

FINAL REPORT

STUDY PROGRAM TO IMPROVE FUEL CELL
PERFORMANCE BY PULSING TECHNIQUES

by

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ABSTRACT

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It has been observed that under certain conditions, heavy discharge pulses show varying degrees of improvement on the performance level of different types of fuel cell electrodes. In this investigation these conditions were defined on six different types of electrodes: Union Carbide plastic bonded and baked carbon electrodes; American Cyanamid electrodes; Justi-type electrodes; platinum sheet electrodes; and porous nickel electrodes. Studies were also conducted to determine the effect of pulsing on performance level and electrode life.

The results obtained indicated that pulsing is primarily a catalyst reactivation treatment and is most effective in improving the performance level of electrodes that are catalyst limited from the start, or become catalyst limited during the life of the electrode. Electrodes such as Union Carbide catalyzed electrodes that contained less than 2 mg/cm² of catalyst normally showed improvements of about 10 mv per pulse when operated in the current density range of 20-100 ma/cm². Electrodes containing high catalyst concentrations such as American Cyanamid electrodes (9-40 mg/cm²) normally showed improvements of about 2 mv per pulse when operated in the current density range of 30-250 ma/cm². Studies on nonporous platinum metal electrodes show that these electrodes show rapid losses in catalytic activity with time in H₂-saturated alkaline solutions. However, the catalytic activity can be restored electrochemically by oxidative pulses or by chemical oxidation.

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SUMMARY

The conditions under which heavy discharge pulses improved the operating level of electrodes were determined for platinum sheet, Union Carbide plastic bonded, catalyzed porous nickel, Union Carbide baked carbon, American Cyanamid and Justi-type electrodes.

Platinum sheet electrodes were pulsed as anodes in hydrogen-saturated alkaline solution and as cathodes in O_2 -saturated alkaline solutions. Improved activity of platinum sheet anodes resulted when pulses drove the polarization between $\eta = 0.3$ v to $\eta = +1.6$ v. The stronger the pulse, the greater the improvement in activity. Platinum sheet cathodes were improved in activity by any cathodic pulse. Improvements resulting from pulsing cathodes were not as large as those which resulted from pulsing anodes.

Platinum sheet anodes were observed to decline in activity with time in H_2 -saturated alkaline solutions. This activity could then be restored either by a heavy discharge pulse or by chemical oxidation of the platinum. The decline in activity with time was related to the concentration of trace metal ions in solution. Treating electrolytes by pre-electrolysis for several weeks or more slowed down the decline of activity with time in H_2 -saturated solutions.

The effect of adding a metallic impurity on the rate of activity decay of a platinum electrode was determined for iron. The current at a fixed polarization of +10 mv declined about 10 per cent in four minutes on a Pt electrode in a solution containing less than 1 ppm Fe (pre-electrolyzed) compared to a 90 per cent decline in four minutes in the same solution to which 5 ppm of Fe was added. Current-voltage scans of solutions containing Fe(II) showed an additional current peak at a potential of +1.1 v which was not present in iron-free solutions. This suggests that iron can be oxidized or desorbed off a "poisoned" electrode under certain conditions.

The potential range attained during pulsing in which some beneficial effects were observed on Union Carbide composite anodes was from -0.70 to 0.66 v with

respect to an HgO reference electrode. The potential range attained during pulsing in which beneficial results were observed on composite cathodes was from -1.04 to +0.03 v.

The porous nickel electrodes that were available for pulsing experiments did not respond favorably to pulsing because their operation appeared to be diffusion limited rather than catalyst limited.

Union Carbide catalyzed, baked carbon anodes showed improvements of several millivolts as a result of a single pulse when driven to potentials between approximately -0.6 and +0.5 v versus a mercuric oxide-reference electrode. Improvements of 10 mv or more resulted only if the circuit was opened for about one minute before reapplying the normal load. Baked carbon cathodes showed improvements of only 1 to 3 mv as a result of a single pulse when pulsed to potentials negative to -0.1 v versus a mercuric-oxide reference. These results for beneficial pulsing were approximately in the same potential region as were composite electrodes catalyzed in the same way.

Beneficial pulsing effects on American Cyanamid electrodes were quite small (i. e., 10 per cent or less) and were observed only after a few days of operation. This indicates that initial performance is not catalyst limited. Gas reversal, i. e., exchanging gas feed lines to the cell, appeared to be especially beneficial for cells of this type which used the same electrodes for anodes and cathodes.

Justi-type anodes (porous nickel, no platinum metal catalyst) and Justi-type cathodes (porous silver) showed only very small beneficial effects from pulsing. Results on anodes were highly scattered and improvements were not always positive.

Pulsing tests on Union Carbide composite electrodes with two levels of catalyst concentrations (1 and 3 mg/cm²) showed that the "pulsing effect" is higher at low catalyst concentrations. For Pt catalyzed electrodes the average improvement resulting from a single pulse was 7.2 mv for the 1 mg/cm² catalyst level and 3.5 mv per pulse for the 3 mg/cm² catalyst level. Experiments using smooth and platinized platinum showed that the rate of decline in catalytic activity decreased with increasing platinization. The decay rate was negligible for electrodes platinized two minutes or more. Both of these results, therefore, as well as the pulsing results on the heavily catalyzed Cyanamid electrode, show that the "pulsing effect" is largest on catalyst limited electrodes.

Temperature dependence data were obtained on Union Carbide composite electrodes and on sheet platinum electrodes. The temperature dependence of the "pulsing effect" was very small on the Union Carbide electrodes in the range 23° to 70°C. Statistically significant temperature dependence, however, was obtained on sheet platinum anodes in the range 26° to 90°C. The percentage improvements (in current) resulting from a single pulse at the various temperatures were as follows: 26°C, 30%; 45°C, 32%; 70°C, 60%; and 90°C, 240%.

Life tests were performed in which the performance level of nonpulsed cells under otherwise identical conditions were compared with pulsed cells. The Union Carbide pulsed cells (pulsed twice per day at 1050 ma/cm² for two seconds) averaged 0.830 and 0.823 v. The nonpulsed cells averaged 0.762 and 0.802 v. A 25-day life test on AB-40 Cyanamid electrodes was performed where one cell (No. 4) was pulsed once daily at 1200 ma/cm² for 30 seconds. Cell No. 3 was not pulsed during this 15-day period. After 15 days (for the next 10 days) Cell No. 3 was pulsed and Cell No. 4 was not. The average cell voltage at 100 ma/cm² for the initial 15-day period was 0.79 v for Cell No. 3 (nonpulsed) and 0.83 v for Cell No. 4. For the latter period the average cell voltage for both pulsed and nonpulsed cells was 0.80 v. Justi-type anodes were not significantly helped by pulsing in the one life test that was performed. Justi-type cathodes appeared to be slightly helped by pulsing. A cathode on test declined in performance from -0.072 v to -0.114 v during the first 17-day period on test during which time it was not pulsed. After the electrode was pulsed the performance improved to a maximum of -0.080 v but then declined to -0.102 v. It appeared to stabilize at this level, but pulsing was not able to bring it to a higher operating level. A cathode that was pulsed improved its performance level from -0.085 to -0.054 v during a 17-day period in which it was pulsed once daily. Thereafter, it declined in performance to -0.080 v during the following 10-day period when it was not pulsed.

MEETINGS AND CONFERENCES

There were several meetings between NASA and Carbide personnel at both NASA and Union Carbide's Parma Technical Center to discuss various aspects of the program. The dates of the visits and personnel involved were the following:

<u>Date</u>	<u>NASA</u>	<u>Union Carbide Corp.</u>
November 13, 1964	M. R. Unger W. Aldred	M. L. Kronenberg G. E. Evans
February 15, 1965	M. R. Unger W. Aldred	M. L. Kronenberg
March 26, 1965	M. R. Unger W. Aldred	M. L. Kronenberg K. V. Kordes

May 18, 1965	M. R. Unger	M. L. Kronenberg
May 21, 1965	M. R. Unger	M. L. Kronenberg
May 24, 1965	M. R. Unger	M. L. Kronenberg
May 27, 1965	M. R. Unger	M. L. Kronenberg
	W. Aldred	G. Sprogis
		G. E. Evans
June 8, 1965	M. R. Unger	M. L. Kronenberg
June 10, 1965	M. R. Unger	M. L. Kronenberg
	W. Aldred	
June 30, 1965	M. R. Unger	M. L. Kronenberg
	W. Aldred	G. E. Evans
	W. Robertson	
September 3, 1965	M. R. Unger	M. L. Kronenberg
	W. Robertson	

Dr. M. L. Kronenberg attended the 127th Meeting of the Electrochemical Society and presented a paper entitled, "A Study of the Effects of Heavy Discharge Pulsing on Fuel Cell Electrodes," by M. L. Kronenberg and K. V. Kordesch.

INTRODUCTION

In the course of a recent survey¹ on the effect of mechanical and electrical pulsing on the performance of fuel cell electrodes, it was observed that under certain conditions heavy discharge pulses significantly improved the sustained performance level of fuel cells. Preliminary results indicated that this "pulsing effect" was related to catalyst reactivation. Because of the great importance of catalyst reactivation in extending useful fuel cell life, it was decided to conduct a detailed investigation of this pulsing effect.

The purpose of this investigation was to define the conditions under which pulsing improved the performance level and operating life of six different types of electrodes. Studies were also conducted to see how the pulsing effect was dependent on catalyst type, concentration, temperature, and presence of impurities in the electrolyte.

The general procedure used throughout the investigation was to use current at a fixed polarization as a measure of electrode activity. The electrode was then pulsed under a given set of conditions, and the activity level following a pulse was noted. The pulsing was regarded as having been "beneficial" if the activity level improved as a result of the pulse.

FACTUAL DATA

Task I - Definition of Effect.

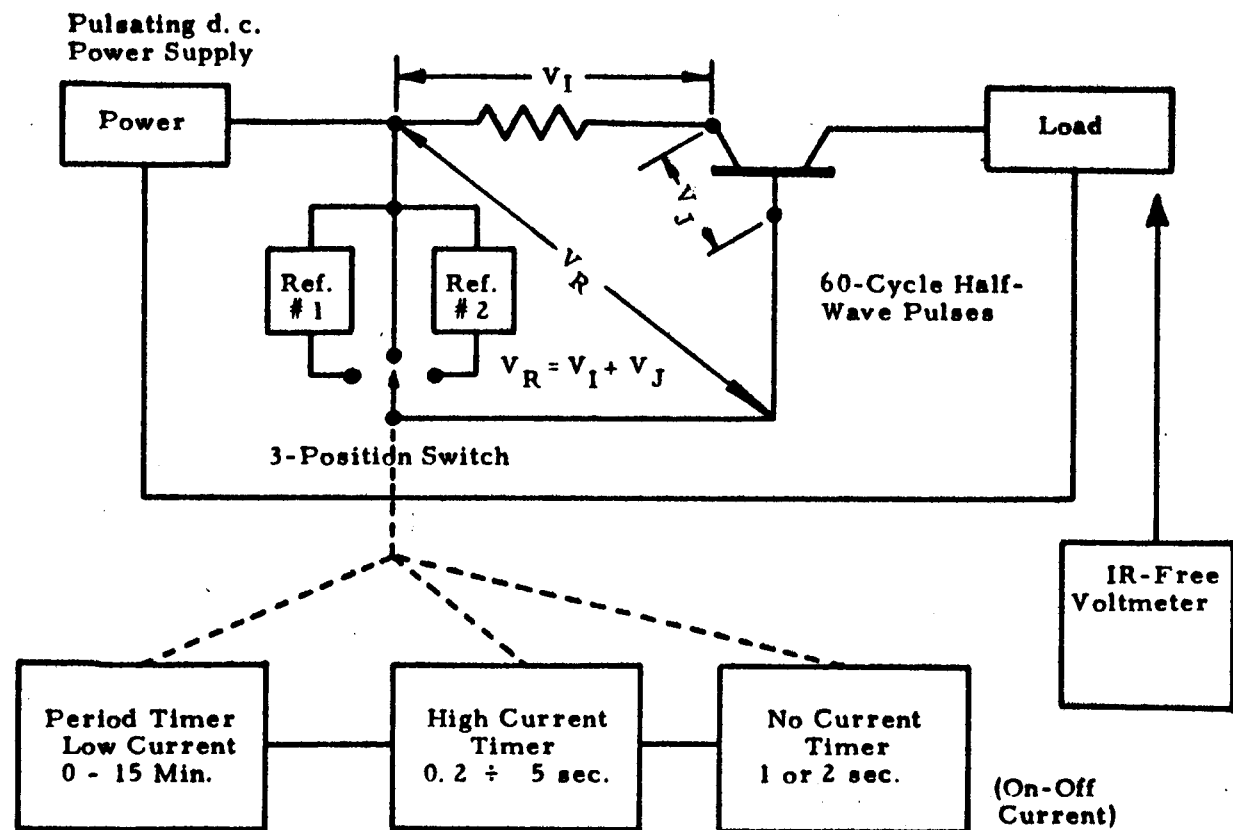
I.A. Purpose and Scope.

The purpose of this Task is to obtain experimental information about conditions under which heavy discharge pulsing shows a maximum beneficial effect. This information is to be obtained on solid platinum electrodes; Union Carbide thin, composite electrodes; and porous nickel electrodes. In order to better understand the problems involved, preliminary pulsing information was also obtained on Union Carbide baked carbon electrodes, American Cyanamid, and Justi-type electrodes.

I.B. Experimental Equipment and Procedures.

Two types of instruments were used in pulsing experiments, i. e., controlled current and controlled potential types. A block diagram of a controlled current instrument that was used is shown in Fig. 1. This instrument was described in an earlier report¹ but was modified to provide controlled discharge pulses from 2 to 3600 ma of 0.2 to 5 seconds duration and steady-state currents from 2 to 1600 ma. The pulses can be applied manually or at controlled intervals from 15 seconds to 15 minutes. A larger capacity instrument of this type was also constructed. This unit provides heavy discharge current pulses up to 50 amperes for time periods of 0.2 to 15 seconds. Both instruments employ the principle of the Kordes-Marko interrupter² enabling resistance-free or resistance-included measurements to be made.

The controlled potential instrument used was a Wenking potentiostat. Use of this instrument eliminates any uncertainty about the potential attained in pulsing experiments since the desired electrode-reference potential is directly imposed by means of the potentiostat. However, the use of the Wenking potentiostat as a pulsing device is limited to low current applications such as pulsing solid metal electrodes. It was not used for porous electrodes which often require many amperes of current to be driven to significant polarization. During the last few weeks of the contract a high current capacity potentiostat (Anatrol potential controller) was available to us for heavy discharge pulsing and for voltage scanning experiments.



Note: Ref. # 1 - Voltage control for low current range.
 Ref. # 2 - Voltage control for high current range.

D-1163

Fig. 1 Dual Range Constant Current Interrupter. Timer Controlled.

The cell used for obtaining pulsing information on thin composite and certain porous metal electrodes is shown in Fig. 2. The electrolyte circulation system was devised in our Laboratory to simulate actual operating conditions experienced by fuel cell batteries. Because of the circulating electrolyte, cells can be run in this system for several months with very little attention.

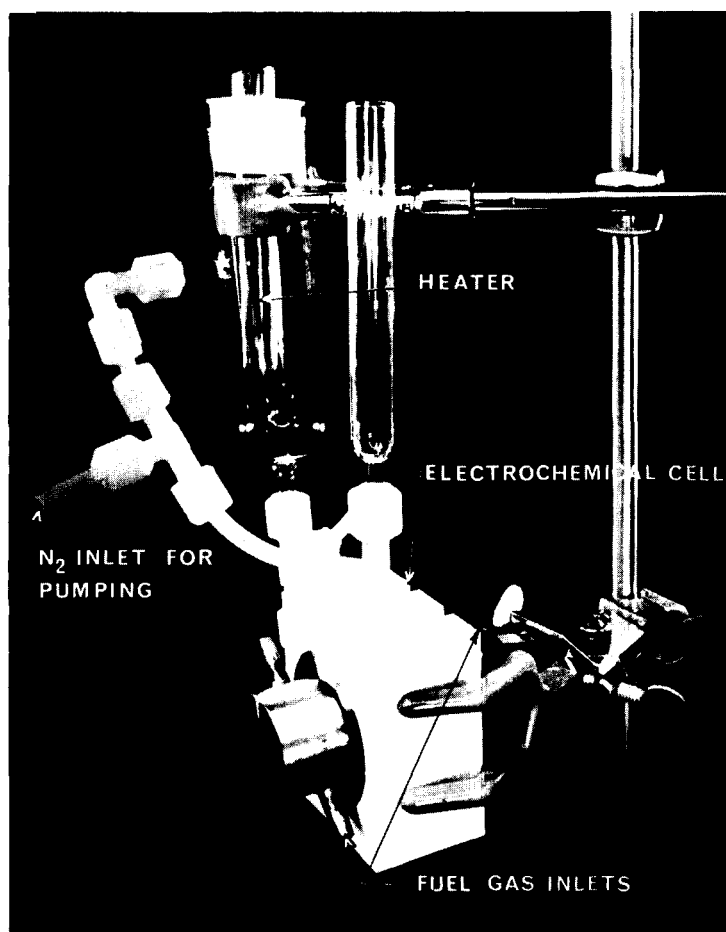
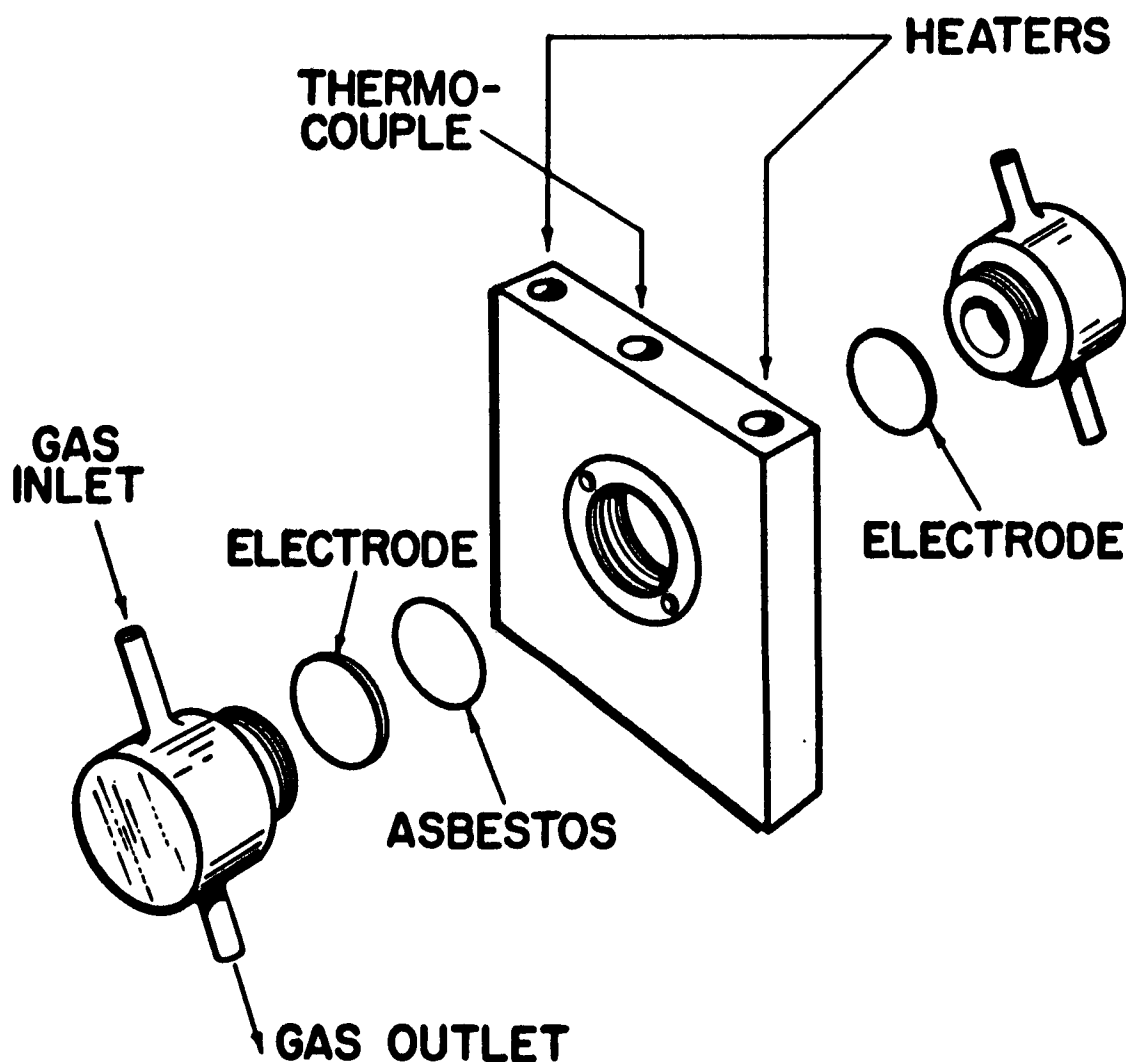


Fig. 2 Cell Used for Composite and Porous Metal Electrodes.

