

SYMPOSIUM ON FUEL CELLS  
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FUEL CELL INTERMEDIATES AND PRODUCTS

By

Maurice J. Schlatter  
California Research Corporation, Richmond, California

I. INTRODUCTION

Studies of fuel cell intermediates and products were carried out with two different objectives. The first work, supported by California Research Corporation, was initiated in December 1958. It consisted of an exploratory evaluation of fuel cells as reactors for producing chemicals. Concurrently, pilot studies aimed at utilizing hydrocarbons or petroleum-derived fuels in power fuel cells were initiated. Early in 1960, this latter phase was expanded as a fundamental program supported by Army Ordnance and under the general direction of Diamond Ordnance Fuze Laboratories. Initial objectives of this project include the determination of the kinetics and detailed reaction mechanisms of low temperature oxidations of hydrocarbons and hydrocarbon oxidation intermediates at fuel cell anodes. The methanol product studies reported here are a part of this continuing program.

When our work was initiated, there were few reported product data for fuel cells or for low voltage anodic oxidations in the potential range obtainable at fuel cell anodes. Scarcely more information was available on the low temperature fuel cell performance of fuels other than hydrogen. Therefore, it was necessary for us to screen many compounds in order to select some that were sufficiently active in fuel cells for initial product studies. Results of these experiments are also of interest in the interpretation of product data and are included in this report.

II. APPARATUS

A. Fuel Cell Electrodes

Electrodes were our most important apparatus problem. We were not concerned with preparing the best possible electrodes for a particular fuel cell reaction but rather with making versatile, reproducible electrodes for comparative screening tests and electrodes capable of producing sufficient reaction to allow isolation and identification or analysis of the reaction products.

Electrode forms used in most of the later product work are shown in Figure 1. These hollow, cylindrical, porous carbon electrodes are suitable for use in acidic or in basic electrolytes. They can be used as noncatalytic electrodes or impregnated or plated with catalytic materials. They are equally useful with gases, with liquid reactants insoluble in the electrolyte, and with soluble reactants. Stackpole Porous Carbon No. 139\* was the most satisfactory of the porous carbon supports which we tested. This material came to our attention through the electrode studies of Anthony and Humphrey. (1)

Platinized electrodes were used as fuel anodes in most of the work reported here. They were also used as oxygen cathodes in acidic and sometimes in basic electrolytes. They were prepared by plating porous carbon electrodes for 20 minutes at a current density of 40 ma/cm<sup>2</sup> of geometric area and an initial temperature of 25°C. The plating electrolyte contained 10 grams of platinum per liter and was prepared by dissolving pure chloroplatinic acid in 0.12 N hydrochloric acid. It was contained in a cylindrical "Karbate"\*\*\* impervious graphite cup which served as anode. After allowing the electrode to stand in the electrolyte for 10 minutes, current was passed through the system and electrolyte was drawn into the electrode and forced out again every two minutes. Equally active electrodes were sometimes obtained with less platinum. However, this was not always the case; and the longer plating time which did give reproducible results was adopted as standard.

\*Stackpole Carbon Company

\*\*National Carbon Company

Table I

Relative Reactivities of "Reductants" in  
Basic Electrolyte Fuel Cell

Group	Potential Relative to H <sub>2</sub> -O <sub>2</sub> Fuel Cell, <sup>a</sup> %	Reductant	Group	Potential Relative to H <sub>2</sub> -O <sub>2</sub> Fuel Cell, %	Reductant
A	85	Hydrazine Formaldehyde	E	(50-65) <sup>b</sup>	n-Octanol n-Decanol Ethylamine Acetone Ethylene <sup>c</sup> Propane <sup>c</sup> Acetylene <sup>c</sup> Butadiene <sup>c</sup> n-Dodecanol
B	50-75	Ethanol Benzyl alcohol <sup>c</sup> 2-Aminoethanol Isopropanol n-Propanol Ethylene glycol Methanol Glycerol Sorbitol Glucose Isobutanol sec-Butanol n-Butanol	F	(25-35) <sup>b</sup>	n-Tetradecanol
			G	(1-6) <sup>b</sup>	Soluble Starch Cumene p-Xylene Toluene
C	20-40	Sodium formate Sodium glycolate n-Pentanol Hydroxylamine Benzaldehyde <sup>c</sup> Ammonia Sodium tartarate n-Hexanol Allyl alcohol	H <sup>d</sup>	Inactive	t-Butanol Sodium acetate Sodium maleate Sodium succinate Sodium citrate Potassium oxalate Ethyl ether Dioxane Potassium m-toluate
D	2-5 (65-70) <sup>b</sup>	Sucrose n-Heptanol			

- a Percentages relative to hydrogen compared at current densities corresponding to H<sub>2</sub>-O<sub>2</sub> potential of 0.7 volt in the cell used for the comparison.
- b Figures in parentheses are based on comparison made at current density corresponding to 0.9 volt H<sub>2</sub>-O<sub>2</sub> potential.
- c Assignment of relative position may be subject to considerable error.
- d Compounds in this group may have slight activities.

Table II

Relative Reactivities of "Reductants" in Basic and  
Acidic Fuel Cells According to Pavela<sup>3</sup>

Group	Electrolyte	
	1 N NaOH	1 N H <sub>2</sub> SO <sub>4</sub>
Good reactivity	Methanol Ethanol Ethylene glycol	Methanol Ethanol Formic acid
Fair reactivity	Benzyl alcohol Propylene glycol Sodium formate Isopropanol sec-Butanol	
Bad reactivity	n-Propanol n-Butanol α-Phenylethyl alcohol	
No effect	t-Butanol Phenol Ethyl ether	Acetic acid Benzoic acid

Silver-silver oxide catalyzed oxygen cathodes were generally used with basic electrolytes. These were prepared by plating at 25°C. in 10% silver nitrate solution using a concentric, cylindrical silver anode. Silver was deposited in three one-minute intervals at a cathode current density of 10 ma/cm<sup>2</sup>. Between platings, the electrode was rinsed with distilled water and loose silver removed by wiping with filter paper. The electrode was activated by electrolytic oxidation at 20 ma/cm<sup>2</sup> using a cylindrical "Karbate" cup as cathode. Three per cent sodium hydroxide was drawn through the electrode during the 10-minute electrolysis.

## B. Test Procedures

The electrodes were used in various ways. In many screening experiments in basic electrolytes, a platinized porous carbon anode was used with a cathode of silver-silver oxide on porous carbon. The fuel or reductant\* under test was dissolved in the electrolyte. Oxygen was passed through the porous cathode. With this arrangement, fuel cell activity is observed when the reductant reacts selectively at the platinized anode and does not combine rapidly with oxygen at the cathode.\*\* Some reductants insoluble in the electrolyte were screened by drying the electrode under helium and then saturating with the compound under test. Other materials were passed through the electrode as gas or vapor or sometimes in an inert carrier gas. The "fuel cell" consisted of anode and cathode immersed in electrolyte contained in a beaker or in a "U" tube.

Some compounds, such as hydroquinone, sulfides, and mercaptides, when dissolved in basic electrolyte will react at an uncatalyzed porous carbon anode and will also react directly with oxygen at the cathode. To test these materials in basic electrolyte, a three-compartment fuel cell (Figure 2) was used with Nalfilm-2\*\*\* cation exchange membrane separations. These separators are effective in retarding the diffusion of reactants and products from the anolyte to the catholyte.

Cathodes consisting of silver-silver oxide on porous carbon were unsatisfactory in acidic electrolytes. However, platinized porous carbon electrodes were effective in acid and were used for oxygen cathodes as well as for fuel anodes. When soluble reductants were studied, it was necessary to separate anolyte and catholyte. This was done using the three-compartment fuel cell and Nalfilm-1 anion exchange membrane separators.

Product studies, too, were ordinarily carried out in the three-compartment cell.

Over-all cell voltages were recorded. Cell currents were held constant with an automatically controlled, variable load resistance. Individual electrode potentials were measured against a Beckman saturated calomel electrode using a Luggin capillary bridge containing cell electrolyte. Potentials were measured with a Beckman Model G pH meter.

