \log \frac{(.393)^2 \times 1}{(5.2) \times 1 \times 1}$$

$$= 1.239 \text{ v}$$

In a similar way, equations (e) and (h) can be corrected to give:

<u>50 (wt)% carbonate</u>	<u>E_{rev}</u>
(c′) $CH_3OH + \frac{3}{2} O_2 + CO_3^= = 2HCO_3^- + H_2O$	1.239 v
(e′) $CH_3OH + O_2 + OH^- = HCOO^- + 2H_2O$	1.231 v
(h′) $HCOO^- + \frac{1}{2} O_2 + CO_3^= + H_2O = 2HCO_3^- + OH^-$	1.256 v

The composition of the carbonate-bicarbonate mixture electrolyte is calculated in Appendix C.

$(HCO_3^-) = 2.95$ M

$(CO_3^=) = 2.05$ M

$(OH^-) = 2.43 \times 10^{-4}$

(See Section 4 on Reference Potentials.)

Equations (c), (e), and (h) can also be corrected by the Nernst equation for this electrolyte.

Carbonate-Bicarbonate Mixture Electrolyte		E_{rev}
(c'')	$CH_3OH + \frac{3}{2} O_2 + CO_3^{=} = 2HCO_3^{-} + H_2O$	1.218 v
(e'')	$CH_3OH) + O_2 + OH^{-} = HCOO^{-} + 2H_2O$	1.184
(h'')	$HCOO^{-} + \frac{1}{2} O_2 + CO_3^{=} + H_2O = 2HCO_3^{-} + OH^{-}$	1.287

Some current measurements have also been made in 20 (wt)% potassium hydroxide electrolyte. The hydroxide activity for this electrolyte is 6.26 M.[37] The Nernst Equation is used to adjust equation (b) for the complete oxidation of methanol in hydroxide electrolyte.

20 (wt)% hydroxide		E_{rev}
(b')	$CH_3OH + \frac{3}{2} O_2 + 2OH^{-} = CO_3^{=} + 3H_2O$	1.311 v

2. Oxygen Half Cell Potentials

The standard electrode potential for oxygen in one molar hydroxide is + 0.401 v.

	E^o
$4 e^{-} + O_2 + 2H_2O = 4 OH^{-}$	+0.401

This may be corrected for any hydroxide concentration by the Nernst equation:

$$E_{rev} = E^o - \frac{0.05915}{4} \log \frac{(A_{OH^-})^4}{(A_{H_2O})(P_{O_2})}$$

The activity of water is approximated as unity. For the carbonate electrolytes, the hydroxide activities have been calculated in section 4 of this Appendix.

20 (wt)% potassium hydroxide[37] $E_{rev} = +0.348$

50 (wt)% potassium carbonate $E_{rev} = +0.425$

carbonate-bicarbonate electrolyte $E_{rev} = +0.615$

3. Methanol Half Cell Potentials

The methanol half cell potentials may be determined by subtraction of the complete cell potentials of section 1 from the oxygen half cell potentials.

20 (wt)% potassium hydroxide	E_{rev}
$CH_3OH + 8\ OH^- = CO_3^= + 6\ H_2O + 6\ e^-$	-0.963
50 (wt)% potassium carbonate	
$CH_3OH + CO_3^= + 6\ OH^- = 2\ HCO_3^- + 4\ H_2O + 6\ e^-$	-0.814
$CH_3OH + 5\ OH^- = HCOO^- + 4\ H_2O + 4\ e^-$	-0.806
$HCOO^- + CO_3^= + OH^- = 2\ HCO_3^- + 2\ e^-$	-0.831
carbonate-bicarbonate electrolyte	
$CH_3OH + CO_3^= + 6\ OH^- = 2\ HCO_3^- + 4\ H_2O + 6\ e^-$	-0.603
$CH_3OH + 5\ OH^- = HCOO^- + 4\ H_2O + 4\ e^-$	-0.569
$HCOO^- + CO_3^= + OH^- = 2\ HCO_3^- + 2\ e^-$	-0.672

(The above equations may not truly represent the actual consumption and production of hydroxide and bicarbonate in the solution, due to the equilibrium:

$$H_2O + CO_3^{=} = HCO_3^{-} + OH^{-}$$

However, the calculated values of E_{rev} are independent of how the reaction is written as long as the correct concentrations are used in each case.)