D-1529

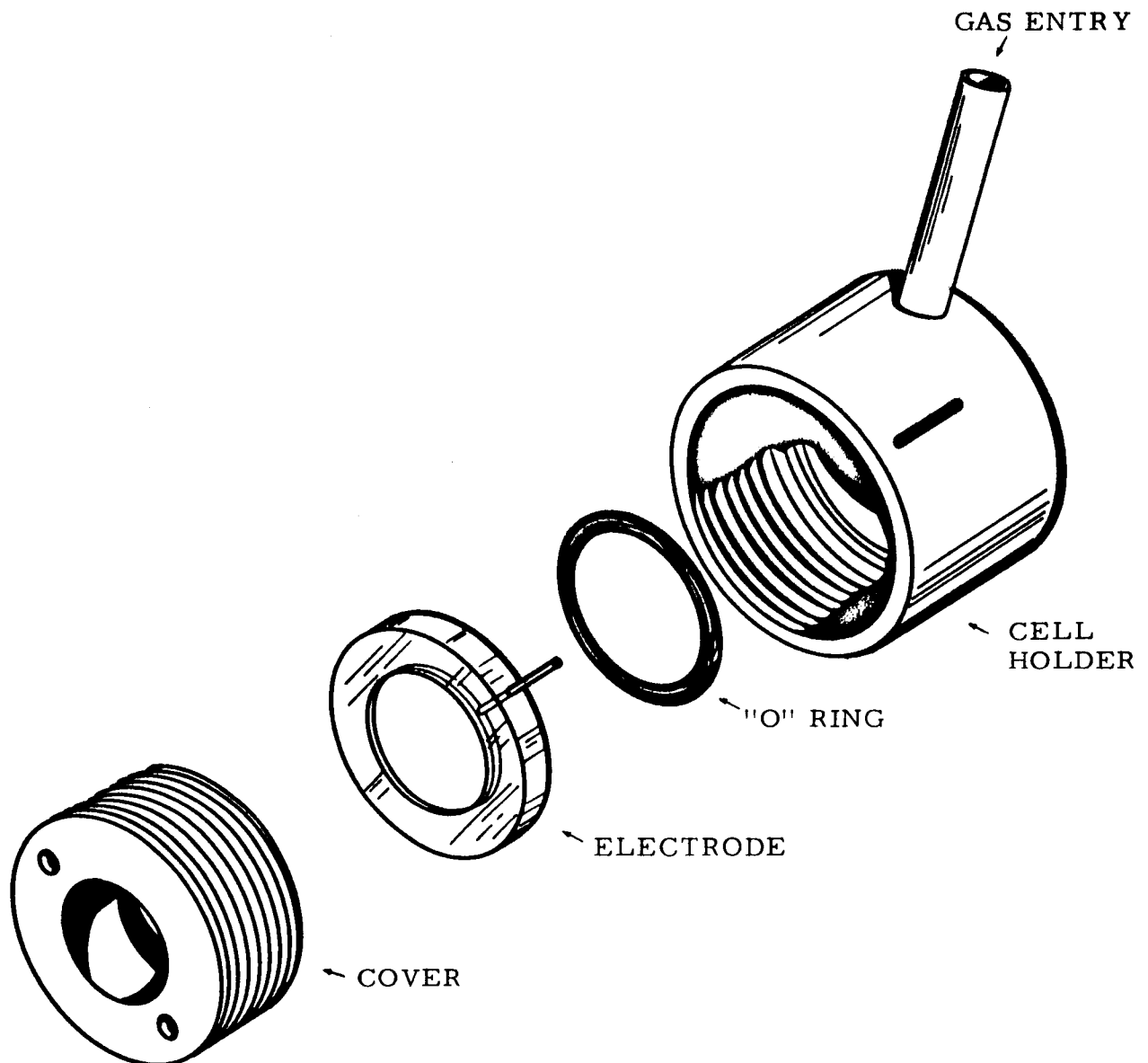
The cell used for testing electrodes that required immobilized electrolytes (KOH-soaked asbestos) is shown in Fig. 3. With this type of cell it is necessary to saturate the inflowing gases with water vapor at the same vapor pressure as the electrolyte. The gases are then fed to the cell at about ten times the galvanic utilization rate and vented off. This procedure permits considerable flexibility in cell loading without water-balancing problems.



D-1963

Fig. 3 Test Cell for Electrodes Requiring Asbestos Matrix.

A Teflon cell that was designed for testing Justi-type anodes and cathodes is shown in Fig. 4. These electrodes are tested as half cells and operated at 15 psig.



D-2224

Fig. 4 Teflon Cell for Testing Justi-Type Electrodes.

The cell used to obtain pulsing information on solid metal electrodes is shown in Fig. 5. The ground glass joints and liquid seal outlets permit the electrodes to be run under a controlled atmosphere. Concentration polarization is minimized by stirring at a controlled rate by means of the magnetic stirrer shown, controlled by a Variac. For special high purity runs with nonporous electrodes, a Teflon-glass cell was constructed. All cell components in contact with the electrolyte are Teflon or metal. A drawing of this cell is shown in Fig. 6. The H_2 used was electrolytic grade which was further purified by passing through a Serfass Model CH-A hydrogen purifier (palladium-silver alloy type).

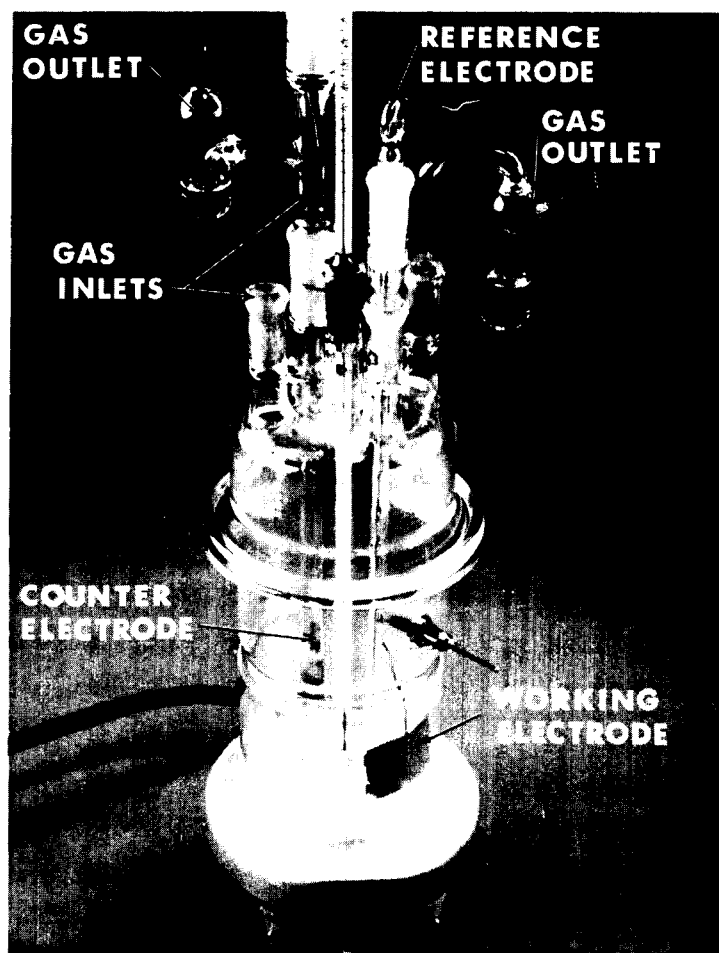
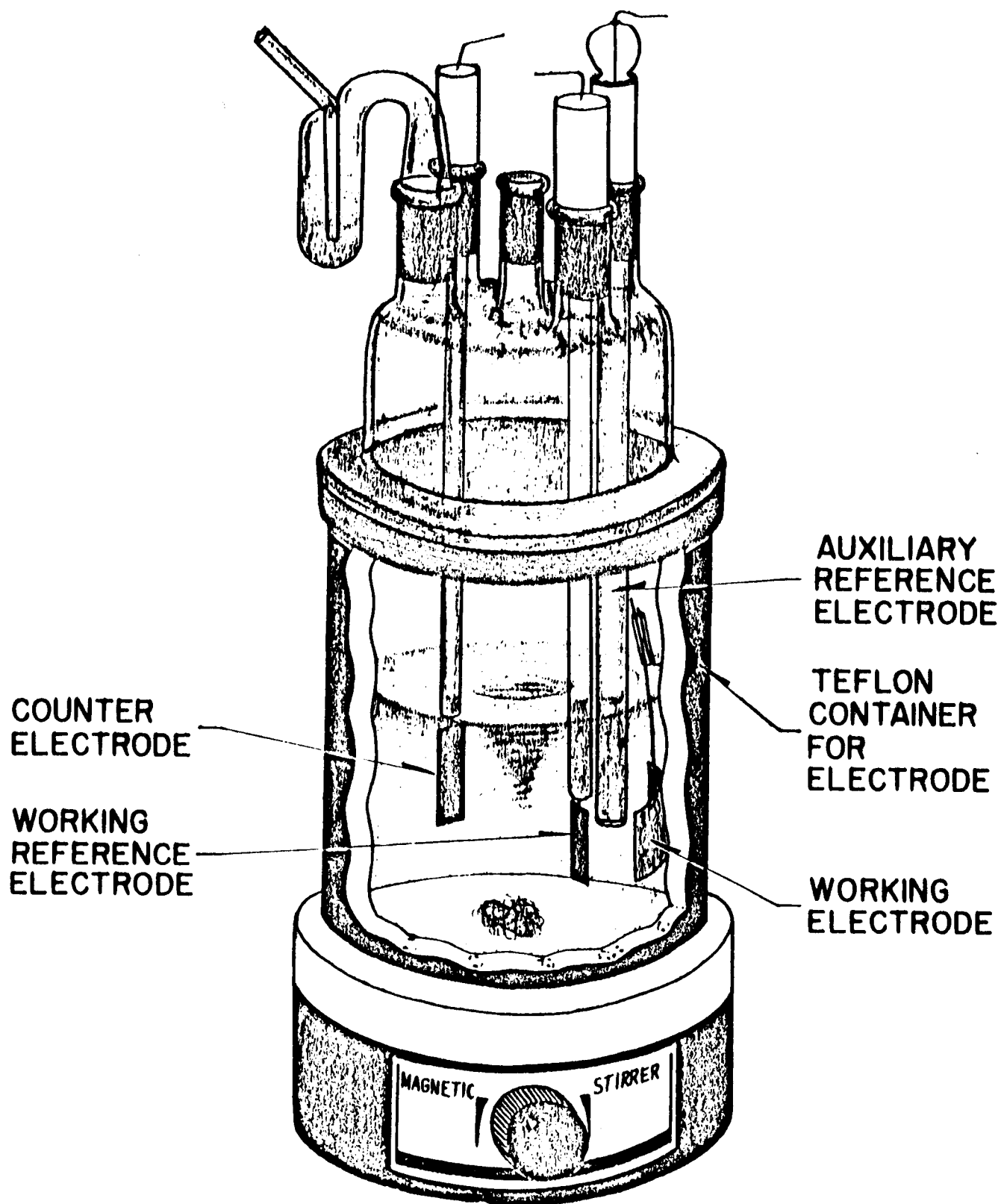


Fig. 5 Cell Used to Obtain Information on Solid Electrodes.

D-1245



D-1984

Fig. 6 Teflon-Glass Cell Used for Polarization Measurements on Nonporous Electrodes.

In general, the following procedure was used for obtaining pulsing information on electrodes with the controlled current pulsing units: The cell was run at steady-state current prior to pulsing. The current density employed depended upon the nature of the electrode and operating conditions and was adjusted to a steady-state value sufficient to polarize the working electrode 25 mv or more. The cell was then pulsed and the potential of the working electrode with respect to a reference electrode was noted before, during and after pulsing. The polarizations immediately before and after pulsing are compared at the same steady-state currents. Pulsing is regarded as having improved the electrode performance (beneficial pulsing) when the polarization is less immediately after pulsing than immediately before. Preliminary experiments indicated that the potential to which an electrode was driven during the heavy discharge pulse was one of the main factors in determining whether beneficial pulsing occurs. For this reason, the electrode potential attained during the discharge pulse is noted as a measure of the pulse intensity. Since it is obvious that an electrode cannot improve indefinitely (e. g. , to negative polarizations) the condition of the electrode immediately before pulsing must also be a factor in determining whether the electrode performance will improve as a result of a single heavy discharge pulse. In addition it must be noted that driving an electrode to a given potential level means that the electrode has passed through a potential range while getting to that level and again when returning to its steady-state potential following the pulse. It cannot be readily established therefore whether an improved performance resulted from driving the electrode to the maximum polarization observed or to some intermediate polarization along the way.

In later experiments, this procedure was modified slightly in that the current at a constant polarization (instead of the voltage) was compared before and after pulsing. With this latter procedure, the criteria for beneficial pulsing was that the current 60 seconds after the pulse was at least 5 per cent greater than the steady-state current immediately before.

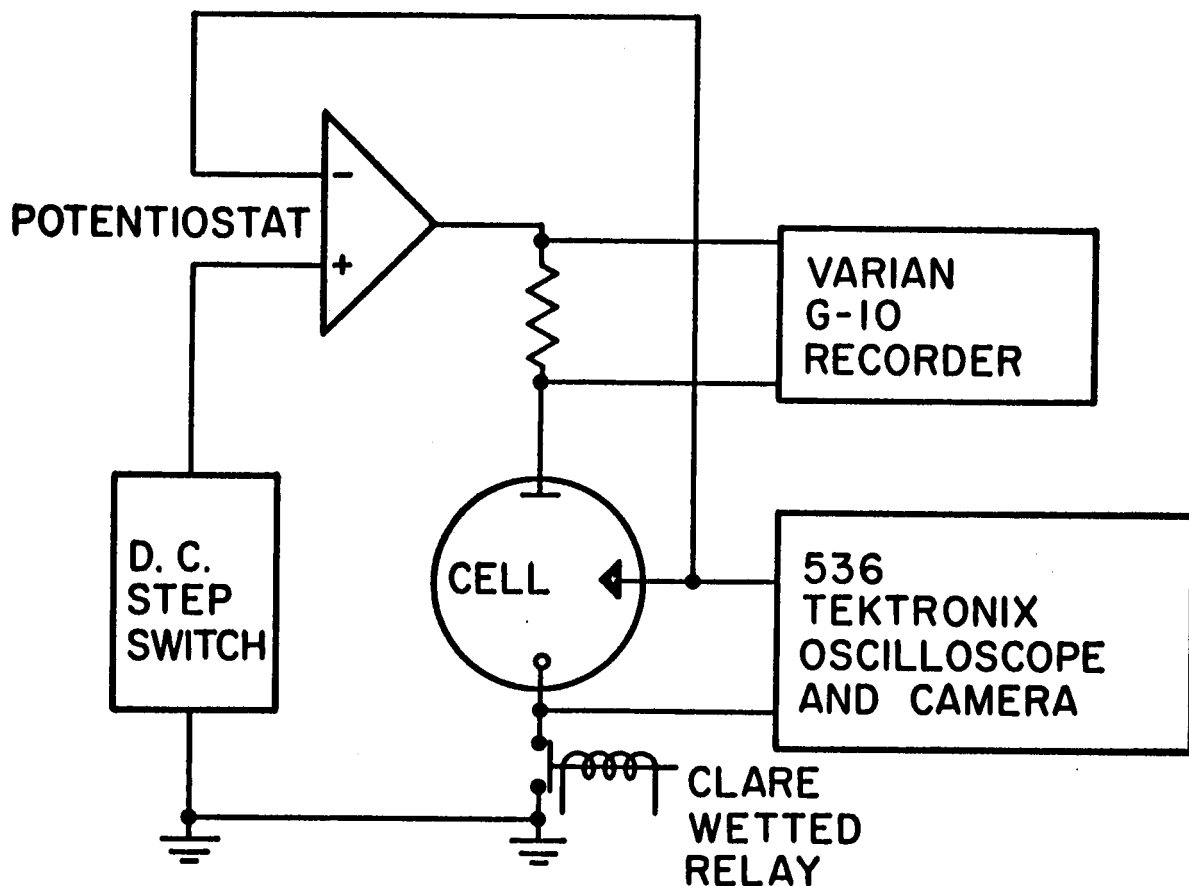
The following procedure was the one that was used to evaluate the activity of electrodes using the potentiostat:

1. The electrode is operated at a steady-state polarization of 10 mv (i. e. , under nonlimiting current conditions), and the current is noted;

2. The potential is abruptly changed by means of a stepping switch to another potential region and allowed to remain there for some short specified time period;

3. The electrode is then returned to its initial steady-state polarization of 10 mv and the current is compared with the steady-state current before the pulse was applied—a higher current is interpreted to mean the potentials applied during the pulse improved the catalytic properties (e. g. , increased the number of active sites of the electrode).

A block diagram of the circuit and experimental arrangement used for measurements with the potentiostat is shown in Fig. 7. A second relay (not shown in the figure) was added to turn off the stirring apparatus several milliseconds before applying the pulse.



D-1630

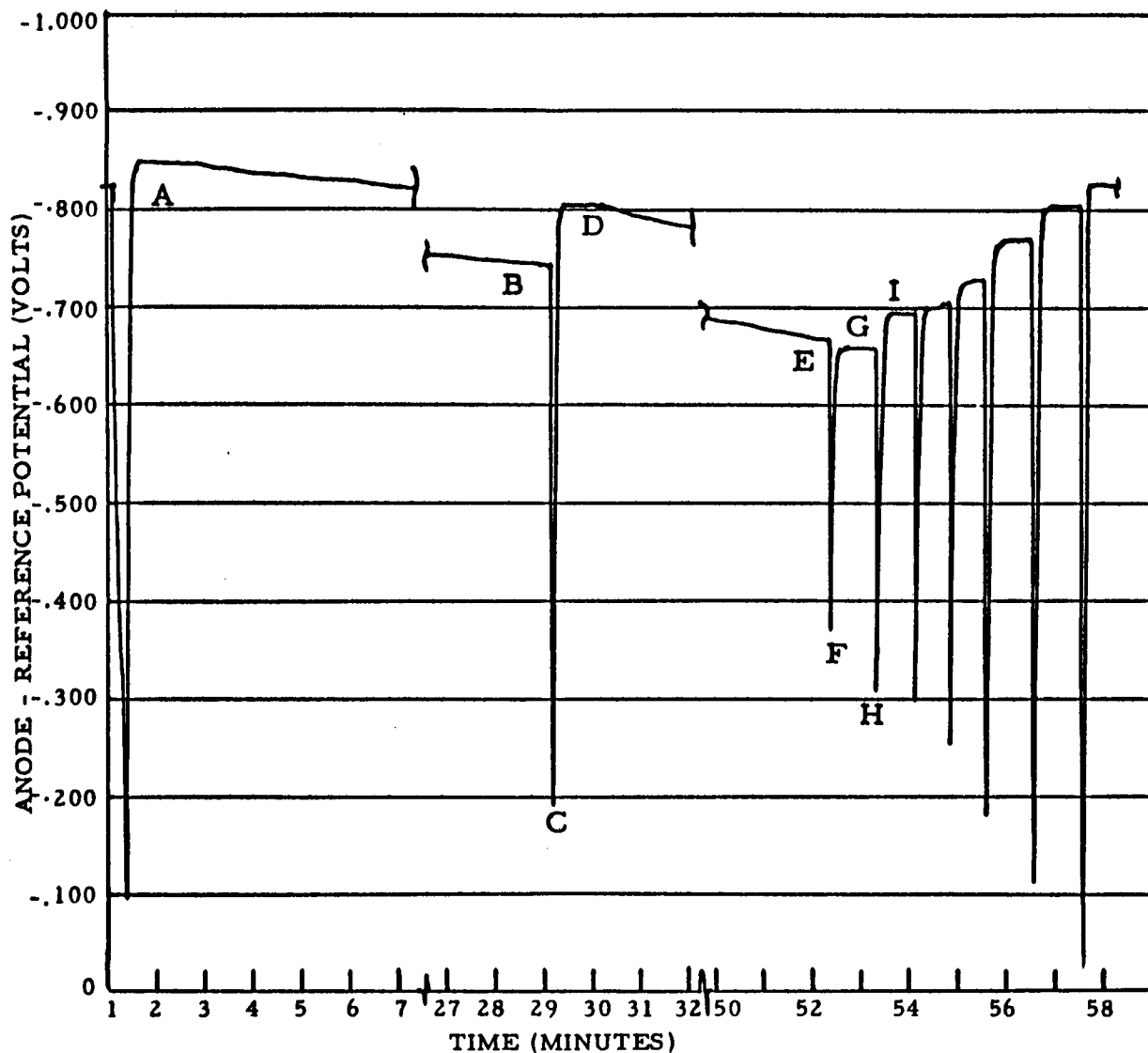
Fig. 7 Potentiostat and Associated Equipment.

I. C. Experimental Results.

I. C. 1. Platinum Sheet Electrodes.

Experiments on smooth platinum sheet electrodes were run using both the current pulsing units and the potentiostat. An example of the way data were obtained using the current pulsing unit and Varian G-10 recorder to record electrode potentials is shown in Fig. 8 for a 20 cm² smooth platinum electrode. The operating conditions were as follows: electrolyte-H₂ saturated 6N KOH, nonpre-electrolyzed; temperature, 26°C; current, 0.23 ma; and a mercuric oxide reference electrode was used. Referring to Fig. 8, the following explanation is pertinent: At point "A" the Pt anode-reference potential (Hg/HgO) was -0.850 v but decayed to -0.743 v (point "B") after 29 minutes. At point "B" a single pulse which drove the electrode to -0.19 v (point "C") caused the electrode to improve to -0.805 v (point "D"). During the next 23 minutes ("D" to "E") the potential deteriorated from -0.805 to -0.669 v. A single pulse to -0.37 v ("F") did not improve the electrode performance because the electrode recovered to only -0.658 ("G") after the pulse. However, the next pulse to -0.31 v ("H") caused the electrode to improve to -0.695 ("I"). As shown in Fig. 8, successive pulses to -0.29, -0.25, -0.18, -0.11 and -0.02 v all continued to improve the electrode to the final value shown here of -0.827 v. Then the recorder scale was changed to zero center (not shown here) to accommodate even stronger pulses (positive values). The electrode continued to show improvement at positive values of pulsing up until +0.08 v. The electrode did not recover at all when pulses drove the electrode beyond +0.08 v. While later experiments showed that a Pt anode driven beyond +0.08 v could be induced to recover by means of a short charging pulse, or by remaining at open circuit for several minutes, the data reported here refer to improvements resulting from a short discharge pulse followed by the immediate restoration of the normal current load.

