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INEXPENSIVE CATALYSTS FOR HYDRAZINE FUEL CELL ANODES

by

John Perry, Jr.

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INEXPENSIVE CATALYSTS FOR HYDRAZINE FUEL CELL ANODES

by

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Electronic Components Laboratory

August 1966

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U. S. ARMY ELECTRONICS COMMAND
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Abstract

The use of elemental iron on porous nickel substrates as a hydrazine anode has been found to give anodic current densities equal to that of palladium catalyst. Anodic current densities of 100 mA/cm^2 at 0.060 V polarization have been obtained at temperatures of 60°C , with fuel concentrations of 3M N_2H_4 in 5M KOH. The Fe hydrazine anode has operated well over 200 hours at 100 mA/cm^2 (showing stable performance). The initial anode potential vs SCE under load was -1.20 V. This voltage was maintained with little variation through the life testing.

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INEXPENSIVE CATALYSTS FOR HYDRAZINE FUEL CELL ANODES

INTRODUCTION

Fuel cells using hydrazine as a fuel have received much attention in recent years due to the high energy levels obtained. In 1965, a contract was awarded to Monsanto Research Corporation by the USAECOM for the development of a 60-watt hydrazine-air fuel cell system to be used as a power supply for military field equipment. Presently, only noble metal catalysts have been used on the anode for the oxidation of hydrazine and other fuels, such as H_2 and methanol, in fuel cell systems. Some investigators have found that less expensive metals, such as nickel boride, can be used effectively as catalysts in the oxidation of hydrazine and hydrogen.¹

Efforts are being made throughout the fuel cell area to drastically reduce the cost of fuel cell components, mainly the catalyst materials. The purpose of this investigation is to develop inexpensive non-noble metal catalysts for the oxidation of hydrazine in the hydrazine-air fuel cell systems. The goal is to obtain both high fuel efficiency and high current densities; both equal to, or better than, those presently obtained with noble metals.

This report describes preparation and test data of a non-noble metal, elemental iron, as a catalyst for the hydrazine anode. The catalyst is formed by the reduction of ferrous chloride in aqueous solution with sodium borohydride to produce fine particles of iron powder on porous sintered nickel substrates. The experimental results show that current densities from this catalyst are equal to those obtained with palladium catalysts; and at the same time, better faradaic fuel efficiencies are obtained.

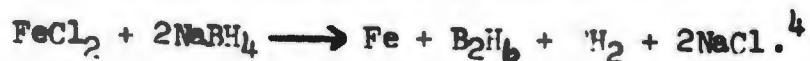
DISCUSSION

Experimental

This report will discuss only the preparation of the iron catalyst in detail and compare its performance with other catalysts. All catalysts investigated were impregnated into pores of porous sintered nickel plaques (1-1/8 x 1-1/8 x 0.030"). The plaques, nickel powder sintered onto a nickel screen, were purchased from Sonotone Corporation. The platinum, palladium, and gold electrodes were prepared by displacement reaction of the respective metals. Copper catalyst was formed by reaction of copper chloride and sodium borohydride within the pores of the plaques.

The iron catalyst was prepared by first impregnating the porous plaques with ferrous chloride solutions (100 gms of ferrous chloride in 100 ml H_2O). This was accomplished by placing the nickel plaque in a vessel containing the iron salt solution, then evacuating the air from the system; thus allowing the solution to fill the pores of the substrate. The plaques, saturated with $FeCl_2$, were shaken slightly to remove excess solution; then immersed for about 20-30 seconds in a 2% solution of sodium borohydride in water. Plaques were removed and washed several times with hot distilled water to remove traces of unreacted sodium borohydride and sodium chloride formed. After washing, the plaques were dried for³ several hours at

120°-140°C in an argon atmosphere. The reaction produced a finely divided black precipitate, which at first was thought to be ferric boride.² X-ray analysis of the precipitate formed showed it to be of Alpha iron patterns, indicating that the following reaction is probably involved



The cathodes used in the experiments were 1/8"-thick carbon electrodes with spinel catalyst (Ag-Co-Al) and wetproofed with paraffin. The cathode performance will not be discussed in this report, since it served only as a counter electrode in completing a single cell. No efforts were made to optimize its performance.

