Limiting Processes at Hydrocarbon Electrodes

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The development of an efficient low temperature, aqueous, hydrocarbon-air fuel cell has been the subject of intensive investigation in recent years. Saturated hydrocarbons would be well suited to commercial fuel cells because of their low cost and high availability. Liquid hydrocarbons are especially preferable because they are easily handled, easily separated from the products of combustion, carbon dioxide and water, and because of their low solubility in the electrolyte, not likely to be oxidized at the cathode.

While the earliest demonstration of the electrochemical activity of a saturated hydrocarbon was made with a non-noble catalyst(1), commercially promising current densities were not observed until electrodes with heavy platinum loadings, thirty and more milligrams per cm^2--were used (2,3). However, hydrocarbon fuel cells will require a reduction in catalyst cost of at least two orders of magnitude before they are commercially practical. One way to achieve this cost reduction is to find an active non-noble catalyst. Efforts along these lines are in progress in several laboratories. A second approach is to improve the utilization of the present catalyst, thereby reducing its requirement per kilowatt of power. To accomplish this end it is necessary to know what processes are limiting the performance of the present hydrocarbon electrodes. In line with this objective, the aim of the present study was to determine whether the steady state performance of operating anodes is limited by the intrinsic electrochemical activity of the catalyst or whether physical factors exert important effects.

This problem is complicated by the fact that the optimum electrodes are complex porous structures consisting of hydrophobic and hydrophilic materials exposed to both fuel and electrolyte. Their activity may be limited by loss of useful electrode area through a failure to be wet by electrolyte, or through total flooding by electrolyte leading to lengthy fuel diffusion pathways. In addition, temperature gradients and the evolution of reaction products may give rise to continuous changes in the location of the fuel-electrolyte interface, which may further complicate the picture(4). These effects are superimposed on the chemical and electrochemical processes occurring on the electrode surface, such as the chemisorption of the fuel and the charge transfer processes associated with its oxidation.

Because of the many possible limiting processes caused by the superposition of physical and chemical variables, relatively little mechanism work has been done on porous diffusion electrodes operating with immiscible fuels. Typical chemical studies have been done on bulk metals (5) or electrodeposited blacks (6). Studies of physical variables have involved model studies of menisci (7) or studies with soluble fuels dissolved in electrolyte which is flowed through the porous electrode (8). The present study attempts to determine which of the many possible physical and chemical processes limits the activity of porous wetproofed electrodes operating on hydrocarbon fuels, and describes some new physical aspects of their operation.

Approach

A number of platinum black catalysts were prepared using different chemical reducing agents. These were formed into porous, wetproofed, interface-maintaining electrodes and tested for steady state performance on butane gas. The activity varied widely, even when corrected for variations in surface area. Next the intrinsic electrocatalytic activities of the catalysts were compared by measuring their ability to oxidize preadsorbed butane. This was done using a voltage-scanning technique under conditions where physical factors limiting the access of fuel to the surface could have no effect. At the same time various physical properties of the catalysts were measured to determine whether these would correlate with the steady state performance. Finally, additional observations of surface effects were made which led to the recognition of a new phenomenon which may be very important in the operation of hydrocarbon electrodes.

Experimental

Preparation and Evaluation of Platinum Catalysts

Five platinum blacks were prepared using various chemical reducing reagents. In addition, a sample of commercial platinum black was included in the study. Each of these was formed into an electrode simply by mixing with Teflon emulsion and hot pressing into a 50 mesh tantalum screen. This type of electrode was chosen because of its ease of preparation and good reproducibility. Optimum electrode formulations perform better than any reported here, giving 100 ma/cm^2 at 0.18 volts polarization and 300 to 400 ma/cm^2 limiting current on butane at 150°C. However, preparation variables must be much more closely controlled with these electrodes to achieve reproducible results.

The electrodes were tested for activity using butane fuel and 14.7 molar phosphoric acid electrolyte at 150°C. A driven "half cell" was used in which the electrode was mounted in a glass flange with 5.7 cm^2 exposed to electrolyte on one side and gaseous fuel on the other. The electrode polarization was measured by means of a calomel-Luggin capillary reference system which was precalibrated against a reversible hydrogen electrode in the same system. Experimental points were run galvanostatically until the polarization reached a constant value. Runs lasted from one to five days.

