FUEL CELLS—I. PROPANE ON PALLADIUM CATALYST*

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Abstract—For the reaction at low temperatures of a gaseous hydrocarbon as a fuel gas at a negative electrode in a fuel cell, the choice of a suitable catalyst is of the first importance.

In the present study, catalysts consisting of palladium reduced by hydrogen and palladium reduced by formate, supported on four types of porous skeleton disks (thin nickel, thick nickel and two types of carbon), were examined. In many cases, the electrodes were given a water-proofing treatment.

The specific fuel cell used involved the prepared fuel electrode using gaseous propane, 30% KOH solution, a carbon-black air electrode and a temperature of 50°C. We attempt to distinguish the behaviour of propane from that due to hydrogen contained in the electrode, mainly on the basis of the relationship between (a) electrode preparation and treatment and (b) the open-circuit potential behaviour of the fuel electrode.

The repetition of small current discharges resulted in open-circuit potentials reaching steady high potentials and in electrodes exhibiting comparatively good dischargeabilities.

Résumé—Le choix d'un catalyseur convenable est particulièrement important pour la réaction à basse température d'un hydrocarbure gazeux au pôle négatif d'une pile à combustible. On étudie ici des catalyseurs au Pd obtenus par réduction au moyen de H_2 ou de formiate et supportes sur 4 types de disques poreux (nickel mince, nickel épais, 2 types au carbone). La cellule, utilisée à 50°C, consiste en l'électrode à combustible, alimentée par propane gazeux, une solution KOH à 30%, une électrode à air à noir de carbone. On a essayé de distinguer le comportement du propane de celui de H_2 contenu dans l'électrode, en relation avec la préparation de cette électrode et son comportement en circuit ouvert.

Zusammenfassung—Für die Oxydation von gasförmigen Kohlenwasserstoffen in einer Niedertemperatur-Brennstoffzelle ist die Wahl eines zweckentsprechenden Katalysators von primärer Wichtigkeit.

In der vorliegenden Arbeit wurden Palladium-Katalysatoren untersucht, welche durch Reduktion entweder mittels Wasserstoff oder mittels Formiat hergestellt und auf vier verschiedene poröse Träger (dünne und dicke Nickelscheiben und zwei Arten von Kohle) fixiert worden waren. In vielen Fällen wurde die Elektrode hydrophobiert.

Die Brennstoffzelle bestand aus der beschriebenen Katalysatorelektrode mit Propan als Brennstoff, einem 30% KOH-Elektrolyt und einer aktiven Kohlen- Luft- Gegenelektrode bei 50°C. Es wurde versucht, zwischen dem Verhalten von Propan und dem in der Elektrode vorhandenem Wasserstoff zu unterscheiden auf Grund der Zusammenhänge zwischen Elektrodenherstellungs-Methoden und Elektrodenbehandlung und dem stromlosen Potential der Brennstoffelektrode.

Wiederholte kleine Entladungen bewirkten, dass das stromlose Potential stationäre hohe Werte erreichte und die Elektroden vergleichbar gute Entladungseigenschaften aufwiesen.

INTRODUCTION

Until recently, most studies of gaseous hydrocarbon fuel cells have been concerned with temperatures higher than 100°C, usually 400–700°C. In one of the few published works on low temperature cells, Rosenbruch[1] indicated that methane behaves, experimentally, like an inert gas for nickel-DSK electrodes. Developments[2,3] have been concerned with a low cost fuel cell using a number of gaseous hydrocarbons at temperatures below 200°C, but experimental details have not yet been published. Data for the open-circuit potentials of ethylene,[4] acetylene[4] and propane[5] have been

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given by Young. Recently, the potential behaviour of various gaseous hydrocarbons have been reported[6] with details of the electrode preparation procedures and galvanostatic studies. Some of these results, obtained with acidic electrolytes, have been presented by Niedrach.[7]

In these studies reduced catalysts were stored under hydrogen (or oxygen-free helium) or other types of prepared catalysts were exposed to hydrogen, prior to the use of the hydrocarbon. In this connexion, it becomes a matter of fundamental importance to distinguish between the electromotive behaviour of a hydrocarbon from that of hydrogen contained in the electrode, and to consider other questions concerning "hydrocarbon potentials". The present study, which approaches these problems mainly in terms of the relationship between electrode preparation procedure and the observed open-circuit behaviour, is specifically concerned with the potential observed at anodes in 30% potassium hydroxide solution using gaseous hydrocarbon fuels at temperatures below 80°C; propane was chosen as a typical saturated hydrocarbon.

