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FUEL CELL

RESEARCH & DEVELOPMENT

RESEARCH ON LOW TEMPERATURE
FUEL CELL SYSTEMS

SPECIAL PROGRESS REPORT NUMBER 18

JUNE 1, 1961 TO SEPTEMBER 30, 1961

CONTRACT NUMBER DA-44-009-ENG-3771

U.S. ARMY

ENGINEER RESEARCH AND DEVELOPMENT LABORATORY

FT. BELVOIR VIRGINIA

AIRCRAFT ACCESSORY TURBINE DEPARTMENT

GENERAL  ELECTRIC

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LYNN, MASSACHUSETTS

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INTRODUCTION

This is a technical progress report of a research program on low temperature fuel cell systems conducted by the General Electric Company under Contract No. DA-44-009-ENG-3771 with the U.S. Army Engineer Research and Development Laboratory. Original work was initiated in October 1958 and under the title "Materials Study Redox Fuel Cell" and was extended in September 1959 under the title "Redox and Related Fuel Cell Systems". In April 1960, the work on the Redox system was concluded and summarized in Report No. 9; however, work associated with the direct conversion of the fuels was expanded to its present concept. Work has continued under the title "Research on Fuel Cell Systems" as outlined in "Exhibit E".

The objective of this program is to develop a technology which will serve as the basis for design and fabrication of fuel cell packs for ground power units and power for traction devices for military applications. A primary aim is the more efficient utilization of conventional liquid hydrocarbon fuels. Close guidance and approval of the direction of this work is given by Mr. E. Cogswell of the U.S. Army Research and Development Laboratories, Ft. Belvoir, Virginia.

These progress reports are issued on a quarterly basis and special summary reports will be issued as indicated. The reader should recognize that this is a progress report covering a particular period of time. The experiments reported are factual, but not necessarily complete, and any conclusions must be considered tentative until a summary report is issued. Comments and suggestions are most welcome.

SUMMARY

The comparative reactivities of a group of saturated hydrocarbons have been determined in platinum anode fuel cells containing both strongly acidic and strongly basic electrolytes over the temperature range 25 to 65°C. Rough values of activation energy for the overall oxidation processes have been calculated in those cases in which the reactivities were sufficiently high. Measurements with the series methane, ethane, propane, isobutane, neopentane show that the tertiary hydrogen in isobutane does not produce any noticeable enhancement in the anodic reactivity of this molecule.

Galvanostatic studies of methane, ethane, propane, isobutane, ethylene and cyclopropane indicate that the rate of adsorption of saturated hydrocarbons on platinum black electrodes is markedly dependent upon the electrolyte. Very slow adsorption occurs in the presence of bicarbonate and caustic. Ethylene and cyclopropane are much more readily adsorbed than the saturated hydrocarbons and both gases adsorb readily in the presence of acidic caustic and bicarbonate electrolytes. The saturated hydrocarbons appear to adsorb dissociatively, and steps attributable to adsorbed hydrogen appear on their galvanostatic oxidation curves. The oxidation of the adsorbed carbonaceous species from all of the hydrocarbons require high overvoltages for their oxidation.

U.S. ARMY ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES

"EXHIBIT E"

RESEARCH ON FUEL CELLS SYSTEMS

19 September 1960

The research to be conducted under this Exhibit E provides for the continuation of research on "other fuel cell concepts" as described in "Amended Exhibit D" dated 20 April 1960, and as provided for in paragraph 5 of "Exhibit D" dated 18 August 1959.

Research shall be conducted on the following tasks:

Task I Study of the adsorption and kinetics of the oxidation of hydrocarbons on different catalyzed electrode surfaces, both in acid and alkaline media.

1. Development of electrodes of different structures, their activation and incorporation of different catalysts.
2. Investigation of the properties of the catalyzed electrodes, developed in 1, concerning the oxidation of pure gaseous hydrocarbons by conducting half cell studies.
 - a. Study of the adsorption of hydrocarbons and their reaction products on the electrode surfaces.
 - b. Study of the oxidation kinetics of hydrocarbons and their reaction products on the electrode surfaces.
 - c. Study of the influence of additives to fuel and electrolyte and influence of pH and process variables (i.e. temperature, pressure, concentration, etc.) on the reaction rates.

3. Development of improved electrolyte structures.
4. Evaluation of these electrolytes in test cells, using the fuel electrodes, developed in 2, concerning:
 - a. The electrical conductivity.
 - b. The mechanical strength and gas-permeability of the electrolyte structures of varying thickness.
 - c. The influence of reaction by-products (H_2O , CO_2 , precipitates) on the conductivity, mechanical strength, etc., determined in long term test.
5. Study of the possibilities of the direct oxidation of heavier liquid hydrocarbons and mixtures thereof according to 2. This task to be initiated pending the completion of 1 through 4 above.

TASK II Study on the kinetics of the oxygen electrode both in acid and alkaline media.

1. Investigation of the rate limiting step in the overall reduction of oxygen on different catalyzed electrode surfaces.
2. Study of the effect of reaction products on the kinetics of the oxygen electrode. (i.e. the formation of hydrogen peroxide and metal oxides.)
3. Study of the influence of additives to the oxygen and electrolyte and the effect of pH and process variables on the kinetics of oxygen reduction.

1.0 TASK I - FUEL ELECTRODE STUDIES

Task I of this contract is directed toward the attainment of fuel electrodes for operation upon non-hydrogen fuels.

The present report is concerned with an area of investigation which was arranged at a meeting between ERDL and the Research Laboratory representatives on May 25, 1961. At that time it was agreed that platinum anode fuel cell performance measurements would be made at ambient temperature and at 65°C. with acidic and caustic electrolytes for ethane, propane, and isobutane as representatives of fuels with primary, secondary and tertiary carbon-hydrogen bonds. It was also agreed that the adsorption of the same fuels would be examined in acidic and alkaline media and at the same temperatures using galvanostatic techniques. This report contains material which comprises the above program and extends somewhat beyond it.

Work on Task I has been performed at the General Electric Research Laboratory by Dr. W.T. Grubb and Dr. L.W. Niedrach with the technical assistance of Miss Carol J. Michalske and Mr. Harvey Alford. Acknowledgement of assistance by any other personnel is contained in the text.

PERFORMANCE OF SATURATED HYDROCARBONS IN FUEL CELLS AS A FUNCTION OF STRUCTURE, ELECTROLYTE AND TEMPERATURE

During the present report period, a special series of experiments has been carried out at the request of our sponsors aimed at obtaining more information about the reactivities of saturated hydrocarbon in fuel cells in the temperature interval from ambient up to approximately 65°C. It was agreed that polarization curves would be obtained for cells containing platinum black electrodes, and strongly acidic and basic electrolytes. It was agreed that at least ethane, propane, and isobutane would be run at 25 and 65°C. in both acidic and basic electrolyte cells. It was proposed by G. J. Young, a consultant to ERDL, that isobutane might prove to be the most reactive of these three fuel gases because of the presence of a tertiary hydrogen in this molecule. It is known that tertiary hydrogen in isobutane exchanges rapidly in the presence of heterogeneous catalysts with deuterium.

If a similar process is rate determining in anodic oxidation of hydrocarbons in fuel cells, it might lead to high reaction rates for isobutane in fuel cells. Alternatively, the finding that this was not the case would be a probable indication that carbon hydrogen bond breaking was not a rate determining step in the overall electrochemical oxidation of hydrocarbons in the fuel cells.

In the pursuit of the above objective, the experiments tabulated in Table I below have been performed.

The performance of all saturated hydrocarbons was very poor in the alkaline electrolyte cells, and in fact so poor that in no case could steady state current densities greater than 1 ma/cm^2 be maintained at temperatures up to 65°C . This is in line with the very slow adsorption of these fuels on platinum electrodes in contact with alkaline electrolyte as described in another section of this report. In strong contrast, and also in line with the adsorption rate measurements, ethylene oxidizes very rapidly at platinum anodes in alkaline electrolyte fuel cells. The emphasis of the present group of experiments is however centered about the saturated hydrocarbons. These are reasonably reactive on platinum anodes in acid electrolyte cells, and give moderately high adsorption rates as discussed in another section of this report.

In Figures 1-6 are presented the polarization curves for several hydrocarbon fuels at various temperatures for the acid cells listed in Table I. Performance always rises with temperature as would be expected; however, the open circuit potential was found to rise with temperature in the case of ethane, and propane but was either constant or slightly falling in the case of isobutane and neopentane. In every case, the polarization curves of Figures 1-6 are presented as solid lines in the region of steady load current and are dashed in the region where the load currents fell off with time. In some cases, this onset of falling performance under load was very sudden at a particular value of the E.M.F. and seemed to indicate a possible change in the character of the electrode reaction or of the surface characteristics of the electrode. The effect of this "switch-over" in the performance curve of the electrode was not however particularly reproducible. In fact, in the case of propane at 25°C , some cells maintained rather low but steady load currents down to 0.15 volts. The onset of falling load currents may be therefore a limiting current effect. This detail of sort of question is obviously not answered by the present data.

TABLE I

Experiments Carried Out to Determine the Comparative Reactivities
Of Several Hydrocarbon Fuels in Fuel Cells

<u>Fuel^(e)</u>	<u>Electrolyte</u>	<u>Temperatures</u>	<u>Type of Measurement</u>
Ethane	Acid ^(a)	25	P.C. ^(c)
		45	P.C.
		65	P.C. CO ₂ ^(d)
Propane	Acid ^(a)	25	P.C.
		45	P.C.
		65	P.C. CO ₂
Isobutane	Acid ^(a)	25	P.C.
		45	P.C.
		65	P.C. CO ₂
Ethane	Alkaline ^(b)	25	P.C.
		45	P.C.
		65	P.C.
Propane	Alkaline ^(b)	25	P.C.
		45	P.C.
		65	P.C.
Isobutane	Alkaline ^(b)	25	P.C.
		45	P.C.
		65	P.C.
Methane	Acid ^(a)	65	P.C. CO ₂
Neopentane	Acid ^(a)	25	P.C.
		65	P.C. CO ₂
Ethylene	Acid ^(a)	28	P.C.
		54	P.C.
		67	P.C. CO ₂

- (a) The acidic electrolyte was Zerolit C-20 saturated with 6 N sulfuric acid.
- (b) The alkaline electrolyte was Zerolit A-20 saturated with 5.5N potassium Hydroxide.
- (c) P.C. means polarization curve, steady state current vs. cell E.M.F.
- (d) CO₂ refers to the determination of the evolved CO₂ by collection in a BaOH₂ bubbler and weighing as barium carbonate. Details of this procedure are presented in the text.
- (e) All fuel gases employed were Matheson C.P. grade or better.

E.M.F. vs. CURRENT DENSITY FOR ETHYLENE-OXYGEN FUEL CELL AT VARIOUS TEMP.
(PT ELECTRODES, ACID ELECTROLYTE)

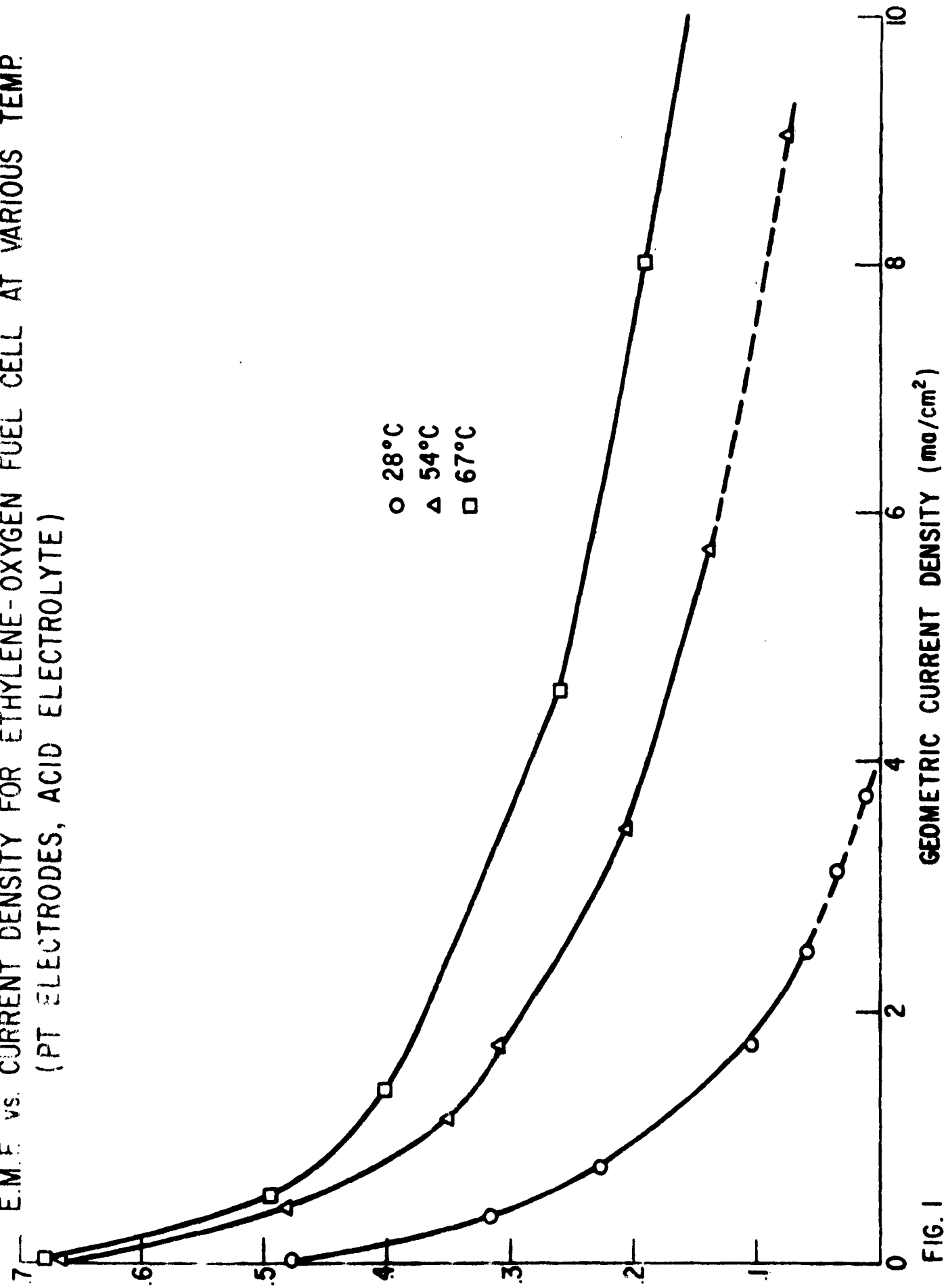


FIG. 1

E.M.F. vs. CURRENT DENSITY FOR ETHANE-OXYGEN FUEL CELL AT VARIOUS TEMP.
(PT ELECTRODES, ACID ELECTROLYTE)