The activity of the catalysts varied by a factor of fifty, whereas the surface areas, measured electrochemically, varied by only a factor of three, as shown in Table 1. The logarithmic standard deviation of the current densities, measured in a related study, corresponded to $\pm$ 1.6%. Thus, the desired wide range of activity was achieved. The next question to be answered was whether the fiftyfold activity variation could be ascribed to differences in the intrinsic chemical reactivity of the catalysts.

Table 1

Activity of Platinum Blacks

No.	Reducing Agent	Current Density at 0.4 volts Polarization (ma/cm^2)	Electrochemical Surface Area $meters^2/gm$*
1	Formaldehyde	2.5	8.9
2	Hydrogen	6	22.5
3	Potassium Borohydride	15	13.4
4	Lithium	19	26.9
5	Commercial (Engelhard) Platinum (Repeat Runs)	92, 90	23.7
6	Formaldehyde + Protective Colloid	130	21.8

* Obtained from voltage scan measurements (see below) assuming theoretical monolayer is 239 m^2/gm , based on 100, 110, and 111 planes weighted according to their X-ray peak intensities.

Evaluation of Intrinsic Electrochemical Activity

A. Indications of Electrochemical Rate Limitations

Before examining the adsorption-oxidation results it should be pointed out that the steady state performance curves gave definite indications of chemical and electrochemical rate limitations. Typical performance curves at both 100° and 150°C showed a Tafel-like region, of slope approximating 0.13 volts per decade, followed by a limiting current region (Figure 1). The energy of activation in the Tafel region was about 18 kcal/mole while that in the limiting region was 10 to 12 kcal/mole (Table 2).

Table 2

Summary of Butane Reaction Parameters

Parameter	Tafel Region	Limiting Region
Tafel Slope (volts/decade)	0.12-0.14	(∞)
Activation Energy (kcal/mole)	17-19	10-12

The slope of 2 RT/F is consistent with the proposals that the oxidation of the platinum surface (9) or the rate of water discharge (5) is limiting in the Tafel region. In the limiting current region an activated step occurring before the electrochemical steps, not involving electron transfer, is indicated to be rate limiting. This could well be the chemisorption of the fuel. True diffusion limited rates, encountered in the adsorptions to be described below, had a very low activation energy.

Assignment of chemical rate limitations to the steady state curves does not preclude the coexistence of physical limitations in the different catalysts. These could shift the curves without changing their shape by making more or less surface area available for reaction. Nevertheless, evidence of the existence of electrochemical rate limitations in the low polarization regions justifies the use of the adsorption-oxidation technique described below.

B. Adsorption-Oxidation Studies

A measure of the intrinsic electrochemical activity of the catalysts was obtained by forming them into totally flooded electrodes and measuring the rate at which they oxidized preadsorbed butane, per unit surface area. The total amount of butane adsorbed at saturation coverage could also be used as a measure of one of the catalytic parameters affecting steady state activity. In this way catalyst structure problems, which limit the accessibility of the fuel or the electrolyte to the surface of the catalyst, were avoided.

Fifty milligrams of the catalyst to be tested were mixed with 5 mg of emulsified Teflon and pressed at 200 psi into a fifty mesh platinum screen attached to the face of a 2 cm^2 platinum foil. This amount of Teflon was sufficient to bind the catalyst to the "flag" electrode, but since it was not sintered or subjected to high pressures it did not wetproof the electrode. The flag, mounted on the end of a long platinum wire, was suspended in 3.7 molar sulfuric acid held at 80°C. Reference and counter electrodes were also mounted in the cell. The potential between the reference and working electrodes was controlled by means of a Duffers Model 600 potentiostat and driven in triangular voltage sweeps by a Servomex Low Frequency Wave Form Generator. Current-voltage diagrams were recorded on a Moseley Model 135 x-y Plotter. The sweep range was from 0.15 to 1.45 volts versus reversible hydrogen in the same electrolyte. Typical scans with and without adsorbed butane are shown in Figure 2. Integration of the area under the oxide reduction peak on the cathodic sweep gave a measure of the platinum surface area. Butane peaks were obtained after exposing the wetted electrode to gaseous butane in the space above the electrolyte. When butane was passed over the surface of the electrolyte with the flag totally immersed, no appreciable butane peaks could be obtained within exposure times of one hour, due to its low solubility.