Subsequent papers will describe studies involving the oxidation of propane and propylene on a platinum catalyst in which the quantity of previously adsorbed hydrogen can be controlled, and certain thermodynamic considerations relative to propylene potentials in low temperature cells.

EXPERIMENTAL TECHNIQUES

Fuel electrode preparation

For experiments 2 and 6–10 (Table 1), a palladium chloride solution was impregnated into porous skeleton electrode disks of sintered nickel or carbon. After drying, the impregnated palladium chloride was reduced by a sodium formate solution.

Two concentrations of palladium chloride solutions were used. The less concentrated solution used in experiments 2, 6, 9 and 10 was prepared by dissolving 1·0 g of $PdCl_2 \cdot 2H_2O$ in dilute hydrochloric acid solution (40 ml water + 1·2 ml 6 M HCl) containing a small quantity of Triton X-100. The more concentrated solution used in the other experiments was prepared from 1·0 g $PdCl_2 \cdot 2H_2O$ in dilute hydrochloric acid solution (10·0 ml water + 0·8 ml 6 M HCl), containing a small quantity of Triton. The sodium formate solution was prepared by dissolving 80 g NaCOOH in 320 ml water.

The nickel disk used in experiment 2 was soaked in the palladium solution for 30 min at room temperature. The excess solution was removed by blotting with filter paper, and the disk was dried in an oven at 60 to 65°C for 10 min. It was then placed in the formate solution at 60–80°C, until the evolution of CO_2 stopped. Then the pH of the solution was adjusted to 1 by the addition of HCl, and the solution with the disk in it was boiled for about 1 min. The disk was removed and washed with boiling distilled water and then treated with boiling dilute HCl and washed with boiling distilled water; this washing procedure was carefully repeated three times. The disk was then dried in an oven at 80°C for 30 min and kept in a vacuum desiccator.

For the carbon electrodes used in experiments 7–9, evacuation was applied for the first 10 min of the soaking stage and then discontinued for 20 min; this procedure was repeated three times. For the nickel electrodes used in experiments 6 and 10, however, the soaking time was reduced to a few minutes in order to avoid dissolution of nickel.

TABLE 1. EXPERIMENTAL SEQUENCE AND EVALUATION OF ELECTRODES TESTED

Expt. no.	Electrode no.	Skeleton disk[a]	Catalyst added	Water-proofing, wax added[b]	Electrochemical characteristics[c]
2	7	Ni–I	Pd(formate)	None	Poor OCP: unstable
6	8	Ni–I	Pd(formate)	Wax–I	Good Dischargeable at 2·10 and 20 mA/cm²
7	14	C–I	Pd(formate)	Wax–I	Poor OCP: −0·90 V for H_2; unstable for propane
8	12	C–II	Pd(formate)	Wax–I	Poor OCP: −0·74 V (unstable) for H_2; unstable for propane
9	10	C–I	Pd(formate)	Wax–I	Poor OCP: −0·886 V for H_2; unstable for propane
10	9	Ni–II	Pd(formate)	Wax–I	Good Dischargeable at 2, 5, 10 and 20 mA/cm²
11	19	C–I	Pd(H)	Wax–I	Good Dischargeable at 2, 5, 10 and 20 mA/cm²
12	17	C–II	Pd(H)	Wax–I	Good Dischargeable at 2, 5, 10 and 20 mA/cm²
13	22	Ni–II	Pd(H)	Wax–I	Good Dischargeable at 2, 5, 10, 20, 50 and 100 mA/cm²
14	23	Ni–II	Pd(H)	Wax–I	*
15	24	Ni–I	Pd(H)	Wax–I	*
16	44	Ni–II	Pd(H)	Wax–II	*
17	45	Ni–II	Pd(H)	Wax–II	*

[a] Properties of skeleton disks used.