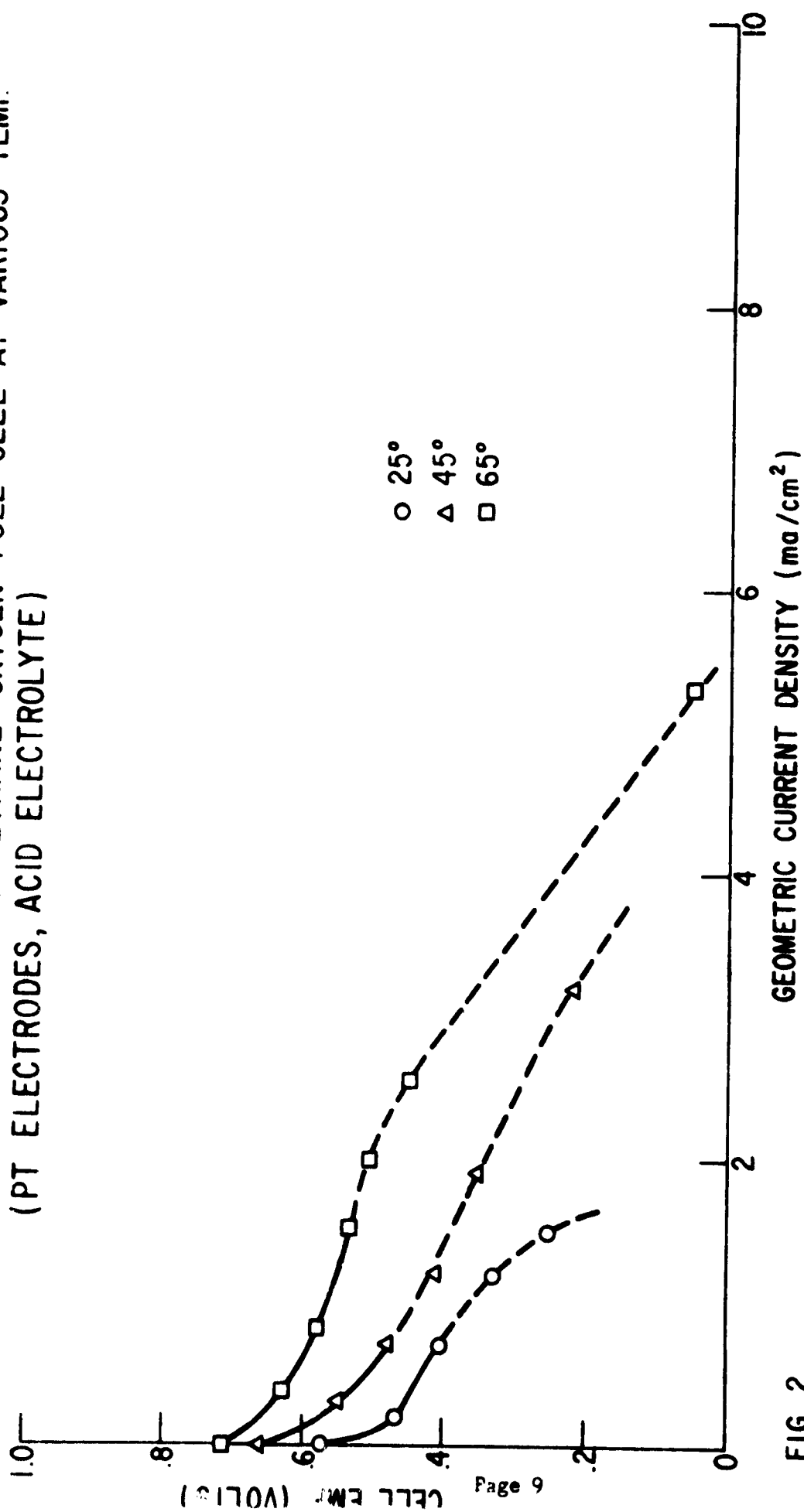


FIG. 2

E.M.F. vs CURRENT DENSITY FOR PROPANE-OXYGEN FUEL CELL AT VARIOUS TEMP.
(PT ELECTRODES, ACID ELECTROLYTE)

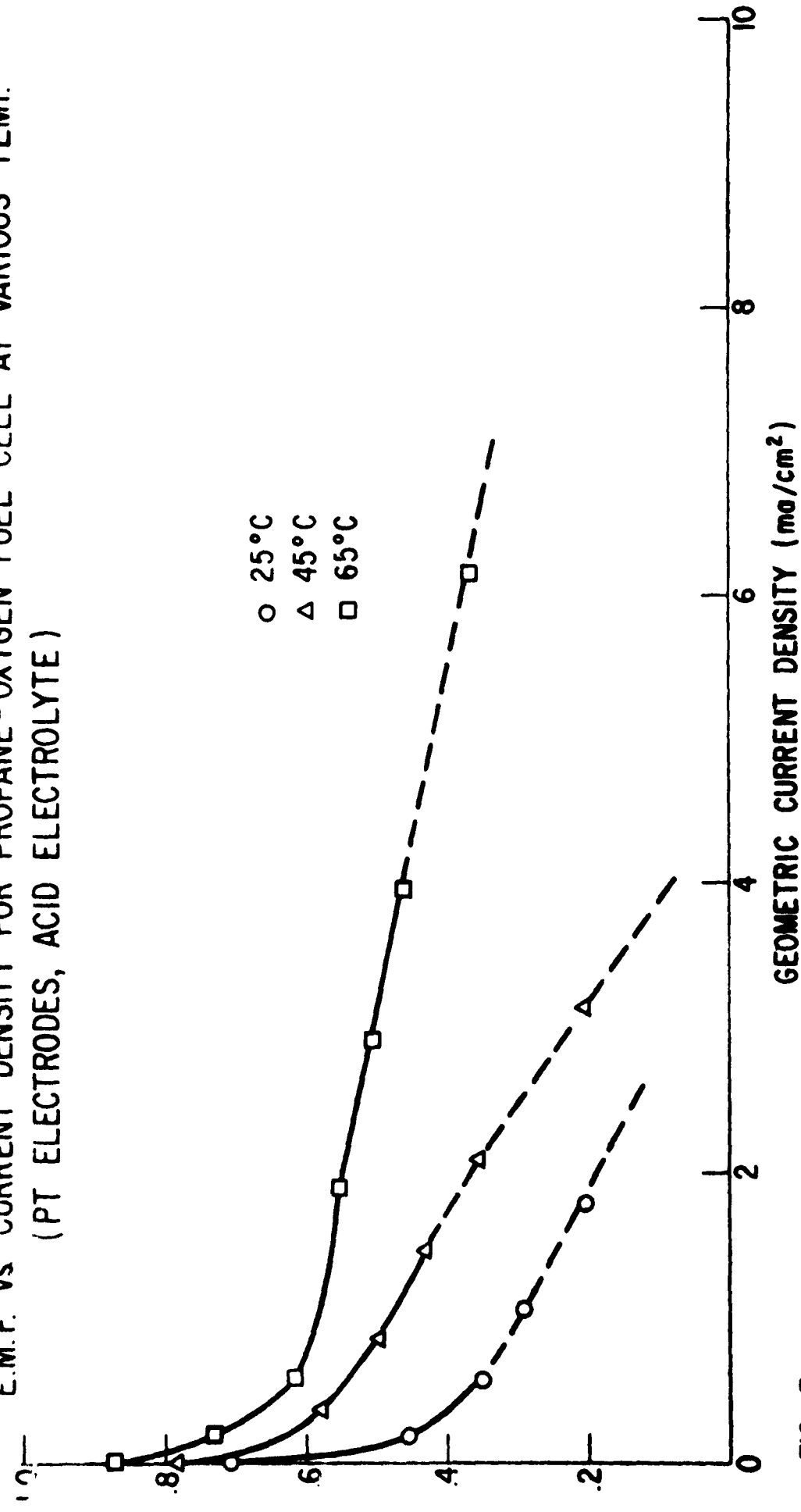


FIG. 3

E.M.F. vs. CURRENT DENSITY FOR ISO-BUTANE - OXYGEN FUEL CELL AT VARIOUS TEMP.
(PT ELECTRODES, ACID ELECTROLYTE)

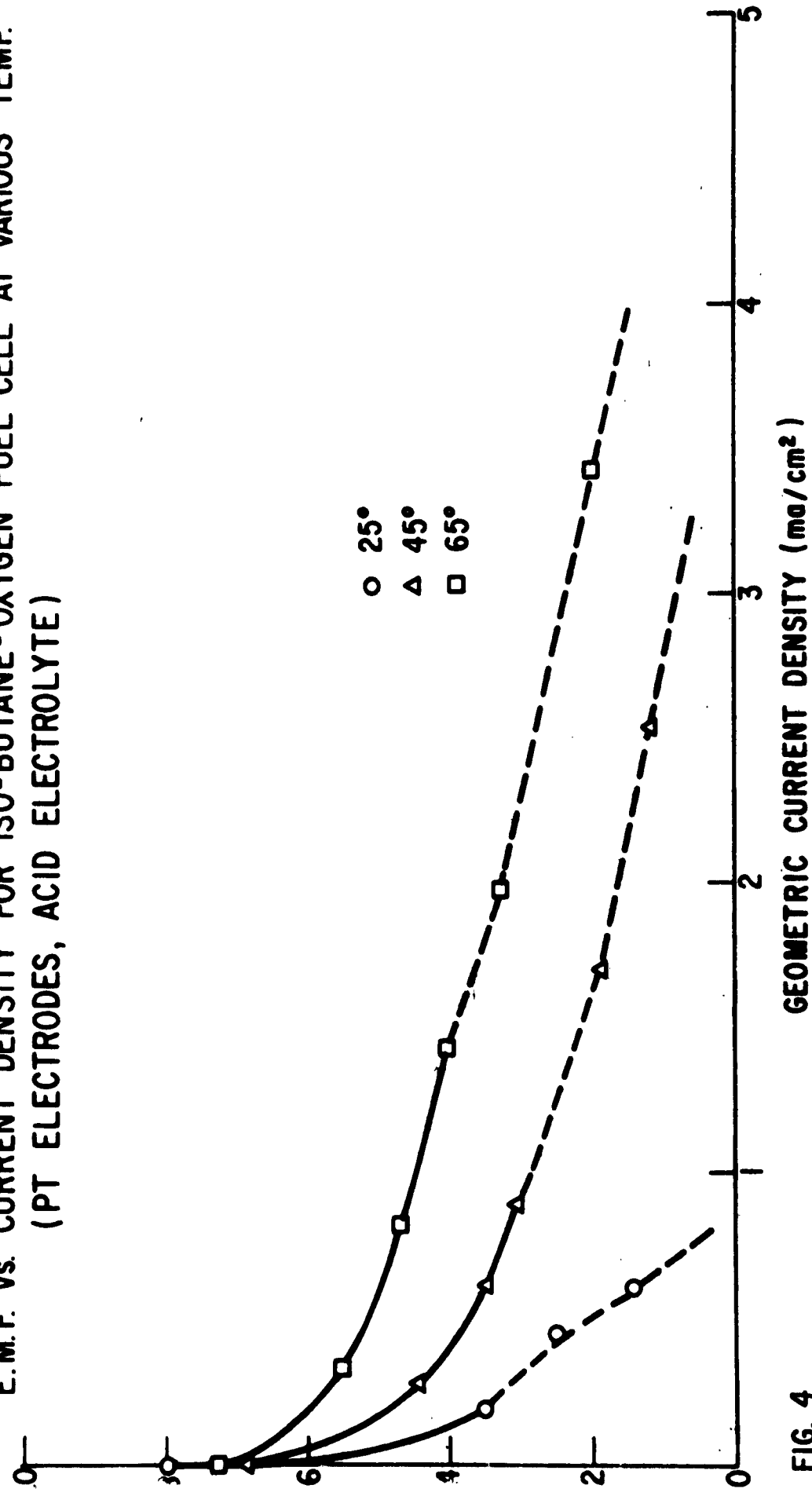


FIG. 4

E.M.F. vs. CURRENT DENSITY FOR NEOPENTANE - OXYGEN FUEL CELL AT VARIOUS TEMP.
(PT ELECTRODES, ACID ELECTROLYTE)

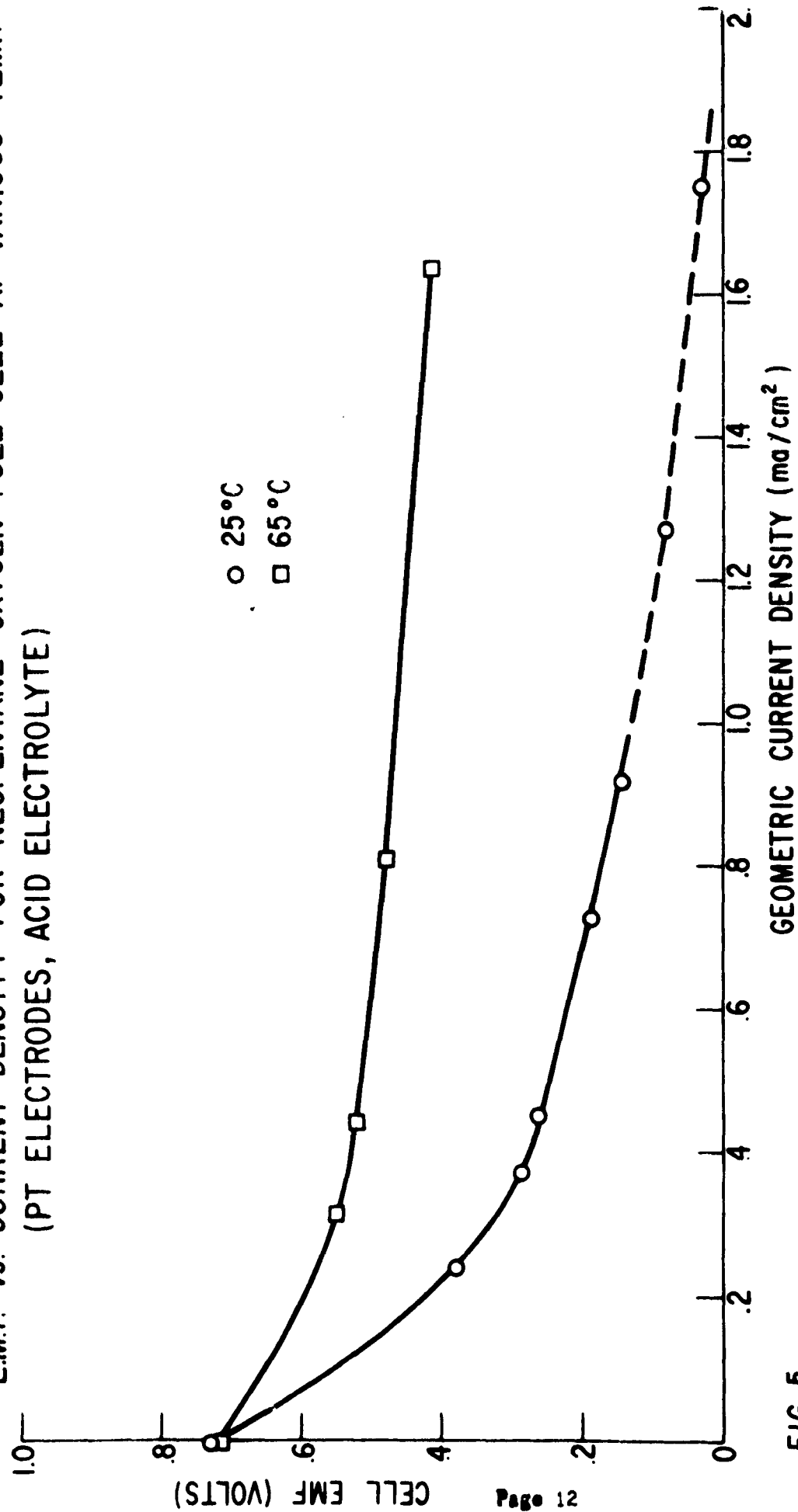


FIG. 5

E.M.F. vs. CURRENT DENSITY FOR METHANE-OXYGEN FUEL CELL AT 65°C.
(PT ELECTRODES, ACID ELECTROLYTE)