This fact made possible a very convenient adsorption-oxidation procedure: The flag electrode was pulled out of the electrolyte until only the lower edge of the platinum foil, an area without catalyst, was immersed in electrolyte. The potential of the electrode could thus be fixed during the adsorption period by the potentiostat. Since only very small currents passed through the wetted layer it is felt that the potential was in relatively good control during the adsorption period. The potential during the adsorption was set at 0.0 volts versus calomel or 0.15 volts versus reversible hydrogen under these conditions. At the end of the adsorption period the electrode was totally immersed in the electrolyte and within one minute thereafter was subjected to anodic and cathodic scans, with the assurance that no significant amount of butane could be adsorbed during the scan period. The number of coulombs in the butane peak was obtained by integration, taking the butane-free base curve into account. Using this technique, fairly rapid adsorption rates could be obtained. These rates were about an order of magnitude less than those obtainable in wetproofed porous electrodes and were clearly diffusion limited, showing a 0-2 kcal activation energy and an approximately linear proportionality of coulombs versus square root of time. These rates were therefore not used in the analysis. Only the total number of coulombs and the shape of the oxidation curve were used as criteria of catalytic activity.

The electrochemical surface areas of the catalysts, as determined from the number of coulombs in the oxide reduction peak, varied by a factor of three as shown in Table 1. However, the ratio of the butane peak at saturation to the oxide reduction peak was virtually constant for all the catalysts at 1.58 with a standard deviation of 0.13. Assuming 26 electrons involved in butane oxidation and 2 in oxide reduction this result indicates 8 platinum sites per butane molecule or one carbon atom per 2 platinum atoms in the surface, independent of the platinum reduction technique.

An index of the rate of the electrochemical oxidation was obtained for all of the catalysts by comparing the observed current at 0.45 volts polarization from butane theory at fixed initial fractional coverage. However, minor variations in the shapes of the curves made this measurement somewhat irreproducible. Therefore, the butane oxidation peak was integrated to 0.45 volts polarization and the catalytic activity expressed in terms of the fraction of the initial adsorbed butane burnt off to 0.45 volts polarization as a function of the initial butane coverage. This method was shown to be able to detect differences in activity: Varying the temperature from 60 to 150°C (using phosphoric acid in the latter case) produced large variations in this ratio. Nevertheless all of the catalysts tested here showed essentially the same relation between fraction reacted at 0.45 volts and initial fractional coverage, indicating all had roughly the same intrinsic electrochemical activity per unit surface area (Figure 3).

From Figure 3 it is also noted that the fraction reacted at 0.45 volts polarized declined severely with increasing butane coverage. This lends credence to the hypothesis that a reaction such as oxidation of, or water discharge on, the uncovered platinum sites is rate determining.

Regardless of the mechanism, however, it is concluded that electrochemically, all of these high surface area catalysts are essentially identical.

Physical Examination of the Catalysts

Following the finding that the intrinsic electrochemical activity of the catalysts could not account for the variation of their steady state performances, they were next examined for variations in their physical properties. The properties measured were: cyrstallite size by X-ray line broadening; bulk density after the settling of aqueous suspensions; B.E.T. nitrogen surface area; the pore volume by nitrogen capillary condensation; and the appearance of the agglomerates under the electron microscope (Table 3).

Table 3

Catalyst Characterization

Sample No.(1)	Bulk Density(2) (gm/cm^3)	Crystallite Size(3) (Å)	B.E.T. Surface Area (m^2/gm)	Pore Volume(4) (cm^3/gm)	Current Density at 0.4 volts Polarization(ma/cm^2)
1	0.27	62	8	0.03	2.5
2	0.65	35	10	0.05	6
3	0.99	82	7	0.13	15
4	0.65	50	26	0.19	19
5	0.46	77	28	0.39	92, 90
6	0.55	45	30	0.40	130

(1) As given in Table 1.
(2) After 24 hours settling of an aqueous suspension.
(3) By X-ray line broadening.
(4) By equilibration with liquid nitrogen in a liquid nitrogen bath.

The physical properties in general varied by a greater factor than the intrinsic electrochemical activities. In particular the pore volume could be correlated with the steady state activity, the more open structures giving the higher activities (Figure 4).

