

NRL Report 6263

UNCLASSIFIED

# Cathodic Pretreatment Effects on the Behavior of a Platinum Electrode

S. SCHULDINER AND T. B. WARNER

*Electrochemistry Branch  
Chemistry Division*

April 28, 1965



U.S. NAVAL RESEARCH LABORATORY  
Washington, D.C.

ABSTRACT

Hydrogen formed by cathodic polarization of a bright Pt electrode in CO-saturated 1M H<sub>2</sub>SO<sub>4</sub> is shown to remain associated with the electrode for relatively long periods of time. Such hydrogen causes unusual open-circuit potential behavior after anodic pulses and can give characteristic hydrogen regions in anodic charging curves. Bringing the electrode potential to a value where hydrogen is normally thought to be absent does not assure that all the hydrogen is removed.

PROBLEM STATUS

This is an interim report on one phase of the problem of electrode mechanisms; additional work on this problem is continuing.

AUTHORIZATION

NRL Problems C05-06 and C05-13  
 Projects SR 007-12-01-0809 and RR 001-01-43-4754

Manuscript submitted February 23, 1965.

## CATHODIC PRETREATMENT EFFECTS ON THE BEHAVIOR OF A PLATINUM ELECTRODE

### INTRODUCTION

The importance of clean electrodes in electrochemical studies is well understood today. In recent years a number of ingenious cleaning or "activation" procedures have been reported in the literature that involve cycling the electrode through various potential regions in a fixed way prior to the electrochemical measurements of interest — the most usual process involves the potentiostatic anodization to  $O_2$  evolution followed by cathodization to the region of interest. It is sometimes reported that reproducible results depend on adherence to the activation process chosen, that reproducible results are not obtained until after a number of activation cycles, or that it is necessary to wait a given amount of time after a cleaning cycle before time-dependent changes related to the cleaning procedure are no longer noticeable.

Recent work from this Laboratory has demonstrated that oxygen anodically generated on the surface of a bright Pt electrode can dissolve inside the electrode (probably in what we have termed the "derma," a relatively few atomic layers of Pt just below the surface layer) in significant amounts and in times as short as  $1000 \mu\text{sec}$  (1). Such dermasorbed oxygen can strongly affect the catalytic activity of a Pt electrode (1) and the rate of attainment of the rest potential of a Pt electrode on open circuit (2). It can also act as a chemical reactant, oxidizing species adsorbed on the electrode surface (3). Thus the activation procedure chosen may contaminate the electrode with dissolved oxygen that can then influence subsequent measurements in an important and generally unsuspected way. The purpose of this work was to show that hydrogen generated cathodically on an electrode (also frequently involved in activation procedures) can also dissolve, probably primarily in the derma, and can also affect subsequent measurements in an important way.

### EXPERIMENTAL METHOD AND DISCUSSION

Using previously reported techniques (4) and apparatus (1), a bright Pt bead electrode in  $1M H_2SO_4$ , saturated with slowly bubbling  $CO$  at 1 atm, was polarized with single  $3.8 \text{ amp/cm}^2$  (all areas based on true area as defined in Ref. 5) constant-current pulses up into the  $O_2$ -evolution region (4) (total charge passed =  $1620 \mu\text{coulomb/cm}^2$ ). No preliminary electrode treatment was used. The electrode was permitted to return on open circuit to its normal open-circuit potential before each successive pulse. The subsequent open-circuit decay of potential was observed on a Tektronix Type 547 oscilloscope using a 10-megohm impedance probe and the Pt wire electrode as reference. The decay was gradual back to the open-circuit potential prevailing before the pulse.

If, however, the working electrode was pretreated by cathodization to  $H_2$  evolution for a few minutes and then allowed to recover on open circuit to 0.36 v (all voltages in this paper versus N.H.E.), open-circuit potential changes following identical, single  $3.8 \text{ amp/cm}^2$  anodic pulses gave decay curve such as are shown in Fig. 1. Electrode potential after each anodic pulse decayed below, i.e., became more cathodic than, the original open-circuit

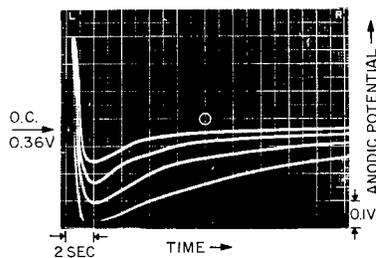


Fig. 1 - Open-circuit decay curves obtained with electrode cathodically pretreated before the first trace. The lowest trace is the first decay curve, the second from the bottom, the second taken, etc. All four traces start at the same open-circuit potential, shown as a dot on the left. Each decay curve was preceded by a  $3.8 \text{ amp/cm}^2$ ,  $425 \mu\text{sec}$  anodic pulse, off scale in the photograph. Between the first decay curve and each subsequent curve, time elapsed and several anodic pulses were applied to help remove hydrogen dissolved in the electrode.

