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STUDY PROGRAM TO IMPROVE FUEL CELL
PERFORMANCE BY PULSING TECHNIQUES

BY

M. L. KRONENBERG

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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QUARTERLY REPORT

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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
M. R. Unger

UNION CARBIDE CORPORATION
DEVELOPMENT DEPARTMENT
PARMA RESEARCH LABORATORY
PARMA, OHIO

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ABSTRACT

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It has been observed that heavy discharge pulses significantly improve the performance level of fuel cells under certain conditions. The purpose of this investigation is to define these conditions.

Results indicate that pulsing is primarily a catalyst reactivation treatment and is most effective in improving the performance of electrodes that are catalyst-limited from the start, or become catalyst-limited during the life of the electrode. Diffusion-limited electrodes show no beneficial effect, and the deterioration of performance of a physically poor electrode cannot be helped by pulsing. Studies on nonporous platinum electrodes show that platinum rapidly loses its catalytic activity as a H_2-anode catalyst with time; however, the catalytic activity can be restored electrochemically by oxidative pulses, or by chemical oxidation.

SUMMARY

Pulsing experiments were conducted on Union Carbide baked carbon, porous nickel, American Cyanamid, and Justi-type electrodes to determine whether pulsing improves the performance level of these electrodes. Improvements of several millivolts were normally obtained as a result of a single pulse on baked carbon and Cyanamid AB-4 electrodes, and with Justi-type cathodes (porous silver) after several days of operation. Electrodes containing large catalyst concentrations, such as Cyanamid 198-A (40 mg/cm²) and Justi-type anodes (porous Raney nickel), did not show any systematic trend upon pulsing. The Pt-Pd catalyzed porous nickel electrodes that were available to us gave erratic responses to heavy discharge pulses, and demonstrated very low recuperative powers, indicative of a diffusion-limited reaction.

Because all of the results obtained thus far can be interpreted to mean that the effect of pulsing depends on the nature and concentration of catalyst, it was decided to investigate in more detail such catalysts as solid platinum which are uncomplicated by porous structures. Potentiostatic studies were conducted to determine how the catalytic activity of a $Pt-H_2$ electrode changed with time. It was shown that the catalytic activity of the platinum (as a hydrogen anode) decreased with time in a hydrogen atmosphere. This activity could be restored by electrochemical or chemical oxidation of the electrode.

These and other experiments with the discharge pulsing unit strongly indicated that both surface-oxidized sites and sites of a reduced or intermediate

oxidation state were desirable for high catalytic activity. Electrode capacitance also decreased with time in a hydrogen atmosphere, along with the electrode activity.

Other experiments on fuel cell electrodes showed that pulsing effects were lower on heavier-catalyzed surfaces, thus, adding weight to the thesis that pulsing is most effective on catalyst-limited electrodes. Also, no significant temperature effect was noted for pulsing in a range 26° to 74°C on smooth platinum electrodes.

A 3-week comparison test was run on pulsed and nonpulsed Cyanamid AB-4 electrodes. Contrary to previous results with Union Carbide composite electrodes which have a lower catalyst concentration, no significant difference was noted in the performance of pulsed and nonpulsed Cyanamid electrodes. The cells were run in a test cell that avoided water balancing problems and permitted monitoring of anode- and cathode-reference potentials.

INTRODUCTION

In order to obtain long life and a high operating level from a fuel cell, the catalyst must maintain its effectiveness for extended periods of time. Since experimental evidence indicates that activity of some types of catalyst deteriorate with usage, the useful life and operating level of a fuel cell depends to a great extent on the rate of catalyst deterioration. For this reason, any technique or method of periodically restoring catalyst activity would be extremely useful in extending life and maintaining performance levels of fuel cells.

In the course of a recent survey[1] 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.

MEETINGS AND CONFERENCES

On 15 February 1965, there was a meeting at NASA, Cleveland, between M. L. Kronenberg of Union Carbide, M. R. Unger and W. Aldred of NASA, and Prof. T. J. Gray of Alfred University. The current state of progress, i. e. , the information included in this report, was presented by Dr. Kronenberg. Prof. Gray presented experimental data relating to his work on the effect of low duty cycle pulses on power output.

FACTUAL DATA

Task I - Definition of Effect.

A. Purpose and Scope.

The purpose of this Task is to obtain detailed 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 fulfill other task requirements, preliminary pulsing information was also obtained on Union Carbide baked carbon electrodes, American Cyanamid and Justi-type electrodes.

B. Experimental Equipment and Procedures.

Two types of instruments were used in these pulsing experiments. One type, already described in earlier reports[1,2] provided controlled discharge pulses from 0.002 to 3.6 amperes at times ranging from 0.2 to 5.0 seconds. Because of higher pulsing current requirements an even larger capacity instrument of this type was constructed. This unit provides heavy discharge current pulses up to 50 amperes for time periods of 0.2 to 15.0 seconds. It employs the principle of the Kordesch-Marko interrupter[3] enabling resistance-free or resistance-included measurements to be made.