4. Reference Electrode Potentials

Two reference electrodes have been used in this work. The saturated calomel electrode has a potential of +0.242 v. (27)

$$Hg_2C\ell_2 + 2\ e^{-} = 2\ Hg + 2\ C\ell^{-} \quad (\text{Sat. KC}\ell) \qquad E^{o}_{SCE} = +0.242$$

The other reference electrode was a mercury-mercuric oxide (red) couple. The standard potential in one molar hydroxide is +0.098 v.

$$HgO(r) + H_2O + 2\ e^{-} = Hg + 2\ OH^{-} \qquad E^{o} = +0.098$$

The electrolyte used for this couple was 50 (wt)% potassium carbonate with a pH of 13.35 at 25°C. Thus, the Nernst equation gives a value of +0.136 v for the reversible potential in carbonate. By actual measurement with a calomel electrode, this potential is +0.140 v.

50 (wt)% potassium carbonate

$$HgO(r) + H_2O + 2\ e^{-} = Hg + 2\ OH^{-} \qquad E_{rev} = +0.140\ v$$

Potassium carbonate was used for the reference electrolyte even when the 20 (wt)% potassium hydroxide or the carbonate-bicarbonate electrolyte was used as the electrode test electrolyte. This added a liquid junction potential to the reference electrode. The net Hg/HgO reference potential (including each liquid junction) was measured with a calomel electrode. They are as follows:

	E_{ref}
$Hg \vert HgO \mid (K_2CO_3)\ 25°C \mid (K_2CO_3)\ 70°C$	0.140 v
$Hg \vert HgO \mid (K_2CO_3)\ 25°C \mid (K_2CO_3, KHCO_3)\ 70°C$	0.131
$Hg \vert HgO \mid (K_2CO_3)\ 25°C \mid (KOH)\ 70°C$	0.164

The hydroxide activity in the carbonate and carbonate-bicarbonate electrolytes at 70°C was determined by measuring the potential of the Hg/HgO couple in each electrolyte with the calomel electrode.

	Potential
$Hg \vert HgO \mid (K_2CO_3)\ 70°C$	+0.122 v
$Hg \vert HgO \mid (K_2CO_3, KHCO_3)\ 70°C$	+0.312 v

The Nernst equation can be used to calculate the hydroxide activity for each case.

<u>50 (wt)% potassium hydroxide 70°C</u>

$$(OH^-) = 0.393\ M$$

<u>carbonate (2.95 M) and bicarbonate (2.05 M) electrolyte 70°C</u>

$$(OH^-) = 2.43 \times 10^{-4}\ M$$

APPENDIX B

Potassium Carbonate-Bicarbonate Mixture Electrolyte

For practical methanol cell operation, an electrolyte is needed which will expel the carbon dioxide product at the operating temperature. A mixture of carbonate and bicarbonate will expel carbon dioxide if the bicarbonate concentration is high enough. This is referred to as an "equilibrium" electrolyte. To achieve maximum electrochemical rates, the electrolyte should also be as concentrated as possible. In order to determine the optimum electrolyte, the carbon dioxide rejection pressure must be known.

A simple mixed fuel cell design is proposed to determine an approximate carbon dioxide partial pressure. (Figure (B-1)

Electrolyte containing methanol is continuously recirculated through an electrode bank (alternating cathodes and anodes). Air is also circulated but is exchanged on each pass. The overall reaction is:

$$CH_3OH + \frac{3}{2} O_2 = CO_2 + 2\ H_2O$$

For each mole of carbon dioxide product, two moles of water are formed and 1.5 moles of oxygen are consumed. A 0.6 mole excess oxygen will be used in order to prevent excessive cathode polarization. The total moles of purged gas per mole of carbon dioxide product can now be calculated.