## III. RELATIVE REACTIVITIES OF REDUCTANTS IN BASIC ELECTROLYTE FUEL CELLS

Relative reactivities reported in this section were obtained from screening experiments. The electrolyte was usually 15 weight per cent sodium hydroxide and the temperature 50°C., though some series were run at 25°C. and 80°C.

These experiments were carried out during the period when different electrode designs and variables were being studied. Because of this, several sets of data involving different compounds were obtained. Typical data plots are shown in Figures 3 and 4. In these, as well as in many similar plots, only directly comparable data obtained in similar systems using the same or similar electrodes are included in each figure.

\* "Reductant" is used in some cases in reference to the fuel or compound oxidized at the anode, especially where partial oxidation to give useful chemical products is being considered.

\*\* Justi and coworkers (2) have also used fuels dissolved in an electrolyte which contacts dissimilar electrodes.

\*\*\*National Aluminate Company. Manufacture of these materials has been discontinued. Alternative materials are being considered.

Table III

Carbon Dioxide Formed from Fuel Cell  
Oxidation of Propane and Ethylene

Hydrocarbon	Gas Rate, ml/hr	Time, hr	Charge Transferred, amp hr	CO <sub>2</sub>	
				Found, mg	% of Theory*
Propane	50	5.63	0.326	80.0	99.5
Ethylene	50	12.63	0.632	160.3	92.7
	44	9.18	0.459	115.0	91.6
	800	4.83	0.242	64.8	97.7
	800	15.28	0.764	200.6	98.5

\* Theory:  $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4 H_2O$  (20-electron change)  
3/20 CO<sub>2</sub> per Faraday = 246.5 mg CO<sub>2</sub> per ampere hour  
 $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$  (12-electron change)  
1/6 CO<sub>2</sub> per Faraday = 274 mg CO<sub>2</sub> per ampere hour

Table IV

Comparison of Relative Fuel Cell Reactivities of  
Propane, Ethylene, and Acetylene on Different Electrodes

Platinized Porous Carbon

1. Ethylene > Acetylene > Propane  
35% KOH > 30% K<sub>2</sub>CO<sub>3</sub>
2. Propane > Ethylene > Acetylene  
5 N H<sub>2</sub>SO<sub>4</sub>
3. Acetylene  
35% KOH > 5 N H<sub>2</sub>SO<sub>4</sub>
4. Propane, Ethylene  
5 N H<sub>2</sub>SO<sub>4</sub> > 35% KOH

Palladized Porous Nickel

Propane > Ethylene > Acetylene  
25% K<sub>2</sub>CO<sub>3</sub> = 27% KOH

Often, different time schedules were used in testing reductants which were later compared. On the figures, the data obtained at each current setting are shown as two points connected by a vertical line. The upper point is the potential one minute after operation at the indicated current density. The lower point is the potential just before the current was increased to the next higher value. The intervening time, in minutes, is shown by the small figures adjacent to this point. For comparison purposes, some adjustments were made in drawing the polarization curves in order to compensate for differences in the test schedules.

"Relative reductant reactivities" were established by comparing the over-all voltages produced by reductant-oxygen fuel cells under equivalent conditions. Compensation for different electrode activities was achieved by relating the reactivity of each compound in a particular test series to hydrogen. For reactive materials, the comparisons were made at the current density which gave 0.7 volt output from a hydrogen-oxygen cell included in each test series. With less reactive reductants, which did not give sufficient current under these conditions, comparisons were made at the current density corresponding to a hydrogen-oxygen cell potential of 0.9 volt. This is illustrated by the dashed lines on Figure 4. The relative reactivities obtained in this way are approximate. Differences in solubility and molecular weight make comparison of different compounds under exactly the same conditions impossible. In general, only one concentration of a soluble reductant in the electrolyte was run. Experiments with some reductants showed that performance is insensitive to concentration above a minimum value. Although this value may not have been reached for all substances tested, we do not believe that this has seriously affected the reliability of the reactivity order.

A reactivity sequence for the compounds tested on platinized porous carbon electrodes in basic electrolyte fuel cells is shown in Table I. The compounds fall into distinct reactivity groups. Assignments of compounds to these groups are quite certain; but within the groups, some transpositions may have occurred between compounds of similar reactivity.

Pavela (3) has also determined a reactivity sequence, based on the rates of low voltage electrolytic oxidations. This is shown in Table II. It is similar to our sequence except for greater differences in the relative reactivities of the C<sub>1</sub>-C<sub>4</sub> alcohols.

Some compounds which do not require catalytic electrodes are not shown in Table I. This group includes hydroquinone, p-aminophenol, mercaptides, and some inorganic sulfur compounds.

#### IV. FUEL CELL OXIDATION INTERMEDIATES AND PRODUCTS

##### A. Hydrocarbons

Gaseous hydrocarbon fuel cell activity was studied in cells operating below 100°C. and at atmospheric pressure. Ethylene, acetylene, and propane were active in hydrocarbon-oxygen fuel cells at 80°C. using platinized porous carbon electrodes with 5 N sulfuric acid, 35 weight per cent potassium hydroxide, or 30 weight per cent potassium carbonate electrolytes.

With 5 N sulfuric acid electrolyte, complete or nearly complete oxidation of propane and ethylene to carbon dioxide and water was obtained. Preliminary evidence for aldehydes and ketones formed in the fuel cell oxidation of ethylene has been reported. (4) In our case, however, preliminary mass spectrographic analyses and vapor-liquid chromatography showed no oxidation products other than carbon dioxide and water. Comparison of the weights of carbon dioxide produced in the cells with the theoretical amounts obtainable from the current produced gave nearly quantitative agreement, as shown in Table III.

These results were obtained in the three-compartment fuel cell (Figure 2) with Nalfilm-1 anion exchange membrane separators. The carbon dioxide in the excess hydrocarbon leaving the anode compartment was determined by absorption in Ascarite after removing water with Anhydrone.

Propane gave the best voltage - current density characteristics of the hydrocarbons studied on platinized porous carbon anodes. In one case, an initial potential of 0.5 volt at a current density of 2 ma/cm<sup>2</sup> was obtained. After seven hours of rather erratic operation, 0.5 volt was still obtainable for short periods but at 1.3 ma/cm<sup>2</sup>.

Propane, ethylene, and acetylene were also active on platinized and palladized porous nickel electrodes with either aqueous potassium hydroxide or potassium carbonate electrolyte.

Table V

Comparison of Methanol-Oxygen Fuel Cells with Acidic and Basic Electrolytes at 24°C (Cylindrical Platinized-Porous Carbon Electrodes)

	Units	Acidic Electrolyte	Basic Electrolyte
Oxygen Half-Cell			
Catholyte		2.3 M H <sub>2</sub> SO <sub>4</sub>	4.5 M NaOH
Cathode Current Density	ma/cm <sup>2</sup>	0	0
Cathode Potential (E <sub>c</sub> )	volt vs SCE	0.825	-0.060
Calculated Oxygen Reference Potential <sup>a</sup> (E <sub>ref</sub> )	volt vs SCE	0.953	0.140
E <sub>ref</sub> - E <sub>c</sub>	volt	0.128	0.200
Methanol Half-Cell			
Anolyte		1.56 M CH <sub>3</sub> OH in 2.3 M H <sub>2</sub> SO <sub>4</sub>	1.56 M CH <sub>3</sub> OH in 4.5 M NaOH
Anode Current Density	ma/cm <sup>2</sup>	0	0
Anode Potential (E <sub>A</sub> )	volt vs SCE	0.215	-0.920
Oxygen-Methanol Fuel Cell			
E <sub>c</sub> - E <sub>A</sub> (Cell Potential <sup>b</sup> )	volt	0.610	0.860

a Calculated for the ideal cathode reactions:  $O_2 + 4H^+ + 4e^- = 2H_2O$   $E_0 = 0.987$  v  
 $O_2 + 2H_2O + 4e^- = 4OH^-$   $E_0 = 0.159$  v

b Corrected for electrolyte and separator resistance.

