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PREPARATION AND EVALUATION OF ADVANCED ELECTROCATALYSTS FOR PHOSPHORIC ACID FUEL CELLS

4TH QUARTERLY REPORT

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ABSTRACT

In this report, results are presented which show that alloy catalysts have hydrogen oxidation performance levels which match those of the best platinum on carbon electrocatalysts. In addition, carbon monoxide poisoning tolerance for the alloy catalysts is as good as the best platinum on carbon electrodes.

Performance testing was conducted in 100% H_3PO_4 and results are shown at temperatures from 120°C to 210°C. Comparison of these results to platinum on carbon catalysts show that the apparent activation energy is similar at 4-6 kcal/mole.

Since surface characterization of this catalyst is important to explain its performance, several approaches and pitfalls to the elucidation of the surface characterization are presented.

1. OBJECTIVE AND SCOPE OF WORK

The overall objective of this electrocatalysis program is to define the feasibility of lowering the electrocatalyst cost and increasing the activity in phosphoric acid fuel cells, as a way to increase the commercial viability of fuel cells for producing electric power.

The specific objectives of the present tasks are the preparation of a series of high surface area electrocatalysts for evaluation in phosphoric acid fuel cells. This involves fabrication of efficient gas-diffusion electrode structures and determining their electrochemical parameters for hydrogen oxidation and oxygen reduction. When possible, new experimental techniques and theoretical interpretations will be forwarded towards an understanding of the relevant electrochemical parameters.

2. Summary of Previous Work

This report covers the fourth quarter period of research and testing on NASA DEN-3-176. Previously, results for the performance of platinum supported on a furnace black (Vulcan XC-72R), for hydrogen oxidation with 100% hydrogen and hydrogen poisoned with 1 and 10% carbon monoxide at temperatures from 125°C to 240°C were given. The catalysts were prepared using an impregnation technique and performance tests were conducted in 104% H_3PO_4. Subsequent testing showed improved performance and tolerance to carbon monoxide when the acid concentration was dropped to 100%. Results were also reported for the oxygen reduction reaction at various temperatures on flooded electrode structures using platinum supported on acetylene black as an electrocatalyst. Since these flooded structures produced an electrode operating under diffusion control, a double Tafel slope was obtained from which the single Tafel slope was calculated. This Tafel slope value was found to be 90-95 mV/decade.

Optimized electrode structures showed the best performance characteristics for this catalyst (10% platinum on Vulcan XC-72R). Hydrogen oxidation and carbon monoxide tolerance measurements for a 10% platinum on Consel I catalyst made into gas diffusion (30% PTFE and flooded (2-1/2% PTFE) electrodes) clearly showed that the extent of carbon monoxide poisoning is electrode structure dependent. Poor electrode structures show greater loss of performance than optimized structures at the same carbon monoxide concentration. Oxygen reduction data for a 10% platinum on acetylene black catalyst were also reported at temperatures from 140°C to 230°C.

Electrodes were tested which contained from 2-1/2% to 30% PTFE and showed that as PTFE content increased and therefore gas diffusion improved, carbon monoxide tolerance improved. A literature survey was conducted which led to the decision to test platinum-palladium alloys as electrocatalysts for hydrogen oxidation. Preliminary tests showed the alloy performance nearly equal to platinum with a significant reduction in electrocatalyst cost.

3. Technical Progress

3.5. Task 5 - Preparation of Platinum-Based Carbon-Supported Electrocatalysts

It was shown in the last quarter that platinum group metal compounds (PGM) could be formed which exhibit activities comparable to platinum for the oxidation of hydrogen in the presence of carbon monoxide. In particular, it was demonstrated that an electrode containing 0.3 mg PGM/cm^2 performed as well as an electrode containing 0.5 mg Pt/cm^2 when the feed stream consisted of 10% CO/balance hydrogen or 30% CO balance hydrogen.

The hydrogen oxidation mechanism, and therefore the reaction rate, will be influenced by the catalyst surface composition. Furthermore, the effect of carbon monoxide poisoning on the reaction rate must certainly be influenced by the surface composition.

The surface composition is related to the bulk composition although it is not likely to be identical because of surface segregation (Burton and Garten, Adv. Mat. in Cat., 33, 1977). Catalysts were prepared, therefore, with different ratios . Electrocatalysts containing 0, 35, 65, and 100 a/o Pt were prepared at 4 w/o PGM loading. The carbon support was Consel I.

Alloy catalysts at the 35 a/o Pt level were prepared at loadings of 2, 4 and 10 w/o PGM to examine the influence of electrode structure on the performance of PGM electrocatalysts. Previously reported results in this contract clearly demonstrated that structure has a dramatic effect on carbon monoxide tolerance (3rd Quarterly Report).

Based on the results of the performance of these catalysts (See Task 7 this report), an additional alloy catalyst containing 75 a/o Pt was prepared. Test results for this catalyst will be reported later.

3.6. Task 6 - Characterization of Platinum-Based Carbon-Supported Electrocatalysts

Characterization of high surface area, supported alloy catalysts is a difficult and challenging problem. With non-alloy supported catalysts, physical characterization is fairly complete when the crystallite size distribution and morphology have been determined. This is not to imply, however, that these determinations are always a simple matter. Electron microscopy may be used to obtain the morphology and crystallite size distribution. Gas phase adsorption methods such as CO slug flow and hydrogen titration provide estimates of the active metal area. Active surface area estimates can also be obtained by electrochemical techniques. In this procedure the area under the hydrogen atom adsorption peaks in the voltammogram is measured to give an estimate of the total coulombic charge required for hydrogen deposition. The active metal area is related to this charge. Finally, x-ray line broadening can also be used to determine both crystallite size and lattice dimensions. The latter has been used to determine bulk alloy compositions (Sinfelt, in Adv. Mat. in Cat., 1, 1977).

Since alloying introduces an additional parameter, i.e. surface composition, interpretation of data obtained from the previously mentioned analytical techniques is difficult. Electron microscopy, for example, would still be capable of providing crystallite morphology and size distribution information, but this technique cannot resolve the surface composition of small crystallites. Gas phase adsorption techniques require knowledge of the nature of chemisorption. The quantity of gas adsorbed is related to the number of available surface atoms, which when coupled with the chemisorption stoichiometry and the metal atom cross section, can be used to estimate the active surface area metal catalysts. Complications may arise when using this method for determination of supported alloy catalyst surface areas.

As a result, the quantity of adsorbed carbon monoxide cannot be directly related to surface area without prior knowledge of the surface composition. Cyclic voltammograms are unique to the metal which is potential cycled. The voltammogram of platinum, for example, is clearly understood so that determination of the active metal area is straightforward.

Addition of an alloying element, however, may sufficiently alter the voltammogram to obscure the interpretation. X-ray line broadening can be used to determine average crystallite size down to about 50 Å. The alloy catalysts prepared in Task 5 should have crystallites on the order of 25-30 Å. The determination of lattice constants of alloys by x-ray techniques have been used to determine bulk alloy compositions (Sinfelt, Carter, and Yates, J. Cat., 24, 283, 1972) by the correlation developed by Vegard (Dekker, Solid State Physics, 104, 1957).

This procedure has been successful for large crystallites and bulk alloys. It is not known if this method can resolve the composition of high surface area supported alloy catalysts.

Based on this discussion, three techniques have been chosen to characterize alloy catalysts. The first method is the CO slug flow technique which has been used to determine surface areas of platinum catalysts in previous tasks. The raw data for a platinum supported on Vulcan XC-72R catalyst is shown in Figure 1. The area between the blank slug and the slug over the 0.11 g catalyst sample is the quantity of carbon monoxide which has chemisorbed on platinum surface atoms. The surface area for this catalyst is estimated to be 100 m^2/g. The difficulties encountered with the application of the CO slug flow method for determination of alloy surface areas have already been described. In addition, it is now clear that a colloidal procedure used to make the alloy catalysts in Task 5 yields catalysts with high impurity coverages which impair adsorption of CO. A more rigorous cleaning technique for the alloy catalysts has been formulated and details of the procedure will be reported at a later date. The second technique is the electrochemical adsorption method. Since little is known concerning the characteristics of alloy ECA's, we are in the process of identifying the location of oxidation and reduction peaks on the voltammograms.

These results will be used to interpret voltammograms for the alloy compositions so that a methodology for estimating alloy surface areas can be defined. The final area of characterization employed in this task is the temperature programmed method. A test stand has been constructed that is capable of performing temperature programmed adsorption, desorption, or reaction. The apparatus is under control of a 16 bit digital microprocessor which allows input of any temperature program by means of software modifications. The component schematic is shown in Figure 2 and the software flow chart is given in Figure 3. Since this hardware and software is quite general, it is capable of programming any heating/cooling system. Some timing sequences may have to be adjusted according to the thermal characteristics of the reactor, but that is trivial. The hardware (digital circuitry and analog control circuitry) were coupled to the micro-computer, the program loaded and the total system performed in the required manner.

3.7 Task 7 - Catalytic Activity of Platinum-Based Carbon-Supported Electrocatalysts

In the 3rd Quarterly Report the performances for two electrocatalysts for hydrogen oxidation were reported. Both of these catalysts contained approximately 10% metal loading.

The performances of gas diffusion electrodes prepared from these catalysts (Figures 14 and 15, 3rd Quarterly Report) compare favorably to the performance of a platinum supported catalyst. These performances for hydrogen oxidation and carbon monoxide tolerance are very promising.

When this catalyst is tested next month, the performance data will show if a minimum exists at this point in the curve.

The alloy catalysts prepared in Task 5 at the 35 a/o Pt level and 2, 4 and 10 w/o PGM were fabricated into gas diffusion electrodes and tested for performance as anodes under H_2, 10% CO/H_2 and 30% CO/H_2. The performance results are reported in Figures 8, 9 and 10. These figures were then used to construct Figure 11 which summarizes the performance data at 25 mV polarization. It is demonstrated in Figure 8 that the expected increase in performance with increased electrode loading is not realized. The electrode thickness has been held constant. The data would suggest that these electrodes are operating in a diffusion limited regime; however, it should be noted that electrocatalyst surface area has not been factored into the analysis. As a result, this interpretation of Figure 11 is not conclusive.

The apparent activation energy for hydrogen oxidation with and without carbon monoxide in the fuel gas is determined by plotting the reaction rate as a function of temperature.

The data reported here can be compared to similar data obtained for platinum on Vulcan XC-72R as reported in our April to June, 1980 Quarterly Report. In Figure 12 the anode performance of electrode P-54 is shown as a function of temperature while operating on 100% H_2. Electrode P-54 was made from a 10% PGM catalyst, and has a loading of 0.5 mg PGM/cm^2. Figures 13 and 14 show the same electrode's performance on 10 and 30% carbon monoxide in H_2, as it varies with temperature. In Figures 15, 16 and 17 we show the performance data for electrode P-55 which is a 4% PGM catalyst at a loading of 0.2 mg PGM/cm^2 on 100% H_2 and 10 and 30% carbon monoxide in H_2. The potential data reported in the Figures 12-17 has been corrected for the potential change due to dilution of the

100% H_2 to 90 and 70% by 10 and 30% carbon monoxide. Comparing the hydrogen oxidation performance of electrode P-54 (0.5 mg PGM/cm^2) with electrode P-55 (0.2 mg PGM/cm^2) it is apparent that at a current density of 200 mA/cm^2 (approximately the fuel cell operating current density) only an additional 1-4 mV polarization is incurred by dropping the loading from 0.5 mg PGM/cm^2 to 0.2 mg PGM/cm^2. The lack of significant performance loss seen on the 0.2 mg PGM/cm^2 electrode versus the 0.5 mg PGM/cm^2 electrode is probably due to a decrease in crystallite size achieved on the lower loaded catalyst, which of course increases the surface area available for reaction.