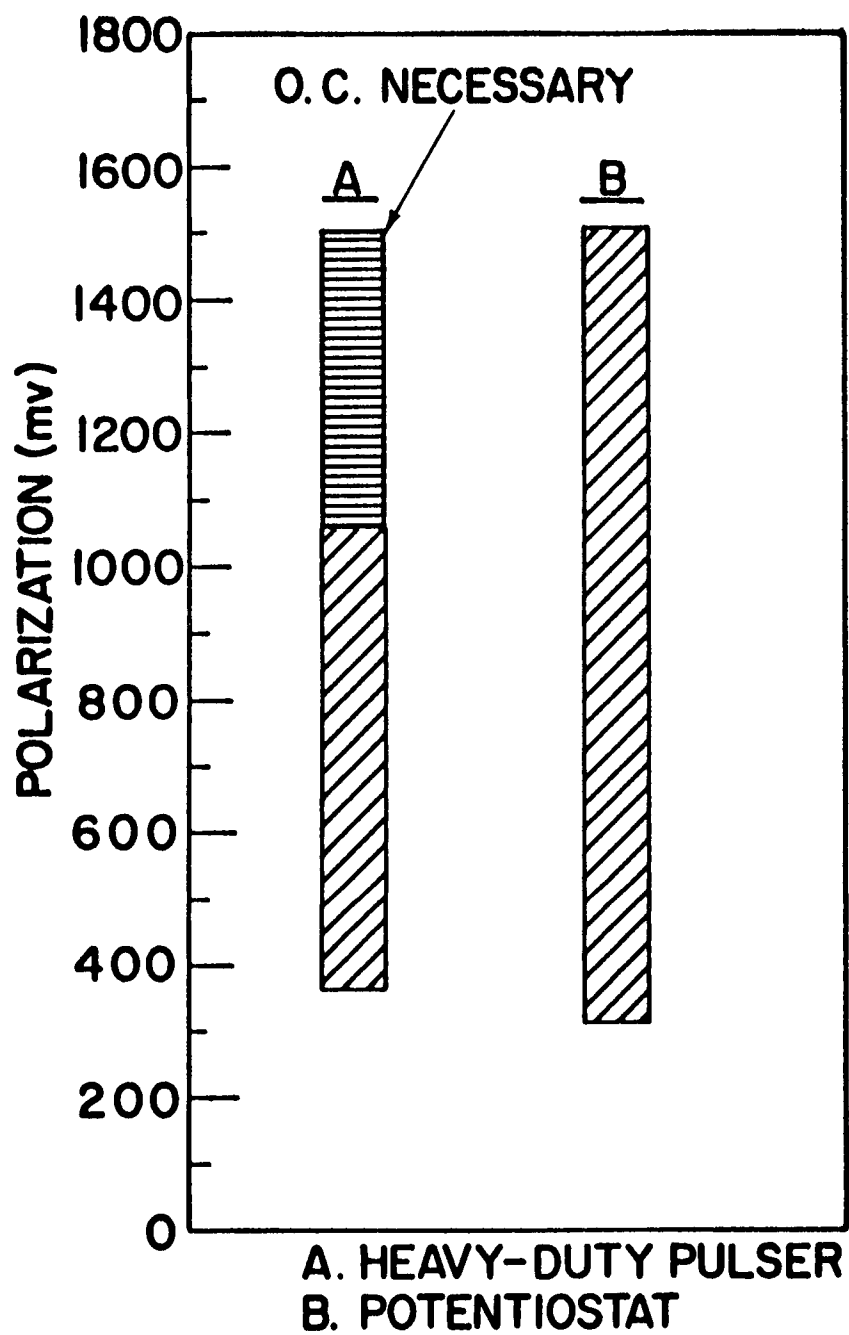
The pulsing region corresponding to improved activity of platinum-sheet anodes was also determined by applying potential-step pulses with the Wenking potentiostat as already described in section I.B. The "beneficial" pulsing region obtained is summarized in Fig. 9, where this region is compared with the "beneficial" region obtained with the current pulsing unit. The results are reported as



D-1531

Fig. 8 Recorder Tape of Anode-Reference Potential.

potentials with respect to a reversible hydrogen electrode in the same solution. This measured difference between an H_2 reference electrode and mercuric oxide reference electrode in 1N KOH was 0.929 v, with the mercuric oxide electrode at a positive potential with respect to the hydrogen electrode.



D-1800

Fig. 9 Range of Potentials for Beneficial Pulsing (Nonporous Electrodes).

As seen in Fig. 9, the potential regions yielding improved catalytic activity are about the same when obtained with the current pulsing unit and with the potentiostat. However, pulsing with the constant current device did require a short open circuit or current reversal period to allow the electrode to recuperate. This difference is not unexpected since the action of the potentiostat is different from the current pulsing unit. The current pulsing unit polarizes the electrode to an unspecified region by virtue of a preset heavy current, and then restores the steady-state current, leaving the electrode to recover on its own. The potentiostat applies the specified potential and then drives the electrode to the comparison potential. Strong oxidation has been reported³ to significantly reduce catalytic activity of platinum. Therefore, the electrode driven to an oxidizing potential by the current pulsing unit remains there, unable to recover. However, if pulsed to the same region by the potentiostat, it would be driven back by the potentiostat. Driving the potential back to the self-recovery potential in a H₂-saturated solution is equivalent to some reduction of surface oxide, so the electrode shows the improved activity characteristic of a partially oxidized surface. Similar results are observed with the constant current pulsing unit if the circuit is opened for several seconds or more immediately after the pulse is applied, before restoring the normal load. The electrode potential recovers slowly at first as surface reduction begins, and then more rapidly as a more active catalytic surface is achieved. This procedure results in improved catalytic activity, even from an anode pulsed to a strongly oxidizing potential region.

Additional experiments to determine beneficial pulsing regions were carried out on platinum cathodes in O₂-saturated electrolytes and on rhodium and palladium anodes and cathodes. The regions of beneficial pulsing obtained for these three metals as both anodes and cathodes in H₂ and O₂ saturated solutions, respectively, are shown in Fig. 10. When anodes were driven to potential regions indicated by the Roman numeral II, the currents after the pulse were always greater than the steady-state currents prior to pulsing. When Pt and Rh electrodes were driven to potential regions indicated by I, the anode potential did not recover upon restoration of the steady-state current but continued to polarize further. It was necessary to open the circuit and wait several minutes for the electrode potential to "recover." This "recovery" could be accelerated by the application of a discharge current.

However, once the electrode recovered after having been pulsed to the region indicated by I, the current at the comparison polarization was normally at least twice as large as the steady-state current before the pulse (i. e., $I_a/I_b \approx 2$ or more). This was significantly greater than the improvement resulting from a single pulse when electrodes were pulsed to potential regions represented by II, where the ratio of current after to current before a pulse was normally 1.1 and 1.2.

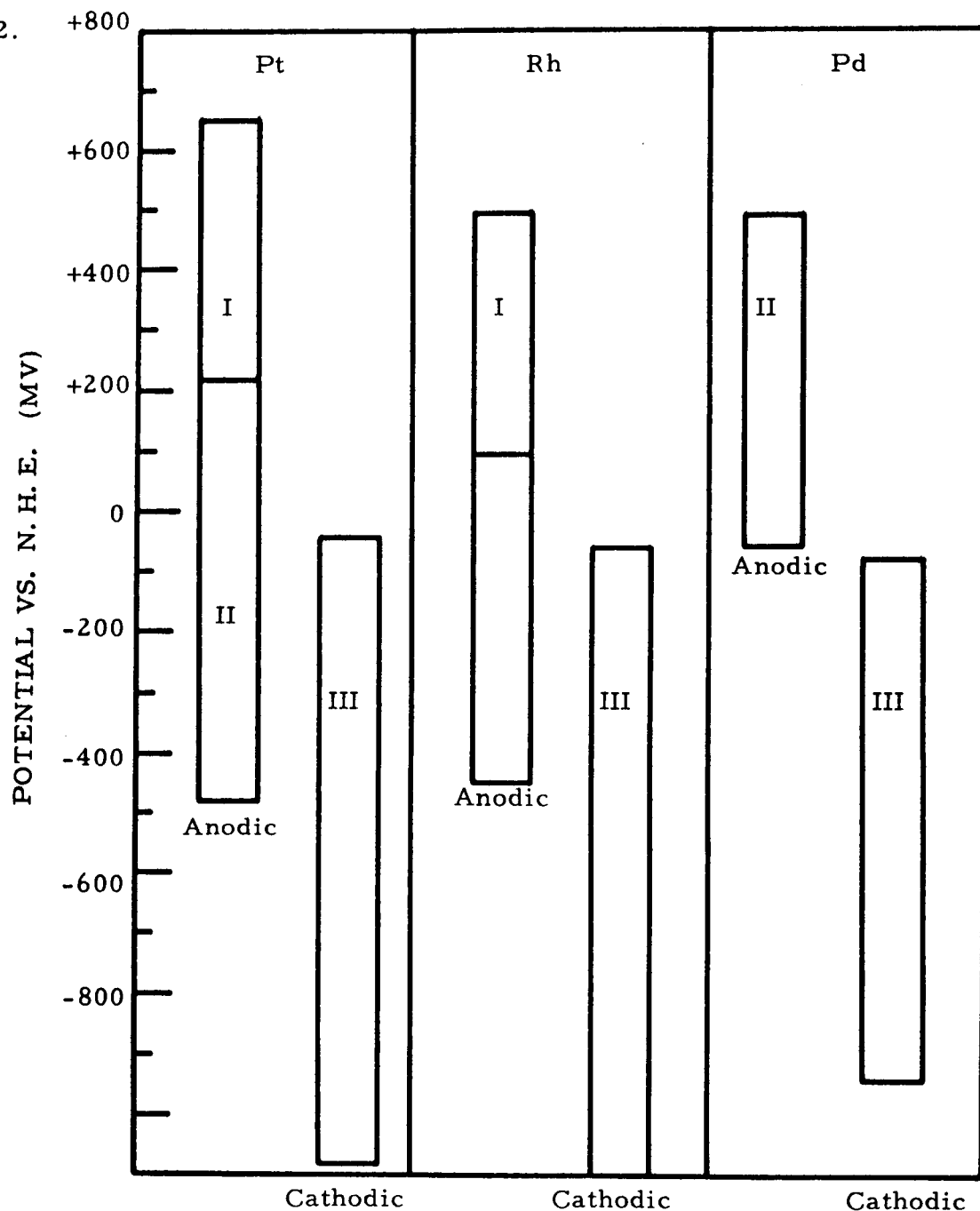


Fig. 10 Polarization Region for Improved Catalytic Activity of Platinum in H_2 -Saturated N KOH Solution.

D-1801R

Palladium anodes behaved quite differently than platinum and rhodium and responded favorably only to strong pulses which polarized the electrodes 700 mv or more. Although it has not been established whether or not the abnormally high solubility of hydrogen in Pd contributes to this difference in response to pulsing, it is not believed to be a significant factor.

The data in Fig. 10 show that cathodic heavy discharge pulsing of the three metals to potential regions corresponding to less oxidized surface states (III) appears to improve catalytic activity for oxygen reduction. The magnitude of improvement in catalytic activity for O_2 reduction resulting from a single cathodic pulse to a favorable potential region was normally 5 per cent or less (i. e., $I_a/I_b \approx 1.05$). This is significantly lower than the increased catalytic activity attained as a result of pulsing H_2 electrodes ($I_a/I_b \approx 1.1-2.0$).

Some of the early data obtained on solid metal electrodes determined in a range too close to limiting current conditions show a more narrow spread than those presented here. (The anodic polarization was set at approximately 50 mv and 6N KOH solutions were used.) Subsequent work indicated that for nonporous, metal electrodes in H_2 -saturated solutions, it is preferable to use 1N KOH solutions and to remain in the 10-20 mv polarization range.

Experiments were conducted to determine the length of time an activation pulse must be applied in order to reactivate Pt metal catalyst. Potential pulses to +1.6 v were applied to Pt anodes in H_2 -saturated 1N KOH solutions for times ranging from 0.01 to 10 seconds. A circuit employing the sweep timer of a 536 Tektronix oscilloscope was used to time the pulses.

The activity versus time curves for a smooth 5 cm² platinum electrode are shown in Fig. 11. The steady-state current prior to the pulse at $\eta = 10$ mv was 0.97 ± 0.03 ma for all four cases. The results show that activation of the electrode is complete after approximately one second, i. e., the one-second and ten-second pulse had about the same degree of activation and decay rate. The 0.01-second pulse did not activate the electrode, and the 0.1-second pulse partially activated the electrode. (The rise time of the Wenking potentiostat under these conditions is approximately 0.0001 second to 95 per cent of final value.)

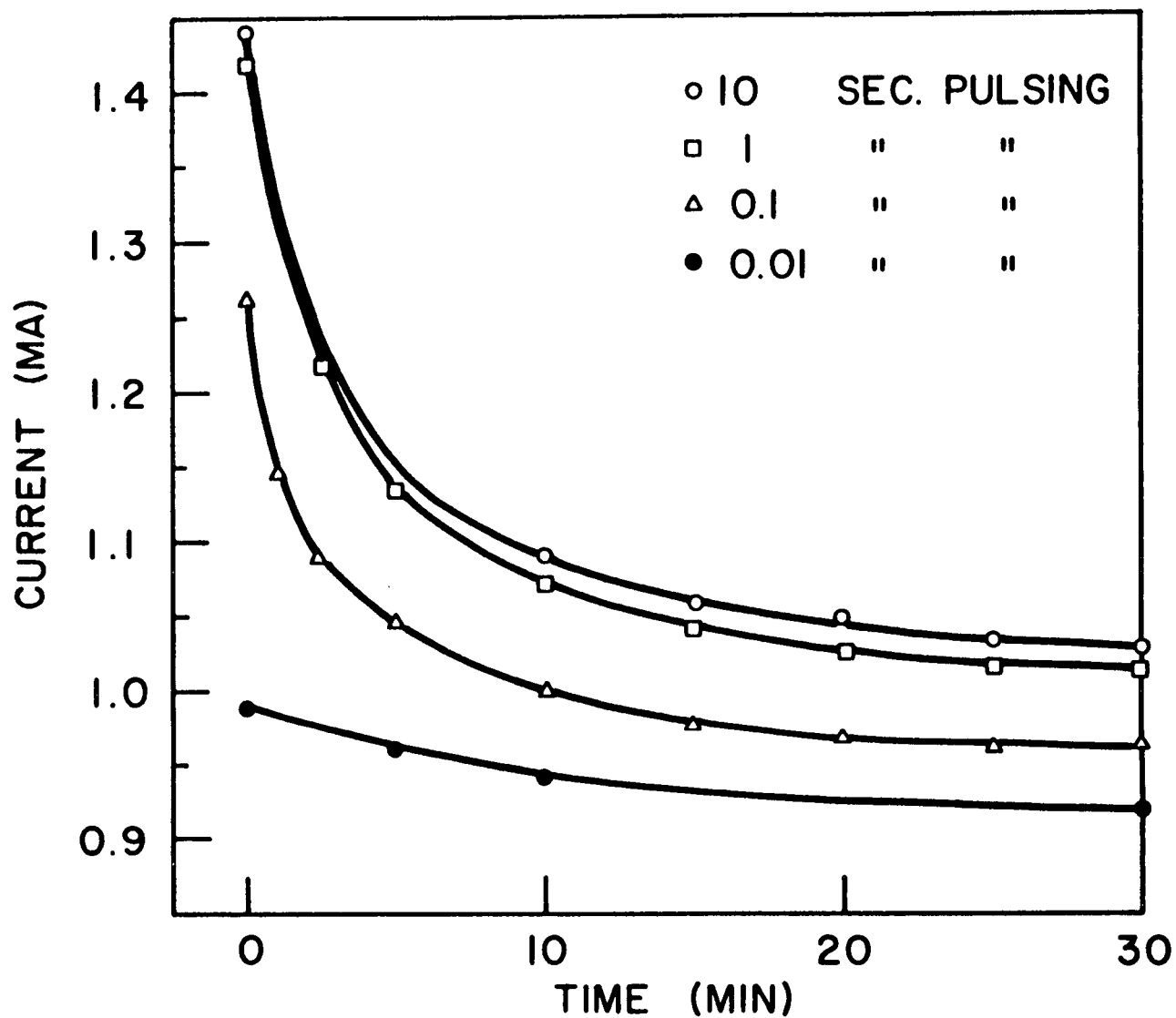


Fig. 11 Current Versus Time Curves Illustrating the Effect of Pulse Time.

D-2049

In Fig. 12 are shown oscilloscope traces of current-time scans from $\eta = 0.010$ to 1.6 v for 10^{-4} , 1.0 , 2.5 and ten-second scan rates.* The total time during the 0.010 to 1.60 v scan was six seconds, after which the smooth Pt was returned to the comparison potential of $+0.010$ v. Referring to Fig. 12, Curve 1, in each case, represents the steady-state current before the scan at $\eta = 10$ mv; Curve 2 the current during the scan; and Curve 3 the current after the scan at $\eta = 10$ mv. In Fig. 12a (10^{-4} second scan), the electrode was at $+1.6$ v for virtually six seconds; in (b) for about three seconds; and in (c) and (d) just attained $+1.6$ v at the end of the scan. The vertical level of Curve 3 above Curve 1 represents the increased current following the pulse. This is slightly greater for the longer durations near $+1.6$ v which were attained by the faster scan rates. The sharp initial rise in current during the rapid pulses is attributed to double layer charging currents, which at the 10^{-4} -second rate would be approximately

$$\text{current density} = C \frac{de}{dt} = 30 \times 10^{-6} \times 10^4 = 0.3 \text{ amp/cm}^2 \quad (3)$$

where C = double layer capacity (F/cm^2)

$$\frac{de}{dt} = \text{rise time of potentiostat (volts/second)}.$$

* The scan rate is the RC time constant in seconds, i. e., it gives the time to attain 63 per cent of the final value. Our scans were usually for 6 or 12 seconds, so rates slower than 2.5 seconds were set to higher voltages so that they could reach the intended voltage within this scanning time. The voltage, V , at any time, t , is given by Equation 1:

$$V = V \text{ final } (1 - \exp^{-t/RC}) \quad (1)$$

and the scan rate at any time t by Equation 2:

$$\frac{dv}{dt} = \frac{V \text{ final}}{RC} \exp^{-t/RC} \quad (2)$$

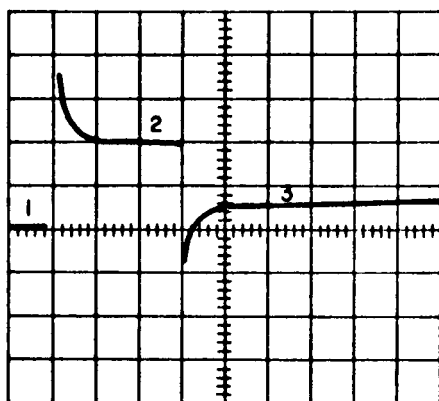
$$\text{where } \frac{dv}{dt} = \text{scan rate in volts/second}$$

$$V \text{ final} = \text{final voltage setting}$$

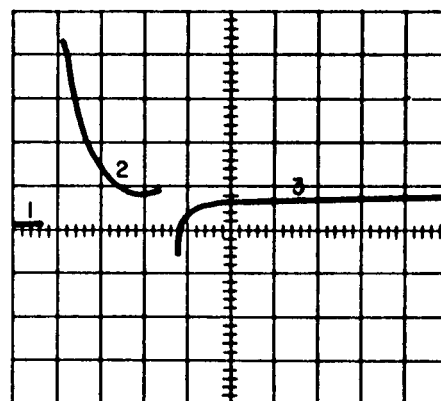
$$RC = \text{time constant in seconds}$$

thus when $t \approx 0$ (at the beginning of a scan) the scan rate equals the final voltage divided by the time constant.

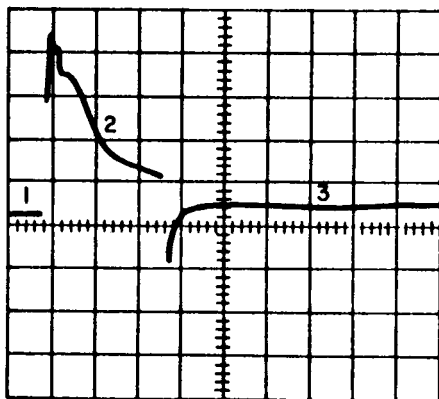
VERTICAL SCALE 2 MA/CM
HORIZONTAL SCALE 2 SEC./CM



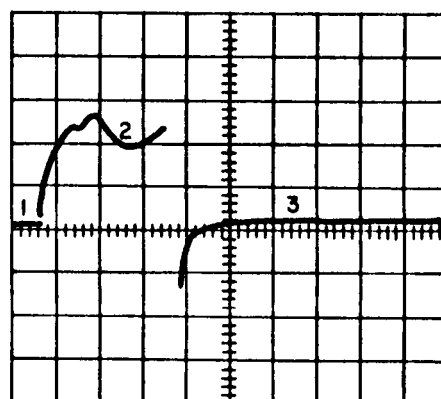
(a) 10^{-4} SEC. SCAN RATE



(b) 1 SEC. SCAN RATE



(c) 2.5 SEC. SCAN RATE



(d) 10 SEC. SCAN RATE

D-2141

Fig. 12 Oscilloscope Traces of Current-Time Scans
on Smooth Platinum.

Experiments were also conducted on platinized platinum sheet electrodes to determine whether these more active electrodes would respond to pulsing and decline in activity with time in a manner similar to the observations on smooth platinum electrodes. Accordingly, nonporous platinum electrodes were platinized for specified times at 10 ma/cm^2 and placed in H_2 -saturated 1N KOH solutions. The activity of these electrodes was determined as a function of time by determining the current at 10 mv polarization with respect to a heavily platinized platinum, H_2 -electrode in the same solution. Capacitance measurements were taken at the same time to note changes in surface condition. After the activity decreased to a small fraction of the initial activity, the electrode was pulsed to one of the following ranges versus H_2 in the same solution: a strong oxidizing potential where vigorous O_2 evolution and substantial surface oxidation occurs (1.7 v); an intermediate oxidation potential (1.05 v , where significant oxygen chemisorption occurs); and a low voltage, low adsorption region (0.65 v). A chemical oxidation treatment was also given (chromic acid immersion for one minute at 80°C). The data for these various treatments are summarized in Table I and graphically shown in Fig. 13. The relative decay of the catalytic activity was far more pronounced, when the ratio of the current at the time specified, to the initial current was plotted versus time. Maintaining the potential in the strong oxidation region (1.7 v ; O_2 evolution and PtO_x formation) produces the highest active catalytic surface after the electrode is driven back by the potentiostat to the comparison potential at $\eta = 10 \text{ mv}$. These data suggest that both, strongly oxidized sites and sites of a reduced or of an intermediate oxidation state must be present for an especially active catalytic surface to exist.

The data in Table I and Fig. 13 also show that electrochemical oxidation to 1.05 v appears to restore the initial activity of the electrode but does not increase the activity to the extent observed by pulsing to higher potentials. Pulsing to the 0.65 v region only partially restored activity. Chemical oxidation is very effective in restoring catalytic activity to platinum.