The other instrument used for pulsing was a Wenking potentiostat. This procedure eliminates any uncertainty about the potential attained in pulsing exper-iments since the desired electrode-reference potential is directly imposed by means of the potentiostat. However, the use of the potentiostat as a pulsing device is limited to low current applications such as solid metal electrodes, and was not used for porous electrodes which often require many amperes of current to be driven to significant polarizations.

The potentiostat was used to evaluate the effect of potential on the surface condition and activity of platinum. Differential capacitance measurements were made by noting the steady-state current prior to pulsing, and rapidly opening the circuit (by means of a mercury-wetted relay).

(*) Beneficial pulsing refers to instances where polarization is reduced as a result of the heavy discharge pulse; i.e., polarization immediately before and after pulsing as compared at the same steady-state current.

A block diagram of the circuit and the experimental arrangement used for electrode activity and surface condition measurements is shown in Fig. 1. A second relay (not shown in the figure) was added to turn off the stirring apparatus several milliseconds before applying the pulse. The general procedure used to evaluate the activity and surface condition of the solid platinum electrodes is the following:

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);

4. Capacitance measurements are also made before and after a series of pulses to determine changes in surface condition.

The capacitance was determined from the initial slope of the voltage-time curve displayed on an oscilloscope according to the following expression:

$$C = i \times dt/d\varepsilon$$

where C is the differential capacitance in farads; i the steady-state current in amperes prior to opening the circuit; $dt/d\varepsilon$ the reciprocal of the potential change in volts relative to the time change in seconds obtained from the oscilloscope trace.

An example of the capacitance calculated by this procedure is given in Fig. 2. The three oscilloscope traces shown are on the same electrode taken at one-minute intervals. There is a faradaic contribution to the capacitance determined in this way also related to the surface area. The faradaic effect and double layer capacitance give a measure of relative surface condition when determined at a constant potential.

The cell used for obtaining pulsing information on solid electrodes was described in our last Report. A Pt-Pt, H_2-reference electrode is used in measurements with this cell whenever possible and this is periodically checked against an Hg/HgO-reference electrode in the same solution. Because adsorption of impurities could strongly influence the results obtained in experiments

of this nature, precautions were taken to avoid impurities. 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). Analytical-grade reagents were used to make up the solutions which were further purified by pre-electrolysis using Pt-Pt electrodes for 1 week or more in a specially designed cell. Initial experiments on solid electrodes were carried out in 6 N KOH, but this was changed to 1 N KOH because of the fivefold greater H_2 solubility in the less concentrated electrolyte.[4]

The effect of variables other than pulsing are currently being studied on Pt electrodes to determine their effect on the activity of these electrodes. These include surface area changes; environmental changes, i. e. , hydrogen, oxygen, and argon atmosphere; coulometric vs. open circuit; temperature effects; and chemical oxidation.

C. Experimental Results.

1. 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 approx. -0. 6 and +0. 5 volt 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 volt versus a mercuric oxide reference. These results for beneficial pulsing are in approximately 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 approx. 10 mv, and followed no distinguishable pattern. As an example of the way the data was obtained, the results for Anode 264-a are tabulated in Table I. Here the pulse was always initiated when the anode-reference potential reached -0. 850 volt with respect to a Hg/HgO-reference electrode. The current density at this potential varied between 25 and 35 ma/cm^2. The pulse time was varied between 0. 5 and 5. 0 seconds in other experiments, but was maintained at 3 seconds for most of the results shown in Table I. In this and all tabulated data to follow, a positive value in the "Improvement" column denotes the extent of improvement in mv resulting from a single pulse.

TABLE I

PULSING DATA - BAKED CARBON ANODE 246a
(Area: 2 cm^2 - Temperature 50°C - Electrolyte 6 N 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

2. <u>Porous Nickel Electrodes</u>[*] - A small pulsing effect was observed on cells made up with Pt-Pd catalyzed porous nickel electrodes. 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 6 N KOH to support the pressures required to operate the cell. The cells were run at a potential of 0.850 volt prior to pulsing, and subjected to pulses of varying intensity. Representative results are shown in Table II, indicating the change in mv resulting from the pulse. The cells were operated at pressures

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

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, unlike composite or solid-metal electrodes where recovery takes place within several seconds.

TABLE II

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/cm²)	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 most of it seemed to arise from the porous structure since the thinner Cyanamid electrodes (see next section), which also are used with an electrolyte

matrix, did not exhibit this limitation to the same extent. 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.

3. <u>American Cyanamid Electrodes</u> - Beneficial pulsing effects of only several millivolts or less were noted on <u>cells</u> made up with AB-4 electrodes. The NA-198-A electrodes did not show any improvement as a result of heavy discharge pulsing. This latter result is not surprising since the NA-198-A electrodes are catalyzed to the extent of 40 mg/cm^2 with platinum black, and are not likely to be catalyst-limited in initial stages of operation. The AB-4 electrodes contain 9 mg/cm^2 of catalyst which is of a concentration comparable to the catalyst concentration on the porous nickel electrodes described in the preceding section. Unlike the porous nickel electrodes the AB-4 and NA-198-A electrodes are not diffusion-limited in initial performance.

