

## OPERATING CHARACTERISTICS OF PALLADIUM-SILVER ANODE ON IMPURE HYDROGEN STREAMS

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### INTRODUCTION

The practicality of using non-porous hydrogen diffusion anodes in fuel cells has been described by Oswin and Chodosh<sup>(1)</sup>, Elmore and Tanner<sup>(2)</sup>. The advantages in manufacture and operation of these electrodes are considerable and have stimulated work on these palladium membrane electrodes to lower electrode costs and permit their use with cheaper fuels than pure H<sub>2</sub>. Modifications of the electrode surfaces have been developed to extend anode performance and permit wider application of the non-porous anode.<sup>(3, 4, 5,)</sup>

Most of the work has been related to the palladium-silver alloys which appear to be remarkably suited for fuel cell applications. A unique property of the alloys is their selective permeability to hydrogen, and some of the metallurgical factors involved have been discussed by Makrides<sup>(6)</sup>. Recently von Sturm and Kohlmüller<sup>(7)</sup> using palladium membranes have derived a relationship between concentration polarization (with respect to H atoms), the membrane thickness, current density and partial pressure of hydrogen in the gas phase. In this work, however, the membrane surfaces were activated by an undisclosed technique, and the effects of the surface activation are not apparent.

Although originally conceived<sup>(8)</sup> for use with relatively pure H<sub>2</sub> streams, the greatest potential application of palladium-silver anodes is with carbonaceous fuels. To obtain efficient anode performance with carbonaceous streams, there are two prime requirements:

1. The electrode must exhibit high limiting currents with low partial pressures of hydrogen, and
2. The electrode must be stable in the presence of materials other than hydrogen. Specifically, the limiting currents (H<sub>2</sub> flux) at low p<sub>H<sub>2</sub></sub> values must not be lowered significantly by gases and substances present or formed in the fuel streams.

The palladium-silver anode can be used in a fuel stream in at least two ways. The fuel can be externally reformed, to provide a gas rich in free hydrogen which is then circulated behind the Pd-Ag electrode and the hydrogen extracted electrochemically. In this case the external reformer is operated at a higher temperature than the fuel cell. The fuel cell with palladium-silver anode can then be operated at any convenient temperature.

The second method of operation which has been developed recently<sup>(9, 10)</sup> consists of reforming the fuel stream to hydrogen in the anode chamber behind the palladium alloy membrane. This "internal reforming" process requires operating the fuel

cell at a temperature high enough to reform the fuel rapidly: the endothermicity of this process is satisfied by the polarization losses in the fuel cell itself. Continuous extraction of  $H_2$  down to lower than equilibrium values of  $p_{H_2}$  permits very efficient utilization of the fuel.

Before either of these types of fuel cell could be developed; however, it was necessary to provide a highly efficient  $H_2$ -extracting anode<sup>(1)</sup> with low sensitivity to contaminant gases.

The work presented here describes progress with this type of anode and some of the preliminary studies carried out with various types of  $H_2$ -containing streams.

### EXPERIMENTAL PROCEDURES

The experiments were performed at 200°C in 75% potassium hydroxide. Potential measurements were made versus a reversible 75 Pd/25 Ag/hydrogen reference electrode in the same electrolyte, and all values reported are on the  $E_h$  scale. A Luggin capillary was employed at the surface of the membrane to measure anode potential. Studies for the most part were conducted on one inch diameter, 1.5 mil and 5 mil thick 75% palladium - 25% silver membranes operating against a Pt mesh counter electrode. The experimental apparatus is presented in Figure 1. All anodes studied were activated as described in the following section.

### ELECTRODE PREPARATION

Many activation procedures have been investigated at Leeson<sup>(5)</sup> in an attempt to improve operating parameters such as limiting current density, polarization, and stability. The activation procedure used in this work was satisfactory and entirely reproducible.

75 Pd/25 Ag membranes were first abraded with 50 micron aluminum powder. The membranes were then cathodized in 5% KOH solution using two Pt mesh counter electrodes to maintain proper geometry: this cathodization resulted in the saturation of the membrane structure with hydrogen. The structures were then immersed in a 2% palladium chloride solution (2-molar HCl) for approximately 4 minutes. The hydrogen previously introduced into the lattice chemically reduces the palladium ions from the plating solution to form a palladium black on both of the membrane surfaces; the quantity of black deposited was a function of plating time and anode thickness. This procedure resulted in an adherent, active palladium black; most structures studied had activations of approximately 4 to 5 milligrams per square centimeter. Although the amount of Pd activation is not a critical factor over the range  $\sim 1-15 \text{ mg/cm}^2$  <sup>(5)</sup> the 5 milligram level of activation was arbitrarily selected for experimental convenience.