The capacitance values qualitatively follow the decline in activity as determined by the current at $\eta = 10 \text{ mv}$.

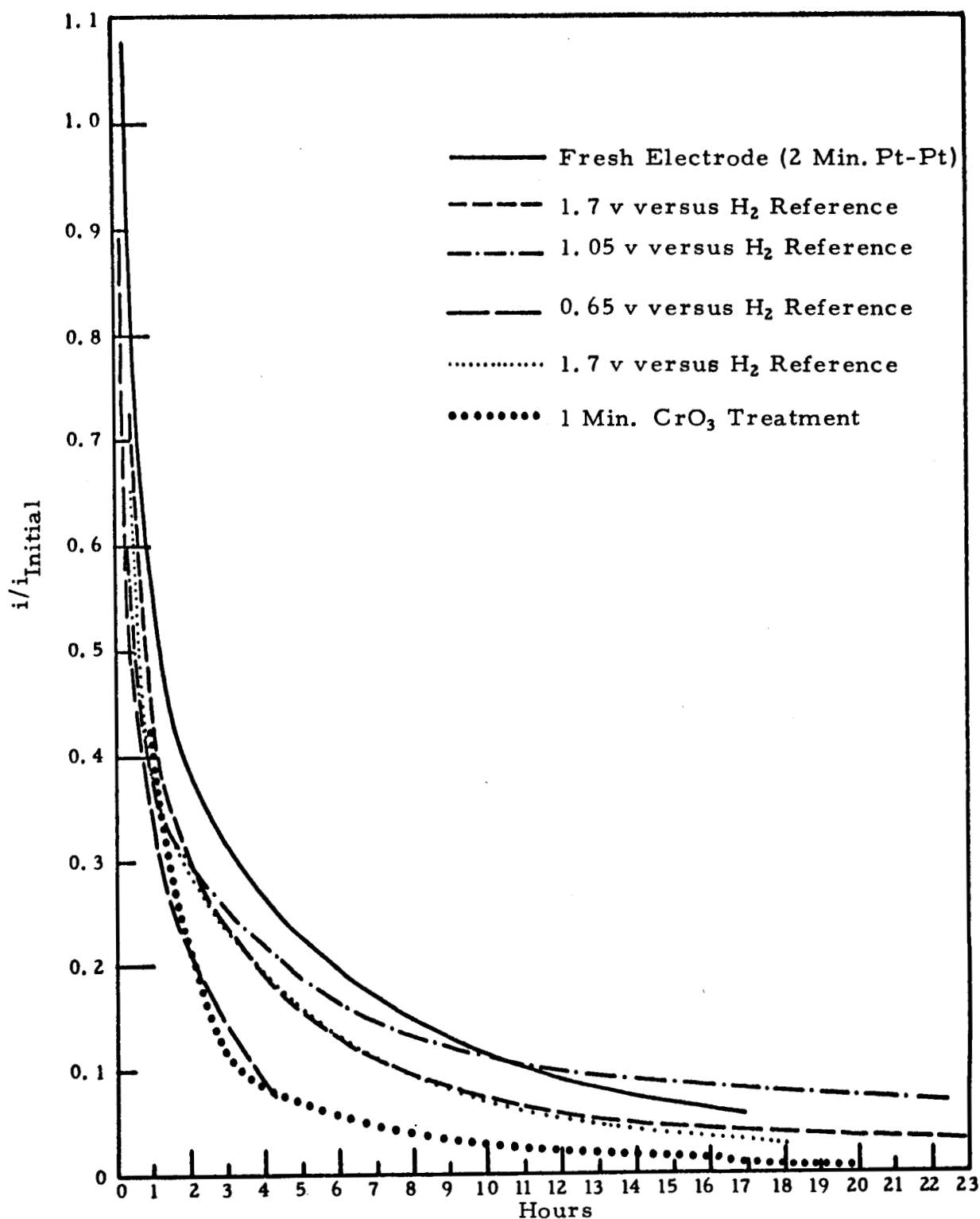
In addition to rejuvenating a catalytic platinum surface by oxidation, an electrochemical pulse could also improve catalytic activity by desorption or dissolution of impurities which might deactivate an active catalytic center through adsorption or deposition.

TABLE I

DECAY OF PLATINUM ELECTRODE ACTIVITY
AND CAPACITANCE AFTER PULSING

(In H₂-Saturated 1 N KOH Solution; Electrode Area: 20cm²; 2 Min. Platinization)

Time (Hrs.)	Current at $\eta = 10$ mv (ma)	Capacitance $\mu F \times 10^{-3}$	i/i initial
0.15	1.730	171.00	1.000
0.33	1.860	130.00	1.070
0.75	1.060	77.80	0.610
1.10	0.920	58.00	0.530
1.50	0.705	61.70	0.405
1.75	0.710	47.80	0.410
16.80	0.100	32.80	0.058
16.90	0.110	33.30	0.063
Maintain at 1.7 v for 15 minutes and continue measuring activity and capacitance vs time.			
0.03	5.200	142.00	1.000
0.40	3.780	86.80	0.725
1.00	2.210	62.40	0.425
1.60	1.700	51.50	0.328
2.70	1.110	46.30	0.214
4.40	0.920	36.00	0.177
6.20	0.650	36.40	0.125
23.50	0.160	17.15	0.031
Maintain at 1.05 v vs H ₂ for 15 minutes and continue measurements.			
0.03	1.580	44.70	1.000
0.33	0.940	41.60	0.595
1.10	0.560	25.40	0.355
3.85	0.320	14.00	0.203
6.25	0.250	13.10	0.158
22.55	0.100	12.60	0.063
23.65	0.100	11.30	0.063
Maintain at 0.65 v vs H ₂ for 15 minutes and continue measurements.			
0.03	0.370	13.60	1.000
0.25	0.330	14.60	0.890
1.00	0.130	15.00	0.350
1.50	0.100	11.20	0.270
4.15	0.030	14.50	0.081
Hold at 1.7 v vs H ₂ for 15 minutes and continue measurements.			
0.03	5.960	94.60	1.000
0.50	3.900	39.80	0.655
0.80	2.340	44.40	0.393
17.60	0.140	16.00	0.023
18.20	0.220	16.40	0.037
Treat electrode in strong oxidizing agent (CrO ₃ at 80°C) for 1 minute.			
0.13	4.000	111.20	1.000
0.95	1.700	38.60	0.425
2.00	0.900	29.60	0.225
3.00	0.450	28.20	0.112
20.00	0.040	11.80	0.010



D-1727

Fig. 13 Preliminary Data Illustrating Decay of Catalytic Activity of a Pt-Pt Electrode with Time, and Restoration by Electrochemical and Chemical Oxidations.

The effect of adding a metallic impurity on the rate of current decline was determined for iron. The decay rate for a ten-second platinized electrode in a 30-day pre-electrolyzed 1N KOH solution was determined and is shown as (a) in Fig. 14. This decay rate was then obtained following the addition of FeSO_4 solution to bring the concentration of Fe to (b) 1 ppm; (c) 5 ppm.

The effect on decay rate is shown in Fig. 14. The decay rate is much higher for solutions of relatively high iron content. Since the solubility product for $\text{Fe}(\text{OH})_2$ is only 1.8×10^{-15} , there must be an equilibrium between colloiddally suspended $\text{Fe}(\text{OH})_2$ and ionic iron species in solution. To make certain that iron "poisoned" the electrode by adsorption or deposition rather than ferrous ion reduction of an active-oxidized site, the effect of 5 ppm addition of $\text{Fe}_2(\text{SO}_4)_3$ was noted. This is shown in (d) of Fig. 14. Here too, the current decay was much more rapid than without Fe addition.

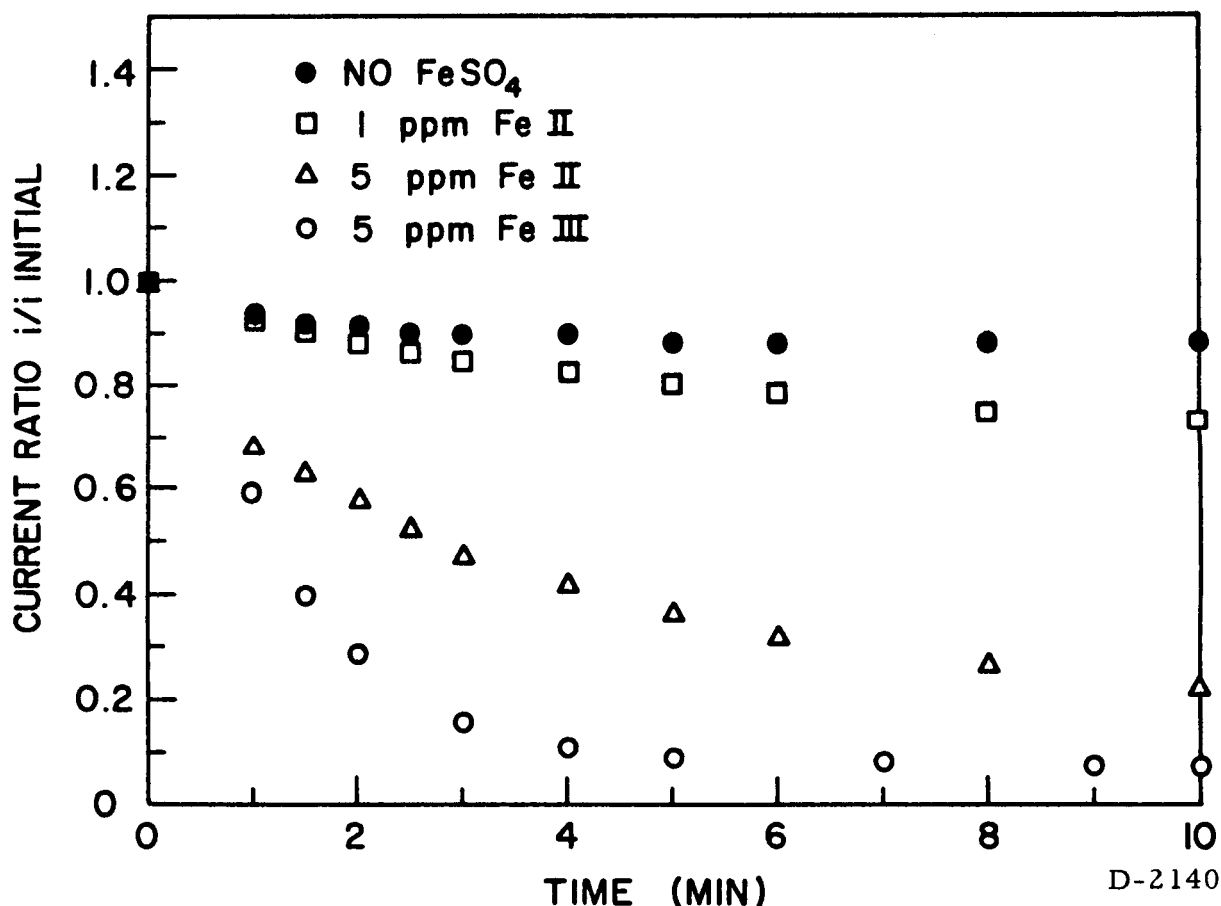


Fig. 14 Normalized Current-Time Curves after Addition of Fe to the Electrolyte.

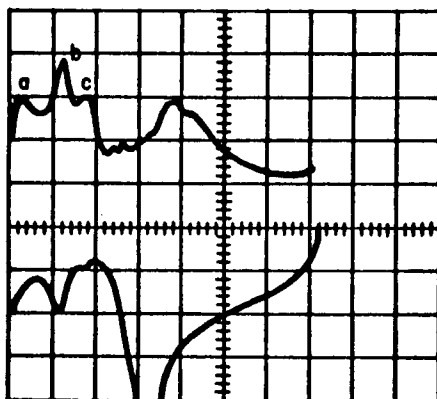
Current-voltage scans were also run on lightly platinized electrodes to determine whether there would be any significant difference between these scans in solutions free of Fe II and those to which Fe II was added. In Fig. 15 are shown current-voltage forward and reverse scans for a lightly platinized electrode in a) 30-day pre-electrolyzed 1N KOH and b) 1N KOH containing 5 ppm Fe II. Peaks a, b and c (15a) are due to molecular and adsorbed hydrogen dissolution currents and peaks d and e are attributed to surface oxidation currents. The forward scan for the same electrode in an electrolyte containing 5 ppm Fe (II) shows a lack of peak definition (low hydrogen currents) which is characteristic of a "poisoned" electrode.

Another characteristic of the "poisoned" electrode is that there is an additional current peak slightly positive to the second oxidation peak of platinum. This is indicated by an arrow on Fig. 15b. This occurs at about +1.1 v and is related to Fe II addition. At this anodic potential it is more likely indicative of Fe II cation desorption, rather than the oxidation of deposited Fe which occurs at -0.877 v in alkaline electrolyte.⁴

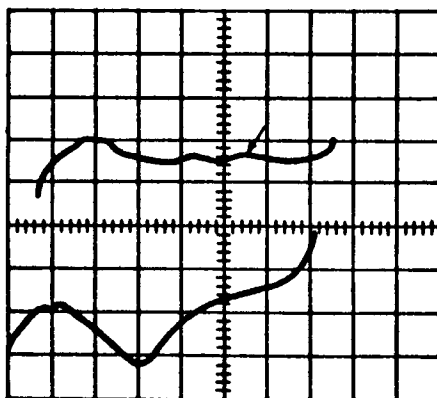
I. C. 2. Composite Electrodes (Plastic Bonded).

Pulsing experiments on Carbide electrode composite were run with the current pulsing unit according to the procedure described in Section I.B. The following variables were investigated: steady-state current density (20 to 100 ma/cm²); pulse duration (0.5 to 5.0 seconds); and pulse intensity (500 to 1800 ma/cm²). A summary of the data obtained on Union Carbide catalyzed, plastic-bonded electrodes for two levels of current density, pulse duration and pulse intensity is given in Table II. Anode-reference and cathode-reference data were obtained separately versus a Hg/HgO electrode in the same 12N KOH electrolyte. The data reported in Table II was obtained at 50°C. The results reported were read one minute after a single pulse was applied, and the time interval between pulses was one hour. The change in potential at constant current resulting from a single pulse is given in the far right column. A positive value denotes the extent of polarization in millivolts. The results summarized in Table II and other results obtained on composite electrodes which were not tabulated, indicated that the degree of improvement resulting from a single discharge pulse (within practical limitations) was directly related to the following factors.

UPPER CURVE - FORWARD SCAN
 LOWER CURVE - REVERSE SCAN
 VERTICAL SCALE = 5 MA/CM
 HORIZONTAL SCALE = 0.2 VOLT/CM



(a) PRE-ELECTROLYZED 1 N
 KOH



(b) 1 N KOH CONTAINING 5-
 P.P.M. Fe II

D-2149

Fig. 15 Current-Voltage Forward and Reverse Scan
 on Lightly Platinized Electrode.

TABLE II

PULSING DATA ON UNION CARBIDE PLASTIC-BONDED ELECTRODES

Temperature = 50°C

Electrolyte = 6N KOH

Time on Test (Days)	Electrode Type	Current Density (ma/cm ²)	Potential vs HgO (Volts)			Pulse C. D. (ma/cm ²)	Pulse Duration (Sec)	Improvement (mv) After - Before
			Before	During	After			
2	anode	20	-.933	-.79	-.933	500	1	0
2	"	20	-.933	-.53	-.938	1800	1	+ 5
2	"	20	-.935	-.60	-.939	500	5	+ 4
2	"	20	-.934	-.44	-.941	1800	5	+ 7
2	"	100	-.911	-.80	-.911	500	1	0
2	"	100	-.911	-.54	-.918	1800	1	+ 7
2	"	100	-.912	-.60	-.918	500	5	+ 6
2	"	100	-.911	-.45	-.921	1800	5	+ 10
3	cathode	20	-.071	-.10	-.070	500	1	+ 1
3	"	20	-.071	-.12	-.068	1800	1	+ 3
3	"	20	-.068	-.12	-.066	500	5	+ 2
3	"	20	-.068	-.19	-.062	1800	5	+ 6
3	"	100	-.086	-.11	-.085	500	1	+ 1
3	"	100	-.085	-.13	-.083	1800	1	+ 2
3	"	100	-.084	-.12	-.081	500	5	+ 3
3	"	100	-.082	-.20	-.076	1800	5	+ 6
17	anode	20	-.912	-.69	-.913	500	1	+ 1
17	"	20	-.912	-.47	-.923	1800	1	+ 11
17	"	20	-.914	-.53	-.923	500	5	+ 9
17	"	20	-.913	-.27	-.932	1800	5	+ 19
17	"	100	-.889	-.70	-.890	500	1	+ 1
17	"	100	-.889	-.51	-.899	1800	1	+ 10
17	"	100	-.894	-.50	-.909	500	5	+ 15
17	"	100	-.898	-.31	-.923	1800	5	+ 25
18	cathode	20	-.079	-.10	-.078	500	1	+ 1
18	"	20	-.079	-.12	-.076	1800	1	+ 3
18	"	20	-.077	-.12	-.072	500	5	+ 5
18	"	20	-.075	-.21	-.065	1800	5	+ 10
18	"	100	-.096	-.11	-.095	500	1	+ 1
18	"	100	-.096	-.13	-.093	1800	1	+ 3
18	"	100	-.092	-.13	-.082	500	5	+ 6
18	"	100	-.087	-.20	-.079	1800	5	+ 8

1. Length of time the electrode was on test.
2. Polarization attained during the heavy discharge pulse.
(This is directly related to the duration and intensity of the pulse and the condition of the electrode prior to the pulse.)
3. Length of time between pulses.
4. Nature and concentration of catalyst (to be discussed in more detail under Task II).

The potential range attained during pulsing in which some beneficial effects were virtually always observed on composite anodes was from -0.70 to +0.66 v with respect to an HgO reference electrode. In certain instances, on very strong pulses, it was necessary to open the circuit for several minutes, or briefly apply a current reversal before reapplying steady-state discharge current.

The potential range attained during pulsing in which beneficial effects were observed on composite cathodes was from -1.04 to +0.03 v with respect to an HgO reference electrode.

I.C. 3. Porous Nickel Electrodes*

These electrodes were first tested in the cell shown in Fig. 2. The electrodes that were available to us could not support a gas pressure greater than 1 psi due to random pores larger than 27 microns in the nickel substrate. Therefore, a gas barrier in the electrolyte was provided by means of an asbestos matrix soaked with 6N KOH to support the pressures required to operate the cell. The cells were run at a potential of 0.850 v prior to pulsing, and subjected to pulses of varying intensity. Representative results are shown in Table III, indicating the change in mv resulting from the pulse. The cells were operated at pressures ranging from 2 to 14 psig. Beneficial effects noted as a result of a single pulse were normally only several millivolts or less, and often the cell voltage was lower after the pulse than before. The recovery in cell voltage after a pulse was normally quite slow, requiring several minutes in many cases.

* These electrodes were furnished to us by Prof. T. J. Gray of Alfred University.

TABLE III
PULSING DATA ON POROUS NICKEL CELLS
(Pt-Pd Catalyzed)

Note: Prior to Pulse, Cell Voltage Adjusted to 0.850 Volt.								
Cell No.	Gas Press. (psig)	Temp (°C)	C. D. (ma/cm ²)	Cell Potential (Volt)		Change (mv)	Intensity (ma)	Pulse Time (Sec)
				During	After*			
250	14	50	100	0.62	0.854	+4	480	2
250	14	50	100	0.00	0.848	-2	850	4
251	2	60	35	0.56	0.860	+10	350	2
251	2	60	37	0.26	0.852	+2	750	2
251	12	60	58	0.33	0.850	0	575	2
251	12	60	58	-0.03	0.843	-7	1150	2
251	12	60	49	0.24	0.854	+4	490	2
251	2	60	30	0.36	0.858	+8	295	2
251	2	60	30	0.00	0.846	-4	590	2
251	4	60	30	0.36	0.855	+5	300	2
251	4	60	30	0.00	0.846	-4	600	2
251	6	60	31	0.36	0.855	+5	305	2
251	6	60	31	0.00	0.850	0	620	2
251	8	60	32	0.35	0.858	+8	320	2
251	8	60	33	0.00	0.852	+2	650	2
251	10	60	33	0.00	0.848	-2	670	2
251	10	60	33	0.34	0.853	+3	335	2
251	12	60	34	0.32	0.855	+5	340	2
251	12	60	35	0.00	0.845	-5	695	2
253	8	45	30	0.61	0.846	-4	300	2
253	8	45	30	0.48	0.847	-3	590	2
253	8	45	29	0.41	0.847	-3	750	2
253	8	45	29	0.28	0.846	-4	1000	2

(*) Slow recovery.

Slow recovery is characteristic of a diffusion-controlled reaction. The diffusion control may arise in part due to the use of an electrolyte-soaked matrix, but may also be due to excessive tortuosity in the porous structure. These porous nickel electrodes are heavily catalyzed and are not likely to be catalyst limited. Therefore, their failure to respond to the pulsing treatment which is believed to improve catalyst performance through catalyst reactivation is not a surprising result. A heavy discharge pulse in a diffusion-controlled electrode is harmful, since products can accumulate at reaction sites and reactants are depleted. The system then requires time for the products to diffuse away and for reactants to diffuse before recovering. This is the general behavior that was observed on porous nickel electrodes, indicating that the electrodes were primarily diffusion-controlled rather than catalyst-limited. The harmful effect of heavy drain on a diffusion-limiting process may, in some instances, outweigh any beneficial effects to be derived from catalyst reactivation, thereby producing erratic results.

These electrodes were also tested in the cell shown in Fig. 3. A single 0.020", 6N KOH soaked asbestos matrix was used as the electrolyte. The cell was operated at 50°C and the H₂ and O₂ gases which were fed to the cell were saturated with water vapor at 35°C. The H₂ and O₂ pressures were 6 psig. The gas flow rate was adjusted to ten times the galvanic utilization rate, and the gases were vented off. The polarization curve for the cell before and various times following a ten-second pulse at 500 ma/cm², which drove the cell to -1.4 v, is shown in Fig. 16. Curve 16b was taken several minutes after the pulse, since the cell required this amount of time at open circuit to recover from the pulse. The improved performance resulting from the pulse lasts about 90 minutes.