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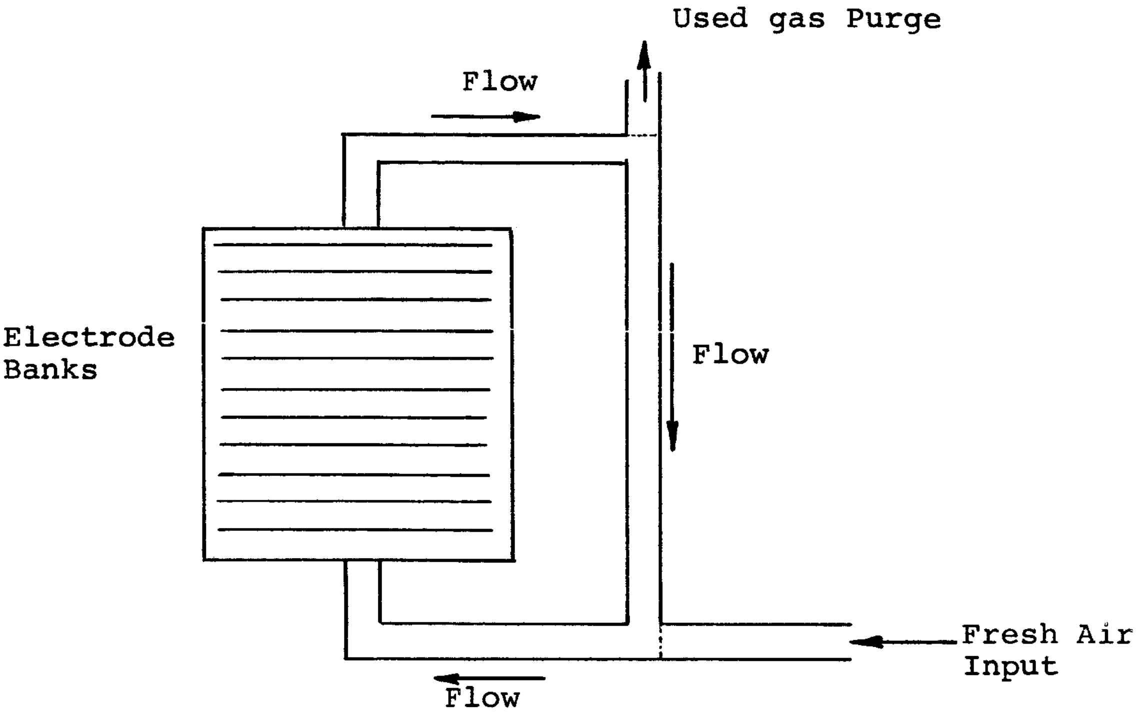

Figure B-1. Methanol-Air Cell

(a) Excluding Water Vapor

1.0 mole carbon dioxide

0.6 mole oxygen

8.4 mole nitrogen (4 times oxygen input)

10.0 mole

(b) Including Water Vapor

The approximate vapor pressure would be 130 mm Hg. This is 17.1% out of a total of 760 mm Hg. If x = moles water vapor,

$$.171\ (10 + x) = x$$

$x = 2.06$ moles water vapor in purge gases

The partial pressure of carbon dioxide in purge gases is:

$$\frac{1 \text{ mole } CO_2}{12 \text{ mole total}} \times 760 \text{ mm Hg} = 63 \text{ mm Hg}$$

The equilibrium constant of Sieverts and Fritzsche[43] at 70°C will be assumed to be approximately valid in concentrated solutions.

$$0.068 = \frac{(KHCO_3)^2}{(K_2CO_3)(P_{CO_2})} \qquad (P_{CO_2} \text{ in mm Hg})$$

For $P_{CO_2} = 63$ mm Hg,

$$\frac{(KHCO_3)^2}{(K_2CO_3)} = 4.30$$

By trial and error, a concentrated solution at 70°C was found which satisfied this equilibrium. (Reference on the solubility of potassium carbonate and bicarbonate: Rubtzov[42].)

The equilibrium solution is:

20 (wt)% potassium carbonate, anyd.
21 (wt)% potassium bicarbonate, anyd.
59 (wt)% water

The density of this electrolyte mixture was measured to be 1.41 gm/ml. This mixture can only be used at 70°C, or higher, because the salts are not completely soluble at a temperature below 65°C. The molar concentrations in this solution are:

$(KHCO_3) = 2.95$ M

$(K_2CO_3) = 2.05$ M

APPENDIX C

Electrode Fabrication

Platinized Wire Gauze Electrodes

These electrodes consisted of a wire gauze which had been electrolytically platinized. Both nickel and platinum-10% rhodium wire gauzes were used. The nickel screen was 150-mesh with 0.0026 inch diameter wire. The platinum-rhodium gauze was 80-mesh with 0.003 inch diameter wire.

The platinizing solution was prepared by dissolving 4 gm of reagent grade chloroplatinic acid in 200 ml distilled water. The gauze was immersed in the stirred solution and a cathodic current of 50 ma/(cm^2 of face area) was applied for 3 minutes. The platinized platinum screen was activated by immersion in concentrated sulfuric acid for several hours. No activation was necessary for the platinized nickel screens.