Symbol	Type	Thickness mm	Porosity %	Pore size μm
Ni–I	Thin porous sintered nickel (Clevite Co., No. 4)	0·76	80–85	9–15
Ni–II	Thick porous sintered nickel (Clevite Co., No. 2)	3·17	80–85	9–15
C–I	Porous Carbon (Speer Carbon Co., 33/7716)	3·15	25	0·8–10
C–II	Porous Carbon (Morganite, CY111)	3·15		

[b] Wax–I and Wax–II refer to paraffin waxes obtained from Schering-Kahlbaum, A. G. (m.p. 68–72°C) and National Wax Co. (m.p. 77–81°C), respectively.

[c] OCP is "open-circuit potential".

* These electrodes were used in the experiments described in the section entitled "Persistence of Hydrogen in Electrodes".

In experiments 11–17, the more concentrated palladium chloride solution was impregnated into porous sintered nickel disks. After being dried, the electrodes were reduced at 195–205°C for 15 h in a hydrogen furnace. The wt-% Pd was between 0·4 and 2·4. After reduction, the electrodes were kept in a desiccator filled with hydrogen.

The palladium catalyst reduced by a formate is designated as Pd(formate), and the palladium catalyst reduced by hydrogen as Pd(H).

The reduced electrodes were subjected to a waterproofing treatment, impregnation with a paraffin wax of m.p. 68–72°C (Schering Kahlbaum, A.G.) or 77–81°C (National Wax Co.). After being soaked in a solution of the wax in petroleum ether (b.p. range 60–75°C.) or methylcyclohexane, the electrodes were dried in an Abderhalden drying apparatus at the temperature of condensing $CHCl_3$ (61·3°C). The weight percentage of the impregnated wax were in the range 1 to 4.

A nickel wire (B.S. No. 28) lead was joined to the skeleton disk by electrical welding for the nickel disks and by means of silver paint for the carbon disks. The silver paint was prepared from silver powder and Eccobond 26 (Emerson and Cuming, Inc.).

Air electrode

The water-repellent properties of an activated carbon block designed for air-cell use (Union Carbide Corporation) were tested in 30% aqueous KOH solution at 50°C. A 1- to 2-mm thick surface layer was slowly wetted by the KOH solution but the block could be re-used by removing the wet layer with a knife.

Hydrogen furnace

The hydrogen furnace used for reduction of fuel electrodes consisted of a 6-ft stainless steel combustion tube around which was placed an electric tube furnace with water-cooled chambers on either side. A chromel–alumel thermocouple was placed in the combustion tube, which had a side tube for the purpose. Hydrogen gas (Matheson Co.) was supplied to the furnace through a purifying train consisting of a tube filled with copper ribbon, bottles of concentrated NaOH solution, a furnace filled with palladium-impregnated ceramic pieces, cylinders containing Drierite, a flow-meter and a second copper-wire cylinder. The absence of oxygen in the hydrogen was checked with yellow phosphorus. The necessary stop-cocks were arranged and supported on a Flexaframe assembly, using Tygon tubing for connexions.

For the packing of the palladium furnace unit, crushed pieces of a porous ceramic dish were soaked in palladium chloride solution and dried at about 100°C; the surface palladium chloride layer was then reduced to metallic palladium by hydrogen at about 400°C; these operations were repeated two or three times in order to build up a substantial palladium layer.

Cell: arrangement and measurement

A small glass cell, conceived in the fashion of a Hildebrand hydrogen electrode, was used to screen electrodes. The negative electrode, which was a porous sintered nickel or porous carbon disk of ⅝ in diameter, was fixed with one or two Neoprene rings and paraffin wax at the bottom (open end) of a glass cylinder (approximately

$\frac{5}{8}$ × 3 in) having gas inlet and outlet tubes. A relatively large piece of the carbon block (ca 2 × 2 × 10 cm), used as the positive electrode, was exposed to the air and had a much larger capacity than that of the small negative electrodes. The two electrodes and a Luggin capillary, containing 30% KOH solution and agar-agar, were situated in a rectangular glass jar (ca 4 × 6 × 9 cm) containing 30% KOH solution.

The experimental cell and a HgO reference electrode half-cell in 30% KOH solution were kept at 50°C in a liquid bath, which also contained an electric immersion heater connected to an automatic electric relay, a thermostat, an electric stirrer and a mercury thermometer. The bath was a large glass jar, insulated with a glass wool mat.