In studying the anode half-cell, a complete single cell was used (anode, separator and cathode) with a liquid junction connecting the reference to the anode as shown in Fig. 1. The two half-cells (anode and cathode) were bolted together with an ion exchange membrane and an asbestos separator in between. The ion exchange membrane served to prohibit O₂ leakage from cathode to the anode compartment; thus, allowing for more accurate gas evolution measurements at the anode. The fuel was mixed with the electrolyte and supplied to the anode compartment from a 200 ml externally connected reservoir. The fuel mixture was fed to the anode compartment by gravity. During operation the nitrogen gas generated by the reaction lifts the anolyte back into the reservoir; thus, providing anolyte circulation for the cell. When operating at elevated temperatures, the fuel was preheated in the reservoir and then fed to the cell.

Measurements

The anode potential was measured against a mercury/mercuric oxide reference electrode in the initial experiments. After the initial screening of anode catalysts for hydrazine oxidation, using Hg/HgO reference electrodes, a saturated calomel electrode was introduced into the fuel electrolyte reservoir for a closer check and evaluation of polarization data. When using HgO reference electrodes at elevated temperatures, gas bubbles appeared in the reference electrode vessel arm or leg, causing erratic readings. The use of a commercial standard saturated calomel electrode eliminated this problem.

Faradaic efficiencies were calculated using the following formula

$$\eta_F = \frac{\text{theoretical } V_{N_2}}{\text{theoretical } V_{N_2} + \frac{\text{meas. gas } V - \text{theoretical } V_{N_2}}{3}}$$

The theoretical yield of N₂ gas evolved during direct electrochemical oxidation of N₂ is 2.49 cc/min at 100 mA/cm² using electrodes of 7.28 cm² in area. However, due to high activity of hydrazine in the presence of most catalysts some self-decomposition of the hydrazine occurs producing N₂ and H₂. Thus, the measured gas volume will include gas produced from the electrochemical reaction, plus gas evolved through auto-decomposition of hydrazine (N₂ + N₂ + 2H₂). Gas measurements

were made by collecting the gas evolved from the anode compartment in a buret over water. Gas volumes were corrected for temperature, pressure and water vapor

$$V_1 = V_2 \times \frac{T_1}{T_2} \times \frac{P_2 - \text{Vap Pres H}_2\text{O}}{P_1}$$

The cell was operated at a constant load for one hour or more to allow for stable electrode performance and gas evolution. The gas was collected for a total of ten minutes to determine rate.

Voltage-current measurements were made using the Kordes-Marko current interrupter technique to eliminate IR losses.

Catalyst Study

The first set of experiments was to examine the polarization characteristics of several catalysts at room temperature, using a fuel electrolyte concentration of 3M $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in 5M KOH. The first experiment was conducted using uncatalyzed porous nickel plaques. Several uncatalyzed sintered nickel electrodes were tested; their performances varied from electrode to electrode, probably due to oxide films formed during storage. No effort was made to clean the electrodes. It was felt that the influence of the oxide in the study of the various catalyst materials would be void after catalyzing the nickel substrates.

Gold, copper, palladium, platinum, nickel boride and iron were catalysts studied on sintered nickel substrates. Fig. 2 shows the potential-current density data obtained from these catalysts (anodes vs Hg-HgO reference). The initial experiment at 24°C showed Pt to be superior to the others with iron, Ni_2B , and Pd next best in descending order. Gold and copper catalysts gave performance less than the uncatalyzed nickel plaques. An ammonia odor was detected from the cells with Au and Cu after several hours of operation. This was probably an indication of an ammonia reaction mechanism taking place. The high performance of iron catalysts was both surprising and interesting in that iron has not been considered as an anode catalyst in fuel cell studies. This is because the overvoltage is excessive for the oxidation of a simple fuel such as H_2 . Several investigators have stated that hydrazine is not oxidized directly at the anode, but is decomposed to nitrogen and molecular hydrogen. This hydrogen is absorbed on the electrode and subsequently oxidized.