Electron microscope examination of the catalysts provided further evidence of their structural variation. While quantitative comparisons were not possible there appeared to be definite differences in appearance between the low activity, low pore volume catalysts and the high activity, high pore volume materials. The latter were characterized by a lacy agglomerate structure with the individual crystallites forming a network of low coordination number. The poorer catalysts had much less lacy material, large dense areas and some indications of well formed edges of relatively large crystals. The best and the worst catalysts are compared in Figures 5 and 6.

It, thus, appears that the fiftyfold variation in steady state catalytic activity was due not to changes in chemical reactivity of the catalyst surfaces, but to changes in the physical nature of the catalysts, having to do with the openness of the structure and the ease of diffusion within it.

Operation of Porous, Hydrophobic Electrodes

The finding that physical parameters governed the operation of hydrocarbon electrodes led naturally to a consideration of their physical mode of operation, and to what may be an important new phenomenon. There have been two general approaches to the understanding of the operation of porous diffusion electrodes. One involves diffusion of the dissolved fuel into the porous structure flooded with electrolyte (8). The other considers pores containing meniscuses such as are illustrated by the model experiments of Will (7). Diffusion alone, without flow, cannot account for the activities observed. A simple calculation shows that the butane can penetrate only about 5 microns into the structure by diffusion alone from the surface, since its solubility is so low, relative to the reactivities shown in Figure 1. The importance of internal meniscus formation is cast in doubt by the facts that liquid and gaseous decane give about equal performance (Figure 7), whereas the electrolyte meniscus is inverted in going from gaseous to liquid hydrocarbon fuels. Whereas for gases the electrolyte meniscus in concave upwards, for liquid hydrocarbons it is concave downward. That is, the platinum is perferentially wetted by the hydrocarbon. (See Appendix I and Figure 8 for details).

The phenomenon of gasification, or boiling, within the pores of a wetted hydrophobic matrix, at temperatures far below the normal boiling point, may help explain how fuel penetrates into the depths of porous electrodes, and why gases and liquids perform equally well. It has been observed that certain Teflon-wetproofed electrodes mounted in their normal operating configuration, begin to spontaneously emit a stream of bubbles on the electrolyte side, when the temperature is raised to within 30° of the normal electrolyte boiling point. This phenomenon will occur in the absence of any pressure excess on the fuel side, and will even overcome a considerable electrolyte head. It is observed even with liquid decane in the fuel chamber. It can be shown thermodynamically that the boiling point of a liquid in a porous hydrophobic matrix can be lowered by 30° and more, due to the preferential wetting of the surface by gas rather than liquid. (See Appendix II for derivation and example illustrating the effect.) However, the thermodynamics do not explain the continuous bubble release observed in certain electrodes. This may be due to temperature and pressure gradients, turbulence and pore junctions within the electrode.

In any case, a picture of hydrocarbon electrode operation is proposed in which localized electrolyte boiling within the small hydrophobic pores provides a stream of vapor which carries the gaseous or vaporized fuel into the depths of the catalyst bed. Thus, the contact area magnification necessary to provide adequate diffusion into a relatively thick electrode is obtained. Meniscuses exist transiently along the stream of bubbles, continually being renewed by their passage. In a sense, the "dynamic interface" referred to as necessary for the operation of electrodes for immiscible fuels is thus set up. This phenomenon may explain why electrode activity has been observed to rise to a maximum about 8° below the boiling point of the electrolyte (2).

Summary and Conclusions

A series of platinum blacks prepared with different reducing agents showed a fiftyfold variation in steady anodic activity with butane at 150°C. The intrinsic electrochemical activity of the catalysts as measured by their ability to oxidize preadsorbed butane, however, was shown to be essentially equal. The observed activity was shown to be a function of the physical structure of the catalyst as determined by internal pore volume measurements and electron microscopy. It appears then that the different reducing agents either did not affect the growth and morphology of the platinum crystallites or that these factors have little affect on chemical reactivity. The reducing conditions did have marked effects on the way the crystallites agglomerated, however. Pore volumes varying from 60 to 900% of the solids volume were achieved. This in turn had a marked affect on performance, the finer more open structures giving the best performance.