### THE EFFECT OF HYDROGEN PARTIAL PRESSURE

The driving force for the diffusion of hydrogen through the metal lattice is the differential activity of hydrogen, and it was important at the beginning of this study to determine the relation between hydrogen partial pressure, limiting current density and polarization. This was desirable since in later studies it permitted separation of the relative effects of partial pressure and impurities. This data was obtained using streams containing predetermined mixtures of hydrogen and nitrogen. A low

utilization was used to simulate a constant partial pressure of hydrogen across the membrane. Using structures of 15, 10, 5, 3 and 1.5 mils in thickness and partial pressures of .025, .125, 0.25 and 2.5 psia hydrogen, the relationship shown in Figure 2 was obtained. Figure 2 indicates that down to 2.5 psia the process is bulk controlled over the range of thicknesses studied. At lower pressures, a degree of surface control is evident. Corresponding polarization data is shown in Figure 3. The variation of OCV with  $H_2$  partial pressure follows the Nernst relationship within experimental limits.

As with any electrode operating on an impure reactant, the concentration of reactive species in the stream (in this case hydrogen) will decrease during passage over the electrode. The concentration of hydrogen in the exit purge stream should ideally approach zero, and the extent of approach will be determined by the ability of the electrode to operate at a low effluent concentration of hydrogen. The actual partial pressure of  $H_2$  (over a given range) behind the electrode will be determined by the extent of back-mixing within the anode gas chamber. This will be a function of the geometry of the chamber, the gas flow-rates and the electrode current density. The mixing profile was not determined in these preliminary studies.

Hydrogen utilization studies were conducted employing a stream of 70% hydrogen and 30% nitrogen. The relationship between utilization and  $I_{lim}$  was determined experimentally by fixing the current density and reducing the flow to the newer stable value. An overall hydrogen mass balance was established by analyzing the composition of the effluent gas. This analysis was performed continuously by a thermal conductivity cell.

Measurements were taken at current densities of 139, 179 and 487 mA/cm<sup>2</sup> with an inlet hydrogen partial pressure of 25 psia. At the lower current densities hydrogen utilizations of 90% were observed. This value fell to 80% when the current density was increased to 487 mA/cm<sup>2</sup>. Since this is below the limiting current range at moderate  $H_2$  partial pressures, polarization was virtually unchanged over the range of utilizations studied. These results established that low polarization and high hydrogen utilization could be obtained simultaneously when operating on impure hydrogen streams.

It was next necessary to determine the extent to which this result is dependent on the identity of the particular impurities. The following sections present the data related to the ammonia-, methanol-, and hydrocarbon-derived streams.

#### AMMONIA-CONTAINING STREAMS

Simulated "cracked"  $NH_3$  streams containing 2 to 5%  $NH_3$ , and a balance of hydrogen and nitrogen in a ratio of 3  $H_2$ :1  $N_2$  were used. The fuel was prepared by introducing  $NH_3$  into a 75%  $H_2$ , 25%  $N_2$  stream; the concentration of ammonia in the effluent was determined by adsorption in 0.856 N  $H_2SO_4$  and titration with 0.01 N NaOH.

The effect of 3  $H_2$ :1  $N_2$  streams containing 4.3% and 2.2%  $NH_3$  on anode polarization and limiting current density is shown in Figure 4, and it is apparent that:

1. At similar limiting current densities (350 mA/cm<sup>2</sup>), a hydrogen utilization of 75% is obtained with the ammonia-free stream compared to a hydrogen utilization of 54.7% for the 4.3%  $NH_3$  feed.

2. Reducing the ammonia concentration to 2.2%, it is possible to increase the hydrogen utilization to 74.4% with only a slight reduction in limiting current (325 mA/cm<sup>2</sup>). Operation at these conditions for a period of 9 hours produced no change in  $I_{lim}$  or polarization.
3. A return to operation with pure hydrogen/nitrogen mixtures after exposure to ammonia resulted in a fairly rapid (but not instantaneous) return to the original performance level, indicating the reversibility of the ammonia effect.

From these results, it is evident that ammonia exerts a more profound influence on hydrogen anode performance than does nitrogen in similar concentrations. The ammonia clearly influences not merely the hydrogen partial pressure but also the adsorption kinetics on the palladium surface. This would be expected in view of the known adsorption of ammonia on transition metals. On the other hand, its demonstrated reversibility indicates that ammonia cannot be regarded as a strong poison. For good H<sub>2</sub> utilization at high current densities, the temperature and space velocity in the ammonia cracker must be optimized to maintain the NH<sub>3</sub> concentration below 2%.

#### SIMULATED METHANOL REFORMER STREAM

The cracking of methanol to yield CO + H<sub>2</sub> followed by the shift reaction with water to yield CO<sub>2</sub> + H<sub>2</sub> provides a gas of the approximate composition 70% H<sub>2</sub>, 23% CO<sub>2</sub>, 1 - 2% CO + unreacted methanol and water. The effects of these various compounds on anode behavior is discussed below:

##### 1. Effect of CO<sub>2</sub>

Streams of 75% H<sub>2</sub>, 25% CO<sub>2</sub> have been studied. CO<sub>2</sub> behaves as a totally inert diluent, and limiting current density is a function only of the reduction in hydrogen partial pressure. No poisoning effects with CO<sub>2</sub> have been observed on structures operated for periods of hundreds of hours.

##### 2. Effect of CO

The initial exploratory studies employed a stream of 75% H<sub>2</sub>, 20% CO<sub>2</sub>, and 5% CO. This amount of CO is substantially greater than that normally expected from methanol reformed at 250°C.

