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ELECTROCATALYSIS STUDIES OF TRANSITION-METAL SILICIDES,(U)
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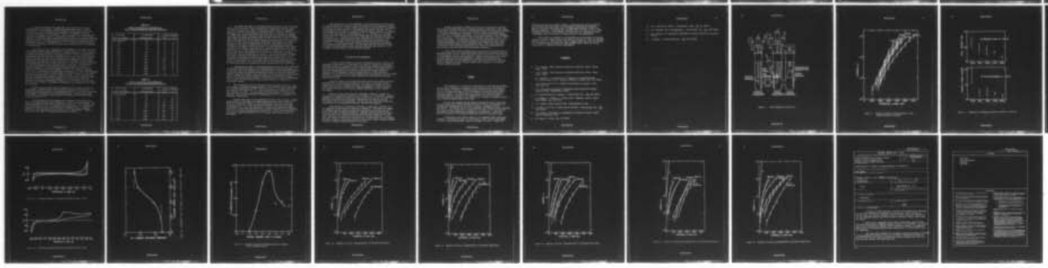

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⑥ ELECTROCATALYSIS STUDIES OF TRANSITION-METAL SILICIDES,

by

D. Fouchard and C. Gardner

⑩ David T. /Fouchard
Christopher L. /Gardner

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ELECTROCATALYSIS STUDIES OF TRANSITION-METAL SILICIDES

by
D. Fouchard and C. Gardner
Energy Conversion Division
Chemical Sources Section

DECEMBER 1978
OTTAWA

ABSTRACT

A series of transition metal silicides were evaluated as catalysts for the anodic oxidation of hydrogen in acid medium. Overall levels of activity were very low and relative levels of activity were very similar for all the compounds except Cr_3Si which showed an activity roughly three times the others.

Each of the compounds formed highly irreversible passive films when polarized anodically making them quite stable in acid medium. The usefulness of the compounds as catalyst support materials, however, is hindered by difficulties in obtaining efficient electrodeposition of active metals onto the compounds.

The study also revealed that erroneous results can easily be obtained in electrocatalysis studies if care is not taken to exclude all traces of platinum from the test cell as platinum was found to migrate about the cell when platinum counter electrodes were used.

RÉSUMÉ

Plusieurs siliciures de métaux de transition ont été évalués comme catalyseurs d'oxydation anodique de l'hydrogène en milieu acide. On a trouvé que l'activité de tous ces composés est très faible et presque semblable pour tous sauf Cr_3Si qui a une activité environ trois fois plus élevée.

Quand ces composés sont polarisés anodiquement, il se forme une couche inerte hautement irréversible qui les rend très stables en milieu acide. Cependant, il semble que ces siliciures ne soient pas très utiles comme support de catalyseurs à cause de la difficulté d'obtenir des dépôts de métaux actifs sur la surface de ces composés.

Cette étude a démontré que les études électrocatalytiques peuvent aisément conduire à des résultats erronés si l'on n'enlève pas complètement le platine de la cellule expérimentale, car on a constaté une migration du platine quand on l'utilise comme contre-électrode.

INTRODUCTION

A Canadian Armed Forces requirement for silent continuous sources of power has long been recognized. One of the candidates for filling this requirement has been the fuel cell. Fuel cells unfortunately, have always suffered the disadvantage of high cost, with a considerable portion of this high cost being due to the fuel cells' requirement for expensive noble metal catalysts to make the electrochemical reactions proceed at reasonable rates. The search for inexpensive catalysts to replace the presently-used noble metals is therefore a continuing research effort in many parts of the world.

The selection of candidate materials for catalyst evaluations becomes difficult when one considers the extremely corrosive environment in which they must operate, usually either strong alkali or acid coupled with a wide range of electrical potentials. One group of compounds which appeared promising for acid environments were the transition metal silicides. Most of these compounds are very stable in acid and exhibit high conductivity(1,2). Surveys of the literature gave evidence of catalytic properties towards hydrogen. Samsonov et al(3) reported activity for several silicides in catalysing the dehydrogenation of ethylbenzene to styrene. Sandler(4) reported catalytic activity for vanadium and molybdenum disilicides in the deuterium-hydrogen exchange reaction. Data, however, on the electrocatalytic properties of these compounds for hydrogen oxidation reactions is somewhat confusing with some authors reporting no activity whatsoever(5,6) while others report considerable activity(7).

In view of this, a study of several transition-metal silicides was undertaken at DREO to determine their activities as hydrogen anode catalysts. Although a great deal of activity was not anticipated, it was hoped that the relative levels of activity between the compounds could be correlated with various physical properties of the compounds and so gain an insight into the catalytic mechanisms involved. Such information could be very useful in predicting the catalytic activity of untested compounds.

EXPERIMENTAL

The test materials, namely $CrSi_2$, Cr_3Si, $ZrSi_2$, $MoSi_2$ and VSi_2 were obtained in powder form (-200 to -325 mesh, 99% pure) from 'Materials Research Corporation' in Orangeburg New York. A sample of platinum black was also obtained (from the Aldrich Chemical Company) for comparison purposes. The powders were fabricated into hydrophobic gas-diffusion electrodes in the following manner. Discs of tantalum screen (Exmet Corp.) 1 cm^2 were punched out, cleaned and dried, then swirled in a slurry of 70% catalyst/30% Teflon 30B (Dupont Corp.). The discs were hung to dry in an oven at 125°C for 2h and then sintered at 350°C for 5 minutes. The resulting electrodes contained approximately 20 mg of catalyst.

Electrodes were tested in an all-glass cell illustrated in Fig. 1. Two types of electrode mounting arrangements were used, the gold spring arrangement shown in the diagram and, secondly, a simple spot-welding of the electrode tab to a platinum wire. By varying the electrolyte level, the electrode could be tested either in a floating position or submerged. A reversible hydrogen electrode (RHE) was used as a reference throughout and all potentials are referred to this. Counter electrodes used were either gold foil or gold-plated platinum foil. All testing was done in 1M H_2SO_4 at 22°C, the H_2SO_4 solutions being prepared from pyro-distilled water(8) and 'Ultrex' H_2SO_4 (J.T. Baker Chemical Co.).

Instrumentation for the testing consisted of a Princeton Applied Research (PAR) potentiostat and universal programmer in conjunction with a Hewlett-Packard X-Y recorder. IR drops in the electrolyte were measured with an interrupter circuit constructed in-house.

Electrochemical testing of the electrodes generally consisted of four types of tests, namely measurements of the hydrogen oxidation activity, the hydrogen evolution characteristics, the corrosion behaviour and the electrochemical surface area. In addition to this, the purity of the electrolyte solutions was monitored electrochemically throughout the study.

Testing for hydrogen oxidation activity was done in the following manner. The electrode was clamped in the gold electrode holder, installed floating on the electrolyte and allowed to equilibrate overnight with the cell saturated with nitrogen. The electrode was then cycled at 10 mV/sec over the range +0.14V - +1.30V for 1h to oxidize any impurities present on the electrode. The cell was then saturated with hydrogen and the electrode scanned at 1 mV/sec from 0V to approximately +0.6 V to determine its hydrogen oxidation characteristics.

Testing for hydrogen evolution characteristics was done with the electrodes vertical and submerged in the electrolyte. Electrical connection to the electrodes under test was by means of a platinum lead-in wire spot welded to the electrode tab rather than by the gold spring arrangement. The cell was saturated with hydrogen and the potential of the electrode was taken progressively more negative in steps, while the corresponding current was recorded when it stabilized, usually after several minutes equilibration.

Corrosion behaviour was studied with the electrodes again placed vertically and submerged, but with the cell saturated with nitrogen. Slow (10 mV/sec) potential scans were conducted over a wide range of potentials, generally -0.3 V to +2 V.

Electrochemical surface areas were determined as follows. The electrodes were submerged in nitrogen saturated electrolyte then wetted according to the procedure of Giner(9). The surface area was then determined by integration of the hydrogen adsorption peaks. This procedure is, of course, limited to those materials which have distinct hydrogen adsorption peaks, which in this study turned out to be only the platinum standards.

The electrolyte purity monitoring, mentioned previously, was carried out regularly to ensure that no large buildup of chemisorbable impurities occurred which could mask true catalytic activity. A gold foil, precleaned in a hot solution of 10% HNO_3 in concentrated H_2SO_4, was used to detect the impurities. The electrode was potentiostated at +0.05 V in a N_2 saturated electrolyte sample for exactly 30 min. during which time impurity adsorption occurred. The 0.05 V value was chosen because it is as cathodic as one can go and still be sure that no significant H_2 evolution will occur. Following the adsorption step the electrode was scanned at 10 mV/sec out to +1.3 V. The presence of chemisorbed impurities was indicated by the appearance of distinct anodic peaks on the voltammogram as the impurities were oxidized off the electrode surface. Analysis of the magnitude and position of the peaks was used to evaluate the condition of the electrolyte.

A number of platinum deposition experiments were carried out in the course of the study and the procedure for the deposition was as follows. A stock solution of 10^{-4} M $Pt(SO_4)_2$ in 1 M H_2SO_4 was prepared and standardized spectrophotometrically using the stannous chloride method(10) against standards prepared from pure platinum metal. The volume of this solution required to achieve the desired doping level was calculated, then added to the test cell with the test electrode potentiostated at a suitably cathodic potential (0 V to -0.8 V in this study). The electrode was left at this potential for 30 min., at which time it was presumed that all the platinum was out of solution. Following the deposition the electrode was subjected to the previously mentioned electrochemical tests.

Physical testing of the electrode materials consisted of chemical stability testing and BET surface area measurements. The chemical tests simply consisted of measuring the weight loss of samples of the powders after sitting in 1 M H_2SO_4 for 1 week at room temperature. For the BET surface area measurements, two types of apparatus had to be utilized due to the widely varying values encountered. A fairly conventional apparatus constructed in-house was utilized for the high surface area powders such as the platinum-black reference material. A micro-BET apparatus similar to that of Hayes(10) was constructed for measuring relatively low ($<1\ m^2/g$) surface areas such as the silicide powders. Measuring procedures were similar in both cases. Samples were outgassed at 150°C for 2 h under the maximum available vacuum (approximately 10^{-4} torr). Gas adsorption was measured at 77°K using helium as a blank then nitrogen for the actual measurement. Calculations of the actual surface area were based on a nitrogen molecular area of $16.2\ (\mathring{A})^2$.

RESULTS AND DISCUSSION

PLATINUM-BLACK STUDIES

Initially, a series of teflon-bonded platinum-black electrodes were constructed and tested in order to establish a basis of comparison for the new materials.

BET surface area measurements of the platinum powder yielded an average value of $13.6\ m^2/g$.