Relative fuel cell reactivities of the hydrocarbon gases studied varied with different catalytic electrodes and with different electrolytes. These differences are summarized in Table IV.

Some of these reactivity relationships may be subject to correction. However, they do serve to show the order of complexity that may be expected in dealing with these reactions.

## B. Alcohols

### 1. Methanol in Basic Electrolyte

Methanol product studies were carried out in a three-compartment fuel cell using platinized porous carbon electrodes at a cell current of 50 ma (anode current density, 1.27 ma/cm<sup>2</sup>). The anolyte was 1.56 M methanol in 4.5 M sodium hydroxide. Sodium hydroxide (4.5 M) was used in center and cathode compartments.

Net products formed at 24°C. and 53°C. are plotted in Figures 5 and 6 against ampere-hours produced. As 100 ml of anolyte was used in these experiments, molar product concentrations are approximately 10 times the net moles of product produced. The actual concentrations were slightly less because the net product curves are corrected for analytical samples which were withdrawn at intervals and replaced with equal volumes of a feed stock retain.

Samples from the anode compartment were analyzed for formaldehyde and formate immediately after they were taken from the cell. Formaldehyde was determined by a sensitive colorimetric method using chromotropic acid in sulfuric acid as the colorimetric reagent, (5) Formate was determined by reduction with magnesium and hydrochloric acid, followed by colorimetric determination of the formaldehyde formed. The method used was adapted from a procedure described by Grant. (6) In the formate analysis of these fuel cell products, the amount of formaldehyde was small enough to be neglected.

Formaldehyde was definitely formed in these fuel cells, though the amount which appeared in the electrolyte was very small compared with the quantity of methanol oxidized. The concentration reached by the end of the experiment at 24°C. was only  $2.5 \times 10^{-4}$  M, and  $3.5 \times 10^{-4}$  M at 53°C. By contrast, the amount of formate initially formed corresponded closely to theory assuming that formate is the only product. With time, as the formate concentration increased, more formate was oxidized, presumably to carbonate.

Air oxidation and electrochemical oxidation of methanol in base can both give formaldehyde. Although air was not excluded from the anode in our experiments, it is evident from Figure 7 that most of the formaldehyde found in the basic electrolyte fuel cells came from electrochemical processes. In the experiment which produced the data shown, no current was drawn from the cell for 168 hours. During this period, the formaldehyde concentration increased gradually as the result of air oxidation of the methanol in the basic anolyte. Then the cell was operated intermittently at 50 ma load. Each time current was drawn, the formaldehyde concentration increased rapidly at first, tapering off as the formaldehyde concentration increased.

Apparatus and electrolyte were identical with those used in the methanol fuel cell experiment which gave the data for Figure 5.

Platinized porous carbon electrodes also have the property of catalyzing non-electrochemical reactions of formaldehyde. This too is evident from the data plotted in Figure 7. In addition to the fuel cell which was operated intermittently, a control air oxidation was carried out with 150 ml of the methanol-in-base which was used as anolyte in the fuel cell. This was contained in a 250-ml volumetric flask. During the first 217 hours, samples were drawn for analysis with minimum disturbance of the contents of the flask. In the remainder of the experiment, the flask was shaken vigorously when each sample was withdrawn. The formaldehyde concentrations are shown by a dashed line in Figure 7.

In the first part of the control experiment, formaldehyde was produced by direct air oxidation at a constant rate. Under similar conditions and at null current, the rate of increase of formaldehyde in the fuel cell anode compartment was about half that in the control. Also, when the fuel cell current was interrupted after a period of operation under load, the formaldehyde concentration decreased. The rate of this decrease was greater at higher concentrations.

Table VI  
 Effect of Chemical Structure on "Reductant"  
 Activity in Basic Electrolyte Fuel Cell

Active	Inactive or Very Slightly Active
<p><u>Simple Alcohols</u></p> $\begin{array}{c} \text{H} & & \text{H} & & \text{H} & & \text{CH}_2\text{OH} & & \text{CH}_2\text{CH}_2\text{OH} \\   & &   & &   & &   & &   \\ \text{H}-\text{C}-\text{OH} & , & \text{CH}_3-\text{C}-\text{OH} & , & \text{CH}_3-\text{C}-\text{OH} & , & \text{C}_6\text{H}_5 & & \text{C}_6\text{H}_5 \\   & &   & &   & &   & &   \\ \text{H} & & \text{H} & & \text{CH}_3 & & & & \end{array}$ <p><math>\text{CH}_3(\text{CH}_2)_n\text{OH}</math>: Activity decreases as n increases</p>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$
<p><u>Polyols and Dihydric Phenols</u></p> $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}, \text{HO}-\text{CH}_2-\overset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{OH}, \text{C}_6\text{H}_4(\text{OH})_2$ <p>Glucose, Sorbitol <math>\gg</math> Sucrose <math>\gg</math> Soluble Starch</p>	$\text{C}_6\text{H}_5\text{OH}$
<p><u>Substituted Alcohols and Phenols</u></p> $\text{CH}_2=\text{CHCH}_2\text{OH}, \text{NH}_2\text{CH}_2\text{CH}_2\text{OH}, \text{C}_6\text{H}_4(\text{NH}_2)(\text{OH})$	
<p><u>Hydroxy Acids</u></p> $\begin{array}{c} \text{H} \\   \\ \text{HOCH}_2\text{COO}^\ominus, \text{HO}-\text{C}-\text{COO}^\ominus \\   \\ \text{HO}-\text{C}-\text{COO}^\ominus \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_2-\text{COO}^\ominus \\   \\ \text{HO}-\text{C}-\text{COO}^\ominus \\   \\ \text{CH}_2-\text{COO}^\ominus \end{array}$
<p><u>Other Carboxylic Acids</u></p> $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^\ominus$	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^\ominus, \text{O}^\ominus-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^\ominus, \text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^\ominus$ $\text{O}^\ominus-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^\ominus, \text{O}^\ominus-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^\ominus$
<p><u>Carbonyl Compounds</u></p> $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}, \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}, \text{C}_6\text{H}_5\text{CHO}$	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
<p><u>Ethers</u></p>	$\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3, \text{C}_4\text{H}_8\text{O}$
<p><u>Nitrogen Compounds</u></p> $\text{NH}_2\text{NH}_2 \gg \text{NH}_3, \text{NH}_2\text{OH} > \text{CH}_3\text{CH}_2\text{NH}_2$	
<p><u>Sulfur Compounds</u></p> $\text{HS}^\ominus, \text{CH}_3\text{S}^\ominus, n\text{-BuS}^\ominus$ $\text{S}^\ominus \text{ (as polysulfide)}$	$\text{S}_2\text{O}_8^\ominus, \text{SO}_4^\ominus, \text{SO}_3^\ominus, \text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$ <p>(5 N <math>\text{H}_2\text{SO}_4</math> electrolyte)</p>

The forms of the decreasing formaldehyde concentration curves, which were obtained at zero current, were probably determined by the rate at which formaldehyde was produced by air oxidation reduced by the rate of the catalytic conversion of formaldehyde to other products. The ascending curve was determined by these factors together with the rates of electrochemical formation and subsequent electrolytic oxidation of formaldehyde at the electrode and attendant mass transfer effects between electrode and solution.

It is possible that all or part of the decrease in formaldehyde concentration is due to platinum-catalyzed reduction of water by formaldehyde, giving hydrogen and formate as the products.

The decrease in formaldehyde concentration may also be due to disproportionation to give methanol and formate. This occurs slowly in basic solution at room temperature but is known to be accelerated by platinum. (7)

## 2. Methanol in Acid Electrolyte

Products formed from the fuel cell oxidation of 1.56 M methanol in 2.3 M sulfuric acid at 23°C. are shown in Figure 8. Some data from a 24°C. basic electrolyte experiment (Figure 5) are included for comparison. Formic acid and formaldehyde concentration curves are plotted in addition to net product in order to show the approach to steady state concentrations. The saw-tooth shape of these curves is the result of replacing analytical samples, drawn at intervals, with feed stock to maintain a constant anolyte volume.