The experimental procedure employed was as follows: (1) an anode was operated in pure H<sub>2</sub> measuring polarization and limiting current density; (2) at 150 mA/cm<sup>2</sup> using the H<sub>2</sub>, CO<sub>2</sub>, CO stream and a given vent rate (hydrogen utilization) the polarization was observed over a half-hour period with the following results:

<u>% Hydrogen Utilization</u>	<u>Increased Polarization After 1/2 Hour Under Load</u>
8.33	no change
20	no change
33	no change
38.1	7 mV
57.1	23 mV

It is apparent that CO has an increasingly deleterious effect on anode polarization as the utilization is increased. This is also demonstrated by its effect on limiting current densities as seen in Figure 5. Increasing the utilization at 150 mA/cm<sup>2</sup> from 8.33% to 38.1% halved the limiting current density; this is greater than can be expected from the presence of an inert diluent, demonstrated in the previous H<sub>2</sub>/N<sub>2</sub> utilization studies.

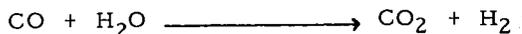
It was also observed when changing from a CO-containing stream to pure H<sub>2</sub> that recovery of the initial limiting current could be obtained, but only after extensive purging with pure H<sub>2</sub>. This indicates that the CO is strongly, but not irreversibly adsorbed onto the gas side surface.

Further studies were then conducted on streams containing 0.01, 0.1 and 1% CO in the presence of H<sub>2</sub>O and CO<sub>2</sub>. Water was included since it was expected to be present normally in the low temperature shift effluent. Each experiment was conducted for the period of time it took to either double the initial polarization at 150 mA/cm<sup>2</sup>, or 50 hours, whichever came first. H<sub>2</sub> utilization was maintained at 50%.

The results of these experiments are summarized in Table 1 below:

Gas (°C)	Composition(%)				The Effect of CO on Anode Polarization		Electrode Diameter(in.)
	CO	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub>	Poisoning Under Load (Hours Required To Double Polar.)	Recovery (Hrs. of H <sub>2</sub> Purge Needed)	
200	0.01	0	0	Bal.	slow (~20)	slow (~10)	1 & 5
	0.1	0	0	Bal.	rapid (< 1)	slow (~10)	1 & 5
0.1	0	2	Bal.	none (> 50)			1
	1	0	2	Bal.	none (> 50)		1
0	26	0	Bal.	none (> 50)			1
	0.1	25	0	Bal.	rapid (10 - 20)	slow (~10)	1
1	25	0	Bal.	rapid (< 10)		slow (~10)	1

The data shows clearly that CO (either alone or in the presence of CO<sub>2</sub>) poisons the gas side reaction, but that in the presence of water (~2%), no deterioration in anode polarization is observed. This is explained by the shift reaction occurring on the gas side of the palladium black activated membrane:



The effect of this process can be measured by the observation that as little as .01% CO is deleterious when present in the dry form, whereas 1% CO can be safely tolerated in the presence of water.

#### EFFECT OF METHANOL AND H<sub>2</sub>O

The effect of the expected concentration of unreacted methanol (1 - 2%) and H<sub>2</sub>O (1 - 2%) in the reformer stream was evaluated. The desired hydrogen stream was synthesized by passing hydrogen through a glass absorption column containing the proper H<sub>2</sub>O/methanol composition. The stream composition was analyzed by

gas liquid chromatography. Using streams containing the desired impurity content, an anode was kept under a load of  $150 \text{ mA/cm}^2$  for 25 hours with a vent rate equivalent to 50%  $\text{H}_2$  utilization. Potential under load was steady for the period studied, and polarization curves indicated no change in limiting current density after this exposure to the impure stream. The utilization was increased to 80% at the same load with no change in stability. Subsequent runs using actual (internally) reformed methanol showed no poisoning of the anode over periods exceeding 200 hours. These experiments were carried out at  $200 - 250^\circ\text{C}$  with hydrogen utilization of 80 - 90% and current densities of  $150 \text{ mA/cm}^2$ .

#### EFFECT OF $\text{CH}_4$

Dependent on the efficiency of reforming, substantial concentrations of saturated hydrocarbons may be encountered when operating on fuels such as kerosene, gasoline, etc. Methane in particular will be present, even with methanol feed, due to the methanation of carbon monoxide. Tests with  $\text{CH}_4$  showed it to be an inert diluent.

#### UNSATURATED HYDROCARBONS

Unsaturated hydrocarbons may be present in significant quantities either as impurities in the feed, or as a result of partial dehydrogenation during the reforming process. It was considered possible that because of their tendency to chemisorb on transition metals, some poisoning of the  $\text{H}_2$  diffusion process might be observed. Tests, however, failed to confirm this, and stable operation for the periods specified was observed with ethylene. However, a reduction in the limiting current was noted which corresponded almost exactly to the loss of hydrogen required for hydrogenation of the unsaturated species. The original polarization and limiting current conditions were observed immediately on restoring the hydrogen partial pressure.