Hydrogen oxidation activity measurements of the electrodes generally gave linear current/potential relationships up to the current limit of the potentiostat (1 A). Currents were quite high for $1\ cm^2$ electrodes indicating a fairly efficient electrode structure. Using +0.2 V (IR free) overpotential as a reference point, the average hydrogen oxidation current obtained for 15 samples was 490 mA (±21%).

Electrochemical surface area measurements on the electrodes gave active areas ranging from $1215\ cm^2$ to $3053\ cm^2$ (±5%). Comparison of the measured electrochemical surface areas with calculated surface areas based on the BET surface area and the catalyst loading was used as a criterion of catalyst utilization. The average value so obtained was (47 ± 8)%, indicating that roughly half the platinum in the electrodes was electrochemically active.

SILICIDE EVALUATIONS

PHYSICAL PROPERTIES

The transition-metal silicide samples were evaluated initially to determine their chemical stability in the 1 M H_2SO_4 electrolyte and their BET surface areas. The results of these initial tests are summarized in Table I. Note that the average weight losses due to corrosion over the 1 week period are generally low, ranging from 0.55% to 2.30% (±0.05), indicating relatively good stability. Surface areas of the powders are also low, ranging from 0.040 m^2/g to 0.087 m^2/g (±10%). These low surface area values indicate that the powders are essentially non-porous since calculated surface areas for spheres of the same mesh size are of the same order of magnitude.

TABLE I

Chemical Stability and Surface Areas of the Transition-Metal Silicides

Compound	Stability (% wt loss in 7 days) (±0.05)	BET Surface Area (m^2/g) (±10%)
$CrSi_2$	0.84	0.081
Cr_3Si	1.55	0.040
$ZrSi_2$	0.76	0.073
$MoSi_2$	0.55	0.056
VSi_2	2.29	0.087

HYDROGEN ACTIVITY

Evaluation of the hydrogen activity of the compounds consisted of measuring the hydrogen oxidation and evolution characteristics of the electrodes. The hydrogen oxidation measurements yielded very little information as in each case the oxidation currents measured with and without hydrogen present in the cell were very similar. The hydrogen evolution measurements however gave somewhat more resolution in distinguishing the relative levels of hydrogen activity, and these are shown in Fig. 2. The order of activity appears to be Cr_3Si, VSi_2, $ZrSi_2$, $CrSi_2$, $MoSi_2$, although with the degree of scatter in the data the trend must be considered subtle at best. If one corrects however for the varying surface areas of the compounds the trend becomes quite different and much more obvious. This is illustrated in Fig. 3. This figure shows the hydrogen evolution currents at -0.4 V for each of the compounds, first with the current as measured, and secondly with the current expressed as true current density. After making the correction for surface area it becomes apparent that only Cr_3Si differs significantly from the rest, with an activity roughly three times the others.

The reason for the higher activity exhibited by Cr_3Si no doubt lies in its high metallic content as compared to the others. The fact that the other four are so similar suggests that their surface compositions must be very similar, with a silica type of surface predominant.

ELECTROCHEMICAL BEHAVIOUR

General corrosion testing of the silicide electrodes showed that all the compounds were reasonably stable in the sulfuric acid electrolyte over quite a wide range of potentials. Anodic potential scans showed the gradual buildup of a passivating film on all of the compounds with the film thickening on each successive cycle. Oxygen evolution was negligible at potentials as high as 2 V, no doubt because of a large voltage drop across the film preventing the potential at the electrode/solution interface from becoming anodic enough to evolve oxygen. Only one of the compounds, Cr_3Si, showed electrode dissolution in the range of potentials studied (-0.3 V to +2 V). With this compound, anodic current increased sharply above +1.3 V accompanied by the production of a soluble yellow species in solution. All the others showed relatively high currents on the first few cycles but gradually passivated to a relatively stable, inert form. This stable form is, we believe, a silica (SiO_2) type of surface.

The initial formation of the passive layer on each of the electrodes is illustrated in figures 4 through 8. A linear potential sweep of 10 mV/sec was used in each case, starting from the rest potential. The electrodes had no pretreatment other than an overnight soak at open circuit.

The behaviour of the $MoSi_2$ and $ZrSi_2$ electrodes was quite similar in that the major portion of the film was formed during the first cycle in each case and this involved a similar quantity of charge, 36.1 and 30.7 mC, respectively. The amount of oxide coverage that this corresponds to is 2.3 and 1.5 monolayers respectively if one assumes that all the charge is converting Si to SiO_2. The behaviour was also similar in that both started the film formation at approximately 0.6 V and both showed a broad current peak in the 1.5 to 2.0 V range with considerable current instability present over this range. This instability is considered to be associated with the formation of a poorly conductive film (as one would expect of SiO_2).

The $CrSi_2$ electrodes behaved somewhat differently in that the film formation started at a much higher potential (approx. 1.4 V) and considerably more charge was involved, 173 mC on the first cycle, corresponding to a film thickness of 8.9 monolayers. Their behaviour resembled the $MoSi_2$ and $ZrSi_2$ electrodes in that the major portion of the films was also formed on the first cycle, and the same broad, spikey, current peak was present in the 1.5 - 2.0 V region.

The Cr_3Si electrodes, as mentioned previously, decomposed above 1.3 V and as a result very little film formation occurred. The VSi_2 electrodes, on the other hand, formed a unique type of surface in that an enormous quantity of charge was involved in the passivation process, 2.4 C in cycle 1, corresponding to a theoretical coverage of 78 monolayers. All signs of current instability were absent. The reason for this unique behaviour is not clear at this point.

Details of the behaviour of the electrodes following prolonged cycling are illustrated in figures 9 through 13. The electrodes in each case had been cycled at 10 mV/sec over the potential range shown for 4 h, at which time all the voltammograms were essentially stable with time. Both the $MoSi_2$ and $ZrSi_2$ electrodes exhibited broad flat voltammograms with no distinct oxidation or reduction peaks. Oxidation currents occurred over a wide range of potentials and the electrode reduction currents tended to be masked by hydrogen evolution currents. The Cr_3Si electrodes exhibited a small reduction peak centered around +1.1 V immediately following sweep reversal at +1.3 V. The size of this peak was dependent on the anodic sweep limit and increased noticeably when the electrode was held at +1.3 V for a period of time, indicating some degree of reversibility in the oxidation of the electrode.

The $CrSi_2$ and VSi_2 electrodes also showed considerable detail in their stable voltammograms. The $CrSi_2$ electrode exhibited a broad range of oxidation from 1.3 V to 2.0 V followed by a distinct reduction peak at 0.75 V on the return sweep, again indicating some degree of reversibility. The VSi_2 electrodes were the only ones to show an oxidation peak (+0.8 V) but exhibited no distinct reduction peak, the reduction reaction occurring at very low potentials (<-0.4 V) along with some hydrogen evolution.

PLATINUM MIGRATION IN 1M H_2SO_4

During the course of the investigation, it became very apparent that erroneous results can be obtained in electrocatalysis studies if care is not taken to exclude all traces of platinum from the system. The use of platinum counter electrodes was found to introduce significant quantities of platinum into solution which ended up on the test electrodes, greatly increasing their hydrogen activity. One simply cannot assume that platinum is inert in most electrolytes even in a non-complexing medium such as the sulfuric acid used in this study.

Four types of counter electrodes were utilized in the study: gold, platinum; gold plated platinum; and silicide electrodes similar to those under test. The differences found in the hydrogen oxidation activity of various test electrodes after cycling against the different types of counter electrodes (10 mV/sec, 0.05 V to 1.3 V for 2 h) plainly showed that platinum contamination was occurring. This is shown in Table II.

TABLE II

Changes in Hydrogen Activity with Different Counter Electrode Materials

Electrode		H_2 Oxidation Current Max at 10 mV/sec (μA)		
#	Mat'l	Au counter	Pt counter	Silicide counter
1	$MoSi_2$	20	–	–
2	"	20	270	–
3	"	–	1170	–
4	"	33	200	–
5	"	–	365	–
6	"	–	570	–
7	"	10	–	–
8	"	10	–	–
1	$ZrSi_2$	10	–	–
2	"	10	–	–
3	"	–	120	–
4	"	–	240	–
1	$MoSi_2$	10	–	–
2	"	–	–	10
3	"	–	–	10

Note that the use of a platinum counter electrode increased the activity by more than an order of magnitude.

The above data were obtained with the electrodes mounted in the gold spring electrode holder previously shown in Fig. I. When the electrodes were separated from the holder and each tested separately it was found the virtually all the activity was coming from the gold holder rather than the test electrodes, indicating that the platinum deposition occurs preferentially on the gold. Needless to say this can cause very misleading results.

A brief investigation was made into the conditions under which platinum migration can occur. Platinum electrodes were held at various potentials or cycled between various potentials using a pure gold foil as a counter electrode. Following each treatment, the hydrogen oxidation activity of the gold foil was checked. Since pure gold is a relatively poor catalyst for hydrogen oxidation, any platinum transferred from the working electrode to the gold counter electrode is easily detected by greatly increased hydrogen activity. The gold foil was therefore made the working electrode and scanned from 0 V to approximately 1.2 V in a hydrogen saturated solution to monitor its hydrogen oxidation activity and thereby indicate the presence of any platinum.

The first series of experiments were designed to investigate the rate of platinum migration under conditions of constant potential. The platinum electrode was simply potentiostated at a constant potential for 30 minutes in a nitrogen saturated solution. Following this, the cell was saturated with hydrogen and the gold electrode previously used as the counter electrode was made the working electrode and its potential was scanned anodically (using another gold electrode as a counter electrode) to determine if any increase in hydrogen oxidation activity had occurred due to platinum migration from the platinum working electrode to the gold counter electrode. Following this, the cell was resaturated with nitrogen and the experiment repeated at a different potential. In determining the hydrogen oxidation activities, a 10 mV/sec scan was used over the range 0 V to +1.2 V. Although the anodic limit of 1.2 V was higher than would have been preferred, it was found necessary to scan this high in order to fully remove all adsorbed impurities and hence observe the true hydrogen activity of the electrode. Solution stirring was also used (700 RPM with a magnetic stirrer) to overcome mass transport limitations and thereby increase the sensitivity of the platinum detection. Although this stirring arrangement leaves a lot to be desired from the theoretical point of view, it was simple, convenient, very reproducible and could be calibrated.

Results for this first series of experiments are shown in Table III. As expected, a steady increase in the activation potential brings out a corresponding steady increase in the hydrogen activity of the counter electrode indicating an increasing rate of platinum migration. Potentials as low as 1 volt (RHE) can dissolve a small amount of platinum, and the effect seems to peak at about +1.7 V.

The second series of experiments were designed to investigate the rate of platinum migration under conditions of linear cycling potential. In these experiments the platinum electrode was cycled for 1 h at 10 mV/sec over a potential range of +0.4 V to various anodic sweep limits. A smooth gold counter electrode was once again used and its hydrogen activity changes monitored in the same manner as the previous set of experiments. Results for this second series of experiments are shown in Table IV.