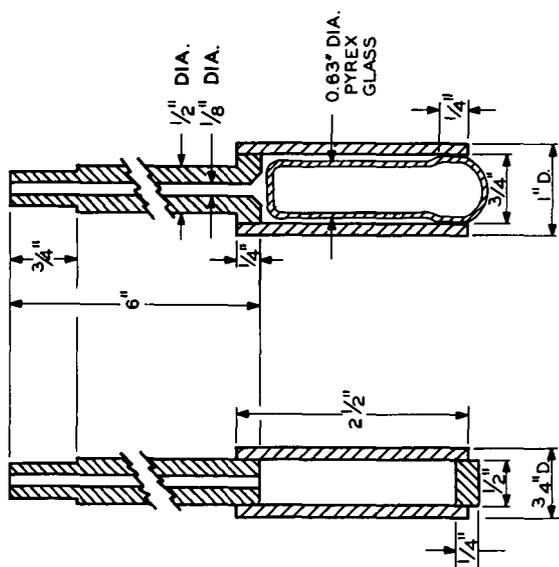
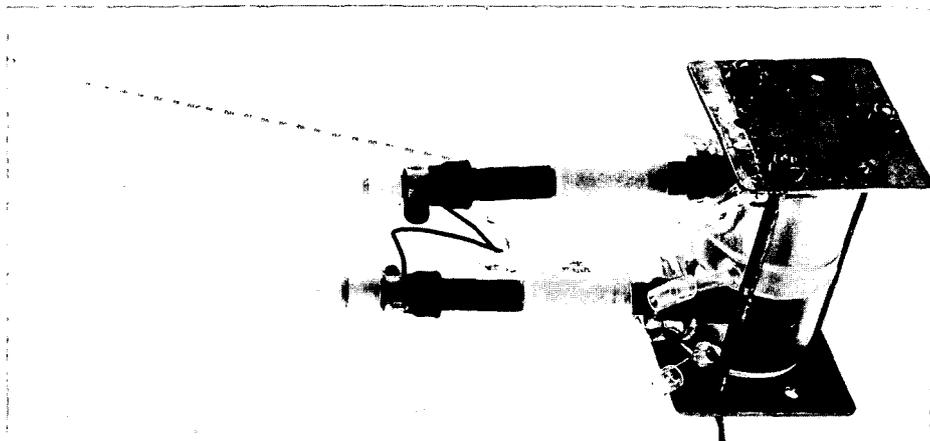
Formaldehyde analyses were carried out as described for the basic electrolyte experiments. Formic acid analyses proved to be more difficult. Both sulfuric acid and formaldehyde in appreciable amounts interfere in the formate-formic acid analysis used in the basic electrolyte experiments and, therefore, had to be removed before satisfactory analyses could be obtained. This was accomplished by converting most of the formaldehyde present into the nonvolatile phenylhydrazone. The volatile formic acid, added water, and excess methanol were then distilled at room temperature *in vacuo* into a Dry Ice-cooled side arm of a special distillation tube. An aliquot of the distillate was analyzed for formic acid as described for the basic electrolyte. Some of the formaldehyde in the original sample is not removed by the phenylhydrazine treatment. Therefore, a second aliquot of the distillate was analyzed for formaldehyde and a suitable correction was applied. The analytical procedure is still far from satisfactory. Our most consistent results were obtained by running analyses in quadruplicate and arbitrarily using the highest value obtained. Standards were treated in a manner as nearly identical with the fuel cell electrolyte as possible. Unexpected difficulty was experienced with large reagent blanks which varied from day to day. The reason for these variations is still not clear. In the experiment shown, the data points obtained fell on a smooth curve; but difficulties in relating this to reproducible standards were such that we can only place the steady state formic acid concentrations between 4.5 and  $6.5 \times 10^{-3}$  M.

In contrast with basic methanol solutions, no formaldehyde was formed by air oxidation of methanol in a retain sample of the acid electrolyte.

The relative amounts of formaldehyde and formic acid produced in fuel cell oxidations of methanol are quite different in acidic compared with basic electrolytes. In acid, the concentration of formaldehyde was several times the highest concentration attained in base. Formic acid was not the principal product, as was the case with formate in base, but reached concentrations of the same order as those of formaldehyde. The total amounts of formaldehyde and formic acid together accounted for only a very small fraction of the methanol oxidized. Carbon dioxide was probably the principal product in acid. Its presence was shown qualitatively, but quantitative data were not obtained.

During the product studies, it was also observed that the potential of the methanol-oxygen fuel cell was significantly lower in acid than in base. This was true at open circuit and also at equivalent loads. The data in Table V show that the oxygen electrode performs as well in acidic as in basic electrolyte at the low current densities used in these experiments. Therefore, the poorer over-all cell performance in acid must be due to the methanol half-cell.

FIGURE 2. THREE COMPARTMENT FUEL CELL



 'KARBATE' IMPERVIOUS GRAPHITE (NATIONAL CARBON CO.)

 POROUS CARBON NO.139 (STACKPOLE CARBON CO.)

JOINTS SEALED WITH EPON 826-Z RESIN (SHELL CHEMICAL CO.)  
HEATED 30 MIN. AT 100°C BETWEEN APPLICATIONS, FINISHED FOR 1 HOUR  
AT 150-160°C.

FIGURE 1. ELECTRODE CONSTRUCTION

### 3. Ethanol, Isopropanol, and Benzyl Alcohol in Base Electrolytes

Limited product studies were made with ethanol, isopropanol, and benzyl alcohol. The ethanol data were obtained early in our program. Ethanol (5 volume per cent) was dissolved in 15 weight per cent sodium hydroxide electrolyte. This solution was contained in a small beaker at room temperature. It contacted a 1/4-inch diameter platinized porous carbon anode (6 cm<sup>2</sup> area) and a similar silver-silver oxide on porous carbon cathode. Oxygen was forced through the cathode at a slow rate. Analysis of the electrode after 173 hours of operation at 10 ma current (1.67 ma/cm<sup>2</sup>) gave 37% of the theoretical amount of acetic acid based on the amount of electricity produced. No acetaldehyde was detected.

The isopropanol and benzyl alcohol product studies were made in the three-compartment cell.

The isopropanol experiments were carried out at room temperature using 5 volume per cent isopropanol dissolved in 5 weight per cent potassium hydroxide as anolyte. A 10 cm<sup>2</sup> platinized porous carbon anode and a silver-silver oxide on porous carbon oxygen cathode of similar size were used. Rapid deactivation of the anode occurred with isopropanol, and it was necessary to replace anodes several times during 12 hours of fuel cell operation at 20 ma current (2.0 ma/cm<sup>2</sup>). Steam distillate from the basic electrolyte contained 14.5% of the theoretical amount of acetone.

The benzyl alcohol experiments were carried out at 50°C. in 35 weight per cent potassium hydroxide electrolyte. Similar 30 cm<sup>2</sup> platinized porous carbon electrodes were used for anode and oxygen cathode. The anode was dried by warming in a test tube while passing helium through the electrode. Air was excluded, and the electrode was saturated with benzyl alcohol. A total of 0.997 ampere-hour was drawn from the cell over a period of 41 hours at currents from 10 to 50 ma (0.3-1.67 ma/cm<sup>2</sup>). Pure benzoic acid amounting to 78% of theory was recovered. No benzaldehyde was detected in the excess benzyl alcohol contacting the anode. In a similar experiment, the two Nalfilm-2 diaphragms separating anode, center, and cathode compartments in the product fuel cell ruptured. In this case, some benzaldehyde was found, presumably formed by direct oxidation of benzyl alcohol with oxygen.