The performance of Pd, Ni_2B , and Fe catalysts had a spread of approximately 0.025 volts at 100 mA/cm² indicating that the performance of these catalysts is nearly equal at room temperature. The Fe electrode catalyst was chosen for further study because it is an inexpensive metal with very low hydrazine auto-decomposition rates on both open circuit and on drain at room and elevated temperatures. Table No. I shows the rates of gas evolved at open circuit indicating auto-decomposition of the N_2H_4 by the catalysts ($\text{N}_2\text{H}_4 + \text{catalyst} \rightarrow \text{N}_2 + 2\text{H}_2$). Note in this table that the catalyst Fe shows a lower gas evolution rate at open circuit than Ni, indicating that it is less active in promoting auto-decomposition at room temperature. When auto-decomposition occurs at open circuit and closed circuit conditions,

the fuel energy is being wasted and passed off in the form of hydrogen gas. The build-up of gaseous products could cause high internal resistance and concentration polarization by prohibiting fuel contact at the catalyst sites. The use of iron as catalyst on sintered nickel plaques has been shown to reduce the self-decomposition of hydrazine and at the same time maintain good electrical and electrochemical characteristics.

Practical hydrazine-air fuel cell systems will operate at a temperature range of 125°F to 175°F. A temperature of 60°C (140°F) was selected to study the various catalysts, for it is in this range that most hydrazine-air fuel cells will be operated. It was found that both Pt and Ni₂B gave higher potentials at the same current densities as compared to the others. Figure 3 shows voltage-current curves of these catalysts tested at 60°C. The voltage is recorded as anode vs the SCE electrode. Surprisingly, the uncatalyzed nickel oxide plaques gave current densities near that of Pd and Fe catalysts. The potential of iron catalyzed electrodes is probably a mixed potential caused by both the nickel substrate and iron catalyst, but it is significant to note that the addition of iron improves the electrode performance. This being an exploratory investigation of catalysts, no effort was made to optimize the catalysts loadings for maximum performance. The catalysts loadings in Fig. 3 were: Fe (4 mg/cm²), Pd (15 mg/cm²), Pt (1.5 mg/cm²), and Ni₂B (5 mg/cm²). The performance of nickel plaques with iron deposited on the surface was lower than the electrodes with Pt and Ni₂B catalysts. Yet, it is being considered here as a good electrode and warrants further investigation, because of its high faradaic fuel efficiency of 98% as compared to the other metals of 89% and lower. The fuel utilization can be an important factor in practical fuel cell systems, from a logistical standpoint. It seems that the Fe catalysts on the nickel plaques retard the self decomposition of N₂H₄ during the oxidation process. Table I shows a comparison of gas evolution rates of the various catalysts at 100 mA/cm² drain operating at 60°C.

Life Testing

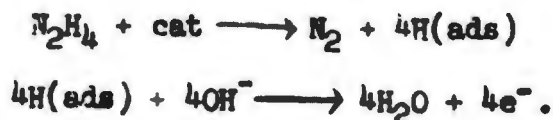
A life test was conducted using an Fe catalyzed electrode; the cell performance and life is shown in Fig. 4. The cell was operated at room temperature for 110 hours (intermittent loads of 8 hours a day) at 100 mA/cm² to measure the voltage stability of the electrode. After 110 hours of operation at ambient room temperature the temperature of the fuel mix in the reservoir was increased to 70°C and the cell operated at 60°C. The anode potential increased under load to 1.20 V vs SCE and maintained this average for more than 120 hours before signs of decrease in performance; at which time the wax wetproofing on the cathode began to breakdown. As can be seen in the Fig. 4, the potential was fairly stable at the 60°C temperature. It is believed that the wax wetproofing diffused across the matrix and began to poison the anode electrode.

Figure 5 shows the performance of the cell after 162 hours of operation at 100 mA/cm². The anode potential was approximately 0.974 volts vs H₂ electrode. The oxidation potential of hydrogen is 0.825 volts vs H₂ reference; thus, indicating that the oxidation reaction is not solely that of H₂, brought about by the decomposition of N₂H₄ into N₂ + 2H₂. The same anode has operated over 200 hours as of the date of this writing.

Figure 6 shows another life test of an Fe anode using a Teflon wetproofing on the cathode.

SUMMARY

It has been shown that Fe, an inexpensive metal, can be used as a catalyst for the hydrazine anode. The iron catalyst used in this study reduces the auto-decomposition of hydrazine and also the tendency of the substrate materials (sintered nickel) to oxidize H_2 . No effort was made during this period to determine the exact electrode mechanism. It is believed, however, that probably a mixed oxidation potential is involved resulting in partial oxidation of hydrazine through $N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^-$ route and the other reaction through the decomposition of hydrazine by the following¹



In conclusion, it is believed that iron can be used as an anode electrode catalyst on sintered nickel to give practical current densities and to increase faradaic fuel efficiencies.