TABLE III

Effect of Potential on the Migration Rate of Platinum-Constant Potential Conditions

Activation	H_2 Oxidation	Activity Change	
Pot'l (V vs RHE)	Activity (μA)	(μA)	%
no activation	40	-	-
1.00	58	18	45
1.10	68	10	17
1.20	71	3	4
1.30	88	17	24
1.40	111	23	26
1.50	197	86	77
1.60	325	128	65
1.70	590	265	82
1.80	820	230	39
1.90	1080	260	32
2.00	1130	50	5
2.05	1200	70	6

TABLE IV

Effect of Potential on the Migration Rate of Platinum-Cycling Potential Conditions

Anodic Sweep	H_2 oxidation	Activity Change	
Limit (V vs RHE)	Activity (μA)	(μA)	%
no activation	21	-	-
1.00	20	1	5
1.10	24	4	20
1.20	60	36	150
1.30	260	200	333
1.40	775	515	198
1.50	1430	655	85
1.60	1700	270	19
1.70	2000	300	18
1.80	2250	250	13

Once again the degree of platinum migration increases with increasing anodic potential limits, but differs from the steady-state results in that the overall currents are higher, indicating a greater degree of platinum migration, and the effect peaks at a lower potential, 1.3 V as opposed to 1.7 V. The higher rate of platinum dissolution under cyclic conditions as opposed to steady-state anodic potentials could be because this avoids the strongly-bound oxygen situation encountered when platinum electrodes are held at fairly high anodic potentials which could suppress the platinum dissolution reaction. This is probably also the reason why the platinum dissolution rate tends to decline in both cases at high anodic potentials. The peaking at a lower potential in the cyclic situation may be due to differences in platinum "collection efficiency" in the two cases. In these experiments, the counter electrode is in essence being used as a platinum collector; but it is also functioning as a counter electrode and we have no control over its potential. Much of the time it is probably not in a potential region where it would effectively reduce platinum ions in solution. In the steady-state situation the counter electrode will always be at very cathodic potentials (<-0.5 V) resulting in efficient reduction of platinum ions. However under cyclic conditions the potential of the counter varies widely and potentials as high as +1.5 V were noted. This could cause some of the deposited platinum to re-dissolve on each cycle resulting in poor platinum collection efficiency.

Quantifying the amount of platinum migrating under the above conditions is therefore difficult because of the aforementioned collection problems. A calibration curve was constructed by doping a gold electrode with known amounts of platinum (using the standard deposition procedure), then monitoring the hydrogen oxidation activity of the electrode in the same manner as the previous tests. One must be careful however in comparing the calibration results with the experimental results because of the different collection efficiencies in each case, and this quantification procedure should be considered as approximate at best.

The calibration curve for platinum on gold is shown in Fig. 14. The first signs of increased hydrogen activity on the gold electrode corresponded to a platinum doping level of 10^{-10} moles (19.5 ng). At a doping level of approximately 10^{-7} moles (19.5 μg), the electrode behaved essentially as a pure platinum electrode. If one assumes even distribution of the deposited platinum, these levels correspond to approximately 1/20 of a monolayer to 50 monolayers respectively.

Relating this back to the experimental results, Fig. 15 gives a rough quantification of the degree of platinum migration that occurred when the platinum electrode was cycled to the varying anodic end points mentioned previously (Table IV). Here the amount of migrated platinum is expressed in monolayers on a 1 cm^2 electrode and it is shown as a function of anodic sweep limit. This shows that repetitive cycling to moderately high potentials (1.35 V) can transfer a monolayer of platinum to a 1 cm^2 counter electrode and slightly higher potentials (+1.5 V) can raise this level to close to 2 monolayers.

The significance of this phenomenon in electrocatalysis studies cannot be underestimated and no doubt accounts for some of the discrepancies reported in earlier literature. Several authors (11,12,13,14) have studied the stability of platinum in acid solutions in considerably more detail than here and all agree reasonably well with our results in that the anodic stability of platinum in 1 M H_2SO_4 only extends to approximately 1.1 V. Therefore, if a platinum counter electrode must be used one must ensure that its potential does not stray above 1.1 V. Isolating the counter electrode solution from the working electrode solution while maintaining high conductivity is difficult since the commonly-used glass frits will only slow down platinum diffusion not prevent it. A flowing junction is perhaps the best solution to the problem if a platinum counter must be used. On the other hand one should not forget to consider other possible counter electrode materials such as gold or, if possible, the same material as the working electrode.

PLATINUM-DOPING EXPERIMENTS

In view of the extremely low levels of hydrogen activity found for the compounds it was decided to investigate the effects of doping the electrodes with small amounts of platinum to see if the silicide substrate would have any effect on the electrochemical activity of the platinum. The characteristics of the platinum deposits were studied by testing the hydrogen oxidation behaviour and the hydrogen evolution characteristics of the electrodes. Comparison of the results with those obtained with platinum-doped gold electrodes was used to determine if the silicide substrate was affecting the platinum deposit in any way.

Previous studies of platinum deposition on gold (see previous section) indicated that a gold electrode doped with 10^{-7} moles of platinum behaved essentially as a pure platinum electrode. A deposition potential of 0 V for 30 min. was found to be adequate for complete deposition. These conditions were therefore chosen for the initial doping experiments on the silicide electrodes.

Results of this first series of experiments showed no evidence for the presence of significant quantities of platinum on the electrodes. Hydrogen oxidation and evolution currents were down by more than an order of magnitude. Deposition potentials were then made increasingly more negative and the electrodes tested in the same manner. In each case the electrode became more platinum-like as the deposition potential was made more negative.

The dependance of deposition efficiency on deposition potential for the compounds is illustrated in figures 16 through 20. This shows the change in hydrogen evolution characteristics when electrodes were doped with 10^{-7} moles of platinum at various potentials. Hydrogen evolution characteristics are shown rather than hydrogen oxidation characteristics simply because the former proved to be a more sensitive method of platinum detection. In each case, more negative deposition potentials give correspondingly greater hydrogen evolution currents at any given potential, indicating a higher platinum loading and hence a higher platinum deposition efficiency.

In each case however, overall currents are far below those obtained with a gold electrode doped with a similar quantity of platinum. Even using a deposition potential of -0.8 V, the hydrogen evolution and oxidation currents of the doped electrodes are between one and two orders of magnitude below the similarly treated gold electrodes. Since the electrodes evolve hydrogen freely at -0.8 V it seems unusual that the platinum deposition reaction should be so inefficient. The reason for this is probably the surface state of the silicide electrodes. As mentioned previously, the electrodes tend to form highly irreversible oxide layers and perhaps the platinum deposition only occurs where defects exist in this oxide covering. This could cause poor utilization of the deposited platinum since it would be concentrated in a few discrete locations rather than being highly dispersed.

In any case, there certainly does not appear to be any enhancement of platinum activity due to interaction between the silicide substrates and the platinum deposit, in fact if an interaction effect does exist it would appear to be detrimental rather than beneficial. Highly passivated surfaces such as these simply do not lend themselves to effective electrodeposition. Further experiments on the reduction of the surface oxides of the compounds would be required in order to better assess their suitability as electrocatalyst support materials.

SUMMARY

The evaluation of a series of transition metal silicides as catalysts for the anodic oxidation of hydrogen in acid medium revealed extremely low overall levels of activity. Relative levels of activity were very similar for all the compounds except Cr_3Si which showed an activity roughly three times the others. This higher level of activity was attributed simply to the higher metallic content of the compound while the similar relative activity levels of the others was attributed to a similar, presumably silica-type, surface predominating in each case.

Each of the compounds formed highly irreversible passive films when polarized anodically, making them quite stable in the acid electrolyte, but probably also bringing about the very low levels of hydrogen activity encountered. The passive nature of the compounds also hindered their usefulness as catalyst support materials as evidenced by the great difficulty that was encountered in electrodepositing platinum on the compounds, a difficulty which we attribute to the highly irreversible nature of the oxide films.

A reduction of the surface oxides of the compounds might bring about a change in the activity level, but this would no doubt involve high temperatures in a reducing atmosphere (such as hydrogen) in order to effect the

reduction and keep the catalyst reduced. In this way one could explain why the silicides often work well for heterogeneous hydrogenation reactions where the reaction often takes place at temperatures upwards of 600°C in a hydrogen atmosphere. Unfortunately, catalysts which are only active at high temperatures are out of the question for most fuel cell applications where a reasonable level of activity is required even at low temperatures.

This study also pointed out the problems one can encounter in electrocatalysis studies if great care is not taken to exclude all traces of platinum from the test cell. Platinum was found to migrate about the cell when exposed to only moderate anodic potentials, and extremely small quantities caused large errors in hydrogen activity measurements.

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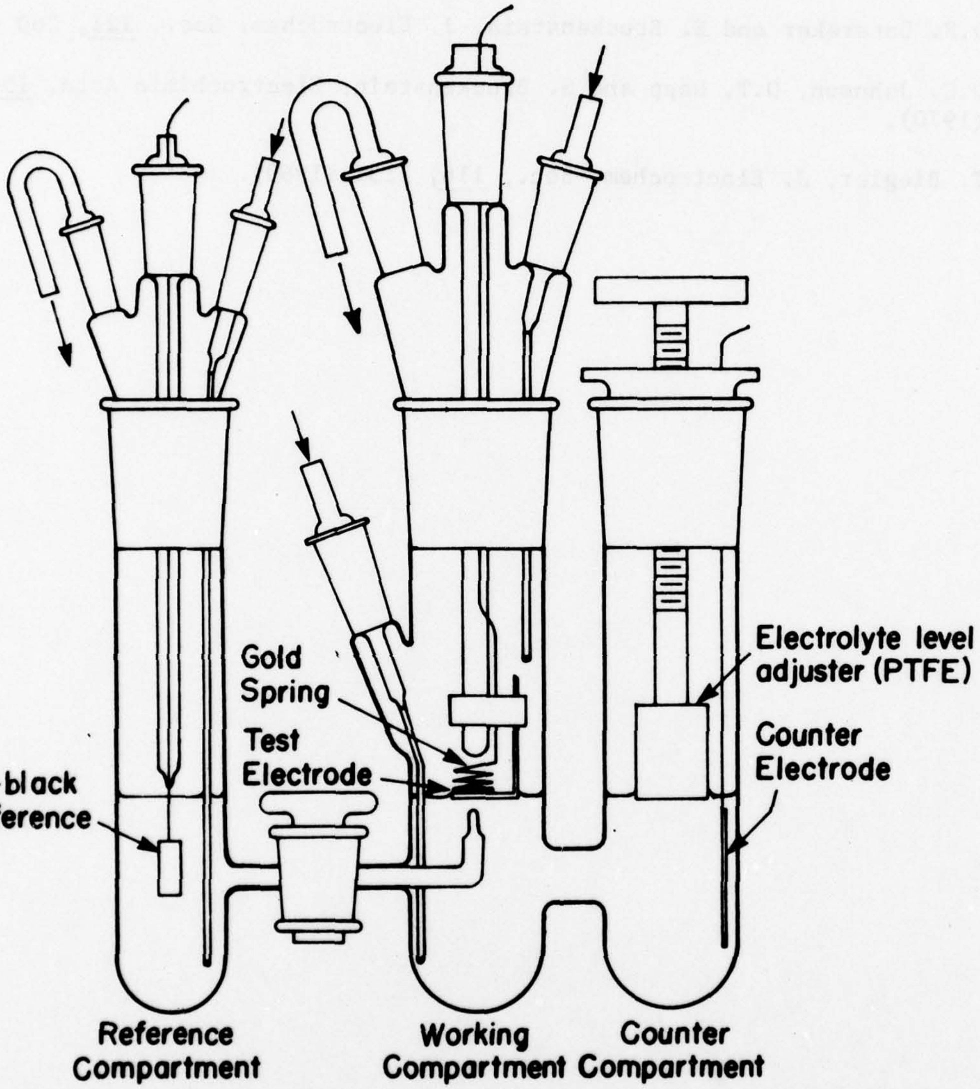

Figure 1. Electrochemical Testing Cell.