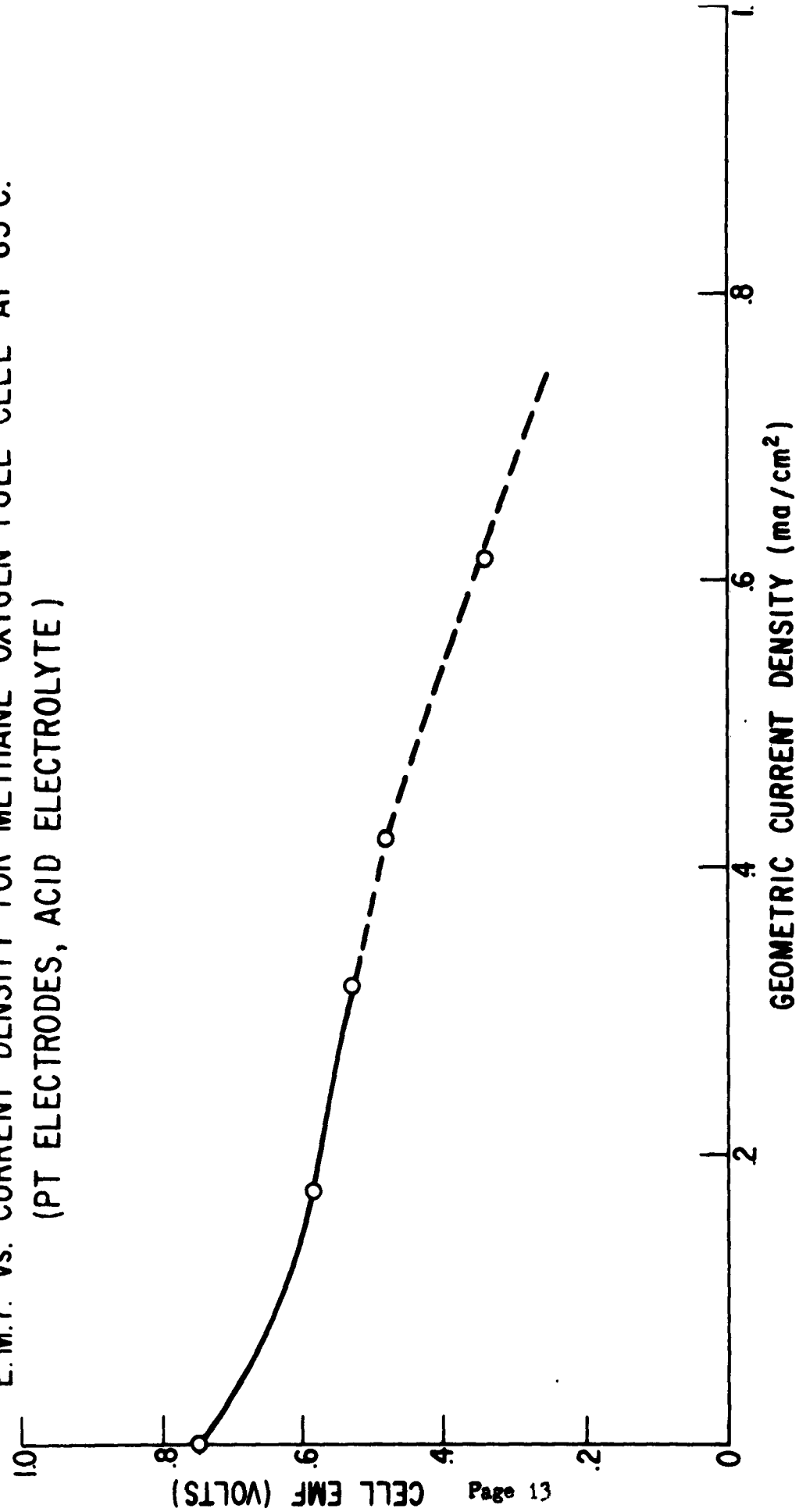


FIG. 6

From the temperature coefficient of the current at a constant value of polarization (i.e. open circuit minus load voltage) one can calculate a gross overall activation energy for the electrochemical oxidation of the several fuels. This has been done for the case of ethylene and the value of 11 kcal/mole was found using the data from an acid electrolyte cell (cf preceding progress report). The present data on ethane, propane, and isobutane have been analyzed in the same manner with the results tabulated below.

TABLE II

<u>Fuel</u>	<u>ΔH</u>
Ethylene	11 $\pm$ 2 kcal/mole
Propane	6 $\pm$ 2 " "
Ethane	6 $\pm$ 4 " "
Isobutane	7 $\pm$ 4 " "

Fuel cell performance alone could not be considered a fair criterion for judging the relative merits of hydrocarbons of different structure, since high performance from a fuel which oxidized only slightly, e.g. propane to acetone, or propionic acid would be very inefficient and undesirable from the practical point of view. Therefore a second criterion of fuel cell performance was the determination of the amount of CO₂ formed from a fuel cell accompanying the production of measured amounts of electric charge. These results are tabulated in Table III below.

TABLE III

<u>Fuel</u>	<u>% of Theoretical CO₂</u>
ethylene	27,23
ethane	31,57,36
propane	49,48,34
isobutane	33
neopentane	116,120*
methane	53

*Possible leaking membrane or rearrangement reaction?

The various numbers in the right-hand column represent replicating experiments in which different cells were used except in the case of ethane in which the 3 numbers were determined using the same cell.

The CO_2 analysis was performed by weighing barium carbonate collected in a centrifuge tube containing saturated barium hydroxide.

A calibration of this procedure by introducing various known amounts of gaseous CO_2 into similar centrifuge tubes showed that the method was accurate to about 5%.

In a typical CO_2 collection experiment, an acidic electrolyte fuel cell was operated on propane at a total cell current of slightly more than 20 milliamperes (geometric current density of 1.75 ma/cm^2) for 100 minutes at 65°C . During this time interval with intermittent purging of the fuel gas through the anode compartment and the barium hydroxide bubbler, the current from the cell was constant within a few percent of its initial value. In fact it is sometimes observed with propane at 65°C that the current rises slightly with time after application of the load to the cell when moderate load currents are drawn. It is surprising to find such steady load performance from a fuel molecule as complex as propane at a temperature of only 65°C .

Considerable discussion of the actual magnitude of the CO_2 recovered from the cells as a percentage of the theoretical amounts for complete oxidation of the fuel, would appear to be in order at this point. However, the rather wide variation of values from one cell to another of presumably identical construction and from one run to the next on the same cell would seem to obviate the value of a detailed analysis of these data at this time. The rate wide variability of the results may be caused by the formation of partially oxidized intermediates that are either further oxidized to CO_2 and water or desorbed from the anode surface into the electrolyte.

A number of qualitative attempts have been made to detect intermediates in the electrolyte phase from cells operated on hydrocarbon fuels. These tests have shown the presence of aldehyde and/or ketone groups in products from cells operated on ethane and propane but not from isobutane. In the case of one ethane cell, acetic acid was qualitatively detected. This was a cell in which the ethane gave poor performance, and in our best cells operating on ethane, no acetic acid was detected.

It appears that much interesting information about the mechanism of electrode reactions would result from a detailed quantitative analysis of the electrolyte phase. The use of the membrane electrolyte is a definite handicap in that it can not be removed except by disassembling the cell. It would be advantageous if not essential to operate cells with aqueous electrolytes which can be drained out and replaced even during cell operation. Some preliminary attempts to assemble such structures have given encouragement but were not completely successful. Assuming that such a cell can be constructed along the lines of the present cells, there would remain to be solved some difficult analytical problems.

Even the formulation of these cells would require some idea of the quantities of the intermediates present, and their relative abilities to desorb from the anode surface into the bulk electrolyte solution.

The present data establish the following approximate order of reactivity of hydrocarbons on platinum anodes in fuel cells employing the electrolytes described in the footnotes of Table I. The quoted maximum currents refer to operation at 65°C.

<u>TABLE IV</u>		Maximum Steady
<u>Fuel</u>	<u>Electrolyte</u>	Current Density (ma/cm ²)
Ethylene	Alkaline	20 at 0.25 volts
Ethylene	Acid	10 at 0.15 volts
Propane	Acid	4 at 0.45 volts
Ethane	Acid	2 at 0.5 volts
Neopentane	Acid	1.6 at 0.4 volts
isobutane	Acid	1.5 at 0.4 volts
Methane	Acid	0.17 at 0.58 volts

It is a somewhat arbitrary procedure to assign orders of reactivity in the manner of Table IV. The plots of polarization curves for several fuels at 65°C as depicted in Figure 7 show that they differ widely as to form. Some fuels such as ethylene deliver the highest steady load currents but other fuels such as propane produce the best performance at load voltages above 0.5 volts.

The results of Table IV nevertheless clearly indicate that the active tertiary hydrogen in the isobutane molecule does not make it especially reactive in electrochemical oxidation at a platinum fuel cell anode. In a homologous series of hydrocarbons produced by successive substitution of hydrogens in methane by methyl groups, there is a maximum of reactivity at propane. Neopentane, which contains only primary carbon hydrogen bonds is about as reactive as isobutane. This is very strong evidence against the hypothesis that an active tertiary hydrogen contributes high reactivity to hydrocarbon fuels at platinum anodes. No simple hypothesis accounts for the observed order of reactivity except to note that the double bond in ethylene produces a marked activation of the molecule (compared to ethane) in acidic and especially in basic electrolyte cells.

E.M.F. vs. CURRENT DENSITY FOR VARIOUS FUEL-OXYGEN FUEL CELLS AT 65°C.
(PT ELECTRODES, ACID ELECTROLYTE)

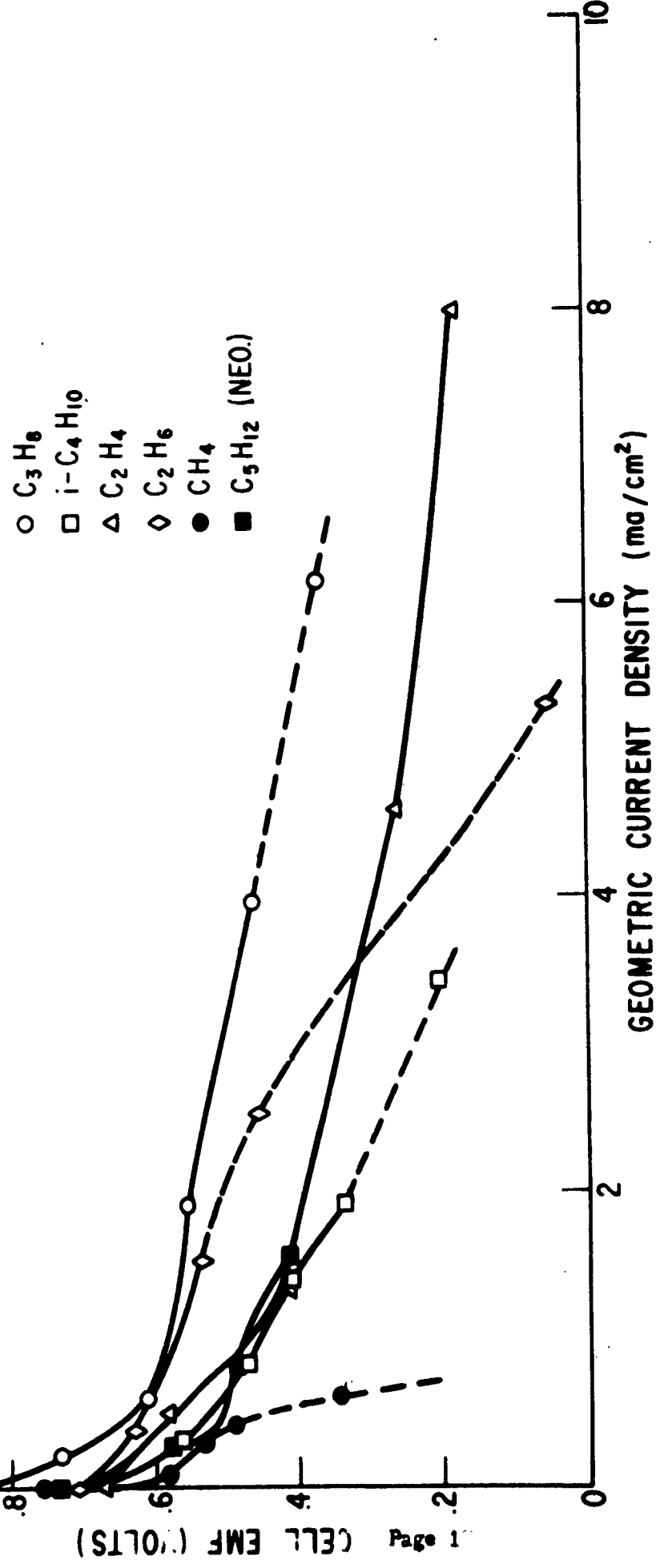


FIG. 7

3.0 GALVANOSTATIC STUDIES OF HYDROCARBONS ADSORBED ON THE SURFACE OF PT-BLACK CATALYSTS

In previous reports of this series, galvanostatic studies of the formation and removal of hydrogen and oxygen films on platinum black electrodes have been described. (Report #14, Oct. 15- Dec. 15, 1960; Report #15, Dec. 15, 1960 - Feb. 15, 1961.) These studies were aimed at characterizing the performance of platinum black catalysts from various sources. In general the voltage-time curves obtained with the catalysts were in agreement with similar data reported for smooth platinum and platinized platinum electrodes (1-3) and indicated that the hydrogen essentially saturates the surface in the ratio of one hydrogen per surface Pt. Data were also reported for the galvanostatic oxidation of adsorbed films of ethane and ethylene on platinum black electrodes (Report #10, Feb. 15 - April 15, 1960). During the present period additional data have been obtained for a variety of adsorbed hydrocarbons at ambient room temperature (25-28°C) and at 65°C in cells employing sulfuric acid, potassium hydroxide, and potassium bicarbonate as the electrolyte.

The purpose of the present experiments was to examine the behavior of a series of hydrocarbons in the presence of a variety of electrolytes to determine whether structural characteristics would have an important influence on their adsorption and oxidation characteristics. The series of saturated hydrocarbons ethane, propane and isobutane (with primary, secondary and tertiary carbon-hydrogen bonds respectively) were examined in all media. Additional tests were run with methane, cyclopropane, and ethylene in some cases in order to uncover other differences in structure that might have bearing on performance.

