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# INVESTIGATION OF MECHANISMS FOR ELECTROCHEMICAL CATALYSIS

## FIRST QUARTERLY REPORT

By

*J. R. Aylward—S. W. Smith*

NOVEMBER 1966

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Technical Report ECOM-02205-1

November 1966

**INVESTIGATION OF MECHANISMS FOR  
ELECTROCHEMICAL CATALYSIS**

**Quarterly Report  
May 1, 1966 to July 31, 1966  
Report No. 1**

**Contract No. DA 28-043-AMC-02205(E)  
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**Prepared by**

**J. R. Aylward and S. W. Smith  
United Aircraft Corporation  
Pratt & Whitney Aircraft Division  
East Hartford, Connecticut**

**for**

**U. S. Army Electronics Command  
Fort Monmouth, New Jersey**

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FOREWORD

This report was produced in accordance with U. S. Army Contract No. DA 28-043-AMC-02205(E) by the Pratt & Whitney Aircraft Division of the United Aircraft Corporation. It discusses the work performed during the period from May 1, 1966, through July 31, 1966.

## ABSTRACT

A program is being conducted to investigate the mechanisms of electrocatalysis with respect to the anodic oxidation of selected fuels by novel electrocatalysts in acid electrolyte at temperatures below 150°C and at ambient pressure. The transition-metal silicides were chosen for study on the basis of previous work which indicated some catalytic activity for these materials for fuel oxidation.

The electrochemical properties of the silicides in acid electrolyte were investigated by measuring the polarization behavior using both potential sweep and steady-state methods. Tests were performed in inert-gas saturated electrolyte to determine corrosion resistance and characteristics of oxide film formation, and then in hydrogen-saturated electrolyte or in electrolyte which is 0.1 molar in methanol to evaluate the catalytic activity.

The results showed that the corrosion current for these materials in acid electrolyte is low, generally about  $10^{-5}$  amp/cm<sup>2</sup>. The oxide films formed on the silicides are good electronic conductors and form through a reversible process. The silicides by themselves were found to have no significant activity for the electrochemical oxidation of hydrogen or methanol, but, when combined with trace amounts of platinum, they demonstrated considerable activity.

10<sup>-5</sup> amp/cm<sup>2</sup>

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## I. INTRODUCTION

A program is being conducted to investigate the mechanisms of electrocatalysis with respect to the anodic oxidation of selected fuels by novel electrocatalysts in acid electrolyte at temperatures below 150°C and at ambient pressure. These studies are especially concerned with exploring how the surface properties of a material influence the catalytic activity and the reaction mechanism. The study is being conducted in order to investigate active, low-cost catalysts for direct energy conversion devices such as fuel cells.

The program is composed of two parts. The first part involves the selection and screening of non-noble materials for corrosion resistance and activity for the electrochemical oxidation of fuels. The selection of materials will be based on several criteria such as the ability to adsorb hydrogen and/or to dehydrogenate hydrocarbons, expected corrosion resistance, and electronic conductivity. The second and major part of the work will be a detailed investigation of selected transition metal silicides for the electrochemical oxidation of fuels. Previous work has indicated that some transition metal silicides show catalytic activity for fuel oxidation. It has also been reported that these silicides are active for the gas phase dehydrogenation of cyclohexane.\* In conjunction with the study of transition metal silicides, the effects of the addition of trace amounts of other materials, such as gold and platinum, will be investigated.

The general physical and chemical properties of the transition metal silicides make this class of compounds interesting from an electrochemical standpoint. They are chemically inert in most environments, showing particularly good characteristics in acid media. They are very hard materials, not likely to sinter or recrystallize in most electrochemical systems. In addition, they have high oxidation resistance and high electronic conductivity except for those which are semiconductors (the silicides of chromium, manganese, and iron). Little is known about their electrochemical behavior in spite of a large body of data on the electrochemical behavior of silicon. The silicides may, in general, be expected to be covered with a layer of oxide in the potential region of interest. Thus, the electrochemical behavior may depend strongly on the sample preparation method, impurities present in the samples, and the presence of surface-active materials in the electrolyte. Inasmuch as the silicides may display some semiconductor properties, modification of the surface by adding small amounts of material may have a large effect on their catalytic properties because of the effect that such activation may have on the space charge.

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\* G. A. Gazien, et. al., Doklady Akedemic Nauk U. S. S. R., 140, 863 (1961).

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The kinetic studies will include the determination of fuel adsorption and oxidation on the silicides and on surface-modified silicides in acid electrolyte as a function of electrolyte concentration and temperature. An attempt will be made to correlate the surface properties of the material with catalytic activity.

## II. PROGRESS

### A. SCREENING OF MATERIALS FOR ELECTROCATALYSIS

Since it was expected that the silicon is the catalytically active element in the silicides, the following silicon-containing materials were selected for screening during this report period:  $\text{CoSi}_2$ ,  $\text{CrSi}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ , and  $\text{SiB}_4\text{C}$ .

The cell used for the screening tests is shown in Figure 1. The electrolyte is circulated through the working electrode compartment by a magnetic stirrer centrifugal pump. In the pumping loop is a glass enclosed electrical heater and a thermometer so that the electrolyte can be maintained at a constant temperature. Power to the electrical heater is controlled by a Variac. Gas is introduced into the electrolyte through a fritted glass disk. The cell has glass O-ring (Viton) joints which hold the working and counter electrodes in place, and these electrodes are separated by a glass frit. The counter electrode is a gold sheet with a porous Teflon 1/8-inch thick sheet gasket which allows any gas generated in this compartment to escape into the atmosphere. A hydrogen reference electrode, at ambient pressure and temperature and with the same electrolyte concentration as the cell communicates with the working electrode compartment via a Luggin capillary. All voltages reported in this document are referenced to this hydrogen electrode.

Materials to be tested in powder form (-325 mesh size) are mixed with 15 weight percent Teflon, which acts as a binder, and pressed onto an inert metal sheet which serves as the current collector. Since these powders mixed with Teflon would not readily stick to a smooth metal sheet, a 100-mesh screen was spot welded to the center of the sheet (see Figure 1). In the early stages of this work, gold screen was not available at the laboratory, and, therefore, a gold-plated platinum current collector was used. Gold plating was used to provide a catalytically inactive current collector.

Polarization data were obtained with a Wenking model 61TRS potentiostat. The current readings were taken after the desired potential had been maintained for 10 minutes, which was sufficient to permit the current to stabilize. Initially, a corrosion run was made at 50 mv intervals from zero to 1.0 volt in a nitrogen-saturated 1-molar  $\text{H}_2\text{SO}_4$  electrolyte at  $50^\circ\text{C}$ . If the corrosion current was less than  $10^{-5}$  amp/cm<sup>2</sup>, the electrolyte was saturated with hydrogen gas and the activity of the material for hydrogen oxidation was measured at 50 mv intervals from 0 to 1.0 volt. The electrolyte was then resaturated with nitrogen and methanol was added to produce a 0.1 molar concentration. The activity for methanol oxidation was then measured. The catalytic activity of each of the materials was evaluated by comparing the results obtained with those for platinum -325 mesh powder under the same conditions.