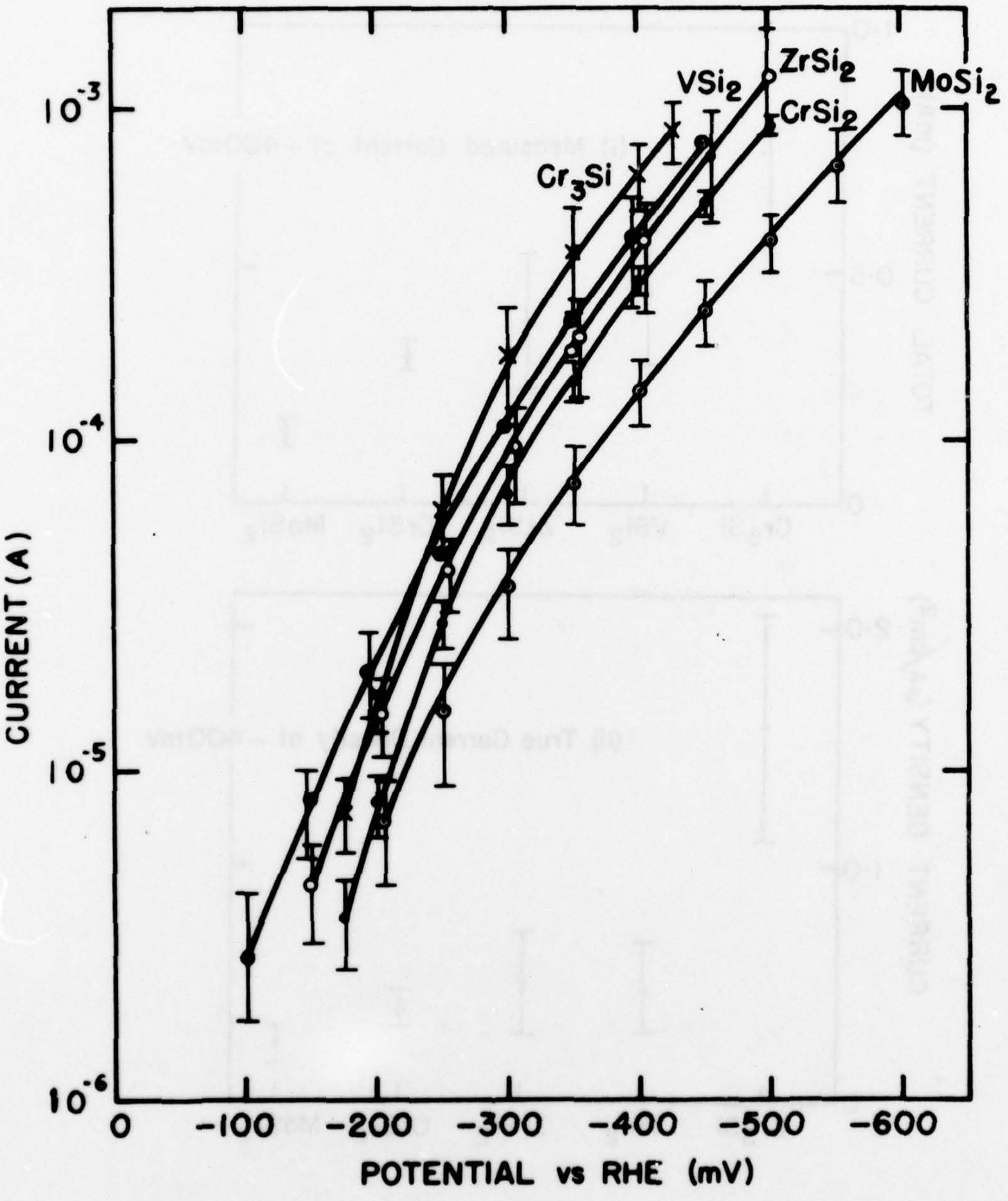

Figure 2. Hydrogen evolution characteristics of the transition-metal silicides.

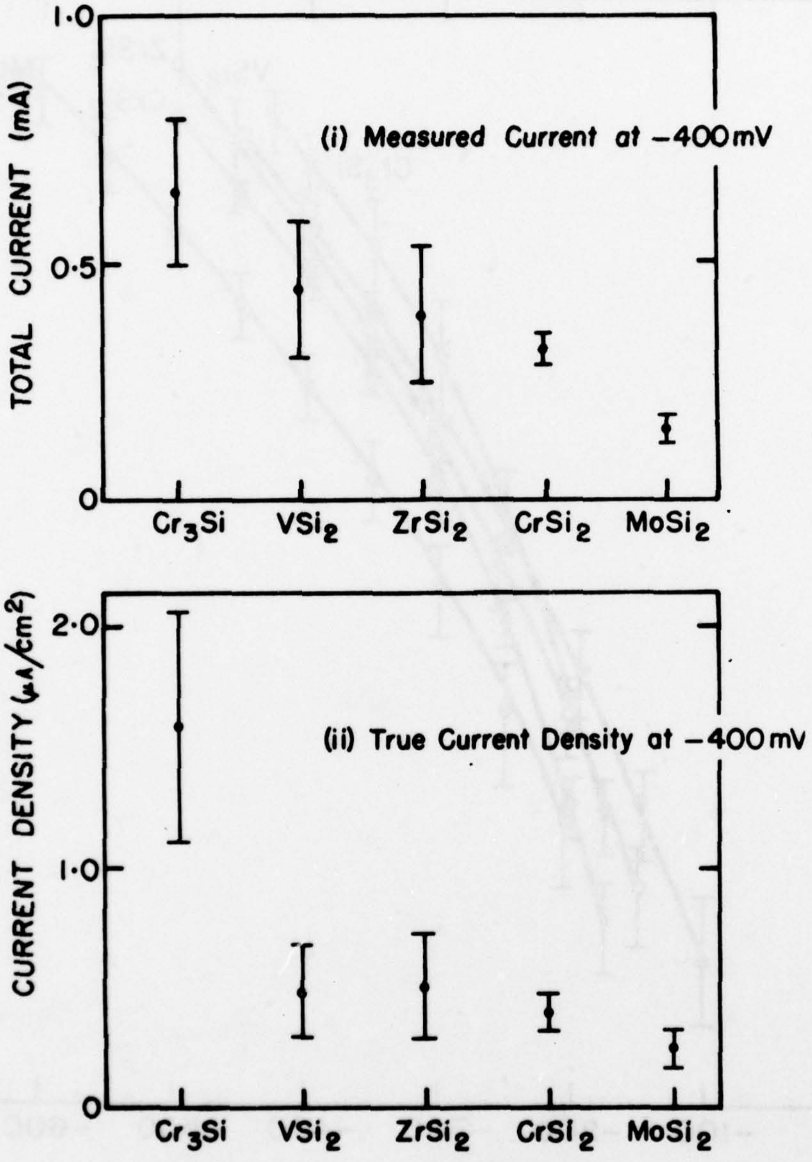

Figure 3. Comparison of hydrogen evolution currents at −400 mV.

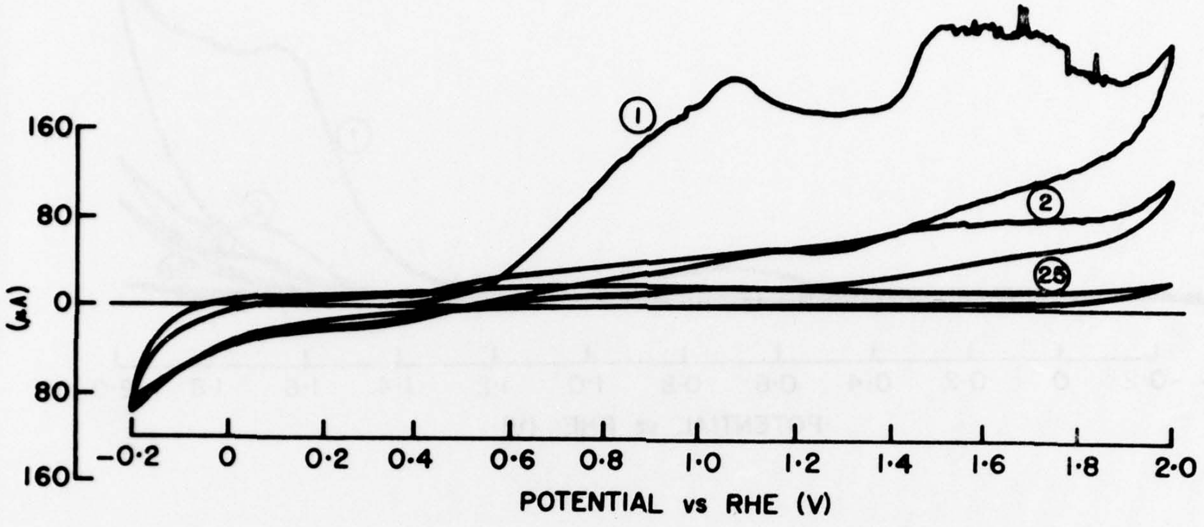

Figure 4. Initial passive film formation on $MoSi_2$.