In making use of galvanostatic oxidation curves to study the adsorbed phase, advantage is taken of the fact that as an adsorbed fuel is oxidized at constant current (in the absence of an additional supply of gaseous fuel), the potential of the electrode changes as the fuel is removed by the oxidation process. From the structure of the potential-time curve one can make deductions about the nature of the adsorbed species and the reactions that occur. In addition it is often possible to determine the amounts of material adsorbed from the transition times between potential steps.

These points are illustrated by the galvanostatic curve for the oxidation of hydrogen adsorbed on platinum black in an acidic system shown in Figure 8.

- 1) A. Slygin and A. Frumkin, *Acta physicochim, URSS*, 3, 791 (1935).
- 2) B. Erschler, *Disc. Faraday Soc.*, 1, 269 (1947).
- 3) M. Becker and M. Breiter, *Z. Elektrochemie*, 60, 1080 (1956).

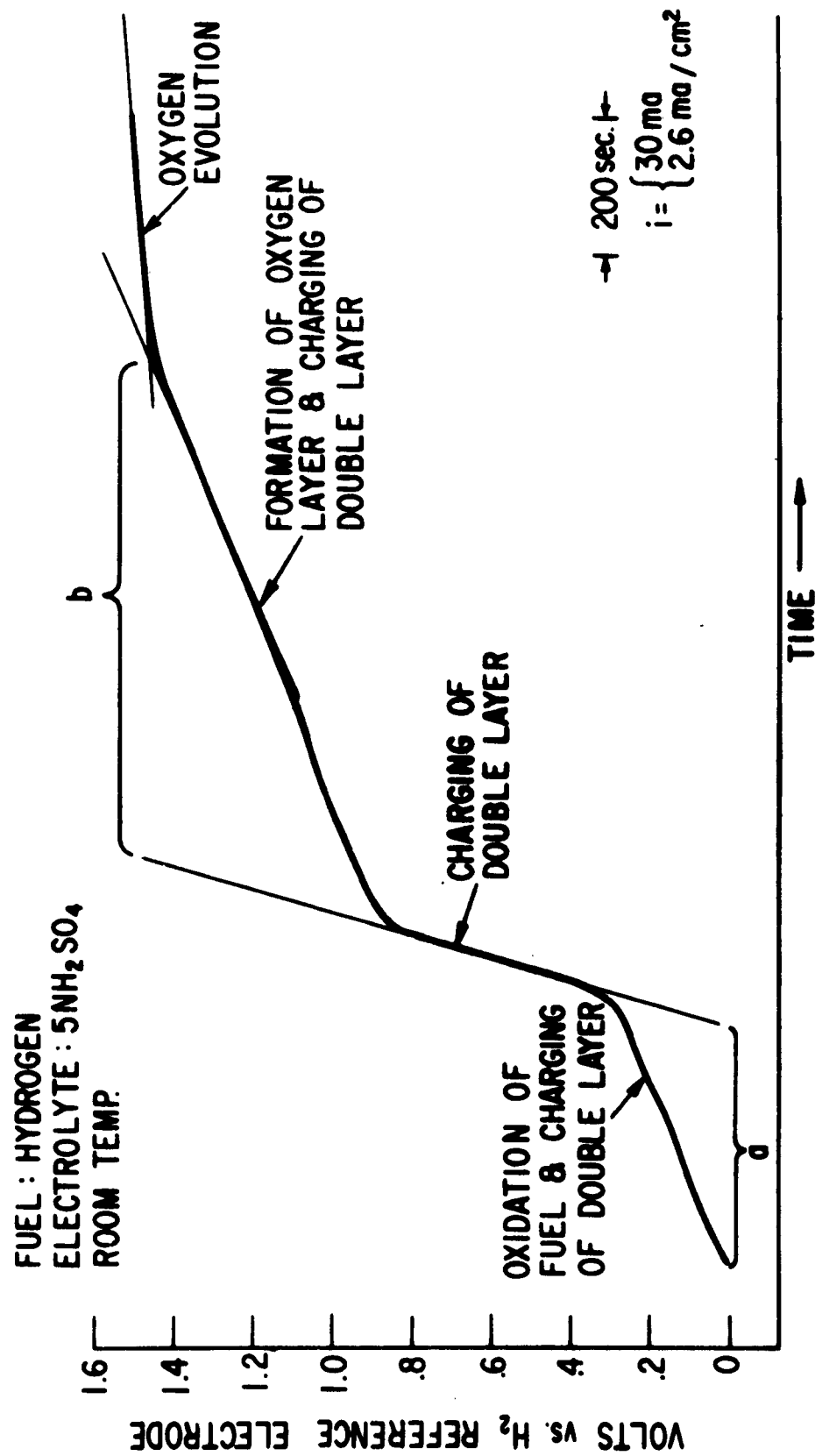


FIGURE 8. GALVANOSTATIC OXIDATION CURVE FOR A PLATINUM ELECTRODE ILLUSTRATING PRINCIPAL FEATURES

At the start, the electrode surface is saturated with adsorbed hydrogen and is in equilibrium with the gas at 1 atmosphere pressure. Its potential is therefore zero versus a hydrogen reference electrode in the same medium. When current is forced through the cell in the appropriate direction, the adsorbed hydrogen is oxidized so that the surface coverage, θ , is reduced. Since this results in a gradual increase in the electrode potential, some current is also consumed in charging the double layer. At a potential of about 0.4V. the electrode is clean; i.e. free of adsorbed hydrogen. A sharp rise in potential then occurs when the only electrode process involved is charging the double layer. This continues until a potential of about 0.8V is reached when another gradual rise in potential occurs as an oxygen film is deposited on the electrode. At a potential of about 1.5 V, oxygen evolution occurs.

The quantities of hydrogen and oxygen on the surfaces may be estimated from the number of coulombs required for their removal and deposition. To arrive at these quantities it is necessary to recall that in the region where hydrogen is oxidized as the deposition of oxygen is occurring, additional current is also required to charge the double layer. The latter may be measured to a first approximation by assuming that the double layer capacity is the same as in the clean region. Then extrapolation of the linear double layer region back to zero volts gives the correction for obtaining the hydrogen coverage from the first break in the oxidation curve. Distance a thus is a measure of the charge consumed in oxidizing the adsorbed hydrogen film. The charge involved in depositing the oxide may be similarly estimated from distance b.

As indicated in a previous report (Report #14, Oct. 15 - Dec. 15, 1960) the amount of hydrogen calculated from distance a corresponds to approximately one hydrogen per available platinum site on the catalyst surface. From a comparison of lengths of a and b it is evident that the oxygen coverage also corresponds to approximately one oxygen per platinum site. This observation is in agreement with related studies of smooth platinum electrodes (4).

A. Experimental Procedures

The procedures and equipment employed in making the measurements with hydrocarbons have been discussed briefly in the earlier reports cited, but it is well to review them at this time. The cell, which employed an auxiliary hydrogen reference electrode, (Report #15, Dec. 15, 1960 - Feb. 15, 1961), is shown in cross section in Figure 9. The test and counter electrodes were the conventional 1.5 inch diameter circular Teflon-bonded structures employed in previous work. Fisher platinum black (Lot #701,281) which had been found previously to have a high surface area and to give uniform performance with hydrogen was employed for the electrodes under test; 0.20 gm bound with Teflon was used. Similar materials were used for the counter electrodes and for the smaller (1/2 inch square) reference electrodes.

(4) M. Breiter, C.A. Knorr and W. Völkl, Z. Elektrochemie, 59, 681 (1955)

The electrolyte was incorporated into suitable matrix by equilibration. A Zerolit C-20 cation exchange membrane was used as the matrix for the sulfuric acid. Zerolit A-20 membranes were used with the potassium bicarbonate and potassium hydroxide electrolytes. In addition, some experiments were performed in which the potassium hydroxide was retained in a matrix of asbestos cloth.

In general, new cells (electrodes, matrix, and electrolyte) were assembled when the electrolyte or temperature was changed. In each cell however, a series of gases were run in the following order, hydrogen, methane (acid system only), ethane, propane, and isobutane. Following the initial tests with hydrogen and these saturated hydrocarbons, additional tests were run with the same materials and in some cases with ethylene and cyclopropane so that replicating and comparison data would be available.

In performing a series of experiments with a cell, a galvanostatic oxidation curve was first obtained for the test electrode after saturating its surface with hydrogen. This was done by admitting hydrogen into Chamber II in Figure 9 and allowing equilibration for several minutes. Chamber II was then completely flooded by forcing in additional electrolyte from a reservoir up to the vent. With the electrode drowned a current of 30 ma (2.63 ma/cm^2) was then forced through the cell in a direction to oxidize the adsorbed gas. Electrolysis was continued through oxygen evolution.

After allowing oxygen evolution for 3-4 minutes the current was interrupted and the free electrolyte was drained from the chamber. Fresh electrolyte was then admitted from the reservoir, and all gas bubbles were eliminated. The current was then reversed to reduce the oxide film on the platinum surface. When the potential had reached a value well within the "double-layer" region (i.e. the region where the electrode surface is clean of oxide and hydrogen films) the current was again interrupted. In the acidic systems the reductions were stopped at a potential of 0.40 V versus the hydrogen reference electrode, in the alkaline and bicarbonate systems at potentials of 0.3 - 0.5 V.

With the electrode clean, the "drowning" liquid was withdrawn from the cell, and the gas to be adsorbed was simultaneously drawn into the chamber through the fuel gas inlet at the top. The system was then allowed to equilibrate for the desired time, usually 30 minutes or 1 hour, with the gas being studied. During this period the potential of the test electrode versus the hydrogen reference was recorded. Attempts to measure the volumes of the hydrocarbons adsorbed were unsuccessful because of excessively high blanks with the cells used.

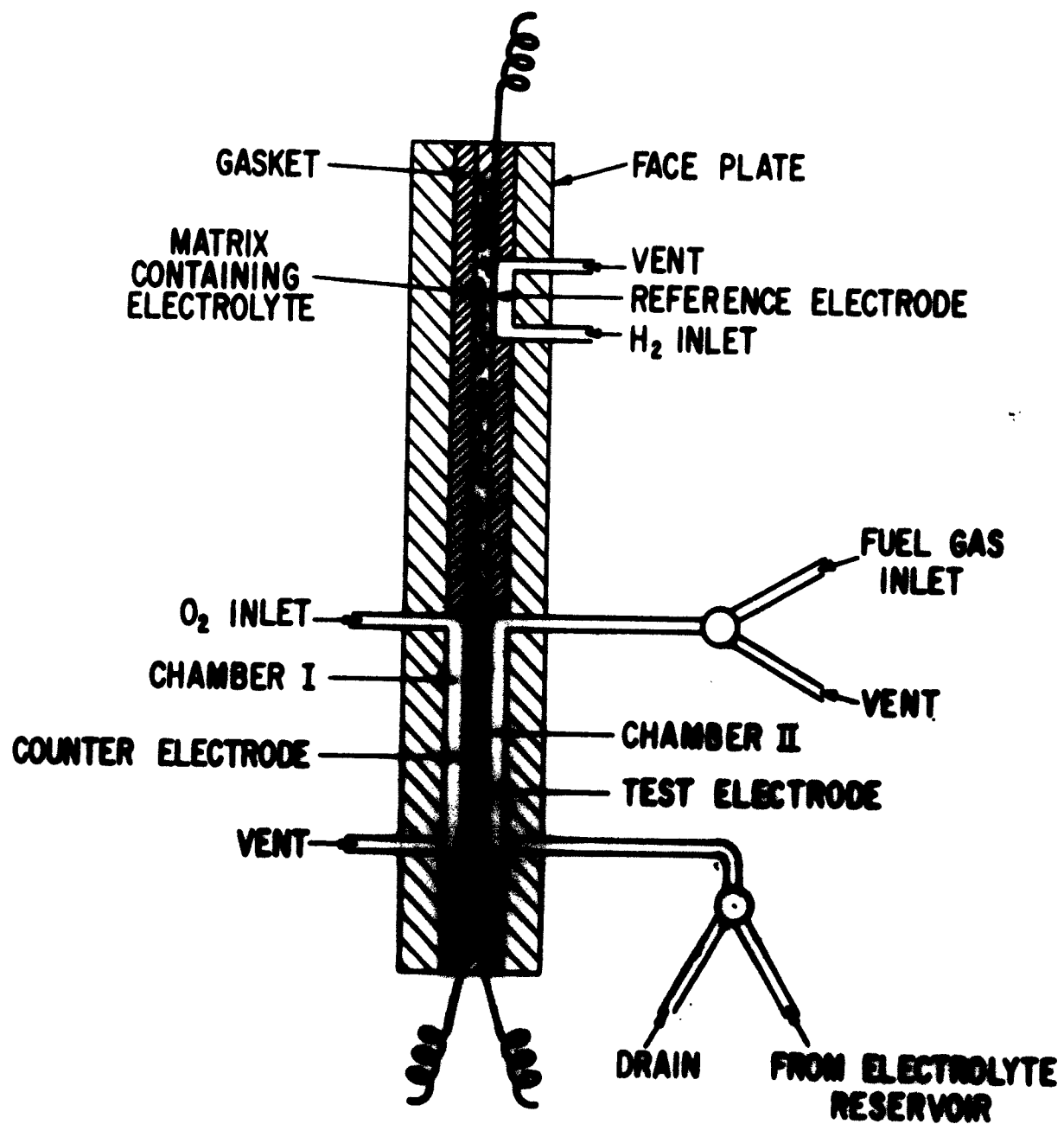


FIGURE 9 TEST CELL

These were caused by the solubility of the gases in the silicone rubber gasketing material. It is intended to obtain such information in future experiments with new cells since the technique has been found to be quite feasible with hydrogen when excellent agreement can be obtained between the volume of gas adsorbed and the number of coulombs that are required for its oxidation.

At the end of the equilibration period the test electrode was again completely "flooded" by filling Chamber II with electrolyte and the adsorbed film was oxidized while the potential was recorded against the hydrogen reference. Again oxidation was continued until oxygen had evolved for 3-4 minutes. At this point the system was treated as after the initial run on hydrogen and when the electrode surface had been cleaned a new gas was adsorbed on the surface and followed as above.

The entire procedure is, of course, dependent upon the fact that the solubilities of the gases being studied are very low and that appreciable amounts can be adsorbed on the catalyst in most cases. In addition, it must be noted that the void volumes in the pores of the electrodes are small so that even were they to contain trapped gas (which is not likely) this would introduce small error into the overall curves. Under these conditions it is therefore possible to obtain oxidation curves than can be attributed to the adsorbed materials.

B. Behavior of the Hydrocarbons

Representative data showing the changes in the working electrode potentials with the time during gas adsorption are shown in Figures 10 thru 15. In Figures 16 and 17 galvanostatic oxidation curves are shown for the adsorbed materials. The galvanostatic curves in each family are superimposed in such a way that the oxygen evolution regions overlap.

In each family of galvanostatic curves, one for hydrogen, as the fuel, is included for reference. It is to be noted in this connection that the curve for the oxidation of adsorbed hydrogen with the bicarbonate medium is irregular in that a high overvoltage is required. This appears to result from a reaction of adsorbed hydrogen with the carbonate to form CO or a related species on the electrode surface. The galvanostatic curve for the electrodeposition of hydrogen on the electrode is shown as a dashed curve. It is seen that a pronounced hysteresis loop is obtained for the cycle. This is in sharp contrast to the behavior of hydrogen in the presence of acid and base, when the oxidation and deposition curves superimpose.

