

DGE/NASA/0794-80/1  
NASA CR-159738

(NASA-CR-159738) ADVANCED SCREENING OF  
ELECTRODE COUPLES (NASA) 56 P HC A04/MF A01  
CSSL 10E

N80-22777

Unclas  
G3/44 18005

ADVANCED SCREENING OF ELECTRODE COUPLES

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FEBRUARY 1980

PREPARED FOR:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
LEWIS RESEARCH CENTER  
CONTRACT NAS3-20794

U. S. DEPARTMENT OF ENERGY  
OFFICE OF CONSERVATION AND SOLAR ENERGY PROGRAMS  
DIVISION OF ENERGY STORAGE SYSTEMS



1. Report No. CR 159738	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle ADVANCED SCREENING OF ELECTRODE COUPLES		5. Report Date February 1980	6. Performing Organization Code
		8. Performing Organization Report No.	
7. Author(s) J. Giner and K. Cahill		10. Work Unit No.	
9. Performing Organization Name and Address GINER, INC. 14 Spring Street Waltham, MA 02154		11. Contract or Grant No. NAS3-20794	
		13. Type of Report and Period Covered Contractor Report	
12. Sponsoring Agency Name and Address U. S. Department of Energy Office of Conservation and Solar Programs Washington, DC 20545		14. Sponsoring Agency Report No. DCE/NASA/0794-80/1	
		13. Type of Report and Period Covered Contractor Report	
15. Supplementary Notes Final report prepared under Interagency Agreement EC-77-A-31-1002. Project Manager, M. A. Reid, Solar and Electrochemistry Division, NASA-Lewis Research Center, Cleveland, Ohio 44135			
16. Abstract The chromium ( $Cr^{3+}/Cr^{2+}$ redox couple (electrolyte and electrode) was investigated in order to determine its suitability as negative electrode for the iron ( $Fe^{3+}/Fe^{2+}$ )-chromium ( $Cr^{3+}/Cr^{2+}$ ) redox flow battery. Literature search and laboratory investigation established that the solubility and stability of aqueous acidic solutions of chromium(III) chloride and chromium(II) chloride are sufficient for redox battery application. Four categories of electrode materials were tested; namely, <u>metals and metalloid materials</u> (elements and compounds), <u>alloys</u> , <u>plated materials</u> , and <u>Teflon-bonded materials</u> . In all, the relative performance of 26 candidate electrode materials was evaluated on the basis of slow scan rate linear sweep voltammetry in stirred solution. No single material tested gave both acceptable anodic and acceptable cathodic performance. However, the identification of lead as a good cathodic electrocatalyst and gold as a good anodic electrocatalyst led to the invention of the lead/gold combination electrocatalyst. This type of catalyst can be fabricated in several ways and appears to offer the advantages of each metal without the disadvantages associated with their use as single materials. This lead/gold electrocatalyst has subsequently been tested by NASA-Lewis Research Center in complete, flowing, redox batteries comprising a stack of several cells. A large improvement in the battery's coulombic and energy efficiency has been observed. In addition to the above, five dissolved organic compounds were tested as possible hydrogen evolution inhibitors, including thiourea, palmitic acid, cetyl alcohol, hexanol and n-propanol. Finally, the cost of large lots of thirteen common chemicals was estimated.			
17. Key Words (Suggested by Author(s)) energy storage, redox, chromium, electrocatalysis, gold, lead		18. Distribution Statement Unclassified - Unlimited STAR Categories 25-04 and 44-02 DOE Category UC-94c	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 48	22. Price*

\* For sale by the National Technical Information Service, Springfield, Virginia 22161

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## ABSTRACT

The chromium ( $\text{Cr}^{3+}/\text{Cr}^{2+}$ ) redox couple (electrolyte and electrode) was investigated in order to determine its suitability as negative electrode for the iron ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ )-chromium ( $\text{Cr}^{3+}/\text{Cr}^{2+}$ ) redox flow battery. Literature search and laboratory investigation established that the solubility and stability of aqueous acidic solutions of chromium(III) chloride and chromium(II) chloride are sufficient for redox battery application.

Four categories of electrode materials were tested; namely, metals and metalloid materials (elements and compounds), alloys, plated materials, and Teflon-bonded materials. In all, the relative performance of 26 candidate electrode materials was evaluated on the basis of slow scan rate linear sweep voltammetry in stirred solution. No single material tested gave both acceptable anodic and acceptable cathodic performance. However, the identification of lead as a good cathodic electrocatalyst and gold as a good anodic electrocatalyst led to the invention of the lead/gold combination electrocatalyst<sup>(7)</sup>. This type of catalyst can be fabricated in several ways and appears to offer the advantages of each metal without the disadvantages associated with their use as single materials. This lead/gold electrocatalyst has subsequently been tested by NASA-Lewis Research Center in complete, flowing, redox batteries comprising a stack of several cells. A large improvement in the battery's coulombic and energy efficiency has been observed<sup>(9)</sup>.

In addition to the above, five dissolved organic compounds were tested as possible hydrogen evolution inhibitors, including thiourea, palmitic acid, cetyl alcohol, hexanol and n-propanol. Finally, the cost of large lots of thirteen common chemicals was estimated.

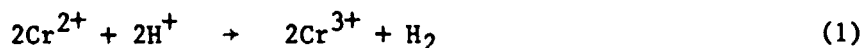


## I. INTRODUCTION

The iron ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ )-chromium ( $\text{Cr}^{3+}/\text{Cr}^{2+}$ ) redox flow battery is an attractive system for bulk energy storage applications<sup>(1)</sup>. The primary objective of this program was to contribute to the development of the redox flow battery concept by investigating the major currently recognized or suspected problems of the chromium electrode. These are: the solubility of reactants, the stability of chromium(II) ion in solution, the efficient electrocatalysis of chromium(III) reduction and chromium(II) oxidation, and the cost and availability of chromium electrolyte.

Concentrated solutions of chromium(II) chloride and chromium(III) chloride in hydrochloric acid are required in order to keep redox flow system costs at a reasonably low level<sup>(2)</sup>. Only a moderate amount of effort in determining solubilities was made under a previous contract<sup>(3)</sup>, so that further work was required.

The long term stability of the aqueous chromium(II) ion is of concern because thermodynamics predict its decomposition. This is illustrated by the Pourbaix diagram of Figure I-1 which shows that  $\text{Cr}^{2+}$  is unstable with respect to oxidation at low pH. The mode of decomposition is given by:



where  $\Delta G^\circ = -18.8$  kcal.

The driving force for oxidation of  $\text{Cr}^{2+}$  by dissolved oxygen is, of course, much larger than this value. It is significant that the process represented by equation (1) is reported to be very slow when chemically pure solutions of  $\text{Cr}^{2+}$  are carefully stored in the absence of air<sup>(4,8)</sup>.

The fundamental reason for the attractiveness of the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  electrode is its negative rest potential with respect to the standard hydrogen electrode over the acid pH range of interest (Figure I-1). For the same reason, difficulties were anticipated in finding stable electrocatalyst materials which exhibit good activity for chromium(III) reduction and chromium(II) oxidation, as well as high hydrogen

overvoltage. By stable electrocatalysts is meant immunity from corrosion (most electrode materials oxidize near the potential range where the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox couple operates). Good activity means that the equilibrium exchange current density ( $i_0$ ) for the reaction considered is very high, so that activation polarization will not be a significant source of energy inefficiency in the redox flow battery. A high hydrogen overvoltage implies a low value of  $i_0$  for the hydrogen evolution reaction so that the coulombic efficiency of the battery remains high. For example, gold had been previously shown<sup>(3)</sup> to have good activity for the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  reaction, but its hydrogen overvoltage is low.

The cost and availability of chromium ores as they relate to redox battery operation had been reviewed by Gahn<sup>(5)</sup>. The information on the cost of large quantities of commonly available chromium chemicals was compiled.

Based on the above information and prior work, five technical tasks were proposed and carried out as described in the following sections.

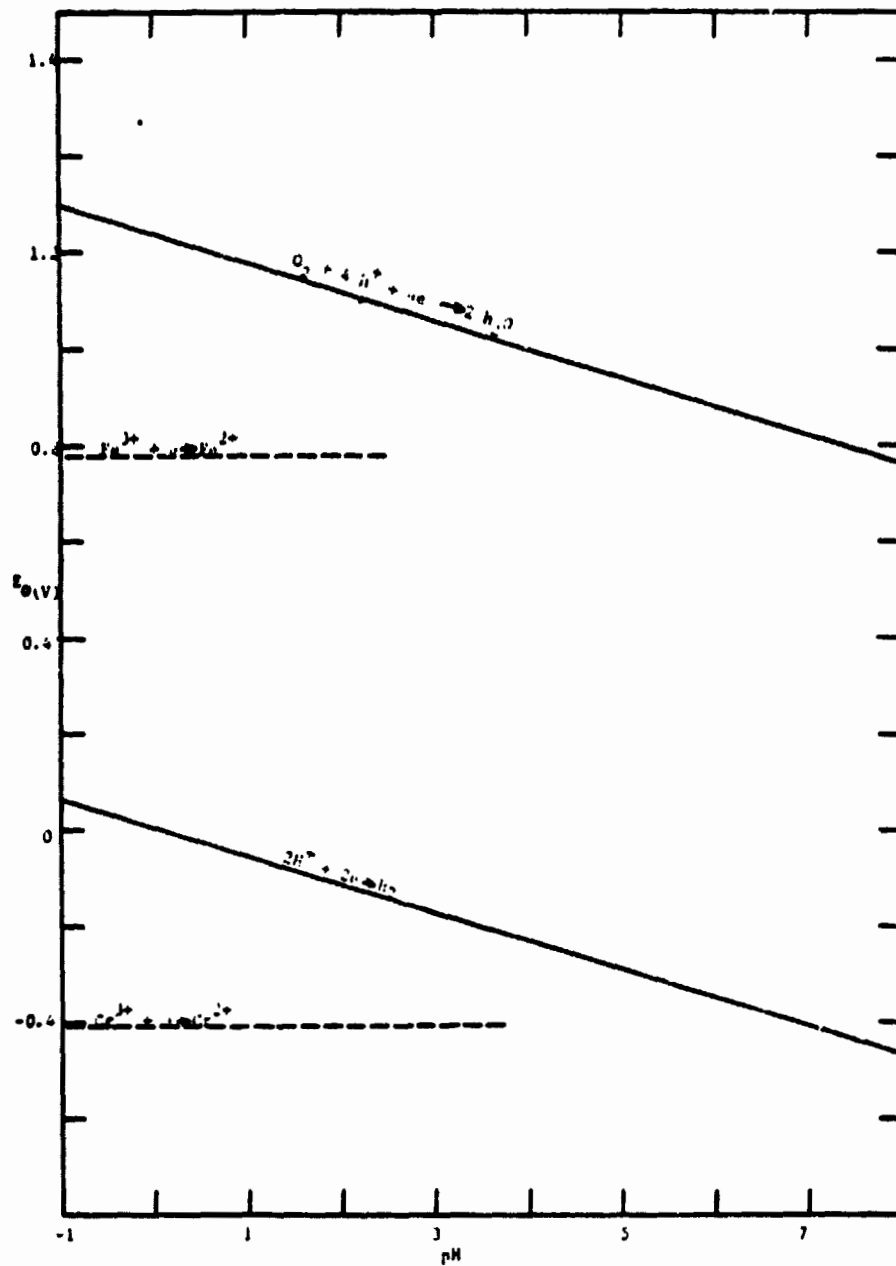


FIGURE I-1 Thermodynamic Stability of  $Fe^{3+}/Fe^{2+}$  and  $Cr^{3+}/Cr^{2+}$  Redox Couples

## II. SOLUBILITY AND STABILITY OF AQUEOUS ACIDIC CHROMIUM(II) CHLORIDE SOLUTIONS

### A. Introduction

In a prior contract<sup>(3)</sup> we were unable to prepare a  $\text{CrCl}_2$  solution in 1M HCl as concentrated as one molar starting from samples of solid  $\text{CrCl}_2$  obtained from several commercial sources. We became convinced that these commercial samples were not genuine  $\text{CrCl}_2$ . Therefore, we conducted a detailed literature search on  $\text{CrCl}_2$  solubility early in the present program to serve as a guide to the experimental work.

### B. Results

The literature search uncovered work done by Lux and Illman<sup>(8)</sup>, which indicated that a solution 3M in  $\text{CrCl}_2$  and .2M in HCl can be made by dissolving pure chromium metal in 21% HCl (approximately 6M). These workers reported that chromium(II) ions remain stable for a long time provided air ( $\text{O}_2$ ) is excluded.

It was deemed desirable to confirm the preparative method and findings of Lux and Illman. To this end, chromium metal obtained from Atchemergic Chemetals<sup>(r)</sup> was dissolved in several concentrations of HCl. The amount of chromium(II) ion produced was determined by potentiometric titration with standard Ce(IV) solution. The final HCl concentration was calculated from the initial HCl concentration and the amount of chromium(II) produced. The results presented in Figure II-1 confirm that solutions up to 3M in  $\text{CrCl}_2$  could be prepared in up to 2.5M HCl and establish the suitability for redox battery operation.

Our exploratory attempts to measure the solubility of  $\text{CrCl}_2$  at higher HCl concentrations showed that the  $\text{CrCl}_2$  solubility is only 0.6M in 5.3M HCl.

The stability of chromium(II) chloride solutions was evaluated by comparison of the amount of chromium(II) ion present in freshly prepared solutions with that in aged solutions. The results are given in Table II-1. The small amount of decomposition observed on long standing is probably due to small intrusion of air. The thermodynamically feasible direct oxidation of  $\text{H}^+$  by  $\text{Cr}^{2+}$  is kinetically inhibited.

In any event, the observed amount of decomposition is small enough to be manageable on the redox flow system level.

Table II-1 also gives the results of tests on the effect of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions on the decomposition of  $\text{Cr}^{2+}$  ions. These experiments indicate no effect of either ions on decomposition of  $\text{Cr}^{2+}$  ions. However, in the case of  $\text{Pb}^{2+}$  we noticed the presence of lead metal at the bottom of the reaction chamber, consistent with the thermodynamically favored reduction of  $\text{Pb}^{2+}$  by  $\text{Cr}^{2+}$  (Figure II-3). Since the total concentration of  $\text{Pb}^{2+}$  is very small relative to  $\text{Cr}^{2+}$ , the results of chemical analysis as reported in Table II-1 are unaffected by  $\text{Pb}^{2+}$  within experimental precision.

Knowledge gained about the properties of gold and lead electrodes (vide infra) enabled us to devise a suitable voltammetry experiment to determine if  $\text{PbCl}_2$  was present in our  $\text{CrCl}_2$  solution in greater than trace quantities. A sample of  $\text{CrCl}_2$  solution was separated from the precipitated solid material and added to an electrochemical half-cell already containing  $\text{CrCl}_3$  in  $\text{HCl}$ . Cyclic voltammetry of this solution at a gold foil electrode is illustrated in Figure II-2. Curve A exhibits  $\text{H}_2$  evolution as expected if no  $\text{PbCl}_2$  is present in solution. As a check, the solution was made  $10^{-3}\text{M}$  in  $\text{PbCl}_2$  and further sweeps were made. Curves B-1 and B-2 show the development of a limiting current due to  $\text{Cr}^{3+}$  reduction in place of  $\text{H}^+$  reduction. This is a consequence of the cathodic deposition of lead.