ACKNOWLEDGEMENT

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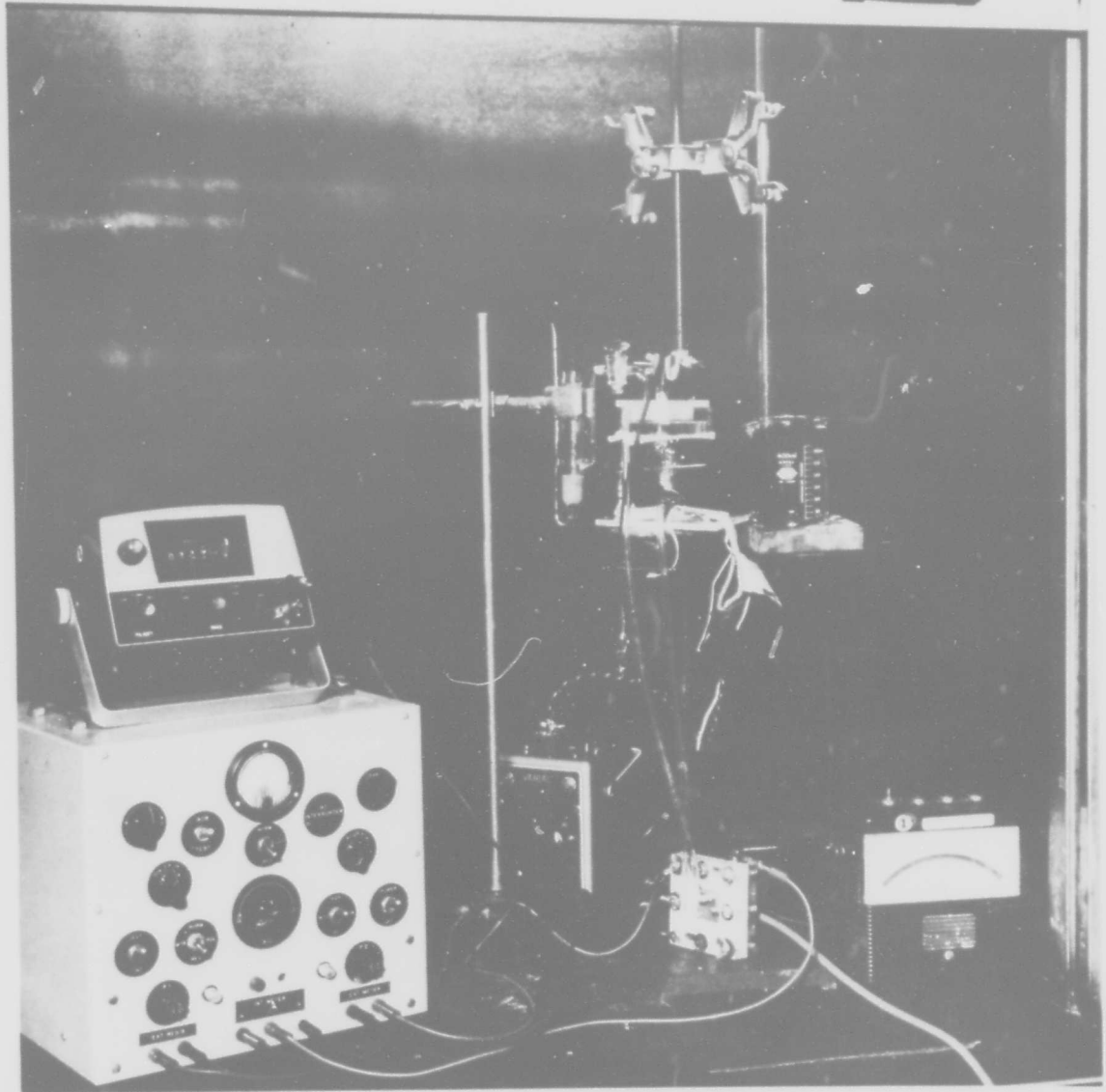