As noted in Section 3.A after the preliminary run with hydrogen, the saturated hydrocarbons were regularly run in each case in the order ethane, propane, isobutane. Methane preceded ethane in the one case when it was run in an acidic cell at room temperature. That fresh electrodes were not used for each gas does not, however, seem to be of great significance in the results to date.

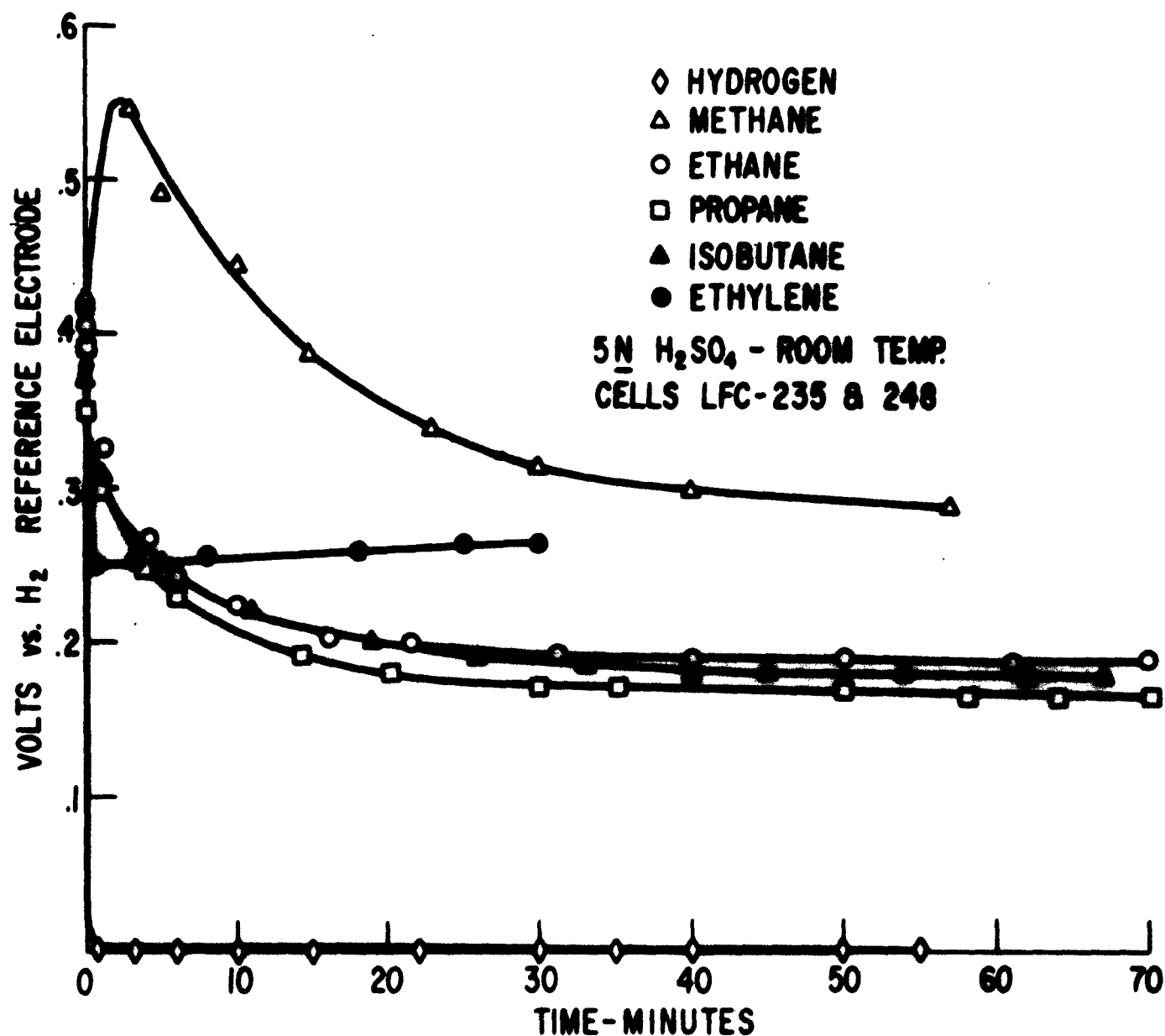


FIGURE 10. CHANGE IN ELECTRODE POTENTIAL WITH TIME
 DURING GAS ADSORPTION WITH ACID ELECTROLYTE AT
 ROOM TEMP.

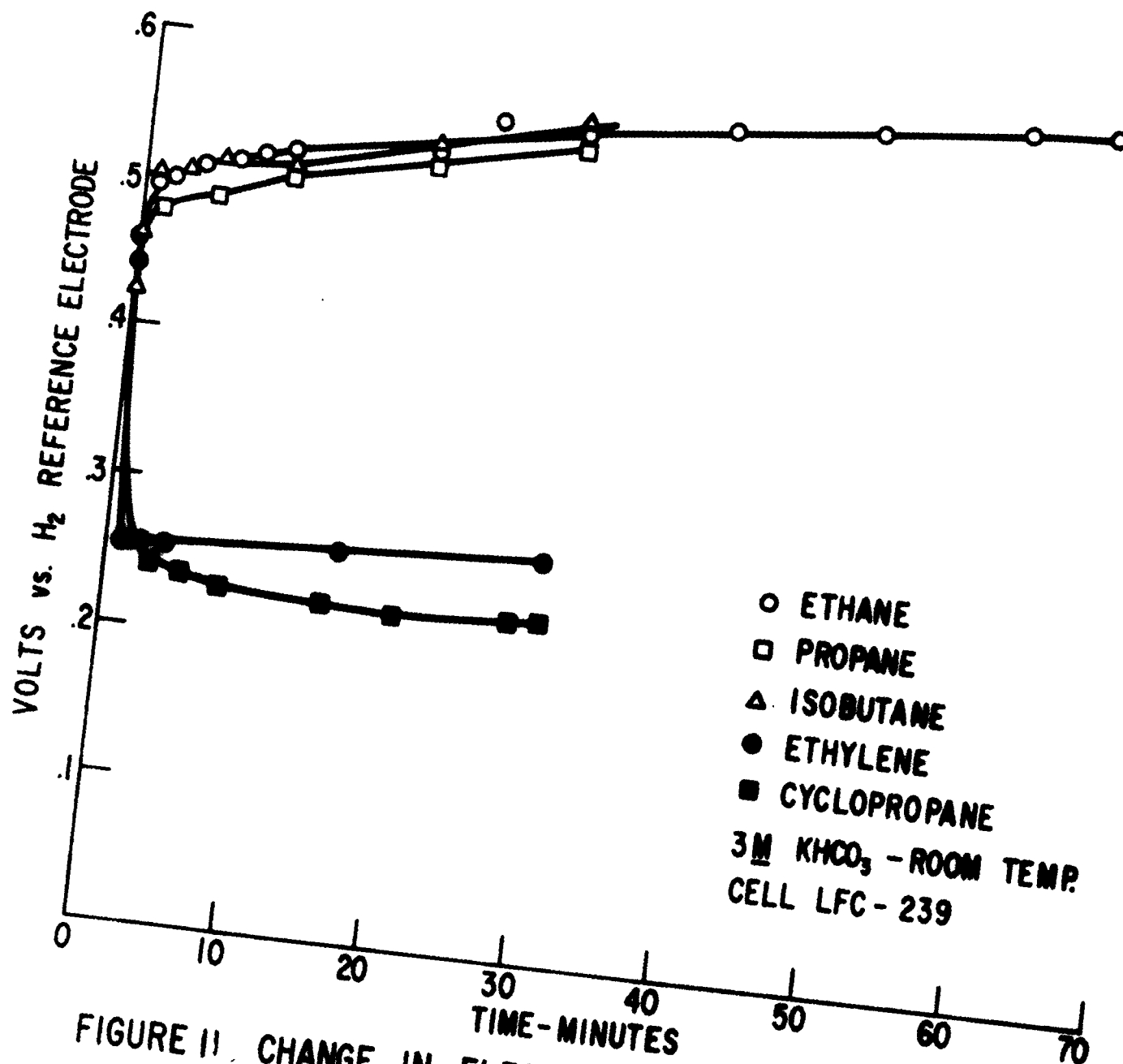


FIGURE 11. CHANGE IN ELECTRODE POTENTIAL WITH TIME DURING GAS ADSORPTION WITH KHCO_3 ELECTROLYTE AT ROOM TEMP.

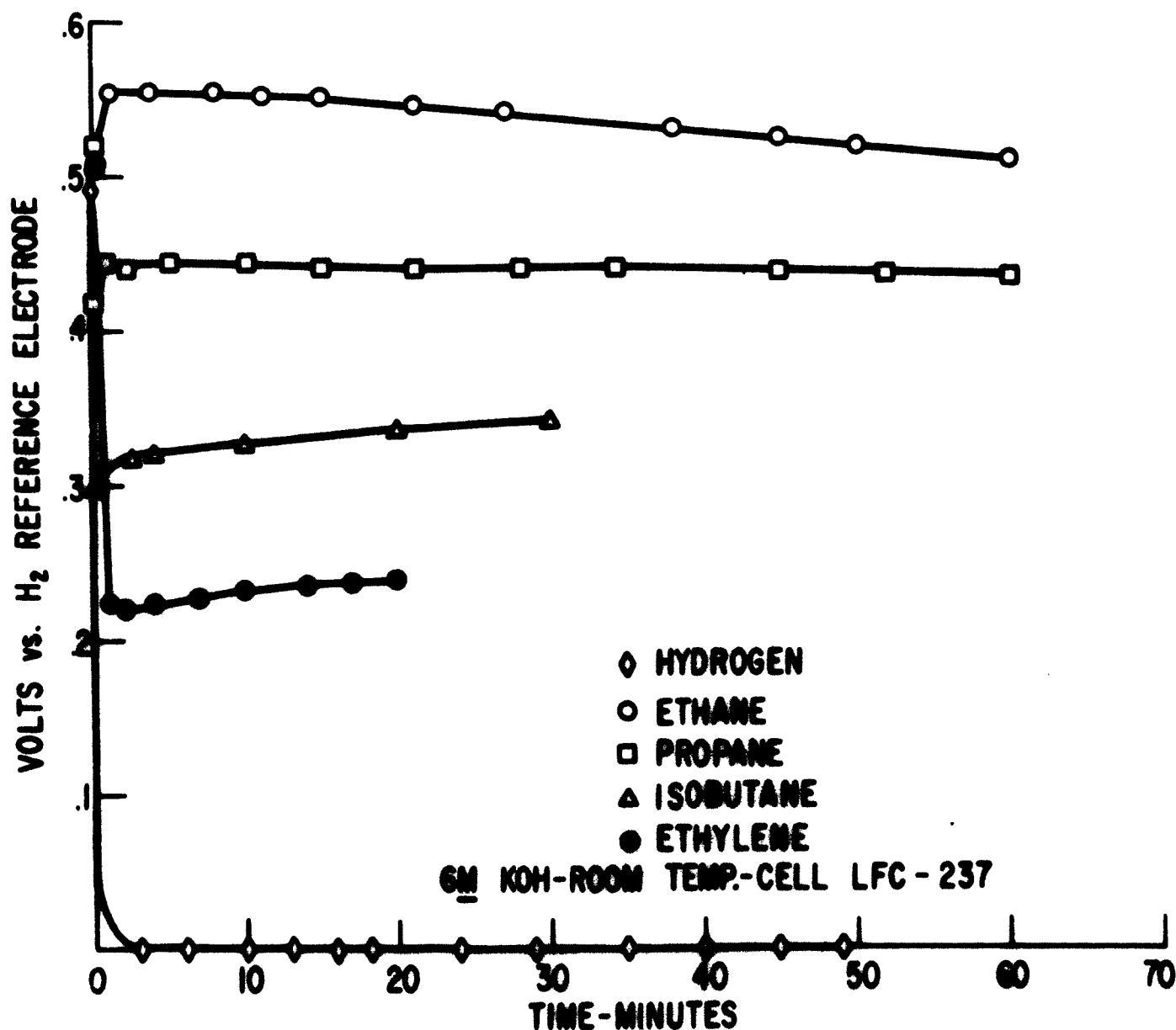


FIGURE 12 CHANGE IN ELECTRODE POTENTIAL WITH TIME DURING GAS ADSORPTION WITH CAUSTIC ELECTROLYTE AT ROOM TEMP.