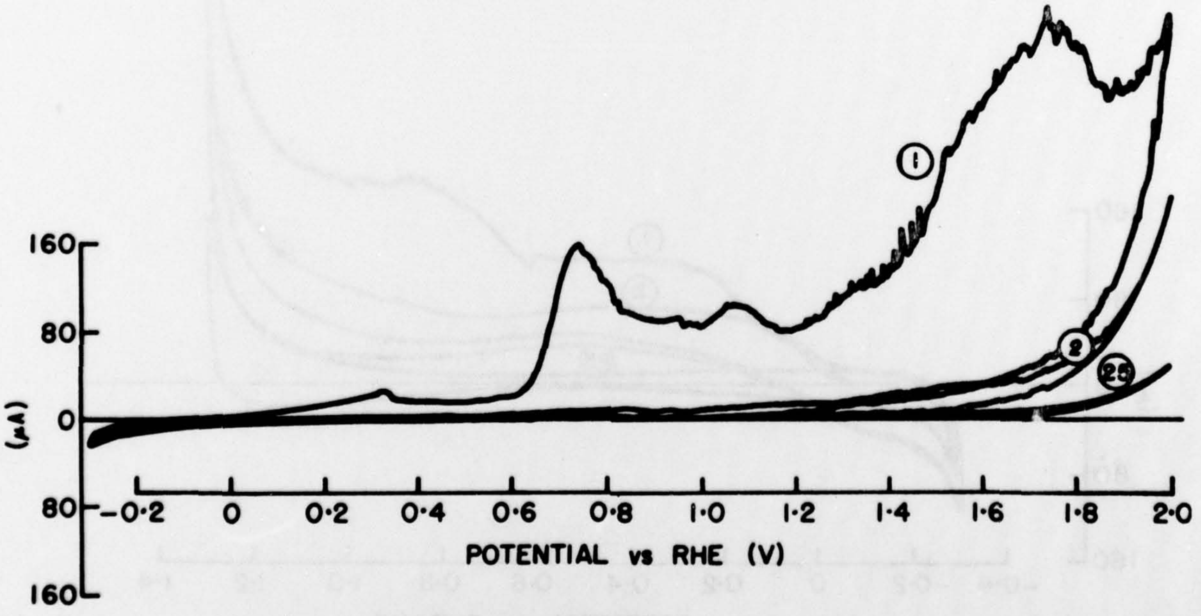

Figure 5. Initial passive film formation on $ZrSi_2$.

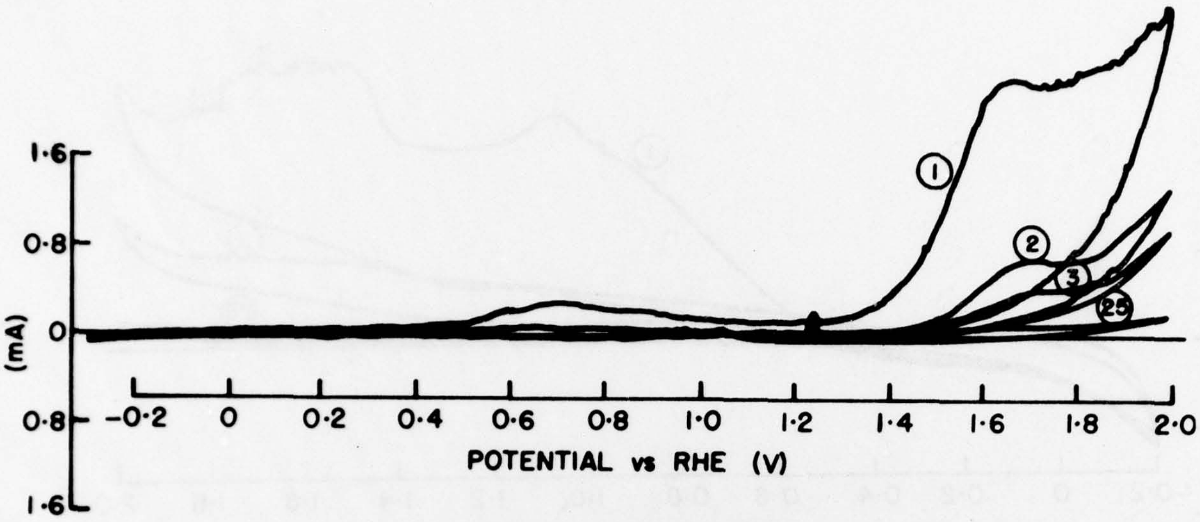

Figure 6. Initial passive film formation on $CrSi_2$.

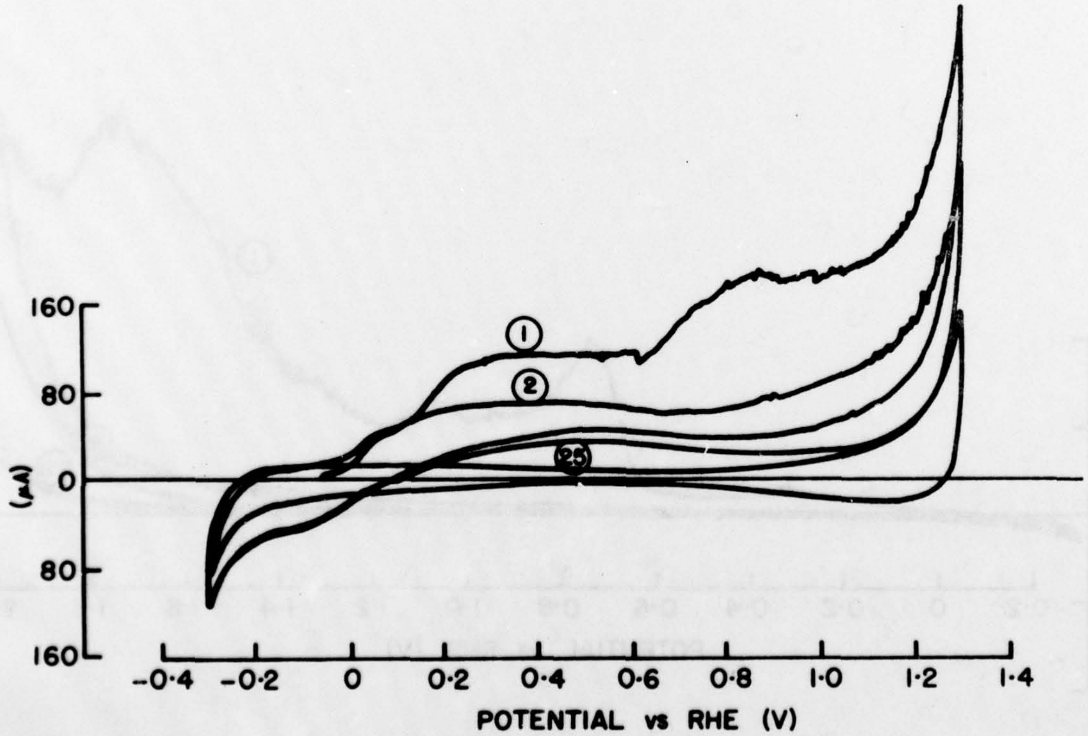

Figure 7. Initial passive film formation on Cr_3Si .

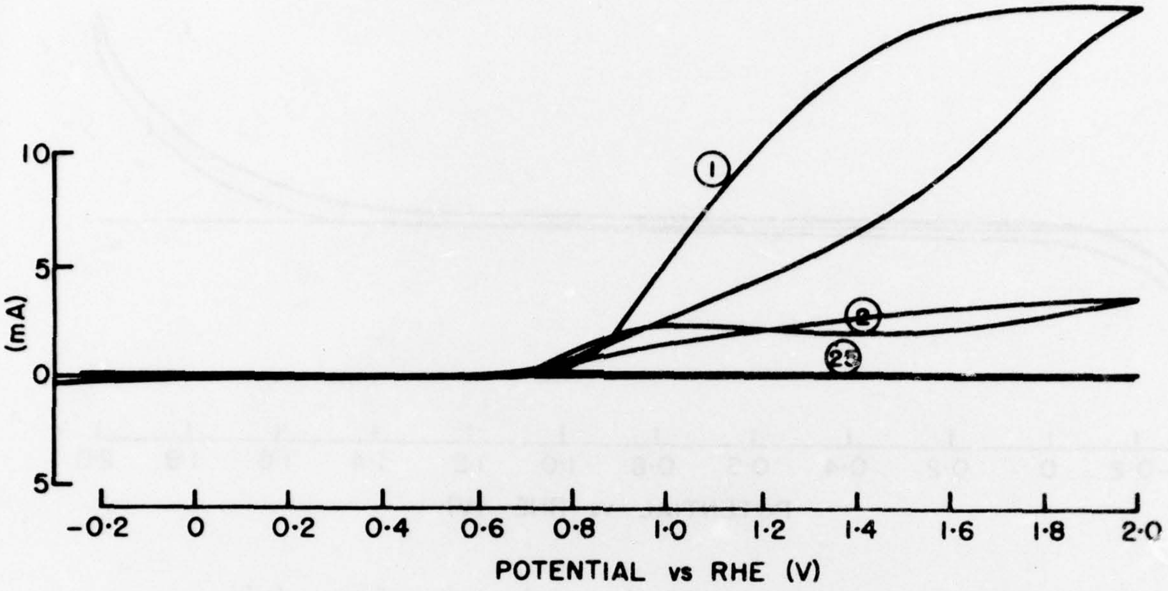

Figure 8. Initial passive film formation on VSi_2.

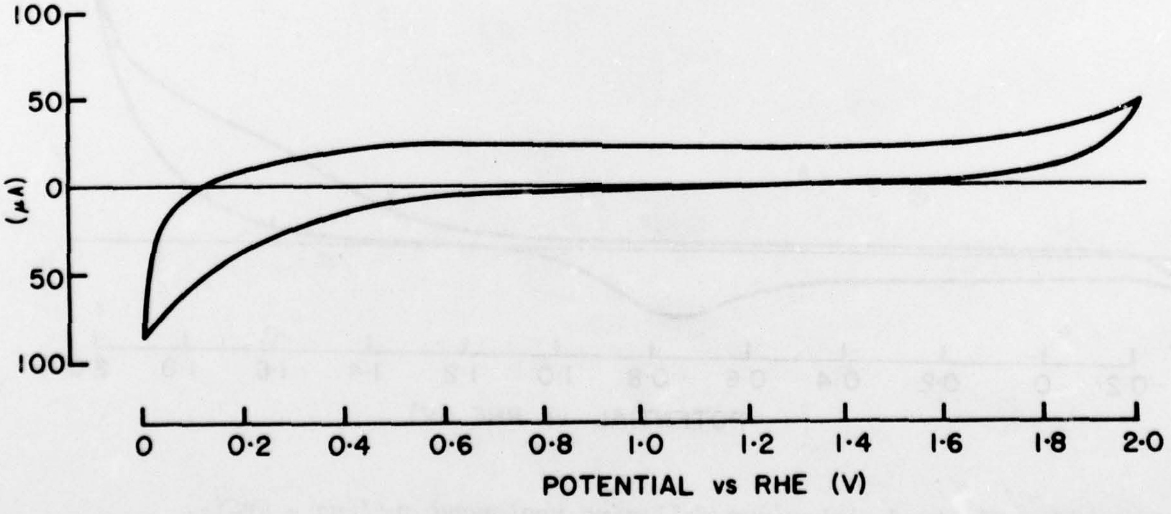

Figure 9. Electrode behaviour following prolonged cycling - $MoSi_2$.