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 6 N KOH, and by a "wicking" arrangement using porous nickel on the electrolyte side with an electrolyte reservoir between the porous nickel electrodes, and 6 N 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 III are shown representative pulsing data for cells made up with AB-4 and cells with 198-A electrodes using an asbestos matrix. (Johns Manville fuel cell asbestos, 2 sheets, 11 mil thick).

TABLE III

PULSING DATA ON AMERICAN CYANAMID CELLS

Operating Variables: H_2 Pressure = O_2 Pressure = 2 psig;
Electrolyte 6 N KOH in Asbestos Matrix;
Cell Voltage Prior to Pulse = 0.900 volt;
Pulse Time = 2 Seconds.

Time	Temp. °C	Electrode Type	C.D. (ma/cm²)	Cell Voltage During	After	Change (mv)	Pulse Current (ma)
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	198-A	250	0.81	0.900	0	2500
"	45	198-A	250	0.79	0.900	0	3000
"	45	198-A	250	0.63	0.900	0	3600
"	45	198-A	170	0.60	0.902	+2	3600
"	70	198-A	200	0.76	0.900	0	2000
"	70	198-A	200	0.72	0.900	0	2500
"	70	198-A	200	0.67	0.900	0	3000
"	70	198-A	200	0.63	0.900	0	3600

The small improvements on the AB-4 type and negligible improvements on the 198-A type are to be noted as discussed above. In Table IV, data are shown on AB-4 electrodes using the wicking arrangement noted above. 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. Preliminary results with the heavy-duty pulsing units (pulses > 3000 ma/cm²) show larger pulsing effects, however, further studies must be conducted before conclusions can be drawn.

TABLE IV

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/cm²)	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

4. Justi-Type Electrodes[*] - A special Teflon holder was designed to accommodate porous Raney silver cathodes and Raney nickel anodes of the Justi-type. These electrodes operate in the range of 13.6 to 16.7 psig, from 10° to 60°C in 6 N ±1 N KOH. Thus far, four cathodes and two anodes have been tested. Pulsing has its most beneficial effect at very high current pulses on cathodes (Table V); however, the effects thus far on anodes are highly scattered and difficult to evaluate (Table VI).

Thermodynamic data from Latimer[5] indicate that oxidation of the nickel anode (to NiO) would occur at approximately -0.82 volt 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 Young[6], the +1 oxidation of silver occurs at approximately +0.25 volt versus HgO, and the +2 state at approximately +0.45

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

TABLE V

PULSING DATA ON JUSTI-TYPE CATHODES

Operating Variables: 6 N KOH Electrolyte; Pressure = 15 psig;
Electrode Area = 9.62 cm²;
Temperature = 55°C

Time	C. D. (ma/cm²)	Cathode Reference During	After	Change (mv)	Pulse Current (ma/cm²)	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

volt 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.

TABLE VI

PULSING DATA ON JUSTI-TYPE ANODES

Operating Variables: 6 N KOH Electrolyte; H_2 Pressure = 15 psig;
Electrode Area = 9.62 cm²;
Temperature = 56°C;
Current Density Prior to Pulse = 50 ma/cm².

| Time | Anode Reference Potential | | | Change (mv) | Pulse Current (ma/cm²) | Pulse Time (Sec.) |
	Before	During	After			
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

5. <u>Potentiostatic Studies on Platinum Electrodes</u> - Because the results obtained thus far indicate that the pulsing effect appears to depend mainly on the nature and concentration of the catalyst, it was decided to investigate in more detail the solid catalyst materials, especially platinum, uncomplicated by a porous structure. The general procedure involving the use of the potentiostat and criteria for activity comparisons have already been discussed in Section B (Experimental Equipment and Procedures).

The first series of experiments was carried out to determine how moving the electrode to various potential regions by means of the potentiostat and bringing it back to a comparison region of 10 mv polarization compared to driving the

potential to that same region by a current pulse. Table VII illustrates how these data were tabulated for a smooth platinum electrode. The left-hand column gives the polarization attained during the pulse with respect to a H_2-reference in the same solution; the middle columns show the steady-state currents before and after the pulse; and I_a/I_b is the ratio of current one minute after the 30-second pulse to the steady-state current immediately before. When this ratio is significantly greater than one, the pulse is regarded as having improved the catalytic activity of the electrode.

TABLE VII

PULSING DATA ON SMOOTH PLATINUM ELECTRODE
USING POTENTIOSTAT

Polarization of Pulse (mv)	Current		$\dfrac{I_a}{I_b}$
	Before Pulse, I_b (ma)	After Pulse, I_a (ma)	
110	0.335	0.345	1.03
210	0.330	0.349	1.06
310	0.290	0.380	1.31
410	0.310	0.440	1.42
510	0.332	0.523	1.58
610	0.355	0.493	1.39
710	0.395	0.506	1.28
810	0.348	0.480	1.38
910	0.320	0.515	1.61
1010	0.320	0.518	1.62
1110	0.400	0.548	1.37
1210	0.430	0.589	1.37
1310	0.390	0.557	1.43
1410	0.400	0.560	1.40
1510	0.420	0.533	1.27
1610	0.435	0.469	1.08

Note: Electrode maintained at indicated polarization for 30 seconds.