### 4. Discussion of Fuel Cell Oxidations of Oxygen-Containing Compounds

Methanol has been suggested as an "ideal" liquid fuel for fuel cells. Although good current densities have been achieved in such cells, they present problems which must still be solved before practical low temperature methanol fuel cells can be developed. In basic electrolyte, formate is formed which is less reactive than methanol. This limits the performance of the cell. To be practical, either formate must be removed, with attendant loss of more than one-third of the energy of the methanol fuel, or means must be found to accelerate the electrolytic oxidation of formate to carbonate. Furthermore, methods must be developed to remove formate and/or carbonate from the cell electrolyte and to replace or regenerate hydroxide. In acidic electrolytes, on the other hand, complete oxidation of methanol to carbon dioxide and water and the removal of these products can be achieved without difficulty. However, the lower over-all cell potentials obtained from methanol in acid, compared with base, mean lower efficiencies. Higher potentials will have to be obtained before practical acidic electrolyte, methanol fuel cells can be realized.

Gross effects of structure on the fuel cell reactivities of alcohols and related compounds in basic electrolytes are summarized in Table VI. Hydroxy compounds having a hydrogen attached to the carbon which carries the hydroxyl group are active. This is true of simple primary and secondary alcohols, polyols, salts of certain hydroxy acids, 2-aminoethanol, and allyl alcohol. *t*-Butyl alcohol and citrate, which do not have this kind of a hydrogen atom, are inactive. Ethyl ether and dioxane, which do have hydrogen atoms on the carbon atoms attached to oxygen but which lack hydroxyl hydrogen, are also inactive. Aldehydes and formate, in hydrated form, contain hydroxyl hydrogen and hydrogen attached to the carbon atom which carries the hydroxyl group. These are active; ketones and other unsubstituted carboxylic acids are not.

The following mechanism for the fuel cell oxidation of methanol in basic electrolyte was presented in a previous paper. (8) It is consistent with the structural requirements for fuel cell reactivity which we have just discussed, with product data, and with the results of kinetic and mechanism studies which were carried out using electrochemical techniques.

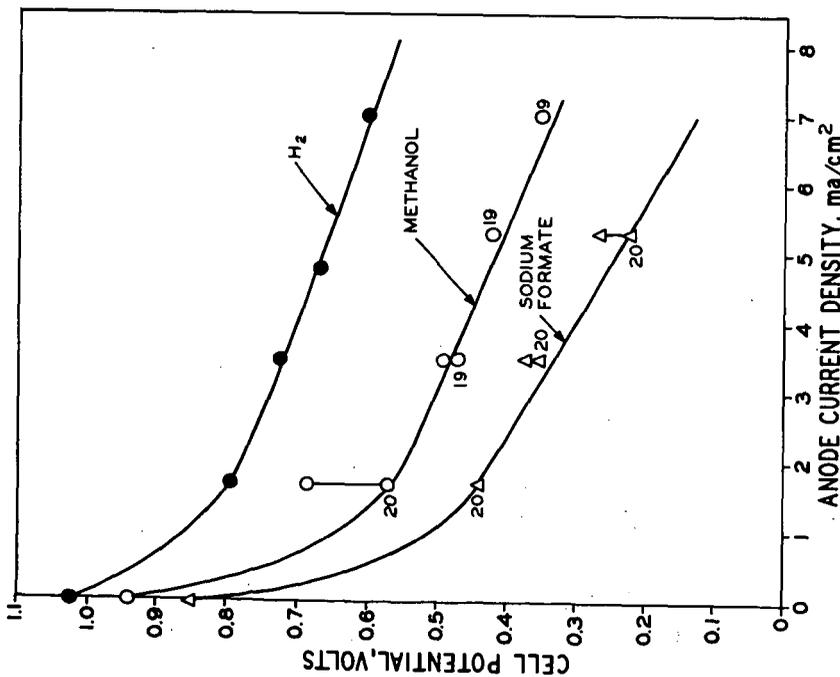


FIGURE 3. FUEL CELL PERFORMANCE OF METHANOL AND SODIUM FORMATE AT 50°C

2 VOLUME PER CENT METHANOL AND 2 WEIGHT PER CENT SODIUM FORMATE IN 15 WEIGHT PER CENT SODIUM HYDROXIDE ELECTROLYTE

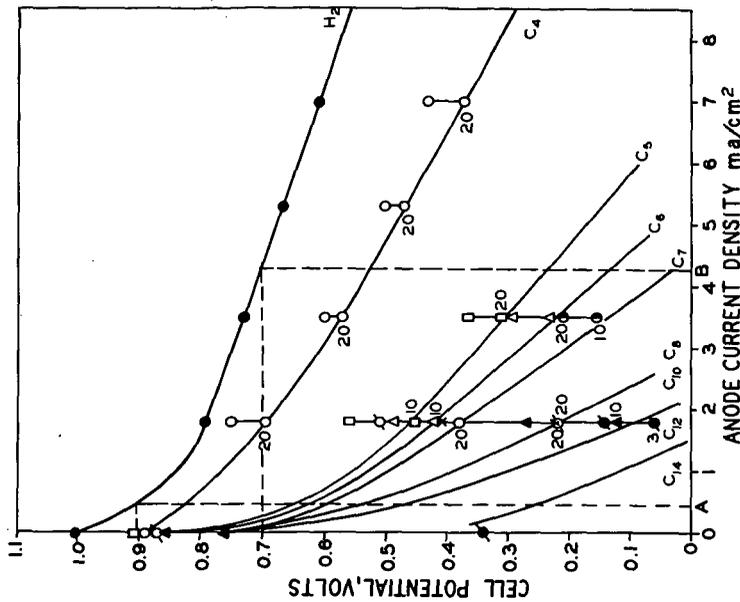
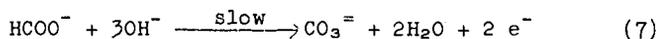
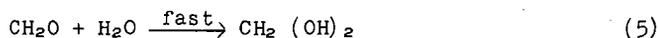
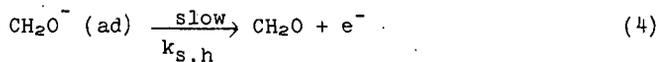
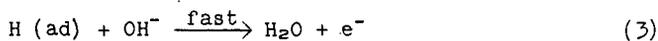
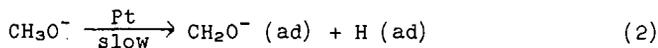
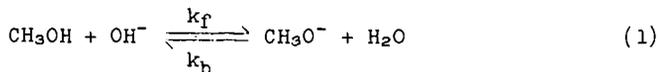


FIGURE 4. PERFORMANCE OF N-C<sub>4</sub> TO N-C<sub>14</sub> ALCOHOLS IN FUEL CELL AT 50°C

ANODE SATURATED WITH ALCOHOL UNDER TEST, 15 WEIGHT PER CENT SODIUM HYDROXIDE ELECTROLYTE

A. CURRENT DENSITY USED IN COMPARING SUBSTANCES HAVING LOW REACTIVITY

B. CURRENT DENSITY USED IN COMPARING REACTIVE SUBSTANCES



The net reactions given by Equations (6) and (7) each occur by a series of steps similar to those detailed for methanol.

The mechanism written for methanol appears to be equally valid when applied by analogy to the fuel cell-reactive hydroxyl compounds discussed above. In these cases, however, the reaction stops when the oxidation product does not satisfy the structural requirements for fuel cell reactivity which we have defined. Thus, we expect ethanol oxidizes to acetate via acetaldehyde, benzyl alcohol to benzoate via benzaldehyde, and isopropanol stops at acetone.

Our exploratory experiments accounted for yields of only 37% acetate from ethanol and 15% acetone from isopropanol. In part, these low yields can be attributed to losses occurring during fuel cell operation and product analysis. In addition, however, the electrode fouling which was particularly noticeable with isopropanol suggests losses by product polymerization at the anode. Similar condensations, giving products which would not have been detected by our analytical method, may have occurred with acetaldehyde formed as an intermediate in the oxidation of ethanol. Yeager (9) reports an acetone yield of greater than 70% from isopropanol. He also notes evidence for acetone condensation products.

Our early experiments also did not rule out the possibility that acetate and acetone formed on an electrode by electrochemical oxidation and not released from the adsorbed state might be more reactive than these same materials tested by the methods used in determining the reactivity sequence. Thus, our low product yields from the oxidation of ethanol and isopropanol might have resulted in part from further oxidation of the expected products. This problem is of great interest in connection with the complete oxidation of fuels in energy fuel cells. It provided a major incentive for the quantitative product studies which we carried out with methanol.