Performance data usually agree within 5 mV at 200 mA/cm^2. Optimization of the electrode structure could eliminate even this small difference and probably improve the performance of this alloy over the performance of pure platinum. The temperature variation of the reaction rate for 100% H_2 for these catalysts (4% PGM/Consel I and 10% PGM/Consel I) are plotted in Figures 18 and 19. Measurements of the slopes at 10 and 25 mV gives an apparent activation energy of 4 kcal/mole at both potentials for the 10% PGM/Consel I catalyst and an apparent activation energy of 5.6 kcal/mole and 4.9 kcal/mole at 10 and 25 mV respectively for the 4% PGM/Consel I catalyst. Within the limitations of the experimental error these values are approximately equal to those found for 10% Pt/Vulcan XC-72R. Such low activation energies usually indicate a diffusion controlled reaction, and we therefore cannot at this time comment upon the mechanism of H_2 oxidation.

The performances of the 10% PGM/Consel I and 4% PGM/Consel I catalysts with 10% and 30% carbon monoxide in the H_2 at various temperatures is shown in Figures 13, 14, 16 and 17. Comparison of these data with 10% Pt on Vulcan catalyst as reported in our April-June 1980 Quarterly Report shows that at low temperature (120°C) the alloy catalysts appear more tolerant to carbon monoxide poisoning in the 200-300 mA range and at least as tolerant to carbon monoxide poisoning at 180°C in the 200-300 mA/cm^2 range. Again optimization of the structure may improve the carbon monoxide tolerance of these catalysts since it has been shown in our Monthly Reports #7 and #8 for 1980 that the structure of the electrode plays an important rôle in carbon monoxide poisoning tolerance.

In Figures 18 and 19 the temperature dependent current density at 10 and 25 mV and 10 and 30% carbon monoxide levels is plotted along with the 100% hydrogen data. By plotting the data this way in Figures 18 and 19 it is easy to generate the apparent adsorption isotherms for carbon monoxide on the catalyst as a function of temperature and electrode potential. Figures 20 and 21 show the results of these calculations. We take the liberty to draw a curve through two points since we know that at zero percent carbon monoxide, $1-\theta_{CO}$ is equal to 1.0, therefore it seems logical that the trend will curve upward at low carbon monoxide percentages in a manner similar to that shown for 10% Pt/Vulcan XC-72 shown in Figure 5 of our April-June 1980 Quarterly Report. Comparison of site availability as shown in Figures 20 and 21 for these two catalysts (4% PGM/Consel I and 10% PGM/Consel I) with previously generated data on platinum (10% Pt/Vulcan XC-72) in Quarterly Report for April-June 1980 shows that site availability for PGM catalysts appears to be lower than that for platinum.

The above site availability comparison must be approached carefully. Although the site availability of the PGM catalyst is apparently lower than that for platinum, we cannot be totally certain that structural (diffusion) factors are not rendering such a comparison invalid at this time. Only if both catalysts are under 100% activation control or have the same mix of diffusion and activation control would this comparison be valid. Optimization of electrode structures will change the $1-\theta_{CO}$ ratios.

Even though the relative number of sites for hydrogen oxidation for our catalysts (4% PGM and 10% PGM) is lower than that for 10% platinum on Vulcan XC-72, it may be possible that the total number of active sites is greater and that a greater dispersion has been achieved.

Our progress in reducing the cost of the anode is shown in Figure 22. The solid line is the performance versus cost for 10% Pt on Vulcan XC-72R at various electrode loadings and is constructed from data obtained in this laboratory. The performance is based on the polarization at 200 mA/cm^2 for a 10% CO/90% H_2 fuel. The dollar cost is normalized to the cost of a 0.5 mg Pt/cm^2 electrode. As a further point of reference, the commonly accepted performance value for 80% H_2, 2% CO and 18% CO_2 with .25 mg Pt/cm^2 at 180°C is 25 mV polarization at 200 mA/cm^2. This point is shown as the solid circle in Figure 22. It is clear that any electrocatalyst which falls below the line for the state-of-the-art 10% Pt on Vulcan XC-72R electrocatalyst will result in lowering the cost of the anode. All of our alloy preparations operate in this region of lower cost, with the P-50 catalyst combination preferred at this time.

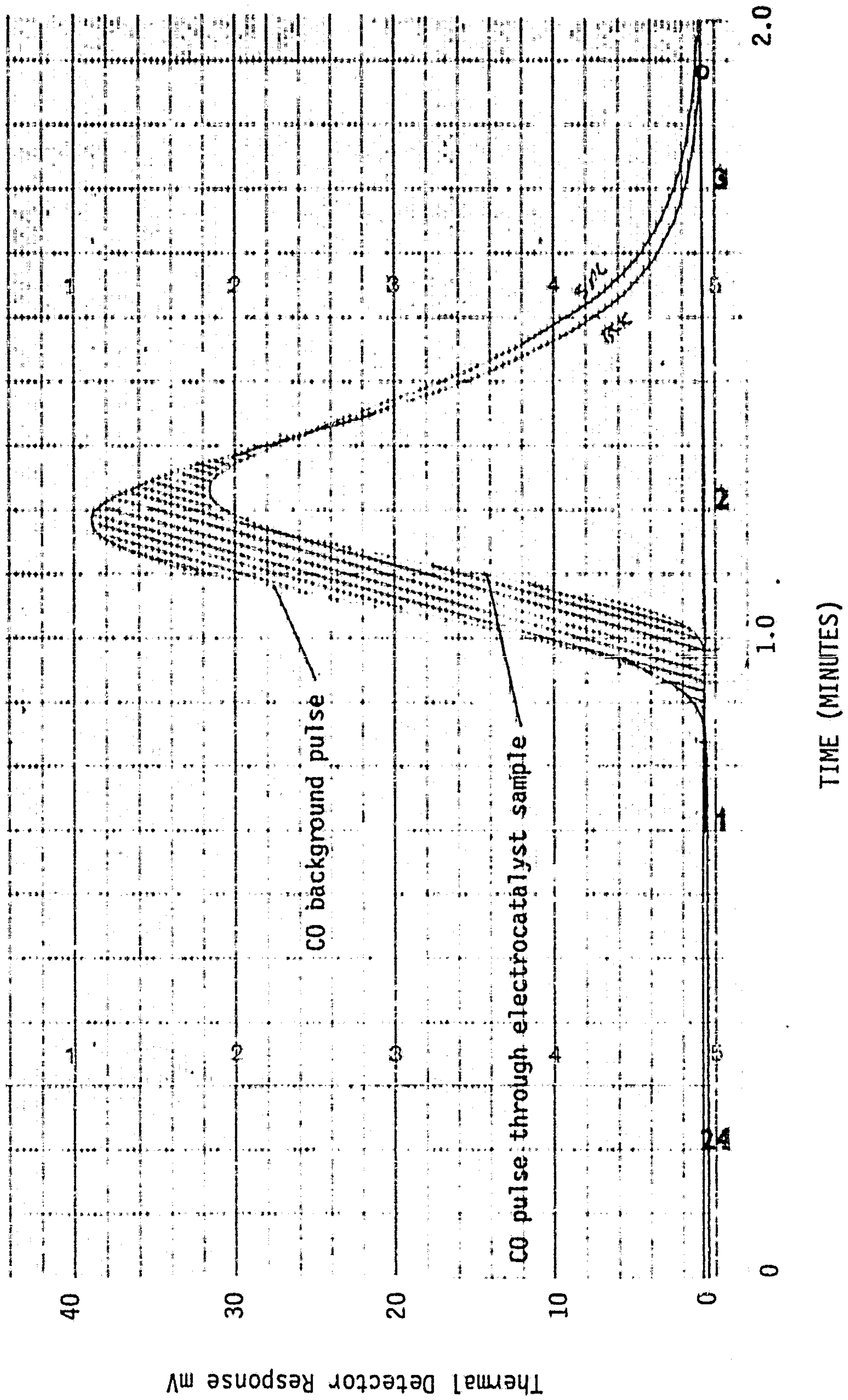

CO background pulse
CO pulse through electrocatalyst sample
TIME (MINUTES)
0
1.0
2.0
Thermal Detector Response mV
0
10
20
30
40

Figure 1.

COMPONENT SCHEMATIC

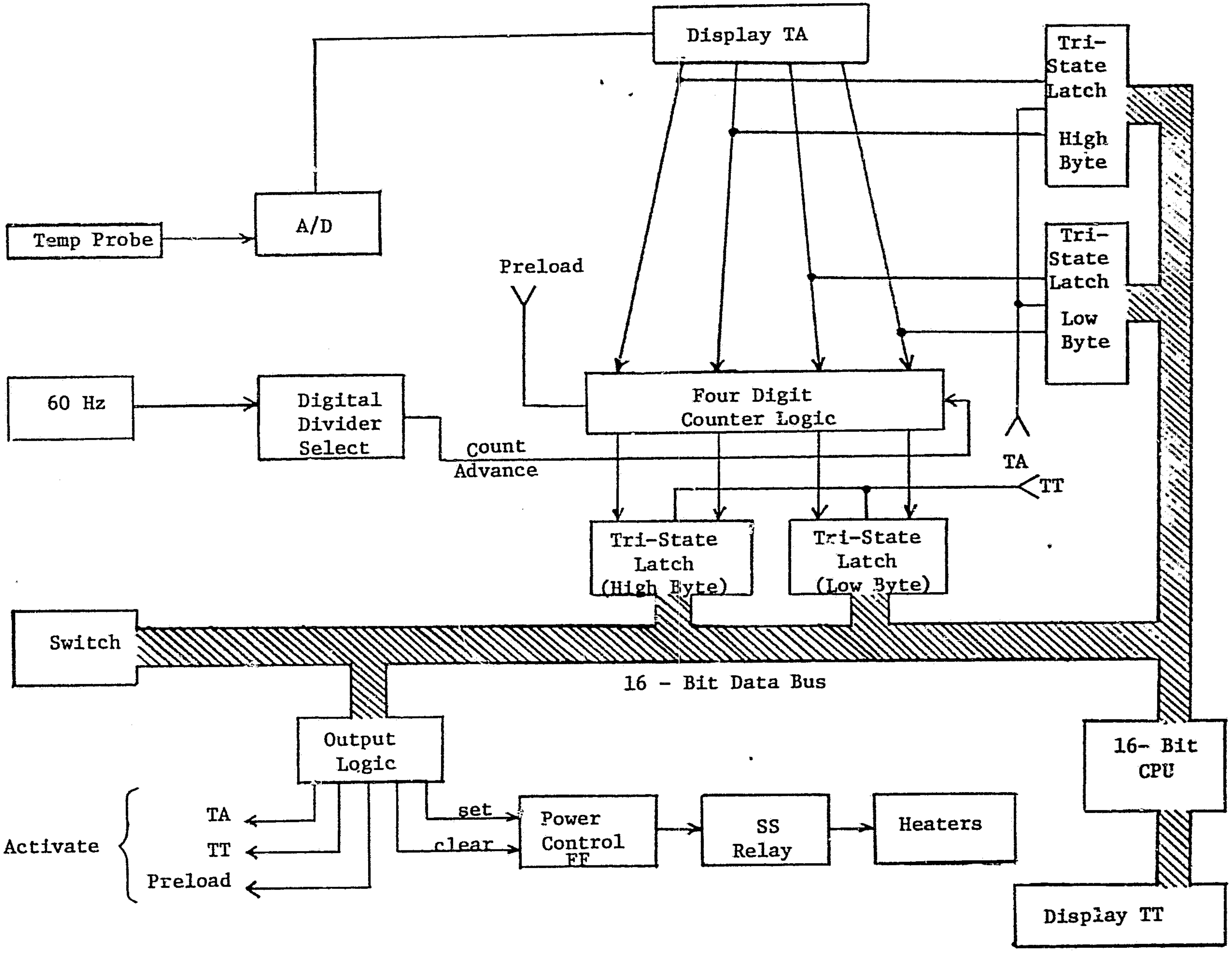
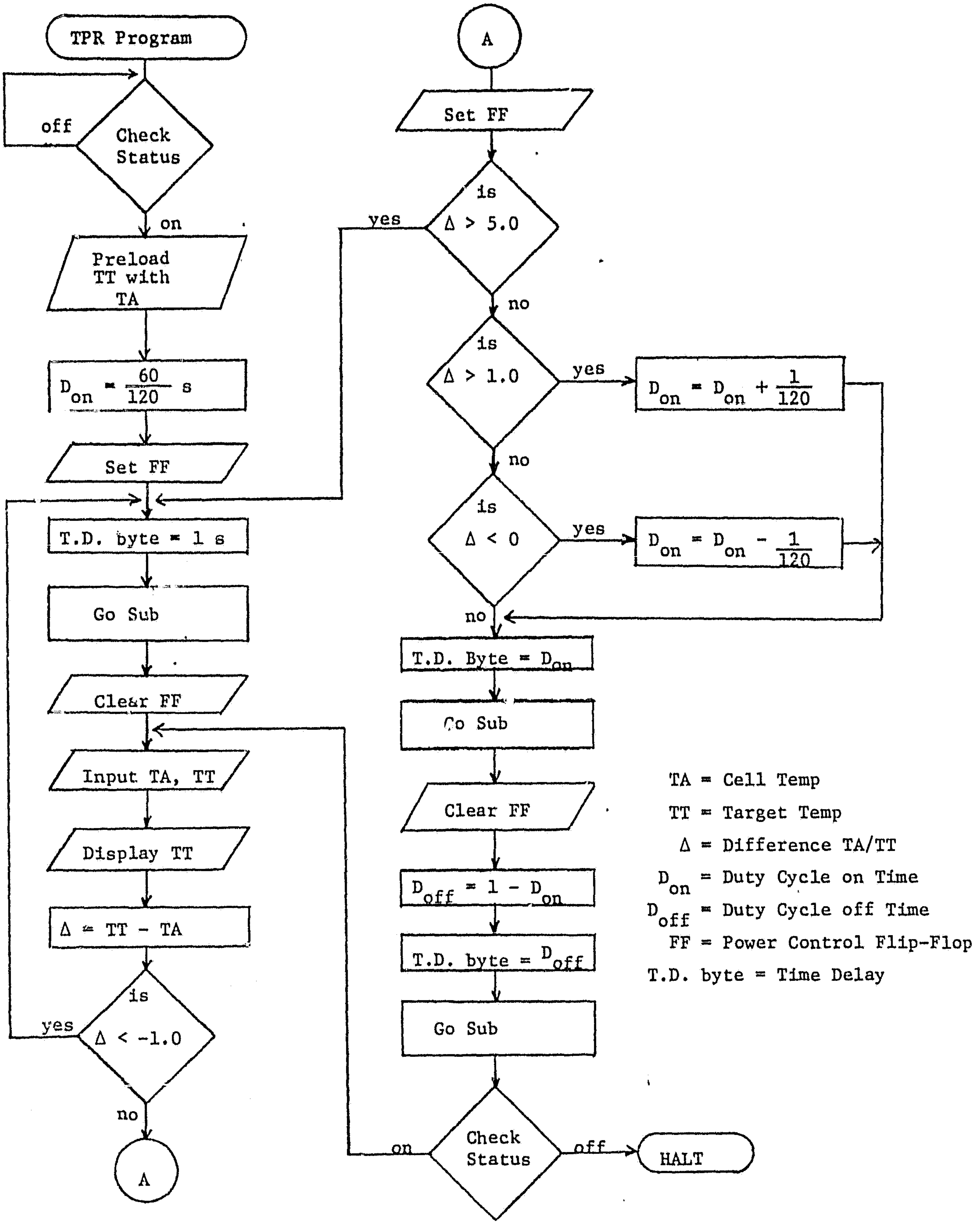