In Fig. 3, a comparison is made between the potential region resulting in improved catalytic activity, recently obtained under nonlimiting current conditions, with the pulsing unit and with the potentiostat. The potential region causing improved activity obtained with the potentiostat is much broader, especially at strong positive potentials (region of significant surface oxidation). This difference is not unexpected since the action of the potentiostat is quite different

from the discharge pulsing unit. The discharge pulsing unit polarizes the electrode to a potential region which can normally be estimated by virtue of a heavy current; it 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. If strong oxidation significantly reduced catalytic activity, the electrode driven to the oxidizing potential by the pulsing unit would remain there, unable to recover. However, if pulsed to the same region by the potentiostat, it would be driven to a recovery potential by the potentiostat. Driving the potential back to the recovery potential in a H_2-saturated solution reduces the surface oxidation so the "over-oxidized" electrode may show the improved activity characteristic of an intermediate oxidation state, or of a partially oxidized surface. Similar results are observed with the discharge pulsing unit if the circuit is opened for several minutes immediately after a pulse is applied instead of 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. When the potential has recovered to within 10 mv of the normal open circuit potential, the steady-state current prior to pulse is restored. This procedure results in improved catalytic activity, even from an electrode pulsed to a strong oxidation region. The electrode can be forced to recover more rapidly by means of a several-second current reversal (charging pulse) after a pulse to a strong oxidation region.

It should be noted from Table VII that potentiostatic pulses to vigorous O_2 evolution did not change catalytic activity to an optimum level. It has been suggested[6] that PtO_2 may form at potentials $> +1.5$. Platinum dioxide is soluble in alkaline solution[7] and, even if formed, any possible inhibiting effect it may have on activity would probably be of short duration. More experiments are planned to clarify this point.

Since the most active state for a Pt catalyst appears to involve an oxidized surface, it was decided to determine how the catalytic activity of a Pt electrode changed with time in a reducing atmosphere (H_2-saturated solution). Accordingly, nonporous platinum electrodes were platinized for specified times at 10 ma/cm^2 and placed in H_2-saturated 1 N 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 vs H_2 in the same

solution: a strong O_2 evolution potential (1.7 v); an intermediate oxidation potential (1.05 v, significant oxygen coverage); and a low chemisorbed region (0.65 v). A chemical oxidation treatment was also given (CrO_3 soln. -1 min. - 80°C). The data for these various treatments are summarized in Table VIII.

TABLE VIII

DECAY OF PLATINUM ELECTRODE ACTIVITY
AND CAPACITANCE AFTER PULSING
(In H_2-Saturated 1 N KOH Solution; Electrode Area: 20 cm^2; 2 Min. Platinization)

Time (Hrs.)	Current at η= 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

The data in Table VIII are summarized in Fig. 4, where the activity versus time was normalized by plotting the ratio of the current at the time specified to the initial current. It is interesting to note that maintaining the potential in the strong oxidation region (1.7 v; O_2 evolution and PtO_2 formation) produces a very active catalytic surface once the electrode is driven by the potentiostat to the comparison potential at $\eta = 10$ mv. This may indicate that <u>both strongly oxidized sites and sites of a reduced or of an intermediate oxidation state</u> must be present at an active catalytic surface. The possible role of impurity adsorption on catalytic activity will be carefully checked in purified systems by adding known quantities of catalyst poisons.

The data in Table VIII show that strong chemical oxidation is also effective in restoring catalytic activity to platinum. Electrochemical oxidation to 1.05 v restores 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 restores activity.

The capacitance values qualitatively follow the decline in activity as determined by the current at $\eta = 10$ mv. It may be necessary to use a bridge method to obtain more accurate capacitance measurements because of the faradaic contribution to the capacitance. The interruption method currently used is limited in accuracy because of the subjectivity involved in deciding how to draw the slope of the $d\epsilon/dt$ trace after opening the circuit.

The curves in Fig. 4 all have the same general shape and imply a relationship that suggests that it may be logarithmic with time, which would indicate first order kinetics with respect to decrease in catalytic activity with time. The data are somewhat scattered, however, and continuously monitored experiments will be run over longer periods.

Task II - <u>Effect of Catalyst Concentration.</u>

The purpose of this task is to determine whether pulsing effects are related to catalyst concentrations as well as the nature of the catalyst. These tests were run on composite electrode substrates, and compare pulsing effects for 1 and 3 mg/cm^2 applications of various catalysts. These tests have been completed using Pt, Rh-Pd, and Union Carbide catalysts, and show that the degree of beneficial pulsing is significantly higher at low catalyst concentrations.

As an example, Union Carbide catalysts applied at 1.0 and 3.0 mg/cm^2 were pulsed at intensities ranging from 850 to 1800 ma/cm^2 for 1, 3 and 5 seconds. The average improvement (of 34 pulses) resulting from a single pulse was <u>27.8 mv</u>

for the 1.0 mg/cm² catalyst level and 20.6 mv for the 3.0 mg/cm² level. For Rh-Pd catalysts the average improvement per pulse was 8 mv for 1.0 mg/cm² and less than 1 mv per pulse for 3 mg/cm² catalyst. For Pt catalyzed electrodes it was 7.2 mv per pulse for 1.0 mg/cm², and 3.5 mv per pulse for 3.0 mg/cm² catalyst. Although 3X catalyst concentration very likely does not mean 3X the amount of catalyst at the active sites, it can be assumed that the greater catalyst concentration has more catalyst at active sites for the electrochemical reaction.