The results indicate that with unsupported platinum catalysts physical variables affect performance more than chemical. Further understanding of the physical operation of porous electrode is therefore desirable. One or two aspects of this problem have been treated here. The miniscus shape within the pores is probably not critical since a liquid hydrocarbon fuel, with an inverted meniscus, gave activities essentially identical to the same fuel in the gas state. The solubility and diffusion mode of fuel transport from the surface of the catalyst bed is inadequate by itself to account for the observed activities. The phenomenon of internal gasification caused by a lowering of the boiling point of the electrolyte due to its being present in a high surface area, hydrophobic bed helps account for the activity. It can provide a large area increase by exposing the deep innards of the catalyst bed to gaseous fuel.

There are important implications of this work in the development of new electrode catalysts: It is clear that steady state performance testing will not necessarily detect catalysts of intrinsically greater chemical reactivity. As a corollary, catalysts with superior intrinsic activities will not necessarily operate best in finished electrodes. Probably the physical structure of new catalysts will have to be optimized individually to secure optimum performance.

Acknowledgment

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Appendix I

Evidence for Inverted Meniscus with Liquid Hydrocarbons

As was demonstrated by F. Will with hydrogen,[7] an area of increasing current output is obtained as a potentiostatted plate or wire electrode is withdrawn from submersion in an electrolyte up through the fuel-electrolyte interface. This is because the meniscus is concave upwards and forms along the partially protruding surface. With liquid hydrocarbons, however, an area of increasing current density was observed as the bottom of an electrode was lowered from total submersion in the fuel through the electrolyte interface. This phenomenon was more easily observed in the presence of a surfactant where the active area extended as much as one cm. below the nominal interface. Figure 8 illustrates the data with liquid heptene-2 at 80°C. The film of heptene was observable under the electrolyte by means of the phenomenon of total reflectance at an angle of 70 to 80° from the normal.

Thus, there is no doubt that the liquid hydrocarbon-electrolyte meniscus is concave downwards into the electrolyte, along the electrode face. Consideration of the wetting properties of platinum makes this result seem reasonable. Sulfuric acid or phosphoric acid wets clean platinum foil. However, liquid hydrocarbons displace the electrolyte. A platinum foil immersed in decane was not wet by a droplet of 3.7 M sulfuric acid. Instead of spreading it remained on the surface as a globule with a very high contact angle. On the other hand, a droplet of decane placed on the under surface of a platinum foil immersed in electrolyte spread on it immediately, displacing the electrolyte from the surface. This phenomenon has not been studied as a function of potential but it is known that platinum is more hydrophobic at reducing potentials than at oxidizing.

Appendix II

Thermodynamics of Boiling Point Lowering in a Hydrophobic Matrix

A porous hydrophobic body is considered to be totally immersed in a vessel of electrolyte, which has filled all the pores. Within the porous body the liquid is in equilibrium with a bubble of its own vapor. The vapor is not at the external pressure, however. A difference in pressure between the external and vapor pressures is necessary to maintain the liquid within the hydrophobic matrix.

$$P_v = P_o + (\gamma_{gs} - \gamma_{ls})\,\sigma \qquad (1)$$

where P_v = pressure of vapor within matrix

P_o = external pressure (1 atm)

γ_{gs} = gas solid interfacial tension

γ_{ls} = gas liquid interfacial tension

σ = surface to volume ratio of matrix

Equation (1) will be recognized as that used in porosimetry, where $\Delta\gamma$, which is negative in this case, is written as $\gamma_{gl} \cos \theta$ (θ is the contact angle), and σ for pores of radius r equals 2/r. Establishment of equilibrium within the porous body requires that the temperature be lowered until the vapor pressure of the liquid equals that given by equation (1). The exact thermodynamic treatment is quite complex, but an approximate idea of the size of the effect can be obtained from the Clausius-Clapeyron equation in the form:

$$\frac{dP_v}{dT} = \frac{\Delta H}{TV_v} \qquad (2)$$

where T is the equilibrium temperature (boiling point)
ΔH is the heat of vaporization of the liquid
V_v is the molar volume of the vapor