Figure 2.

SOFTWARE FLOWCHART



TA = Cell Temp
TT = Target Temp
Δ = Difference TA/TT
D_{on} = Duty Cycle on Time
D_{off} = Duty Cycle off Time
FF = Power Control Flip-Flop
T.D. byte = Time Delay

Figure 3.

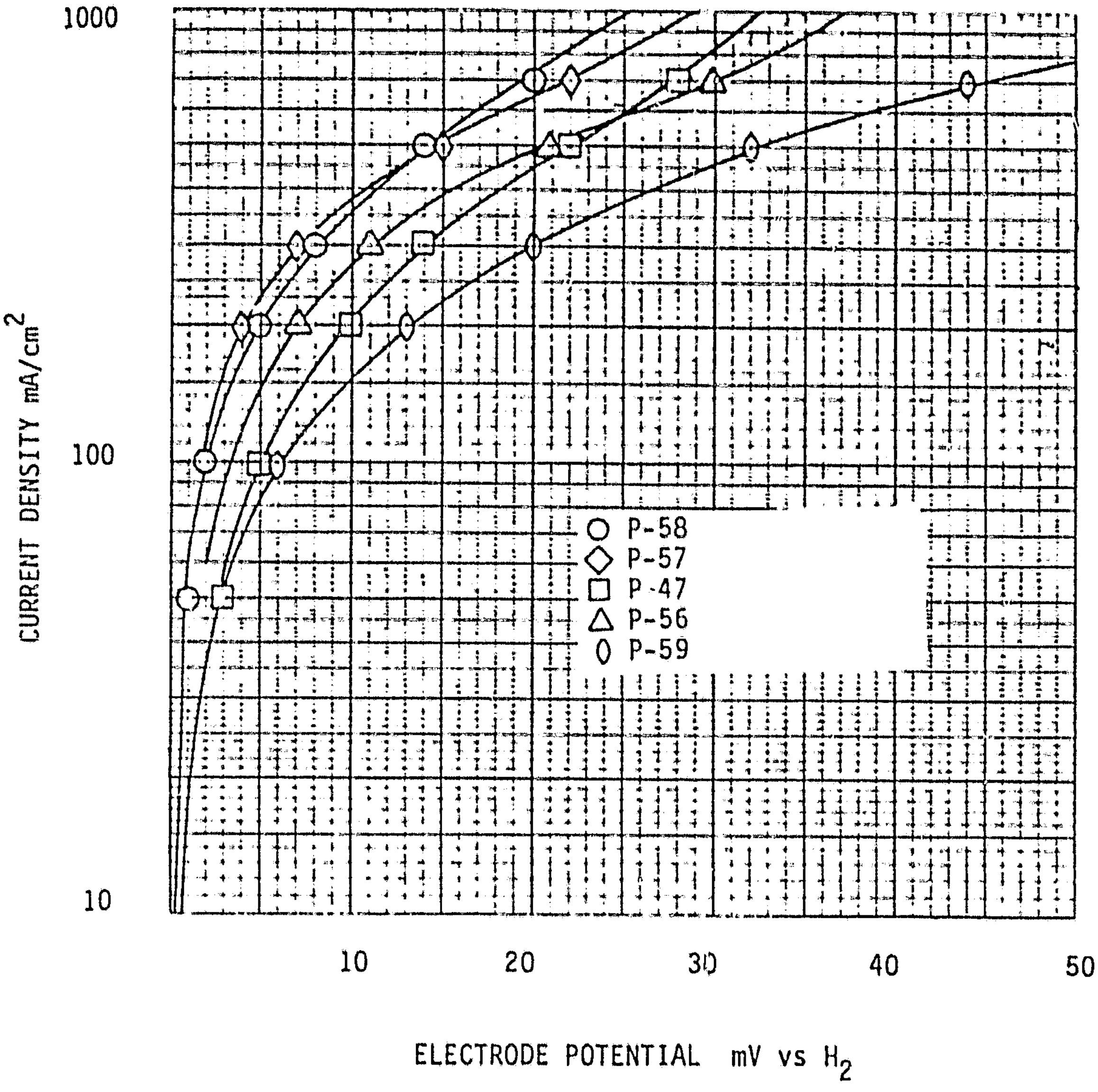


Figure 4.

Electrodes contained 30% PTFE and were run in 100% H_3PO_4 at 180°C. The electrodes were made from 4% PGM on Consel I and have a loading of 0.2 mg/cm^2.

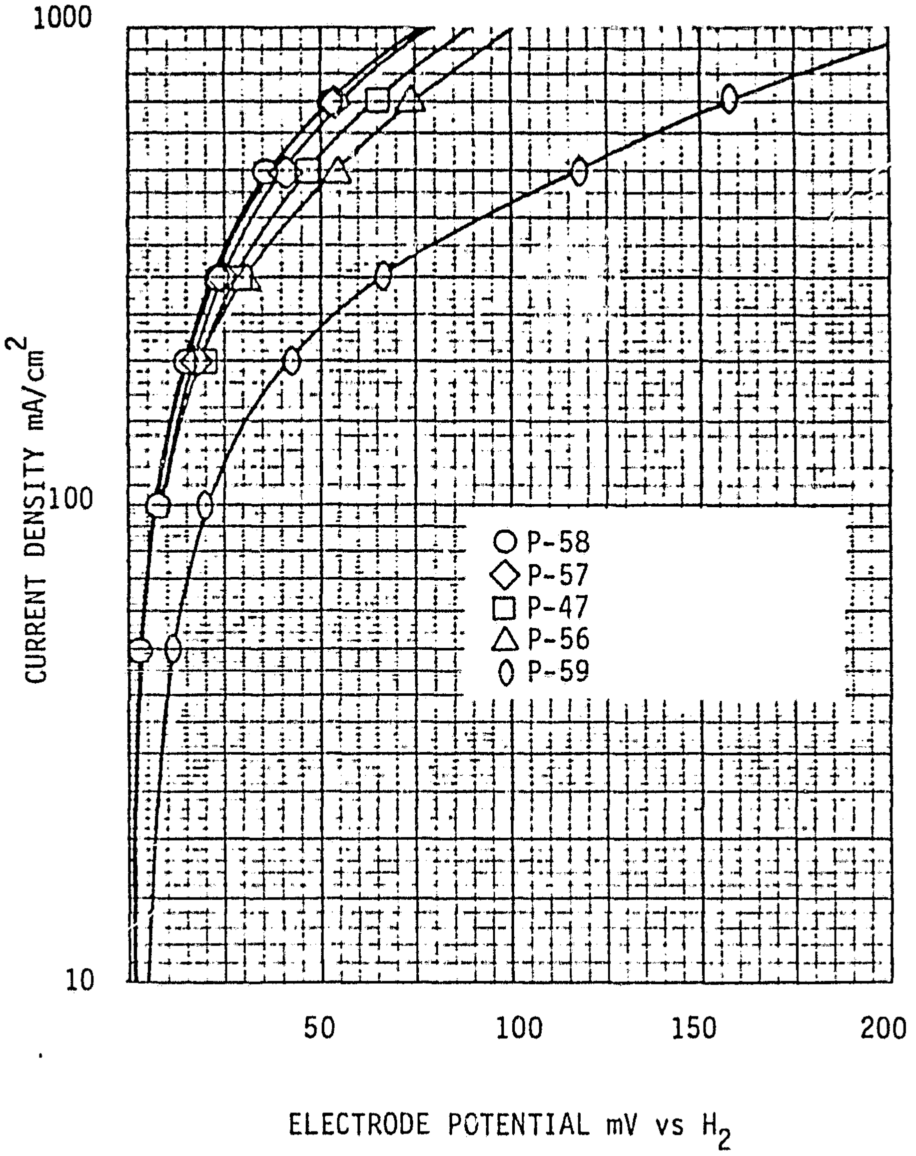


Figure 5.

The catalyst is 4% PGM on Consel 1 and was fabricated into gas diffusion electrodes (30% PTFE) with a loading of 0.2 mg PGM/cm^2. The test was conducted in 100% H_3PO_4 at 180°C.