#### OTHER SPECIES - ACTUAL REFORMER STREAMS

Additional qualitative experiments have indicated that severe and irreversible poisoning can occur in the presence of significant quantities of acetylene or of sulfur. The exact limits of tolerance for these species have not been established, but operation with actual reformed streams from both methanol and hydrocarbon fuels in internal-reforming cells has shown no gas-side deterioration over operating periods of 500 hours. From this it can be concluded that any species generated during reforming but not explicitly considered in these studies must be present in low concentrations which do not noticeably affect the diffusion process.

#### DISCUSSION

The data presented clearly show that a suitably prepared palladium-silver anode can be used efficiently to extract hydrogen from impure streams within certain limits.

The limits of operation are set by the temperature (fixed in these studies at  $200^\circ\text{C}$ ), the required  $\text{H}_2$  utilization, i.e., exit  $p_{\text{H}_2}$ , and the reversibility of the chemisorption of various impurity species.

$\text{H}_2$  utilization at fixed current density is a function of  $p_{\text{H}_2}$ , flow rate and the extent of impurity adsorption. The data obtained with  $\text{H}_2/\text{N}_2$  mixtures show that below  $p_{\text{H}_2} = 2.5 \text{ psia}$ , gas-phase adsorption is limiting. When poisons which can be strongly

adsorbed are present in the hydrogen, a significant fraction of the surface is covered by the poisoning species even when  $p_{H_2} = 2.5$  psia. Under these conditions, the surface (hydrogen - adsorption) process is rate-limiting at higher partial pressures of hydrogen. Only when  $p_{H_2}$  is high enough so that  $H_2$  competes successfully for surface sites with the poisoning species and causes an increase in  $\Theta_H$  is there any reduction in the extent of limitation by the surface step.

$N_2$ ,  $CO_2$ ,  $H_2O$ ,  $CH_4$  and  $CH_3OH$  do not appear to affect the  $p_{H_2}$  - limiting current relationship and all of these species act as inert diluents: they are likewise known not to chemisorb strongly on metals such as palladium.

Ethylene appears to be an intermediate case. The evidence (rapid desorption) is that it does not chemisorb strongly under these conditions and hydrogenates very rapidly to ethane which by inference must be completely inert. By contrast, acetylene is an irreversible poison; this is explainable by its tendency to form strongly-bonded, surface species on most Group 8 metals. Neither acetylene nor ethylene have been observed in steam-reformed effluents and are not considered to be likely poisons.

Ammonia, known to chemisorb extensively, but reversibly on Pt and Pd, is tolerable up to the level of 2% of the stream content.

The case of carbon monoxide is very important from a practical point of view since the most efficient shift catalysts in use today cannot reduce CO below 0.1% level at useful space velocities. In the absence of water it is demonstrated that CO chemisorbs strongly and extensively on the palladium surface, significantly lowering  $\Theta_H$  and limiting currents. In the presence of water vapor, however, this is not the case, and the palladium acts as a remarkably good shift catalyst, so that limiting currents are unaffected. Thus, by inference,  $\Theta_H$  must be higher and  $\Theta_{CO}$  smaller than when water is absent. In turn, this would imply that the rate of the shift reaction is far greater than the rate of adsorption of CO.

In recent practice<sup>(9, 10)</sup> it has been demonstrated that the anodes can be operated efficiently for long periods on reformed streams of methanol/water and hydrocarbon/water. Under these conditions<sup>(9)</sup>, the membrane surface is exposed to mixtures of CO,  $CO_2$ ,  $H_2$ ,  $H_2O$  and fuel: the composition of this gas at any point on the surface being determined by temperature, space-velocity, pressure and the extent of back-mixing. The least favorable case (for  $H_2$  adsorption on the membrane surface) exists at the exit point where the values of  $p_{CO}$ ,  $p_{CO_2}$  will be highest and  $p_{H_2}$  lowest. Operating at conditions where 85% of the methanol has been decomposed and 90% of the resulting hydrogen 'extracted' by the anode, the anode has operated without increased polarization at exit values of  $p_{CO} > 1\%$ . This seemingly high level of  $p_{CO}$  can be tolerated since it is unstable with regard to the shift equilibrium:



Thus, when the CO is adsorbed on the palladium surface, it is unstable, and rapidly converts to  $CO_2$  and  $H_2$  since the palladium is an efficient shift-promoting catalyst under these conditions.

Sulfur, especially in the form of  $H_2S$ , is of course one of the most strongly adsorbed poisons on metal surfaces. Experience has shown, however, that all reforming catalysts are sensitive to sulfur poisoning, and fuel streams must be pre-treated to

remove sulfur in order to obtain good reformer-catalyst lifetimes. In this respect, the pre-treatment of fuel and the removal of sulfur traces by the reformer catalyst significantly reduce the chance of sulfur-poisoning of the palladium membrane by the H<sub>2</sub> stream, and the quantitative tolerance of the membrane surface to sulfur is therefore of academic interest at this point.

It is apparent that from a practical point of view, the non-porous diffusion anodes when operated under correct conditions can provide very efficient fuel utilization at high current densities, and that they are operable in the presence of a wide variety of impurities and by-products of fuel-reforming.