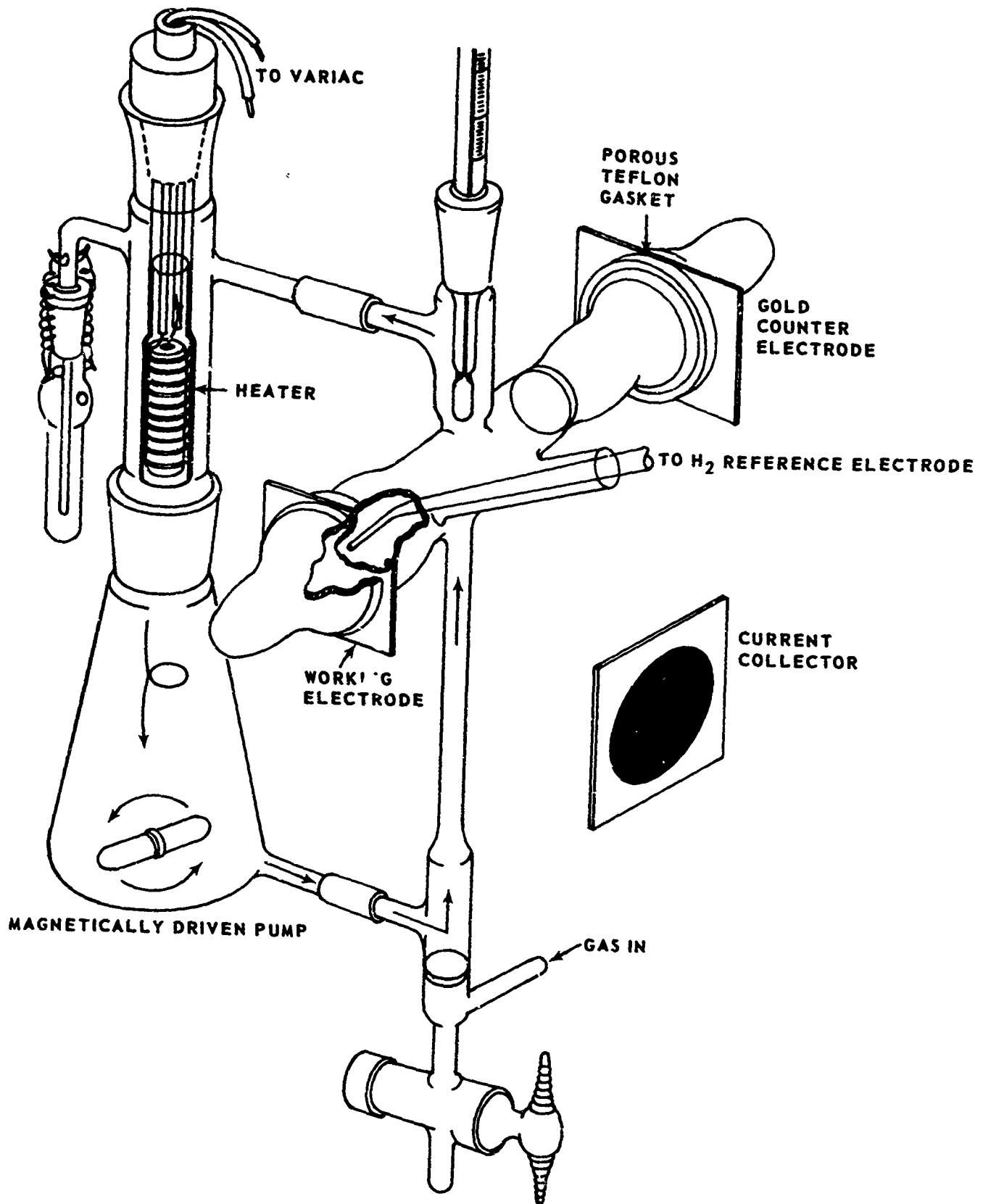


Figure 1 Electrochemical Cell for Catalyst Screening

Prior to testing any of the selected materials, the background activity of the gold-plated platinum current collector for methanol oxidation was measured to establish that the current contribution from this source was negligible. Since the gold plate, as with all plates, was expected to have some pin holes, which would leave a very small platinum surface exposed to the solution, the activity of the current collector before gold plating was also measured to find the maximum catalytic activity to be expected from the current collector. The results are shown in curves 1 and 2 of Figure 2.

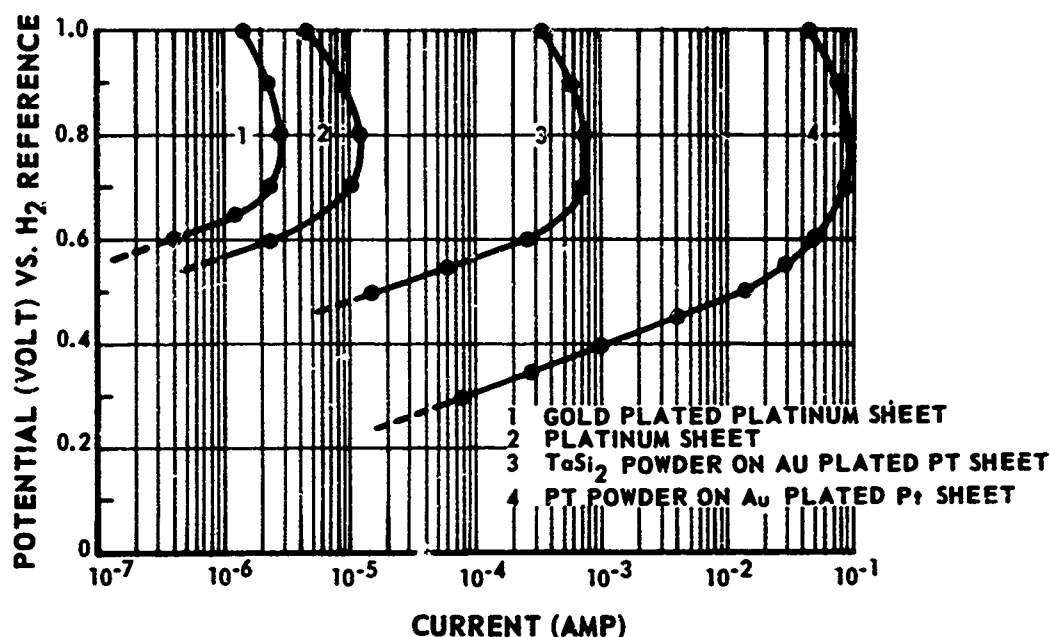


Figure 2 Background Activity for Methanol Oxidation on Current Collector Without Powders and With TaSi<sub>2</sub> and P<sub>t</sub> Powders

The maximum current for methanol oxidation was  $3 \times 10^{-6}$  amp on the gold-plated platinum sheet and  $1.3 \times 10^{-5}$  amp on the unplated platinum sheet. In contrast to these results, when the gold-plated platinum sheet was used as the current collector for TaSi<sub>2</sub> and P<sub>t</sub> powders (both -325 mesh), the current maximum was much higher, being  $8 \times 10^{-4}$  and about  $10^{-1}$  amp for the TaSi<sub>2</sub> and the Pt, respectively. From these results, it was concluded that the gold-plated platinum sheet was sufficiently inert to be used as a current collector, and it was reasoned that the current maximum, when compared to that obtained on platinum in the same form, could be used as a relative measure of the catalytic activity for the materials being screened.

Five materials,  $\text{CoSi}_2$ ,  $\text{CrSi}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ , and  $\text{SiB}_4\text{C}$ , were obtained from Cerac, Inc., Butler, Wisconsin in the form of -325 mesh powders. These materials were screened for corrosion resistance and catalytic activity for hydrogen and methane oxidation in 1-molar concentration  $\text{H}_2\text{SO}_4$  solution at  $50^\circ\text{C}$ . The results, shown in Table 1, indicate that none of these materials are promising as anode catalysts. Also shown in Table 1 are the results of previous testing of several other materials, namely,  $\text{TiSi}_2$ ,  $\text{VSi}_2$ ,  $\text{MoSi}_2$ , and  $\text{Si}$ , as well as  $\text{Pt}$ . These silicides were selected for the more detailed kinetic studies discussed in the following section.

TABLE 1

Results of Material Screening Tests for  
Corrosion Resistance and Catalytic Activity  
in 1-Molar  $\text{H}_2\text{SO}_4$  Electrolyte at  $50^\circ\text{C}$

<u>Material</u>	<u>Maximum Current (ma)</u>		<u>Corrosion Resistance</u>	
	<u><math>\text{H}_2</math></u>	<u>0.1 M <math>\text{CH}_3\text{OH}</math></u>	<u>Current (ma)</u>	<u>Voltage (Volts)</u>
	$\text{CoSi}_2$	0.15	0.4	$< 3 \times 10^{-2}$
$\text{CrSi}_2$	0.3	0.3	$< 1 \times 10^{-2}$	$\leq 0.9$
$\text{Si}_3\text{N}_4$	---	---	material dissolves	
$\text{SiC}$	0.15	0.02	$< 1 \times 10^{-2}$	$\leq 1.1$
$\text{SiB}_4\text{C}$	0.5	---	$< 5 \times 10^{-2}$	$\leq 0.4$
$\text{TiSi}_2$	1.2	1	$< 1 \times 10^{-2}$	$\leq 0.6$
$\text{VSi}_2$	2.5	0.01	$< 1 \times 10^{-2}$	$\leq 1.2$
$\text{TaSi}_2$	1.2	0.7	$< 1 \times 10^{-3}$	$\leq 1.1$
$\text{MoSi}_2$	1.0	0.3	$< 1 \times 10^{-2}$	$\leq 0.8$
$\text{Si}$	0.8	0.04	$< 1 \times 10^{-2}$	$\leq 0.6$
$\text{Pt}$	100	95	---	---

## B. KINETIC STUDIES OF TRANSITION METAL SILICIDES

### 1. Effect of Electrolyte Composition and Temperature on Corrosion and Catalytic Activity

The same cell and equipment used for the screening tests were used for this phase of the work. Polarization curves with various electrolytes for the oxidation of 0.1 molar methanol on  $\text{TaSi}_2$  were determined. Tests were also conducted with ethane and ethylene, but no activity could be detected with either of these fuels. The electrolytes used were 1- and 3-molar  $\text{H}_2\text{SO}_4$  and 1-, 3-, and 9-molar  $\text{H}_3\text{PO}_4$ . Tests were conducted at temperatures of 25, 50, and 75°C. The first series of tests were made using the gold-plated platinum current collector, but during the quarter, 100-mesh gold screen became available, and, therefore, a second series of tests were performed using an all-gold collector and other silicides in addition to  $\text{TaSi}_2$ .