I. C. 4. Baked Carbon Electrodes

Union Carbide catalyzed, baked carbon anodes showed improvements of several millivolts as a result of a single pulse when driven to potentials between approximately -0.6 and +0.5 v versus a mercuric oxide-reference electrode. Improvements of 10 mv or more resulted only if the circuit was opened for about one minute before reapplying the normal load. Baked carbon cathodes showed improvements of only 1 to 3 mv as a result of a single pulse when pulsed to potentials negative to -0.1 v versus a mercuric oxide reference. These results for beneficial

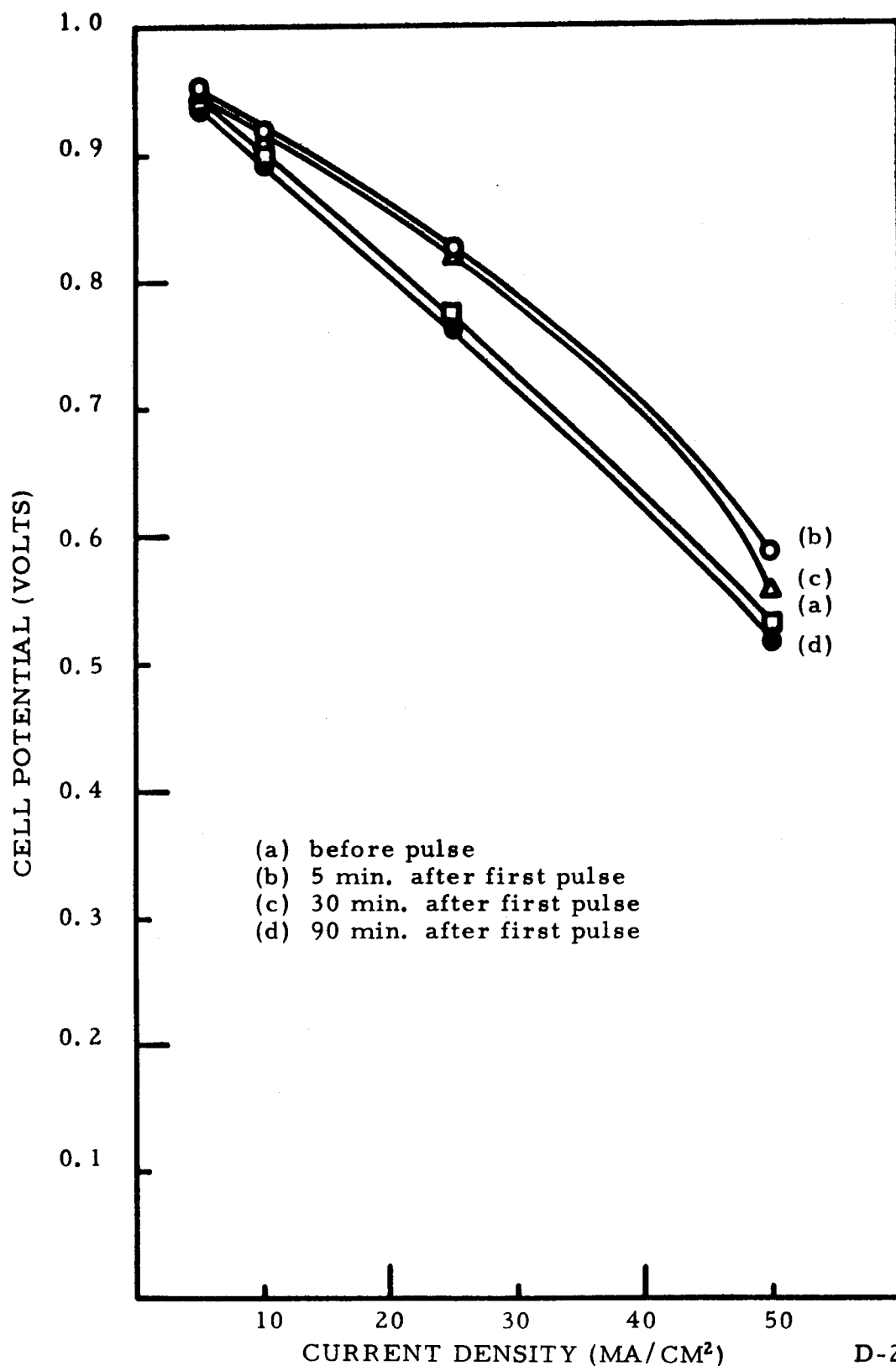


Fig. 16 Polarization Curves on Pt-Pd Catalyzed, Porous Nickel.

pulsing were approximately in the same potential region as are composite electrodes catalyzed in the same way. This lends support to previously reported results that also indicated that the "pulsing effect" was primarily a catalytic effect, independent of the substrate. The experiments were repeated several times and the potential range over which these small improvements were noted was in good agreement. However, the magnitude of the improvements resulting from a single pulse ranged from 1 to approximately 10 mv, and followed no distinguishable pattern. As an example of the way the data were obtained, the results for Anode 264-a are tabulated in Table IV. Here the pulse was always initiated when the anode-reference potential reached -0.850 v with respect to an Hg/HgO-reference electrode. The current density at this potential varied between 25 and 35 ma/cm². The pulse time was varied between 0.5 and 5.0 seconds in other experiments, but was maintained at three seconds for most of the results shown in Table IV. A positive value in the "Improvement" column denotes the extent of improvement in mv resulting from a single pulse.

I. C. 5. American Cyanamid Electrodes

American Cyanamid electrodes beneficial pulsing effects of only several millivolts or less were noted on cells made up with AB-4 electrodes. The AB-40 electrodes did not show any improvement as a result of heavy discharge pulsing during the first few days of operation. This latter result is not surprising since the AB-40 electrodes are catalyzed to the extent of 40 mg/cm² with platinum black and are not likely to be catalyst limited in initial stages of operation. The AB-4 electrodes contain 9 mg/cm² of catalyst which is of a concentration comparable to the catalyst concentration on the porous nickel electrodes described in the preceding section.

Since the Cyanamid electrodes have a very open structure, it is necessary to use a gas barrier between the electrodes. Furthermore, in order to use the electrode surface efficiently, the electrode must have some support on both the electrolyte and gas sides. This was accomplished in two different ways—by means of an asbestos matrix soaked with 6N KOH, and by a "wicking" arrangement using porous nickel on the electrolyte side with an electrolyte reservoir between

TABLE IV

PULSING DATA - BAKED CARBON ANODE 246-a
(Area: 2 cm² - Temperature 50°C - Electrolyte 6N KOH)

Anode Ref. Potential (Volts, HgO Ref.)			Improvement (mv)	Pulse Current (amps)	Pulse Time (secs)	Time (hrs)
Before	During	After				
-.850	+.290	-.852	+2	0.85	5	0
-.850	-.014	-.854	+4	1.25	3	1.25
-.850	+.060	-.856	+6	1.7	3	2.0
-.850	.000	-.854	+4	2.1	3	4.1
-.850	-.110	-.856	+6	2.5	3	25.0
-.850	-.050	-.861	+11	2.8	3	118.0
-.850	-.110	-.854	+4	3.2	3	119.0
-.850	-.140	-.855	+5	3.6	3	122.0
-.850	-.560	-.855	+5	2.8	3	124.0
-.850	-.080	-.858	+8	3.2	3	143.0
-.850	-.200	-.855	+5	3.6	3	146.0
-.850	-.195	-.853	+6	2.8	3	166.0
-.850	-.118	-.856	+3	3.2	3	167.0
-.850	.000	-.855	+5	3.6	3	173.0
-.850	-.018	-.859	+9	2.8	3	190.0
-.850	.000	-.854	+4	2.8	3	191.0
-.850	.000	-.854	+4	1.7	3	192.0
-.850	-.250	-.856	+6	2.1	3	194.0
-.850	+.066	-.856	+6	2.8	3	195.0
-.850	-.072	-.858	+8	2.8	3	214.0
-.850	-.110	-.855	+5	2.8	1	216.0
-.850	+.120	-.857	+7	2.8	5	218.0
-.850	+.200	-.867	+17	2.5	3	238.0

the porous nickel electrodes, and 6N KOH-soaked matrices between the working electrodes and porous nickel sheet. The latter system has two important advantages in testing electrodes, i. e., a reference electrode can be readily used to monitor individual electrode performance, and rigid water balance is not required.

In Table V are shown representative pulsing data for cells made up with AB-4 and cells with AB-40 electrodes using an asbestos matrix. (Johns Manville fuel cell asbestos, two sheets, 11 mil thick.)

TABLE V
PULSING DATA ON AMERICAN CYANAMID CELLS

Operating Variables: H ₂ Pressure = O ₂ Pressure = 2 psig; Electrolyte 6N KOH in Asbestos Matrix; Cell Voltage Prior to Pulse = 0.900 volt; Pulse Time = 2 Seconds							
Time	Temp. °C	Electrode Type	C. D. (ma/cm ²)	Cell Voltage		Change (mv)	Pulse Current (ma)
				During	After		
1st Day	45	AB-4	100	0.78	0.900	0	1000
"	45	AB-4	100	0.68	0.902	+2	2000
"	45	AB-4	115	0.62	0.906	+6	3000
"	45	AB-4	143	0.55	0.905	+5	3600
4th Day	45	AB-4	34	0.70	0.900	0	335
"	45	AB-4	34	0.60	0.906	+6	685
"	45	AB-4	37	0.57	0.902	+2	742
"	45	AB-4	37	0.49	0.904	+4	1000
"	45	AB-4	39	0.36	0.907	+7	2000
"	45	AB-4	42	0.31	0.905	+5	3000
"	45	AB-4	45	0.33	0.904	+4	3600
1st Day	45	AB-40	250	0.81	0.900	0	2500
"	45	AB-40	250	0.79	0.900	0	3000
"	45	AB-40	250	0.63	0.900	0	3600
"	45	AB-40	170	0.60	0.902	+2	3600
"	70	AB-40	200	0.76	0.900	0	2000
"	70	AB-40	200	0.72	0.900	0	2500
"	70	AB-40	200	0.67	0.900	0	3000
"	70	AB-40	200	0.63	0.900	0	3600

The small improvements on the AB-4 type and negligible improvements on the AB-40 type are to be noted as discussed previously. In Table VI, data are shown on AB-4 electrodes using the wicking arrangement noted previously. These data show that the improvements in performance resulting from pulsing were quite small and occurred more regularly at the anode than at the cathode.

TABLE VI

PULSING DATA ON AMERICAN CYANAMID AB-4 ELECTRODES

Operating Variables: 6 N KOH "Free Electrolyte"; Hg/HgO Reference; Temperature = 50°C.							
Electrode	C. D. (ma/cm ²)	Electrode Ref. Potential			Change (mv)	Pulse Current (ma)	Pulse Time (Sec.)
		Before	During	After			
Anode	230	-0.850	-0.20	-0.856	+6	2500	3
Anode	250	-0.850	-0.18	-0.855	+5	2800	3
Anode	250	-0.850	-0.17	-0.853	+3	3200	3
Anode	250	-0.850	-0.16	-0.852	+2	3600	3
Anode	260	-0.850	+0.03	-0.852	+2	3600	5
Cathode	100	-0.021	-0.63	-0.020	+1	2100	3
Cathode	100	-0.020	-0.71	-0.023	-3	2500	3
Cathode	100	-0.021	-0.73	-0.021	0	2800	3
Cathode	100	-0.021	-0.56	-0.020	+1	3200	3
Cathode	100	-0.019	-0.28	-0.021	-2	3600	3

Some experiments were performed on American Cyanamid AB-40 electrodes using the heavy-duty current pulsing unit. These data are summarized in Table VII. In obtaining these data, the electrode reference potential, before and after the pulse, was compared at the same potential. The pulse duration was five seconds. The cells were pulsed six to ten times per working day in the course of a two-hour period to obtain the data. When anodes were pulsed to positive potentials with respect to a mercuric oxide reference electrode, it was necessary to open the circuit for several minutes before restoration of steady-state current to permit the electrode potential to recover to its normal operating value.

TABLE VII
PULSING DATA FOR CYANAMID AB-40 ELECTRODES

Electrode	Time (days)	Electrode Ref. Pot. (Volts, IR-Free)		Current Density (ma/cm ²)			Ratio of Current After ÷ by the Current Before
		Before	During	Before	During	After	
Anode	1	-0.875	-0.694	180	1050	172	0.96
	1	-0.875	-0.605	172	1250	172	1.00
	1	-0.875	-0.491	172	1600	172	1.00
	1	-0.875	-0.454	172	1800	172	1.00
Cathode	1	0.0	-0.091	195	1050	195	1.00
	1	0.0	-0.178	190	1400	190	1.00
	1	0.0	-0.250	190	1800	195	1.02
Anode	2	-0.875	-0.626	180	1400	182	1.01
	2	-0.875	-0.463	182	1600	188	1.03
	2	-0.875	-0.436	180	1800	182	1.01
Cathode	2	0.0	-0.077	192	850	192	1.00
	2	0.0	-0.131	197	1050	200	1.01
	2	0.0	-0.236	200	1400	200	1.00
	2	0.0	-0.246	200	1800	200	1.00
Anode	6	-0.875	-0.595	160	1750	160	1.00
	6	-0.875	-0.160	200	3250	215	1.08
	6	-0.875	+0.330	245	4500	267	1.09
Cathode	6	0.0	-0.217	170	1250	175	1.03
	6	0.0	-0.460	160	2300	160	1.00
	6	0.0	-0.600	160	3000	165	1.03
Anode	14	-0.875	-0.750	250	1125	240	0.96
	14	-0.875	-0.580	255	1850	270	1.06
	14	-0.875	-0.130	287	3000	320	1.08
	14	-0.875	-0.040	320	3500	340	1.03
	14	-0.875	+0.320	345	4600	355	1.03

Beneficial pulsing effects for these electrodes were quite small (i. e. , 10 per cent or less) and were observed only after several days of operation. This indicates that initial performance is not primarily catalyst limited. Anodes appear to have derived some beneficial effects from pulsing since the performance level at a constant potential of -0.875 v versus a HgO reference improved with time. The cathode performance decreased slightly with time, as normally expected with cell operation, with no special effects noted from pulsing in this case.

An electrode potential equivalent to that obtained by a heavy discharge pulse can be achieved by "gas reversal," i. e. , exchanging the gas feed lines to the cell. When this is done, the hydrogen electrode is driven to the oxygen potential and the oxygen electrode is driven to the hydrogen potential. With a cell using the same electrodes for anodes and cathodes (Cyanamid), it is not necessary to reverse back to the original state, and the electrodes have had the electrochemical equivalent of a heavy discharge pulse. In addition, unfavorable concentration gradients are reversed by this treatment. A test of this type was performed on an AB-40 electrode cell, operating at 50°C and 100 ma/cm² for two days. The results obtained are given in Table VIII.

TABLE VIII
CELL VOLTAGE VERSUS TIME FOR GAS REVERSAL
(Data from Tape No. A-102)

Time (Minutes)	Cell Voltage (IR-Free)	Comments
0	0.811	Followed by gas reversal which took 3.5 minutes.
3.5	0.910	
7.5	0.902	
27.5	0.874	
67	0.859	Followed by gas reversal which took 2.0 minutes.
69	0.908	
73	0.900	
85	0.894	
89	0.893	
91	0.867	

I.C.6. Justi-Type Electrodes*

These electrodes were tested in the specially designed Teflon half-cell shown in Fig. 4. The cathodes are made up of Raney silver and the anodes of Raney nickel. Both types are operated in the range of 13.6 to 16.7 psig. Pulsing has its most beneficial effect at very high current pulses on cathodes (Table IX). The effects on anodes are highly scattered and difficult to evaluate (Table X).

Thermodynamic data from Latimer⁴ indicate that oxidation of the nickel anode (to NiO) would occur at approximately -0.82 v versus HgO. This indicates that a relatively small pulse would cause surface oxidation to the +2 oxidation state since this amounts to only 130 mv of polarization. Pulsing to higher polarizations would result in higher surface oxidation states, which are not well defined. According to a recent review by Young⁵, the +1 oxidation of silver occurs at approximately +0.25 v versus HgO, and the +2 state at approximately +0.45 v versus HgO. This indicates that normal cathodic operation probably occurs on an oxygen chemisorbed surface and that the effect of cathodic discharge pulses tend to further reduce the oxygen adsorption on this surface.

Task II - Catalyst Type and Concentrations.

The purpose of this task is to determine whether pulsing effects are related to catalyst concentrations as well as the nature of the catalyst. Tests were run on composite electrode substrates to determine whether the degree of pulsing improvements were related to catalyst concentrations. Experiments were also run to compare the inherent rate of catalytic activity decay on smooth and platinized platinum surfaces.

II.A. Composite Electrode Substrate.

In these tests, 1 and 3 mg/cm² concentrations of Pt, Rh-Pd and Union Carbide catalysts were applied to composite electrode substrates. The Pt and Rh-Pd catalysts were applied to the substrate by brushing on an appropriate amount of salt solution. This was followed by reduction with a 10 per cent hydrazine solution, washing and drying. The Union Carbide catalysts were applied

* These electrodes were purchased from Varta, A. G., Frankfurt A. M., West Germany.

TABLE IX
PULSING DATA ON JUSTI-TYPE CATHODES

Operating Variables: 6 N KOH Electrolyte; Pressure = 15 psig; Electrode Area = 9.62 cm ² ; Temperature = 55°C						
Time	C. D. (ma/cm ²)	Cathode Reference During	After	Change (mv)	Pulse Current (ma/cm ²)	Pulse Time (Sec.)
1st Day	50	-0.225	-0.027	0	360	1
"	50	-0.245	-0.027	0	360	2
"	50	-0.245	-0.027	0	360	3
"	50	-0.245	-0.027	0	360	4
"	50	-0.245	-0.027	0	360	5
2nd Day	200	-0.135	-0.095	0	285	5
"	200	-0.171	-0.095	0	385	5
"	200	-0.173	-0.094	+1	385	5
"	200	-0.211	-0.094	0	470	5
3rd Day	200	-0.205	-0.103	0	450	5
"	200	-0.235	-0.096	+1	700	5
"	200	-0.290	-0.095	+2	700	5
"	200	-0.325	-0.095	+1	800	5
"	200	-0.385	-0.094	+2	1000	5
"	200	-0.445	-0.092	+2	1240	5
"	200	-0.495	-0.088	+3	1450	5
"	200	-0.535	-0.086	+4	1750	5
"	200	-0.545	-0.087	+3	1880	5
5th Day	200	-0.237	-0.112	+1	450	5
"	200	-0.269	-0.108	+4	600	5
"	200	-0.303	-0.109	+1	700	5
"	200	-0.335	-0.109	+1	800	5
"	200	-0.371	-0.109	+1	900	5
"	200	-0.405	-0.110	+1	1000	5
"	200	-0.465	-0.110	+1	1240	5
"	200	-0.555	-0.109	+3	1600	5
"	200	-0.595	-0.109	+2	1850	5

TABLE X
PULSING DATA ON JUSTI-TYPE ANODES

Operating Variables: 6 N KOH Electrolyte; H ₂ Pressure = 15 psig; Electrode Area = 9.62 cm ² ; Temperature = 56°C; Current Density Prior to Pulse = 50 ma/cm ²						
Time	Anode Reference Potential			Change	Pulse Current	Pulse Time
	Before	During	After	(mv)	(ma/cm ²)	(Sec.)
1st Day	-0.796	-0.395	-0.797	-1	350	2
"	-0.797	-0.375	-0.797	0	500	2
"	-0.801	-0.375	-0.801	0	600	2
"	-0.797	-0.345	-0.797	0	700	2
"	-0.798	-0.345	-0.799	+1	800	2
"	-0.796	-0.335	-0.797	-1	1000	5
"	-0.797	-0.245	-0.797	0	1000	5
"	-0.795	-0.215	-0.789	-6	1350	5
2nd Day	-0.797	-0.375	-0.798	+1	350	5
"	-0.802	-0.335	-0.801	-1	500	5
"	-0.805	-0.303	-0.802	-3	700	5
"	-0.803	-0.295	-0.801	-2	1000	5
"	-0.802	-0.285	-0.802	0	1150	5
"	-0.802	-0.275	-0.799	-3	1350	5
3rd Day	-0.767	-0.260	-0.766	-1	400	5
"	-0.768	-0.280	-0.767	-1	400	5
"	-0.768	-0.230	-0.770	+2	700	5
"	-0.768	-0.210	-0.773	+5	1025	5
"	-0.772	-0.190	-0.774	+2	1340	5
"	-0.771	-0.170	-0.772	+1	1675	5
"	-0.772	-0.130	-0.768	-4	2000	5
"	-0.763	-0.000	-0.764	+1	2375	5

according to proprietary procedures. The electrodes were then operated at 50°C in 6N KOH in cells of the type shown in Fig. 2. The cells were pulsed, beginning with the first day of operation at intensities ranging from 850 to 1800 ma/cm² for one, three and five seconds. The time between pulses was one hour. The average improvement (of 34 pulses) resulting from a single pulse for the three types of catalysts and two levels of concentration is given in Table XI.