FIG. 1 HYDRAZINE FUEL CELL (EXPERIMENTAL) GROUP VIEW. SHOWING COMPONENTS

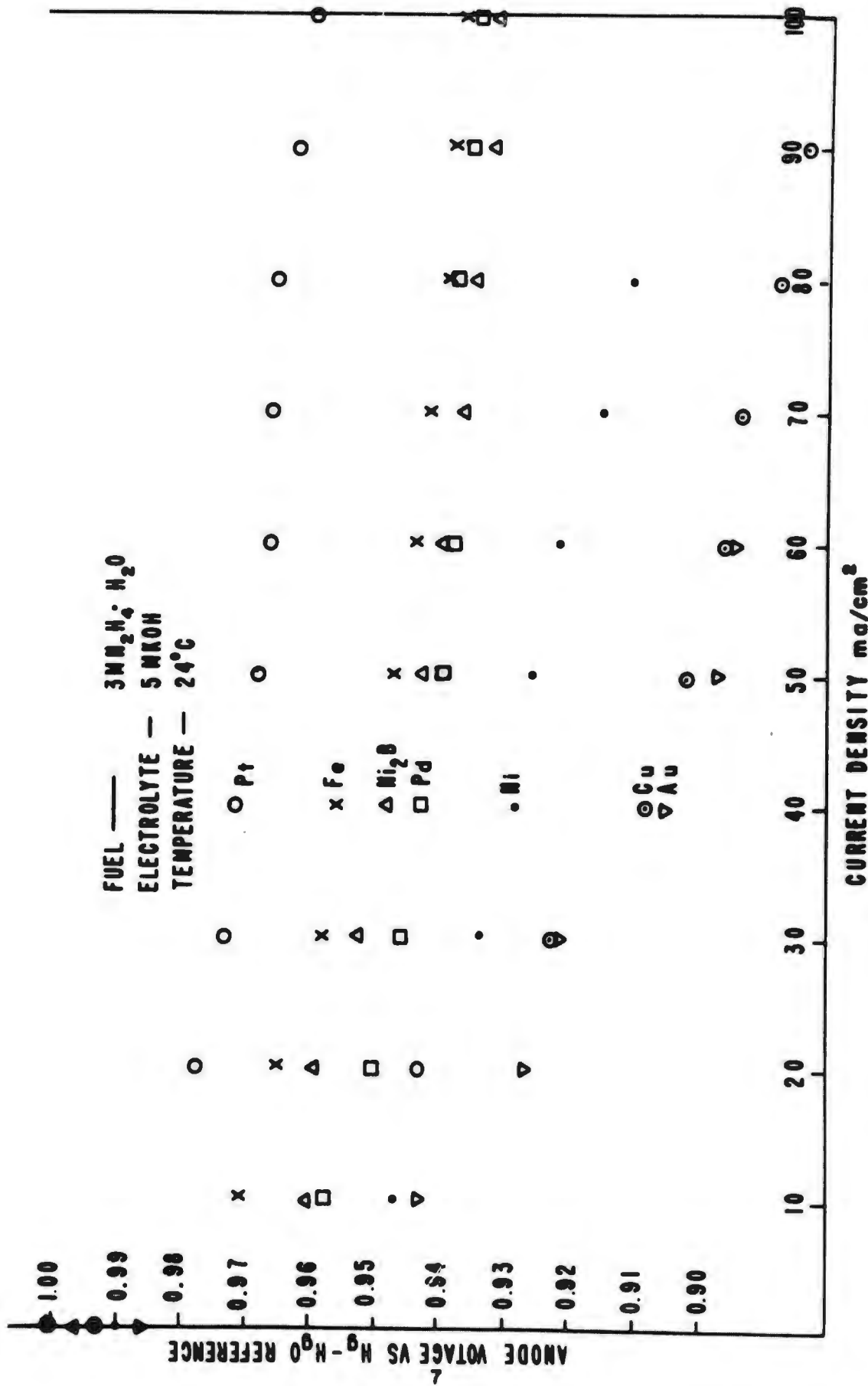


FIGURE 2. VOLTAGE - CURRENT CURVES FOR HYDRAZINE ANODES EMPLOYING POROUS SINTERED NICKEL SUBSTRATES, WITH NICKEL BORIDE, IRON, COPPER AND GOLD AS ACTIVE CATALYSTS