The results of the first series of experiments using the gold-plated platinum current collector were not as expected. One-molar concentrations of the sulfuric and phosphoric acid electrolytes showed normal temperature effects. The activation energy was 11 Kcal/mole in the Tafel region and 5.6 Kcal/mole in the limiting current density region. However, at the higher concentration of both acids, temperature had little effect on the current density at any particular potential. The current density for a given potential decreased with increasing acid concentration, and all concentrations of sulfuric acid tested resulted in higher current densities than those for the concentrations of phosphoric acid tested. The potential-current curves for 1-molar  $\text{H}_2\text{SO}_4$  electrolyte at 25, 50, and 75°C are shown in Figure 3.

The open-circuit potential is a mixed potential and is not reproducible, and, therefore, the "exchange current" has no significance. The Tafel slope is about 0.095 volt. In both acids, the maximum corrosion current for potentials below 1.0 volt increased slightly with temperature but was essentially independent of concentration. The maximum corrosion current was about 0.01 ma at 50°C in both acids.

When similar experiments were performed using the solid-gold current collector, no activity could be obtained on any of the silicides tested. Using the silicides in cylindrical form also resulted in no activity for hydrogen adsorption or oxidation. It might appear that the activity previously assigned to the silicides was, in fact, coming from the gold-plated platinum sheet used for the current collector. However, this hypothesis conflicts with the results obtained with uncoated platinum and gold-plated platinum current collectors. Consequently, three additional background tests on two different unplated platinum sheet current collectors were performed, and maximum currents ranging from

$2 \times 10^{-5}$  amp to  $1 \times 10^{-4}$  amp for methanol oxidation in 1-molar  $H_2SO_4$  at  $50^\circ C$  were obtained. One of these sheets was gold plated and retested. Plating increased the maximum current from  $2 \times 10^{-5}$  amp to  $6 \times 10^{-5}$  amp. The solid-gold sheet was tested, and the maximum current obtained was only  $3 \times 10^{-6}$  amp. Consequently, it appears that gold-plated platinum has a higher catalytic activity than unplated platinum, and that the addition of certain transition-metal silicides raises the activity further. The maximum current for an "active" silicide or a gold-plated sheet is typically about  $1 \times 10^{-3}$  amp for oxidation of both hydrogen and 0.1 molar methanol.

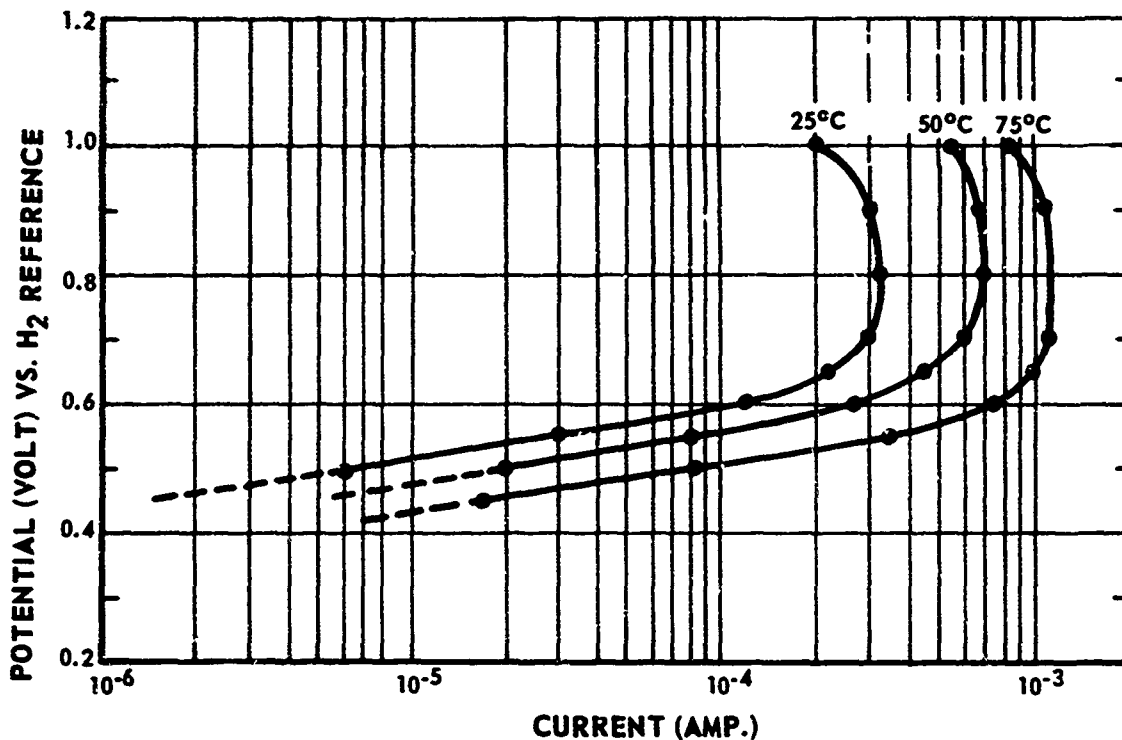


Figure 3 Effect of Temperature on the Electrochemical Oxidation of 0.1-Molar Methanol in 1-Molar  $H_2SO_4$  on -325 Mesh  $TaSi_2$  Powder

It appears that the activity observed is a result of a unique catalytic activity arising from the combination of gold, platinum, and silicide. It was hypothesized that the activity might be solely the result of the gold-platinum combination and that the silicide served only to break through the gold plate and expose more platinum. Tests were conducted with other hard powered materials to determine if this were the case. It was found, however, that maximum currents on the order of 1 ma were obtained only when certain transition-metal silicides were used. It is also noted that with certain silicides the maximum current density for oxidation of hydrogen is significantly greater than for the oxidation of methanol, whereas for other silicides the maximum currents are essentially the same (see Table 1). Consequently, there is definite evidence that all three constituents, the silicide, the gold, and the platinum, play a significant part in the oxidation process.



## 2. Effect of Surface Properties on Catalytic Activity

### a. Apparatus and Sample Description

The study of the effect of surface properties on catalytic activity was started by determining the voltage-current characteristic for the disilicides of molybdenum, titanium, and vanadium immersed in an electrolyte saturated with argon and subsequently with hydrogen. Both steady-state and transient characteristics were obtained. Special precautions were taken to ensure that the electrode surfaces did not become contaminated with platinum or any other catalytically active material. It was also necessary to exclude other impurities since the electrode surface area was quite small, and the adsorption of even small amounts of impurities could affect the results significantly.

Following the experiments with the silicides, an experiment was conducted to determine the effect of activating a  $\text{TiSi}_2$  surface with small amounts of platinum.

The cell used for these tests was the three-compartment cell shown in Figure 4. The working electrode and counter electrode compartments are separated by a fritted glass disk, and the reference electrode compartment terminates in a Luggin capillary beneath the working electrode in the working electrode compartment. The reference electrode is separated from the reference electrode compartment by a flowing junction to prevent contamination of the electrolyte by traces of platinum from the reference electrode. The working electrode passes into the cell through a rotating, water-sealed joint and is rotated at 600 rpm by a synchronous motor. The counter electrode is a gold sheet measuring 2 cm by 2 cm. The electrolyte is prepared in a separate vessel and is transferred to the cell by pressurized argon. Gases are admitted to the cell through glass frits in the bottoms of the working and counter electrode compartments. Gases may also be admitted above the solution in the working electrode chamber to prevent contamination of the cell by water from the rotating seal when the cell is being drained.