potential and then slowly rose back to this potential.\* As Fig. 1 shows, the amount of cathodic overshoot on decay was largest for the first anodic pulse after pretreatment — potentials as low as 0.015 v were observed. As time elapsed and as the electrode was again anodically pulsed, the overshoot decreased, and the time required for the potential to decay back to the open-circuit rest potential decreased. After 30 min or longer, depending on the number of anodic pulses applied, no evidence of the negative overshoot remained, and decay curves were identical with those obtained before pretreatment. The time required for the phenomenon to disappear was directly related to the time and current density of hydrogen generation on the electrode during pretreatment and inversely related to the number of anodic pulses applied in the interval and to the number of coulombs per pulse. Precathodization until visible bubbles of  $\text{H}_2$  adhered to the electrode enhanced the phenomenon.

All of the above experimental evidence is consistent with the following sequence of steps which have been formulated to explain the phenomenon:

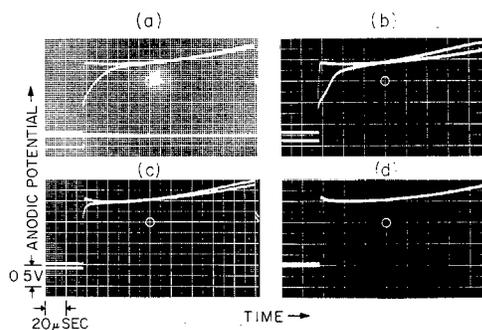
1. Hydrogen generated on the electrode during cathodic pretreatment dissolves in the metal and also forms  $\text{H}_2$  bubbles that adhere to the surface.
2. Subsequently, CO from solution chemisorbs on the surface of the electrode, displacing adsorbed hydrogen, and the electrode potential moves to about 0.36 v, characteristic of a Pt electrode covered with CO (4).
3. A suitable subsequent anodic charging curve strips the CO from the surface and deposits a monolayer of adsorbed oxygen.
4. Desorbed hydrogen and  $\text{H}_2$  dissolving from the adhering  $\text{H}_2$  bubbles quickly diffuse to the electrode surface, remove the adsorbed oxygen by reaction with it, and form a layer of adsorbed H, the surface coverage depending on the amount of hydrogen initially present. The adsorbed H thus governs the open-circuit potential during the cathodic overshoot, before an appreciable amount of CO has had time to re-adsorb.
5. The adsorbed H is slowly displaced with CO and the potential returns to about 0.36 v.

It is reasonable that the dissolution hypothesized in step 1 should occur, particularly in a solution containing a strongly chemisorbable organic compound that can act as an electrode poison. Evidence for hydrogen dissolution in clean Pt in He-saturated solution has previously been presented (1), and it has been shown that diffusion of hydrogen into Pt is greatly increased by poisoning the surface (6).

\*Our observation of this phenomenon is not novel. Others have reported similar behavior in solutions containing formic acid and other organic compounds, but our proposal that this may be related to cathodic pretreatment is believed to be new.

As can be seen in Fig. 2(a) and (b) (the pulses with the shorter rise times), an anodic charging curve taken under the conditions prevailing at the end of step 2 shows no evidence of any hydrogen on the surface nor any hint of any underlying hydrogen. It is, in fact, typical of a CO-covered electrode. This is not surprising, for anodic charging curves taken in solutions saturated with mixtures of  $H_2$  and CO also showed no evidence of the presence of  $H_2$ . Evidently CO does chemisorb tightly enough to displace hydrogen, and apparently a monolayer of CO adsorbed on the surface is sufficient to control open-circuit potential. This differs from the case of the less tightly adsorbed formic acid;  $H_2$  gas in solution can apparently chemisorb preferentially on the surface and contribute a characteristic form to anodic charging curves (7).

Fig. 2 - Anodic charging curves taken during potential decay after initial pulse — both the initial charging curve (the one with the shortest rise time) and the second charging curve taken during the decay show on each photograph. In (a) and (b) the electrode was first cathodically pretreated (and thus presumed to contain hydrogen), and in (c) and (d) it was not pretreated. Figure 2(a) was taken at the bottom of the cathodic overshoot, (b) about 1/2 sec after first pulse (cf. Fig. 1), (c) about 1/2 sec after first pulse and (d) about 1 sec after first pulse.



Step 4 requires (a) that displacement of adsorbed H atoms by CO be a slow process and (b) that dermasorbed hydrogen and dissolved  $H_2$  at the surface/solution interface be able to move to the surface and react with adsorbed O atoms quickly. Indirect evidence (4) has already been found (under slightly different conditions, however) for relatively slow CO adsorption on Pt being anodically polarized, and work currently in process indicates that readsorption on an electrode containing hydrogen is much slower than on an electrode free of hydrogen. Previous results (1) have shown that dermasorbed hydrogen can move to the surface and react with oxygen being anodically generated in times slightly longer than  $1000 \mu\text{sec}$  — a very short time compared to CO readsorption times of seconds.