Fuel gas was introduced into the negative electrode side of the experimental cell by being led from its cylinder through a copper wire-filled tube and drying bottles containing Drierite. The gas pressure was controlled by a single stage regulator (Matheson No. 10510), a low pressure regulator (Matheson No. 70) and a U-type manometer. This gas-supply line could also be connected to the hydrogen or nitrogen lines.

Electrical circuits consisted of (a) the circuit for the fuel-cell discharge and (b) that for measuring and, if desired, recording the electrode potential. The former consisted of booster batteries, rheostats, a milliammeter and a voltmeter, arranged to permit measurement during a constant current discharge. The latter consisted of the HgO electrode, a Leeds and Northrup potentiometer and an automatically recording Minneapolis–Honeywell potentiometer (Model No. 153X17V-X-30). A terminal and switching panel was installed to facilitate measuring operations by one operator.

Since the present study was principally concerned with the behaviour of the fuel or negative electrodes, in many cases only the potential of the negative electrode vs the HgO reference electrode was measured.

RESULTS AND INTERPRETATION

Potentials observed with gaseous propane

The initial aim was the choice of suitable catalysts, but it became a major problem to find a means for obtaining and keeping a reasonably high potential since propane was significantly less reactive than hydrogen at 50°C. Experiments 2 and 6–13 were conducted under conditions which were varied as dictated by the results of each prior experiment, except that

(a) the apparent surface area of each fuel electrode was approximately 1 cm²,

(b) the 30% KOH solution used as electrolyte was exposed to air without stirring,

(c) propane (Matheson Co. instrument grade; 99·5 per cent minimum purity) was used.

The experimental sequence and the evolution of the electrodes tested are summarized in Table 1.

Open-circuit potential. In experiments 6–10, the electrodes were first flushed with hydrogen for a period of 10 to 60 min and then with propane, while the potential change was observed without load.

In the case of three carbon electrodes with Pd(formate) catalyst, the open circuit potentials for hydrogen were comparatively high, —0·900 V after a 30-min flush (stable, Speer carbon 33/7716, Experiment 9). However, these potentials slowly

decreased with time after the change from hydrogen to propane (Fig. 1: curves 7–9).

The open-circuit potential of the thin nickel electrode with Pd(formate) catalyst used in experiment 6 was −0·917 V after a 30-min flush with hydrogen. As soon as the flow of hydrogen was stopped and the cell was flushed with propane, the potential
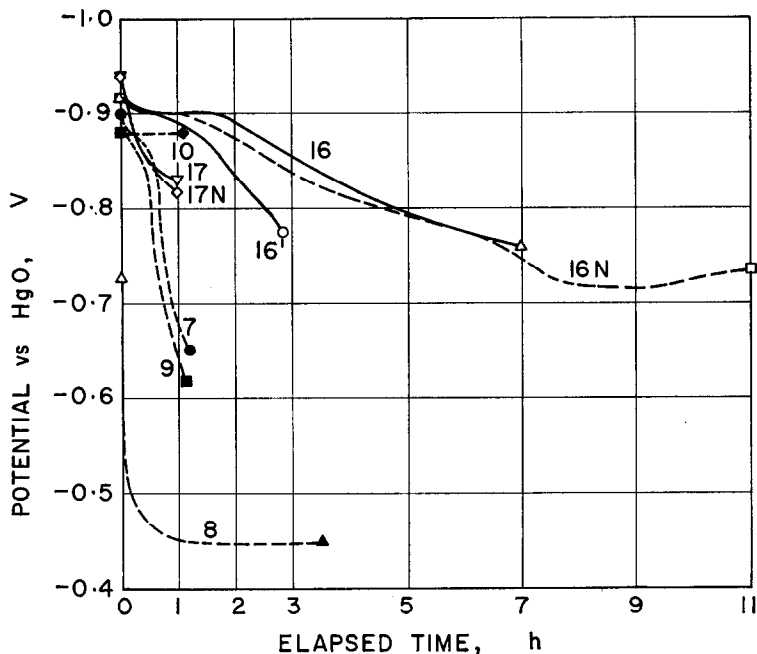

FIG. 1. Changes of open-circuit potentials of fuel electrodes during flushing with propane or nitrogen after pre-saturation with hydrogen.