Task III. - Temperature Effects.

A. Smooth Platinum Electrodes.

Pulsing tests on smooth Pt electrodes were conducted at 26, 48, and 74° C. The average improvement resulting from a single pulse was 21 mv at 26°C, 20 mv at 48°C, and 23 mv at 74°C. This indicates that there is no significant temperature influence on pulsing. However, since this result was based on only 18 single pulses, the series will be repeated.

B. Porous Nickel Electrodes.

Since these electrodes were diffusion-limited (see Task I), 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.
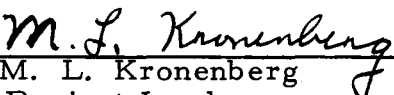
Task IV. - Life Testing.

Comparative life testing was completed for 3 weeks on pulsed and non-pulsed American Cyanamid AB-4 electrodes run as anodes and cathodes. The test electrodes were pulsed twice daily at 1800 ma/cm² for 5 seconds. A wicking arrangement was used to avoid water balancing problems and to permit the use of a Hg/HgO-reference electrode. The daily cathode-reference and anode-reference potential readings on pulsed and nonpulsed cells are shown in Fig. 5. Although small effects were noted as a result of single pulses, pulsing has a negligible effect on the 3-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 indicates that the performance was not catalyst-limited during this 3-week period (catalyst concentration: 9 mg/cm² Pt).

Future Work

1.   Experiments will be continued to determine the effect of surface area and environmental factors such as gas partial pressure, gas atmospheres (H_2, O_2, and Ar), temperature, coulometric effects, and poisons on the inherent activity of platinum electrodes (Task I),

2.   Temperature dependence studies on the pulsing effect will be repeated for smooth platinum electrodes (Task III).

3.   Comparative life testing of pulsed and nonpulsed cells of the Justi-type anodes and cathodes will be made (Task IV).

4.   Practical feasibility of pulsing will be tried on large Union Carbide cells presently on life test in our laboratory.

5.   The effect of longer recovery times (> 5 seconds) on heavily pulsed electrodes will be systematically investigated.

6.   The effect of short charging pulses following heavy discharge pulses will also be investigated.

MLK/jdh

M. L. Kronenberg
Project Leader

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APPENDIX
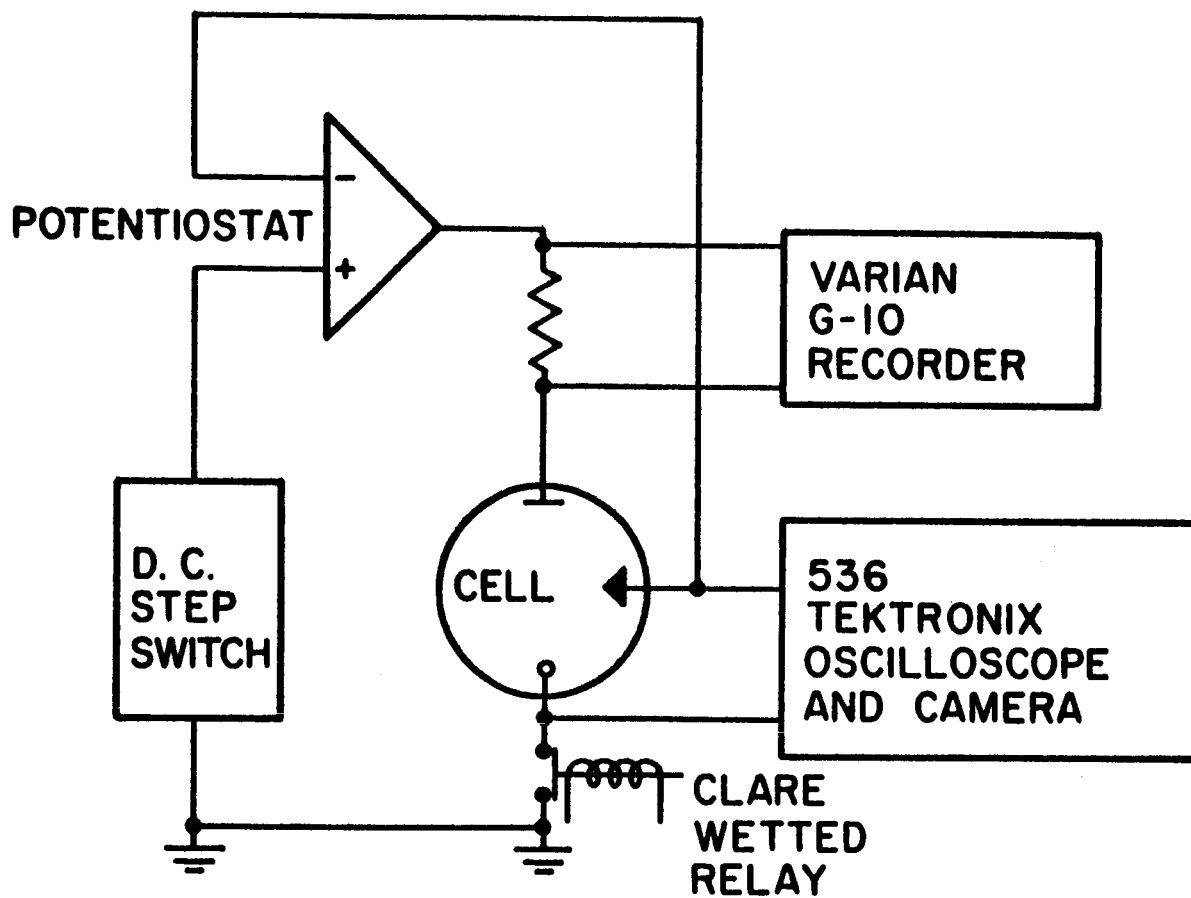
D-1630