Combining [2] with the differential of [1], using the gas law for V_v, and integrating, one finds that:

$$\frac{1}{T_B} - \frac{1}{T} = \frac{R}{\Delta H} \ln\left(\frac{P_o + \sigma \gamma_{gl} \cos\theta}{P_o}\right) \qquad (3)$$

where T_B is the boiling point when σ is zero. Since $\cos \theta$ is negative for hydrophobic matrices $T < T_B$. In heavily loaded platinum black electrodes, for example, σ can be $10^6 cm^2/cm^3$. To obtain a 20°C lowering of the boiling point in this case, a weighted average value of θ of only 90.4° is required. Excessive wetproofing in a region of the electrode can give values of $\sigma \gamma \cos \theta$ greater than one atmosphere. The pores in this region will remain free of liquid at all temperatures. Apparently the proper wetproofing is achieved by correct blending and sintering of the platinum and Teflon.

Figure 1

TYPICAL BUTANE PERFORMANCE CURVES

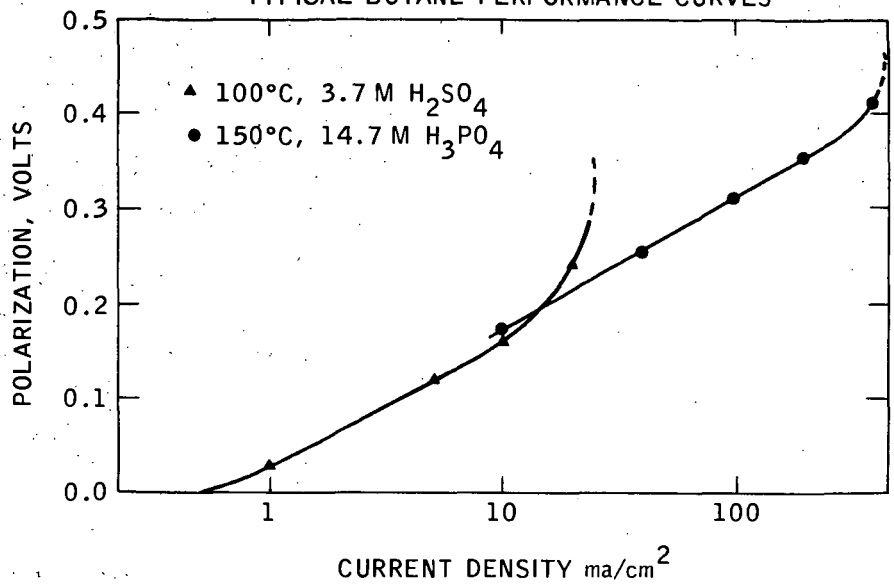


Figure 2

TYPICAL TRACE OF BUTANE VOLTAGE SCANS

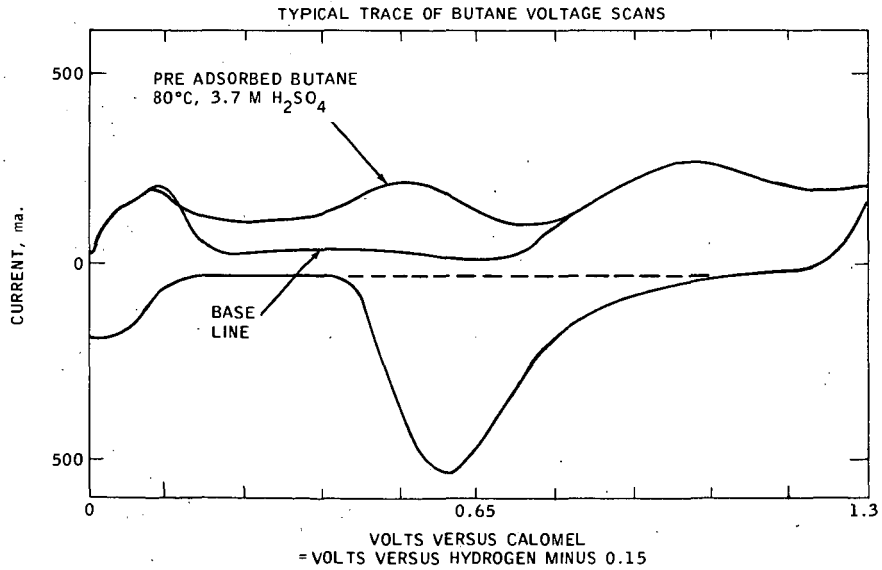


Figure 3

FRACTION BUTANE REACTED VERSUS INITIAL COVERAGE

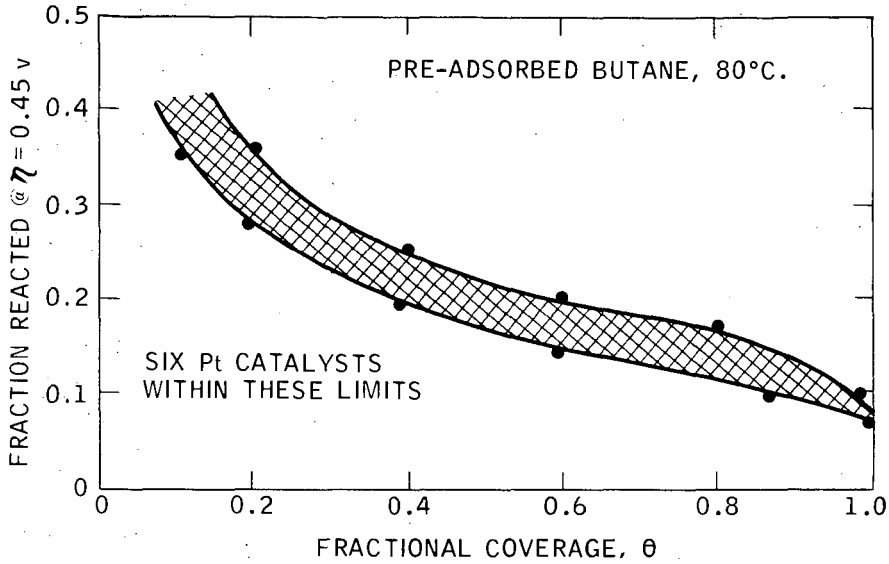


Figure 4

BUTANE PERFORMANCE CORRELATES WITH PORE VOLUME

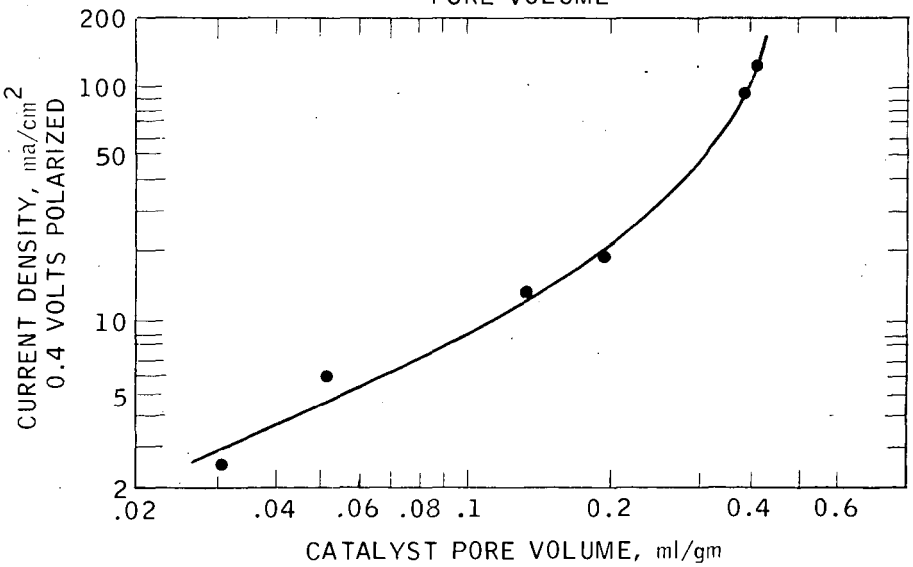


Figure 5

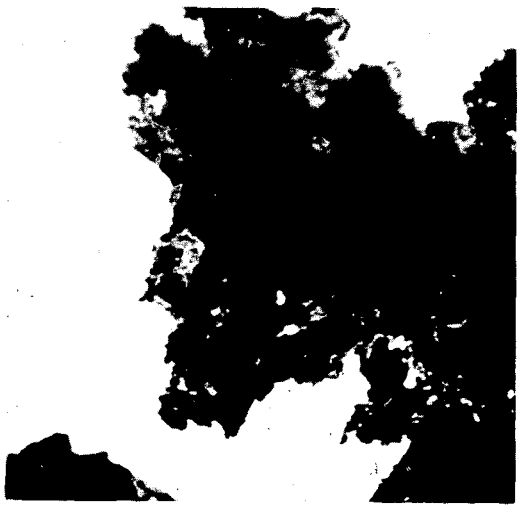
ELECTRON MICROGRAPH OF
HIGH PERFORMANCE CATALYST