For most of the measurements, a group of four gauzes were put in a polyethylene "frame." The gauzes were placed between two polyethylene washers which were then sealed together in a hot press. A polytetrafluoroethylene mold was used (Figure C-1). The polyethylene dimensions were: I.D., 1.59 cm; O.D., 3.3 cm; thickness, $\frac{1}{32}$ in. The exposed electrode face area was 2 cm^2. The polyethylene was sealed at 133°C by application of a pressure of 1000 lb for 60 seconds. A tap extension protruded through the polyethylene frame for attachment to a wire lead.

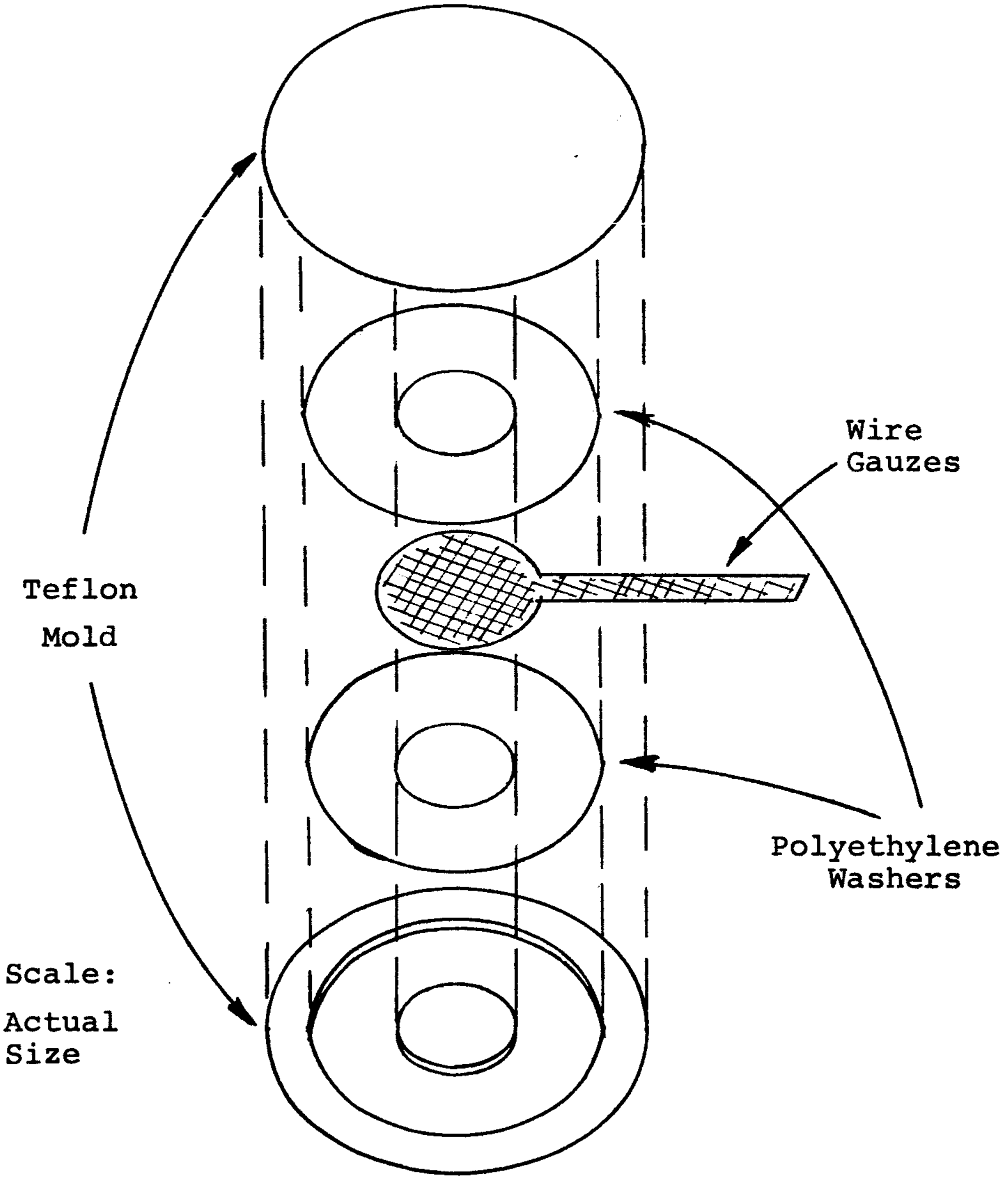

Figure C-1. Electrode Frame Construction

The geometrical wire area was 2.45 $cm^2/(cm^2$ of gauze face area) for the nickel screen, and 1.51 $cm^2/(cm^2$ face area) for the platinum screen. The electrolytic platinum coating contained 4.5 mg of platinum per cm^2 of face area. Thus, if four screens were used as a single electrode, the total electrolytic platinum loading was 19 mg/cm^2. This loading was calculated on the basis of a 3 minute platinization at 50 ma/cm^2. In the case of the nickel screens, the loading may have been slightly larger due to the chemical deposition of platinum by nickel oxidation.