Flushed with propane: 7 and 9; Speer Carbon with Pd(formate); 9; Morganite Carbon with Pd(formate); 10, 16′, 16 and 17; Nickel II with Pd(H$_2$). Flushed with nitrogen: 16N and 17N; Nickel II with Pd(H$_2$)$_2$.

dropped to −0·885 V and remained approximately constant for 30 min. In the case of the thick nickel electrode in experiment 10, the open-circuit potentials with hydrogen and propane were approximately the same as those with the thin nickel electrode used in experiment 6. After hydrogen was replaced by propane, the potential remained constant at −0·880 V for about 1 hr (Fig. 1: curve 10).

When the electrodes are flushed with hydrogen prior to the introduction of propane, uncertainty in interpreting the results exists because of the possibility that some hydrogen might remain adsorbed at the catalyst surface after the propane flush. Therefore, three electrodes, prepared from two different carbon disks (Speer carbon 33/7716 and Morganite CY111) and a thick nickel disk (Clevite No. 2) (all impregnated with Pd(H) catalyst), were tested using only propane.

The open-circuit potential of the Speer carbon electrode (experiment 11) was initially unstable within the range of −0·24 to −0·44 V. However, after repeated discharges of a small current for a few seconds (repeated 20 times during the 6-h flush), the potential gradually rose to −0·894 V. The small current drain resulted

from the circuit consisting of the cell and the automatic recording potentiometer, and was less than 0·1 mA. In the case of the Morganite carbon electrode (experiment 12), an initial potential of about −0·2 V suddenly rose to −0·9 V after four discharges of 2 mA for a few seconds each. In the case of the thick nickel electrode (experiment
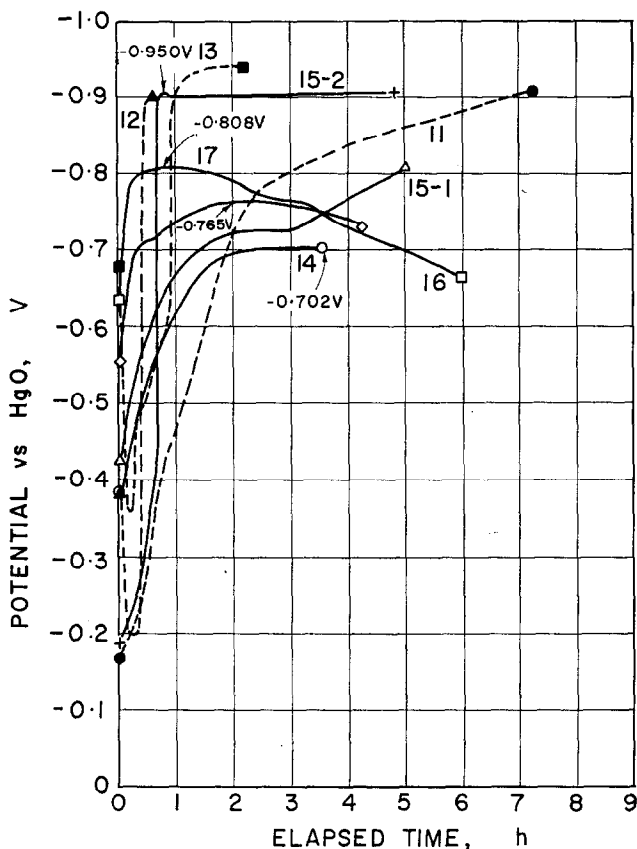

FIG. 2. Changes of open-circuit potentials of fuel electrodes caused by repetition of a short discharge at small currents.
Temperature: 50°C. Electrodes: Pd reduced in hydrogen furnace. Skeleton electrode: Speer Carbon—11; Morganite Carbon—12; Nickel II—13, 14, 16, 17; Nickel I—15–1 (first day), 15–2 (second day).

13), its potential was initially −0·680 V and rose to −0·927 V after repeated discharges in the range of 0·1 to 0·5 mA. These results are shown in Fig. 2, curves 11–13.