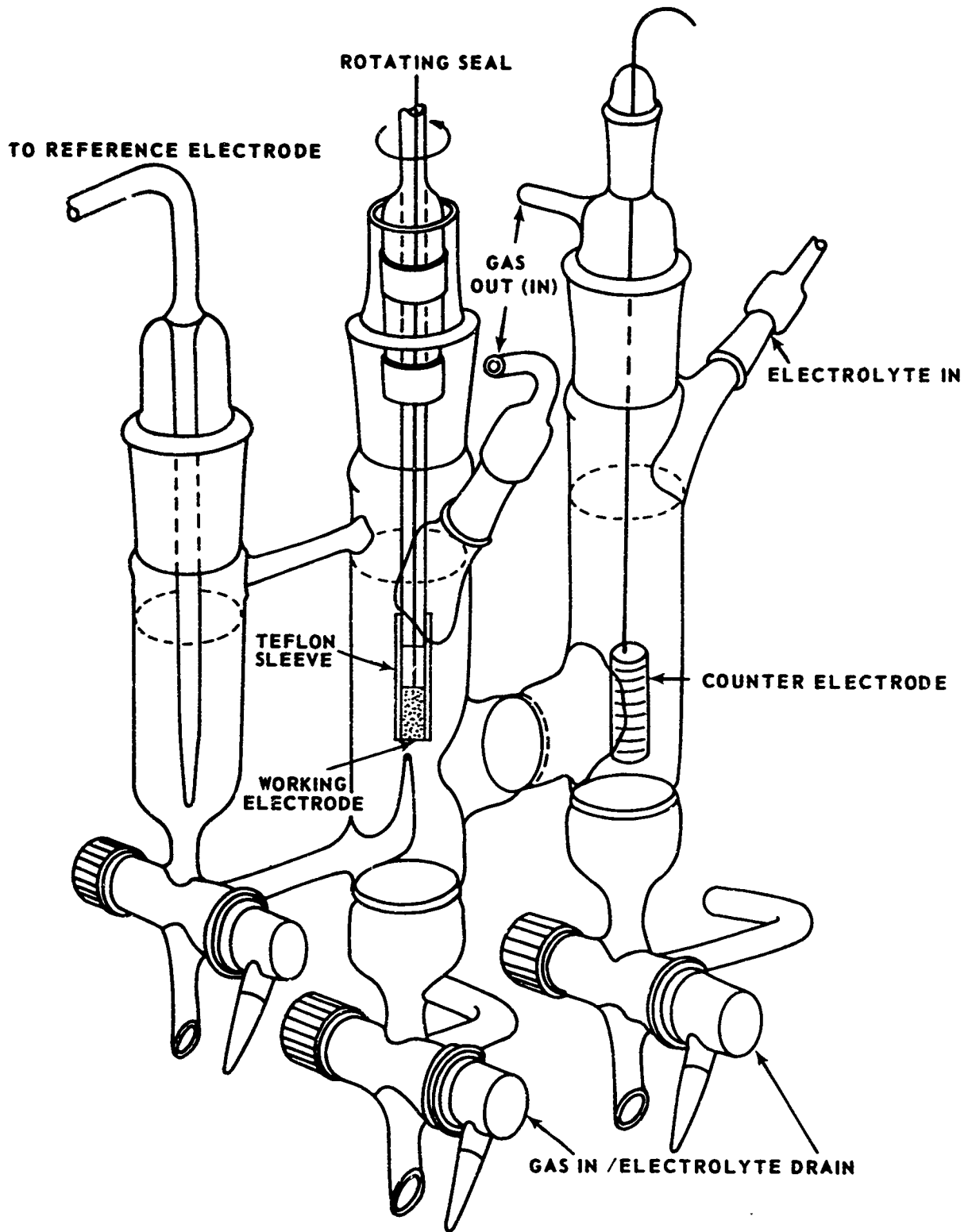


Figure 4 Three-Compartment Cell Used for Kinetic Studies

The electrolyte used was 1-molar  $\text{H}_2\text{SO}_4$ . It was prepared from reagent-grade chemicals and water distilled from alkaline permanganate followed by a double distillation under nitrogen. This water was transferred from the final receiving vessel to a storage vessel by pressurized nitrogen (see Figure 5).

When electrolyte was needed, the water was transferred by gas pressure to a mixing vessel where acid (or base) was added from an integrally fabricated burette. The solution was mixed by gas bubbling and was then transferred to the cell by gas pressure. Thus, the entire water distillation, water storage, electrolyte mixing, and cell systems are sealed from laboratory air and are maintained under inert gas. In addition, all stop cocks in the system are Teflon and all joints are sealed with either electrolyte or water so that traces of greases will not contaminate the electrolyte.

High purity dry grade argon supplied by the Linde company was used. The argon was passed over Cu and CuO at  $800^\circ\text{C}$  to remove traces of  $\text{H}_2$  or  $\text{O}_2$  and subsequently through ascarite to remove  $\text{CO}_2$ . A typical analysis of the argon revealed the presence of 0.5 to 1 ppm moisture, 1 to 2 ppm  $\text{N}_2$ , and 0.5 to 1 ppm  $\text{O}_2$ . The hydrogen used was purified by a palladium-tube diffuser designated as a Model CEA Serfass Hydrogen Purifier.

Plumbing for the gas system was fabricated entirely from copper tubing except for the connection to the glass at the cell. These connections consisted of Teflon tubing inside vacuum rubber tubing to minimize the diffusion of oxygen into the gas stream.

The potential of the working electrode was controlled by a Wenking Model 61RS potentiostat. For transient data, the potentiostat was controlled by a low-frequency function generator (Hewlett Packard Model 202A) producing a triangular wave output. This unit produced potential sweep rates from 0.02 mv/sec to 15 v/sec. The resulting voltage-current curves were displayed on a Tektronix Dual-Beam Model RM561A oscilloscope and were recorded with an oscilloscope camera (Polaroid Model C-12). To obtain slow sweep rates, the potentiostat was controlled by a slow-function generator (P&WA Model 1060-2) which permitted potential sweep rates from 10 mv/sec to 300 mv/min. Slow-sweep curves were recorded on a Mosely Model 135 X-Y recorder. Constant-potential plots of current vs time were recorded on a Sargent Model SR strip-chart recorder. The steady-state potentials were measured with a high-impedance vacuum-tube voltmeter (Knick Ph Meter Type 26 produced by Berlin Zehlendorf).

The silicide samples used were in the form of sintered rods 1.4 cm long and 0.80 cm in diameter. Each rod had a 0.15 cm hole in one end for the insertions of a gold lead wire. The rods were fabricated by Cerac, Inc. by the direct reaction