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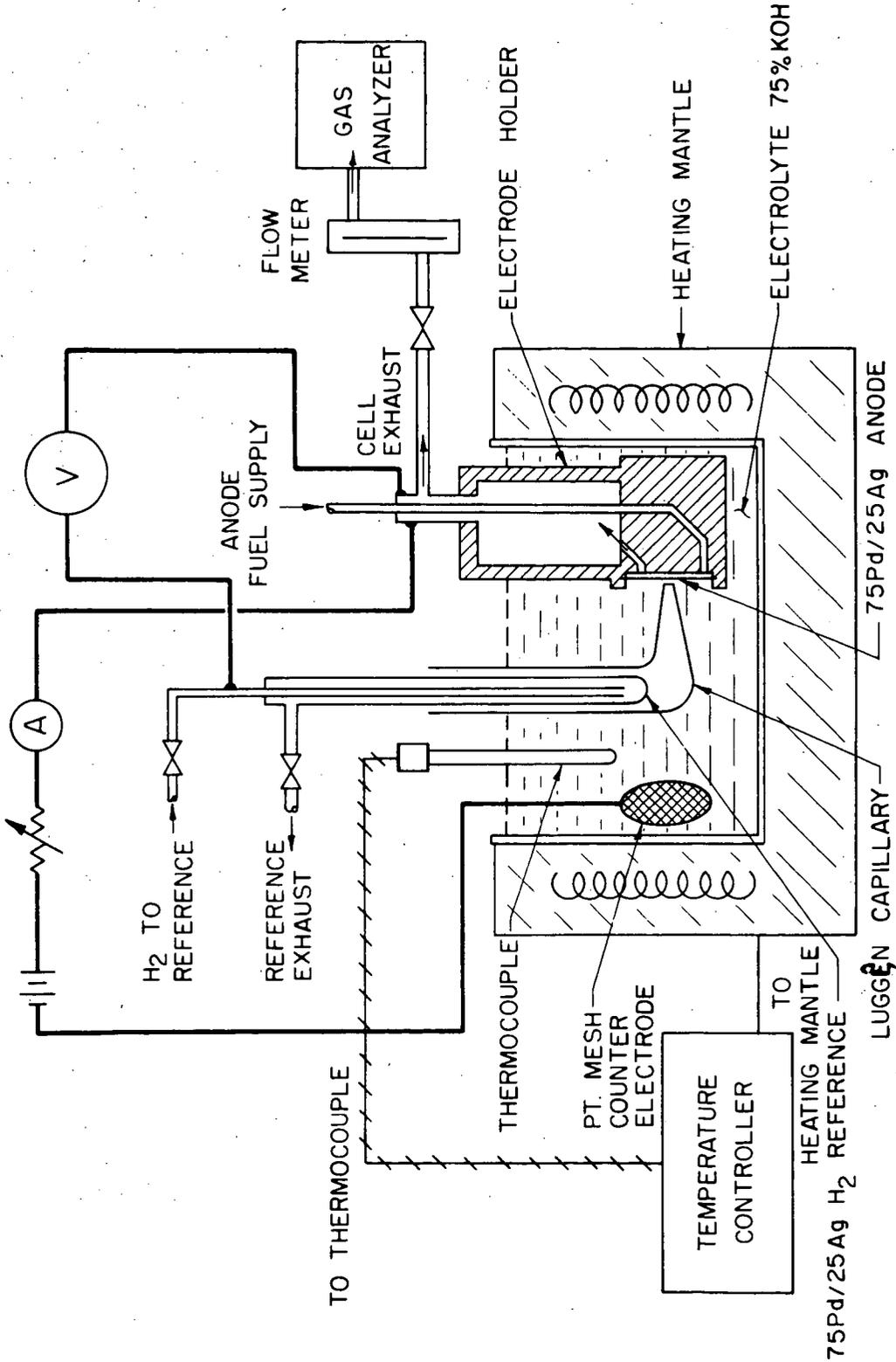