TABLE XI
DEPENDENCE OF "PULSING EFFECT" ON
NATURE AND CONCENTRATION OF CATALYST

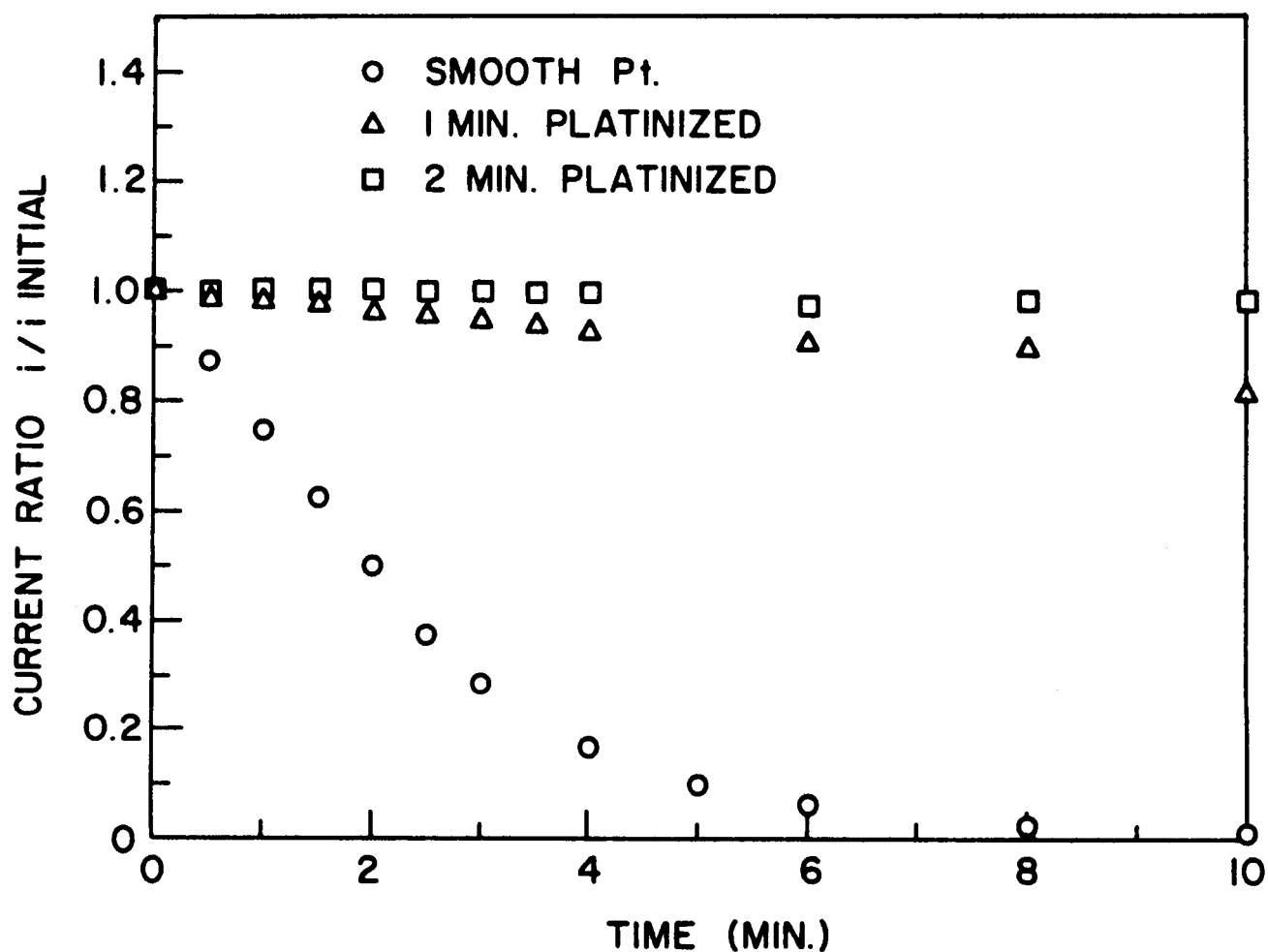
Average Improvement from Single Pulse (mv)		
	1 mg/cm ²	3 mg/cm ²
Platinum	7.2	3.5
Rh-Pd	8.0	1.0
Union Carbide catalyzed	27.8	20.6

These tests show that the "pulsing effect" is higher at low catalyst concentrations. Although 3 mg/cm² catalyst concentration does not necessarily triple the amount of catalyst at active sites as 1 mg/cm² of catalyst, it can be assumed that the greater concentration has more catalyst at active sites.

II. B. Nonporous Platinum Electrodes

A comparison of decline in current with time for smooth Pt and for one and two minutes Pt-Pt in an H₂-saturated, nonpre-electrolyzed 1N KOH solution is shown in Fig. 15. The electrodes were platinized in a 3 per cent PtCl₄ solution containing 0.02 g/100 ml lead acetate at a current density of 20 ma/cm² for the times indicated with current reversal each 15 seconds. The electrodes were pulsed to +1.6 v for ten seconds with respect to a reversible hydrogen electrode in the same solution before measuring the decline in current with time at 10 mv polarization. In Fig. 17 it is seen that the current decay rate

decreases with increasing platinization. Current decay is slow with a heavily platinized electrode because it takes a relatively long time to destroy the activity of an electrode with a large number of active centers to the extent that the current becomes catalyst limiting at a polarization of 10 mv.



D-2139

Fig. 17 Normalized Current-Time Curves Comparing Smooth and Platinized Platinum.

Task III - Temperature Effects.

III. A. Union Carbide Catalyzed Composite Electrodes.

Temperature dependence studies of pulsing effects were conducted on Union Carbide anodes and cathodes at three temperatures. The steady-state currents prior to pulsing were adjusted to permit pulsing effects at three different temperatures to be compared at approximately the same voltage levels. In Table XII are summarized representative results obtained on Union Carbide catalyzed, composite anodes and cathodes.

TABLE XII
TEMPERATURE DEPENDENCE DATA USING
CATALYZED ANODES AND CATHODES

Electrode Type	Temp. °C	Current Density (ma/cm ²)	Potential vs. HgO			Improvement (mv) (After-Before)
			Before	During	After	
Anode	23	25	-.887	-.63	-.890	+3
Anode	40	45	-.887	-.67	-.888	+1
Anode	60	75	-.887	-.66	-.888	+1
Anode	23	25	-.890	-.52	-.898	+8
Anode	40	45	-.889	-.52	-.897	+8
Anode	60	75	-.890	-.64	-.892	+2
Anode	23	25	-.858	+.56	-.901	+43
Anode	40	45	-.860	-.69	-.891	+31
Anode	60	75	-.859	-.60	-.898	+39
Cathode	23	25	-.080	-.148	-.066	+14
Cathode	40	45	-.080	-.159	-.061	+19
Cathode	70	175	-.080	-.140	-.057	+23
Cathode	23	25	-.071	-.147	-.060	+11
Cathode	40	45	-.071	-.159	-.060	+10
Cathode	70	175	-.071	-.150	-.051	+20
Cathode	23	25	-.068	-.147	-.055	+13
Cathode	40	45	-.068	-.152	-.060	+8
Cathode	70	175	-.069	-.147	-.067	+2

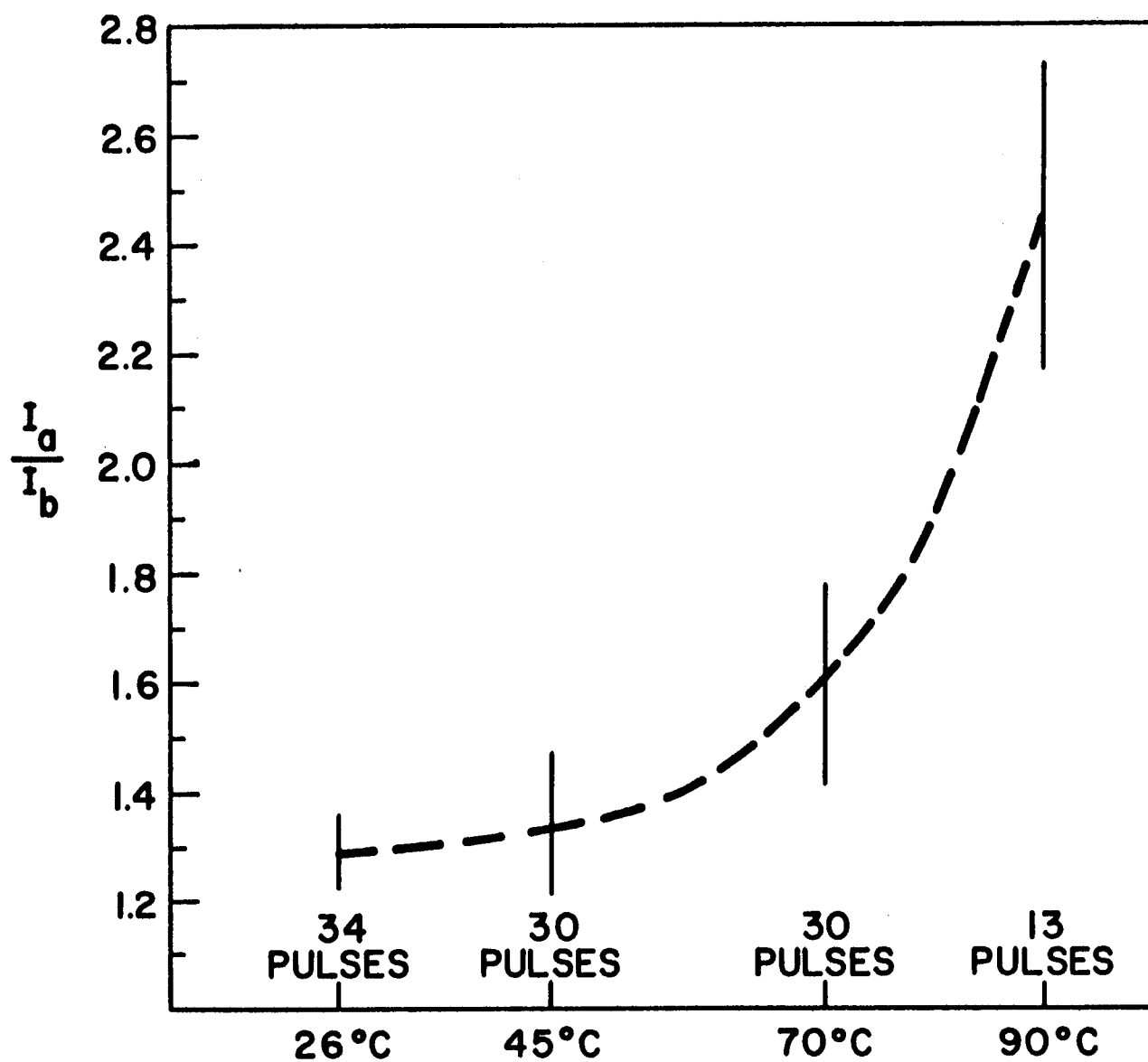
For the three different pulsing conditions presented in Table XII, the anode improvements averaged +18 at 23°C; +13.3 at 40°C; and +14 mv at 60°C. Cathode improvements averaged +12.6 at 23°C; +12.3 at 40°C; and +15 mv at 70°C. Thus, no significant temperature effect was noted on Union Carbide catalyzed electrodes over this temperature range.

III.B. Smooth Platinum Electrodes

A series of experiments were conducted on smooth Pt electrodes in H₂-saturated, 1N KOH solution to determine whether the degree of activation resulting from a single discharge pulse and the subsequent decay rate were temperature dependent. The procedure used was the following:

1. The current at $\eta = 10$ mv was noted immediately before the pulse (i_b).
2. A 30-second pulse to +1.6 v was applied by means of the Wenking potentiostat. The current at $\eta = 10$ mv immediately after the pulse (i_a) was noted. The ratio i_a/i_b was taken as a measure of improvement in catalytic activity resulting from the pulse.
3. The cell was allowed to remain at open circuit for 30 minutes, and the current was again noted (i_c). The ratio i_c/i_a was taken as a measure of decay rate of catalytic activity.

In Fig. 18 are shown the results of i_a/i_b for the four temperatures. The mean values $\pm$ their standard deviations are plotted, and the number of experimental points are shown below at each temperature. The mean value follows the exponential curve, which is shown as a dotted line. Applying the statistical "t" test to the data yielded the "t" values shown in Table XIII. The temperature dependence data support the conclusion that there is a significant temperature effect for pulsing. However, the difference between this temperature effect ranging from 26° to 45°C is evidently quite small, and it was not possible to statistically verify the validity of this small difference for this one comparison.



D-1993

Fig. 18 Temperature Dependence of Improvement of Catalytic Activity Resulting from a Single Pulse; Smooth Pt in H_2 -Saturated 1N KOH Solution; Pulse to $\eta = 1.6$ v for 30 Seconds.

TABLE XIII

STATISTICAL VALUES SHOWING TEMPERATURE DEPENDENCE
OF IMPROVEMENT OF CATALYTIC ACTIVITY OF SMOOTH Pt
ELECTRODES RESULTING FROM A SINGLE PULSE

Temperature Comparison	"t" Value	Confidence Level for Real Difference between the Two Temperatures
26 and 45°C	0.62	< 50%
26 and 70°C	3.30	> 99%
26 and 90°C	8.50	> 99%
45 and 70°C	2.50	99%
45 and 90°C	7.50	> 99%
70 and 90°C	3.02	> 99%

The decay rate after 30 minutes (i_c/i_a) was also determined as a function of temperature, and these values are shown with the average points $\pm$ the standard deviation in Fig. 19. Applying the statistical "t" test to this data yielded the results shown in Table XIV.

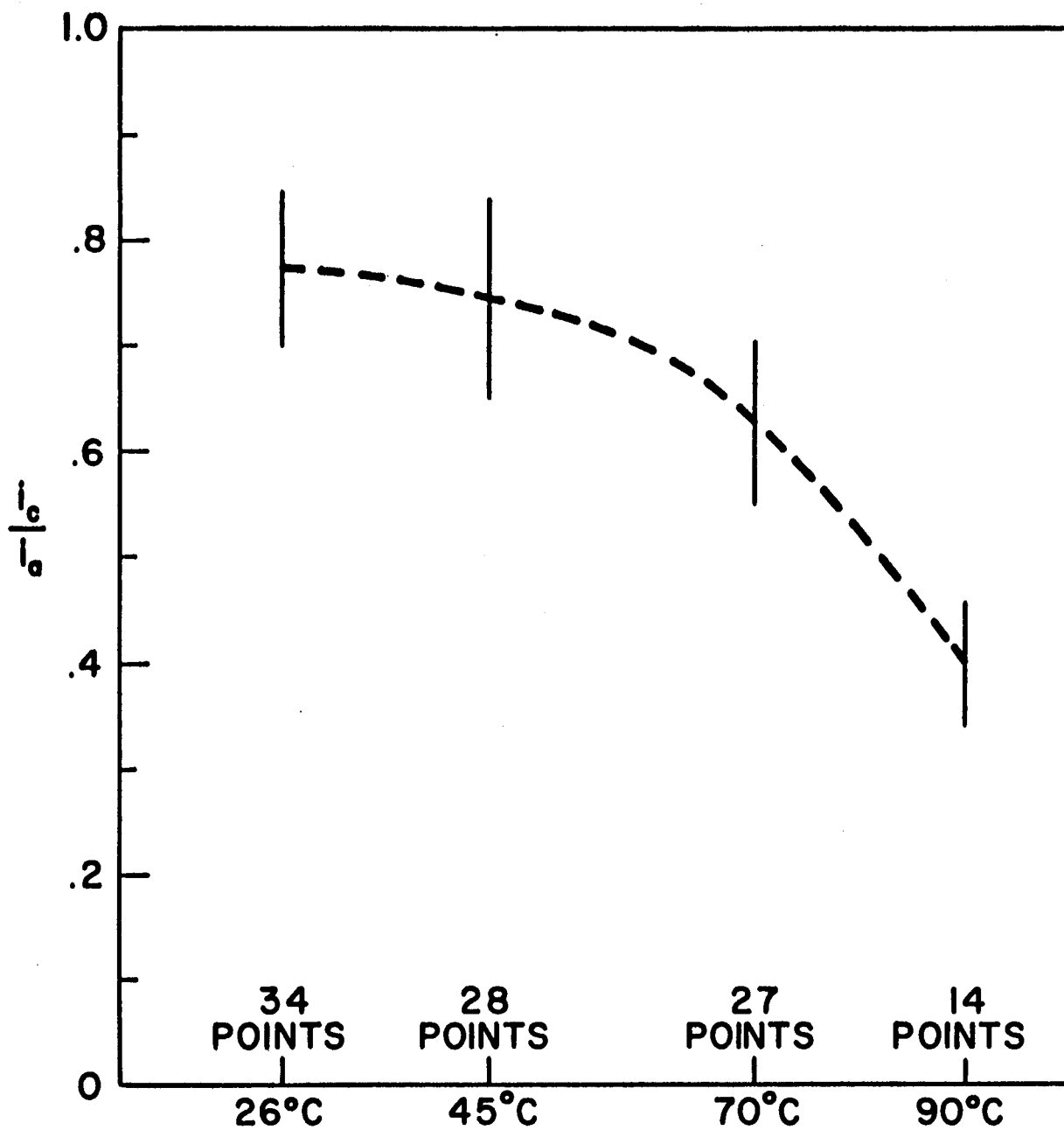
III. C. Porous Nickel Electrodes.

Since these electrodes were diffusion limited (see Section I.C.3), it was not possible to evaluate temperature effects, although pulsing data were taken at 23, 40, 60, and 75°C. The recovery after single pulses was very slow, and depended upon structural limitations rather than catalytic reactivation.

Task IV - Life Testing.

IV. A. Union Carbide Composite Electrodes.

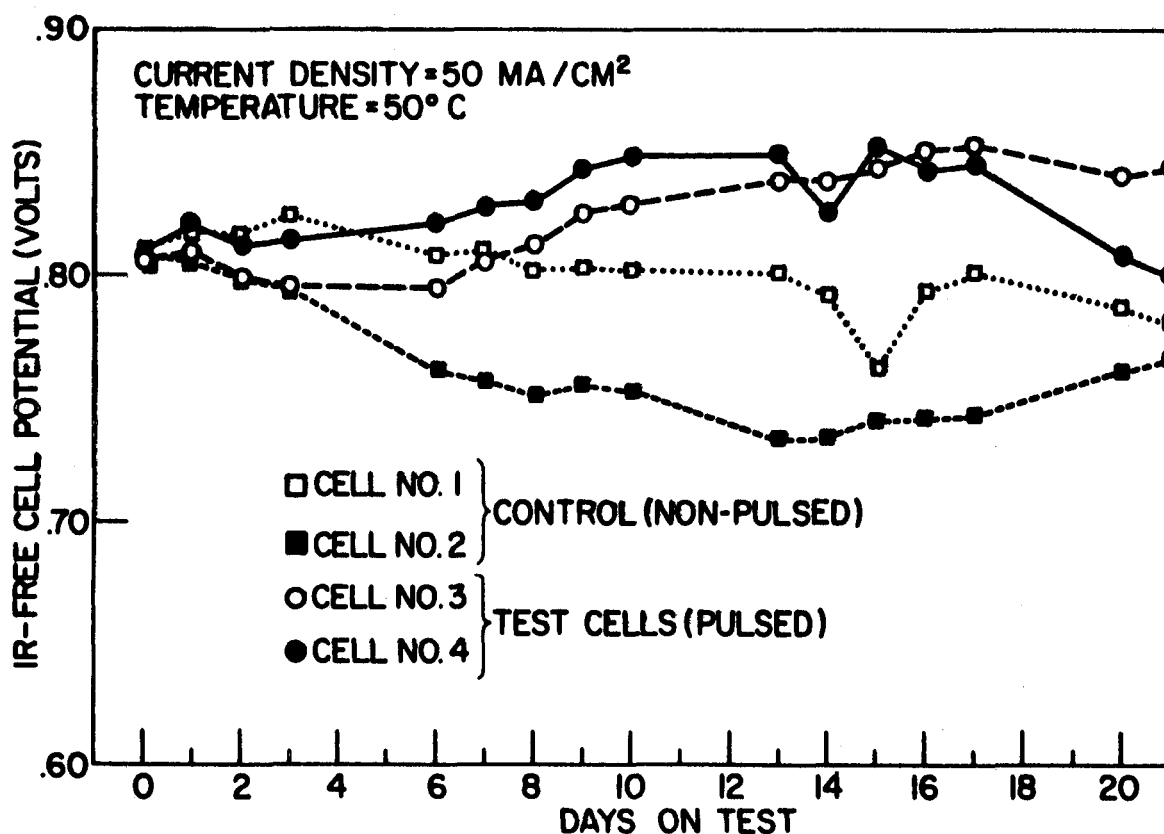
Four Union Carbide composite electrode cells were placed on continuous test at 50 ma/cm² and 50°C. The test cells were of the construction shown in Fig. 2. The electrolyte was 6N KOH. Two of the four cells (hereafter referred



D-1994

Fig. 19 Temperature Dependence of Decay of Catalytic Activity 30 Minutes after Activation Pulse; Smooth Pt in H_2 -Saturated 1N KOH Solution; Pulse to $\eta = 1.6$ v for 30 Seconds.

to as "test cells") were pulsed twice daily at 10 a. m. and 4 p. m. on weekdays. All four cells were run over the weekends, but the test cells were not pulsed during this time. Daily cell voltages were obtained prior to the 4 p. m. pulsing on all four cells. The two control cells were never subjected to pulsing. The test cells were pulsed at 1050 ma/cm^2 for two seconds, with a two-second delay following the pulse. The daily record of cell voltages obtained on the four cells to date is shown in Fig. 20. The average daily cell voltages over the 21-day test period for the pulsed cells was 0.830 and 0.823, respectively; and 0.762 and 0.802 v for the control cells.



D-1496

Fig. 20 Comparison of Cell Voltages for Pulsed and Nonpulsed Union Carbide Composite Electrodes.

The unusual voltage fluctuations in the control cells may indicate that the electrode holders and circulation system do not completely simulate actual operating conditions experienced by full-size cells and batteries. However, the differences between the average voltages of pulsed and control cells appear to be significant and indicate the possibility of achieving similar improvements in the practical fuel cell system.

A practical application of the "pulsing effect" was attempted on 5" x 5" Union Carbide composite electrodes which were on continuous test in our laboratory. Cells were selected which showed far below normal performance for their age and test condition so as to provide a critical measure of pulsing effectiveness. Since these were sealed cells and no prior provision had been made for the insertion of a reference electrode, it was not possible to monitor the potential to which each electrode was driven. An arbitrary pulse of about ten times the steady-state current was applied to each cell. The results obtained on several cells are shown in Table XV. These results are typical of many tested, ranging from minute improvements to improvements of up to 0.2 v as a result of a single pulse. The duration of the improvements ranged from a few hours to weeks.

TABLE XV

EFFECT OF HEAVY DISCHARGE PULSES ON CELL PERFORMANCE

Steady State Current 8 Amps = 50 ma/cm ² ; Pulse Current = 50 Amps (315 ma/cm ²)						
Cell No.	Type	Test Time (Hrs.)	Cell Potential (Volts)		Improvement from Pulse (Volts)	Pulse Duration (Seconds)
			Before Pulse	After Pulse		
656	H ₂ -O ₂	1776	0.81	0.86	0.05	2
657A	H ₂ -Air	3908	0.75	0.78	0.03	1
657A	H ₂ -Air	4312	0.65	0.74	0.09	1
662	H ₂ -O ₂	780	0.82	0.88	0.06	2
665	H ₂ -O ₂	3400	0.68	0.80	0.12	2
665	H ₂ -O ₂	4000	0.68	0.76	0.08	2
688	H ₂ -Air	748	0.65	0.85	0.20	2

IV.B. American Cyanamid Electrodes.