Fig. 1   Potentiostat and Associated Equipment.
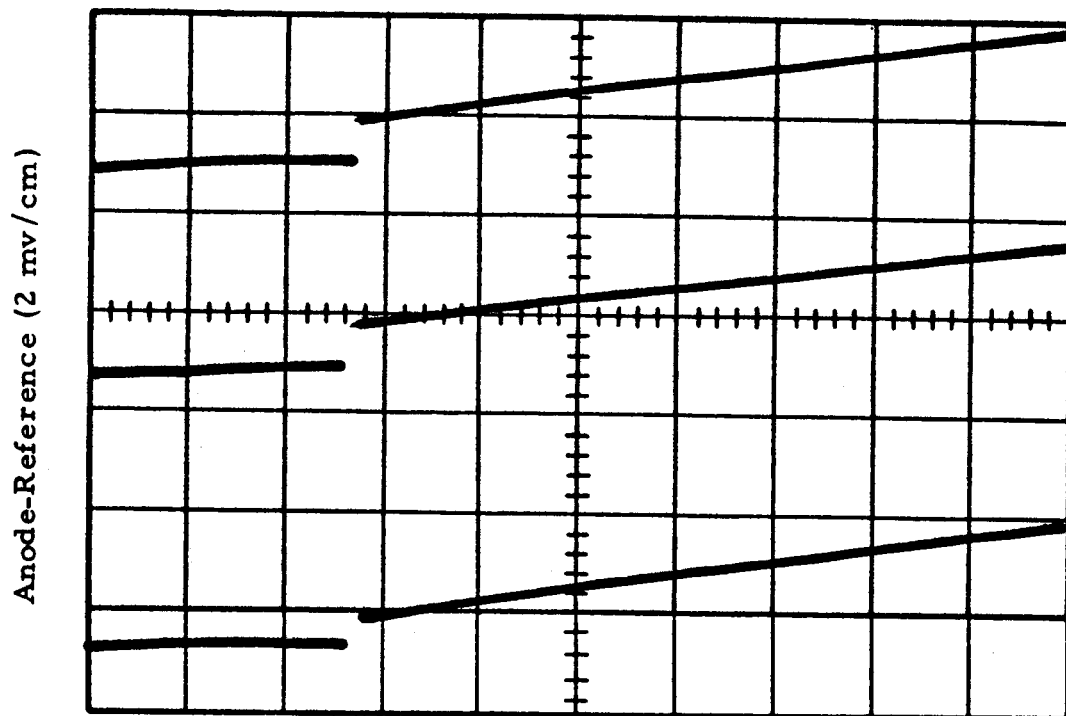
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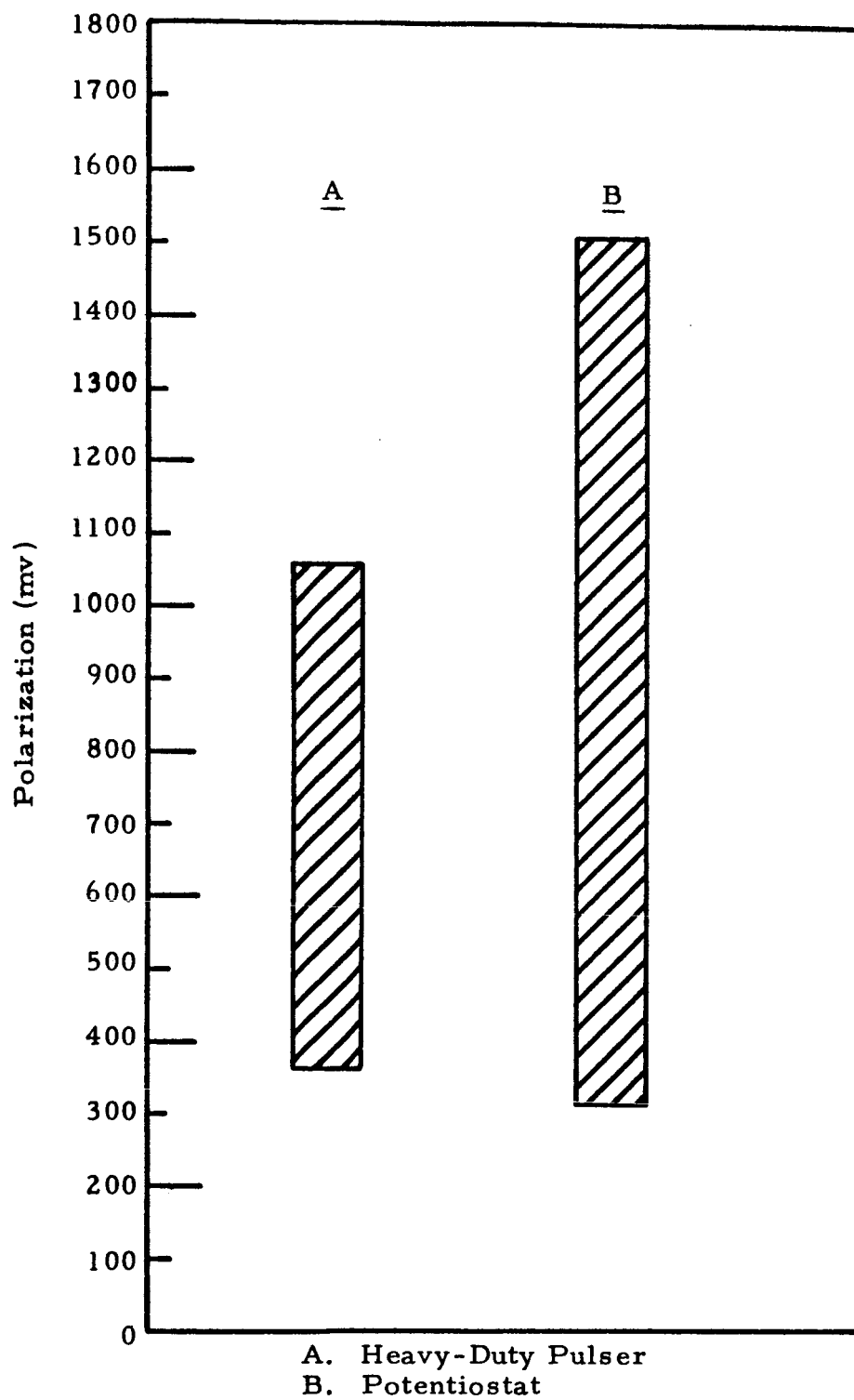
$$C = i \times dt/d\varepsilon$$