FIG. 1 EXPERIMENTAL APPARATUS

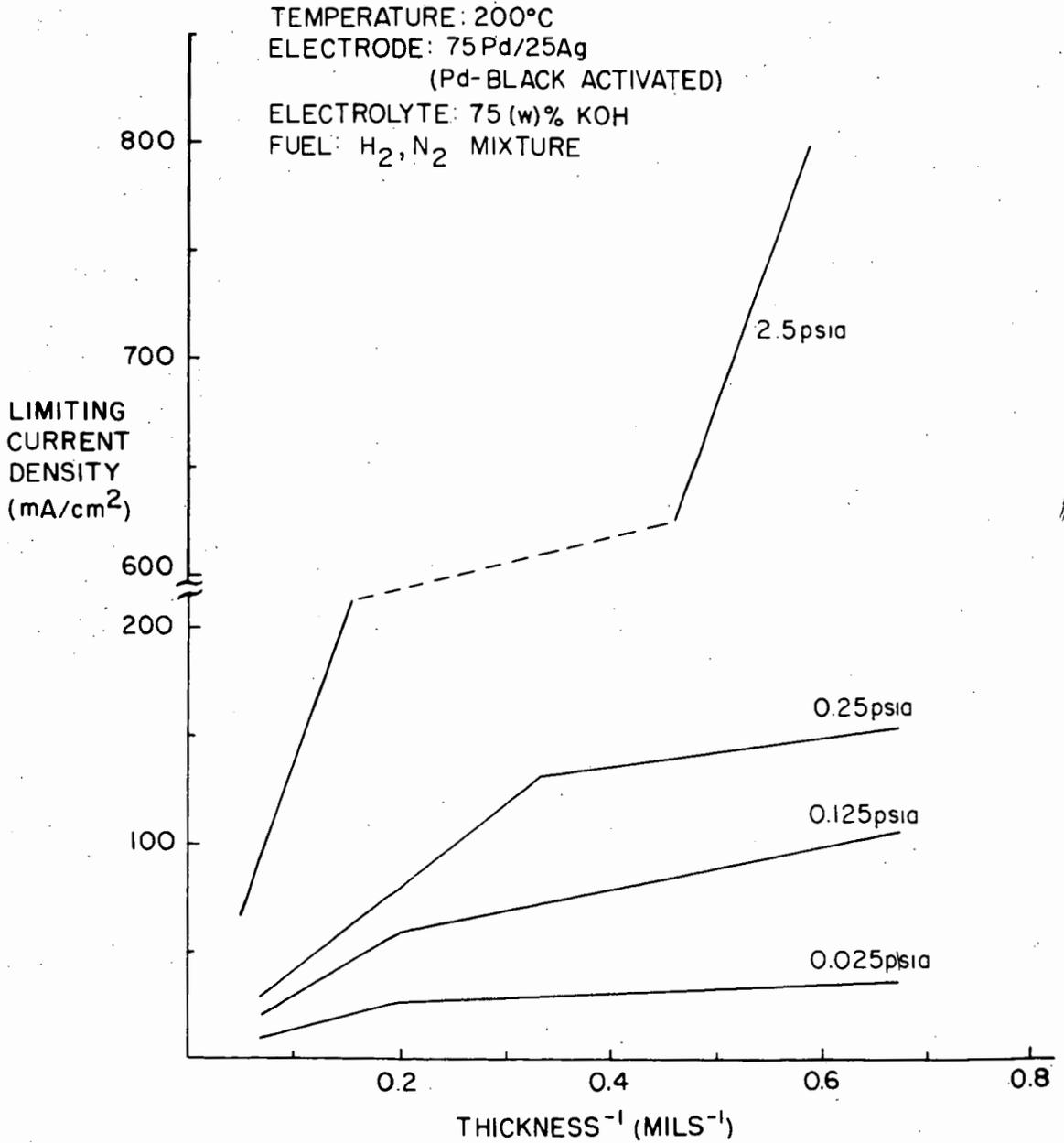


FIG.2 EFFECT OF PH<sub>2</sub> AND ELECTRODE THICKNESS ON LIMITING CURRENTS OF Pd/Ag ANODE

TEMPERATURE: 200°C  
ELECTRODE: .0015", 75Pd/25Ag  
(Pd-BLACK ACTIVATED)  
ELECTROLYTE: 75(w)% KOH  
FUEL PRESSURE: 10psig  
FUEL: H<sub>2</sub>, N<sub>2</sub> MIXTURE  
FLOW RATE OF FUEL: 1025 cc/min/cm<sup>2</sup>