The methanol studies have shown that once a molecule of methanol is attacked on a platinized porous carbon electrode, it need not be completely oxidized to carbonate or even to formate before it is desorbed from the electrode. This is shown conclusively by the escape of some formaldehyde, which is much more reactive than methanol, into the fuel cell electrolyte. It is also clear from comparisons of the amounts of formate in the electrolytes with the amounts theoretically possible assuming complete conversion of methanol to formate (Figures 5 and 6). At the beginning, in these

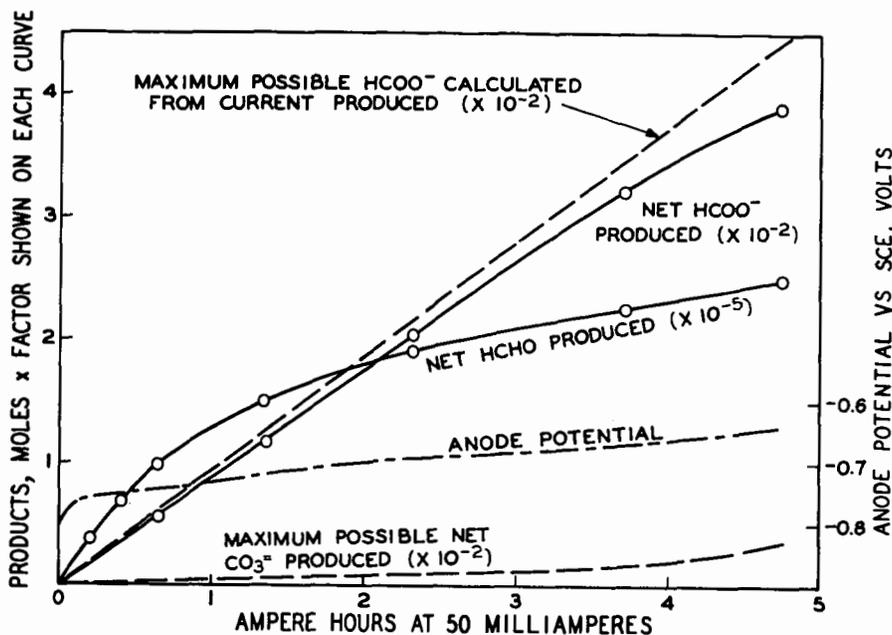


FIGURE 5. FUEL CELL PRODUCTS FROM 1.56 M METHANOL IN 4.5 M SODIUM HYDROXIDE ELECTROLYTE AT 24°C

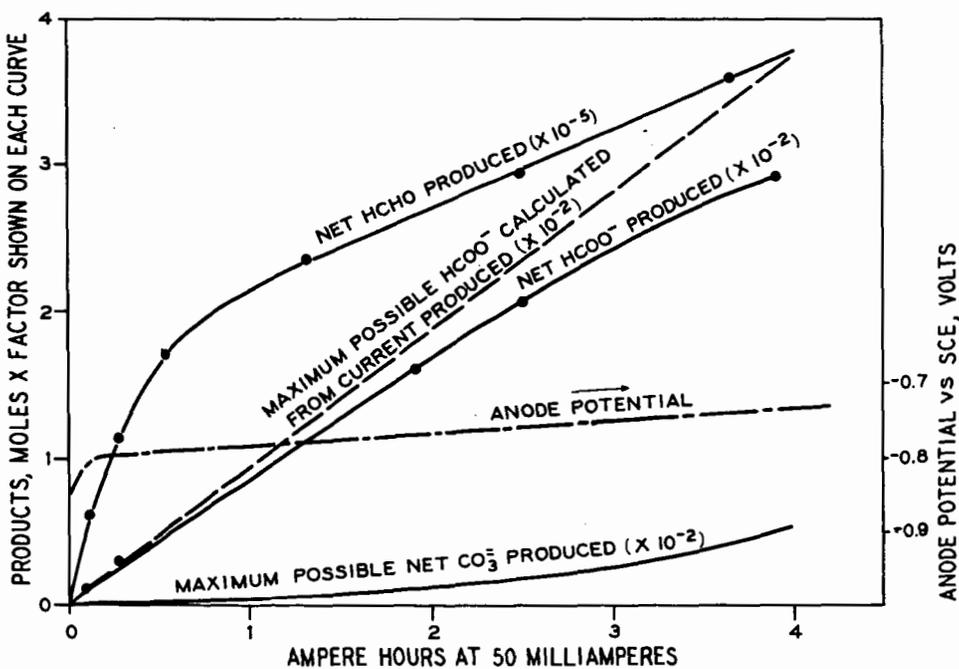
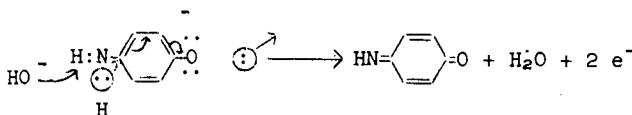
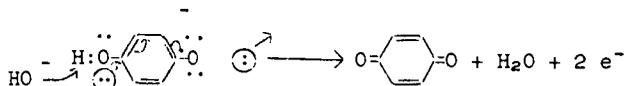


FIGURE 6. FUEL CELL PRODUCTS FROM 1.56 M METHANOL IN 4.5 M SODIUM HYDROXIDE ELECTROLYTE AT 53°C

experiments, very little formate was converted to carbonate; yet later, as the concentrations of formate increased in the electrolyte, more was oxidized further to carbonate. These results are in a sense discouraging. However, they do offer hope for the detection of hydrocarbon oxidation intermediates produced in fuel cells, even when these are much more reactive than the hydrocarbon fuel. Thus, some clues to the complex processes which must occur in the observed complete fuel cell oxidation of hydrocarbons, such as propane, to carbon dioxide and water may be obtainable from analysis of electrolytes and products. Such work is in progress in our laboratories.

In contrast to the compounds discussed above are some reducing agents, such as hydroquinone and p-aminophenol, which do not require catalytic electrodes for electrochemical activity. These compounds exist largely as anions in strongly basic solutions and would appear to be ideally suited for a concerted attack by hydroxyl with the release of two electrons at the anode:



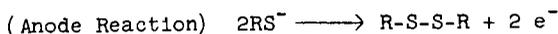
Here, the oxidation probably stops at the stable quinoids.

## V. FUEL CELL PRODUCT STUDIES WITH SULFUR-CONTAINING REACTANTS

Some inorganic, as well as organic, sulfur compounds were oxidized in fuel cells using acidic and basic electrolytes. In general, for this group, compounds that gave good fuel cell activity did not require catalytic electrodes but worked as well on porous carbon alone.

### A. Mercaptans

Mercaptans oxidized readily to pure disulfides in basic electrolyte:



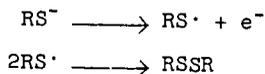
Fuel cell performance of methyl mercaptan and of n-butyl mercaptan dissolved in 2 N sodium hydroxide electrolyte at 50°C. is shown in Figure 9. A platinized porous carbon anode was used with the methyl mercaptan, an untreated porous carbon rod with the n-butyl mercaptan. The reactions were carried out in a three-compartment cell. The oxygen cathode was platinized porous carbon. Sodium hydroxide (2 N) was used as catholyte and center compartment electrolyte.

In both experiments, liquid products began to separate after a short period. These were shown by mass spectrographic analysis to be pure methyl and n-butyl disulfides.

Complete analysis of the product was not attempted. Methyl disulfide recovered by simple separation of the organic layer was 30% of theory based on the methyl mercaptan charged.

The yield of n-butyl disulfide, recovered by simple separation of the organic layer in the anode compartment, was 55% based on the amount of energy produced by the cell.