$i_1 = 1.80$ ma; $C_1 = 135,000$ μF

$i_2 = 1.84$ ma; $C_2 = 132,500$ μF
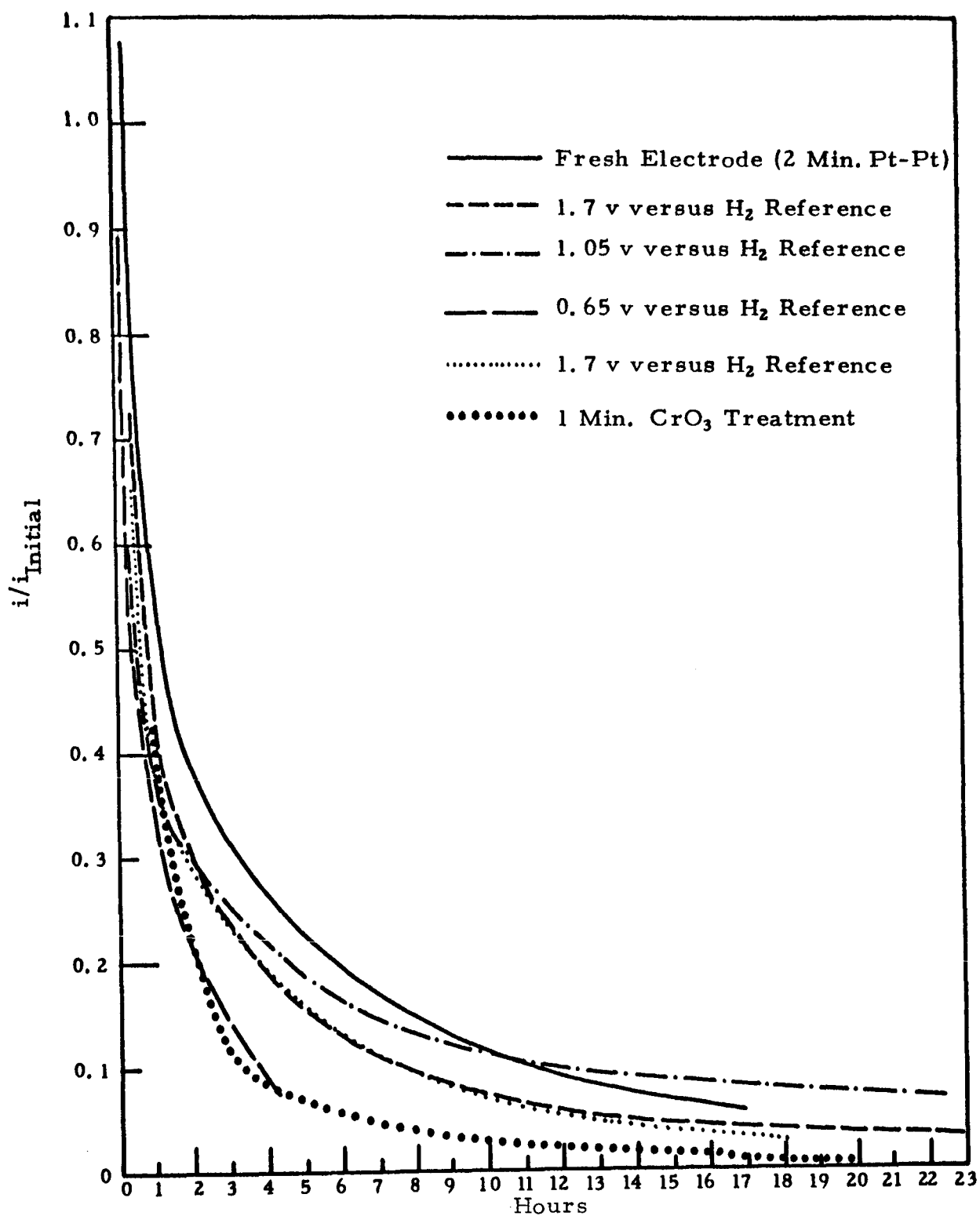
$i_3 = 1.85$ ma; $C_3 = 137,300$ μF