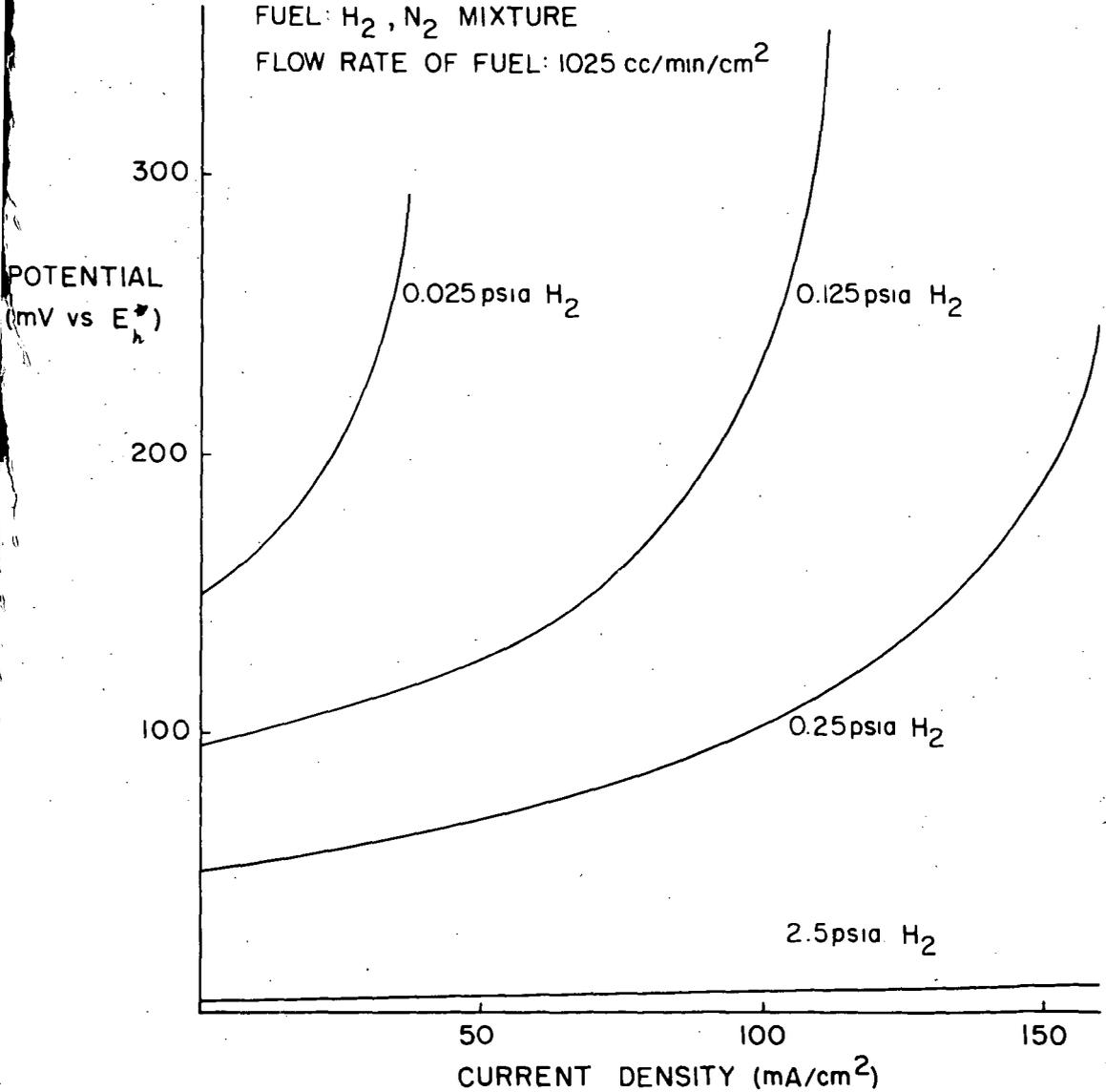


FIG. 3 POLARIZATION OF ANODES OPERATING AT LOW PARTIAL PRESSURES OF HYDROGEN

TEMPERATURE: 200°C

ANODE: .0015", 75 Pd/25 Ag

(Pd-BLACK ACTIVATED)

ELECTROLYTE: 75 (w) % KOH

FUEL PRESSURE: 25 psig

CURVE FUEL MIXTURE

VENT RATE (cc/min)

CURVE	FUEL MIXTURE	VENT RATE (cc/min)
1	100% H <sub>2</sub>	3
2	75% H <sub>2</sub> , 25% N <sub>2</sub>	54
3	75% H <sub>2</sub> , 25% N <sub>2</sub>	10
4	71.1% H <sub>2</sub> , 23.7% N <sub>2</sub> , 4.3% NH <sub>3</sub>	11
5	73.3% H <sub>2</sub> , 24.4% N <sub>2</sub> , 2.2% NH <sub>3</sub>	5