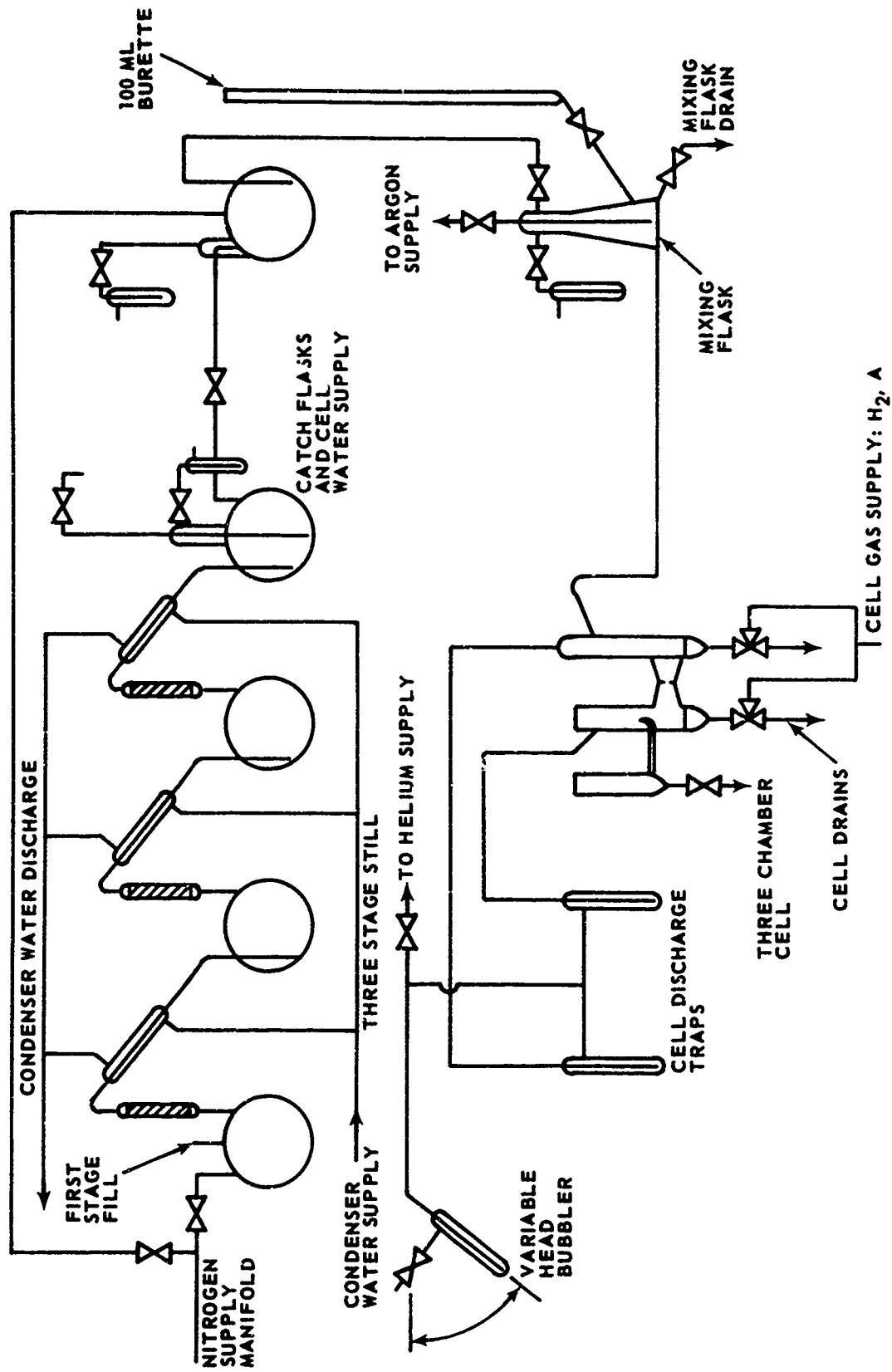


Figure 5 Schematic Diagram of Water-Electrolyte System

under inert atmosphere of the elements in an electrical furnace. After solidification, the resulting material was crushed, ground to a powder, and passed through a sieve to obtain the desired particle size. The powder was then sintered under pressure at a temperature below the material melting point in a graphite mold. As received, the rod samples had a heavy oxide coating. This coating was ground off before any chemical treatment was attempted.

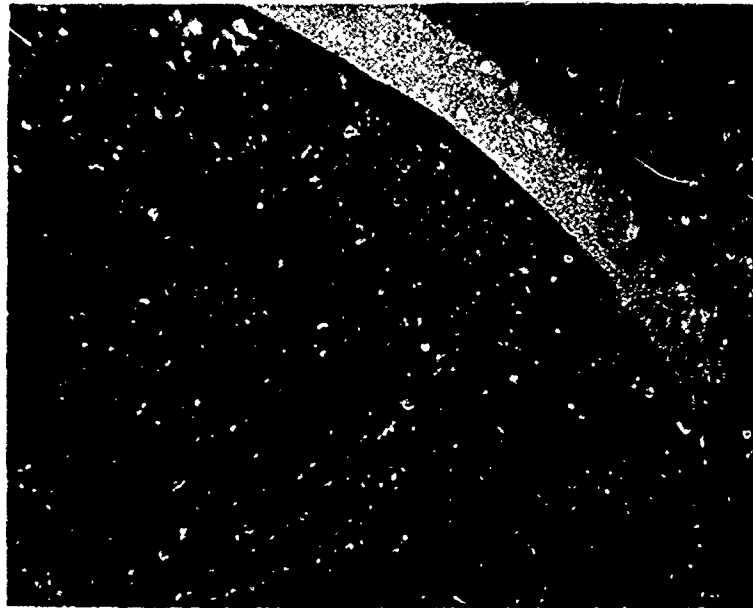
The samples were necessarily porous and could not be polished to a metallurgically smooth finish. However, a macroscopically smooth surface was obtained for each of the samples by chemical treatment. The  $\text{MoSi}_2$  and  $\text{VSi}_2$  samples were treated with a mixture of 2.7 molar HF-14 molar  $\text{HNO}_3$  for one minute at  $90^\circ\text{C}$  followed by 30 minutes in a 3 percent KOH solution at  $90^\circ\text{C}$ . The  $\text{TiSi}_2$  sample was treated in the 2.7 molar HF-14 molar  $\text{HNO}_3$  solution for one minute at  $90^\circ\text{C}$ . Chemical treatment of all samples was followed by rinsing in distilled water. The resulting surfaces were quite irregular as shown in Figure 6, which shows a portion of the  $\text{TiSi}_2$  rod after treatment.

Wet chemical analysis of the powders used to form the samples revealed that the powder composition corresponded to the desired compound with 2 percent. At present, samples of the rods are being examined by electron microprobe and X-ray diffraction analyses to determine the composition of the samples and the distribution of constituents in the surface. Measurements indicate that the rods have a specific resistance of less than 0.005 ohm cm.

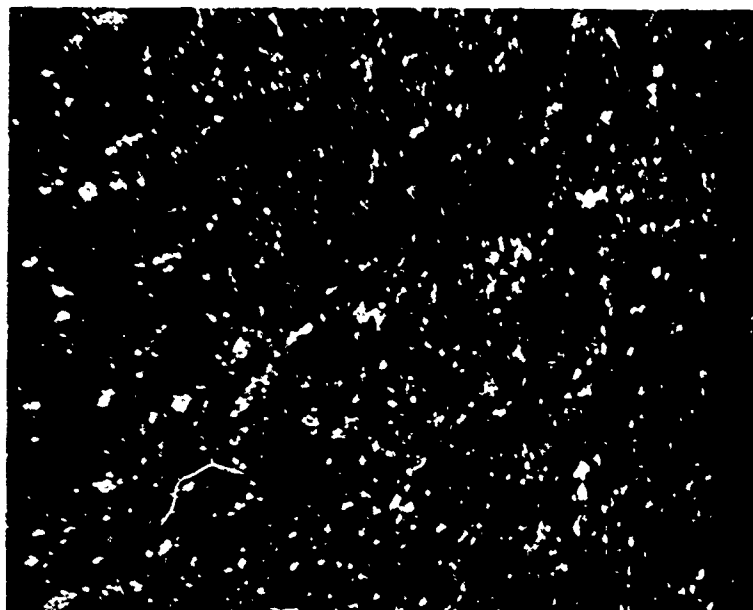
The electrical connection to the rods was made by force fitting a gold wire into the hole in the end of the rod and then applying conductive silver epoxy for mechanical strength. The rod was then forced into a short piece of Teflon tubing until the end of the rod was flush with the tubing. This tubing served to connect the electrode to a glass tube from the stirring motor. After the electrode was positioned in the tubing, the upper end of the electrode was coated with Teflon to prevent seepage of electrolyte between the rod and the Teflon tubing to the electrical connection.

To date, the effective surface area of the exposed portion of the electrode has not been determined accurately. The projected area is  $0.50 \text{ cm}^2$ , but, because of the uncertain surface roughness, meaningful current densities cannot be calculated using this value. Consequently, experimentally measured currents rather than current densities are reported. Determination of the true surface area of the electrodes by electrochemical methods, such as measurement of the double-layer capacity, is complicated by the presence of an oxide layer with a thickness which changes with potential. In addition, a finite faradic current is produced by the oxide formation. The surface area of the rods is too small to measure by the BET method. However, there are several possible procedures for measuring the surface areas. It may be possible to measure

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Mag: 20X



Mag: 60X

**Figure 6** Photomicrographs of  $TiSi_2$  Sample After Chemical Polishing in 2.7 Molar HF-14 Molar  $HNO_3$  for One Minute at  $90^\circ C$

the capacity in a potential region where the oxide is not present, that is, in the hydrogen evolution region. In this region, a correction for the faradic current can be made. Alternatively, the surface might be plated with a monolayer of a noble metal which would result in a surface with essentially the same area and with known behavior.

#### b. Test Results

Initial testing revealed that the porous nature of the silicide rods and the formation of surface oxides caused large electrode capacities, and, therefore, potential sweep rates above about 50 mv/sec would not be meaningful. Consequently, the fast potential sweeps are fast only by comparison to the slower sweeps, which were made at rates from 100 to 200 mv/min.

Before testing, the electrodes were held at -600 mv for 30 minutes to reduce the oxides. In addition, after each sweep the potential was returned to -600 mv to provide a constant, minimum oxide layer for each experiment. The samples were then subjected to a series of triangular potential sweeps from -600 mv to 1100 mv to -600 mv at 34 mv/sec and -600 mv to 400 mv to -600 mv at 20 mv/sec. These same ranges were then covered at 100 mv/min and at steady-state conditions. All tests were performed in 1-molar  $H_2SO_4$  electrolyte at 25°C saturated with either argon or hydrogen.