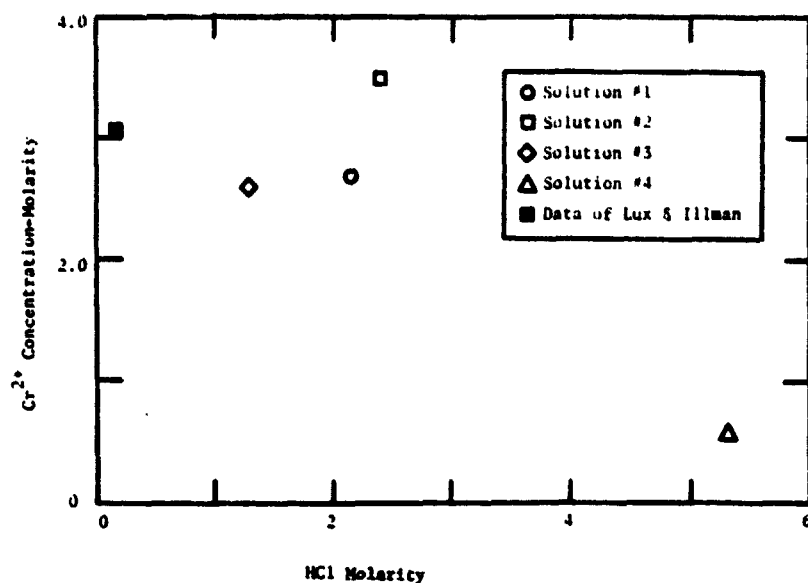
TABLE II-1

Decomposition of Chromium(II) Chloride

<u>Original Solution</u>	<u>4 Days Later</u>	<u>5 Days Later</u>	<u>7 Days Later</u>	<u>9 Days Later</u>	<u>25 Days Later</u>
1M HCl + 2.5M CrCl <sub>2</sub>				2.3	2
1M HCl + 2.5M CrCl <sub>2</sub>				2.25	2
1M HCl + 2.35M CrCl <sub>2</sub>			2.15		
1M HCl + 2.35M CrCl <sub>2</sub> + 10 <sup>-3</sup> M CdCl <sub>2</sub>			2.3		
1M HCl + .4M CrCl <sub>2</sub>	.38				
1M HCl + .4M CrCl <sub>2</sub> + 10 <sup>-3</sup> M PbCl <sub>2</sub>	.38				
* 1M HCl + 1.8M CrCl <sub>2</sub>		1.74			
* 1M HCl + 1.8M CrCl <sub>2</sub> + 10 <sup>-3</sup> M PbCl <sub>2</sub>		1.74			

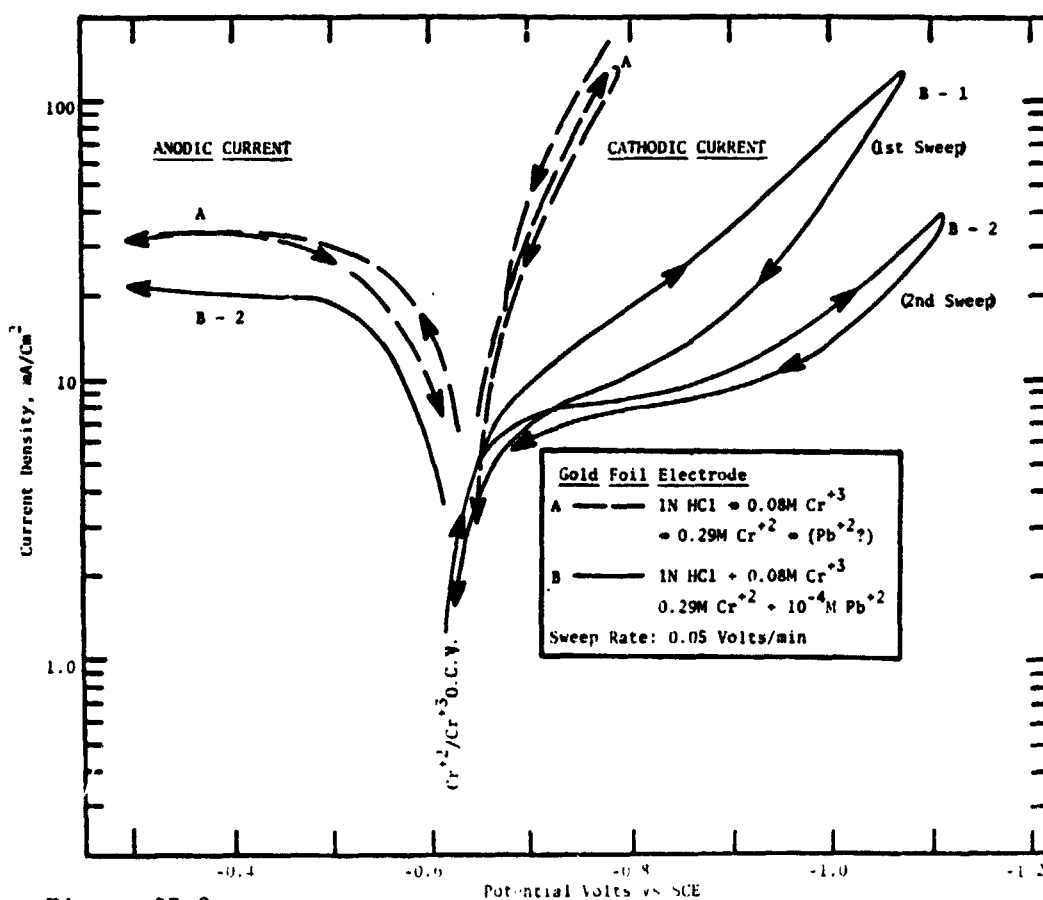
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\*Estimated.



**Figure II-1**

Chromous Chloride Solubility vs.  
Hydrochloric Acid Concentration



**Figure II-2**

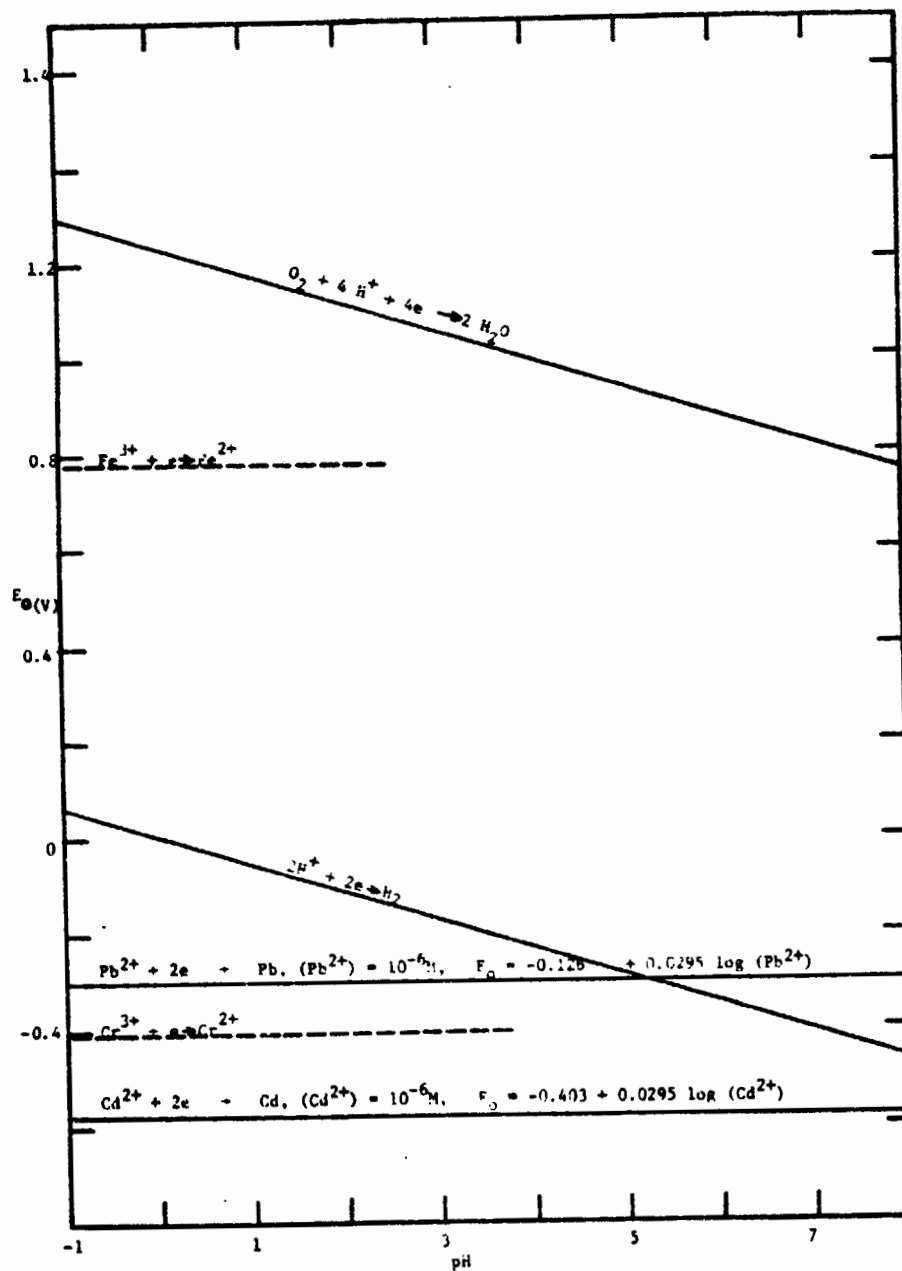


Figure II-3 Thermodynamic Stability of Pb/Pb<sup>2+</sup> and Cd/Cd<sup>2+</sup> Couples.



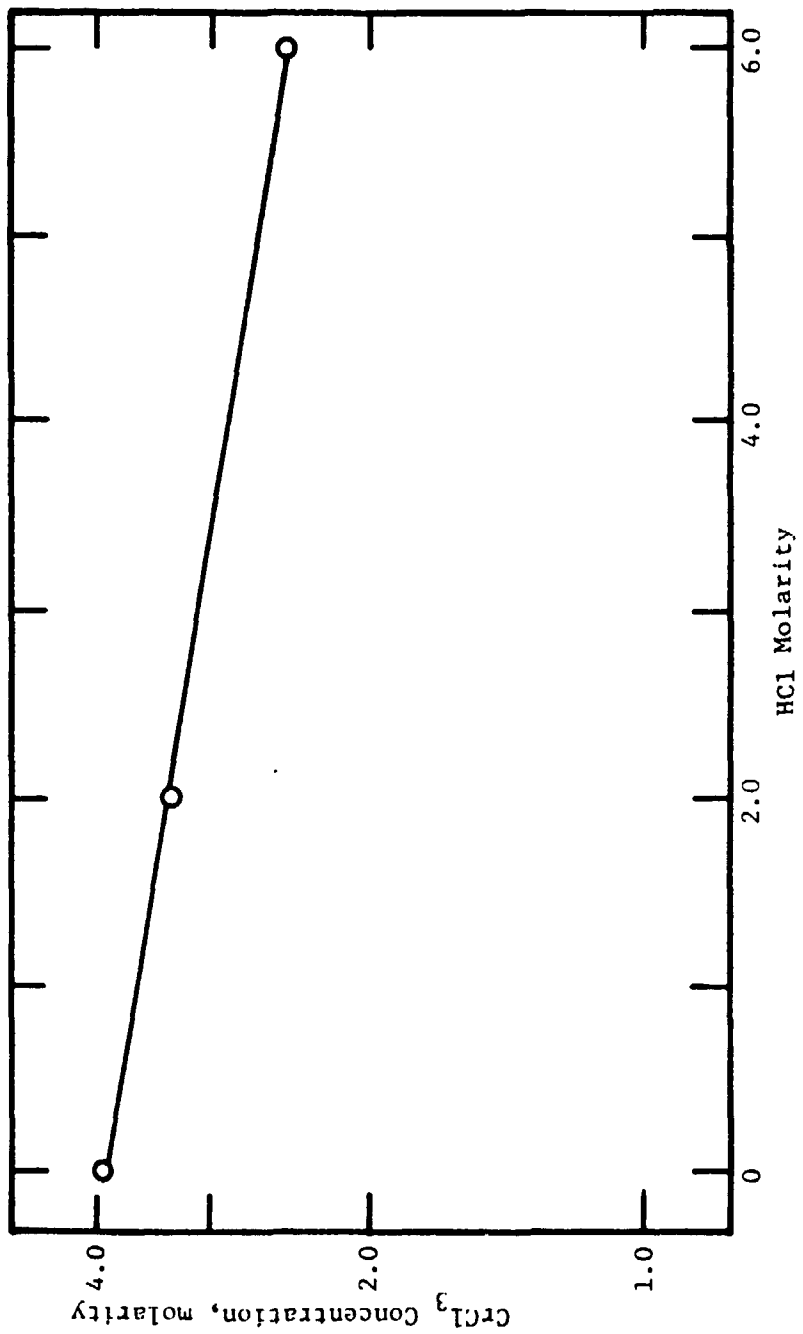
### III. SOLUBILITY AND STABILITY OF AQUEOUS ACIDIC CHROMIUM(III) CHLORIDE SOLUTIONS

#### A. Introduction

There was general agreement that acidic  $\text{CrCl}_3$  solutions are soluble and stable enough for redox battery application. It was of interest, however, to obtain information on the equilibrium solubility of  $\text{CrCl}_3$  in various concentrations of hydrochloric acid.

#### B. Experimental Results

Saturated solutions of  $\text{CrCl}_3$  were prepared by dissolving reagent grade chromic chloride hexahydrate in various concentrations of hydrochloric acid and allowing the supernatant solution to remain in contact with excess solid material at room temperature ( $25^\circ\text{C}$ ) for several days. The solution was then separated from solid and analyzed for chromium using titration and spectrophotometric methods. Results of chromium(III) chloride solubility measurements are given in Figure III-1. In the HCl concentration range of these experiments, the solubility of chromium(III) chloride decreases with increasing HCl concentration.



Chromic Chloride Solubility  
vs. Hydrochloric Acid Concentration

Figure III 1

#### IV. ELECTRODE MATERIAL EVALUATION

##### A. Introduction

Our objective in this portion of the program was to acquire enough knowledge about the electrocatalysis of the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox couple to enable us to recommend suitable electrocatalysts for full cell testing at NASA-Lewis Research Center. This task was accomplished by screening a number of candidate electrocatalyst materials. The candidates investigated included metals and metalloid materials, alloys, Teflon-bonded materials and materials plated on various substrates.

Suitable electrocatalysts should meet all of the following criteria:

- (1) good activity for  $\text{Cr}^{3+}$  reduction;
- (2) good activity for  $\text{Cr}^{2+}$  oxidation;
- (3) high hydrogen overvoltage; and
- (4) good resistance to anodic corrosion.

To screen potentially suitable electrocatalysts, we devised a simple test procedure that consisted of selective slow scan rate linear sweep voltammetry. This procedure provided discriminatory information for the above mentioned four criteria. Most of the materials tested were found unsatisfactory on one or more counts. This required obtaining or preparing and testing of a large number of metals, compounds and alloys in bulk form, supported and composite structures.

##### B. Screening Approach

The screening was conducted in the following steps:

Step 1. The hydrogen evolution reaction of each electrocatalyst was measured by performing sweeps in 1N HCl. A typical sweep begins at some relatively positive potential where only a small residual current is observed and progresses toward more negative potentials where cathodic current due to hydrogen evolution is eventually observed. The current will rise as the sweep is continued, although no limiting current will be achieved. The hydrogen overvoltage of the

different electrodes tested was compared by noting the potential at which the cathodic current first exceeds the arbitrarily chosen value of 1 mA. This cutoff potential was then compared with the open circuit potential of the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox couple.

Step 2. The activity of electrocatalysts for reduction of  $\text{Cr}^{3+}$  was determined in an experiment identical with that performed in Step (1), except that the electrolyte was made .1M in  $\text{CrCl}_3$ . The total Faradaic current observed in these experiments is usually the sum of the currents due to reduction of  $\text{Cr}^{3+}$  and the evolution of  $\text{H}_2$ . In a few cases there is a contribution from an anodic corrosion process. In one case (bismuth) there is a contribution from a cathodic corrosion process. A well defined limiting current due to  $\text{Cr}^{3+}$  reduction was observed when the currents due to competing processes were relatively low. Such cases were judged to have fair activity. An example is Ag-Hg (Figure IV-13). If, in addition to the above, the shape of the current-potential curve indicated low polarization, the electrode material was judged to have good activity for  $\text{Cr}^{3+}$  reduction. An example is Pb (Figure IV-3). In some cases no limiting current due to  $\text{Cr}^{3+}$  reduction was observed. The electrode materials in question were then categorized as not active. An example is  $\text{B}_4\text{C}$  as shown by Figure IV-17.

Step 3. For completeness, anodic corrosion studies in 1M HCl were done on all the materials tested in Steps (1) and (2). The suitability of the candidates screened was evaluated on the basis of the potential at which anodic current first exceeds the arbitrarily chosen value of 1 mA. This cutoff potential was then compared with the open circuit potential of the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox couple.

Step 4. Those materials which still appeared promising after steps (1), (2) and (3), were investigated for their activity towards the oxidation of  $\text{Cr}^{2+}$  using a solution 1N in HCl and .09M in  $\text{Cr}^{2+}$ . All the materials tested in this step showed a well defined limiting current due to  $\text{Cr}^{2+}$  oxidation and were, therefore, judged to have good activity.

Step 5. More detailed investigations were undertaken on selected promising electrode materials emerging from the first four screening steps.

### C. Results

The identity of each candidate electrode, a cross-reference to Figures IV (see below), its physical characteristics, and a brief summary of our conclusions as to its performance (e.g. good activity but low hydrogen overvoltage and poor corrosion behavior) in the four screening steps considered are presented in Table IV-1.

Results of the voltammetry experiments on which screening was based are presented in Figures IV-1 to IV-44 which also include simplified Pourbaix diagrams. Inserts and/or captions indicate the conditions under which an experiment was run. Each figure is also marked with one or more of the screening code numbers (1, 2, 3, 4 and 5) in order to indicate the type of information shown. These screening code numbers correspond to the screening steps described in detail in Section IV.B. of this report.

### D. Recommendations

Based on the first four screening steps, we selected as the most promising electrocatalysts the combination electrodes Ag/Pb, Cu/Pb and Au/Pb. Further investigation (screening Step 5) indicates that a possible problem with Ag is the irreversible formation of an oxide so that the electrode may lose its good performance on repeated cycling. Both the Au/Pb and Cu/Pb electrode were found to have good resistance to anodic corrosion, but Au/Pb is even more resistance than Cu/Pb. Of course, Au is the most expensive material, but it is felt that loadings at microgram levels will be needed to fabricate practical electrodes. Therefore, in spite of a small cost increase, assured reliability warrants the selection of the Au/Pb electrode as most suitable for full cell testing at NASA-Lewis Research Center.