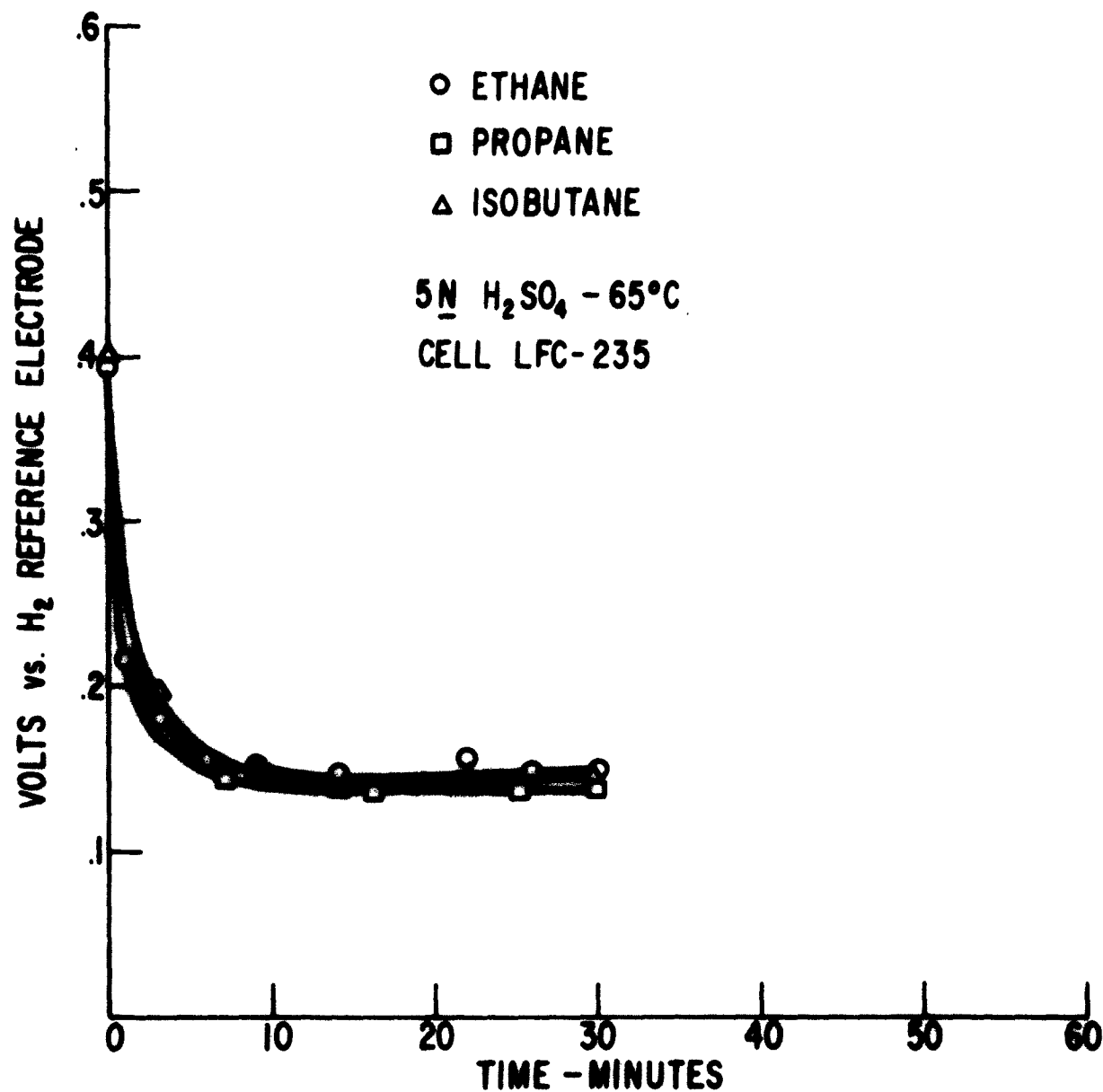


FIGURE 13. CHANGE IN ELECTRODE POTENTIAL WITH
TIME DURING GAS ADSORPTION WITH ACID
ELECTROLYTE AT 65°C

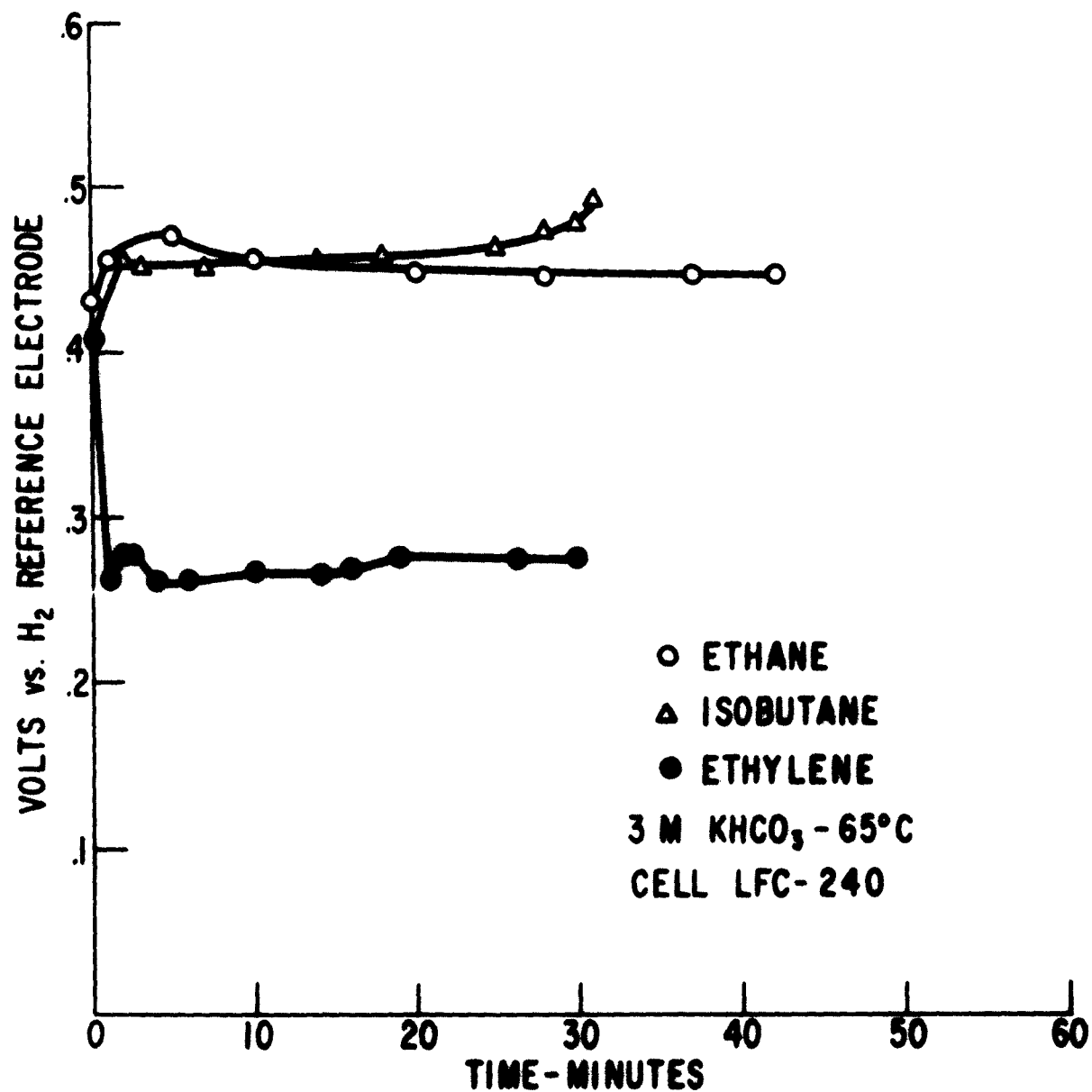


FIGURE 14 CHANGE IN ELECTRODE POTENTIAL WITH TIME DURING GAS ADSORPTION WITH KHCO₃ ELECTROLYTE AT 65°C

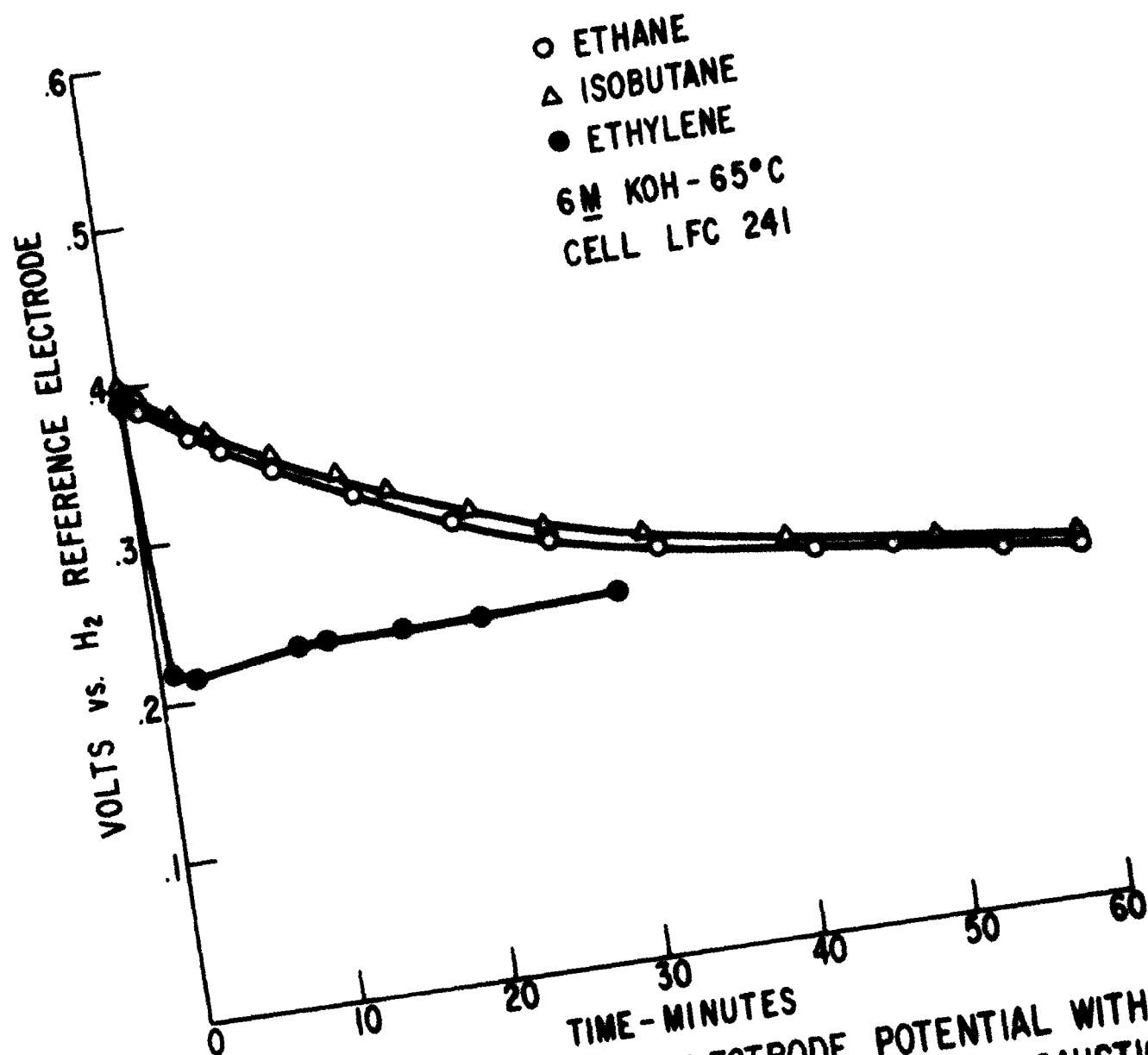


FIGURE 15. CHANGE IN ELECTRODE POTENTIAL WITH TIME DURING GAS ADSORPTION WITH CAUSTIC ELECTROLYTE AT 65°C

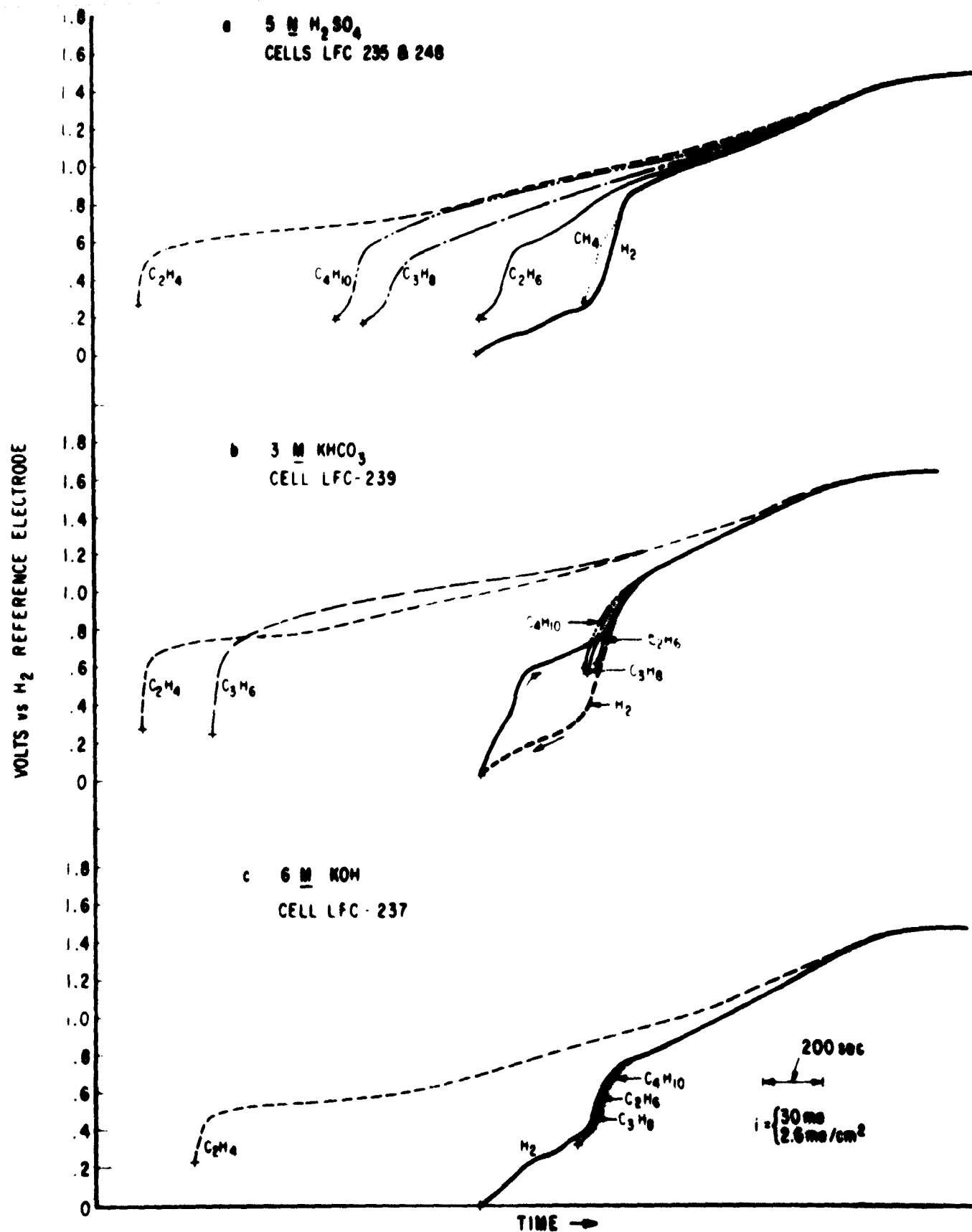


FIGURE 16. GALVANOSTATIC OXIDATION CURVES FOR HYDROCARBONS ADSORBED ON PLATINUM BLACK ELECTRODES AT ROOM TEMPERATURE

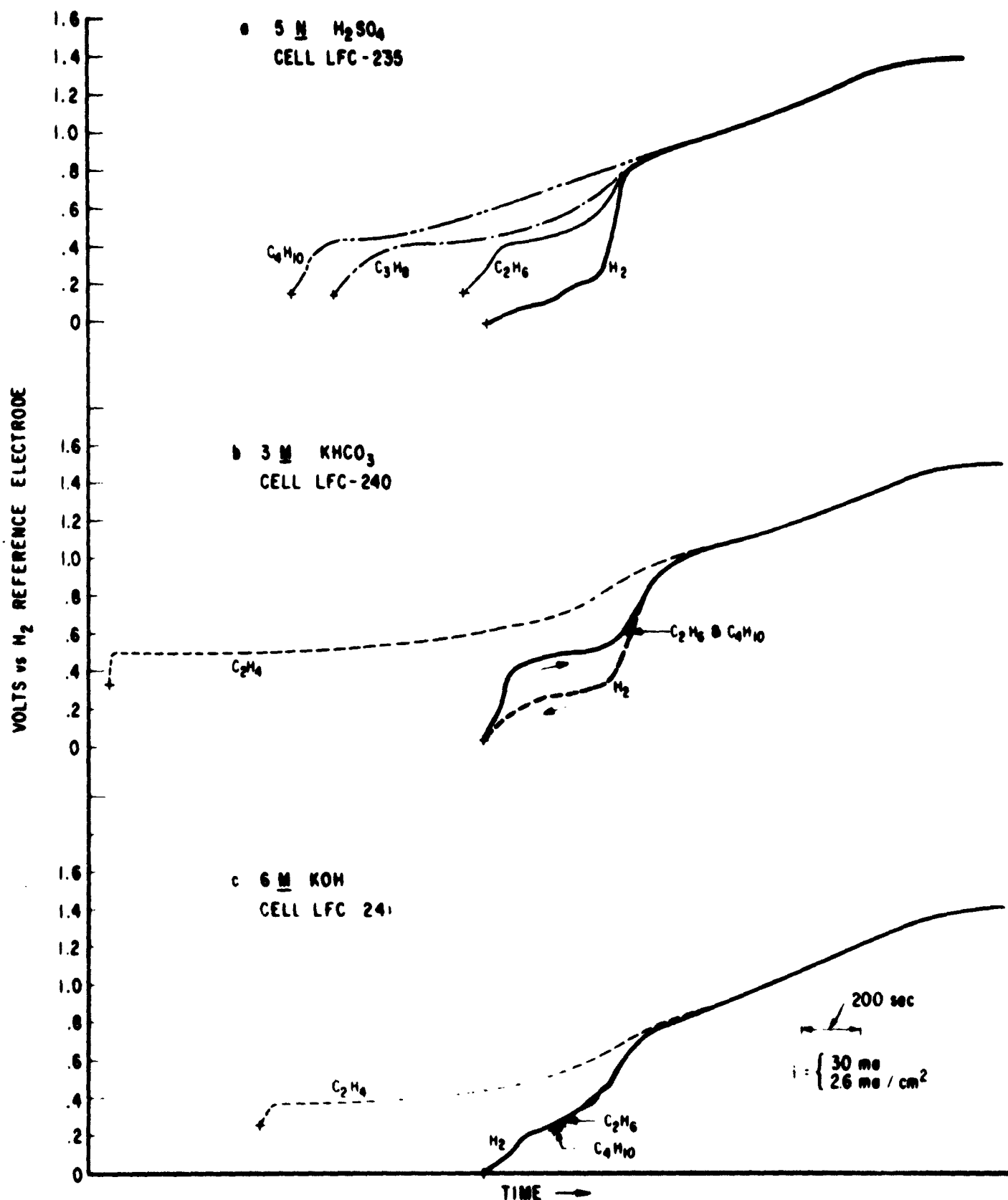


FIGURE 17. GALVANOSTATIC OXIDATION CURVES FOR HYDROCARBONS
ADSORBED ON PLATINUM BLACK ELECTRODE AT 65°C

This was shown by performing a second run with ethane in the acid cell immediately after the run with isobutane. The second run with ethane was in good qualitative agreement with the first and the overall length of the oxidation breaks remained in the order isobutane > propane > ethane > methane. In addition a hydrogen curve obtained after the second run with ethane was in qualitative and quantitative agreement with the initial hydrogen curve; this indicated that appreciable quantities of oxidation intermediates did not remain in the system.

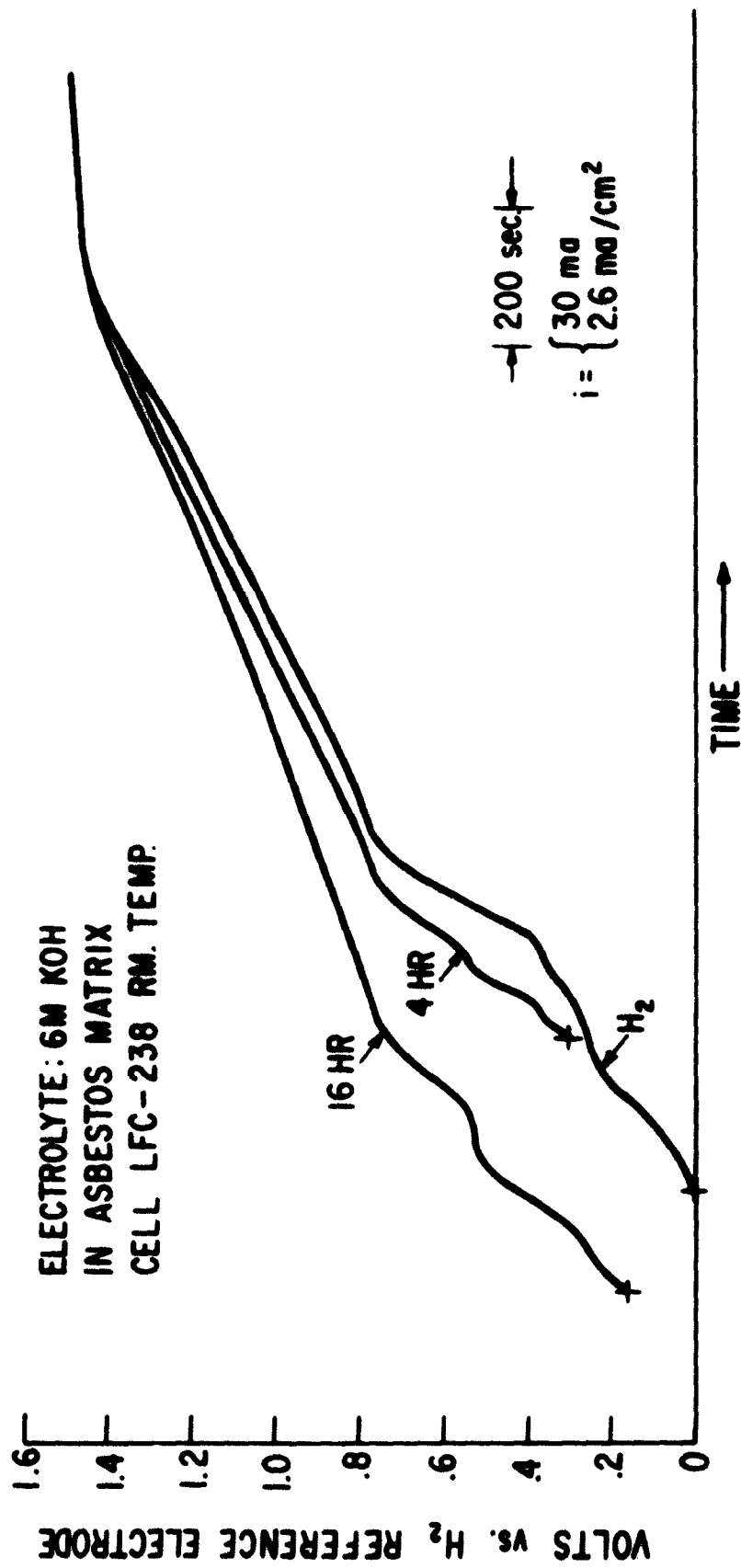
Turning now to the comparison data in the figures, two aspects are most striking. One of these is the vast difference in the behavior of the saturated hydrocarbons in the acidic and the other media. The second is the marked difference between the saturated and the unsaturated hydrocarbons.

Thus one sees from the curves in Figures 16 and 17 that while well developed oxidation waves appear for ethane, propane and isobutane (and to a lesser extent for methane) in the acidic system, evidence for adsorbed material is essentially lacking for the bicarbonate and caustic electrolytes. The slow changes in the electrode potentials with time during adsorption in the latter media (cf Figures 11,12,14 and 15), further indicate that adsorption is at best exceedingly slow in the latter media. Similar results were obtained for both ambient temperature and 65°C equilibrations.

In contrast, the lengths of the ethylene and cyclopropane oxidation waves remain essentially constant in length in all media. Again, the lengths of the breaks are not highly temperature sensitive. In fact in the case of both the saturated and unsaturated hydrocarbons the effect of the increasing temperature is mainly the lowering of the oxidation voltages (overvoltage) and a sharpening of the breaks in the oxidation curves; i.e. a noticeable enhancement of the rate of the oxidation step itself. This in turn manifests itself by smaller deviations in the oxygen film region from that observed with hydrogen.

The marked effect of the electrolyte on the adsorption behavior of the saturated hydrocarbons in contrast to the absence of such an effect with ethylene and cyclopropane was not anticipated, and an explanation is not presently at hand. It would appear, however, to be associated with the fact that a dissociative adsorption involving the breaking of carbon-hydrogen bonds is undoubtedly involved in the case of the saturates. This could imply that the rate and extent of a preliminary physical adsorption of the saturated molecule is markedly hindered by the double layer structure of the electrode in the bicarbonate and caustic media.

The specific nature of this double layer structure is not known. However, because of the use of the anion exchange membrane as the matrix material it was felt that some decomposition products from the resin (amines for example) might be a cause of the effect.



**FIGURE 18. GALVANOSTATIC OXIDATION CURVES FOR ETHANE ON
PLATINUM BLACK AFTER LONG EQUILIBRATIONS IN THE
PRESENCE OF KOH**

To eliminate such a possibility an additional cell was constructed using asbestos cloth as the matrix for KOH. Tests with ethane verified that adsorption was slow in the presence of KOH and negligible over a period of an hour. After equilibration times of 4 and 16 hours, however, adsorption did occur, and oxidation waves similar to those observed with the acidic medium were obtained. These are shown in Figure 18. Similar results were obtained with propane. Further work will be required before the slow adsorption can be explained.

It is now of interest to compare the behaviors of the different gases in the acidic medium where all are adsorbed to appreciable extents. Several stages are encountered during the oxidation of the adsorbed materials. With methane, ethane, propane, and isobutane an initial break is observed at potentials between 0.2 and 0.3 V. (A similar break is evident in the curves in Figure 18 for ethane equilibrated for longer periods in the caustic cell with the asbestos matrix.) Since this potential region overlaps a portion of the break observed for hydrogen, it is reasonable to assume that it corresponds to the oxidation of some hydrogen on the surface resulting from dissociation of the adsorbed hydrocarbons. It is reasonable to assume then that the open circuit potentials of these fuel electrodes are determined by the equilibrium amounts of hydrogen that are formed by dissociative adsorption.