The fast potential sweep curves for  $MoSi_2$  are shown in Figure 7. These curves show no activity for hydrogen, and the only effect of the hydrogen is to decrease the rate of oxide formation. The slow sweeps (see Figure 8) show the same behavior except that it appears that oxidation and reduction occurs in a series of steps in the argon-saturated electrolyte. In the hydrogen-saturated electrolyte, the steps are absent or severely repressed. The steady-state data shown in Figure 9 again indicates that the presence of hydrogen inhibits both the formation of oxides between -25 mv and 250 mv and the reduction of hydrogen ions below -25 mv. This phenomenon may be caused the blocking of reaction sites by adsorbed molecular  $H_2$ , partially excluding water molecules from the surface. The transient curves obtained during step changes in potential are shown in Figure 10. The immediate increase in current followed by a rapid decay indicates that  $MoSi_2$  forms a limited amount of oxide at each potential. This phenomenon was observed for all three silicides tested. From the data, it appears that  $MoSi_2$  could represent a candidate for surface activation.

The electrochemical behavior of  $VSi_2$  is markedly different from that of  $MoSi_2$  or  $TiSi_2$  in that it is the only one of the three silicides which shows any evidence that it catalyzes the oxidation of hydrogen. As shown in Figure 11, hydrogen is used above 0 mv, although the activity is somewhat obscured by the reduction of surface oxidation in the presence of hydrogen, as was observed with  $MoSi_2$ .

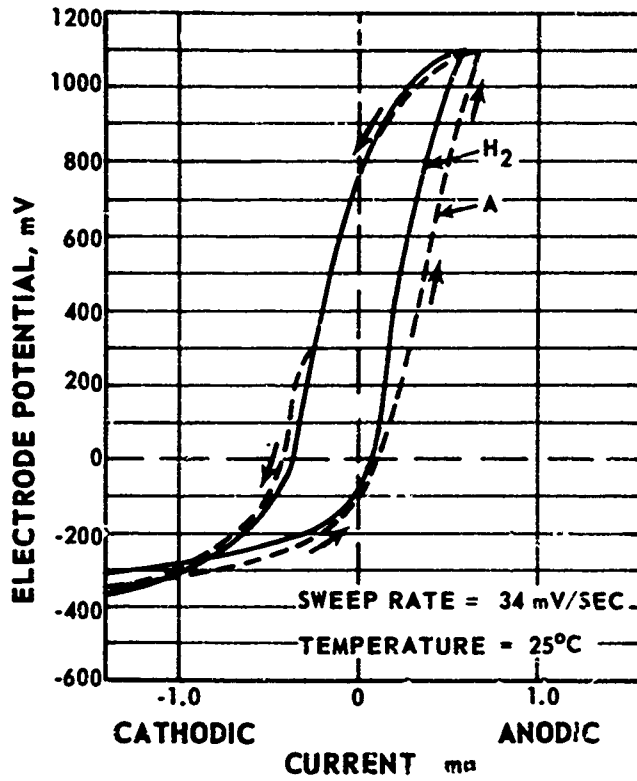


Figure 7 Triangular Potential Sweep Curves for  $\text{MoSi}_2$  With Sweep Rate of 34 mv/sec

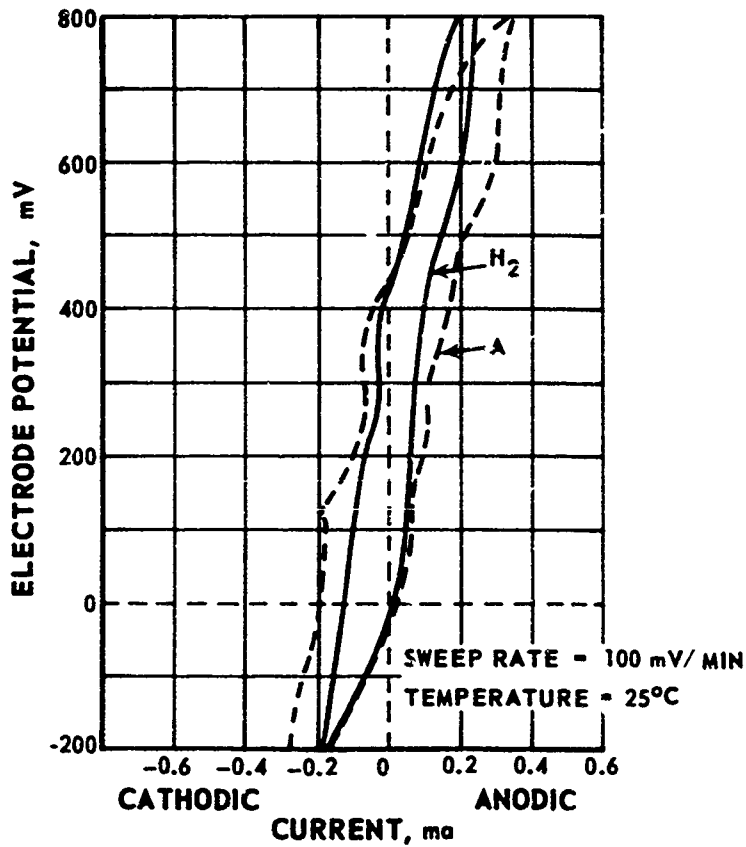


Figure 8 Slow Potential Sweep Curves for  $\text{MoSi}_2$  With Sweep Rate of 100 mv/min



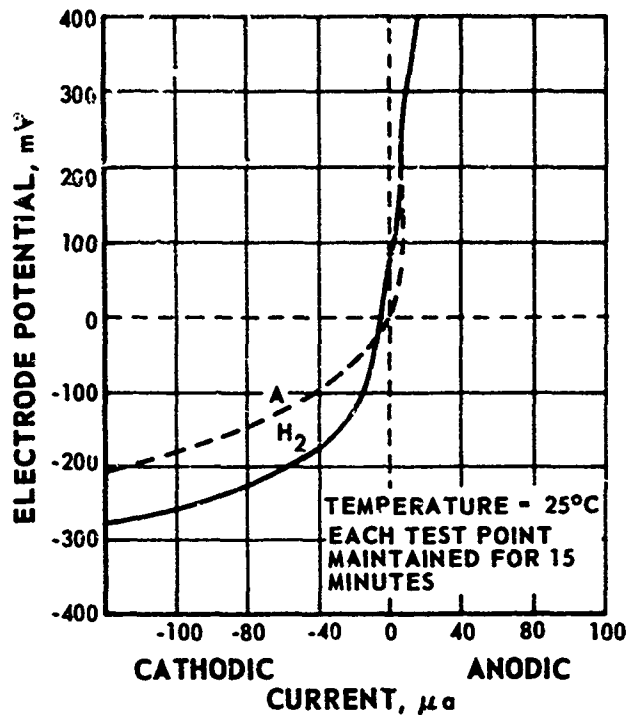


Figure 9 Steady-State Characteristic for  $\text{MoSi}_2$

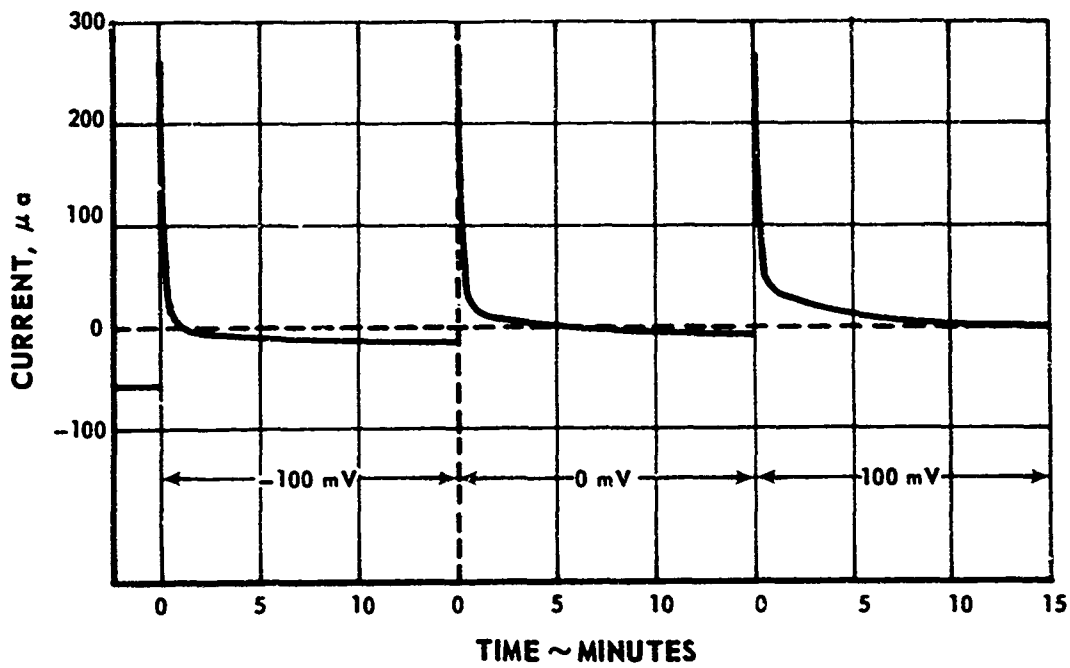


Figure 10 Current Transient Curves for  $\text{MoSi}_2$  Subjected to 100 mv Step Potential Changes