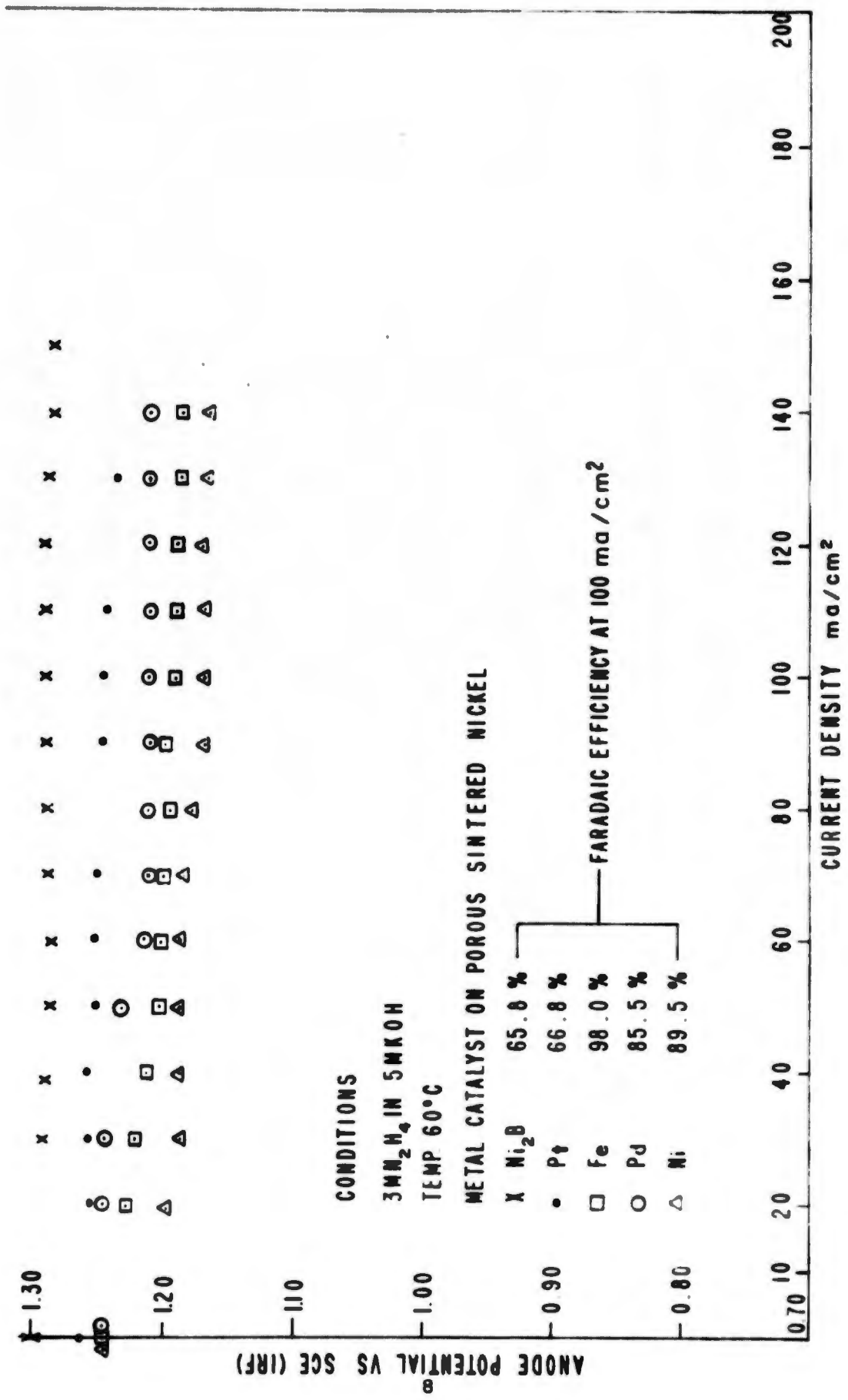


FIGURE 3. VOLTAGE-CURRENT CURVES FOR EXPERIMENTAL HYDRAZINE ANODES OPERATING AT $60^\circ C$

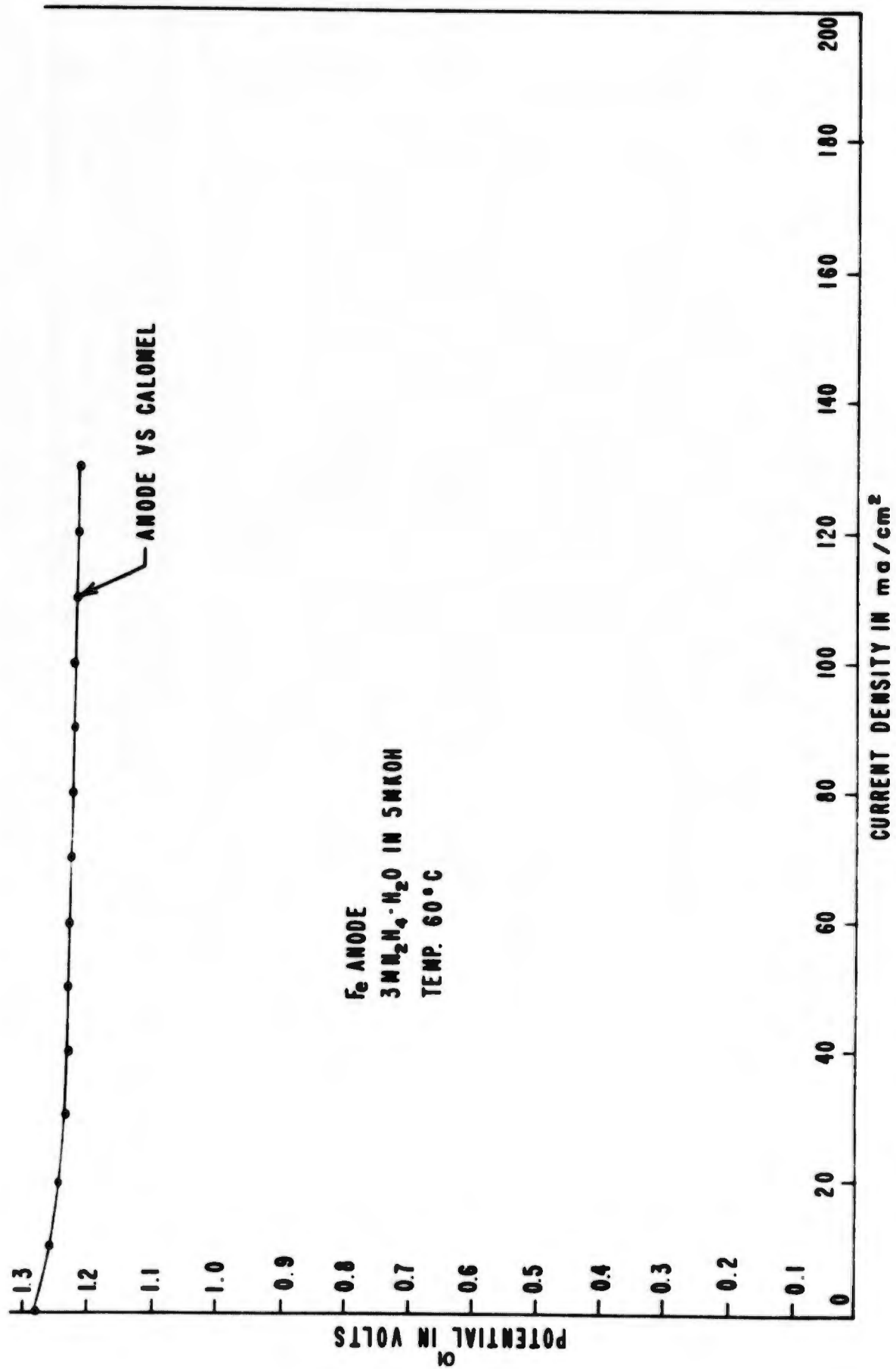


FIGURE 5. VOLTAGE-CURRENT CHARACTERISTICS OF HYDRAZINE ANODE AFTER 162 HRS OF OPERATION AT 100 mA/cm²