Discharge characteristics. After the measurement of initial open-circuit potentials for hydrogen and propane just described, the electrodes studied were subjected to repeated discharge tests at current densities of 2 to 100 mA/cm². These tests were made after the open-circuit potential had reached a steady value near −0·9 V as the result of the repetition of small discharges, *eg* 0·5 to 6 mA/cm², as just described. During these experiments attempts were made to obtain higher potentials. Observations were made of the effect on the potential of (a) gas flow-rate and gas pressure, (b) degree of contamination of the KOH electrolyte, and (c) internal resistances of

the cell. Some of the observed effects, which cannot always be duplicated, were as follows:

(a) The potential change was often greatly influenced by change of gas flow-rate or gas pressure, *eg*

(1) The rate of the potential recovery after discharges increased either suddenly or gradually, on stopping the gas flow.

(2) On the other hand, a potential slowly recovering under no gas flow, decreased on resuming the gas flow.

(3) A sudden jump of the potential sometimes occurred just after a momentary change of gas pressure (produced by momentarily rotating the stopcock connected to a gas source of 5 to 20 mm Hg higher pressure than 1 atm).

(4) A comparatively rapid rise of the potential sometimes occurred when the gas pressure was 5 to 10 mm of dibutyl phthalate less than 1 atm.

(5) The most typical recovery curve of a carbon electrode was a two-step curve, having approximately $-0\cdot7$ V as a steady lower potential and $-0\cdot9$ V as a steady higher potential.

(b) Since the 30% KOH electrolyte was exposed to air without being stirred, it probably was contaminated with carbon dioxide from the air and perhaps some reaction products, and became more concentrated because of evaporation. In experiments 11 and 12, when the open-circuit potentials and the discharge characteristics became very poor after several days' tests, replacing the used KOH solution with fresh solution, without flushing the electrodes with the new solution, seemingly caused most of the potential phenomena to return to the initial status.

(c) The internal resistance of the cell, measured at different current densities during experiment 12 with an impedance bridge, was always in the range of $1\cdot3$ to $2\cdot0\ \Omega$. The magnitude of this variation is not adequate to explain the potential change or to correlate it with the current density.

The discharge behaviour observed under a propane atmosphere was as follows:

The open-circuit potentials of the carbon electrodes with Pd(formate) catalyst (experiments 7–9) were variable and very low. In the case of the carbon electrodes with Pd(H) catalyst (experiments 11 and 12), however, potentials as high as $-0\cdot9$ V were obtained by the repetition of small discharges. The discharge behaviour of the Speer carbon electrode seemed to improve with repeated discharges in the range of 2 to 10 mA; the same tendency was found with the Morganite carbon electrode. However, the potential during discharge sometimes suddenly either rose or fell, exhibiting two different plateau voltages at each current density.

On the other hand, the nickel electrodes used in experiments 6, 10 and 13 had comparatively clean and good discharge characteristics. The plateau voltage in a 10-min discharge was $-0\cdot925$ V (constant) for 2 mA, $-0\cdot906$ V (constant) for 5 mA, $-0\cdot85$ V for 10 mA and $-0\cdot68$ V for 20 mA. Though the discharge curve for 50 mA (and 100 mA) had a large inclination, its approximate voltage for the initial 5-min discharge was $-0\cdot5$ V for 50 mA and $-0\cdot3$ V for 100 mA.

The electrodes used in experiments 6 and 10–13 can be considered to be comparatively good. Figure 3 shows the relationship between approximate plateau voltages and discharge current densities. Each plateau voltage plotted indicates the most marked one obtained for that particular current density. In the case of the carbon electrodes, two plateaus, higher and lower, are shown obtained for each current