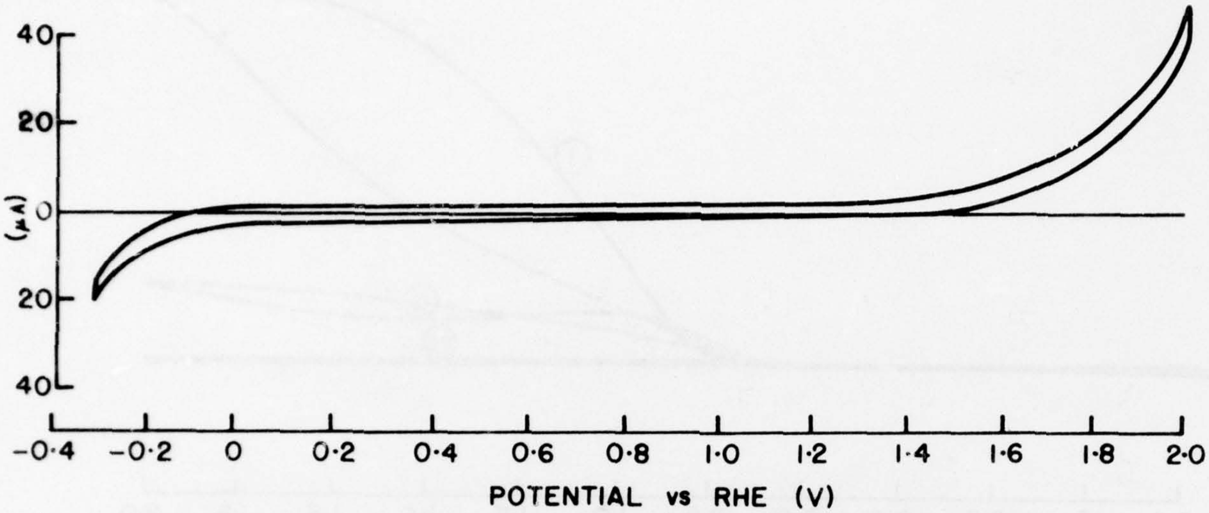

Figure 10. Electrode behaviour following prolonged cycling - $ZrSi_2$.

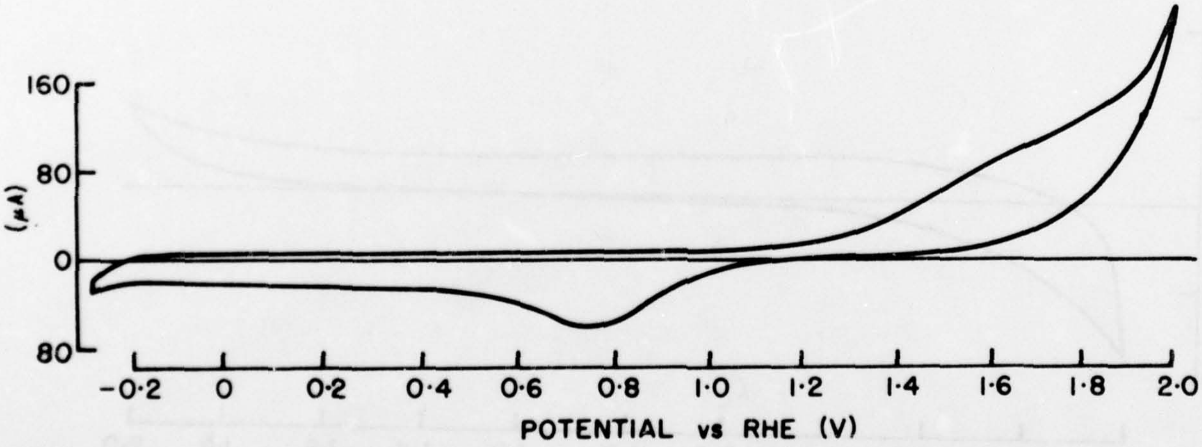

Figure 11. Electrode behaviour following prolonged cycling - $CrSi_2$.

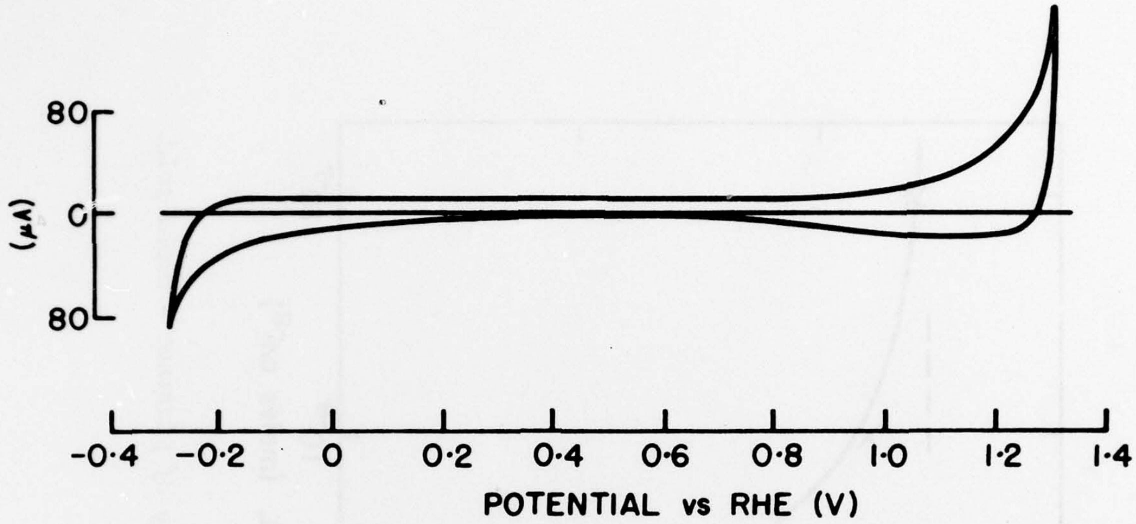

Figure 12. Electrode behaviour following prolonged cycling - Cr_3Si.

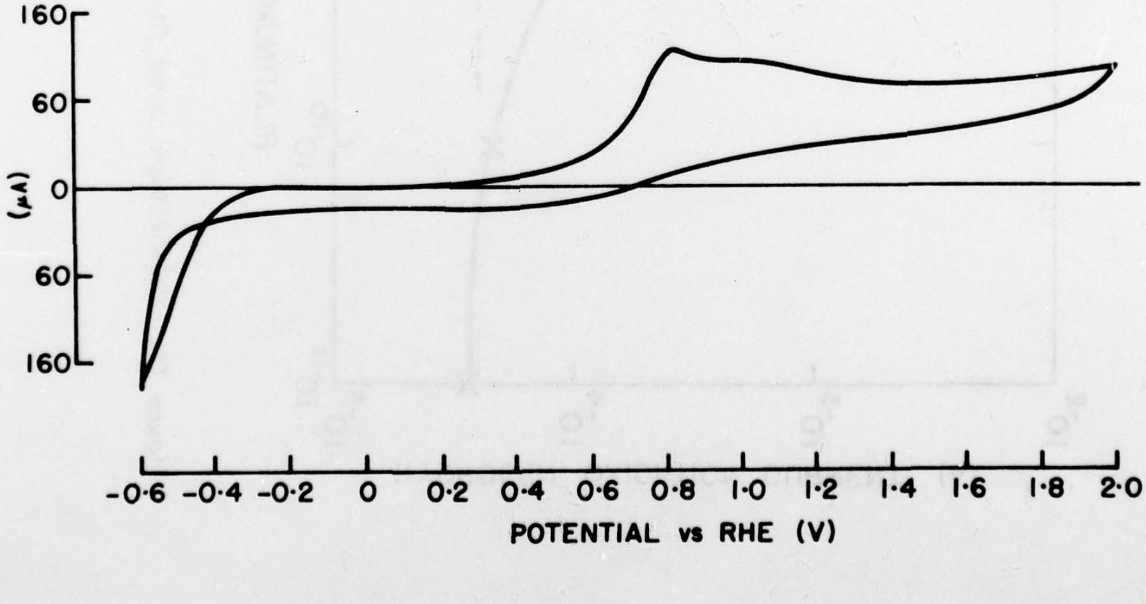

Figure 13. Electrode behaviour following prolonged cycling - VSi_2.

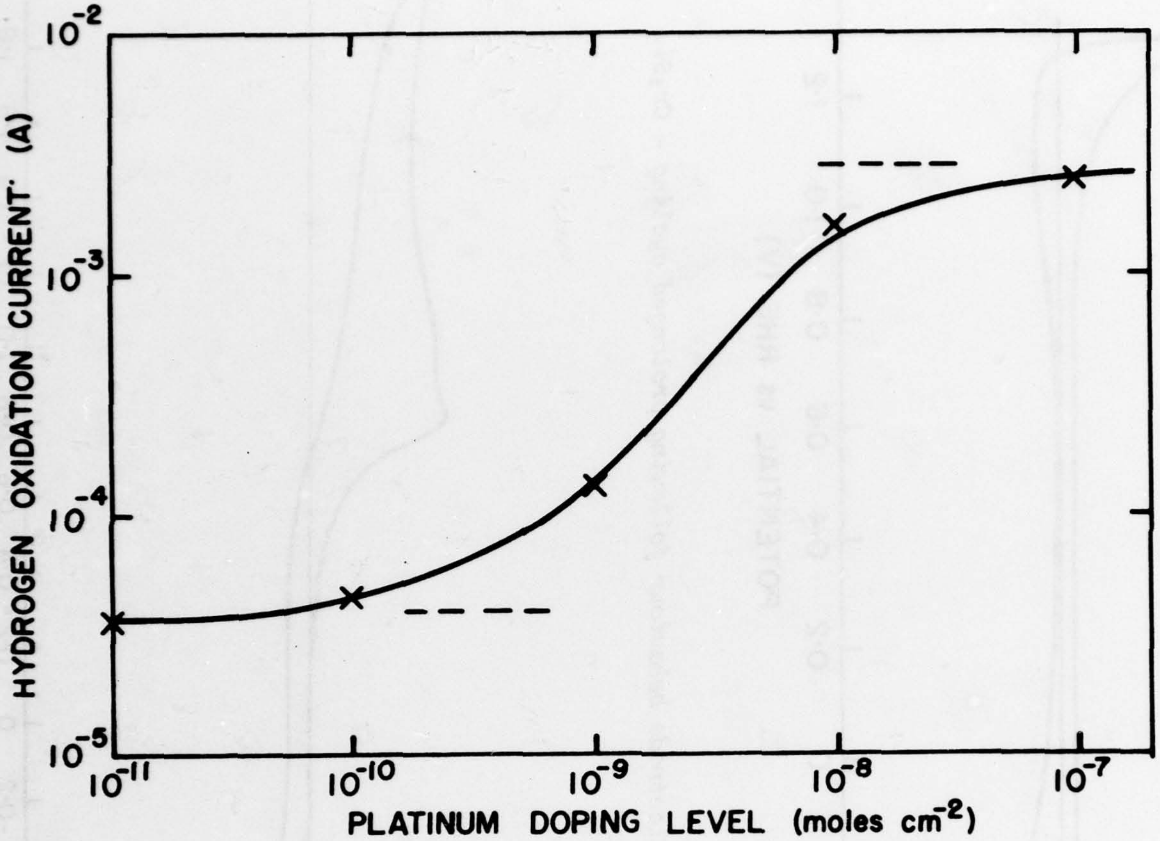

Figure 14. Calibration curve for hydrogen activity of platinum - doped gold.