The investigation of different types of Au/Pb catalysts, including layered (sequential deposition of the two metals), codeposited and underpotential plated was begun in this program. Here codeposition is used in its most general sense -- a

TABLE IV-1

## SUMMARY OF ELECTRODE MATERIALS

(1 of 4)

Electrode	Physical Characteristics	Cathodic Performance	Anodic Performance	Hydrogen Evolution Overvoltage	Corrosion Characteristics	Figure No.
<b>I. METALS &amp; METALLOID MATERIALS</b>						
Au	Foil	Good	Good	Low	Fair	IV-1, -2, -29
Ag	Wire (Ingold)	Good	Good	Low	Fair	IV-11, -32
Au	Foil	Very Good	Very Good	Low	Good	IV-1, -2, -5
Ni	Rod, wrapped with Teflon tape to expose end (Ventron)	Good		High	Fair	IV-7, -8
C (vitreous carbon)	Roughened, rotating disk electrode tip (Beckman)	Fair		Medium	Good	IV-38, -39
C (graphite)	(Ventron) rod, wrapped with Teflon tape to expose end	Poor		Medium	Good	
C (graphite)	(Ultra Carbon) rod, wrapped with Teflon tape to expose end	Fair to Good	Poor	Medium	Good	IV-11, -34
Cd	(Alfa) Foil	Good		High	Very Poor	IV-1, -2, -9
Cu	Foil	Good		Low	Fair	IV-1, -2, -4, -11, -14, -30
In	(Alfa) Foil	Good		High	Very Poor	IV-1, -2, -10

Electrode	Physical Characteristics	Cathodic Performance	Anodic Performance	Hydrogen Evolution Overvoltage	Corrosion Characteristics	Figure No.
Pb	(Fisher) Foil	Very Good		High	Poor	IV-1, -2, -3, -14
Sb	(Alfa) Supported Foil	Fair		Medium	Fair	IV-6
SiC	(Ultra Carbon) Rod, wrapped with Teflon tape to expose end only	Poor to Fair		High		IV-16
Sn	(Ventron) Foil	Fair		Medium		IV-1, -2
Ti	Mesh	Not active		Low		IV-1
W	Wire	Not active		Very Low		IV-1
WO	Wire, heated in flame	Not active		Very Low		IV-1
II. ALLOYS						
Ag/Hg	Etched Ag Foil dipped in Hg	Fair (high polarization)		Very High		IV-12, -13
Cu/Hg	Cu Foil left in Hg	Fair (high polarization)		Very High	Fair	IV-12, -13
Cu/Hg	Etched Cu Exmet dipped in 2% Hg(NO <sub>3</sub> ) <sub>2</sub> · H <sub>2</sub> O	Fair (high polarization)		High		
Pb/Sn	Wire solder	Good		High		IV-12, -13

Electrode	Physical Characteristics	Cathodic Performance	Anodic Performance	Hydrogen Evolution Overvoltage	Corrosion Characteristics	Figure No.
<b>III. TEFLON-BONDED MATERIALS<sup>a</sup></b>						
<b>A. On Amalgamated Copper Foil<sup>b</sup></b>						
TaC	Powder, Teflon-bonded Flag	Not active		Low		IV-25
TaN	Powder, Teflon-bonded Flag	Not active		Low		IV-19
TiC	Powder, Teflon-bonded Flag	Not active		Very Low		IV-23
TiN	Powder, Teflon-bonded Flag	Not active		Very Low		IV-24
ZrC	Powder, Teflon-bonded Flag	Not active		Low		IV-20, -21
ZrN	Powder, Teflon-bonded Flag	Not active		Low		IV-22
<b>b. On Ti Screen</b>						
B <sub>4</sub> C	(Alfa) Powder, Teflon-bonded Flag	Not active		Low		IV-17
Cu/Pb	Powder, Teflon-bonded Flag	Good		Medium		IV-14, -15
WC	Powder, Teflon-bonded Flag	Not active		Low		IV-18
<b>IV. PLATED MATERIALS</b>						
<b>A. Rotating Disk (Beckman) Vitreous Carbon Substrate</b>						
Ag/Pb	Aq <sup>+</sup> , Pb <sup>+2</sup> added to electrolyte	Good	Good	High		IV-41
Au	Au <sup>+</sup> added to electrolyte (10 rps)	Good		Very Low		
Au/Pb	Au <sup>+</sup> , Pb <sup>+2</sup> added to electrolyte	Good	Good	High		IV-36, -37

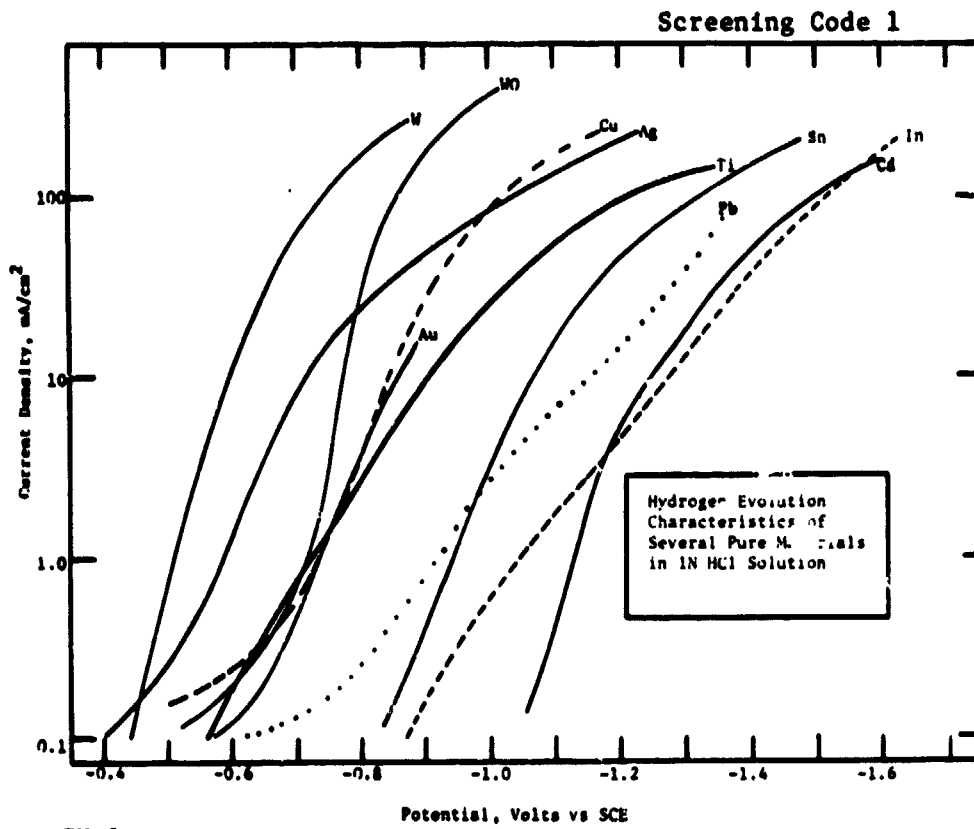
<sup>a</sup>(A) All powders were commercially obtained materials. In view of their overall unsuitability, no attempts were made to characterize their physical properties such as particle size and surface area.

(B) A small quantity of Teflon (usually 20% or less) was used as an inert binder to hold powder materials on amalgamated copper foils.

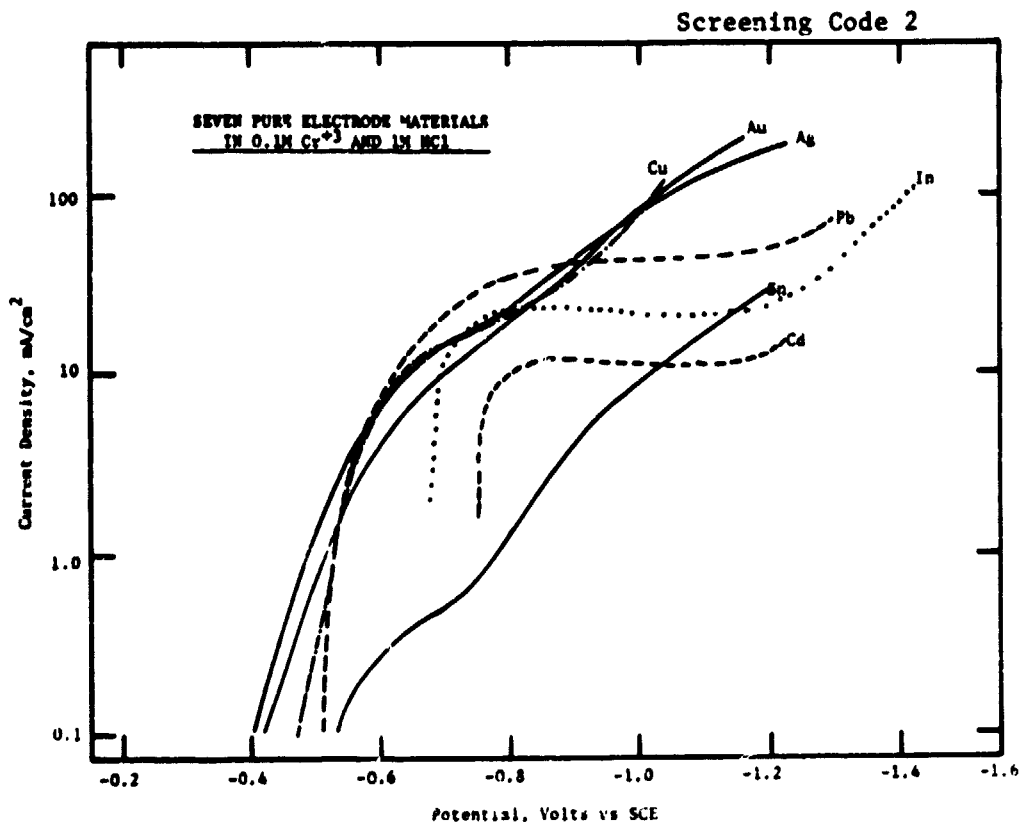


Electrode	Physical Characteristics	Cathodic Performance	Anodic Performance	Hydrogen Evolution Overvoltage	Corrosion Characteristics	Figure No.
Cd	Cd <sup>+2</sup> added to electrolyte	Good		High		IV-38, -39
Cd/Au	Cd <sup>+2</sup> , Au <sup>+3</sup> added to electrolyte	Good		High		IV-38, -39
Cu/Pb	Cu <sup>+</sup> , Pb <sup>+2</sup> added to electrolyte (10 rps)	Good	Good	High		IV-40
Pb	Pb <sup>+2</sup> added to electrolyte	Good		High		IV-35
<b>B. Graphite Substrate</b>						
	Rod, wrapped with Teflon tape to expose end					
Au/Pb	Potentiostatic codeposition in Au/Pb plating solution	Good	Good	High		IV-26, -27, -28
Au/In	Au <sup>+3</sup> , In <sup>+2</sup> added to electrolyte	Good	Good	High		IV-43
In	In <sup>+3</sup> added to electrolyte	Good		High		IV-42
Pb	Pb <sup>+2</sup> added to electrolyte	Good		High		IV-34, -42
<b>C. Other Substrates</b>						
Ag (Pb plated)	Ag foil electrode, Pb <sup>+2</sup> added to electrolyte	Good	Good	High		IV-29
Ag (Pb plated)	Ag wire electrode, Pb <sup>+2</sup> added to electrolyte	Good		High		IV-31, -32
Au (Pb plated)	Au Foil, Pb <sup>+2</sup> added to electrolyte	Good	Good	Medium		IV-33
Cu (Pb plated)	Cu Foil, Pb <sup>+2</sup> added to electrolyte	Good	Good	High		IV-30

simultaneous electrodeposition of Au and Pb from a common solution. In such event, an intimately dispersed mixture of Au and Pb will be deposited; and under some favorable, yet undefined, conditions, either a solid solution of Au and Pb or gold/lead intermetallics may be formed. Further work on this aspect of electrocatalysis is anticipated under NASA Contract No. DEN3-97.