Teflon Type Electrodes

Three types of Teflon bonded porous gas diffusion electrodes were prepared: silver, platinum, and carbon-silver. These electrodes were prepared according to the description of Deibert[15]. The general procedure is to mix and mull the desired powdered catalyst with an aqueous dispersion of Teflon powder. The dough is rolled and thinly spread on an inert screen collector.

The platinum black powder was supplied by Englehard Industries and had an average particle diameter of 100 Å and a specific surface of 25 m^2/gm. The powdered silver was supplied by Monsanto Corporation. It was a non-commercial, high area silver with about a 100 Å particle size. The carbon black, supplied by Cabot Corporation (type "Elf-1"), was the conductive type consisting of non-porous 200 Å particles. DuPont's Teflon dispersion Number 852-201 was used, which is a 50 (wt)% suspension of Teflon particles in water containing a small quantity of organic surfactants. The particles have an average diameter of 1000 Å.

The following weight proportions were used for each of the electrodes:

	Water	Teflon Suspension	Catalyst
Platinum Electrode	45%	10%	Platinum: 45%
Silver Electrode	57%	139%	Silver: 30%
Carbon-Silver Electrode	48%	30%	Carbon: 14% Silver: 8%

These proportions yielded membranes with a Teflon to catalyst volume ratio of about 1:1. The initial water content was about 80-90 (vol)%, so that the dried membranes should have had a porosity of about 80%.

The ingredients were mulled with a mortar and pestle until they formed a rubbery dough. The dough was pressed to a thickness of approximately 0.01 inch between two polyethylene sheets with a rolling pin. This film was then pressed into a 40-mesh Monel screen current collector. The electrode was dried over night at room temperature and then heated successively at 100°C, 200°C, and 300°C for one hour each. The catalyst content per unit electrode area is given in section III.B.

The final electrode membranes were then placed inside a polyethylene frame, as for the wire gauze electrodes. Even though these membranes are rather porous, the pores are far too small for bulk flow. Therefore, three or four small holes (1 mm diameter) were put through these electrodes (around the periphery) to allow for the passage of electrolyte and oxygen.

APPENDIX D

Chemical Analysis

Methanol

The procedure used for methanol analysis was similar to a method reported by Karpov[28]. Standard solutions used were 0.12 N potassium dichromate, 0.04 N ferrous ammonium sulfate, and 0.01 N ferrous ammonium sulfate. Analytical reagent grade potassium dichromate was used as a primary standard and was initially dried in an oven at 100°C. Concentrated sulfuric acid (28 ml) was added to each liter of ferrous ammonium sulfate to stabilize the ferrous ion and to keep ferric hydroxide from precipitating. Even so, the ferrous solution was restandardized each day with potassium dichromate.

N- phenylanthranilic acid was used as indicator for the titration of ferrous into dichromate. About three drops of a 0.1% indicator solution were used for each titration. The indicator produces a violet color after a few milliliters of titrant have been added. The violet sharply turns green at the end point. There is no end point correction.

All analytical glassware was calibrated and all solutions were standardized at a constant temperature (25°C).

The following procedure was used to analyze for 0.01 M methanol in 50 (wt)% potassium carbonate electrolyte.

Standard 0.12 N potassium dichromate (2 ml) was pipetted into a 250 ml G.G. flat bottom flask. A calibrated syringe was used to add 2 ml of the electrolyte. The flask was fitted with a 12 in. condenser and 6 ml concentrated sulfuric acid was slowly added through the condenser while the flask was swirled. Precaution was necessary to prevent the loss of methanol as carbon dioxide was evolved. The flask was then heated for 30-45 minutes over boiling water to completely oxidize the methanol. About 15 ml water was used to rinse the condenser before it was removed, and the flask cooled. The indicator was added and the excess dichromate titrated with 0.01 N ferrous ammonium sulfate.

For the analysis of 0.04 M methanol, the procedure was the same. However, the solutions used were 10 ml dichromate (0.12 N), 10 ml concentrated sulfuric acid, and 0.04 N ferrous ammonium sulfate.