density, although the reproducibility of the higher plateau voltages was not so good. The discharge characteristics of the carbon-based electrodes at high current densities were very poor. By comparison, nickel electrodes, particularly a thick one with Pd(H) catalyst, had relatively reproducible discharge behaviour.
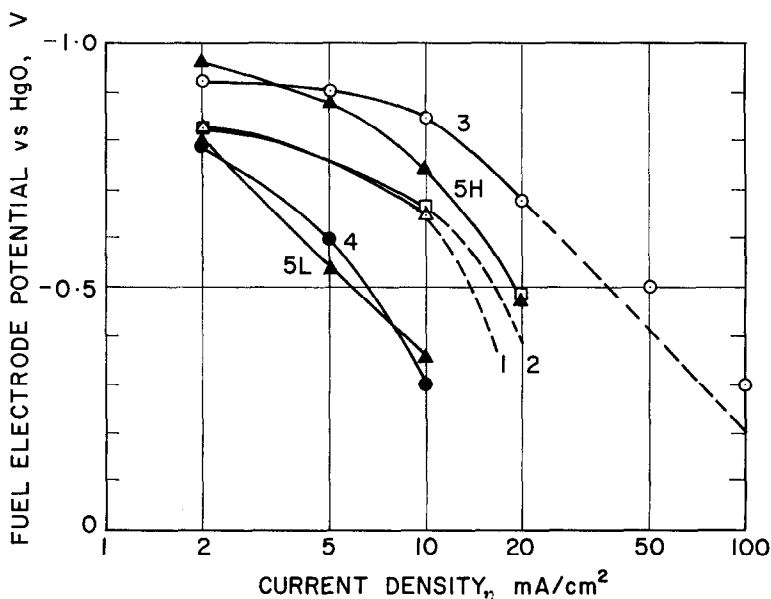

FIG. 3. Discharge plateau voltage of fuel electrode.

Fuel gas: propane. Temperature: 50°C. 1, Nickel I with Pd(formate), Expt. 6. 2, Nickel II with Pd(formate), Expt. 10. 3, Nickel II with Pd(H), Expt. 13. 2, Nickel II with Pd(formate), Expt. 10. 3, Nickel II with Pd(H), Expt. 13. 4, Carbon with Pd(H), Expt. 11; Speer Carbon Co. 33/7716. 5H, Carbon with Pd(H), Expt. 12; 5L, Carbon with Pd(H), Expt. 12; Morganite Inc. CY111; H: higher plateau voltage; L: lower plateau voltage.

Persistence of hydrogen in electrodes

Based on the discharge characteristics, the porous sintered nickel electrode with palladium catalyst reduced in hydrogen had the highest activity of the electrodes described. A high potential and a rather good dischargeability could be obtained, either after repeated short discharges at small current or in the presence of a small quantity of the hydrogen remaining at the catalyst surface. Therefore, it may be suspected that one or more of the following might be occurring: a thin oxidized surface film on the catalyst might be broken by moderate current discharges; the oxidation reaction of propane might be catalytically accelerated by intermediate reaction products; the hydrogen strongly bound to the inner surface of catalyst particles might become exposed to electrolyte as a result of the repetition of the discharges.

Sandler[8] proposed that the oxidation of propane at 610°C may be accelerated by the hydrogen produced as an intermediate product. It was, therefore, a matter of interest to investigate the possibility of this occurring at low temperature. Since the activity of propane is much less than that of hydrogen at low temperatures, it would

be an important part of the electrode process to utilize any hydrogen cracked from propane at the catalyst surface, if the cracking of propane does occur.

Four electrodes, prepared by almost the same procedure as that used for Electrode 13, were used to investigate the accelerated reaction. The electrodes were fixed at
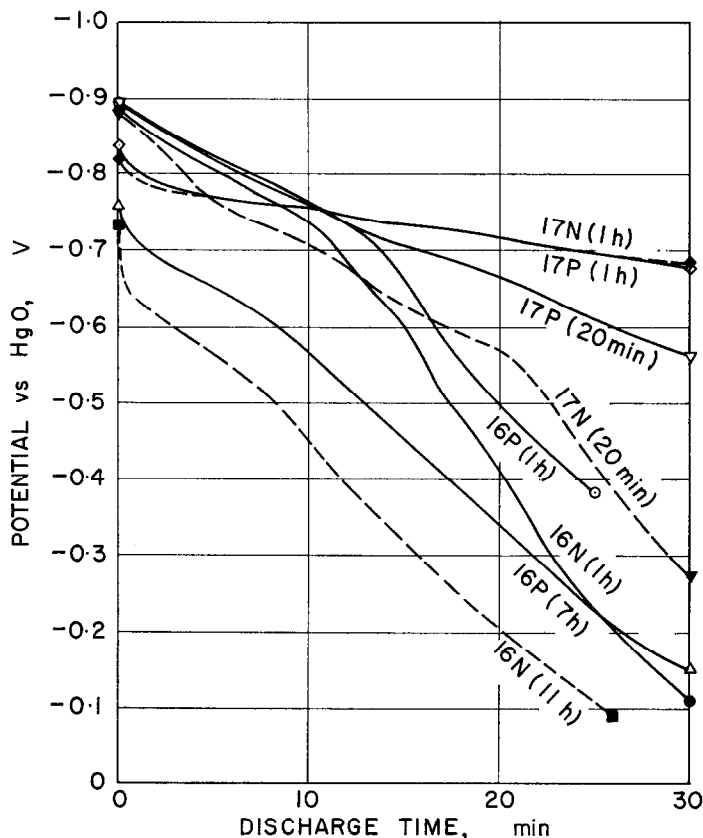