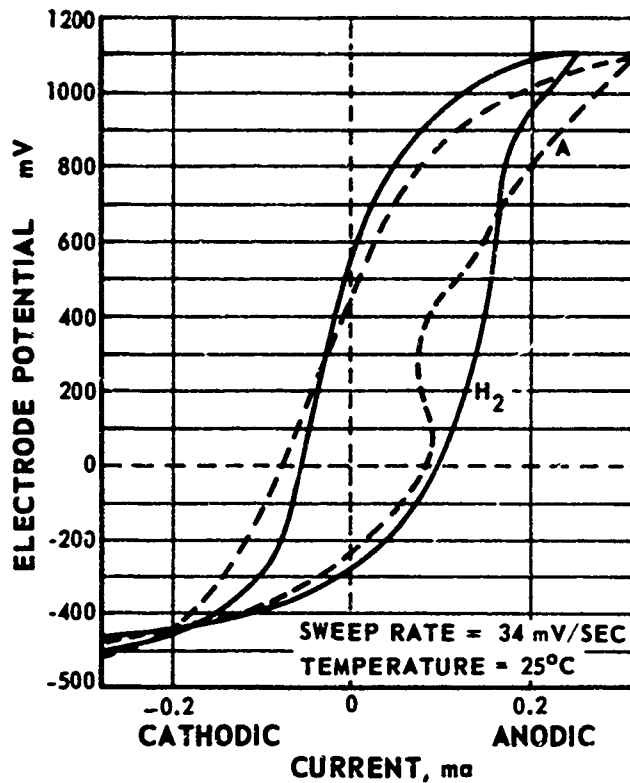


Figure 11 Triangular Potential Sweep Curves for  $VSi_2$  With Sweep Rate of 34 mv/sec

The slow sweep curves (see Figure 12) show that  $VSi_2$  is easily oxidized and reduced, with little difference being apparent between the argon- and hydrogen-saturated solutions. The steady-state curves (see Figure 13) show that the current in a hydrogen-saturated solution is more anodic over the potential range from -500 mv to 1400 mv and has an oxidation peak at -200 mv.

$TiSi_2$  electrodes were tested in both the unactivated and activated states. Tests with the unactivated electrode (see Figures 14, 15, and 16) revealed no activity for hydrogen oxidation. The data also indicated, however, that only a very small amount of surface oxidation occurs, particularly in the potential range of greatest interest, that is, between 0 and 500 mv. It appeared, therefore, that  $TiSi_2$  should provide a very stable surface for activation compared to the other two silicides. Consequently, a  $TiSi_2$  rod was activated by adding  $6 \times 10^{-9}$  moles ( $1.2 \mu gm$ ) of platinum to the electrolyte and holding the potential at -600 mv. If the granular nature of the surface and the porosity of the rod results in a roughness factor of 10, then this amount of platinum should cover 40 percent of the surface with a monolayer. Sweep results are shown in Figure 17. As shown, a considerable amount of activity was achieved.

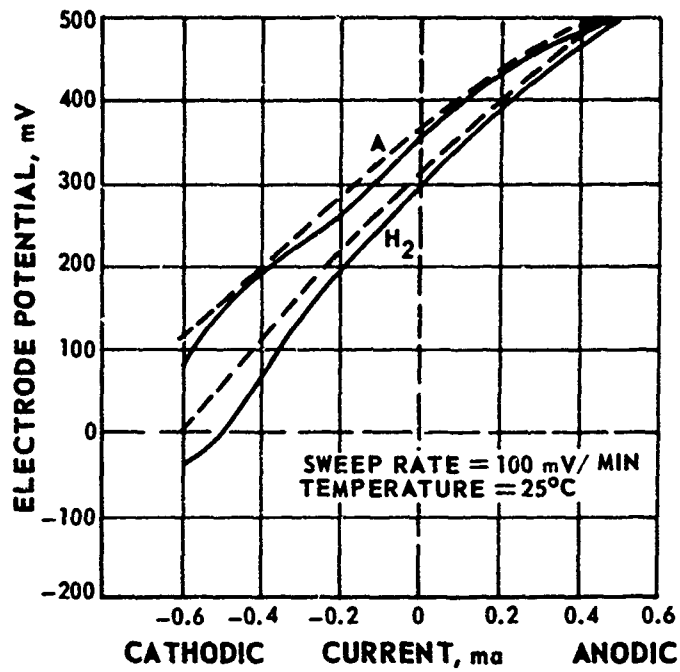


Figure 12 Slow Potential Sweep Curves for VSi<sub>2</sub> With Sweep Rate of 100 mv/min

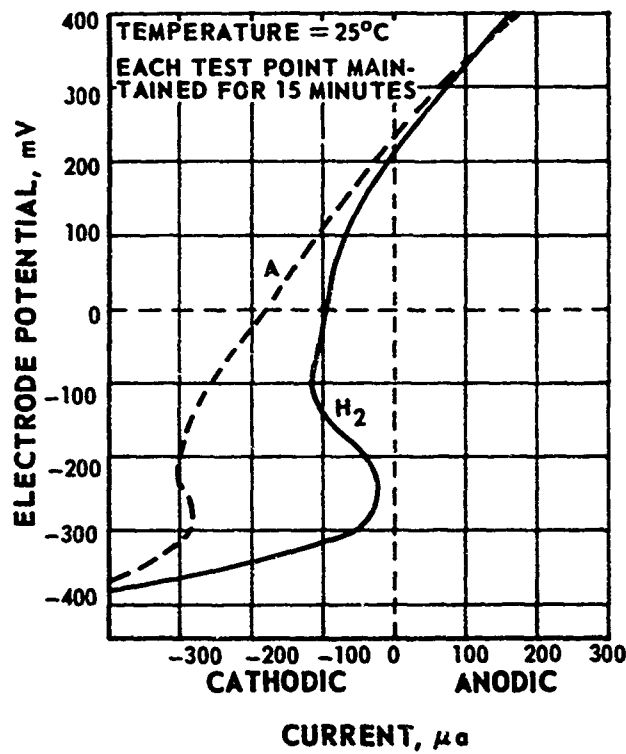


Figure 13 Steady-State Characteristic for VSi<sub>2</sub>

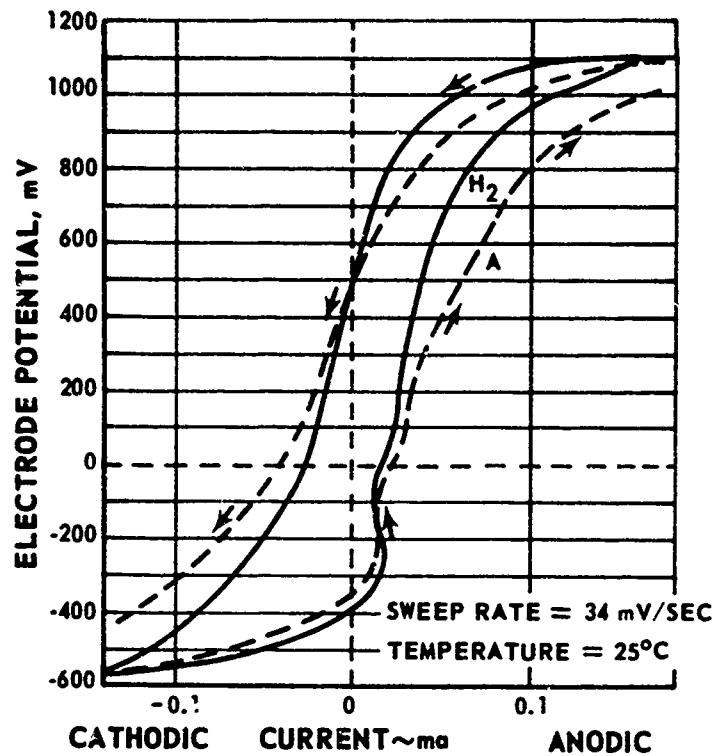


Figure 14 Triangular Potential Sweep Curves for  $\text{TiSi}_2$  With Sweep Rate of 34 mv/sec