Comparative life testing was completed for three weeks on pulsed and nonpulsed American Cyanamid AB-4 electrodes run as anodes and cathodes. The test electrodes were pulsed twice daily at 1800 ma/cm^2 for five seconds. A wicking arrangement was used to avoid water balancing problems and to permit the use of an Hg/HgO-reference electrode. The daily cathode-reference and anode-reference potential readings on pulsed and nonpulsed cells are shown in Fig. 21. Although small effects were noted as a result of single pulses, pulsing has a negligible effect on the three-week performance of these anodes and cathodes. Penetration of electrolyte through the electrodes was a problem, and the penetration may have been more prevalent at the anode because of water production there. This factor, which could result in flooding gas accesses to reaction sites, may have contributed to the deterioration in anode performance for both the test and the control cells. The fact that pulsing had no effect on performance suggests that the performance was not catalyst limited during this three-week period (catalyst concentration: $9 \text{ mg/cm}^2 \text{ Pt}$) but that the other factors noted above were more serious limitations on cell performance than "run down" catalysts.

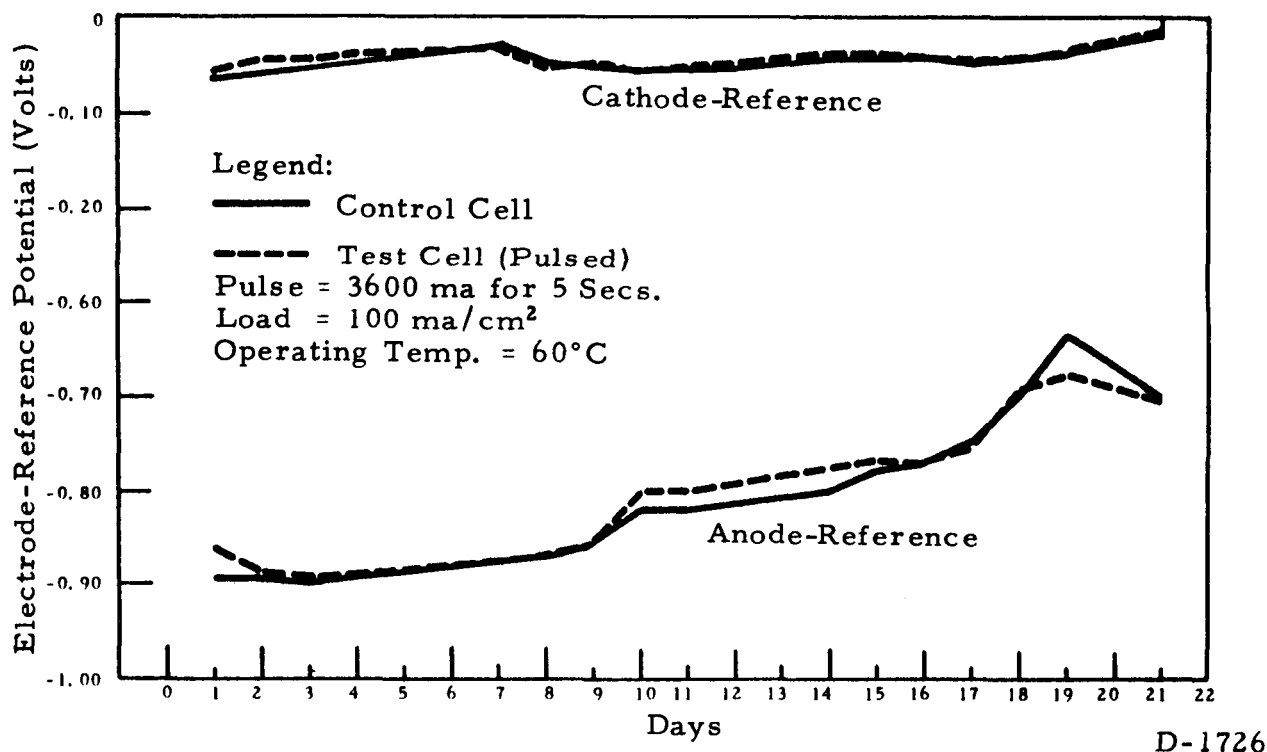


Fig. 21 Comparison of Electrode Reference Potentials for Pulse and Nonpulsed Cyanamid AB-4 Electrodes. Reference Electrode: Hg/HgO.

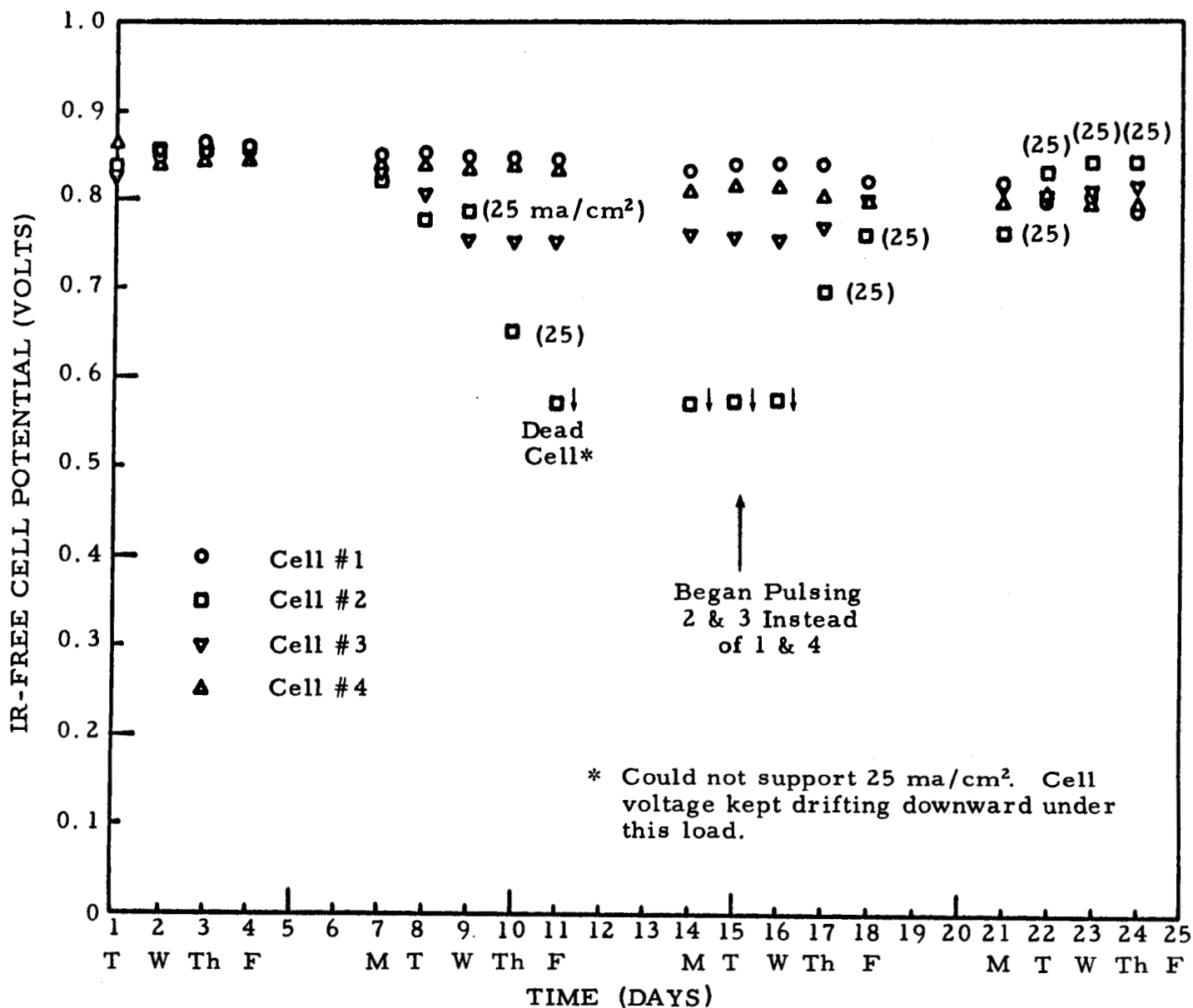
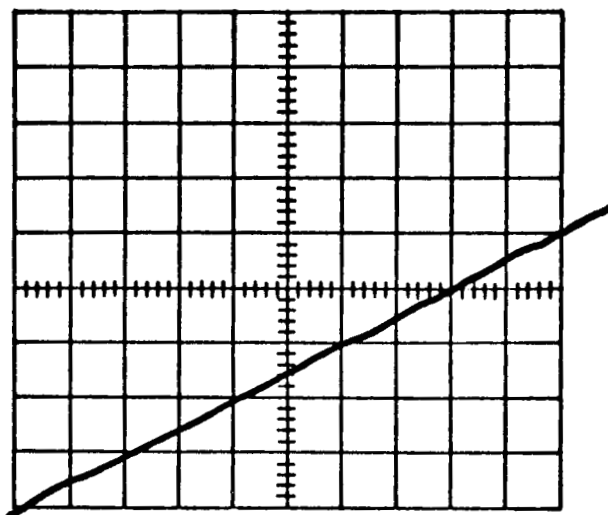


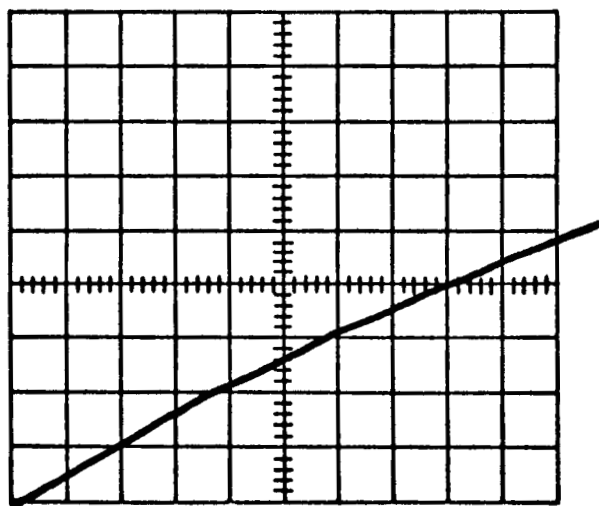
Fig. 22 Performance-Life Studies for Pulsed and Nonpulsed Cyanamid AB-40 Cells Operating at 100 ma/cm².

D-2209

Vertical Scale: 25 ma/cm²/div
Horizontal Scale: 10 mv/div



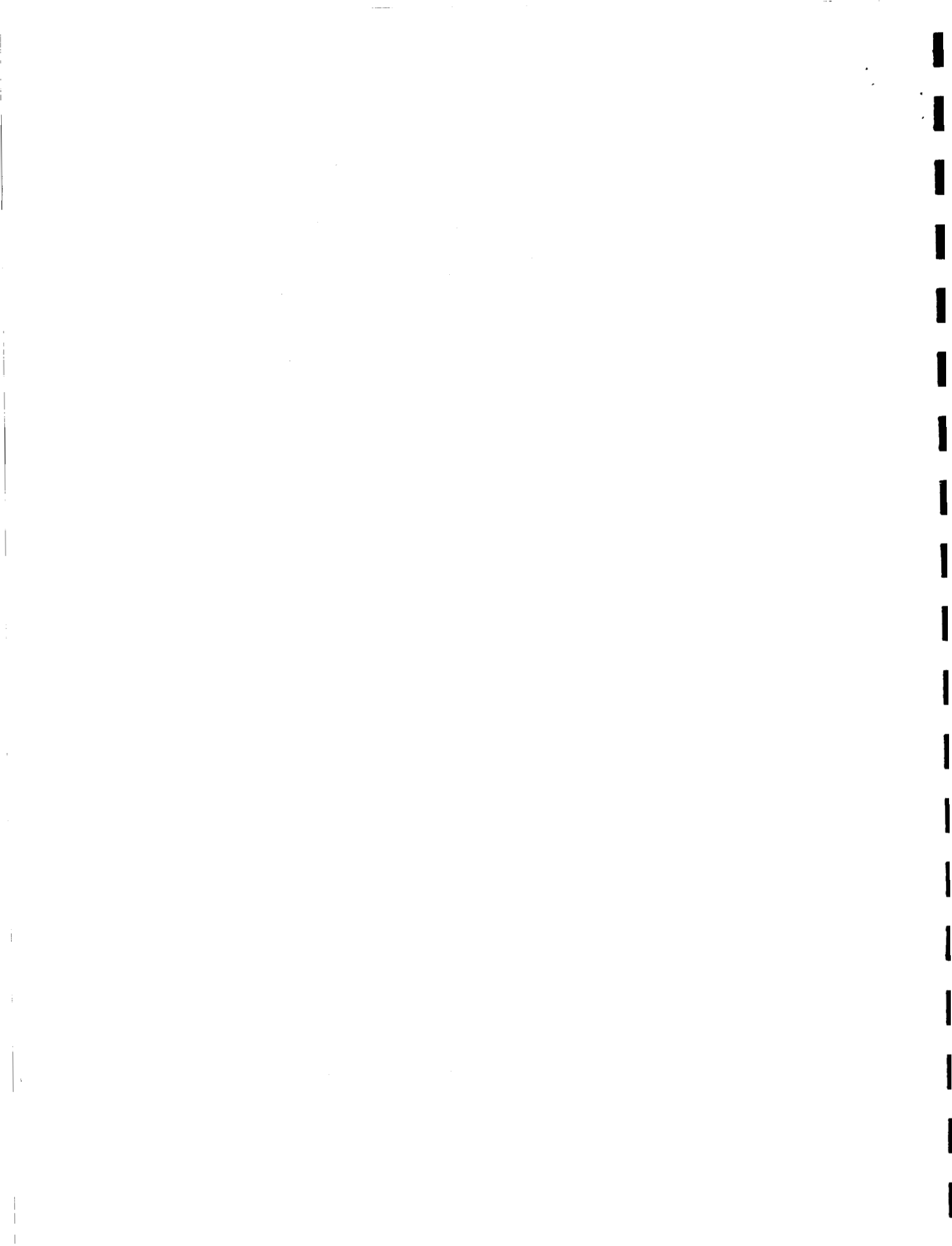
Cell No. 3



Cell No. 4

D-2210

Fig. 23 Oscilloscope Trace of Current-Voltage
Plot on Cyanamid AB-40 Anodes.



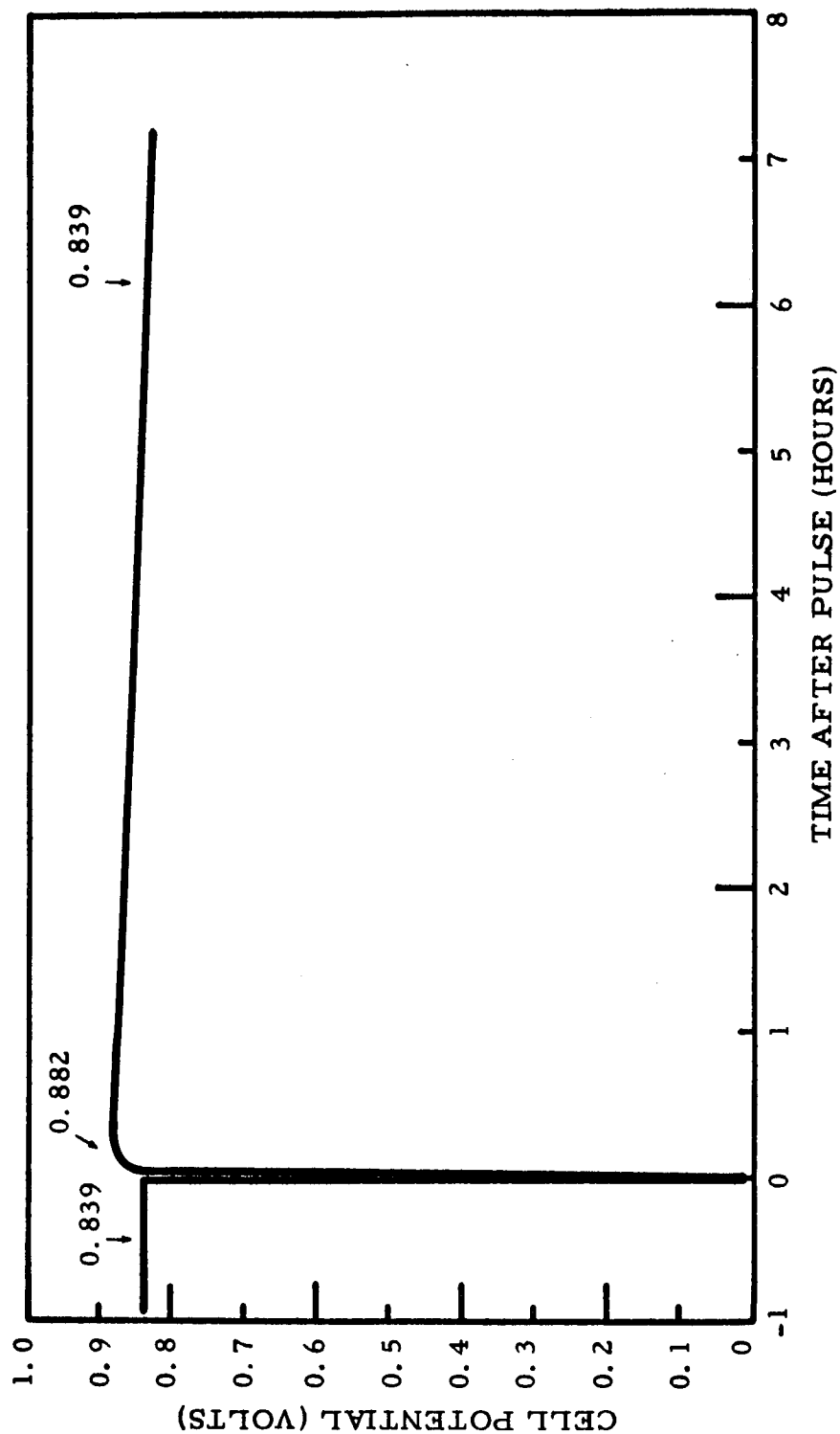
30 seconds, once per day. Once pulsing was begun on cells 2 and 3, the performance level of these cells significantly improved and cell No. 2 was again able to support a 25 ma/cm^2 load at a stable operating potential above 0.8 v. Even after pulsing, however, cell No. 2 could not support 100 ma/cm^2 at a stable potential. Upon conclusion of the tests, the electrodes were examined, and the anode of cell No. 2 had several gaps in the supporting screen where the platinum powder Teflon mix had become separated from the screen. This physical damage which occurred would account for the inability of the cell to perform at its normal operating level. All other electrodes on test were completely intact.

Cell voltages were monitored on pulsed cells before and after a pulse to determine how lasting were the "beneficial effects" of a single pulse. This time varied between 0.5 and seven hours for the cells monitored during the above life test. A typical result is shown in Fig. 24. These results were obtained on cell No. 1 after 14 days on test. The IR-free cell potential at 100 ma/cm^2 before the 1200 ma/cm^2 pulse was 0.839 v. It took six hours of operation after the pulse for the cell voltage to return to this value.

IV. C. Justi-Type Electrodes.

The effect of twice daily pulsing on the performance of Justi-type anodes and cathodes is summarized in Fig. 25. The two lower curves are a daily voltage record for anode half-cells which were run continuously at 50 ma/cm^2 and 60°C . One of the two cells (test cell) was pulsed twice daily at a current density of 500 ma/cm^2 for five seconds. The performance level of the anode test cell began about 10 mv lower than the control cell and ended up 10 mv higher. This improvement is only slight and cannot with certainty be attributed to pulsing because the standard deviation in the performance level of these electrodes is not known to us.

The performance level of the cathode test cell began about 70 mv lower than the cathode control cell and ended up around 15 mv higher. Because of this wide difference in initial performance level between test and control cathodes, this test was repeated. In this latter test, the test cathode (No. 1) was pulsed at 900 ma/cm^2 for 30 seconds, once daily for the first 17 days on test. Afterwards,



D-2211

Fig. 24 Cell Potential at 100 ma/cm² of American Cyanamid (AB-40) Cell
Before and After 30-Second Pulse at 1200 ma/cm².