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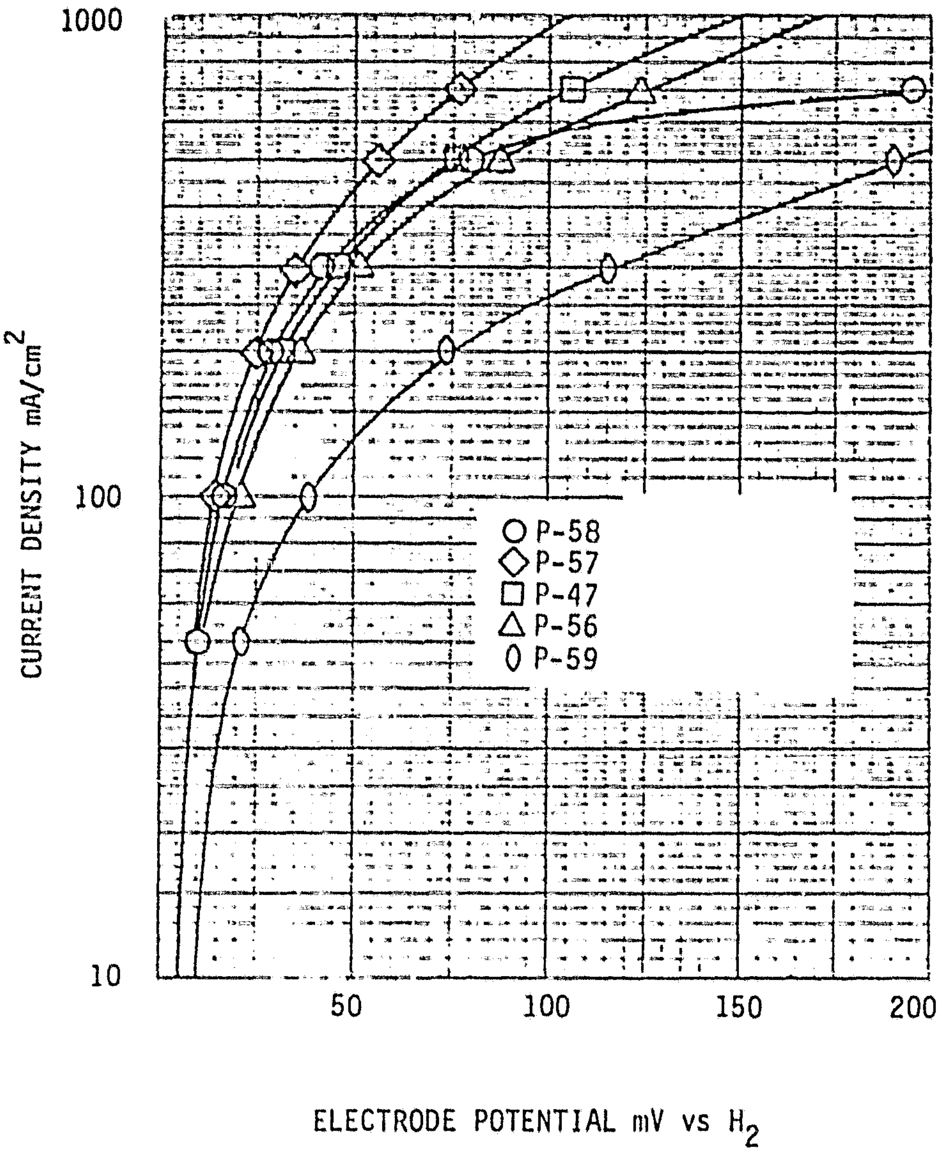

Figure 6.

The catalyst is 4% PGM on Consel I and was fabricated into gas diffusion electrodes (30% PTFE) with a loading of 0.2 mg PGM/cm^2. The test was conducted in 100% H_3PO_4 at 180°C.

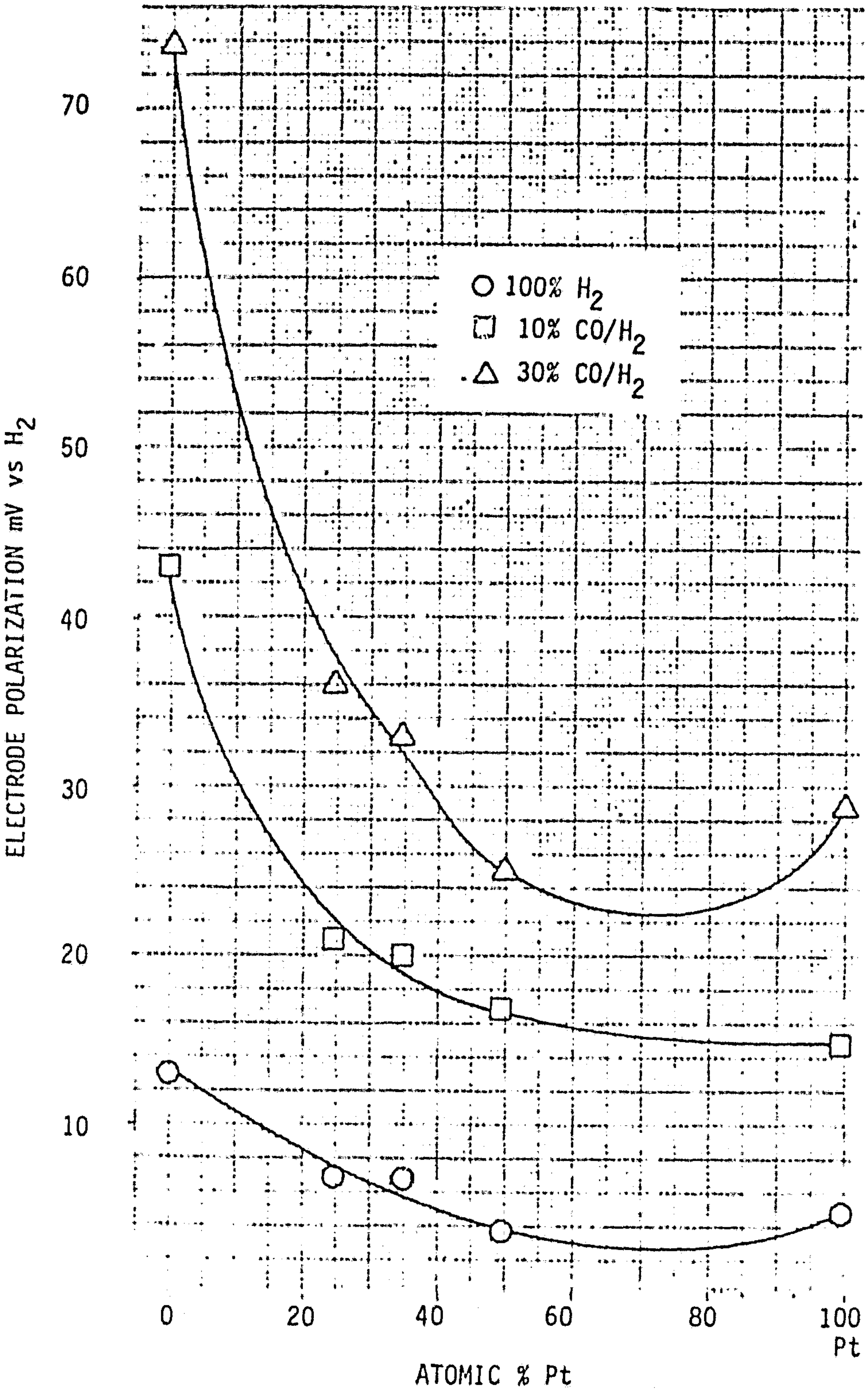

Figure 7.

Anode polarization at 200 mA/cm^2 as a function of a/o platinum for various fuel gases. The catalyst is 4% PGM on Consel I and was fabricated into gas diffusion electrodes (30% PTFE) with a loading of 0.2 mg PGM/cm^2. The test was conducted in 100% H_3PO_4 at 180°C.

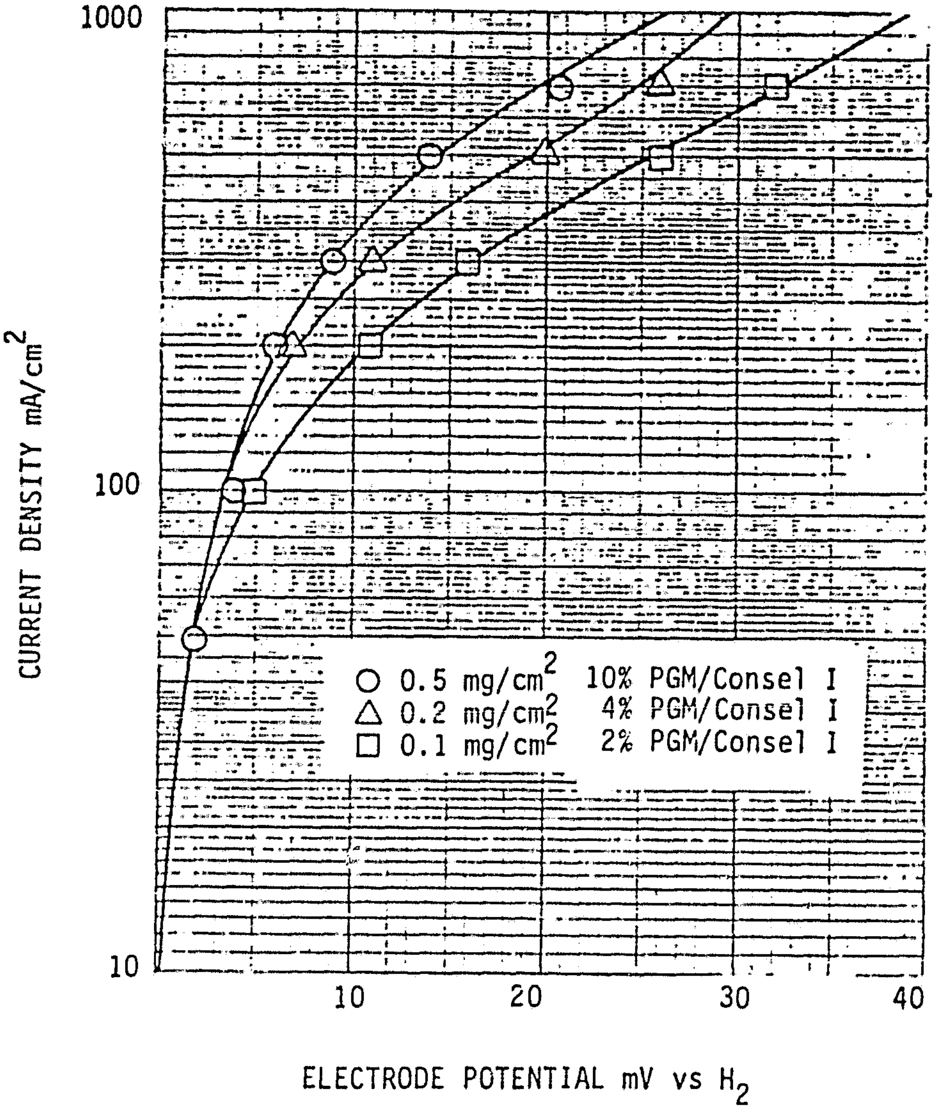

Figure 8.

Electrodes are the same thickness and therefore are loaded with 0.1, 0.2 and 0.5 PGM mg/cm^2 respectively. The catalysts were fabricated into gas diffusion (30% PTFE) electrodes and the test was conducted in 100% H_3PO_4 at 180°C on 100% H_2.