Following this initial hydrogen break there is a sharp rise in potential before a second break is observed in the curves for the saturates. The sharp rise is associated with charging of the double layer to potentials at which oxidation of the carbon containing species can occur on the new plateau that is reached at approximately 0.5 - 0.6 V. in all cases. In the acidic medium, evolution of gas (undoubtedly CO_2 since separate experiments have shown that CO oxidizes at the potentials involved) already occurs as the potential rounds the bend into the plateau. Following the period on the plateau the potential of the electrode gradually rises with continuing gassing. This rise eventually blends in with the rise associated with the formation of a surface oxygen layer on the platinum. Eventually a final plateau is reached when oxygen evolution occurs. While the shapes of the oxidation curves for the saturates are similar, the overall lengths become longer in the series ethane, propane, and isobutane. This, of course, is in the order of their increasing molecular weights and, as a corollary, in the order of increasing number of coulombs required per mole of gas to be oxidized.

In addition, the deviations of the slopes of the curves in the oxygen film region, from that observed when hydrogen is the fuel, became greater with the increasing weight of the hydrocarbon. These deviations are in all likelihood associated with the oxidation of intermediates that accumulate during the early stages of the oxidation. It would not be unreasonable for larger fractions of intermediates to accumulate with the longer chain materials.

A major difference between the curves for the saturated hydrocarbons and those for ethylene and cyclopropane is the absence of the preliminary hydrogen break in the latter cases. This would appear to indicate that these hydrocarbons are not adsorbed dissociatively or that any hydrogen formed by dissociative adsorption of these materials is in turn removed by self-hydrogenation reactions. Apart from this and the obvious greater length of the breaks (indicative of more extensive coverage) the general shape of the curves for ethylene and cyclopropane parallel those for the saturates. This would imply that the carbonaceous species on the surface are similar for the saturates and unsaturates and that the mechanisms of their oxidations are also similar.

C. Additional Observations on the Behavior of Ethane and Ethylene

As noted in the previous section, the behavior of ethane and the higher saturated hydrocarbons appear to be qualitatively similar. For this reason ethane was chosen as a representative of the saturated series for some additional studies with the acidic electrolyte. Concurrently, additional experiments were also performed with ethylene to bring out further relationships between the two materials, since, as noted above, the latter appears to form by dissociative adsorption in the overall reaction of the ethane.

One parameter that was given attention was the effect of the time of equilibration of the electrode with the reactive gas. Galvanostatic oxidation curves for electrodes equilibrated with ethane for different times are shown in Figure 19 and for ethylene in Figure 20.

The breaks in the curves associated with the oxidation of the hydrocarbons increase in both cases with increasing time of equilibration. This is shown further by the data summarized in Table V. Here the number of coulombs associated with the fuel oxidation step have been calculated from the experimental curves. Because the breaks are poorly defined, the total number of coulombs to reach oxygen evolution were first measured. From these values, the length of the oxygen-coverage break obtained with hydrogen was subtracted on the assumption that this value would apply in all cases. An additional correction was made for the double layer charging, again assuming that the value obtained with hydrogen applied.

Also shown in the table are the ratios of the coulombs required for the fuel oxidation to those previously measured for hydrogen oxidation with the same electrodes. These ratios may be compared with the "limiting" values shown in the last column if all sites available to hydrogen could be covered with the fuel species with the assumption indicated in the footnotes. While additional work will be required to establish any direct relationships between the data in the last two columns, it is quite clear that the ethylene is adsorbed to much higher coverages than the ethane.

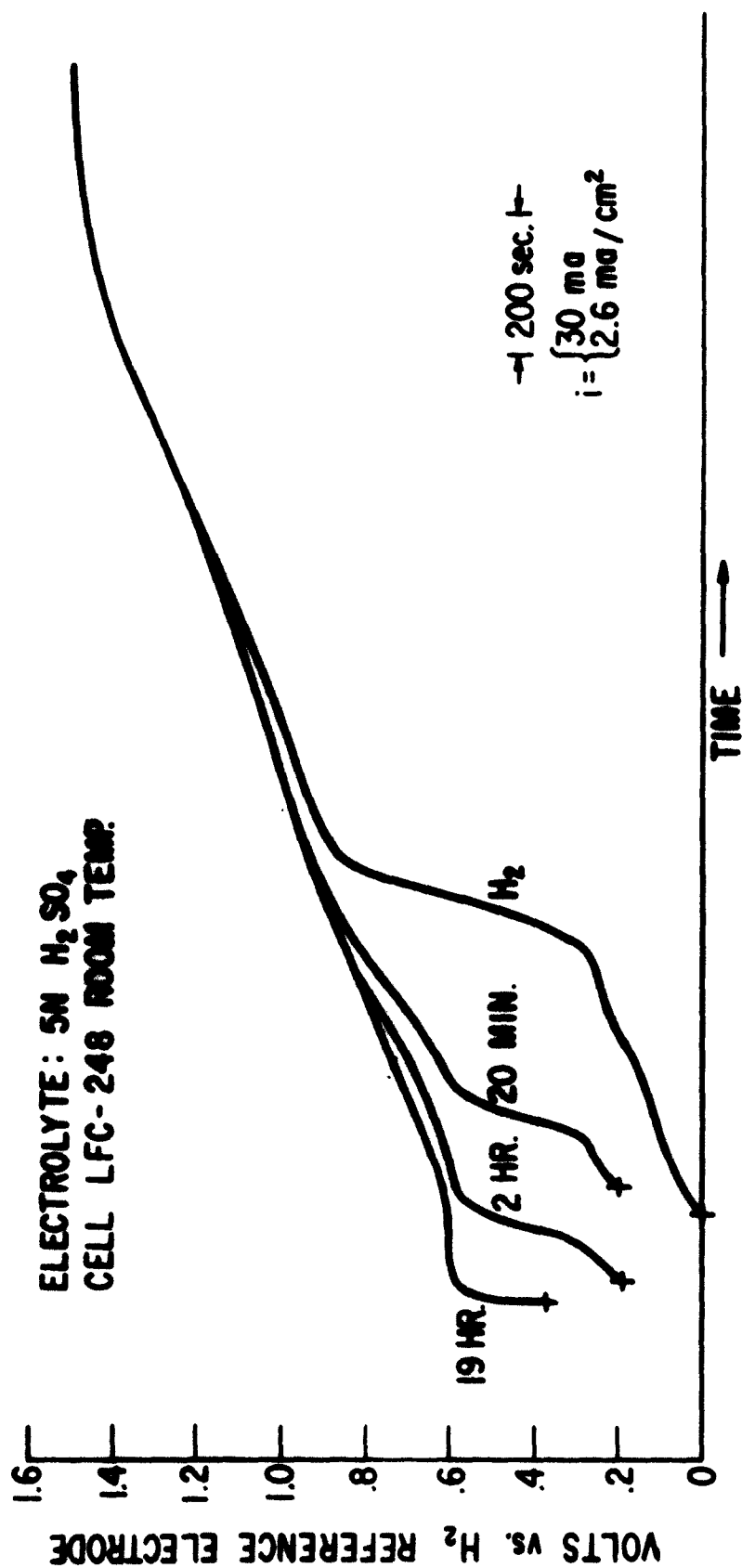


FIGURE 19 EFFECT OF EQUILIBRATION TIME ON GALVANOSTATIC
OXIDATION CURVE FOR ETHANE ON PLATINUM IN THE
PRESENCE OF ACID.