Formaldehyde

The procedure for the colorimetric formaldehyde determination was similar to that reported by Thompsett[45]. Chromotropic acid reagent was prepared by dissolving 0.5 gm chromotropic acid (1:8-dihydroxynaphthalene-3:6-disulfonic acid) in 50 ml water and 75 ml concentrated sulfuric acid. Samples of the reagent (5 ml) were put into test tubes and heated in boiling water. A syringe was used to bubble into each test tube a 0.2 ml portion of 50 (wt)%

potassium carbonate containing a varying quantity of formaldehyde. Likewise, the unknown electrolyte was added to a test tube. The test tubes were heated for 20 minutes to fully develop the violet color. The depth of color in the unknown tube was then compared by eye to the known samples. The formaldehyde concentration in the unknown electrolyte could be determined to ± 8×10^{-7} gm/ml.

APPENDIX E

Sample Calculation of Methanol Reaction Rate

This sample calculation is for a mixed-feed, open circuit run. The electrode was a platinized screen electrode (no holes) and the methanol concentration was 0.04 M.

The procedure was as follows:

(a) First equilibrium mixing (30 min)

(b) First pair of analyses

(c) Run at 70°C (120 min)

(d) Second equilibrium mixing (30 min)

(e) Second pair of analyses

(A detailed description of the procedure is contained in section III.E.—Reaction Rate Measurements.)

The reaction rate was determined from equation (1):

$$\text{Reaction Rate} = \frac{V_S\left[\left(V_{F2} - \frac{.02}{10^3}\right) - V_{F1}\right] C_F \,(1.608)\,(10^6)\,\frac{\text{ma-min}}{\text{equiv.}}}{T \times V_e} - 3.7\ \text{ma} \tag{1}$$

where: V_e = volume of electrolyte analysis sample,

$= 2.005 \times 10^{-3}$ L

V_s = volume of electrolyte in circulating system during run, in L.

V_{F_1} = average volume of standard ferrous solution used for first pair of analysis titrations, in L

V_{F_2} = as V_{F_1}, except for second pair of analyses

C_F = concentration of standard ferrous solution, = 0.04326 N

T = time duration of run, = 120 min

In equation (1), 3.7 ma is subtracted from the first term because there was a 3.7 ma leak rate through the rubber diaphragm of the gas pump. Also in equation (1), 0.02 ml is subtracted from V_{F_2} in order to correct it for the methanol consumed during the second equilibrium mixing.

The volume of electrolyte in the system, V_s, was determined from the first analysis of the concentration and the known amount of methanol added to the circulating electrolyte (M_i). Equation (2) was used.

$$V_s = \frac{M_i V_e}{V_D\, C_D - \left(V_{F_1} - .02 \times 10^{-3}\right) C_F} - 4.5 \times 10^{-3}\ \text{L} \qquad (2)$$

where: M_i = initial amount of methanol put into circulating electrolyte, = 0.03192 equivalents

V_D = volume of dichromate standard solution used in each analysis, = 9.987×10^{-3} L

C_D = concentration of dichromate standard solution, = 0.09977 N

In equation (2), 4.5 ml is subtracted from the first term because this much electrolyte was removed from the system for the first pair of analyses.

The volume of ferrous titrant was:

First Analyses	Second Analyses
11.31 ml	11.72 ml
11.28 ml	11.69 ml
$V_{F_1} = 11.295 \times 10^{-3}$ liter	$V_{F_2} = 11.705 \times 10^{-3}$ liter

Substitution into equation (2) gives:

$$V_s = \frac{(0.03192)(2.005)(10^{-3})}{(9.987)(10^{-3})(0.09977) - (11.275)(10^{-3})(.04326)} - 4.5(10^{-3})$$

$$= 0.1213 \text{ liter}$$

This value for V_s is now used in equation (1):

$$\text{Reaction Rate} = \frac{.1213\left[\frac{11.685}{10^3} - \frac{11.295}{10^3}\right].04326 \cdot 1.608 \cdot 10^6}{120 \cdot 2.005 \cdot 10^{-3}} - 3.7 \text{ ma}$$

$$= 9.8 \text{ ma}$$

APPENDIX F

Error in Reaction Rate Measurements

A repetition of identical runs indicated that there was a random average error of about ±1 ma in the reaction rate measurements. The following calculations will show that most of this error was caused by the chemical analysis.

When 0.04 N ferrous solution was used for titrating, the average difference between duplicate analyses was 0.034 ml. This gives a probable error in the mean of about .015 ml. The probable error in the difference between the first and second pairs of analyses is then about .03 ml.