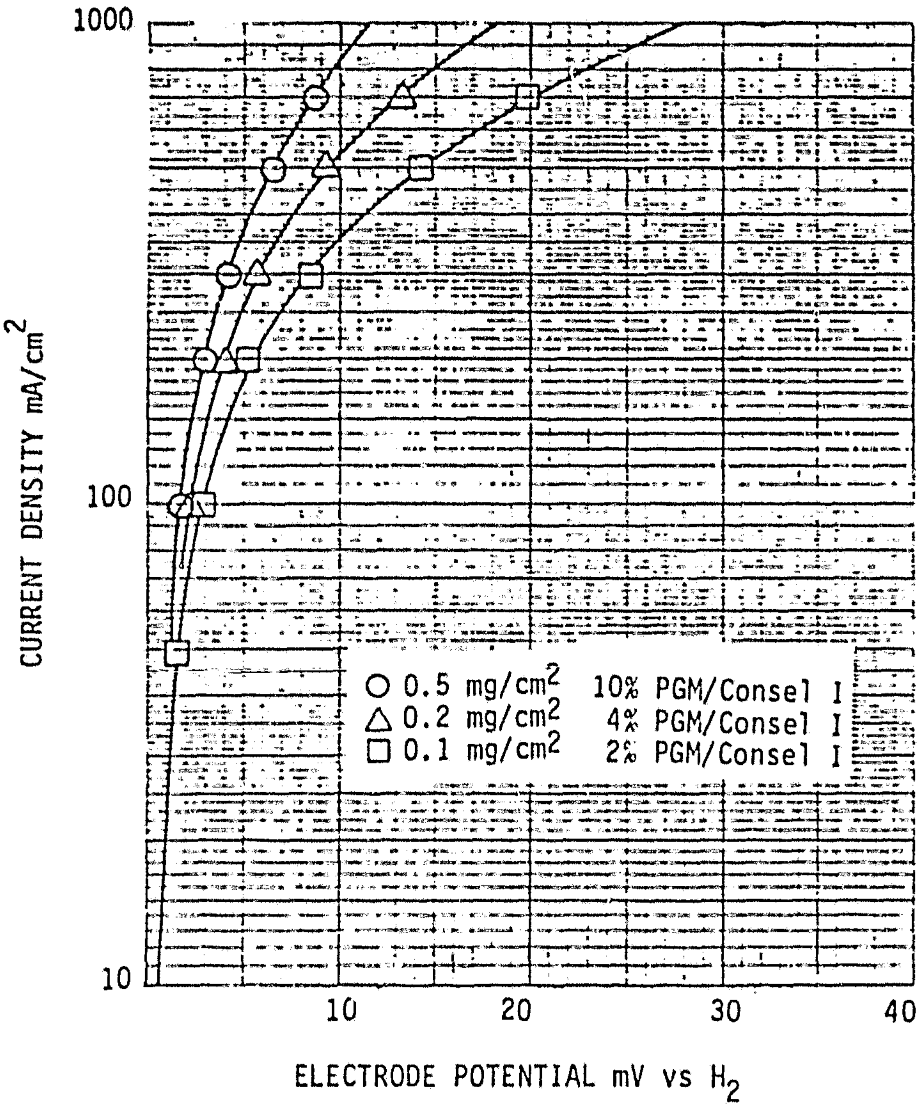

Figure 9.

Electrodes are the same thickness and therefore are loaded with 0.1, 0.2 and 0.5 PGM mg/cm^2 respectively. The catalysts were fabricated into gas diffusion (30% PTFE) electrodes and the test was conducted in 100% H_3PO_4 at 180°C on 10% CO/H_2.

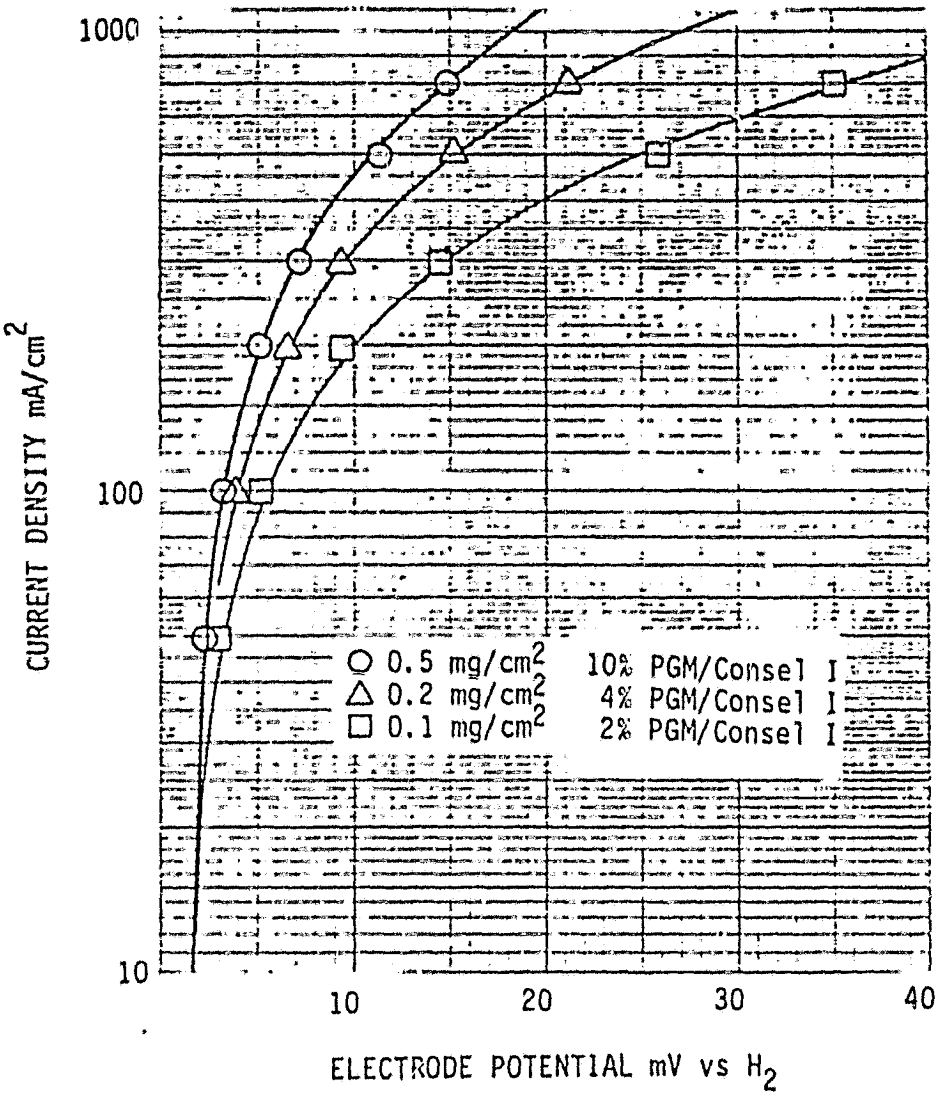

Figure 10.

Electrodes are the same thickness and therefore are loaded with 0.1, 0.2 and 0.5 PGM mg/cm^2 respectively. The catalysts were fabricated into gas diffusion (30% PTFE) electrodes and the test was conducted in 100% H_3PO_4 at 180°C on 30% CO/H_2.

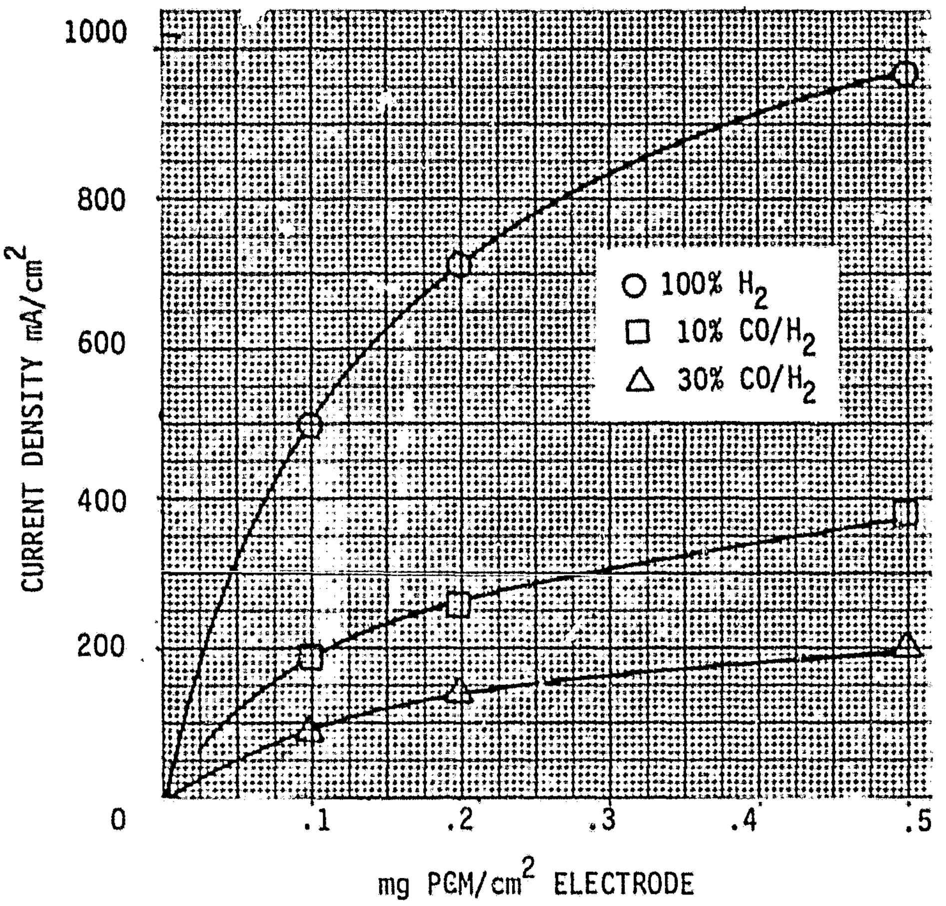

Figure 11.

Current density as a function of catalyst loading for constant thickness electrodes at various CO concentrations.

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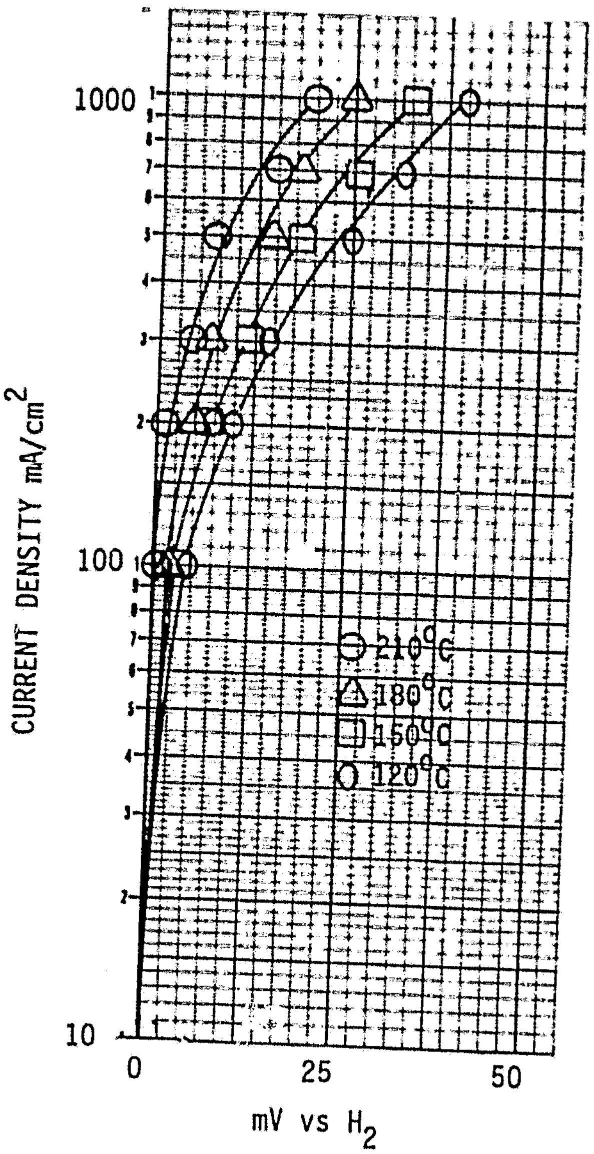

Figure 12.

Anode performance for electrode P-54, 0.5mg PGM/cm^2. Catalyst is 10% PGM/Consel I. Electrode contains 30% PTFE and was run at various temperatures in 100% H_3PO_4 on 100% H_2.