**Figure IV-1**



**Figure IV-2**

Screening Code 1,2,3

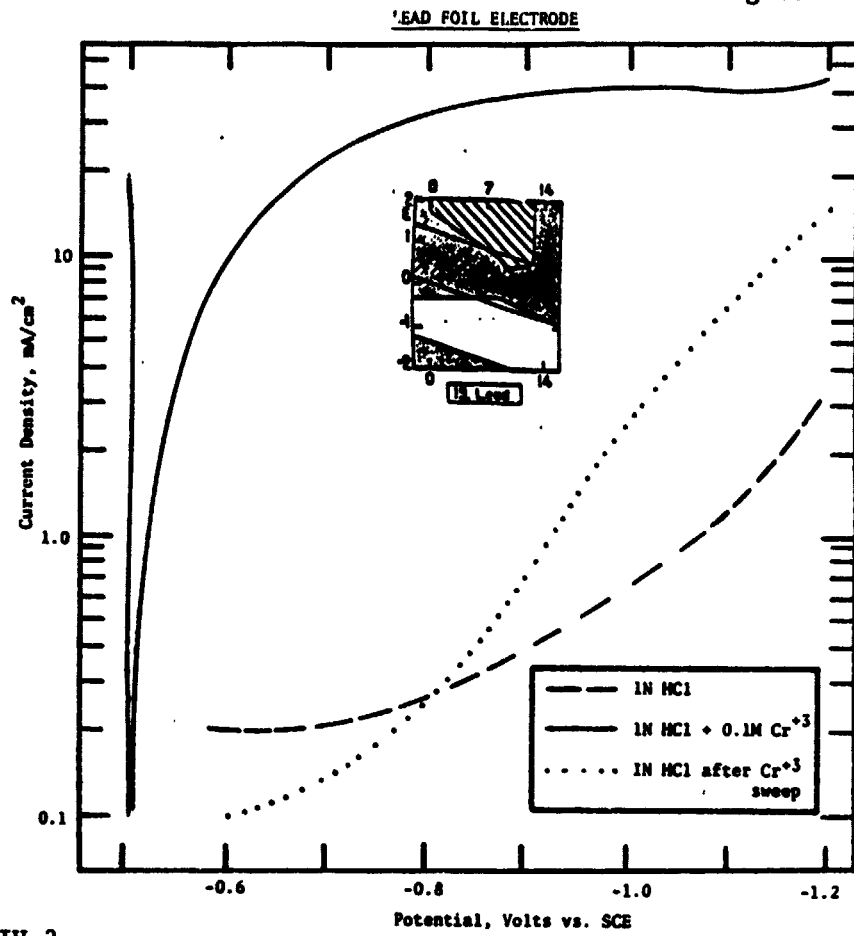


Figure IV-3

Screening Code 1,2,3

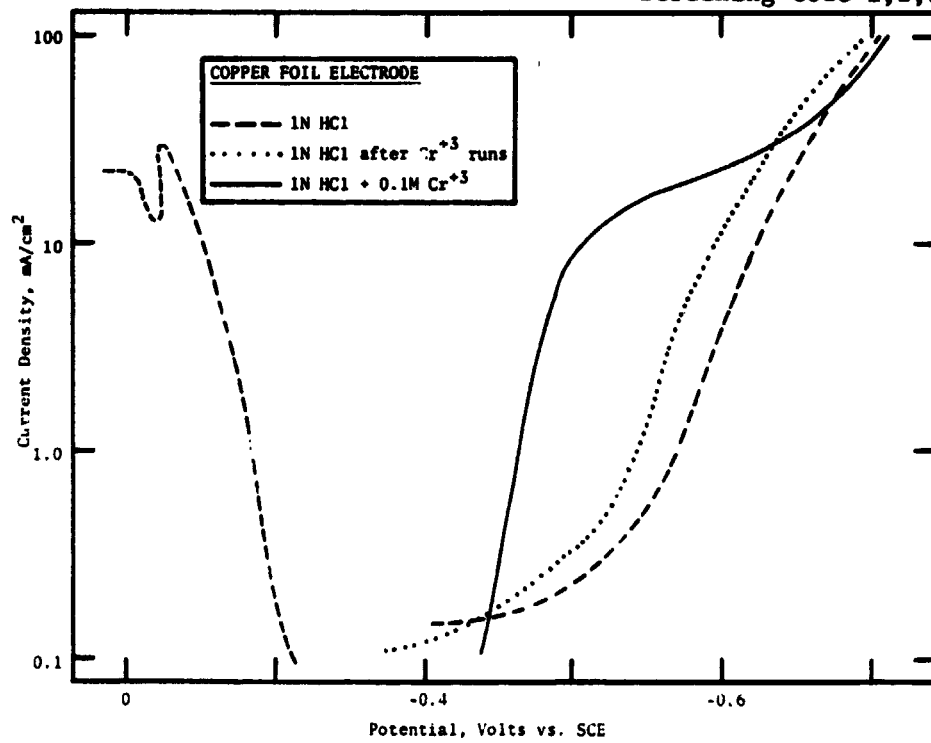


Figure IV-4

GOLD FOIL ELECTRODE

Screening Code 1,2

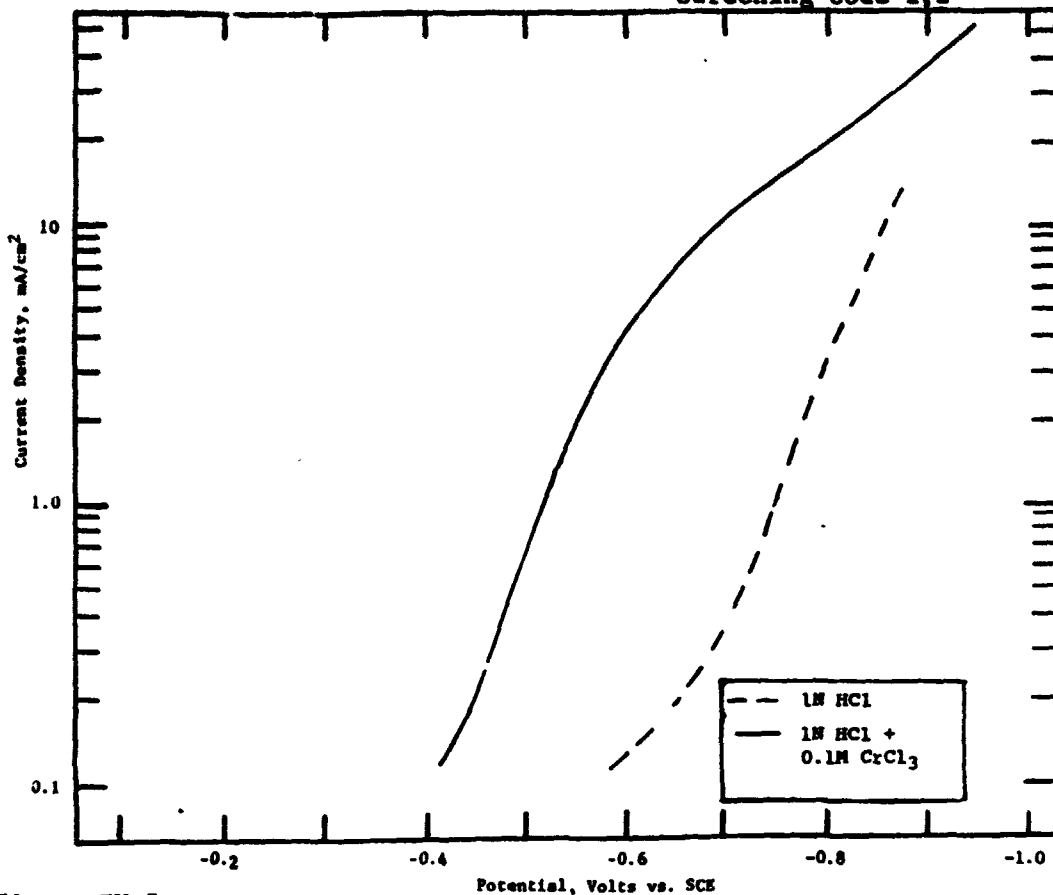


Figure IV-5

ANTIMONY ELECTRODE

Screening Code 1,2,3

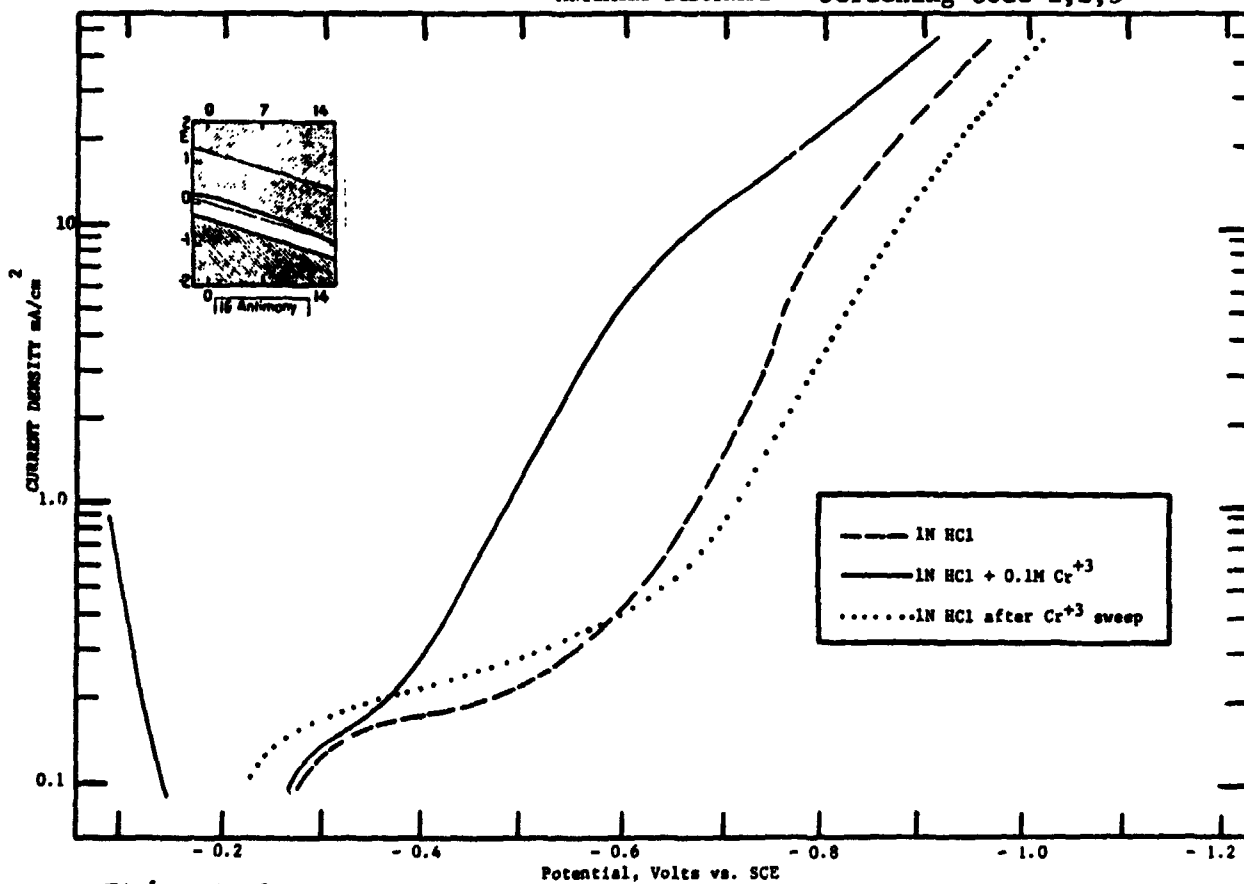


Figure IV-6

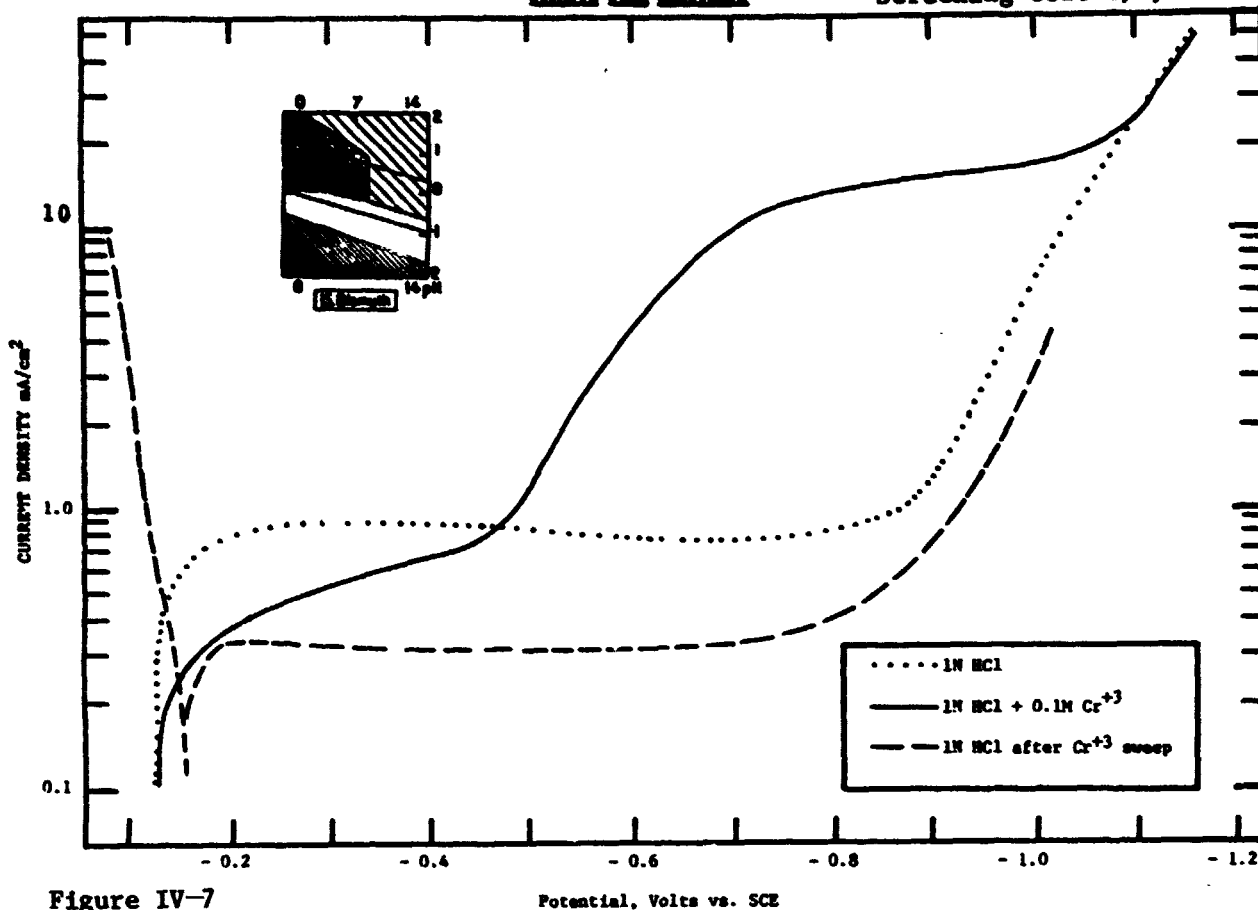


Figure IV-7