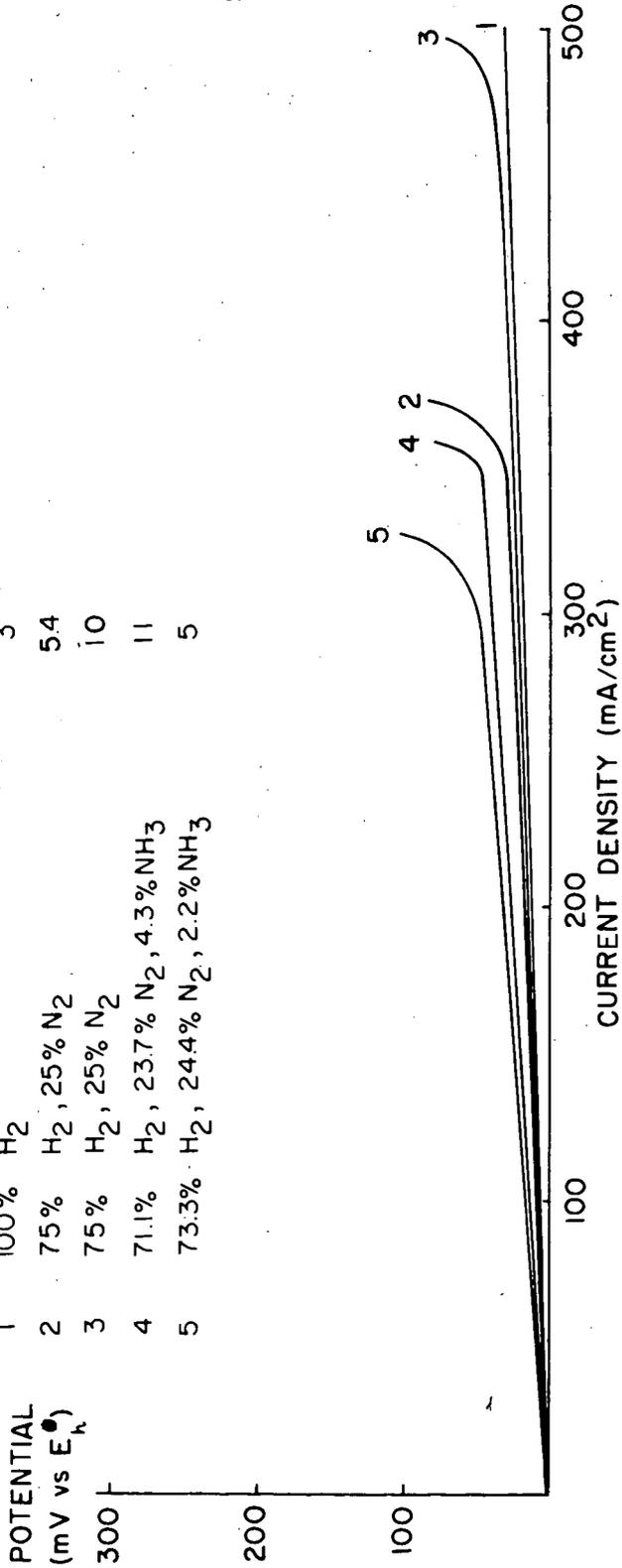


FIG. 4 ANODE POLARIZATION WITH NH<sub>3</sub>/H<sub>2</sub> STREAMS

TEMPERATURE: 200°C  
 ANODE: .0015", 75 Pd/25Ag  
 (Pd-BLACK ACTIVATED)  
 ELECTROLYTE: 75(w)% KOH  
 FUEL PRESSURE: 25 psig  
 FUEL MIXTURE: 75% H<sub>2</sub>  
 20% CO<sub>2</sub>  
 5% CO

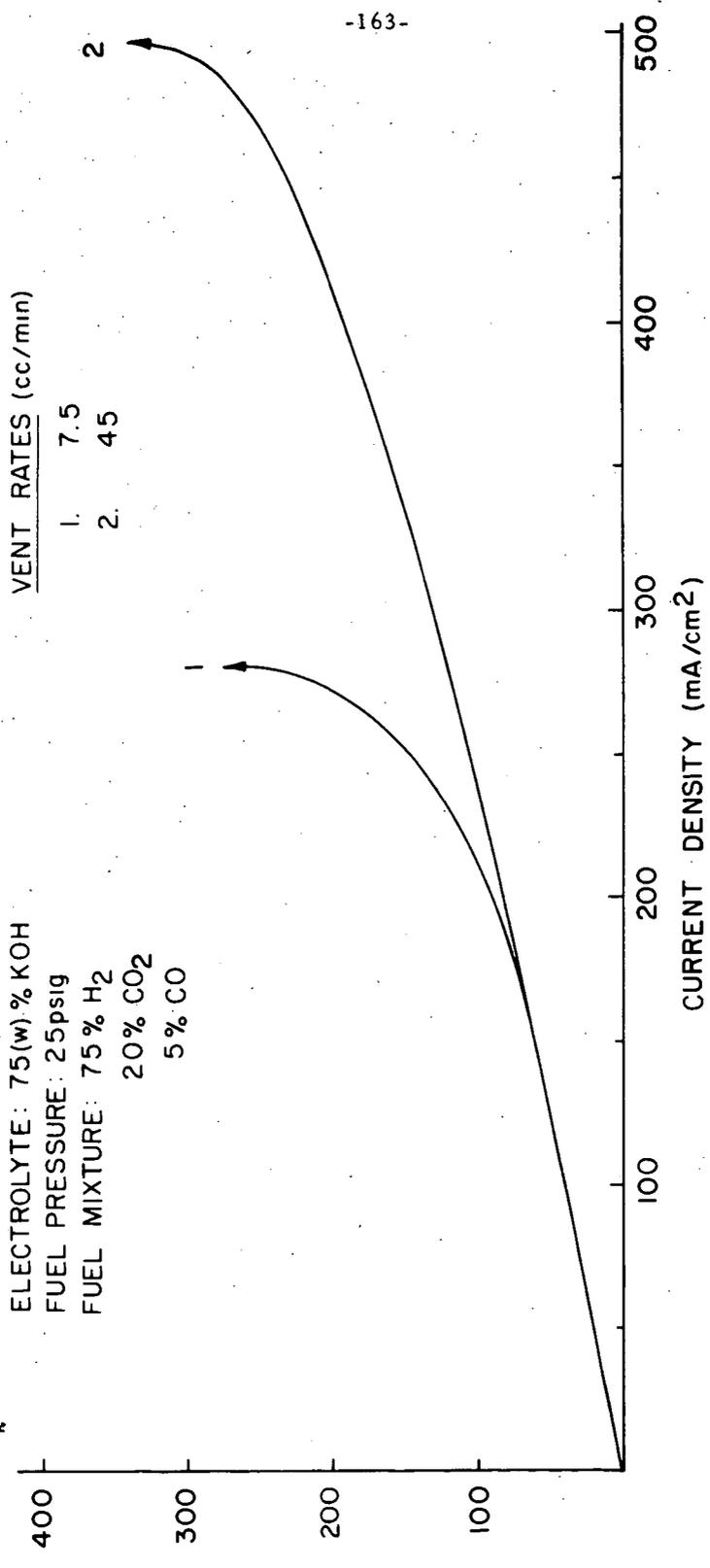


FIG. 5 ANODE POLARIZATION WITH CO/CO<sub>2</sub>/H<sub>2</sub> STREAMS