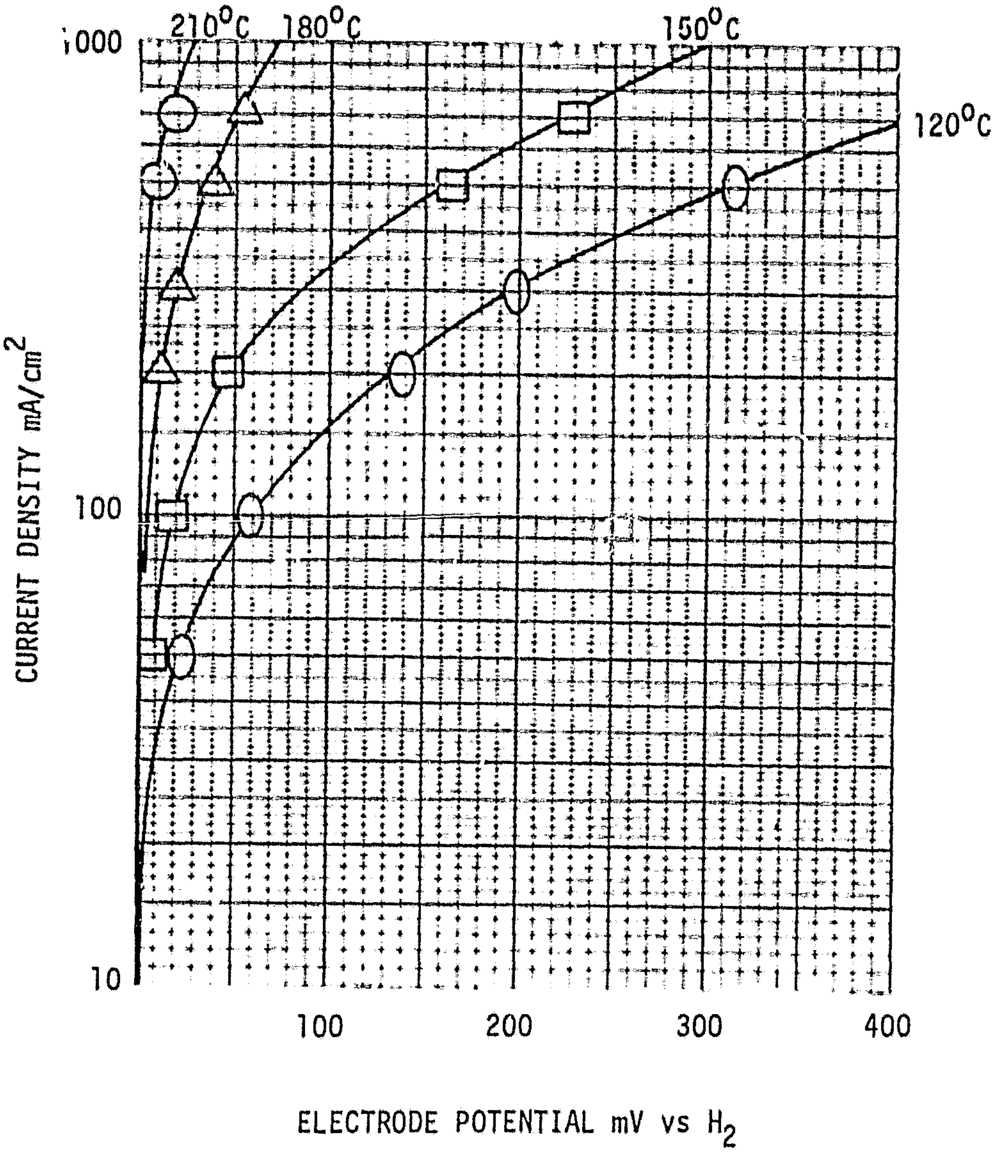

Figure 13.

Anode performances for electrode P-54, 0.5 mg PGM/cm^2. Catalyst is 10% PGM/Consel. Electrode contains 30% PTFE and was run at various temperatures in 100% H_3PO_4 on 10% CO/H_2.

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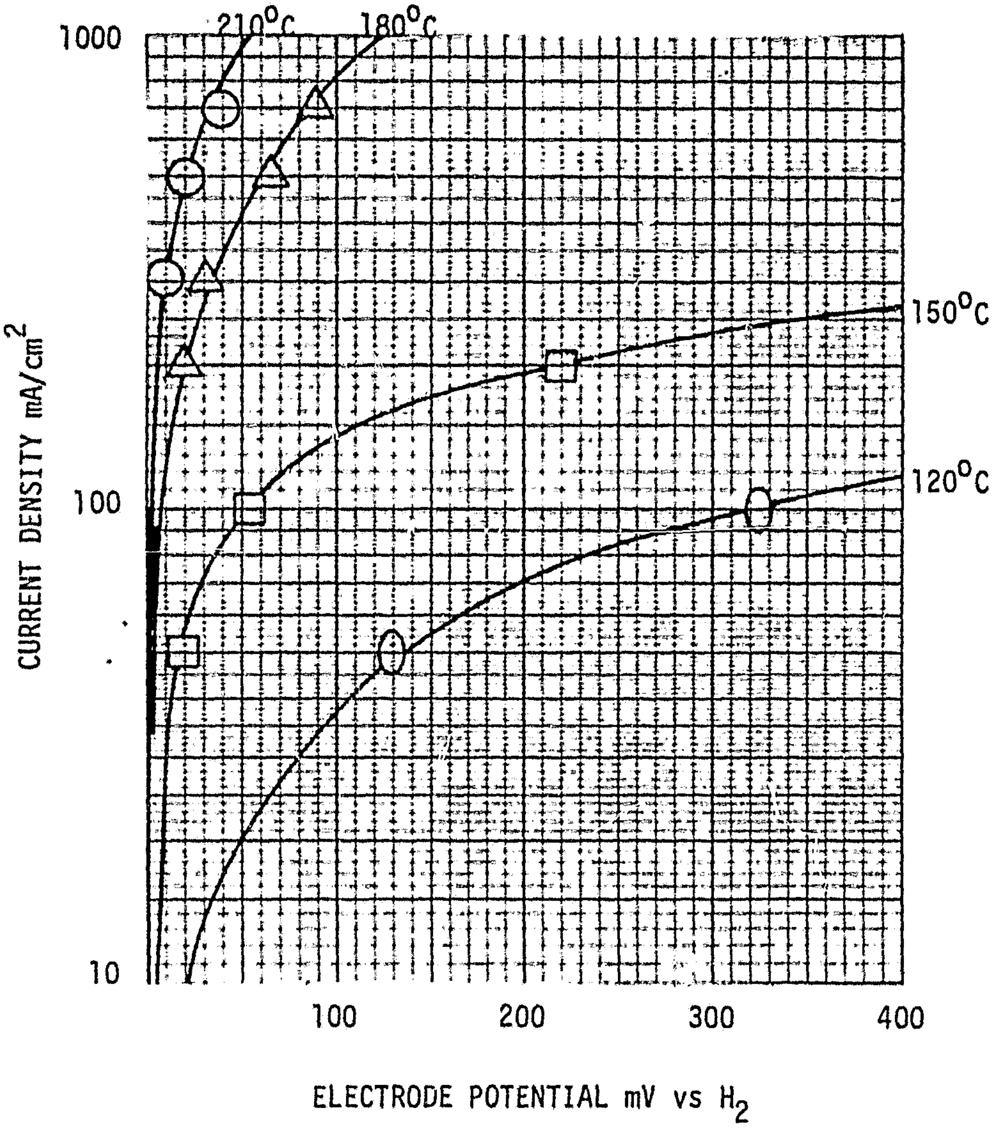

Figure 14.

Anode performances for electrode P-54, 0.5 mg PGM/cm^2. Catalyst is 10% PGM/Consel. Electrode contains 30% PTFE and was run at various temperatures in 100% H_3PO_4 on 30% CO/H_2.

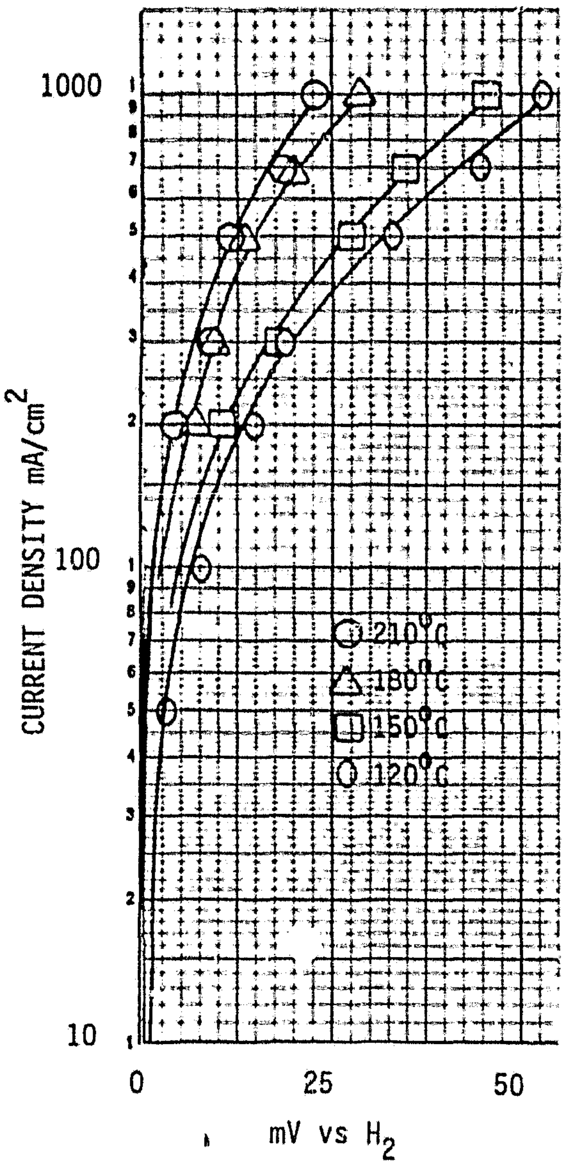

Figure 15.

Anode performance for electrode P-55, 0.2mg PGM/cm^2. Catalyst is 4% PGM/Consel I. Electrode contains 30% PTFE and was run at various temperatures in 100% H_3PO_4 on 100% H_2.

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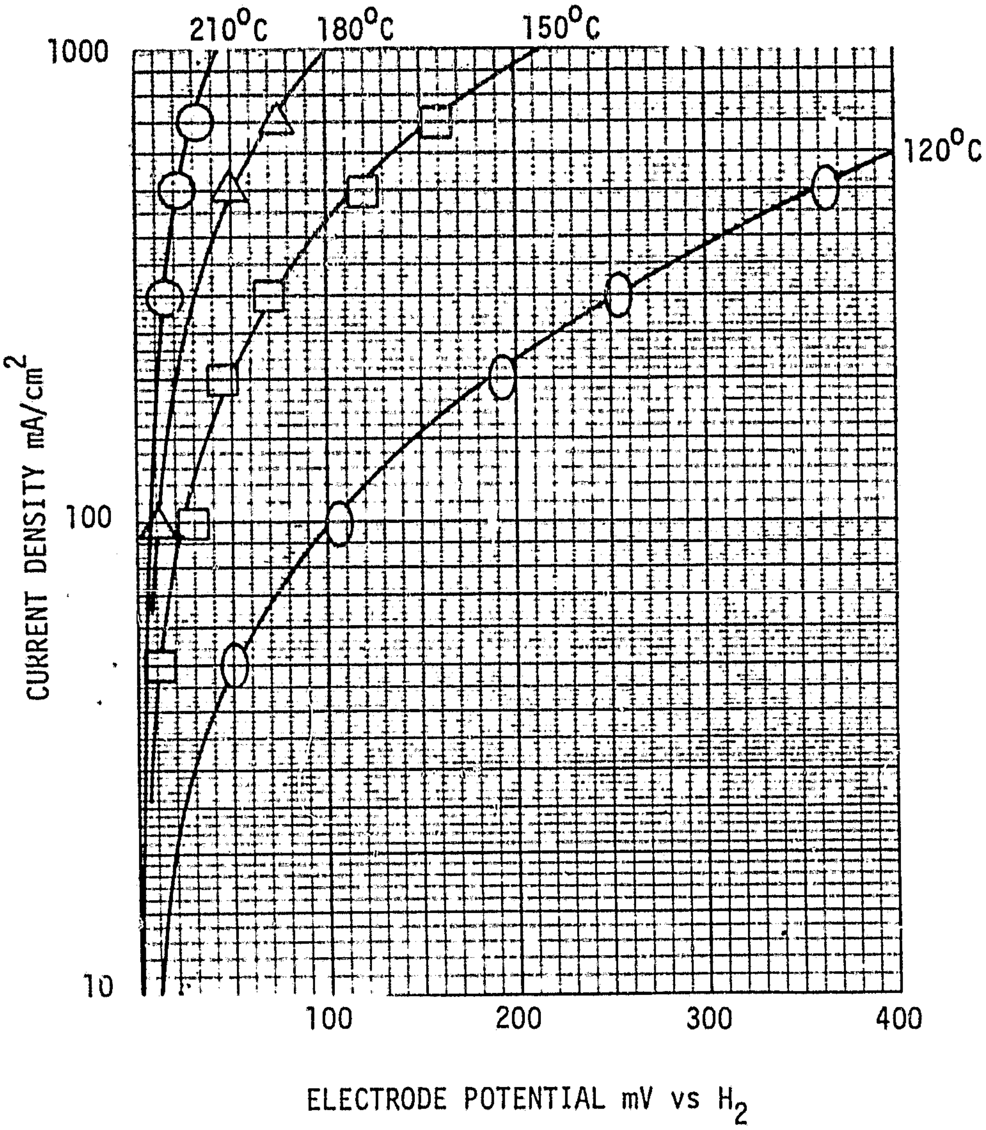

Figure 16.