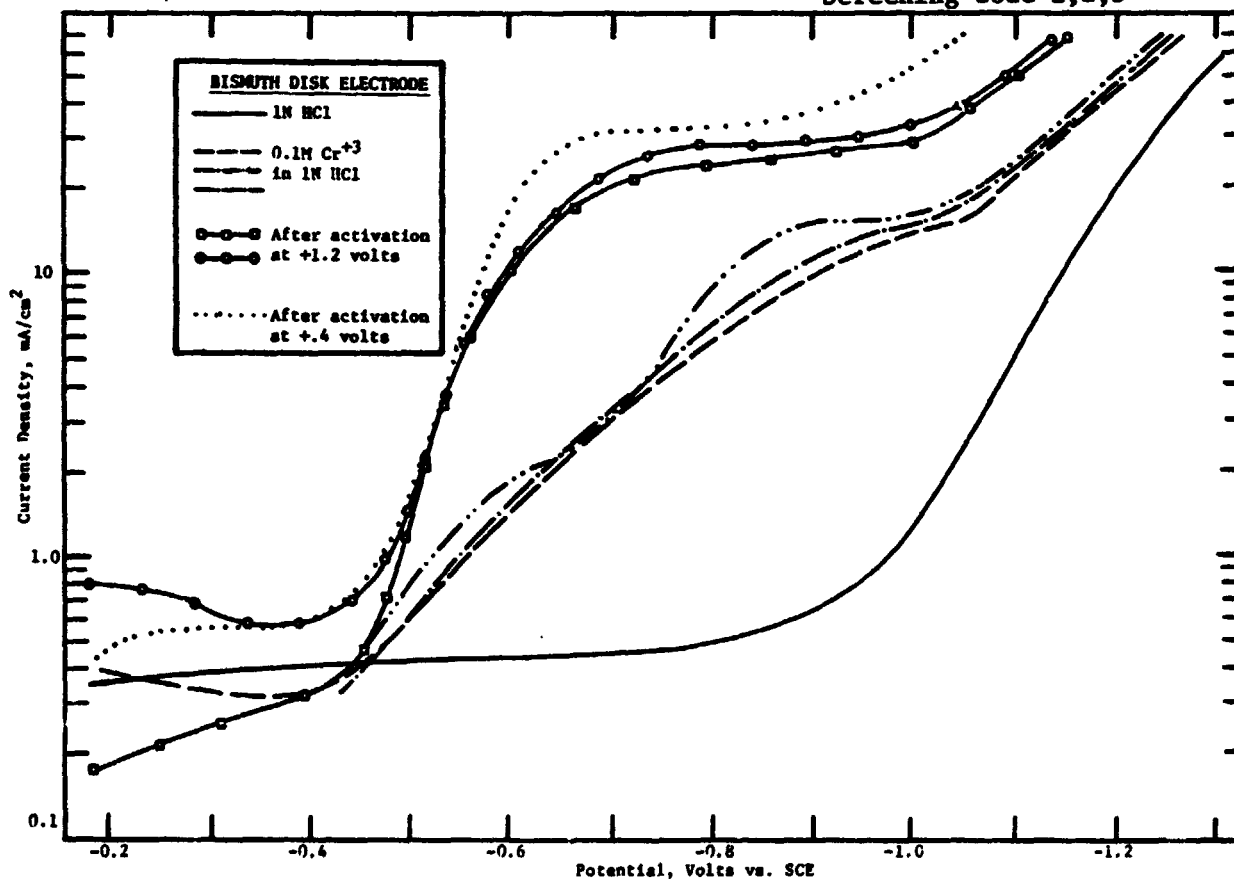


Figure IV-8

Screening Code 1,2,3

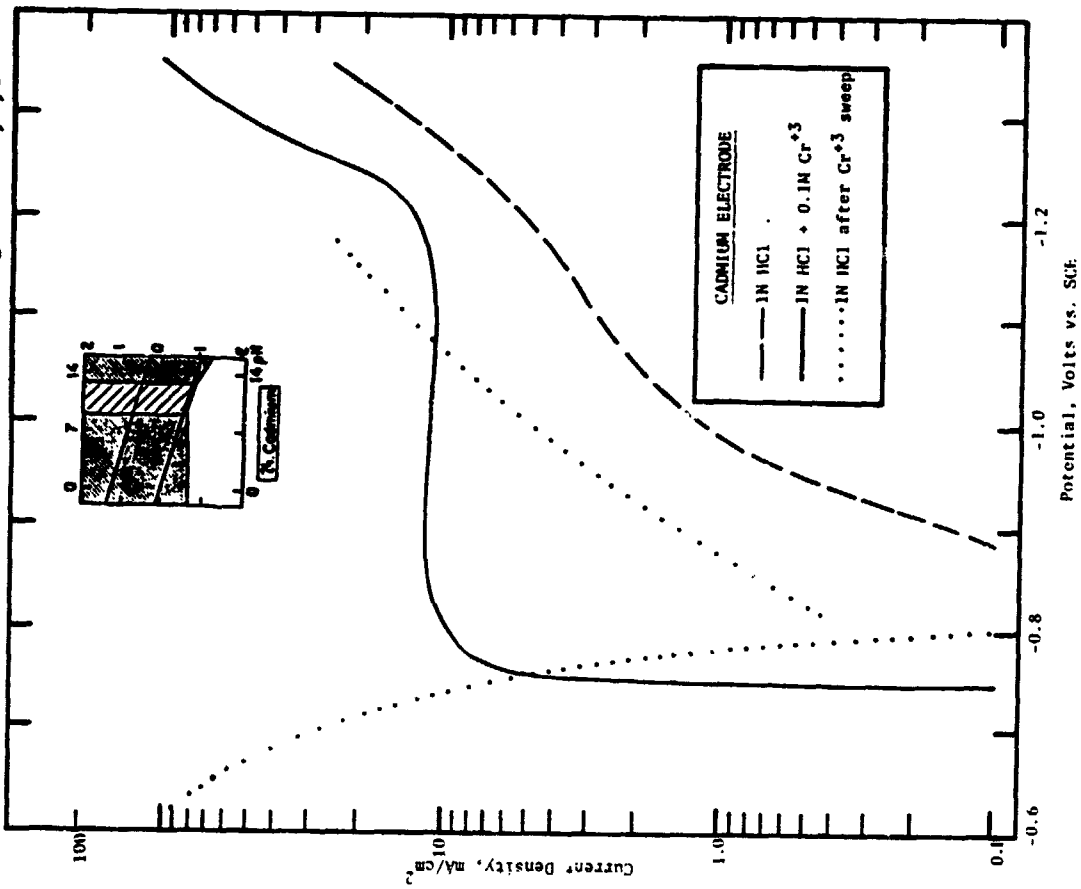


Figure IV-9

Screening Code 1,2,3

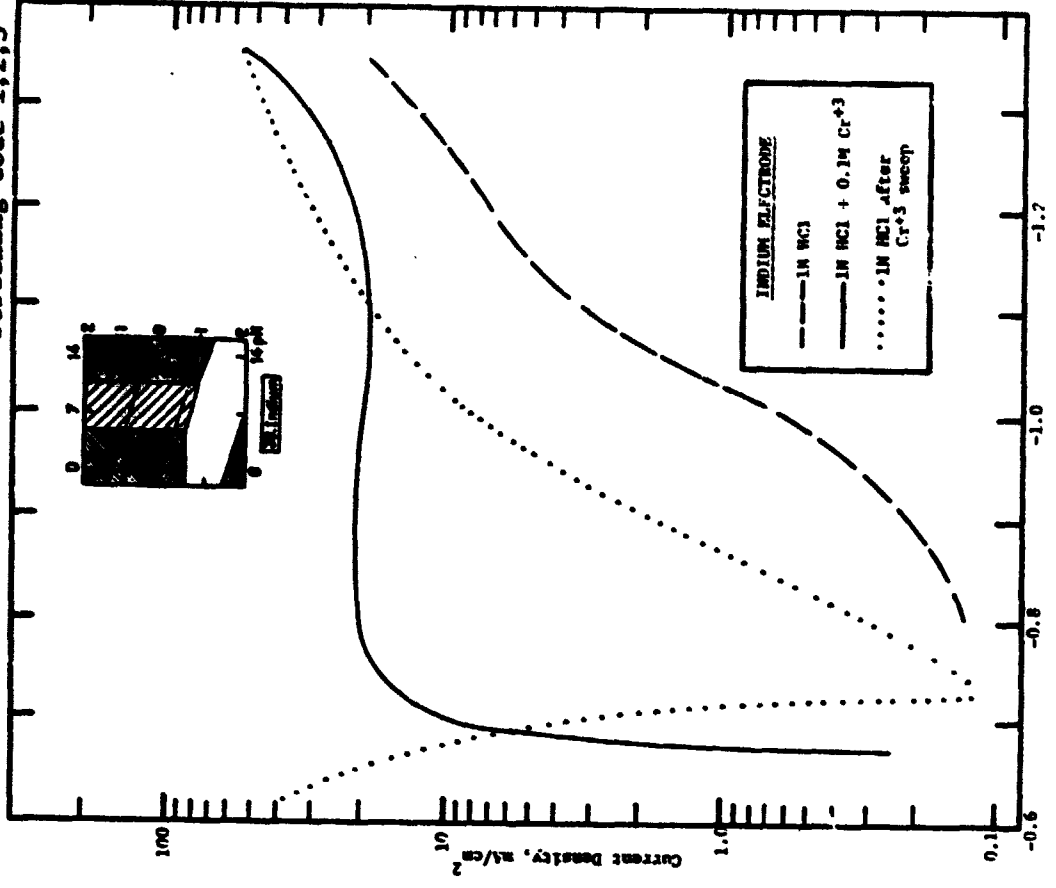


Figure IV-10

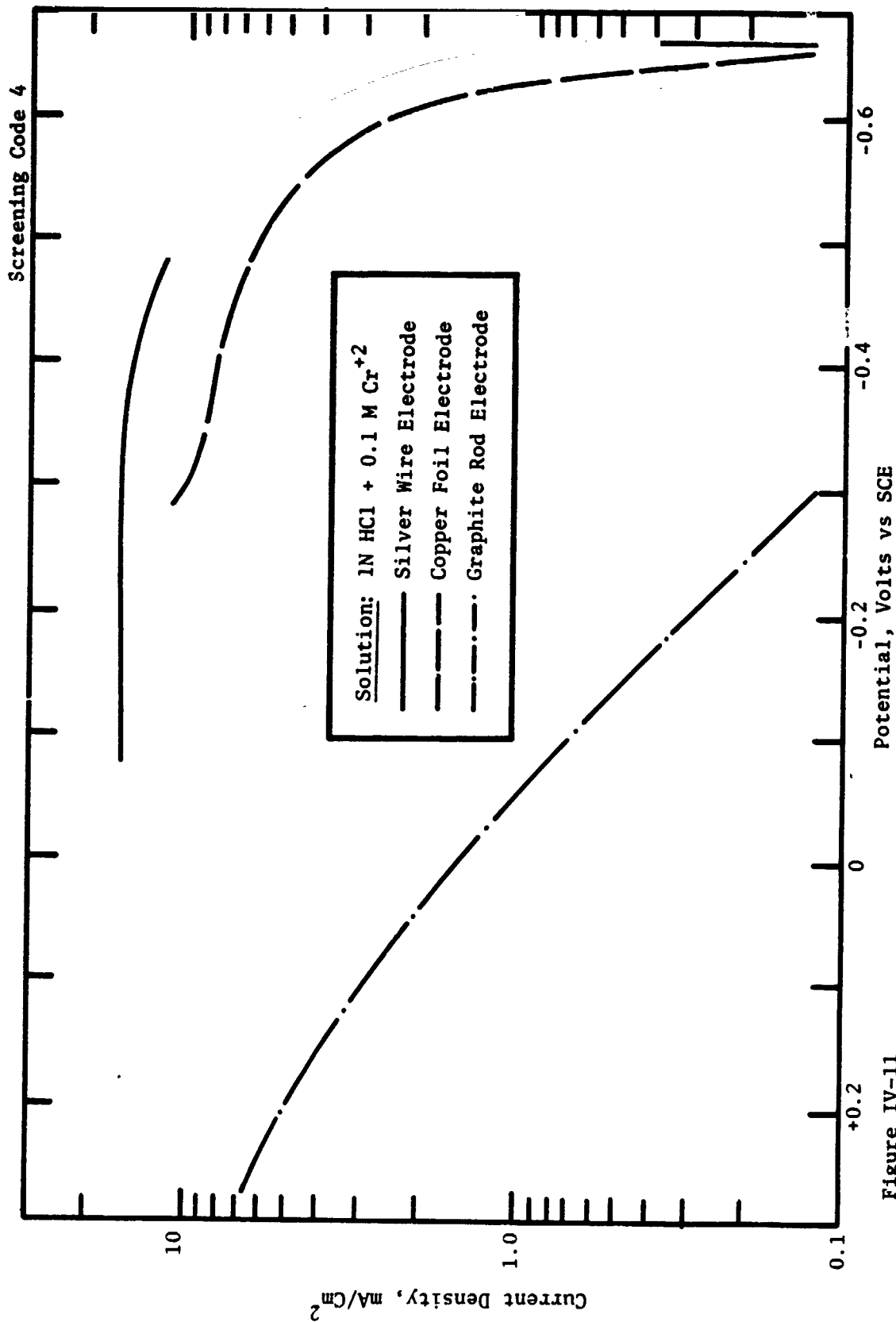


Figure IV-11



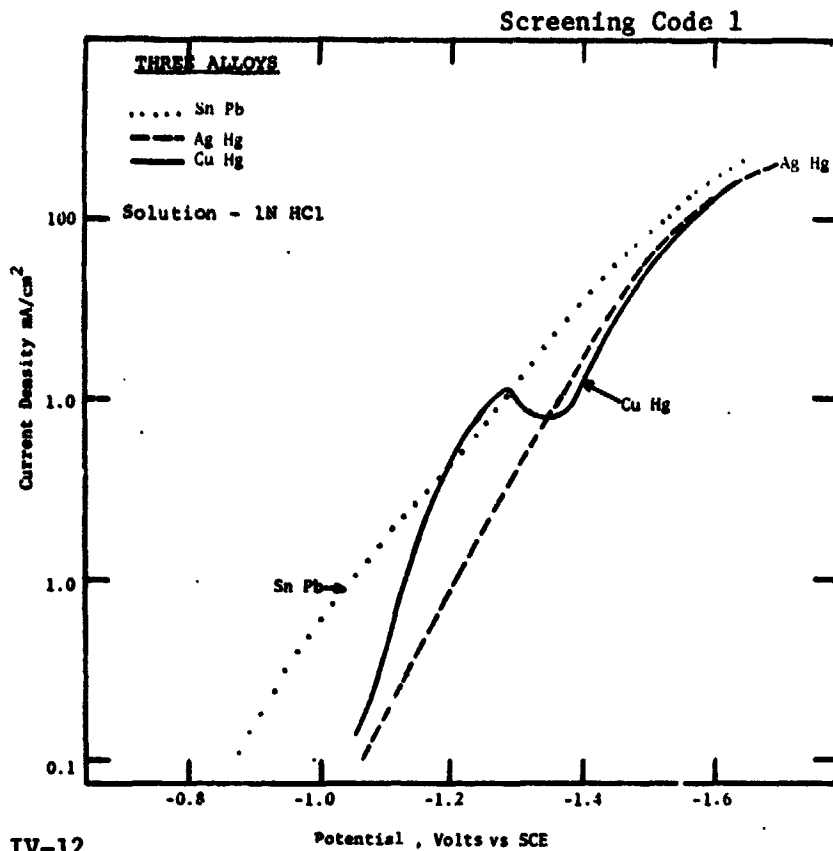


Figure IV-12

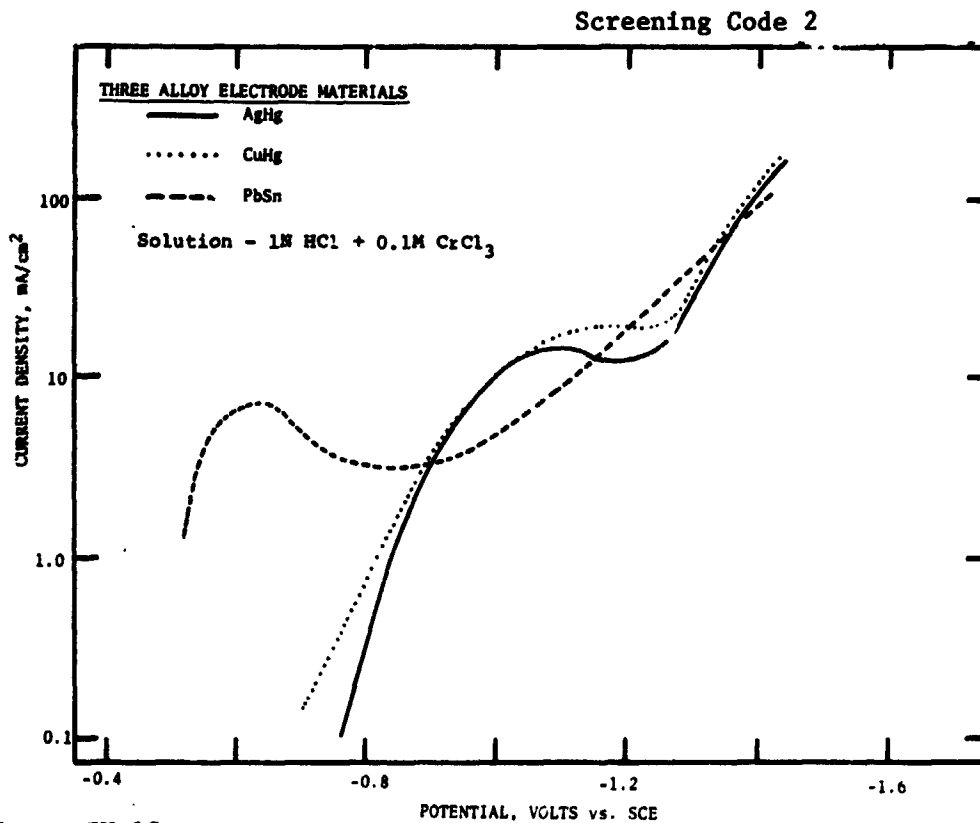


Figure IV-13

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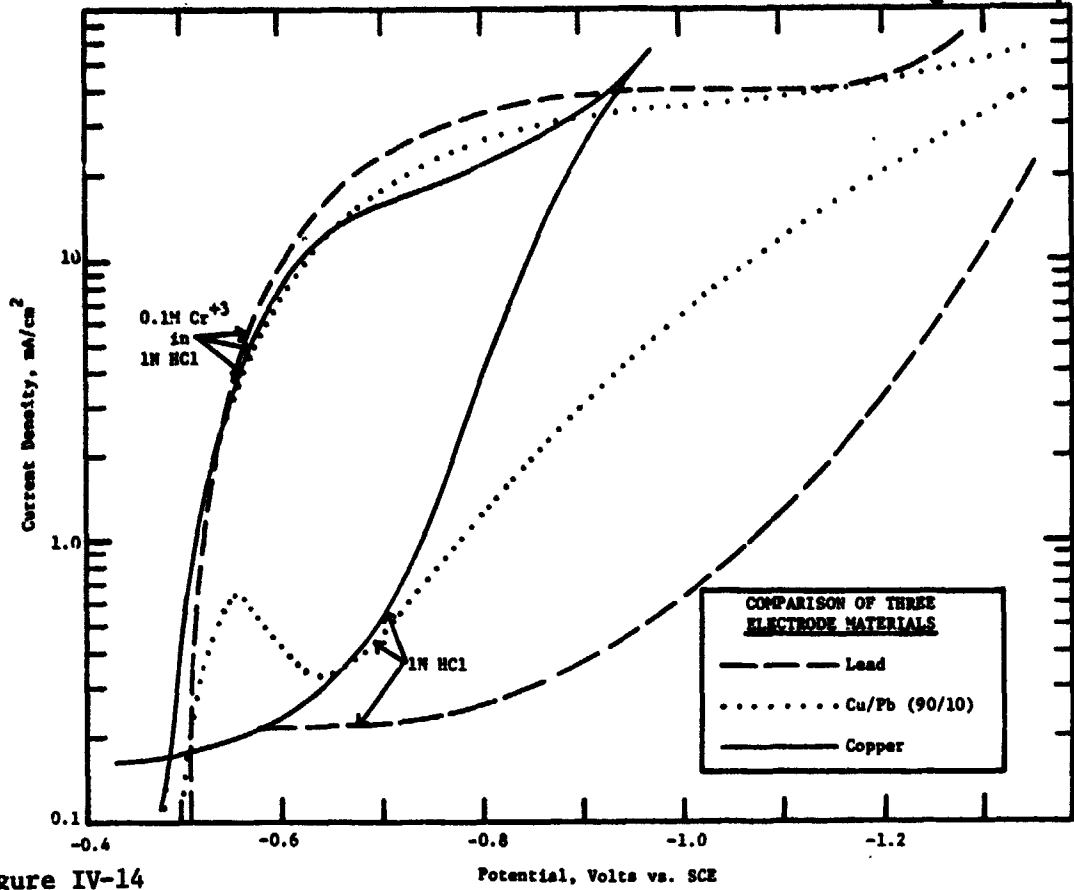