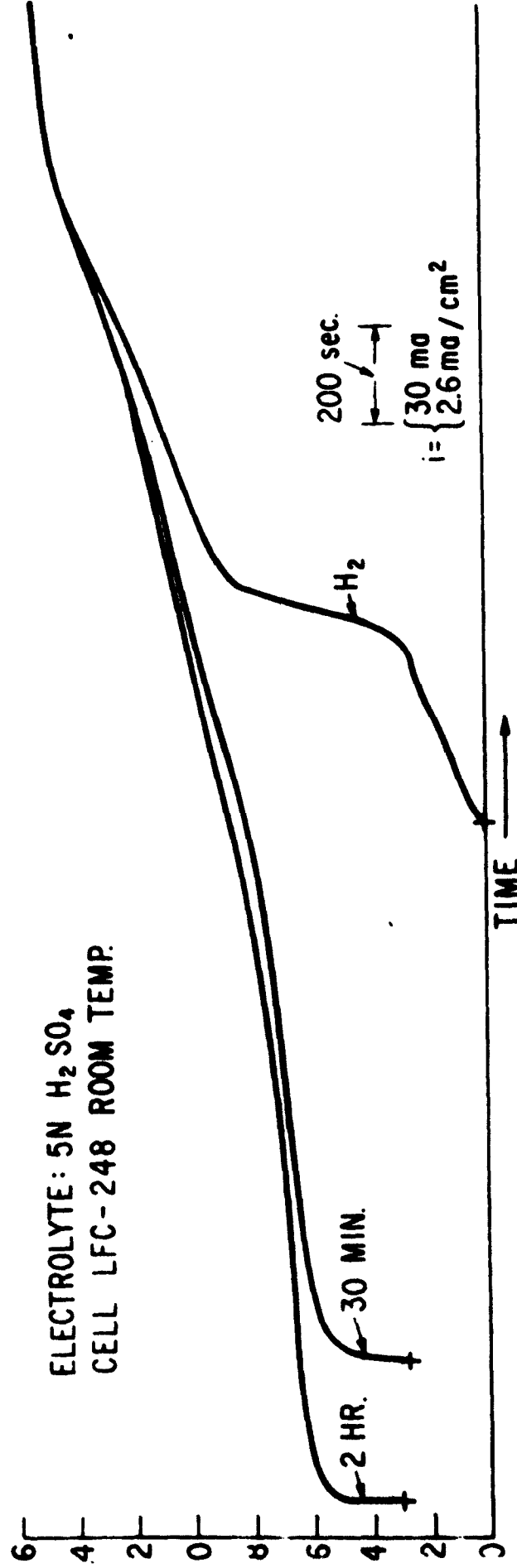


FIGURE 20 EFFECT OF EQUILIBRATION TIME ON GALVANOSTATIC OXIDATION CURVE
FOR ETHYLENE ON PLATINUM IN THE PRESENCE OF ACID

TABLE V

Effect of Equilibration Time on the Number of Coulombs

Required for Fuel Oxidations

<u>Fuel</u>	<u>Equilibration time - hrs.</u>	<u>Coulombs for Fuel Oxidation</u>	<u>Ratio to Coulombs for H Oxidation (a)</u>	<u>Ratio Calculated for Surface Saturated with (b) Adsorbed Hydrocarbon</u>
Ethane	0.33	10.7	0.93	3.5 (c)
"	2.0	14.2	1.2	"
"	19.0	16.2	1.4	"
Ethylene	0.5	44.7	3.9	6 ^(d) ; 5 ^(e)
"	2.0	53.0	4.6	" "

a) 11.5 Coulombs required for H oxidation.

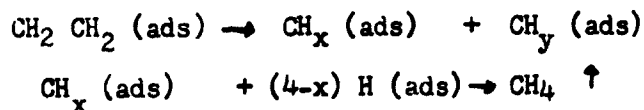
b) Assuming complete oxidation to CO₂ and H₂O.

c) Assuming four site adsorption as $\text{CH}_2 - \text{CH}_2$ plus 2 H.

d) Assuming two site adsorption as $\text{CH}_2 - \text{CH}_2$.

e) Assuming two site adsorption as $\text{CH}=\text{CH}$ after self-hydrogenation.

Additional remarks are in order concerning the 19 hour equilibration with ethane. In this case the galvanostatic curve shows no preliminary break for an adsorbed film of hydrogen, and the equilibrium potential is somewhat higher than normal for ethane. From the recording of the electrode potential with time during the equilibration, it was found that the potential of the electrode fell in the normal fashion during the initial period of equilibration and reached the usual plateau at about 0.2 V. versus the hydrogen reference. The potential then slowly began to rise with time and eventually reached another plateau at about 0.38 V. Two possible explanations suggest themselves: 1) that oxygen diffused through the membrane from the counter electrode and slowly oxidized the adsorbed hydrogen on the surface of the fuel electrode, or 2) that secondary reactions occurring among the adsorbed species resulted in the consumption of the hydrogen and a new set of equilibrium conditions. Such an alternative route for the removal of the hydrogen could be:

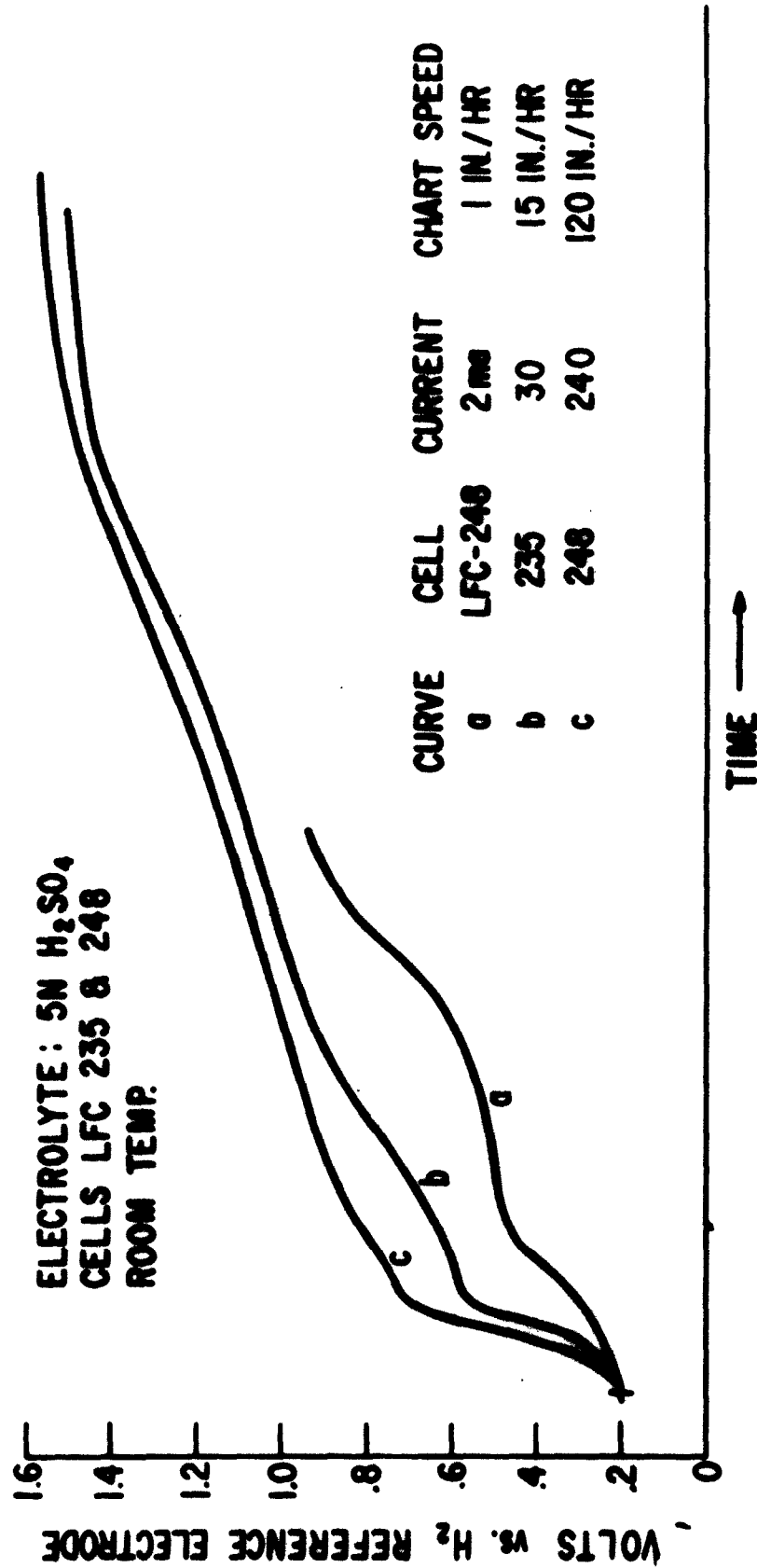


with the methane accounting for the removal of hydrogen from the surface. Such a reaction might be expected to result in an equilibrium potential being established as was indeed observed. Tests will be run for methane in the future. Until then, however, it can be noted that methane has indeed been found to form from ethylene in related fuel cells operating at somewhat higher temperatures (5).

In view of the fact that the oxidation of the hydrocarbon is highly irreversible it was also considered important to examine the effect of the current density employed during the oxidation on the overall behavior. In this connection it is to be noted that the curves for the oxidation of hydrogen are essentially independent of the current density over the range 3 - 240 ma. This is, of course, reasonable, in view of the well known reversible behavior of hydrogen.

Data are shown for ethane in Figure 21 and for ethylene in Figure 22. Current densities were chosen to match available recorder chart speeds. By appropriate matching, the amount of charge transferred per unit length on the time axis could be maintained constant and comparison within a family was facilitated. It is evident from the figures that similar shifts are involved for ethylene and the main oxidation wave for ethane. In the case of the ethane at the low current of 2 ma (0.176 ma/cm^2) a lengthening of the hydrogen break appears to occur. This could result from additional dissociation of the hydrocarbon fragment as hydrogen is depleted on the surface during the oxidation. At this current density, a distinct sharpening of the breaks in the oxidation curve for ethane is also evident. This may result from a reduction in ohmic drop in the pores of the electrode and hence an elimination of gradients that occur at higher current densities. Unfortunately the times involved in performing the experiments at such low current densities are inordinately long and the regular use of low current densities would be impractical in this work.

5) E.J. Cairns, private communication.



**FIGURE 21 EFFECT OF ELECTROLYSIS CURRENT ON GALVANOSTATIC
OXIDATION CURVE FOR ETHANE ON PLATINUM IN THE
PRESENCE OF ACID.**

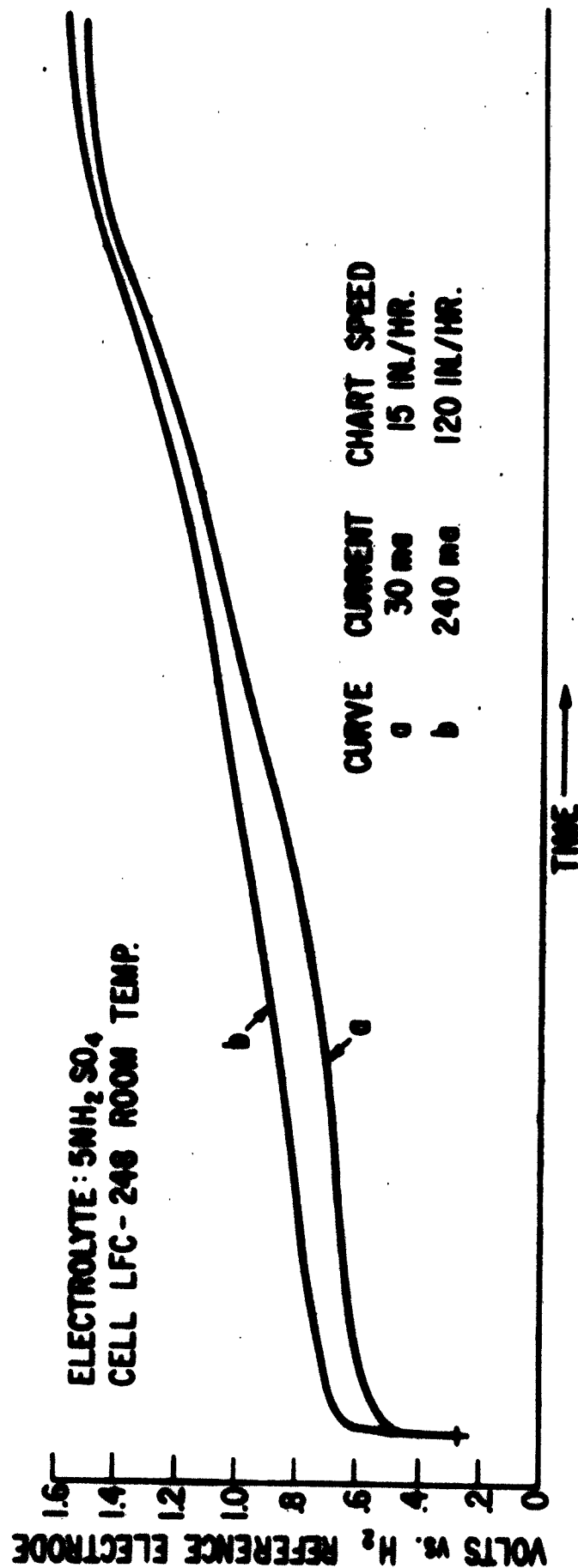


FIGURE 22. EFFECT OF ELECTROLYSIS CURRENT ON GALVANOSTATIC OXIDATION
CURVE FOR ETHYLENE ON PLATINUM IN THE PRESENCE OF ACID

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