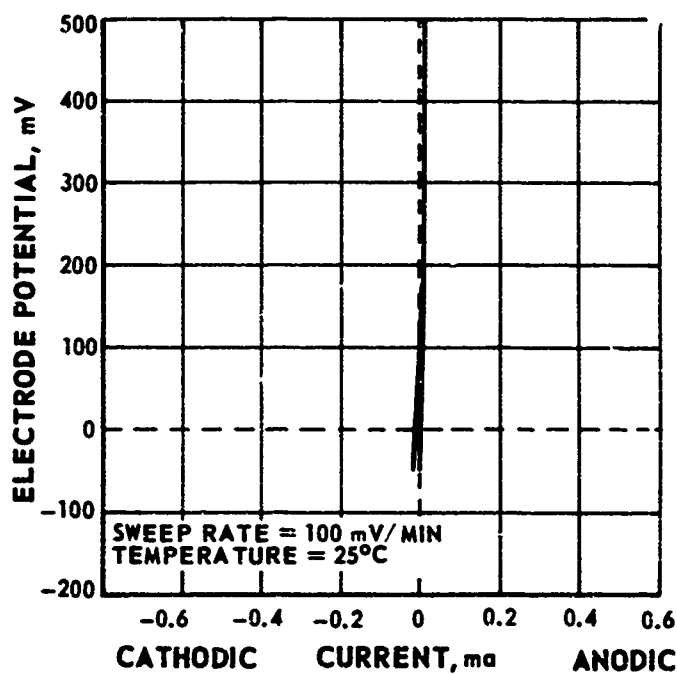


Figure 15 Slow Potential Sweep Curves for  $\text{TiSi}_2$  With Sweep Rate of 100 mv/min

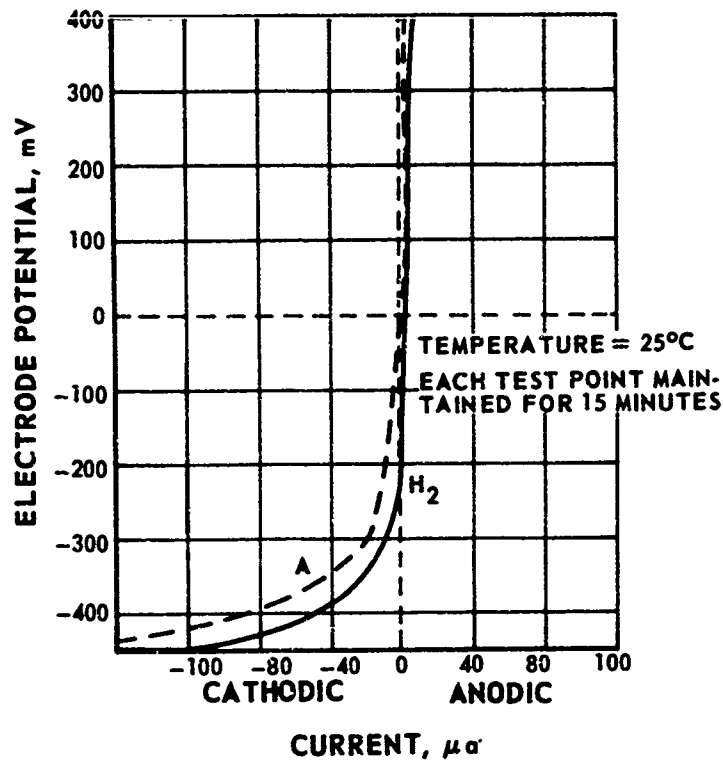


Figure 16 Steady-State Characteristic for  $TiSi_2$

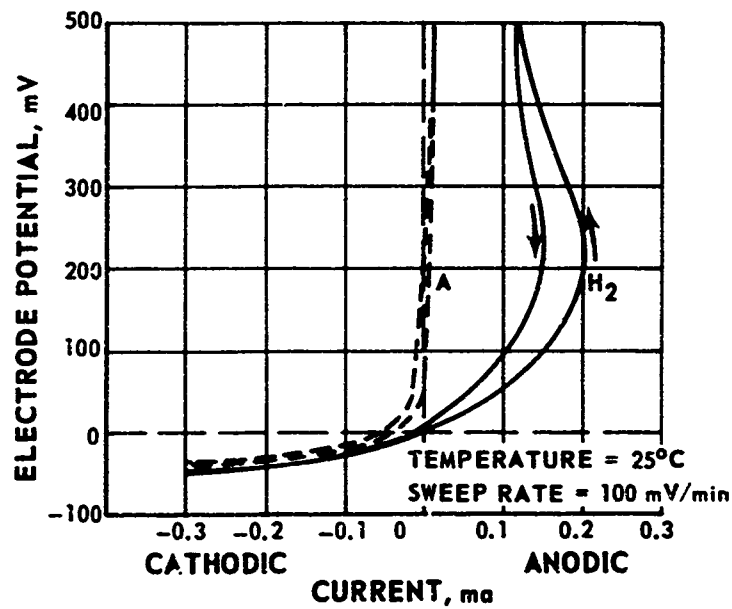


Figure 17 Slow Potential Sweep Curves for Platinum-Activated  $TiSi_2$  With Sweep Rate of 100 mV/min

### III. CONCLUSIONS AND RECOMMENDATIONS

The data obtained during the first quarter shows no evidence that hydrogen can be adsorbed or oxidized on a pure transition-metal silicide surface, although the hydrogen does appear to inhibit the formation of the surface oxide film, particularly on  $\text{TiSi}_2$ . Combining the silicides with small amounts of platinum or platinum and gold results in interesting catalytic activity for the electrochemical oxidation of hydrogen and methanol. Activating the surface of  $\text{TiSi}_2$  with trace amounts of platinum resulted in a considerable amount of activity for hydrogen oxidation.

The oxides of  $\text{TiSi}_2$ ,  $\text{MoSi}_2$ , and  $\text{VSi}_2$  were found to be good electronic conductors, and their formation was found to be reversible up to at least 1.2 volts. That is, within the potential range studied, the oxides can be reduced at lower potentials and presumably completely reduced at potentials below that at which hydrogen evolution occurs.

Below 400 mv, the steady-state corrosion rate of  $\text{MoSi}_2$  and  $\text{TiSi}_2$  at  $50^\circ\text{C}$  is approximately  $10^{-5}$  amp/cm<sup>2</sup>, based on geometrical area. The corrosion current of  $\text{VSi}_2$ , however, increases rapidly at potentials above 200 mv.

The relative true surface area of the sintered silicide samples could not be measured directly by the electrode capacitance when the oxide film is present because of the much smaller capacitance (and, hence, higher impedance) of the film which is in series with the double-layer capacitance. However, it may be possible to measure the surface area by other methods.

In view of the results obtained during the first quarter, it is recommended that future work be directed toward investigating the effects on catalytic activity of modifying the surfaces of a selected transition-metal silicide with platinum or gold. Candidate materials for doping are  $\text{TaSi}_2$ ,  $\text{WSi}_2$ ,  $\text{TiSi}_2$ , and  $\text{MoSi}_2$ , but the corrosion resistance and oxide formation characteristics of  $\text{TaSi}_2$  and  $\text{WSi}_2$  should be studied further before final selection is made. It will also be necessary to investigate other methods of measuring the relative true surface area. The effects of temperature and acid composition on catalytic activity and corrosion should be investigated only after a suitable catalyst has been developed. A minor effort will be given to the screening of new materials using a pure-gold current collector.

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<b>13. ABSTRACT</b>  A program is being conducted to investigate the mechanisms of electrocatalysis with respect to the anodic oxidation of selected fuels by novel electrocatalysts in acid electrolyte at temperatures below 150°C and at ambient pressure. The transition-metal silicides were chosen for study on the basis of previous work which indicated some catalytic activity for these materials for fuel oxidation.  The electrochemical properties of the silicides in acid electrolyte were investigated by measuring the polarization behavior using both potential sweep and steady-state methods. Tests were performed in inert-gas saturated electrolyte to determine corrosion resistance and characteristics of oxide film formation, and then in hydrogen saturated electrolyte or in electrolyte which is 0.1 molar in methanol to evaluate the catalytic activity.  The results showed that the corrosion current for these materials in acid electrolyte is low, generally about $10^{-5}$ amp/cm <sup>2</sup> . The oxide films formed on the silicides are good electronic conductors and form through a reversible process. The silicides by themselves were found to have no significant activity for the electrochemical oxidation of hydrogen or methanol, but, when combined with trace amounts of platinum, they demonstrated considerable activity.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Electrochemical Catalysis		4				
Hydrogen Oxidation		4				
Methanol Oxidation		4				
Silicides		1				
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