If the hypothesized sequence of events is valid, it should be possible to detect hydrogen on the surface of the electrode at the time of the cathodic overshoot. Accordingly, the electrode was first pulsed with a short anodic pulse to just strip off the CO without depositing a substantial amount of adsorbed oxygen. Then, when the cathodic overshoot reached its maximum, a second pulse was photographed (Fig. 2(a), pulse with the slower rise time). The trace was indicative of a small amount of hydrogen on a poisoned surface. When the second pulse was taken more quickly, before much CO could readsorb to poison the electrode, a distinctive plateau characteristic of a small coverage of adsorbed atomic H was seen. Quite a different situation prevailed with an electrode that had not been cathodically polarized. No evidence of hydrogen is seen in the second pulses. The second pulse in Fig. 2(c) (pulse with the longer rise time) closely resembles a slightly poisoned electrode in a He-saturated solution (compare with Fig. 1(a) in Ref. 8), whereas the second pulse in Fig. 2(d) (superimposed on first pulse) shows that the surface is virtually fully re-covered with CO in about 1 sec.

## CONCLUSIONS

1. Cathodic polarization to  $H_2$  evolution can cause hydrogen to become associated with a Pt electrode in such a way (probably dermasorbed with concurrent bubble formation) that effects due to this hydrogen can be observed long after cathodization. Bringing the

electrode potential to a value where hydrogen is normally thought to be absent does not assure that all the hydrogen is removed. This has been studied in CO-saturated  $\text{H}_2\text{SO}_4$ , but is probably quite general.

2. The presence of adsorbed H atoms slows CO readsorption on an anodically charged electrode by more than an order of magnitude. Concomitant presence of dermasorbed hydrogen may or may not be important.

3. Hydrogen formed during cathodic pretreatment can produce spurious open-circuit potential behavior and characteristic hydrogen regions in anodic charging curves.

4. Although this work was done under conditions of actual  $\text{H}_2$  evolution, it is believed that generation of any reasonable amount of hydrogen will cause the same phenomena. This remains to be proven, however.

#### REFERENCES

1. Schuldiner, S., and Warner, T.B., J. Electrochem. Soc. 112:212 (1965); NRL Report 6136, Sept. 1964
2. Warner, T.B., and Schuldiner, S., "Potential of a Platinum Electrode at Low Partial Pressures of Hydrogen or Oxygen," NRL Report 6244, April 15, 1965
3. Schuldiner, S., and Warner, T.B., Anal. Chem. 36:2510 (1964)
4. Warner, T.B., and Schuldiner, S., J. Electrochem. Soc. 111:992 (1964); NRL Report 6058, Apr. 1964
5. Schuldiner, S., and Roe, R.M., J. Electrochem. Soc. 110:332 (1963); NRL Report 5809 July 1962
6. Hoare, J.P., and Schuldiner, S., J. Electrochem. Soc. 103:237 (1956)
7. Munson, R.A., J. Electrochem. Soc., 111:372 (1964)
8. Schuldiner, S., and Warner, T.B., J. Phys. Chem., 68:1223 (1964)

## DOCUMENT CONTROL DATA - R&amp;D

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

1. ORIGINATING ACTIVITY <i>(Corporate author)</i> U.S. Naval Research Laboratory Washington, D.C. 20390		2 a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>	
		2 b. GROUP	
3. REPORT TITLE <b>CATHODIC PRETREATMENT EFFECTS ON THE BEHAVIOR OF A PLATINUM ELECTRODE</b>			
4. DESCRIPTIVE NOTES <i>(Type of report and inclusive dates)</i> An interim report on one phase of the problem.			
5. AUTHOR(S) <i>(Last name, first name, initial)</i> Schuldiner, S., and Warner, T.B.			
6. REPORT DATE April 28, 1965		7a. TOTAL NO. OF PAGES 7	7b. NO. OF REFS 8
8a. CONTRACT OR GRANT NO. NRL Probs. C05-06 & C05-13		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6263	
b. PROJECT NO. SR 007-12-01-0809 & RR 001-01-43-		9b. OTHER REPORT NO(S) <i>(Any other numbers that may be assigned this report)</i>	
c. 4754			
d.			
10. AVAILABILITY/LIMITATION NOTICES Unlimited availability. Available at CFSTI -			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Dept of the Navy (Bureau of Ships and Office of Naval Research)	
13. ABSTRACT  Hydrogen formed by cathodic polarization of a bright Pt electrode in CO-saturated 1M H <sub>2</sub> SO <sub>4</sub> is shown to remain associated with the electrode for relatively long periods of time. Such hydrogen causes unusual open-circuit potential behavior after anodic pulses and can give characteristic hydrogen regions in anodic charging curves. Bringing the electrode potential to a value where hydrogen is normally thought to be absent does not assure that all the hydrogen is removed.			

REF ID: A68502

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Platinum electrode Electrode pretreatment "Activation" procedure Anodization Cathodization Carbon monoxide Hydrogen Oxygen						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.  
It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).  
There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.
14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.