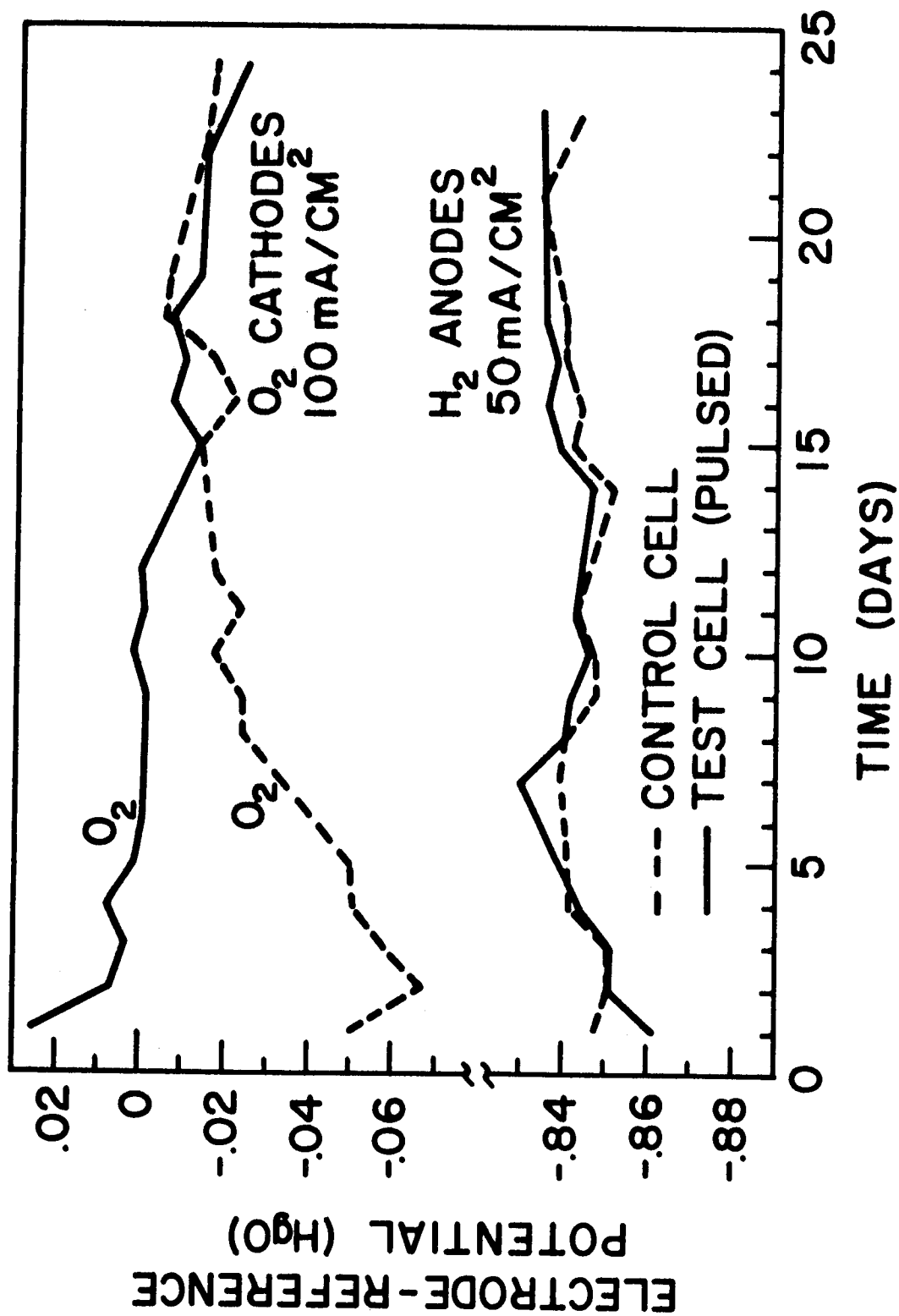
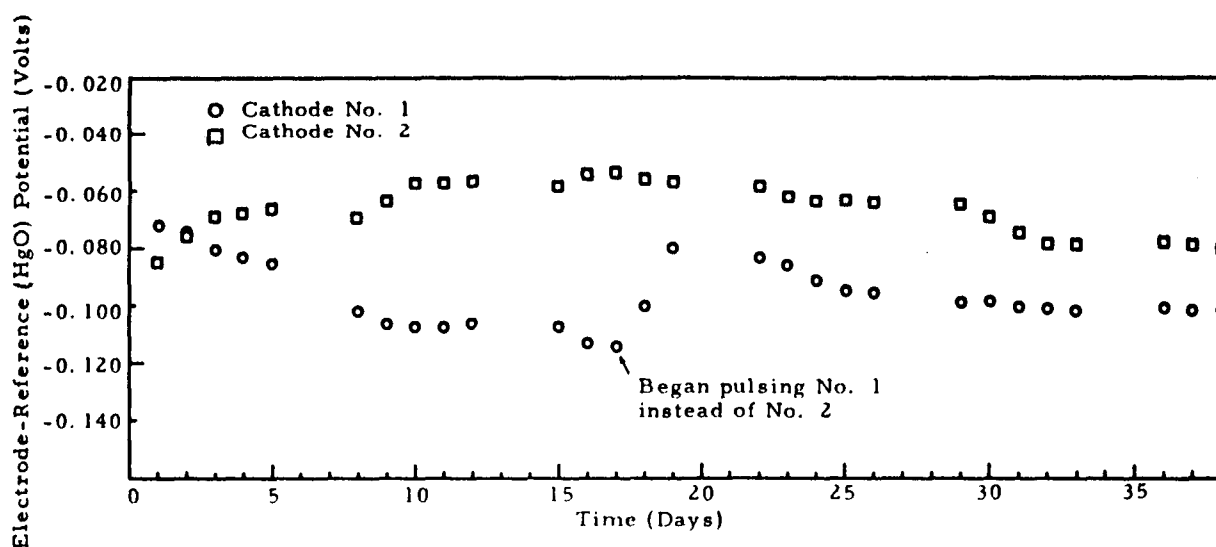


Fig. 25 Comparison of Performance Level for Pulsed and Nonpulsed Operation of Justi-Type (Varta, A. G.) Electrodes.

D-1897

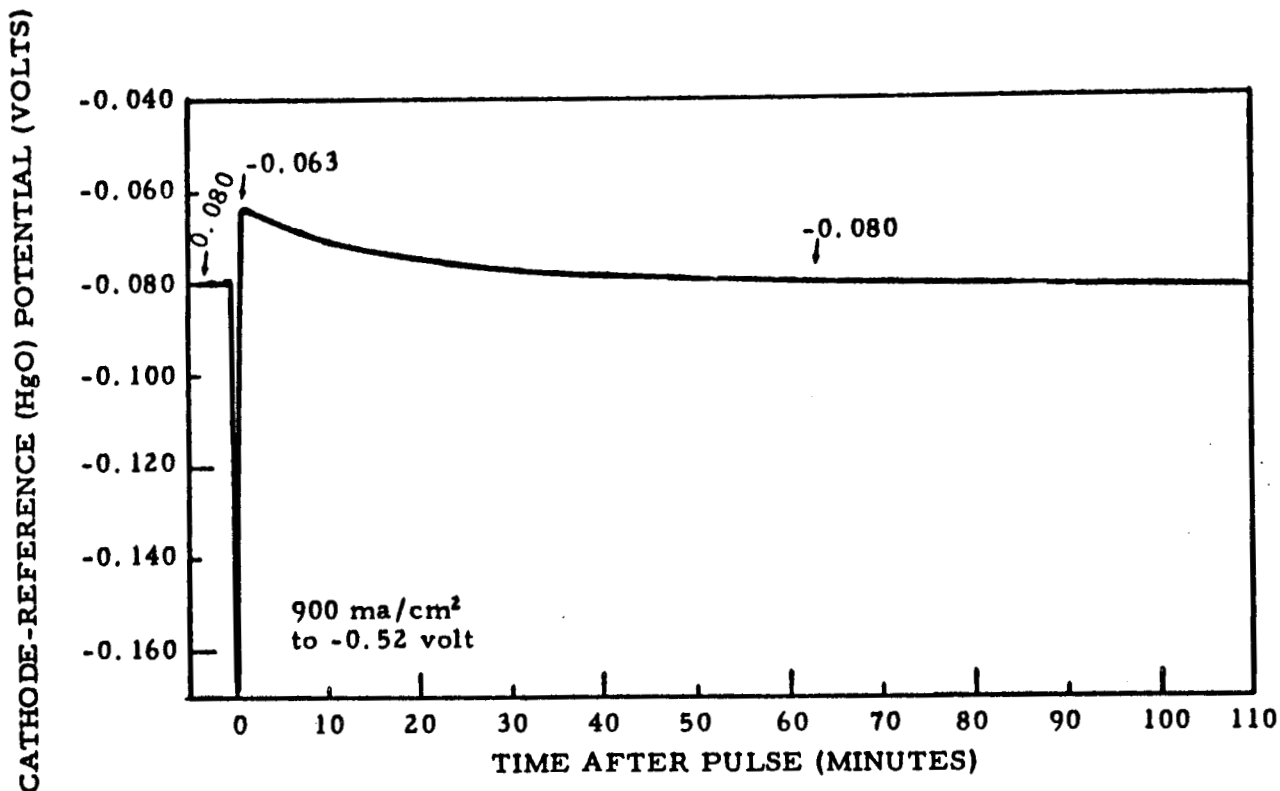
the control cathode (No. 2) was pulsed and the former test cathode (No. 1) was no longer pulsed. The daily voltage record is shown in Fig. 26. Cathode No. 1 declined in performance from -0.072 v to -0.114 v during the first 17-day period when it was not pulsed. After the electrode was pulsed the performance improved to a maximum of -0.080 but then declined to -0.102 v. It appeared to stabilize at this level. Pulsing was not able to bring it to a higher operating level. Cathode No. 2 improved its performance level from -0.085 to -0.054 v during the 17-day period in which it was pulsed, once daily. Thereafter, it declined in performance to -0.080 v but was still at a higher operating level than cathode No. 1.

Electrode potentials were monitored on Justi-type cathodes before and after a pulse to determine how lasting were the "beneficial effects" of a single pulse. This time varied between 45 minutes and three hours for the cathodes monitored during the above life test. A typical result is shown in Fig. 27 (from Tape A-108). These results were obtained on cathode No. 1 on the nineteenth day of the life test. In the result shown here, which was typical, the immediate result of the pulse was a 17 mv improvement in performance level which declined with time. After about one hour, the cell was back to the same operating level as before the pulse. In general, the immediate improvements resulting from a single pulse ranged from 5 to 20 mv and lasted about one hour.



D-2212

Fig. 26 Comparison of Performance Level for Pulsed and Nonpulsed Operation of Justi-Type (Varta, A. G.) Cathodes at 100 ma/cm^2 . Electrolyte: 6N KOH ; Temperature = 60°C .



D-2213

Fig. 27 Cathode-Reference Potential at 100 ma/cm² for Justi-Type Electrodes Before, During and After Second Pulse at 900 ma/cm².

SUPPLEMENTARY RESULTS

At the request of M. R. Unger, NASA Contract Advisor, an experiment was performed to determine whether there are any discontinuities or singular points of response when an H₂-O₂ fuel cell is pulsed at frequencies ranging from 10 to 500 cycles/second.

1. Experimental Equipment and Procedures.

American Cyanamid AB-40 electrodes (40 mg/cm² Pt catalyzed) were run as H₂ and O₂ electrodes at 100 ma/cm² in the D. C. mode at 50 per cent duty cycle. A current diagram of the electronic switch used to provide the 50 per cent duty cycle is shown in Fig. 28. A Hewlett-Packard 200 AB audio oscillator was

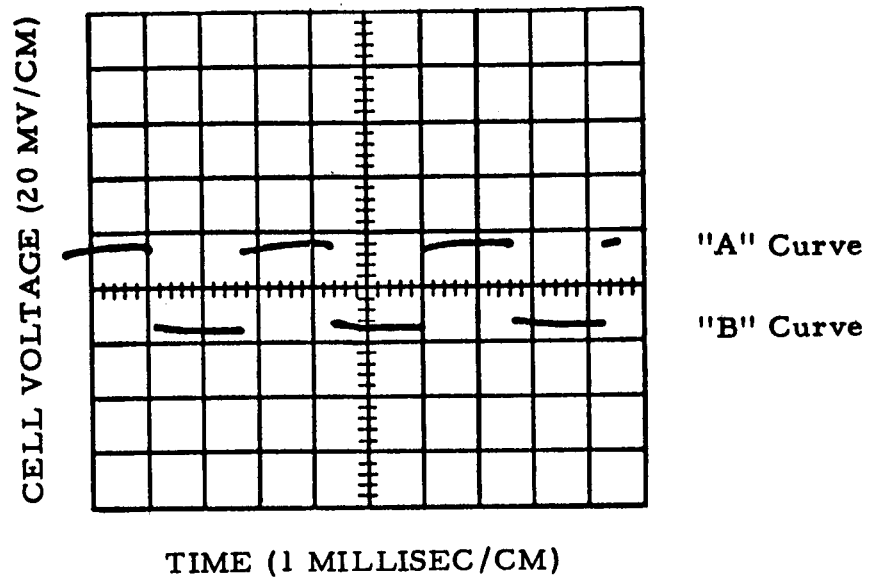
used to provide pulses in the range 10 to 500 cycles/second. The operating current density was provided by the test cell exclusively and was adjusted to 100 ma/cm² by means of the 10 to 50 ohm variable resistors shown in Fig. 28. The voltage drop across the electronic switch was approximately 60 mv at the current employed.

A drawing of the test cell used is shown in Fig. 3. The electrolyte used was 55 per cent KOH soaked in a 0.020 inch ACCO asbestos matrix (furnished by American Cyanamid). The electrolyte temperature was $60^{\circ} \pm 1^{\circ}\text{C}$. The gas flow rates and vapor saturation levels were adjusted to prevent concentration or dilution of the electrolyte. The direct current was interrupted as frequencies ranging from 10 to 500 cycles/second in 10 cycles/second intervals, and the IR-free and IR-included potential was determined using a variable bucking voltage and 536 Tektronix oscilloscope as a null instrument. The cell was pulsed at each frequency for four minutes, and the cell voltage was read at the beginning and end of this period. So that possible changes in cell condition with time will not be confused with frequency variations, the frequency was not systematically increased numerically, but a randomized frequency order was used.

2. Experimental Results and Discussion.

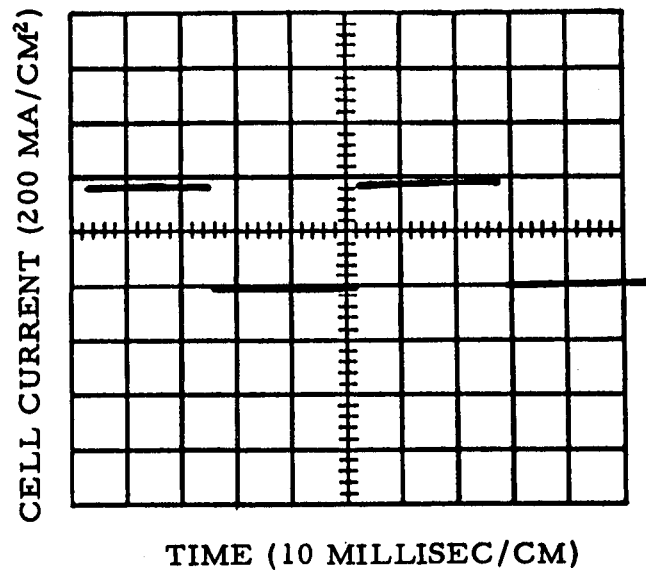
An example of an oscilloscope trace of the cell voltage (minus bucking potential) at 290 cycles/second is shown in Fig. 29. The "A" traces show the cell voltage at 100 ma/cm² and the "B" traces show the polarization decay upon opening the current. Since there is very little activation polarization for these electrodes under these experimental conditions, the virtually instantaneous potential drop of 26 mv is attributed to the resistance of the electrolyte soaked matrix. The resistance is, therefore, $0.026 \text{ volt} / 0.400 \text{ amp} \approx 0.065 \text{ ohm}$. An example of the current trace at 180 cycles/second given in Fig. 30 shows that a satisfactory square wave pulse was produced by the electronic switch.

Table XVI is a summary of the data obtained in the order run. The slight variation (0 to 2 mv) in cell voltage during the four-minute duration at each frequency is attributed to a slight drift in the zero reference level of the oscilloscope. The total variation in cell voltage over the frequency range of 10 to 500 cycles was 10 mv or less.



D-2214

Fig. 29 Cell Voltage Versus Time at 290 Cycles/Second and 50 Per Cent Duty Cycles.



D-2215

Fig. 30 Cell Current Versus Time at 180 Cycles/Second and 50 Per Cent Duty Cycle.

TABLE XVI

DEPENDENCE OF CELL VOLTAGE ON FREQUENCY
USING INTERRUPTED D. C.Electrolyte: initially 55% KOH, finally 50 $\pm$ 10% KOHOperating temperature: 60° $\pm$ 1° C

Open current voltage = 1.06 v

Frequency (cyc/sec)	Cell Voltage			
	Initial		Final	
	IR free	IR included	IR free	IR included
60	.945	.919	.945	.919
220	.945	.918	.944	.917
200	.942	.914	.942	.913
170	.942	.914	.940	.914
40	.939	.914	.939	.913
500	.938	.914	.937	.914
50	.937	.913	.937	.913
330	.940	.913	.940	.913
280	.942	.914	.941	.913
100	.940	.914	.940	.914
410	.942	.914	.941	.914
290	.943	.915	.943	.916
300	.943	.914	.943	.918
420	.944	.916	.943	.914
490	.940	.908	.940	.908
320	.936	.907	.937	.909
120	.937	.912	.939	.913
460	.939	.912	.938	.910
400	.938	.910	.938	.910
210	.939	.913	.939	.913
70	.939	.913	.939	.913
10	.936	.914	.936	.915
250	.937	.911	.936	.911
180	.939	.909	.937	.908
160	.937	.908	.937	.908
350	.937	.906	.939	.906
430	.939	.907	.938	.907
440	.937	.906	.937	.906
270	.939	.907	.939	.907
80	.938	.906	.938	.906
310	.941	.909	.940	.908
140	.939	.911	.938	.911
230	.941	.910	.941	.910
110	.939	.910	.938	.910
450	.941	.909	.940	.908
380	.940	.908	.941	.908
470	.940	.907	.939	.907
340	.940	.908	.941	.907
90	.941	.910	.940	.910
150	.940	.910	.940	.910
20	.939	.915	.939	.915
130	.941	.911	.941	.913
260	.939	.913	.937	.912
360	.938	.911	.938	.911
390	.938	.911	.937	.910
30	.937	.914	.937	.915
480	.940	.912	.940	.913
370	.939	.913	.939	.912
190	.938	.912	.938	.912
240	.937	.911	.937	.912

The data show that there is no special dependence of cell voltage on frequency over this range. There was a slight decrease in the overall cell performance of several millivolts during the 200-minute duration of the experiment which was not related to pulsing frequency.

DISCUSSION

The results obtained in this investigation showed that the discharge pulsing effect is primarily a catalyst reactivation treatment. The controlling factor is the potential region attained by the electrode during the pulse. It is most effective in improving the performance of electrodes that use small amounts of catalysts. The magnitude of the improved performance resulting from a single heavy discharge pulse is related to the length of time the electrode was on test and the elapsed time since the previous pulse.

Since most of the effort was directed toward a study of pulsing effects on specific types of porous electrodes, relatively little effort could be directed toward an understanding of the mechanism of catalyst reactivation. On the basis of the limited work in this direction, there appears to be two different mechanisms for decline in catalytic activity and subsequent reactivation by pulsing. One is so called "oxidation activation," and the other is catalytic poisoning by means of adsorption or deposition of metal ions.

It is quite apparent from the experiments described in this paper involving electrode pretreatment, impurity additions and electrolyte purification that metallic impurities can significantly decrease the catalytic activity of platinum and very likely other catalysts. The results are more apparent on nonplatinized smooth electrodes and low catalyst concentrations since the number of active sites are far lower than on platinized electrodes and electrodes containing large amounts of catalyst. Metallic impurities which may preferentially deposit or adsorb on active sites, must destroy many more active sites on relatively high surface area electrodes to make the hydrogen dissolution reaction catalyst limiting. A heavily platinized reference electrode, thus, often serves as a scavenger to remove certain metallic impurities. This effect was noted in this investigation since freshly prepared (nonpre-electrolyzed) solutions had faster current decay rates than "seasoned" electrolytes which remained in contact with large surface

area reference electrodes in H_2 -saturated electrolytes. Lightly platinized electrodes used as references became "poisoned" relatively soon in freshly prepared electrolytes. Considering the traditional method of preparing platinized platinum, however, it must be concluded that some trace metallics such as Pb do not "poison" a Pt electrode.

The data presented here has demonstrated that certain trace, metallic impurities can "poison" Pt metal catalysts, but the question which has not been resolved is whether the trace impurity effect is the principal or even the only factor that has been really observed in the activation of platinum by pulsing or scanning. Some authors^{7,8} have considered that cyclic pulsing produces a specially activated form of Pt, which has an unstable structure. This structure then settles down in time to the less active stable structure. This model was not consistent with our observations. It has been our observation that repeated cycling of an electrode did not produce a more active surface than one that was strongly oxidized just once and partially reduced. In addition, cleaning an electrode in an H_2 flame for one minute produced a relatively active electrode which would have annealed an unstable structure.⁹ This active electrode declined in activity when placed in a nonpre-electrolyzed, H_2 -saturated electrolyte. In general, although the initial activity of an electrode might vary depending on the pretreatment, the rate of activity decline depended mainly on the impurity level of the electrolyte and the relative surface area of the electrode. Therefore, the experimental facts observed here were more consistent with a trace impurity effect and possibly an oxidation-activation effect rather than a model involving unstable structures.

Another observation of importance was that a strongly oxidized surface (produced by pulsing to $\eta = +1.6$ v or by immersion in hot chromic acid) was a poor catalyst for H_2 oxidation unless some partial reduction took place, after which it was a very active catalyst. This was accomplished rapidly in an H_2 -saturated solution. Further exposure to the H_2 -saturated solution resulted in a decline in activity with time. A surface less strongly oxidized (i. e., produced by pulsing to $\eta = +1.05$ v) produced a catalytic surface of significantly lower activity than the strongly oxidized surface. This yields a difficult to accept conclusion— that if the "oxidation theory" of activation is correct then active catalyst centers are characterized by the simultaneous presence of oxidized and reduced sites rather

than an overall intermediate oxidation state. The active oxidized sites, however, may represent only a small fraction of the total surface. The decline in catalytic activity with time would then be attributed to the reduction of the oxidized site of this active center combination. The fact that platinum oxide can facilitate electron transfer by means of oxygen bridge formation has been discussed by Davis.¹⁰ However, even if a platinum electrode were activated by oxidation, the experimental fact that it can be deactivated by impurity adsorption or deposition cannot be denied. The subsequent reactivation of such a "poisoned" surface by positive potential scans and pulses which oxidize or desorb the impurities and oxidize the surface seem to best explain the experimental observations noted here.

The temperature dependence data (Figures 18 and 19), which showed an increased catalytic activity with increasing temperature, could be attributed either to its effect on oxidation-activation or impurity desorption rates since both would increase with temperature. The increase in the rate of activity decay with temperature also could be explained by both since the rate of surface oxide reduction and the rate of impurity diffusion would be temperature dependent in the direction observed.

Since platinum does not normally build up thick layers of surface oxide,^{11, 12} the pulse-time effect (Fig. 11) does not distinguish between the two possibilities. Times on the order of about one second are sufficient to build up a thin oxide layer or to drive off impurities at moderate current densities.

In conclusion then, while it is possible that oxidation of a platinum electrode may activate the surface if followed by a partial reduction, it appears that this is probably a secondary effect in the presence of iron and very likely other metallic ions. This impurity effect resulting from metal deposition or adsorption is most pronounced on low surface area electrodes.

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Project Leader

MLK:nhf

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