The mechanism of oxidation of mercaptide to disulfide may consist merely in the discharge of the ion at the anode followed by combination of the resulting radicals:



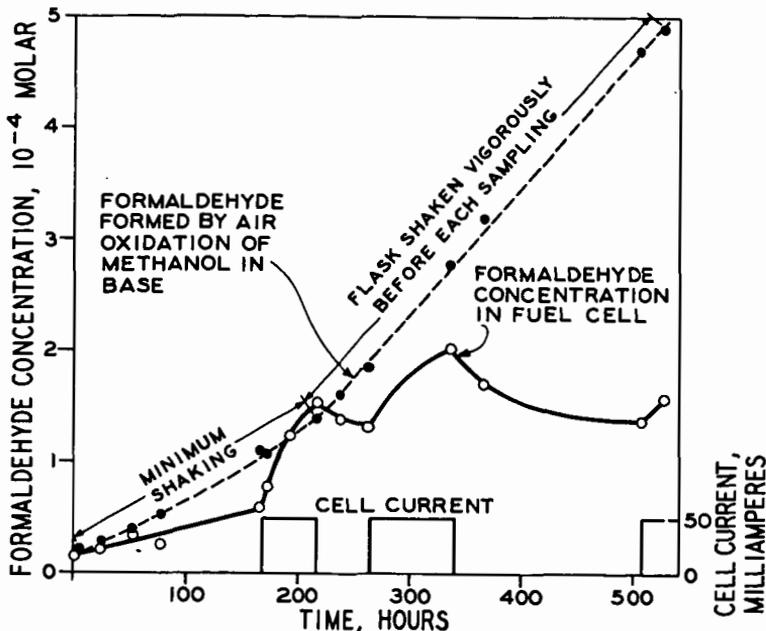


FIGURE 7. CHANGES IN FORMALDEHYDE CONCENTRATION IN A METHANOL FUEL CELL OPERATED INTERMITTENTLY UNDER LOAD AT 24°C

1.56 M. METHANOL IN 4.5 M SODIUM HYDROXIDE ELECTROLYTE

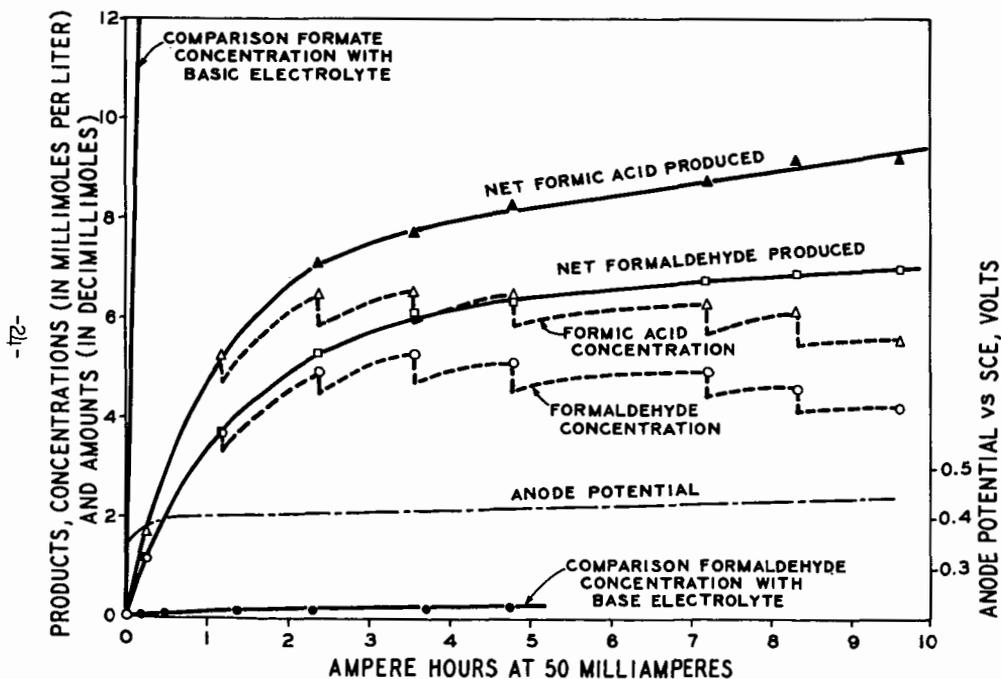
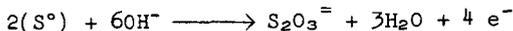
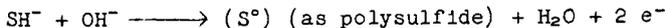
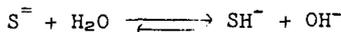


FIGURE 8. FUEL CELL PRODUCTS FROM 1.56 M METHANOL IN 2.3 M SULFURIC ACID ELECTROLYTE AT 23°C

### B. Sodium Sulfide

Sodium sulfide is oxidized at the anode of a fuel cell to thiosulfate via polysulfide:



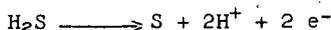
Porous carbon rod electrodes were nearly as effective as platinized porous carbon for the sulfide half-cell. Sodium sulfide alone or with added base was used in the anode section of a three-compartment fuel cell. The other compartments contained sodium or potassium hydroxide solutions as electrolyte. Platinized porous carbon electrodes were used as oxygen cathodes.

In sustained operation under load, the anolyte turned to a deep orange color which then gradually faded to colorless. This is due to the formation of polysulfide which then reacts further, giving thiosulfate. Figure 10 shows the changes in composition occurring and the cell potential as a function of the total energy produced per mole of sulfur of any form in the system. The amount of sulfite present was negligible at all times. Sulfate, present in small amount initially, increased only slightly in concentration.

### C. Hydrogen Sulfide

The possibility of converting hydrogen sulfide to sulfuric acid in a fuel cell using sulfuric acid electrolyte was investigated. Instead of sulfuric acid, elemental sulfur was formed. This collected largely on the surface of the electrode, eventually deactivating it. Extraction with hot xylene and ether followed by heating in boiling water, while passing helium through the electrode, restored most of the original activity. Platinized carbon electrodes were used in these experiments, but later work indicates that porous carbon would work equally well for the hydrogen sulfide anode.

In one experiment, a fuel cell was operated for 23.1 hours at a current of 30 ma (1 ma/cm<sup>2</sup>). Hot xylene extraction of the electrode and evaporation of the extracts gave 0.35 gram of sulfur. This corresponds to 84% of theory, based on the following half-cell reaction,



### D. Sulfur Dioxide

Sulfuric acid production from sulfur dioxide in fuel cells was investigated. Platinized carbon electrodes in 5 N sulfuric acid at 50°C. gave much better performance when separated by Nalfilm-1 anion exchange membranes. In sustained operation at 100 ma cell current (3 ma/cm<sup>2</sup>), the potential only decreased from 0.37 to 0.34 volt in five hours and then remained constant for an additional 11 hours. Cutting the diaphragm at this point dropped the potential sharply from 0.35 volt at 100 ma to 0.18 volt at 60 ma. This decreased further in 20 minutes to 0.128 volt.

Concentrated sulfuric acid from the sulfur dioxide-oxygen fuel cell would be desirable, but increasing the sulfuric acid electrolyte concentration seriously decreased performance (Figure 11).

## VI. PREPARATION OF ANHYDROUS HYDROGEN BROMIDE IN A BROMINE-HYDROGEN FUEL CELL

Reaction of bromine and hydrogen in a fuel cell to give anhydrous hydrogen bromide and by-product electrical energy was investigated. The 48% hydrobromic acid azeotrope was selected as electrolyte in order to permit hydrobromic acid formed in the cell to be separated in anhydrous form by distillation.

The fuel cell used consisted of three compartments separated by Nalfilm-1 anion exchange membranes. Platinized porous carbon electrodes were used initially for both hydrogen and bromine, but later the cathode in the bromine compartment was replaced with a porous carbon rod with no significant change in performance.

Helium saturated with bromine gave a potential of 0.5 volt at a current density of 5 ma/cm<sup>2</sup> at 50°C. No significant loss of activity occurred in 16 hours of operation.