Anode performances for electrode P-55, 0.2 mg PGM/cm^2. Catalyst is 4% PGM/Consel. Electrode contains 30% PTFE and was run at various temperatures in 100% H_3PO_4 on 10% CO/H_2.

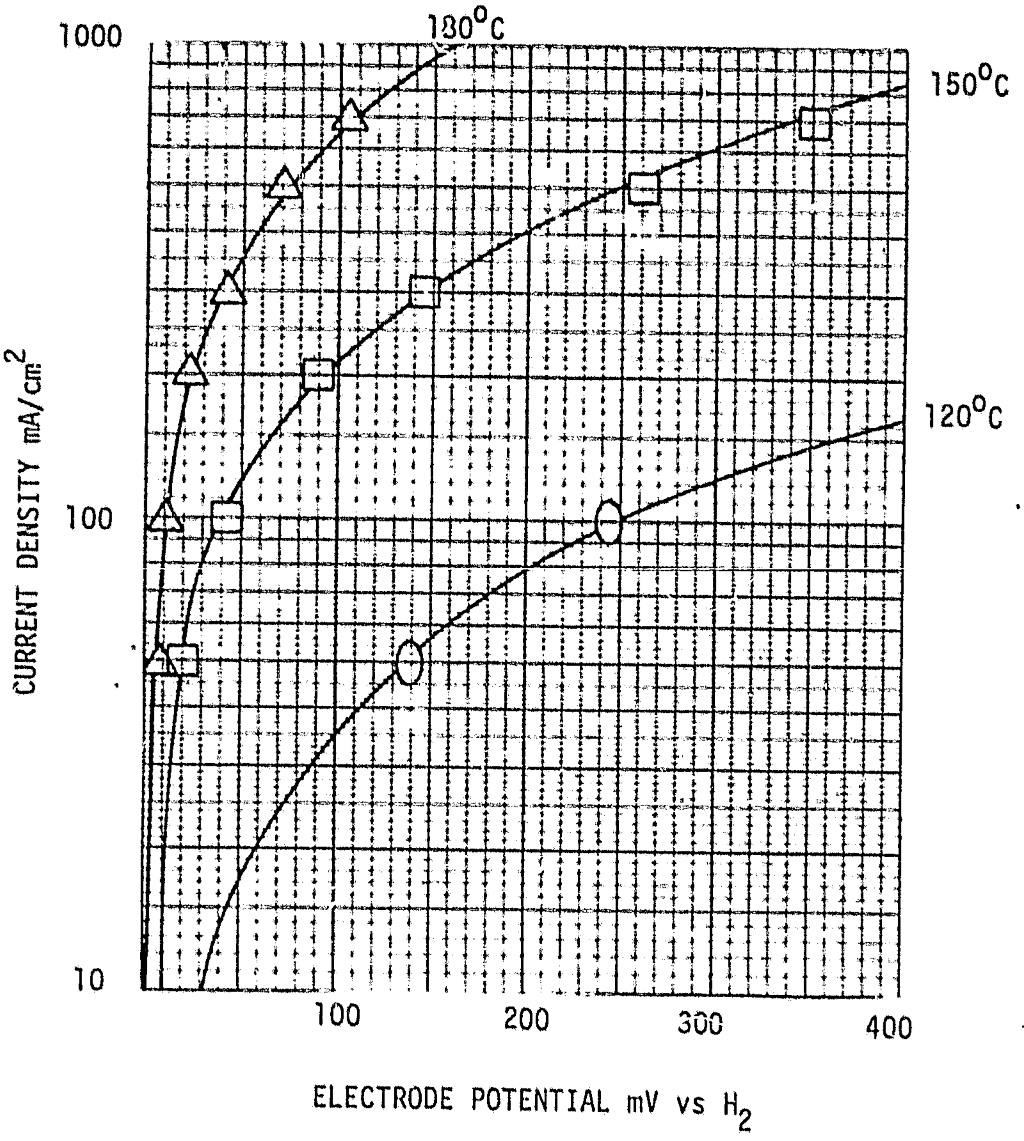

Figure 17.

Anode performances for electrode P-55, 0.2 mg PGM/cm^2. Catalyst is 4% PGM/Consel. Electrode contains 30% PTFE and was run at various temperatures in 100% H_3PO_4 on 30% CO/H_2.

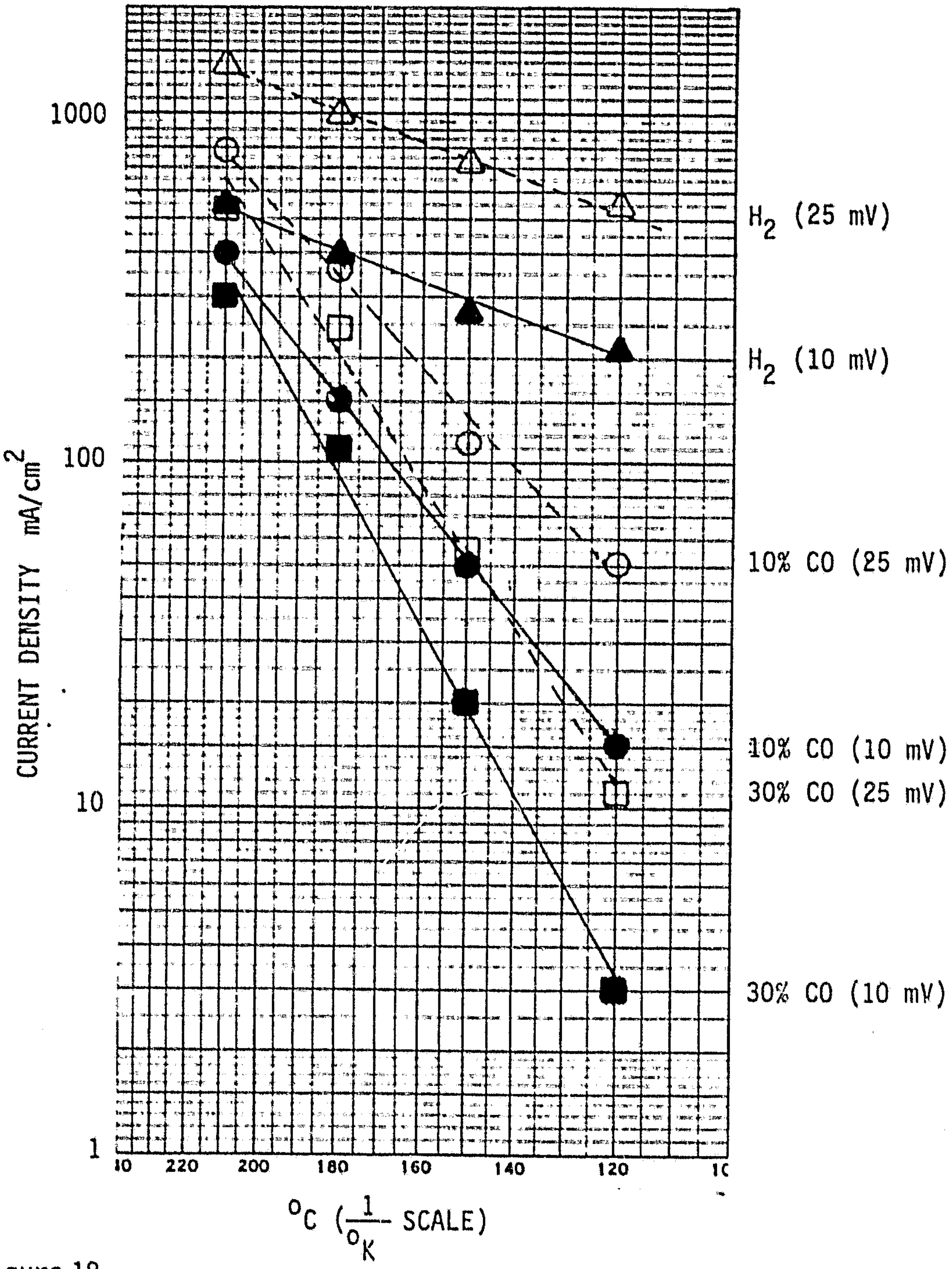

Figure 18.
Current density as a fuction of 1/T for hydrogen oxidation on 100% H_2, 10%CO/H_2, and 30%CO/H_2 at 10mV and 25mV polarization, in 100% H_3PO_4. Electrode number P-54, 0.5mg PGM/cm^2, 30% PTFE. Catalyst is 10% PGM on Consel I.

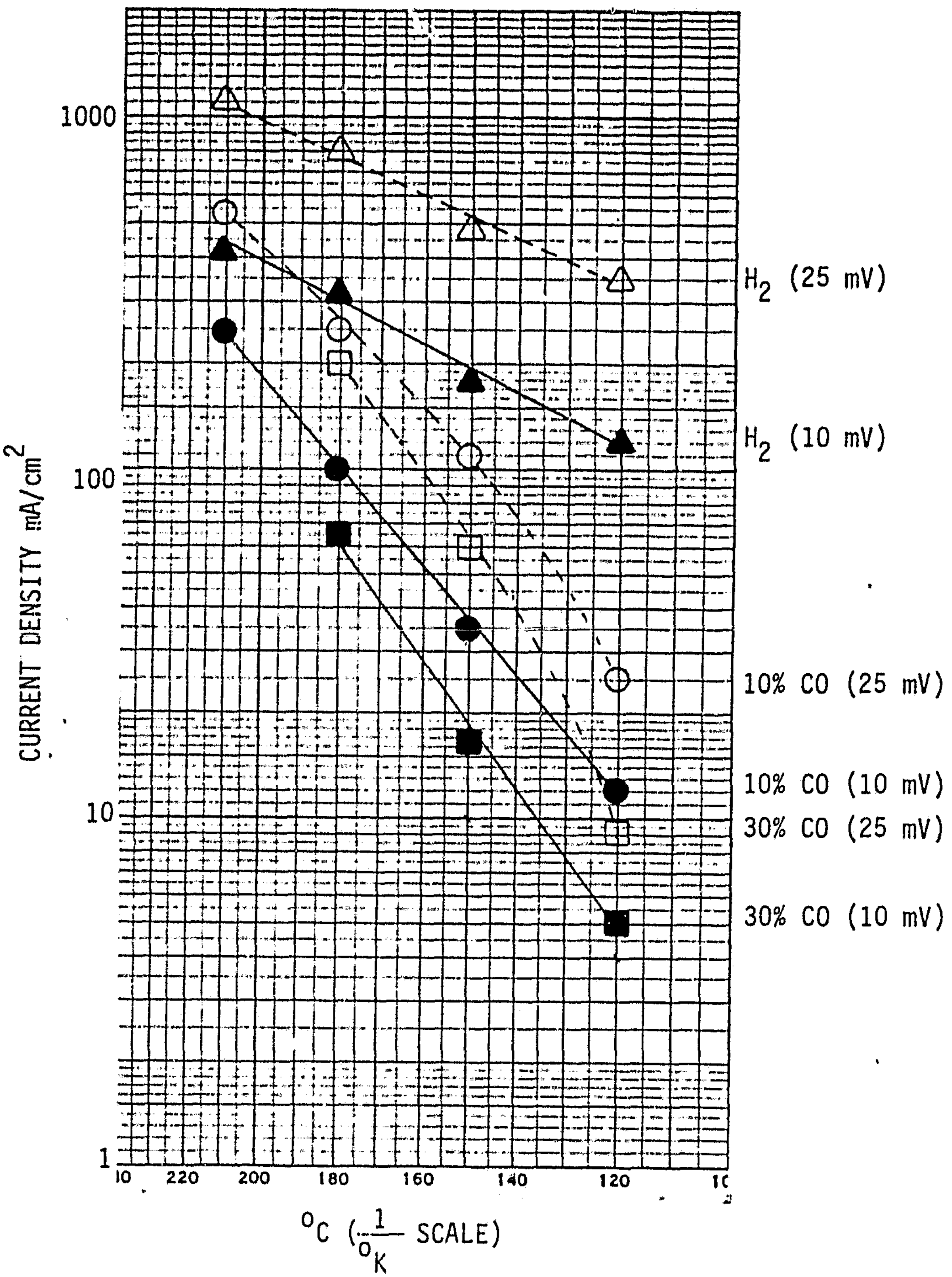

Figure 19.