Equation (1) of Appendix E can be adapted to calculate the probable error in the reaction rate:

$$\text{Error in Reaction Rate} = \frac{(\text{Error in titration}) \times V_s \times C_F \times 1.608 \times 10^6}{T \times V_e}$$

$$= \frac{.3 \times 10^{-3} \times .122 \times .04 \times 1.608 \times 10^6}{120 \times 2 \times 10^{-3}}$$

$$= 1.0 \text{ ma}$$

When 0.01 N ferrous standard was used for titrating, the reaction rate error was only slightly less. The average difference between duplicate analysis was 0.078 ml. This gives a probable error in the reaction rate of 0.6 ma.

There was also an error caused by diffusion of methanol from the reference and dummy side compartments (as discussed in section III.E.). If the initial methanol concentration in the side compartments was the same as the system concentration, then the resulting error in the reaction rate was about 10% low (i.e., a 1 ma error for a typical 10 ma reaction rate). In order to reduce this error, the side compartments were initially filled with a methanol concentration which was approximately equal to the expected final system concentration. The expected concentration could be approximated from previous runs. Obviously, this type of approximation will not completely eliminate the error, but will reduce it. The error then would be less than 5%. Therefore, in most cases, this error was smaller than the error in the chemical analysis.

APPENDIX G

Mass Transfer to Screens

The diffusion limited current for screen electrodes can be calculated by a method used by Reti[41] and Paradis[37]. The diffusion limited current is given by:

$$i_L = 1000\ nFk_LC \quad \text{ma/cm}^2 \text{ geometrical area} \tag{3}$$

where:

n = the number of electrons transferred per molecule of reactant

F = Faraday's Constant, 96,500 coulombs

k_L = the mass transfer coefficient, cm/sec

C = the reactant concentration, gm-moles/cm^2

The mass transfer coefficient can be approximated by adapting a correlation for heat transfer to single cylinders in transverse flow[35].

$$\frac{k_L d}{D} = 0.91\left(\frac{dG}{\rho}\right)^{0.385}\left(\frac{\mu}{\rho D}\right)^{0.31} \tag{4}$$

d = the screen wire diameter, cm

D = the reactant diffusivity, cm^2/sec

G = the mass flow rate, gm/sec-cm^2

μ = the electrolyte viscosity, poise

ρ = the electrolyte density, gm/cm^3

The calculation will be based on an electrolyte temperature of 70°C. The density of the electrolyte is 1.5 gm/cm^3. The diffusivity of methanol is approximated as 2.0×10^{-5} cm^2/sec (the value for methanol in water at 20°C is 1.28×10^{-5} cm^2/sec)[39]. The viscosity for the carbonate electrolyte is similar to that for 20% potassium hydroxide which is 0.0413 poise at 25°C.[41] At 70°C the value for the viscosity of carbonate is approximated as 0.018 poises. The wire diameter is 0.0066 cm.

<u>Flow Rate</u>: 32 cm^2/min, <u>Concentration</u>: $0.011 \times 10^{-3} \cdot \frac{\text{moles}}{\text{cm}^3}$

$$G = 0.40 \text{ gm/sec-cm}^2$$

$$k_L = \frac{D}{d} \times .91 \times \left[\frac{dG}{\rho}\right]^{.385} \left[\frac{\mu}{\rho D}\right]^{.31}$$

$$= \frac{2.0 \times 10^{-5}}{.0066} \times .91 \left[\frac{.0066 \times .40}{1.5}\right]^{.385} \left[\frac{.018}{1.5 \times 2.0 \times 10^{-5}}\right]^{.31}$$

$$= 1.74 \times 10^{-3}$$

Substitution into equation (1):

$$k_L = 1000 \, nFk_LC$$

$$= 1000 \times 6 \times 96{,}500 \times 1.74 \times 10^{-3} \times .011 \times 10^{-3}$$

$$= 11 \text{ ma}$$

There are 2.45 geometric cm^2/(face cm^2) for the 150 mesh nickel screen. For a 4-ply electrode of 2 cm^2 face area, the geometric area is 19.6 cm^2. Thus the limiting current is (11 × 19.6) = 220 ma.