Figure IV-14

COPPER/LEAD 90/10 ELECTRODE

Screening Code 1,2,3

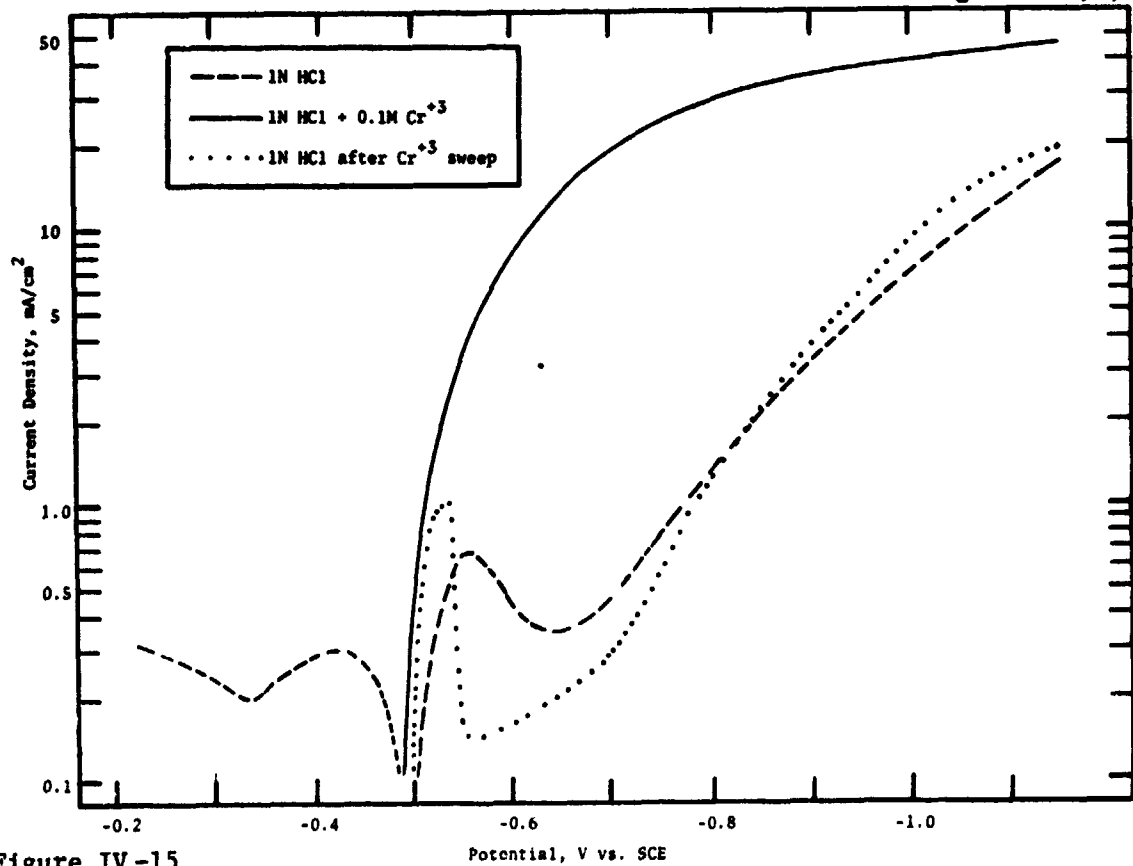


Figure IV-15

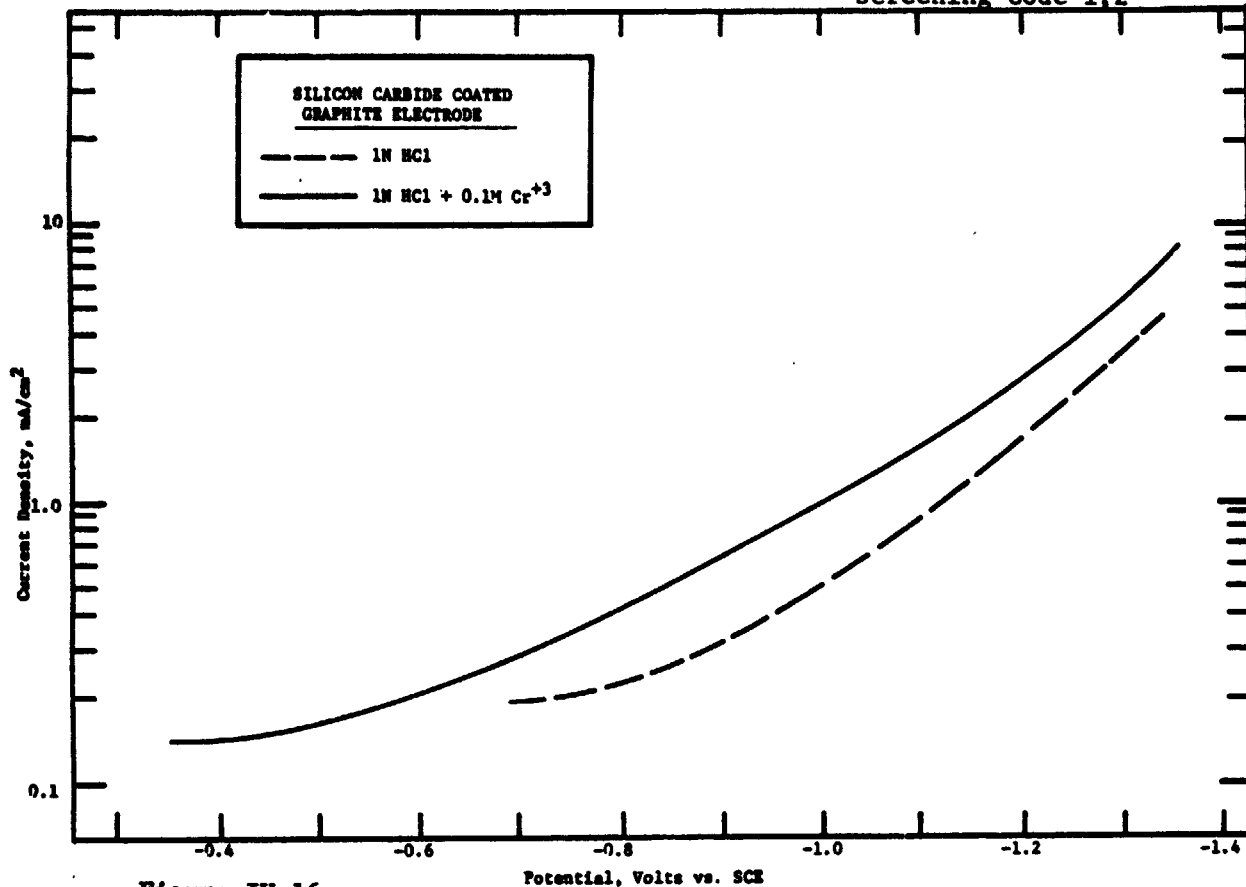


Figure IV-16

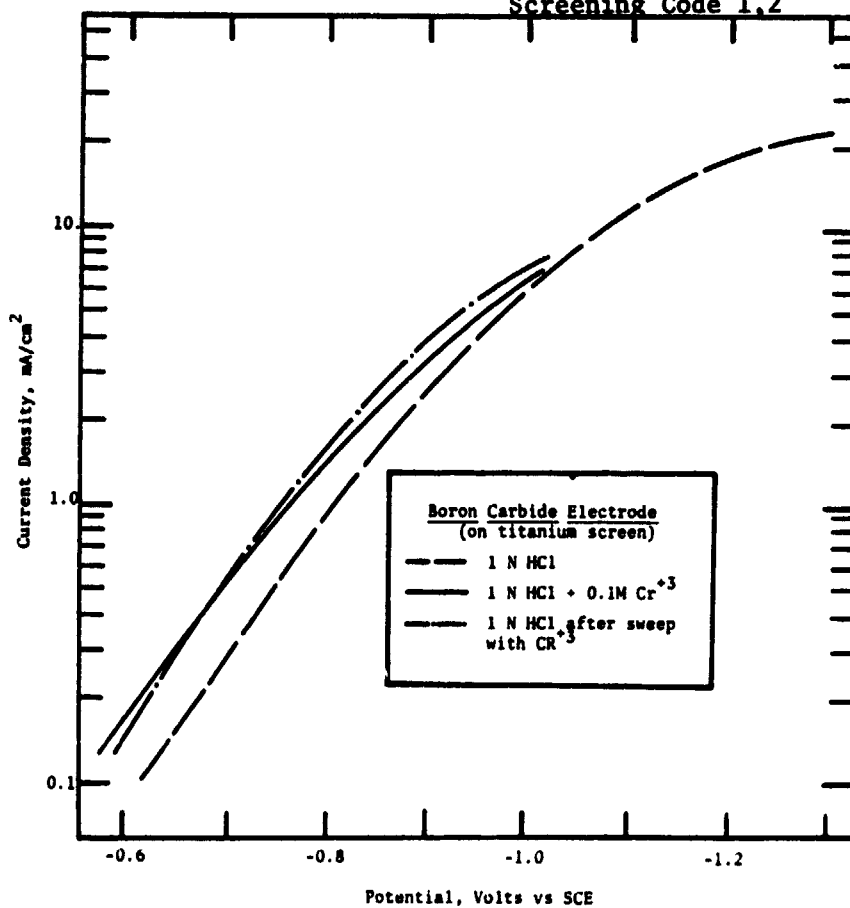


Figure IV-17

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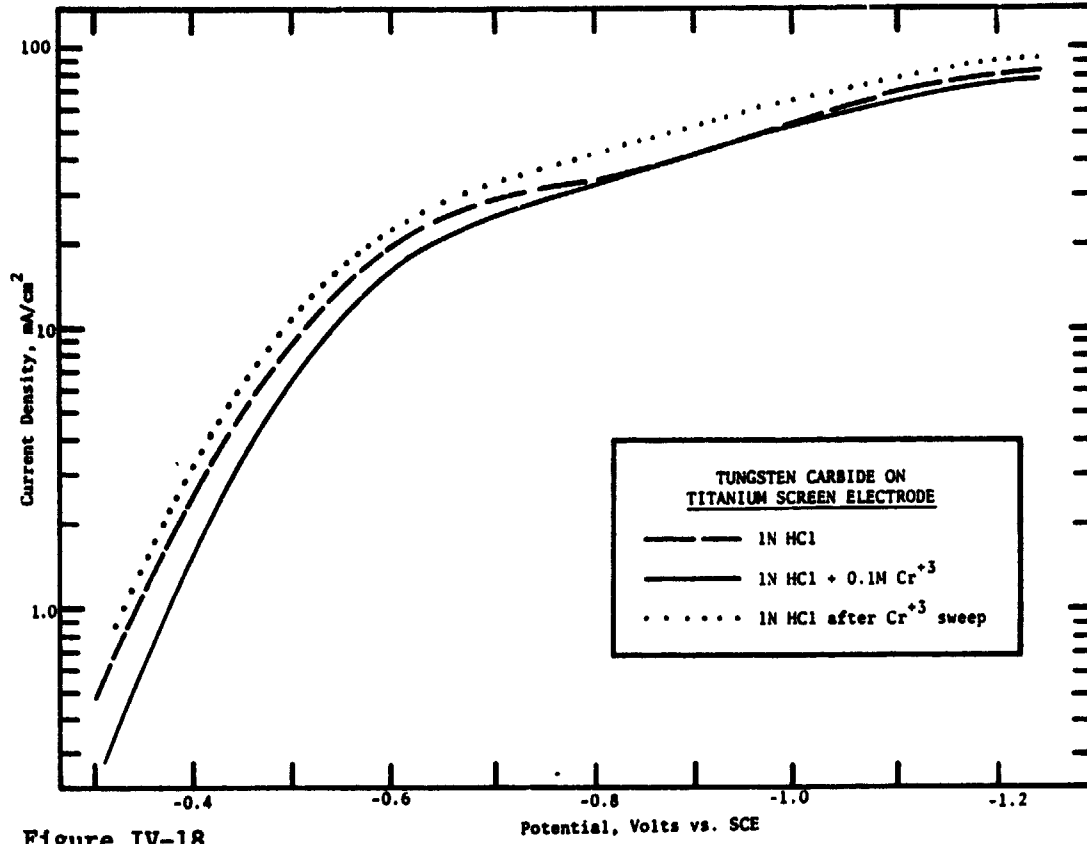


Figure IV-18

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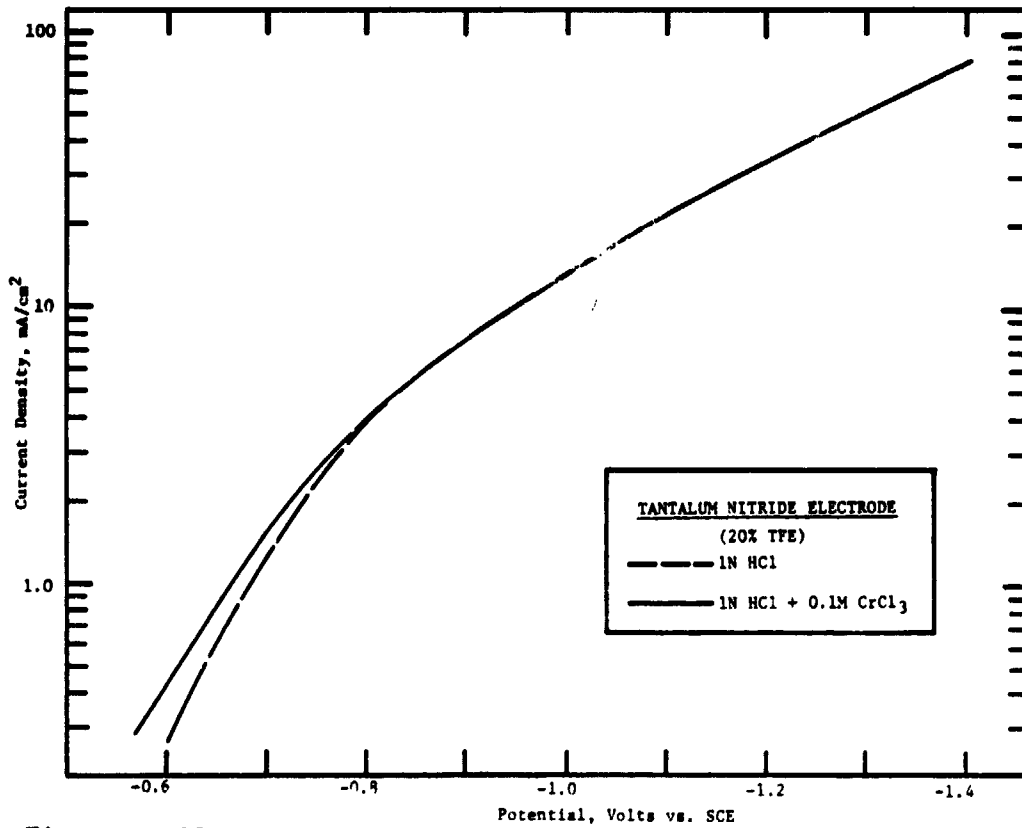


Figure IV-19

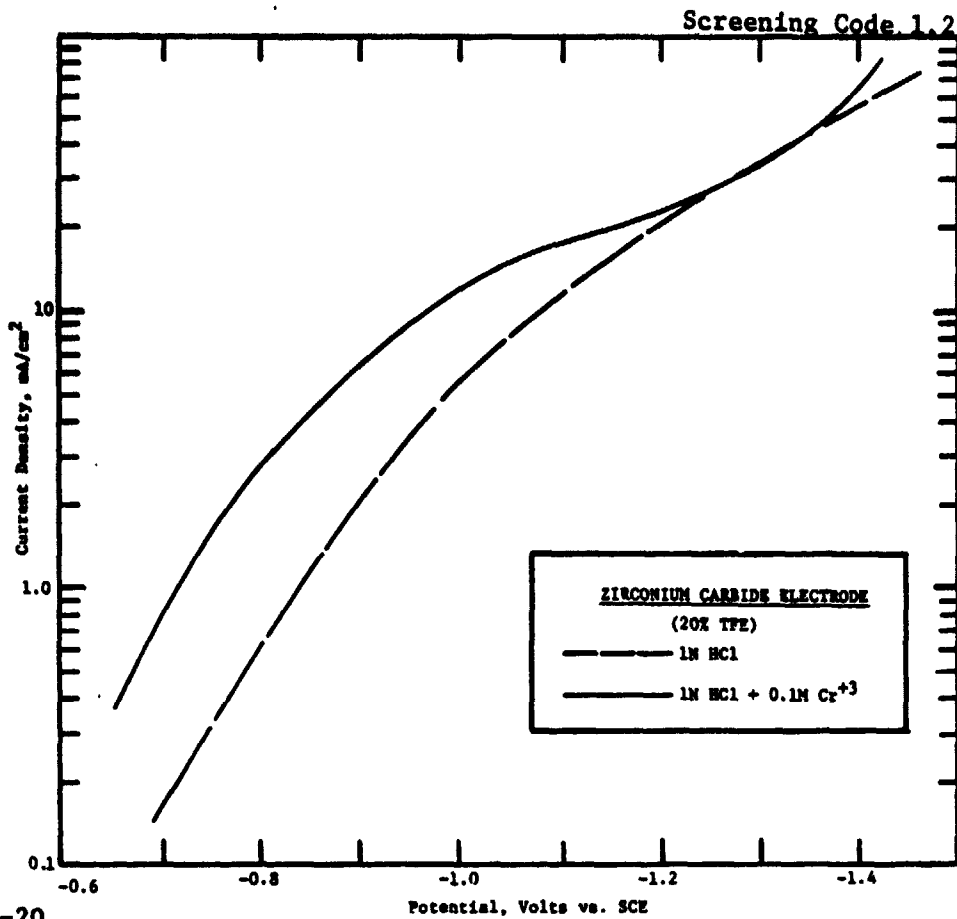


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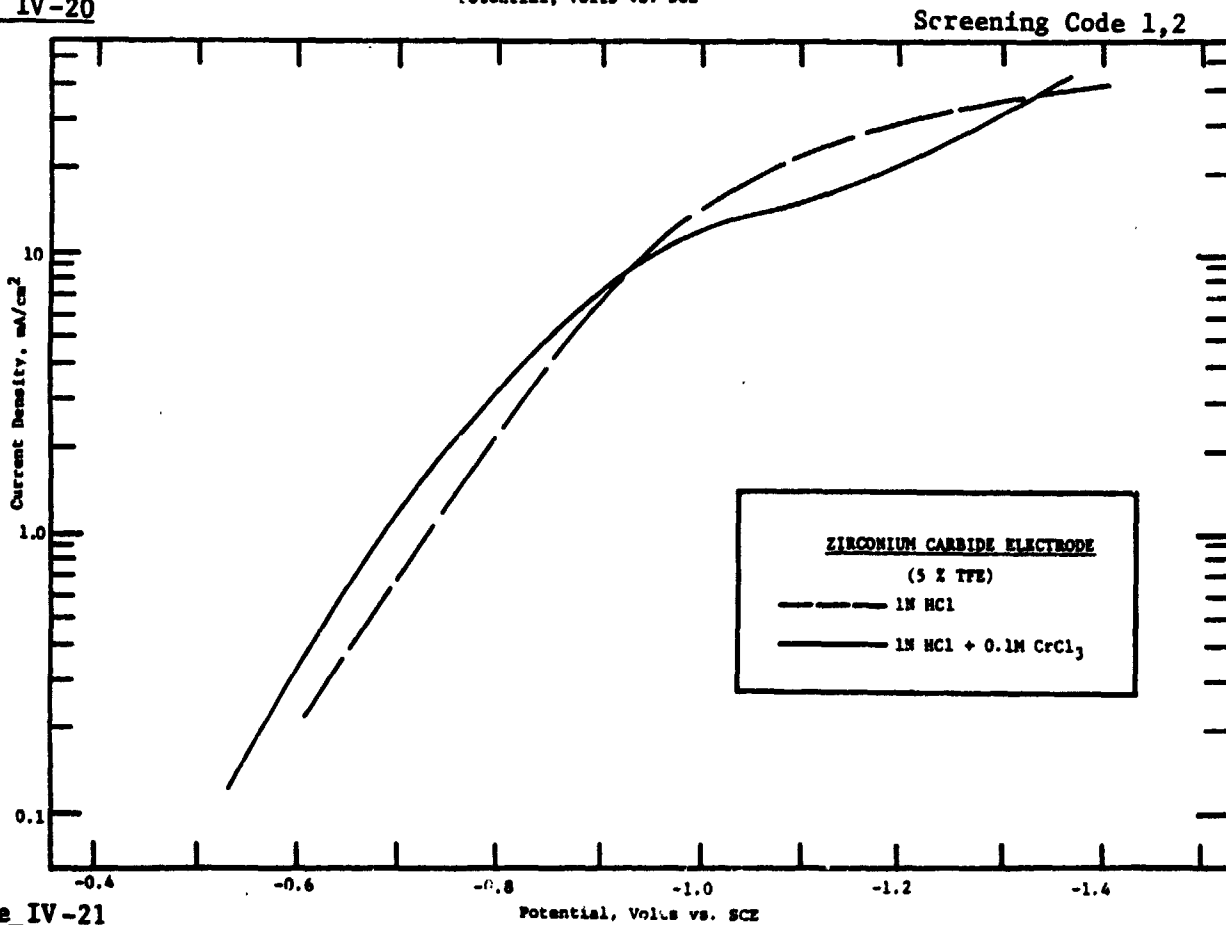