PORE VOLUME=0.4 cm^3/gm

Figure 6

ELECTRON MICROGRAPH OF
POOR CATALYST

PORE VOLUME=0.03 cm^2/gm



1 MM = 300Å

Figure 7

COMPARISON OF LIQUID AND VAPORIZED DECANE ON WETPROOFED ELECTRODE

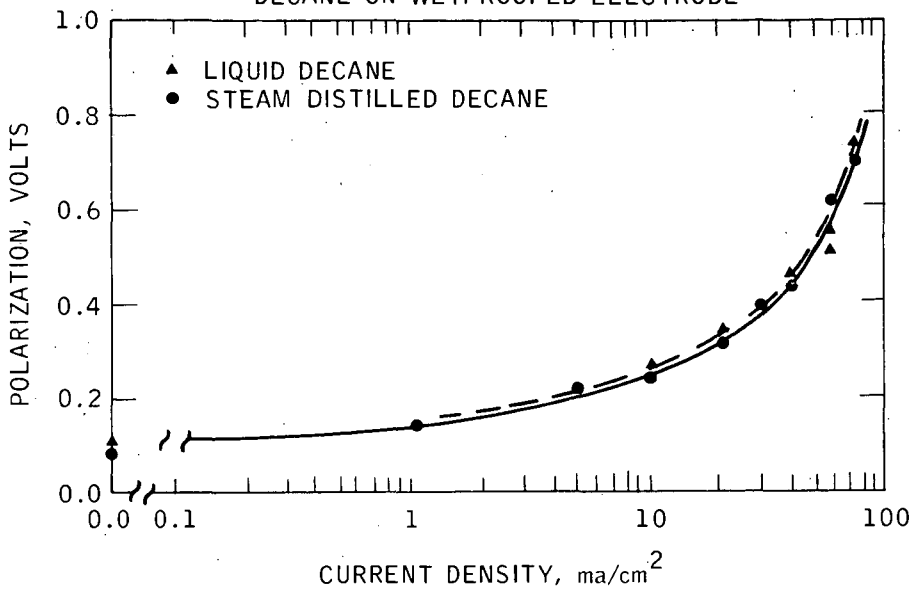
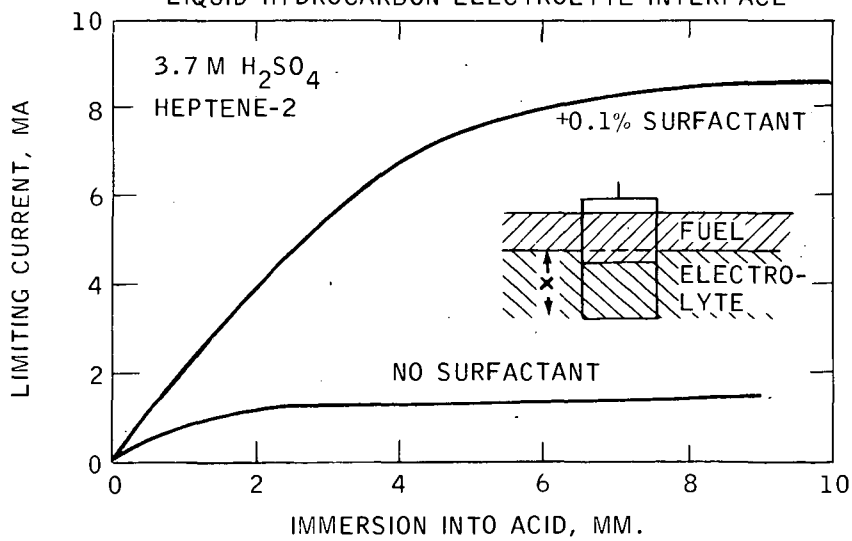


Figure 8

IMMERSION OF PLATINIZED FOIL THROUGH LIQUID HYDROCARBON-ELECTROLYTE INTERFACE