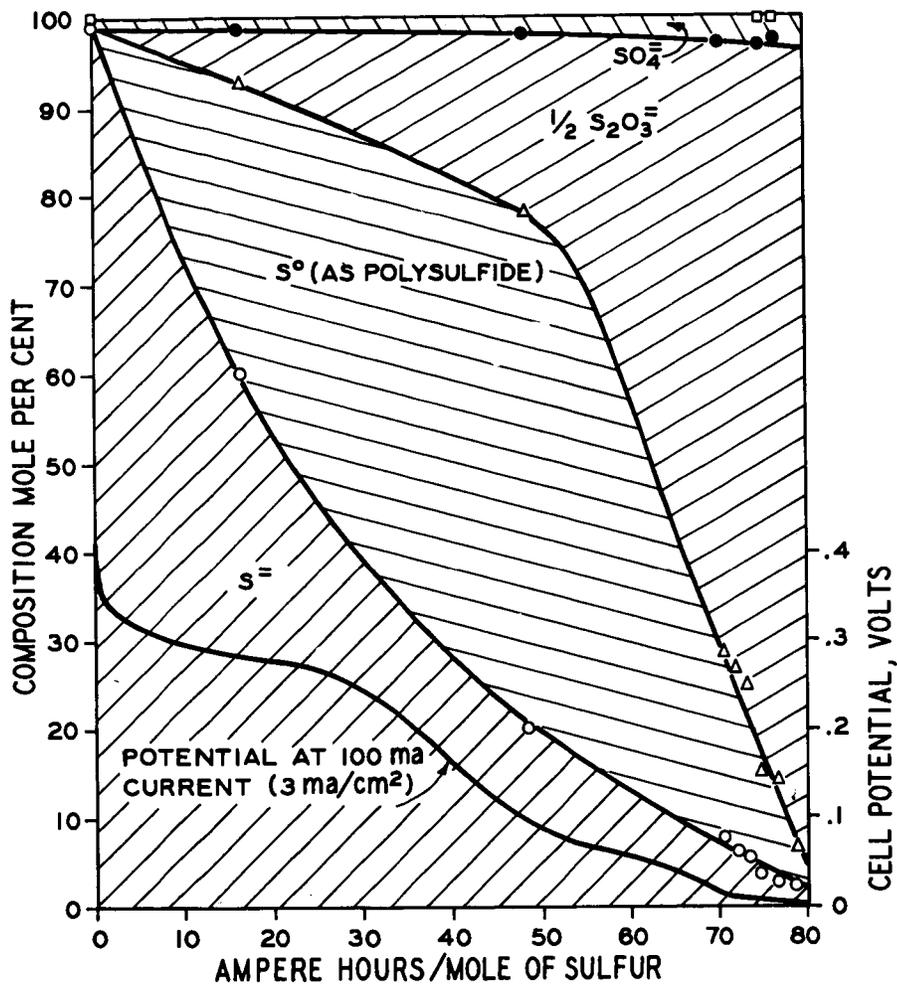


FIGURE 10. CHANGES IN ANOXYTE COMPOSITION IN A BASIC ELECTROLYTE SODIUM SULFIDE-OXYGEN FUEL CELL AT 24°C

□ = NEGLIGIBLE  $SO_3^{=}$  CONCENTRATION

Later, sufficient bromine was added to the cathode compartment to give a second phase and the mixture stirred by rapidly raising and lowering the electrode by means of a motor driven eccentric. Current densities of  $14 \text{ ma/cm}^2$  were drawn for six hours under these conditions. The potential remained at 0.28 volt for two and one-half hours and then gradually decreased to 0.17 volt.

A tenfold improvement in current density, which might reasonably be expected from improved electrode and cell design, would give an anhydrous hydrogen bromide production rate of 1 pound per hour per square foot of electrode surface.

#### VII. ACKNOWLEDGMENT

The author is indebted to Dr. G. H. Denison and Dr. W. G. Toland who were instrumental in initiating and encouraging these fuel cell studies. He also wishes to acknowledge the help of Dr. L. R. Griffith who provided some of the data on the reactivity of hydrocarbons and to thank him with Dr. R. P. Buck and Dr. R. T. Macdonald for helpful discussions and invaluable aid while preparing this paper.

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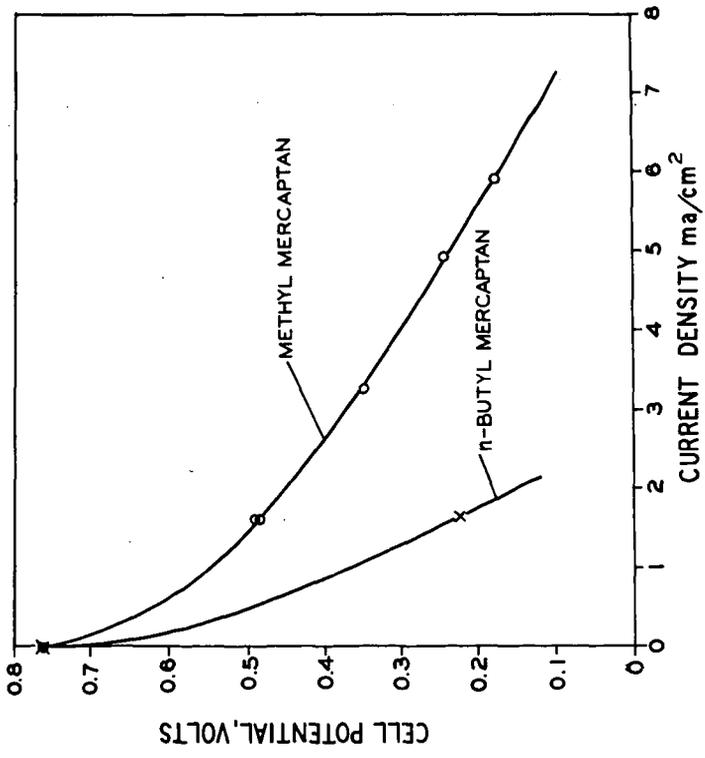


FIGURE 9. PERFORMANCE OF MERCAPTAN-OXYGEN FUEL CELLS AT 50°C  
 1.19 M METHYL MERCAPTAN AND 0.91 M n-BUTYL MERCAPTAN  
 IN 2M SODIUM HYDROXIDE ELECTROLYTE

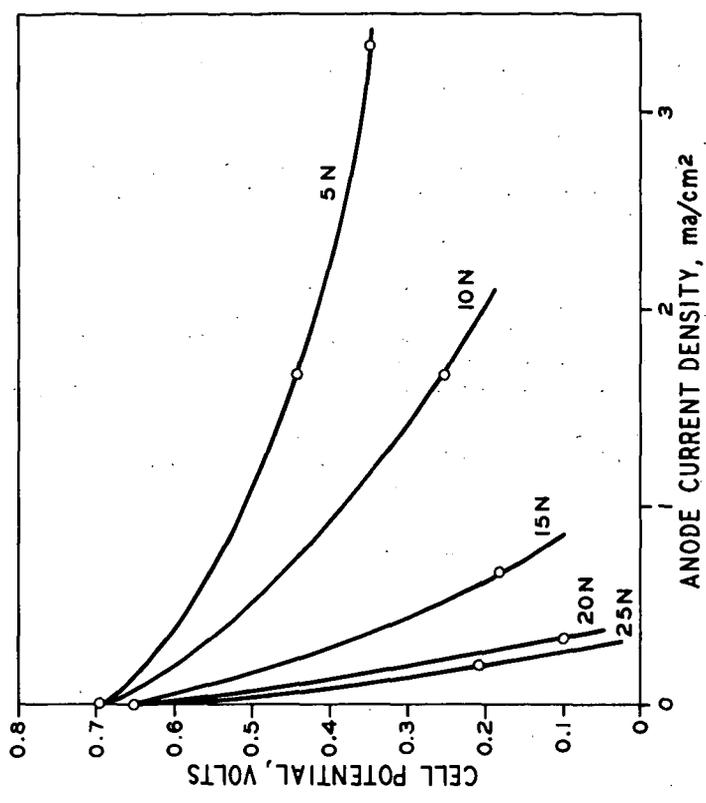


FIGURE 11. EFFECT OF SULFURIC ACID ELECTROLYTE NORMALITY  
 ON SO<sub>2</sub>-O<sub>2</sub> FUEL CELL PERFORMANCE AT 50°C