Figure IV-21

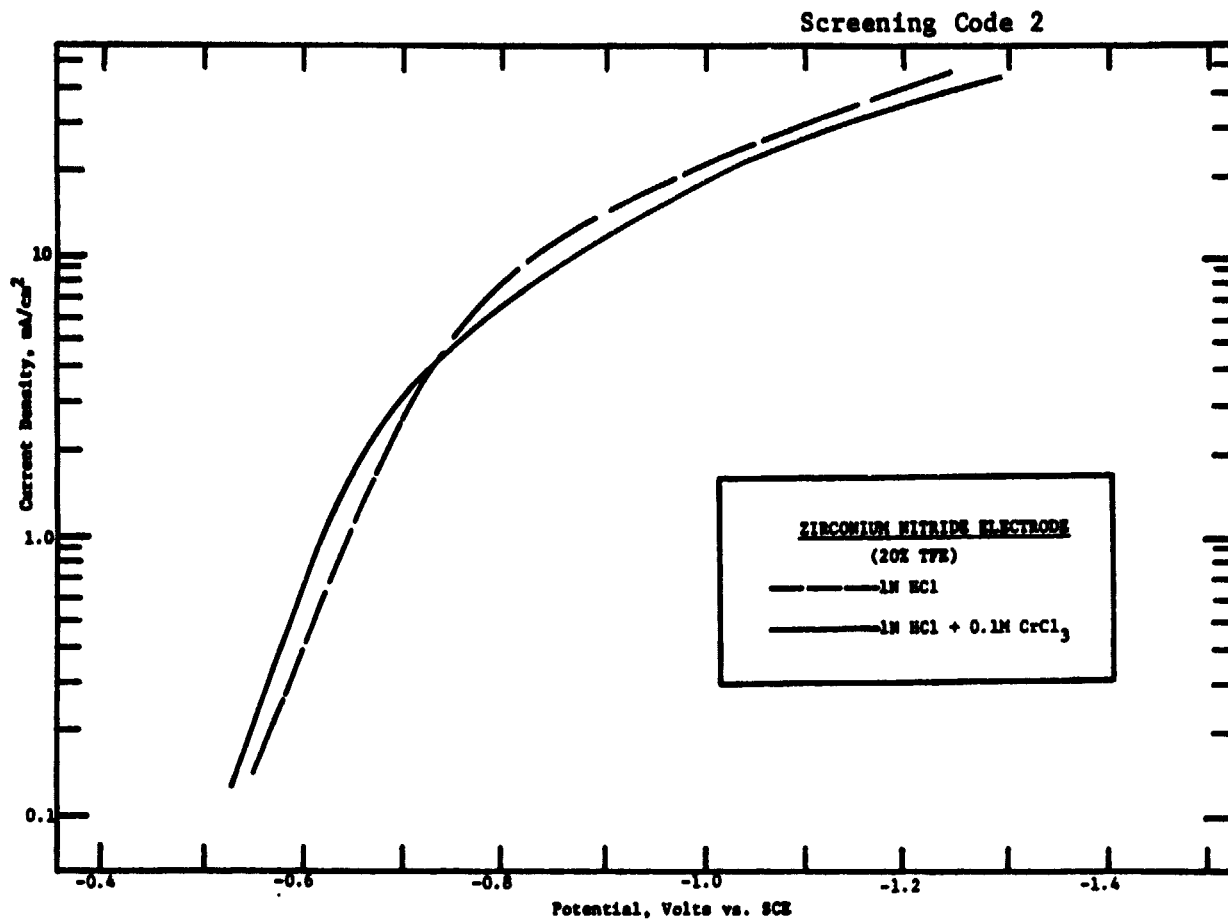


Figure IV-22

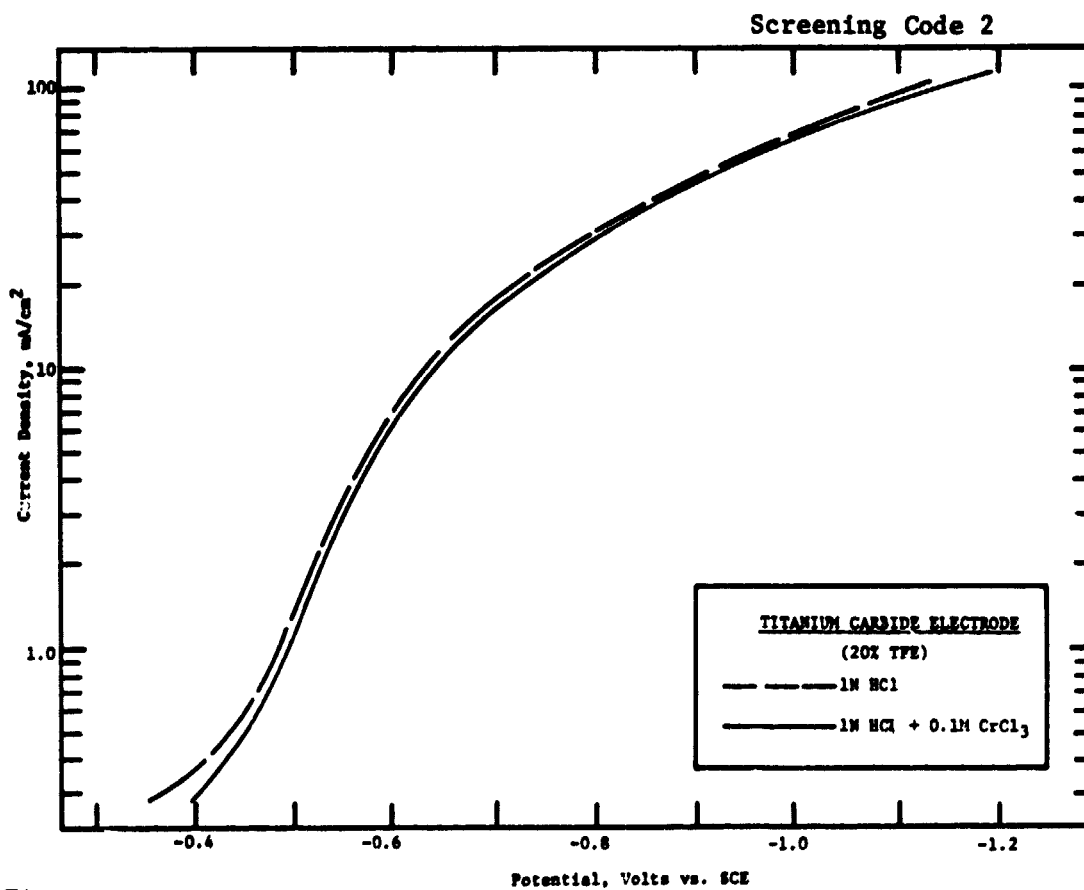


Figure IV-23

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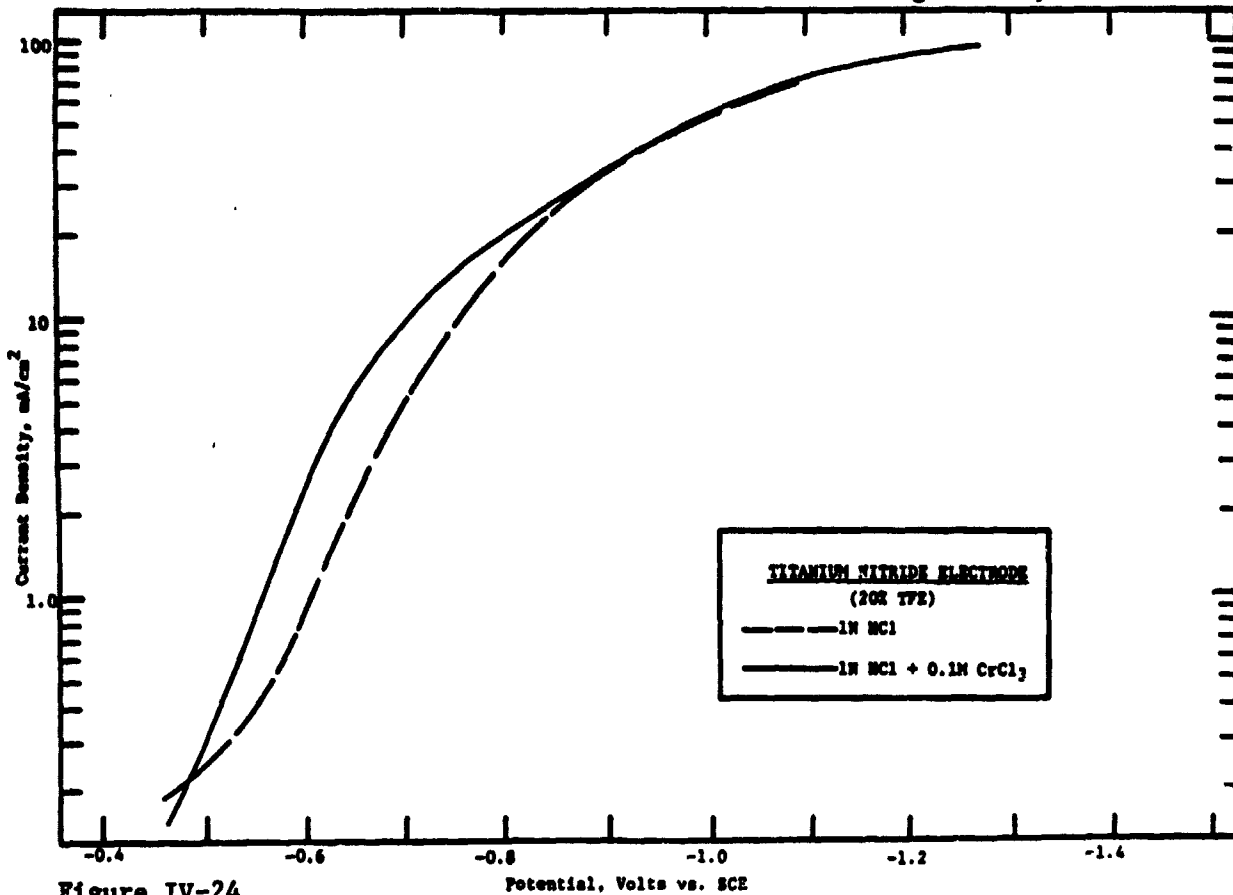


Figure IV-24

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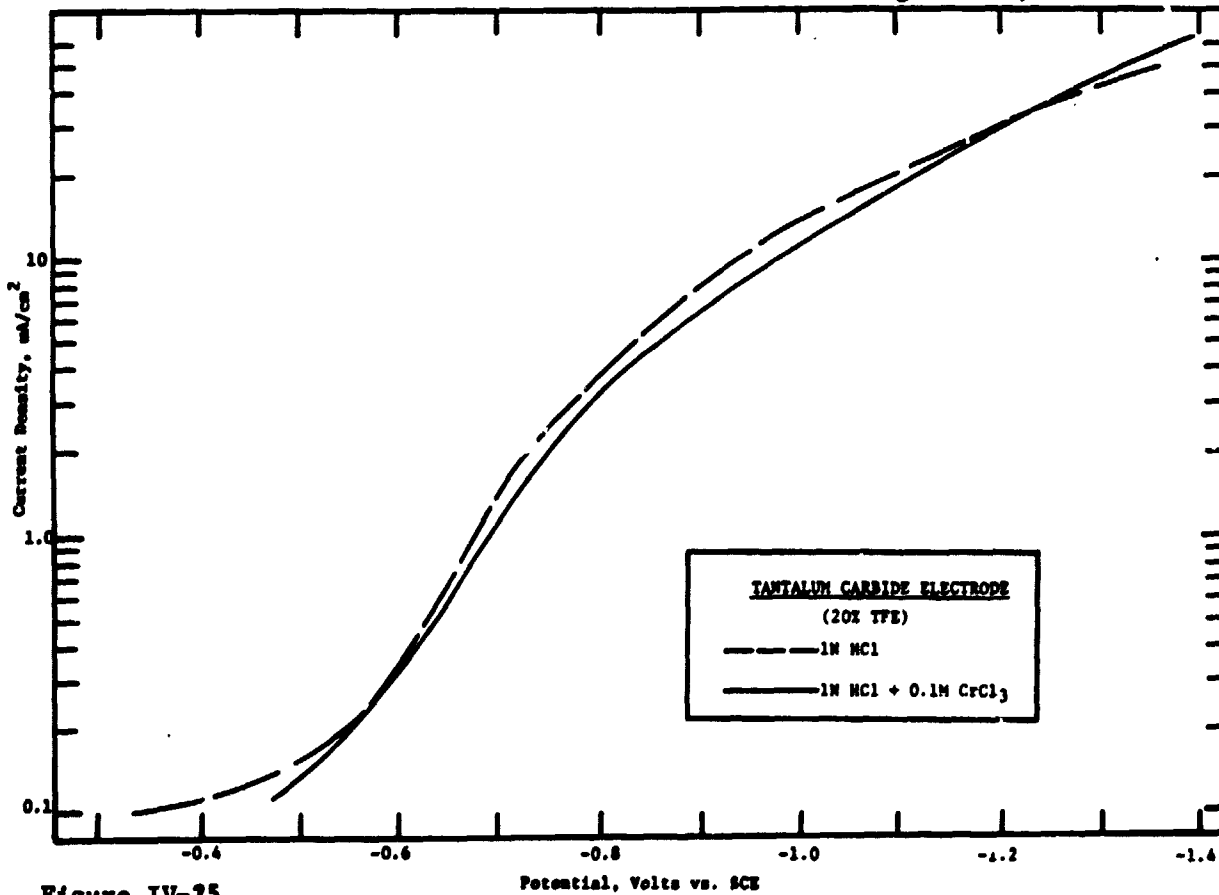
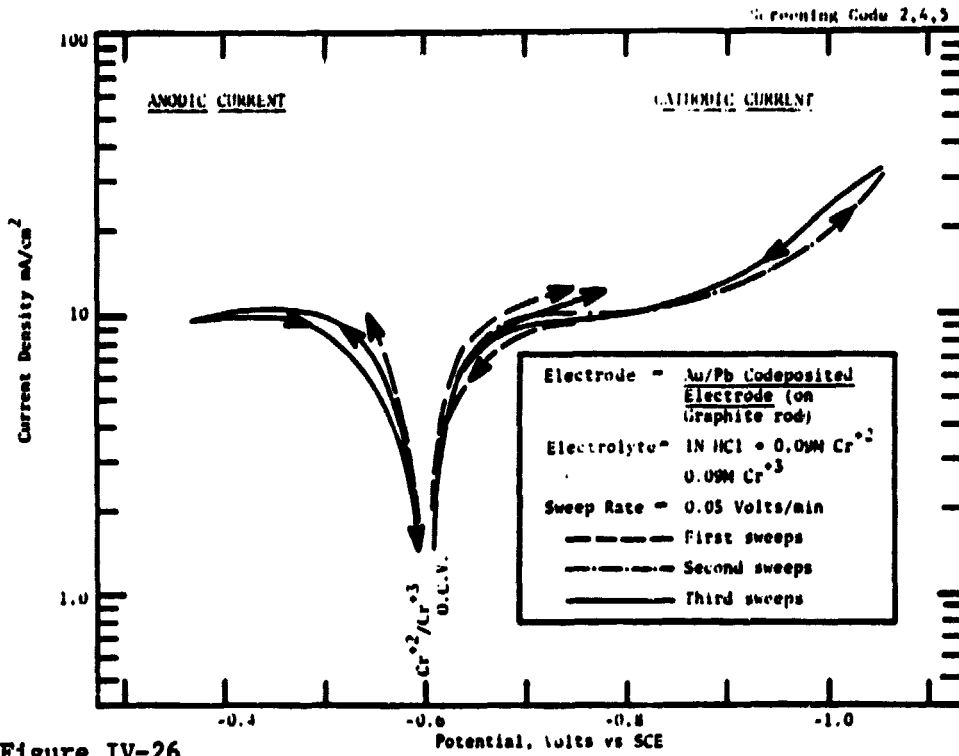
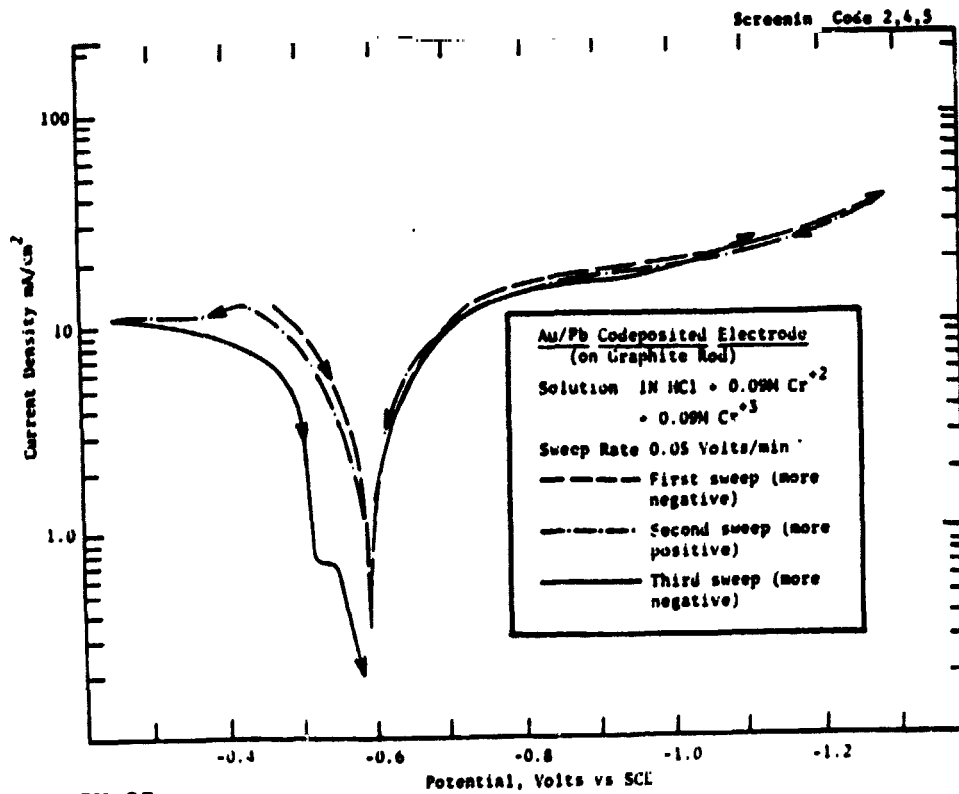