Since the limiting current is proportional to the 0.385 power of the flow rate, a simplified procedure can be used for the calculation at other flow rates:

$$i_{L2} = i_{L1} \left[\frac{G_2}{G_1}\right]^{.385} \tag{5}$$

i_{L1} = 220 ma

G_1 = 0.40 gm/sec-cm^2

Substitution into equation (5) yields:

Flow Rate: 11 cm^3/min: i_L = 143 ma
Flow Rate: 50 cm^3/min: i_L = 255 ma

(for C = 0.011 M)

The limiting current is directly proportional to the concentration of methanol. The following limiting currents may be calculated for the flow rate of 50 cm^3/min (the most commonly used flow rate in this work).

$C = 0.5$ M $\quad i_L = 11{,}600$ ma

$C = 0.1$ M $\quad i_L = 2{,}300$ ma

$C = 0.04$ M $\quad i_L = 930$ ma

The limiting current can be readily calculated for a different number of screens per electrode, or for the platinized platinum screen electrodes. The platinum geometrical area was 1.51 $cm^2/(cm^2$ face area) (compared to 2.45 for nickel).

APPENDIX H

Electrical Resistance of Electrolyte Solutions

The following specific conductivities apply to the potassium hydroxide and potassium carbonate electrolytes and are given in $\text{ohm}^{-1}\ \text{cm}^{-1}$.

References		18°C	70°C
(46)	50 (wt)% Potassium Carbonate	0.147	0.44
(19),(25)	20 (wt)% Potassium Hydroxide	0.500	0.972

The value for potassium carbonate at 70°C was measured by the author with an A.C. conductivity bridge.

These values can be used to calculate the ohmic potential drop in the electrolyte between electrodes. The IR loss is given by:

$$V = \frac{I \times D}{K \times a} \qquad (5)$$

where:

V = electrolyte voltage loss, volts

I = cell current, amps

K = specific conductance of the electrolyte, $\text{ohm}^{-1}\text{cm}^{-1}$

D = distance between electrodes, cm

a = electrode face area, cm^2

For 20% KOH at 70°C and 70 ma:

$$V = \frac{.070 \times 0.1}{.972 \times 2} = 0.0036 \text{ v}$$

For 50% K_2CO_3 at 70°C and 70 ma:

$$V = \frac{.070 \times 0.1}{.44 \times 2} = 0.0080 \text{ v}$$

APPENDIX I

Nomenclature

A	Activity
A_m	Mixed-feed methanol reaction rate, ma
A_s	Single-feed methanol current, ma
a	Electrode face area, cm^2
C	Reactant concentration, gm-moles/cm^2
C_D	Concentration of standard dichromate solution, N
C_F	Concentration of standard ferrous solution, N
D	Distance between electrodes, cm
D	Reactant diffusivity, cm^2/sec
d	Screen wire diameter, cm
E^o	Standard electrode potential, volts vs N.H.E.
E_{ref}	Reference electrode potential, volts vs N.H.E.
E_{rev}	Reversible electrode potential, volts vs N.H.E.
ΔF^o	Standard free energy of reaction, cal/mole
F	Faraday's number, 96,500 coulombs/equiv or 23,100 cal/volt-equiv
G	Mass flow rate, gm/sec-cm^2
I	Cell current, amps
K	Specific conductance, $ohm^{-1}cm^{-1}$
k_L	Mass transfer coefficient, cm/sec
M_i	Initial amount of methanol in flow system, equiv
n	Equivalents per mole

O_m	Mixed-feed oxygen reaction rate, ma
O_s	Single-feed oxygen current, ma
P	Pressure, atm or mm Hg
T	Time duration of run, min
V	Voltage loss, volts
V_D	Volume of dichromate standard solution, L
V_e	Volume of electrolyte analysis sample, L
V_{F_1}	Average volume of titrant for first analysis, L
V_{F_2}	Average volume of titrant for second analysis, L
V_s	Volume of electrolyte in flow system, L
μ	Electrolyte viscosity, poise
ρ	Electrolyte density, gm/cm^3

APPENDIX J

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APPENDIX K

Biographical Note

The author, Stephen Robert Schulze, was born in Santa Barbara, California on September 9, 1941. He attended the public schools of Ventura, California and graduated from Ventura Senior High School in June, 1959.

From September, 1959 to June, 1963, the author attended Harvey Mudd College in Claremont, California. In June, 1963, he graduated with a Bachelor of Science degree in chemistry. After summer employment with the Union Oil Company of California, he entered the Department of Chemical Engineering at the Massachusetts Institute of Technology. The author was awarded a Teaching Assistantship for the 1963-64 academic year.

On June 26, 1965, the author was married to the former Virginia L. McGann of Portland, Maine.