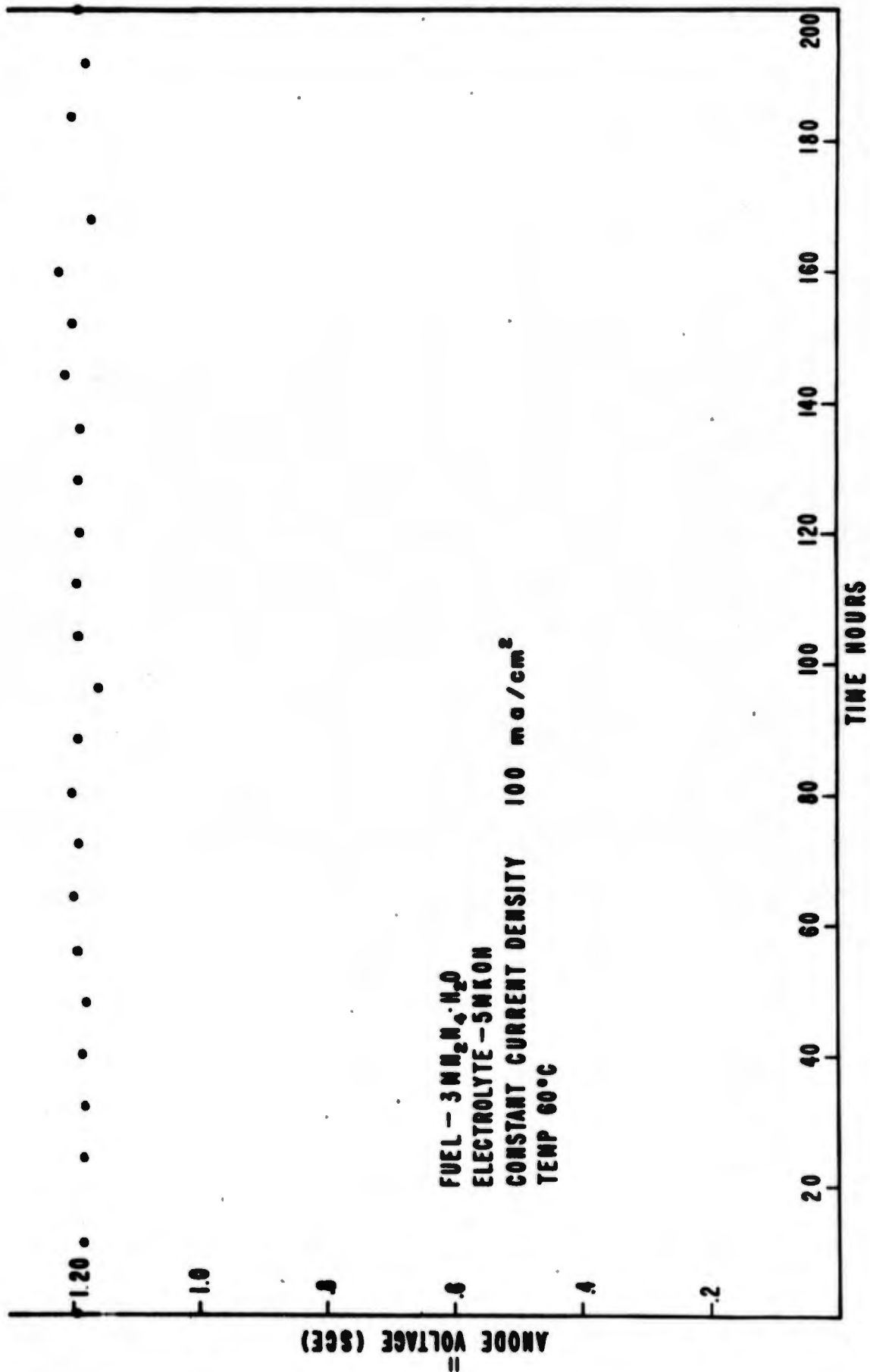


FIGURE 6. LIFE TEST OF F₀ HYDRAZINE ANODE

CATALYST	OCV - 24°C	100 ma/cm ² -60°C	THEORETICAL N ₂ BY PRODUCT AT 100 ma/cm ²
Fe	0.12 cc/min	2.6 cc/min	2.49 cc/min
Pd	0.1 cc/min	3.8 cc/min	2.49 cc/min
Ni ₂ O	0.35 cc/min	6.4 cc/min	2.49 cc/min
Pt	0.5 cc/min	6.2 cc/min	2.49 cc/min
Ni	0.14 cc/min	3.4 cc/min	2.49 cc/min

TABLE I MEASURED GAS EVOLUTION AT VARIOUS EXPERIMENTAL HYDRAZINE ANODES

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14. KEY WORDS Fuel Cell Battery Electrodes Hydrazine	LINK A		LINK B		LINK C	
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