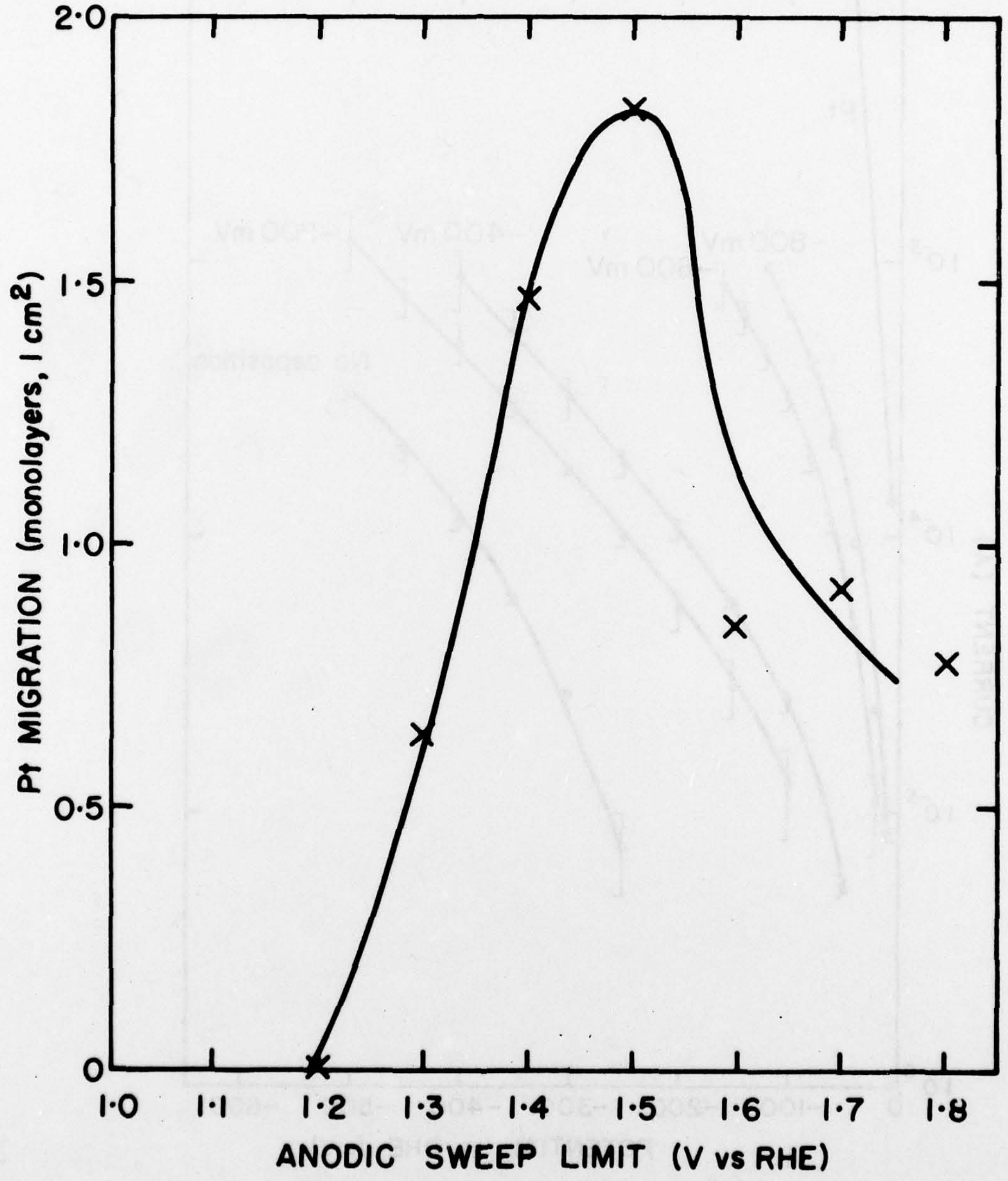

Figure 15. Platinum migration following cycling to various anodic potential limits.

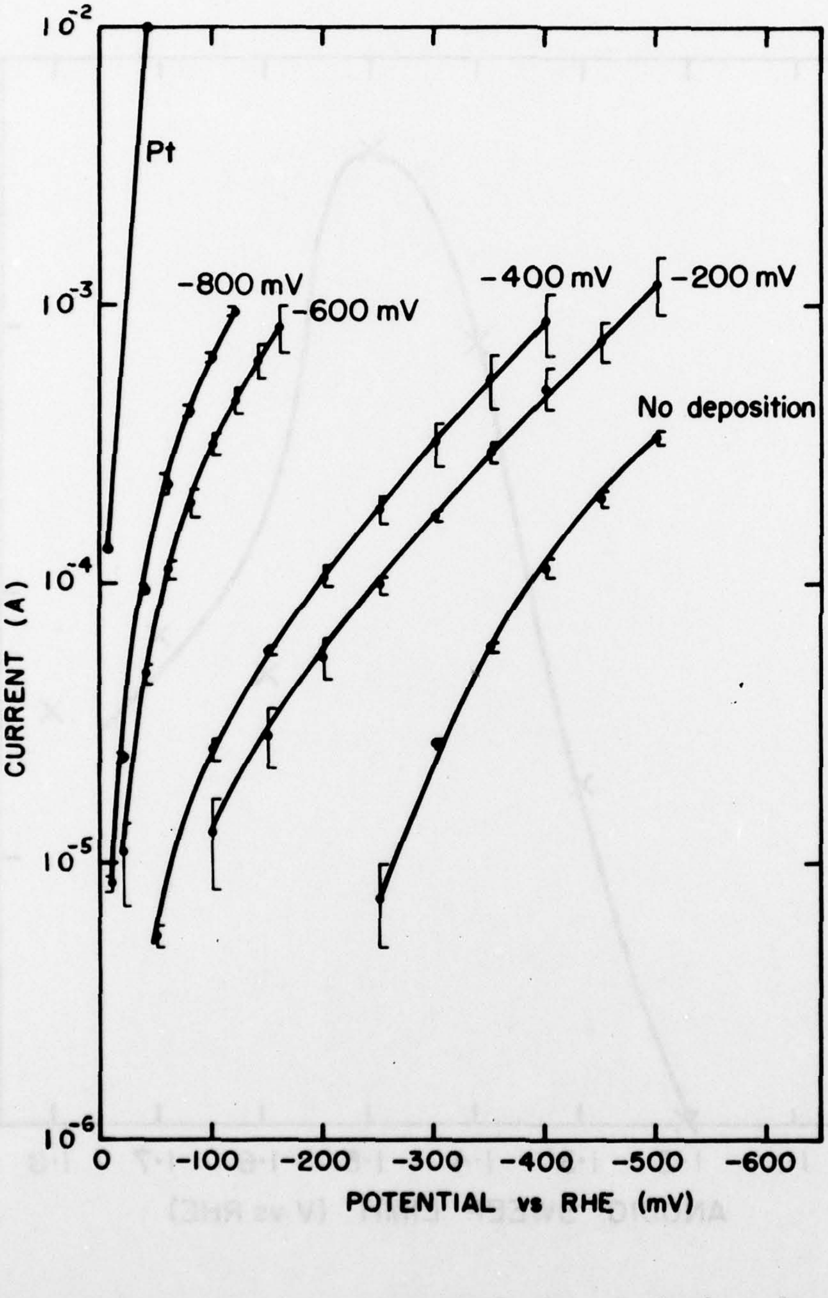

Figure 16. Hydrogen evolution characteristics of platinum doped $MoSi_2$.

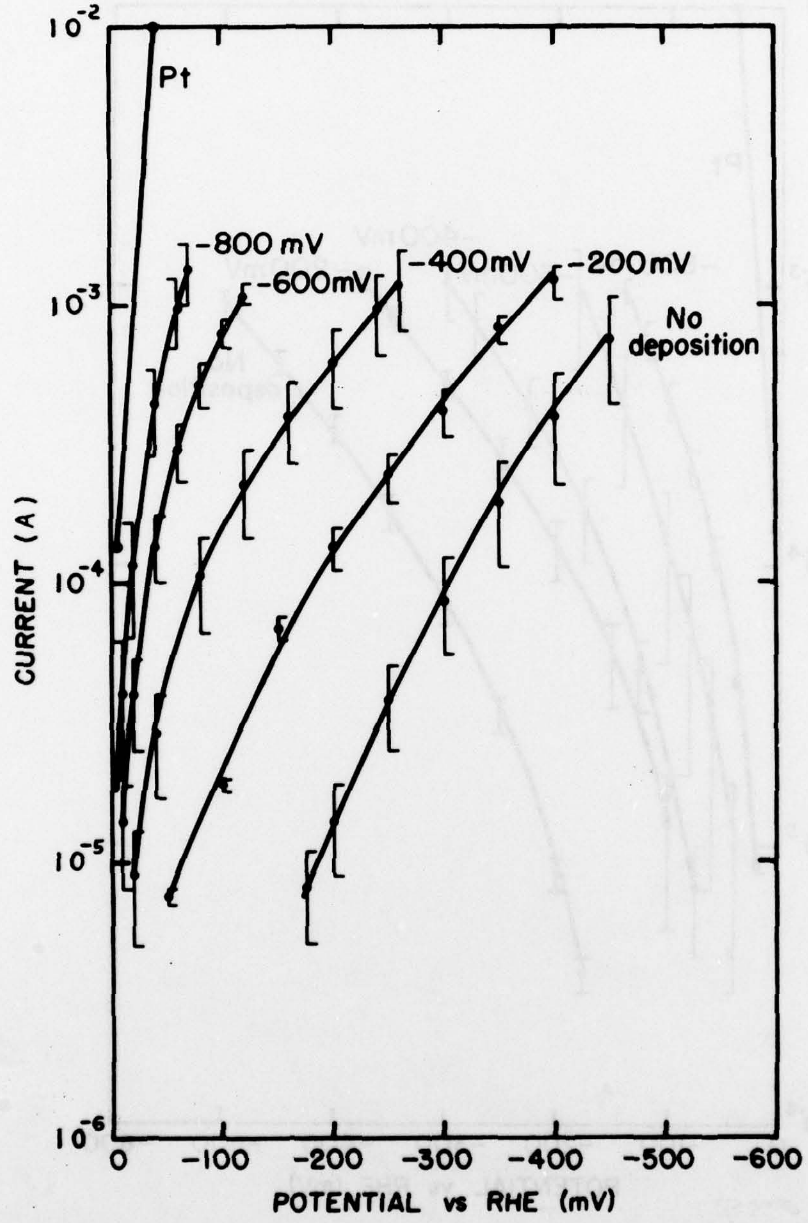

Figure 17. Hydrogen evolution characteristics of platinum doped $ZrSi_2$.