Current Density as a function of 1/T for hydrogen oxidation on 100% H_2, 10%CO/H_2, and 30%CO/H_2 at 10mV and 25mV polarization, in 100% H_3PO_4. Electrode number P-55, 0.2mg PGM/cm^2, 30% PTFE. Catalyst is 4% PGM on Consel I.

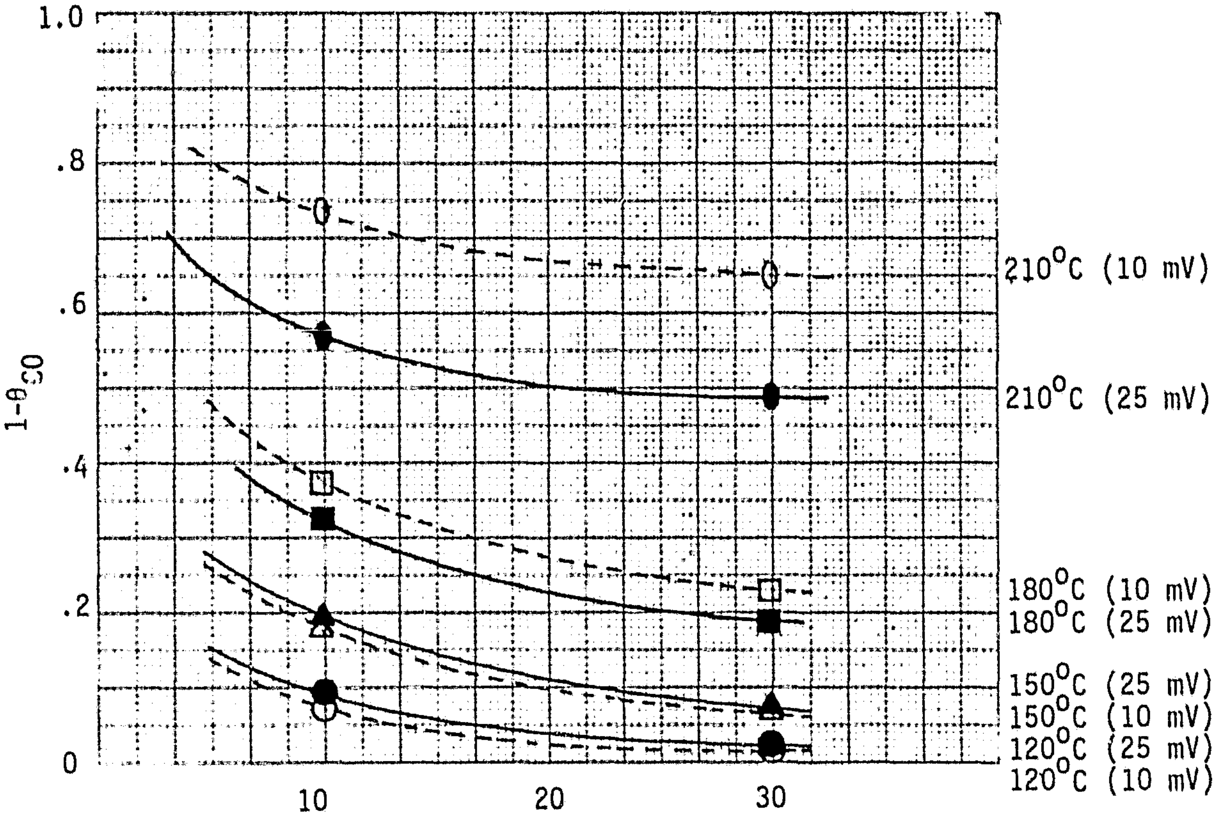

Figure 20.

Site availability on the 10% PGM/Consel I catalyst as a function of carbon monoxide partial pressure, temperature and electrode potential.

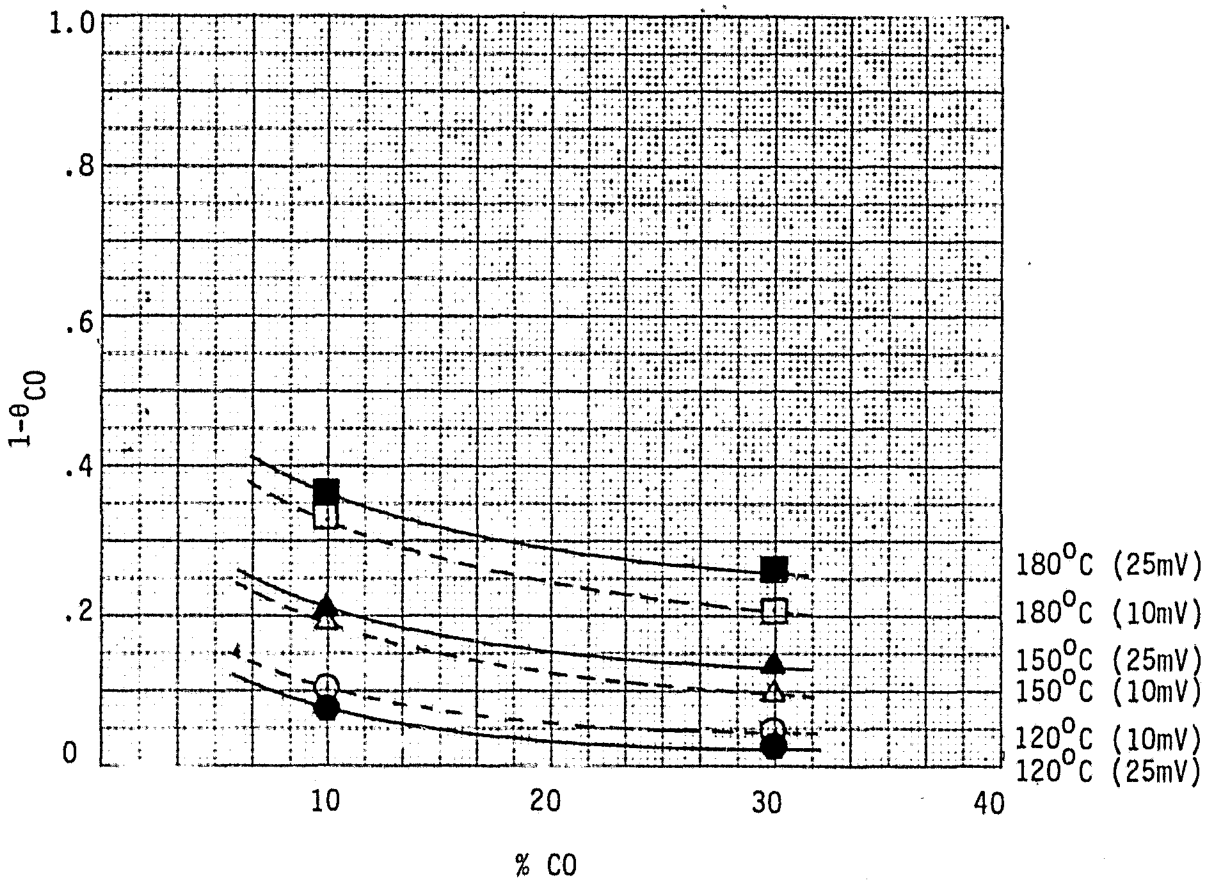

Figure 21.

Site availability on the 4% PGM/Consel I catalyst as a fuction of carbon monoxide partial pressure, temperature and electode potential.

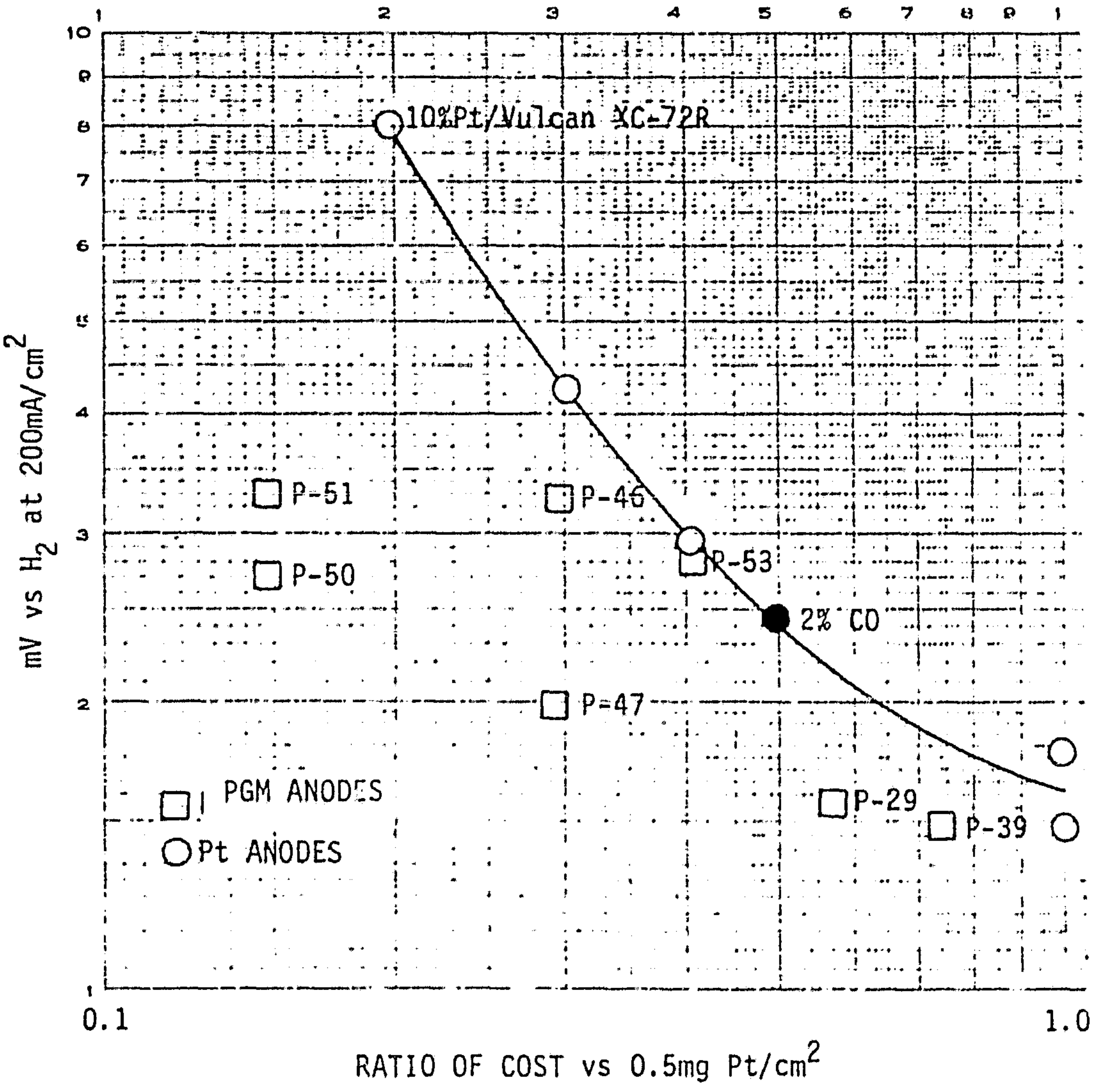

Figure 22.

Comparison of anode electrode performances at 180°C in 100% H_3PO_4 on 10% carbon monoxide 90% hydrogen at 200mA/cm^2 as a function of catalyst cost ratioed to the cost of 0.5mg Pt/cm^2 Pt/Vulcan XC-72R.