FIG. 4. Discharge curves of fuel electrodes at 2 mA after pre-saturation with hydrogen, on flushing with propane or nitrogen.

the bottom of the small cell, which was then flushed with propane for 20 min before being soaked in the potassium hydroxide solution at 50°C. Flushing at a propane pressure nearly sufficient to produce bubbling through the electrodes was carried on for 10 min more and the variation of the open-circuit potential was observed. In order to reach a potential as high as −0·9 V, short-time discharges at a small current were used.

Initial open-circuit potential. The electrodes were initially subjected to flushing with propane with the repetition of small discharges. Variations of the open circuit potential during flushing are shown in Fig. 2. Although the potentials rose, the highest potential reached for each electrode was −0·702 V in experiment 14, −0·905 V in 15, −0·808 V in 16 and −0·765 V in 17.

In experiments 16 and 17, after the introduction of hydrogen into the cells, which resulted in each potential reaching a steady high value (−0·92 V in experiment 16;

—0·94 V in experiment 17), the cells were flushed with propane or nitrogen at a rate of about 2 bubbles/s; the changes in open-circuit potential are shown in Fig. 1. In experiment 16, the potential during nitrogen flushing gradually decreased with time and finally reached a steady value of —0·73 V (Fig. 1, curve 16N). A similar curve was obtained on propane flushing (Fig. 1, curve 16).

Discharge behaviour. Experiments 16 and 17 show the discharge behaviours obtained after flushing the electrodes with propane and nitrogen for a definite time, *eg* 1 h. Every discharge at 2 mA was done after the electrode was flushed with hydrogen for ½ h, resulting in open-circuit potentials of —0·91 to —0·92 V (experiment 16) or —0·93 to —0·94 V (experiment 17).

The discharge behaviour at 2 mA after flushing periods of 20 min, 1 h, 7 h and 11 h are shown in Fig. 4. Even after flushing with nitrogen for 11 h, the electrode had a discharge capacity of more than 1 mA/h, which corresponds to 0·42 ml of hydrogen (curve 16N, Fig. 4). Moreover, there was no distinct difference for the same flushing times between the discharge behaviour using propane and that using nitrogen, although some curves for propane look a little better than those for nitrogen; compare curves 16P (1 h), 17P (20 min) and 17P (1 h) with 16N (1 h), 17N (20 min) and 17N (1 h) in Fig. 4.

CONCLUSION

There remain questions concerning the propane dischargeability from the viewpoints of (a) the dischargeability at a current density lower than that used in the experiments described and (b) the relation between the amount and nature of the hydrogen adsorbed in catalysts and their activities. The literature[9–17] indicates that palladium strongly binds hydrogen and that some portion of the palladium may form a palladium hydride, probably PdH. On the other hand, many investigators have stated that hydrogen plays an important role in the activity of catalysts, in particular Raney nickel catalyst. Even in the case of a palladium catalyst, it is stated that the hydrogen, which is dissolved in palladium metal and diffuses toward the surface, is effective in the catalyst's activity, even though the hydrogen adsorbed at the catalyst surface tends to act like a poison. Accordingly, the removal of hydrogen from a palladium catalyst may change its activity. In experiments 6, 10, 13 and 15, a comparatively good dischargeability was observed after a potential near —0·9 V had been obtained by the repetition of a moderate current discharge. Moreover, such discharge behaviour is much better than that shown in Fig. 4, which was obtained after the electrodes have been saturated with hydrogen and then flushed with nitrogen. It is possible that when a higher potential than —0·9 V has been obtained by repetition of small discharges, the oxidation of propane may catalytically proceed with the help of "activating" hydrogen, which might thus maintain the activity of palladium. To resolve this possibility, it is necessary to use electrodes containing hydrogen in definite amount.

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