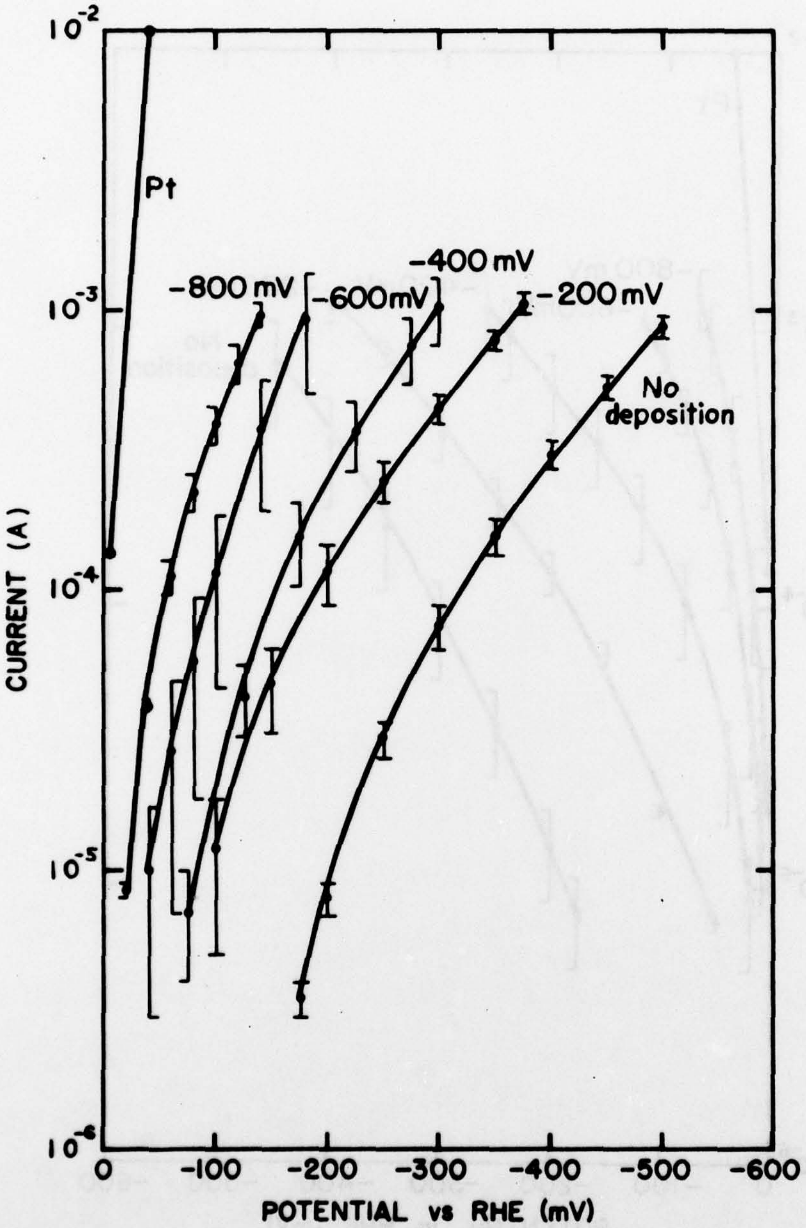

Figure 18. Hydrogen evolution characteristics of platinum doped $CrSi_2$.

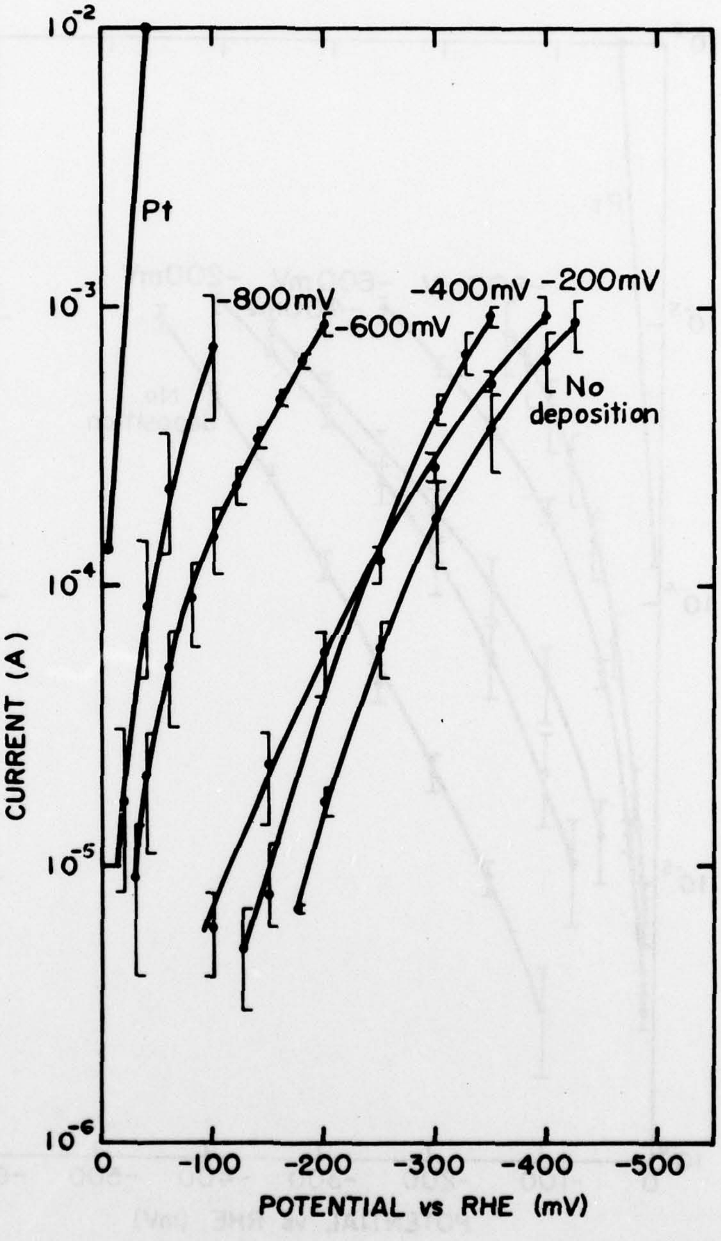

Figure 19. Hydrogen evolution characteristics of platinum doped Cr_3Si.

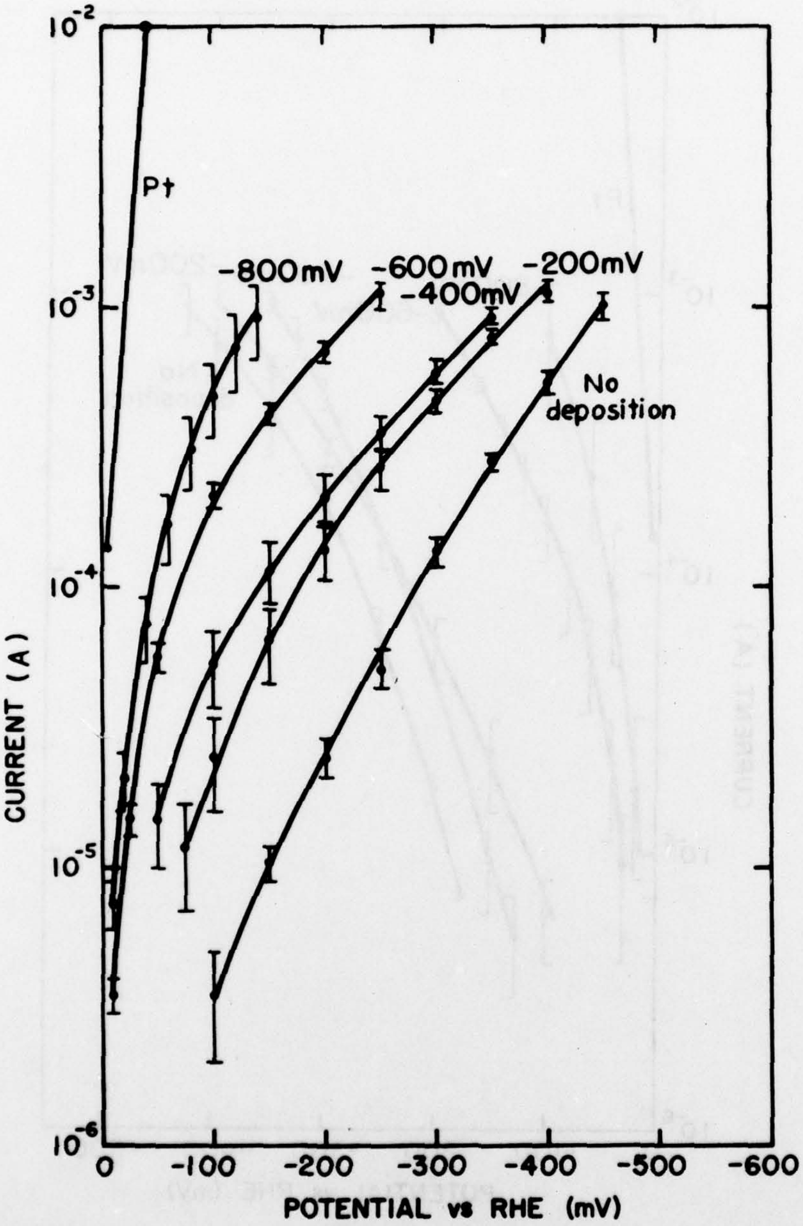

Figure 20. Hydrogen evolution characteristics of platinum doped VSi_2.

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A series of transition metal silicides were evaluated as catalysts for the anodic oxidation of hydrogen in acid medium. Overall levels of activity were very low and relative levels of activity were very similar for all the compounds except Cr_3Si which showed an activity roughly three times the others.

Each of the compounds formed highly irreversible passive films when polarized anodically making them quite stable in acid medium. The usefulness of the compounds as catalyst support materials, however, is hindered by difficulties in obtaining efficient electrodeposition of active metals onto the compounds.

The study also revealed that erroneous results can easily be obtained in electrocatalysis studies if care is not taken to exclude all traces of platinum from the test cell as platinum was found to migrate about the cell when platinum counter electrodes were used.

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