D-1724

Fig. 2   Use of Oscilloscope Trace to Determine
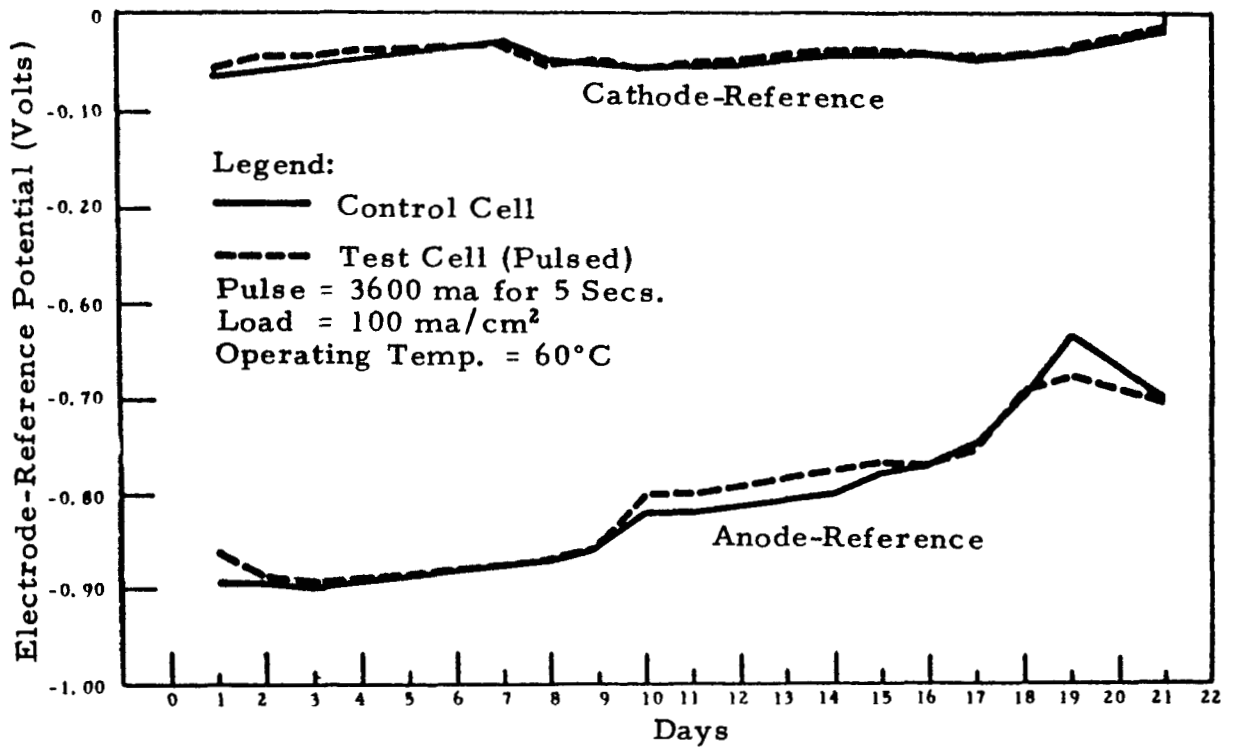Electrode Capacitance.

Fig. 3   Potential Region for Improved Catalytic Activity
Resulting from a Single Pulse.

D-1725

D-1727

Fig. 4   Preliminary Data Illustrating Decay of Catalytic Activity
of a Pt-Pt Electrode with Time, and Restoration by Elec-
trochemical and Chemical Oxidations.

D-1726

Fig. 5   Comparison of Electrode Reference Potentials
for Pulsed and Nonpulsed Cyanamid AB-4 Elec-
trodes.   Reference Electrode: Hg/HgO.

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             SMOFB-EP

U. S. Army Electronics Laboratory
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Attention: Dr. Sidney J. Magram

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Patent Dept.
M. L. Kronenberg (2)
Library (2)