Figure IV-25



**Figure IV-26**



**Figure IV-27**



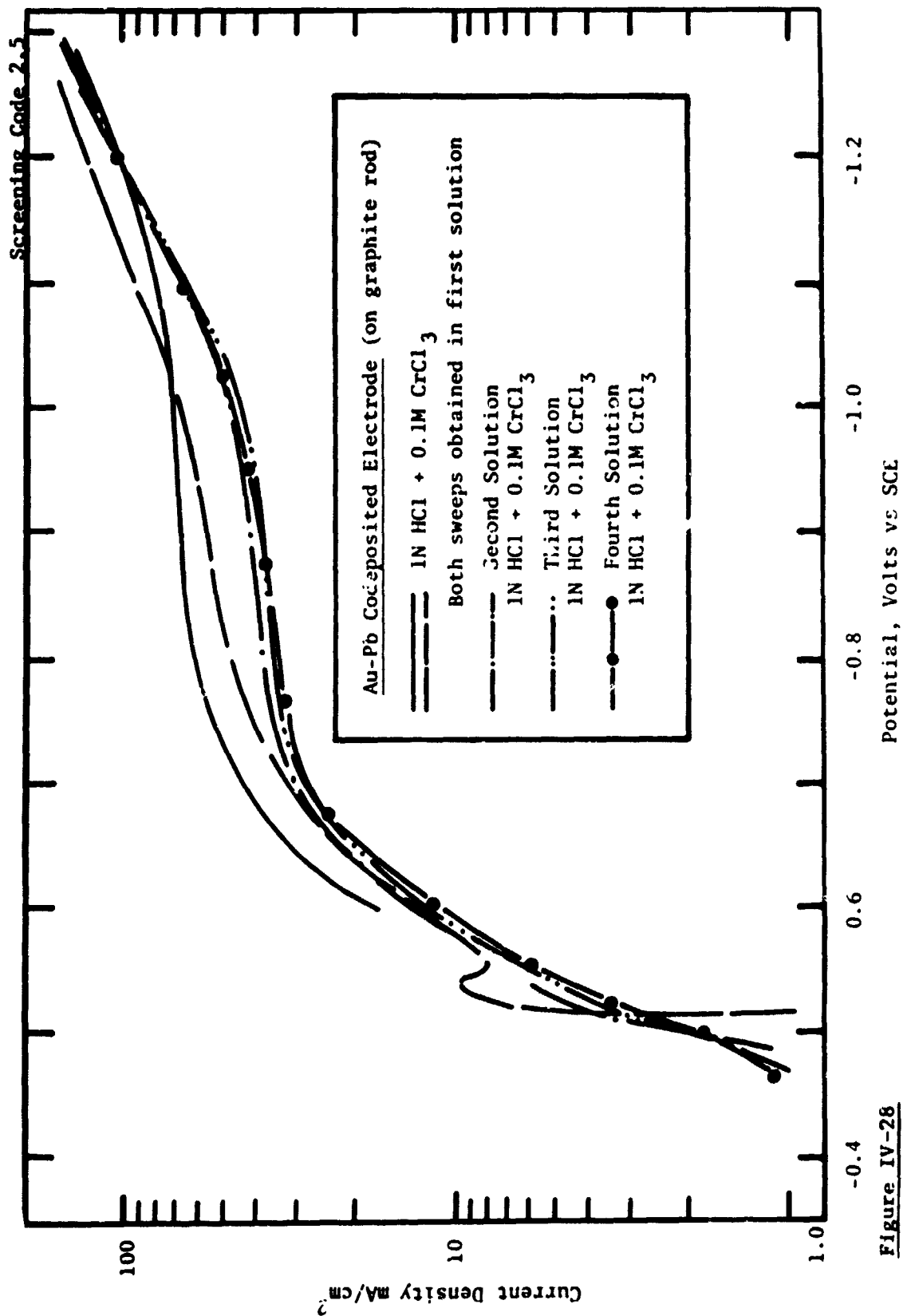


Figure IV-28

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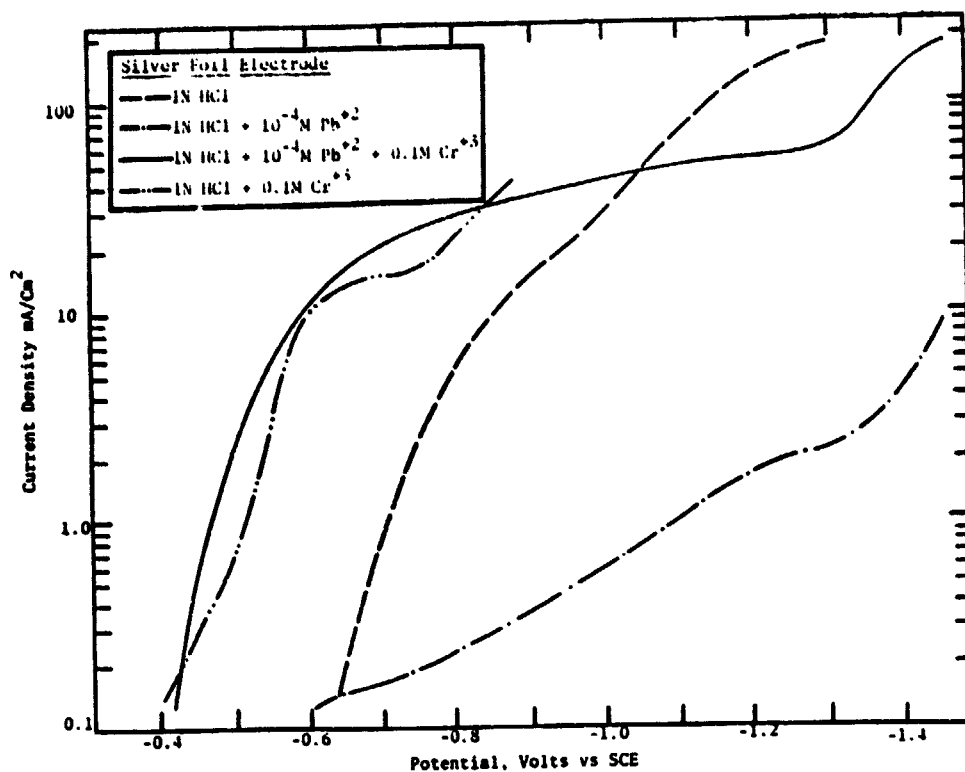


Figure IV-29

Screening Code 1,2

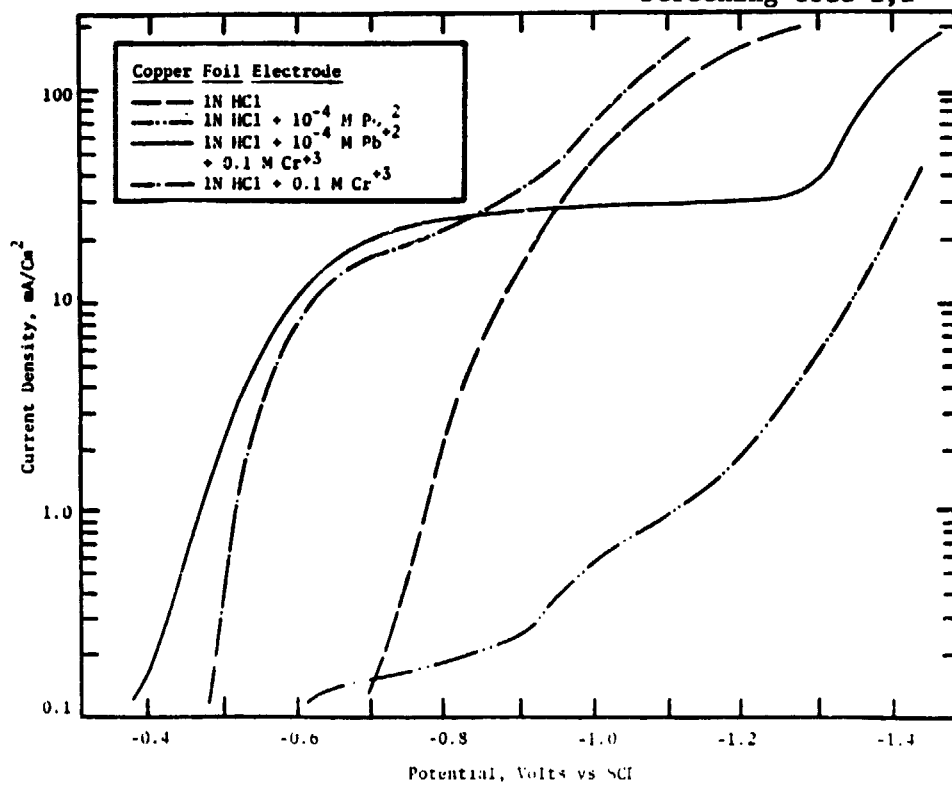


Figure IV-30

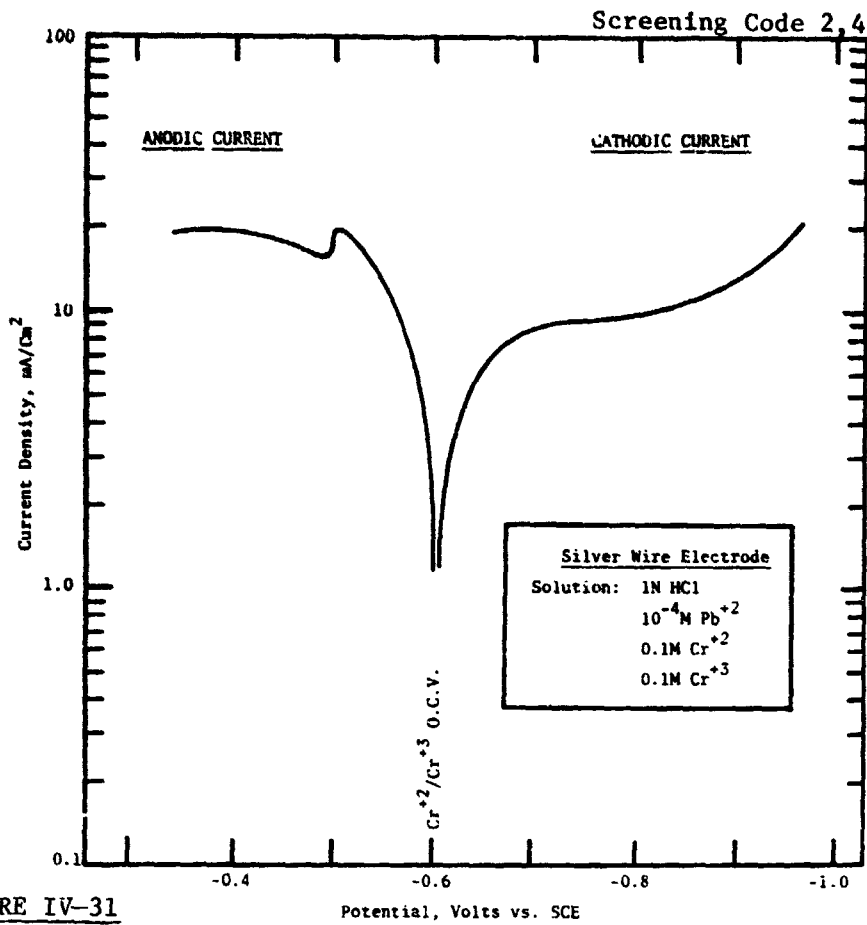


FIGURE IV-31

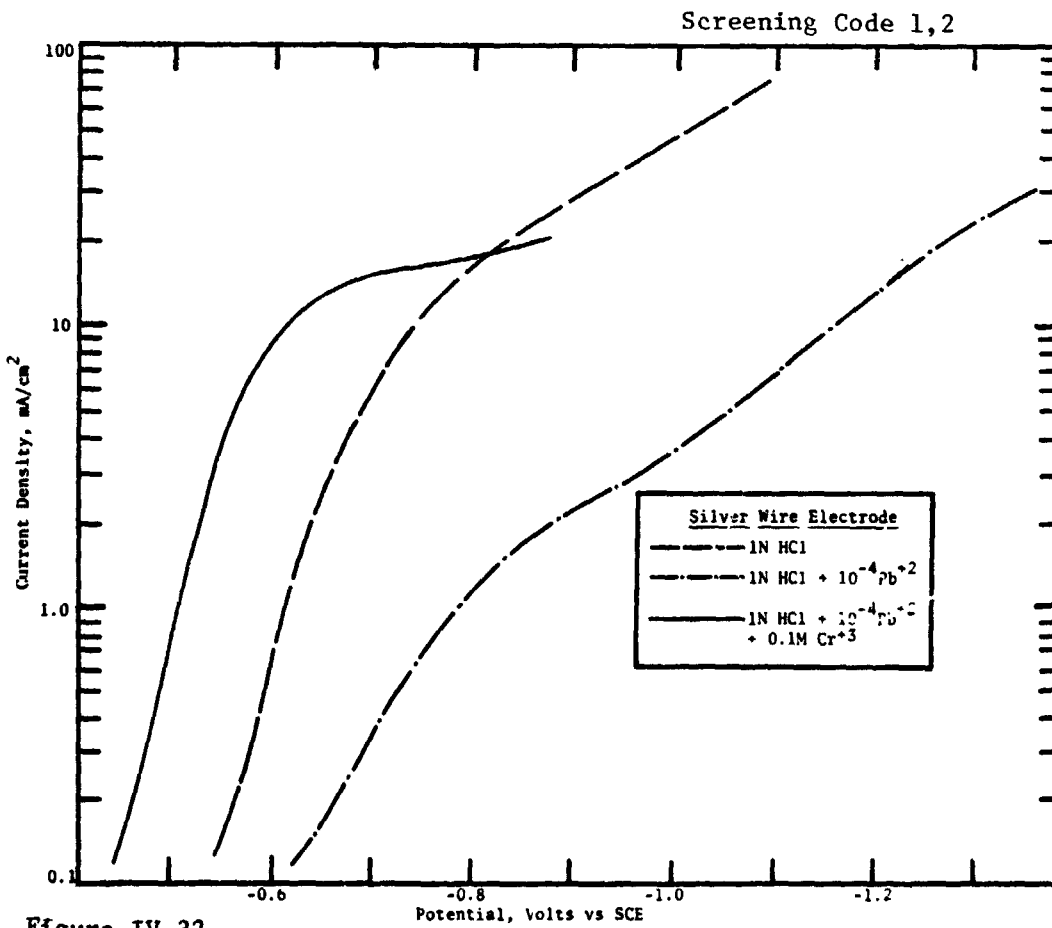


Figure IV-32

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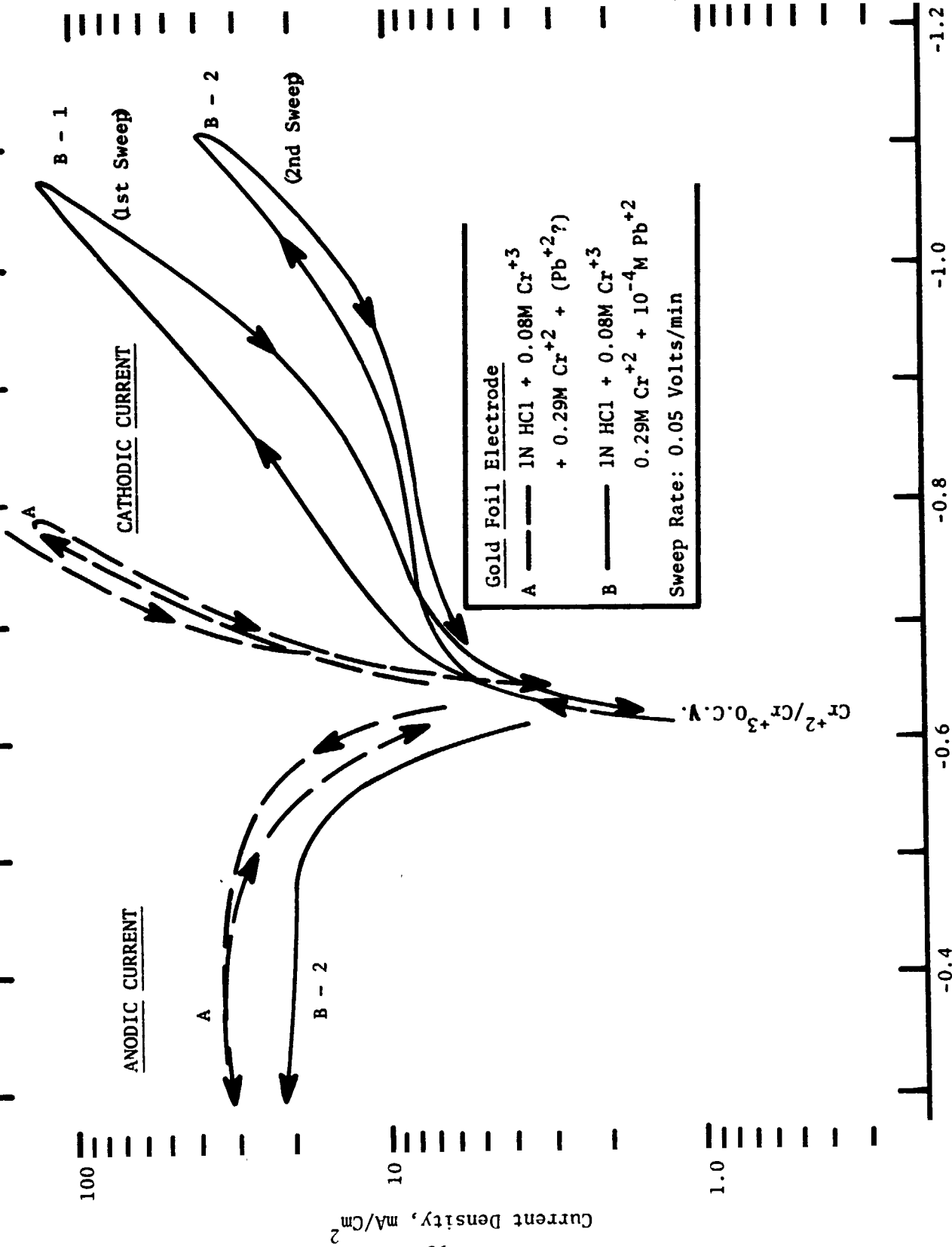


Figure IV-33

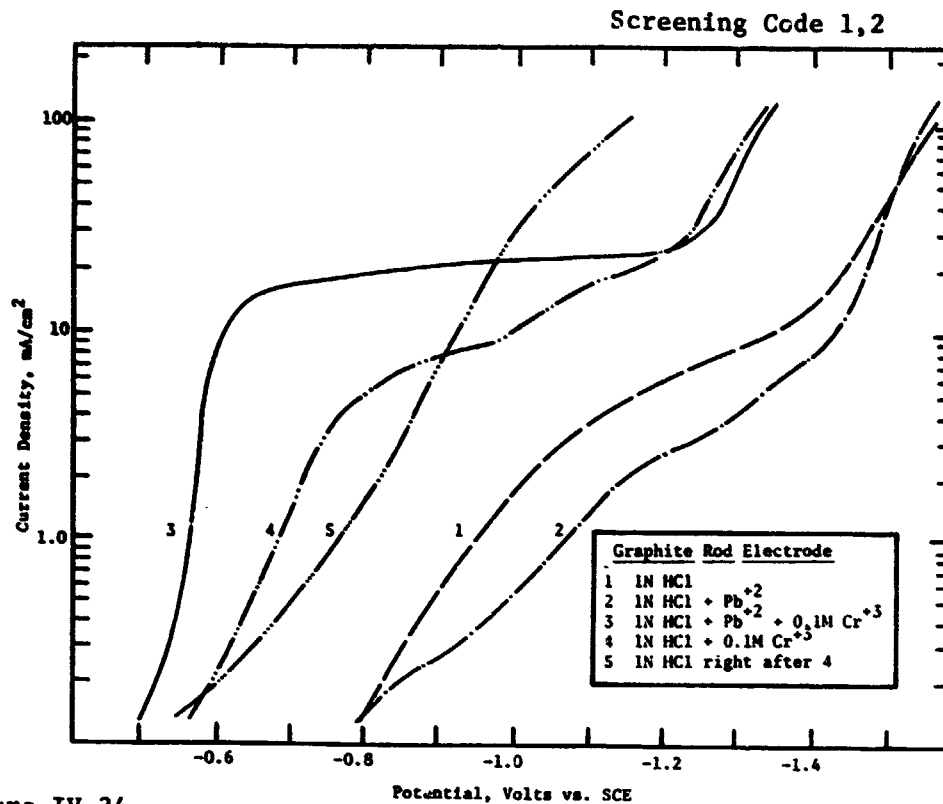


Figure IV-34

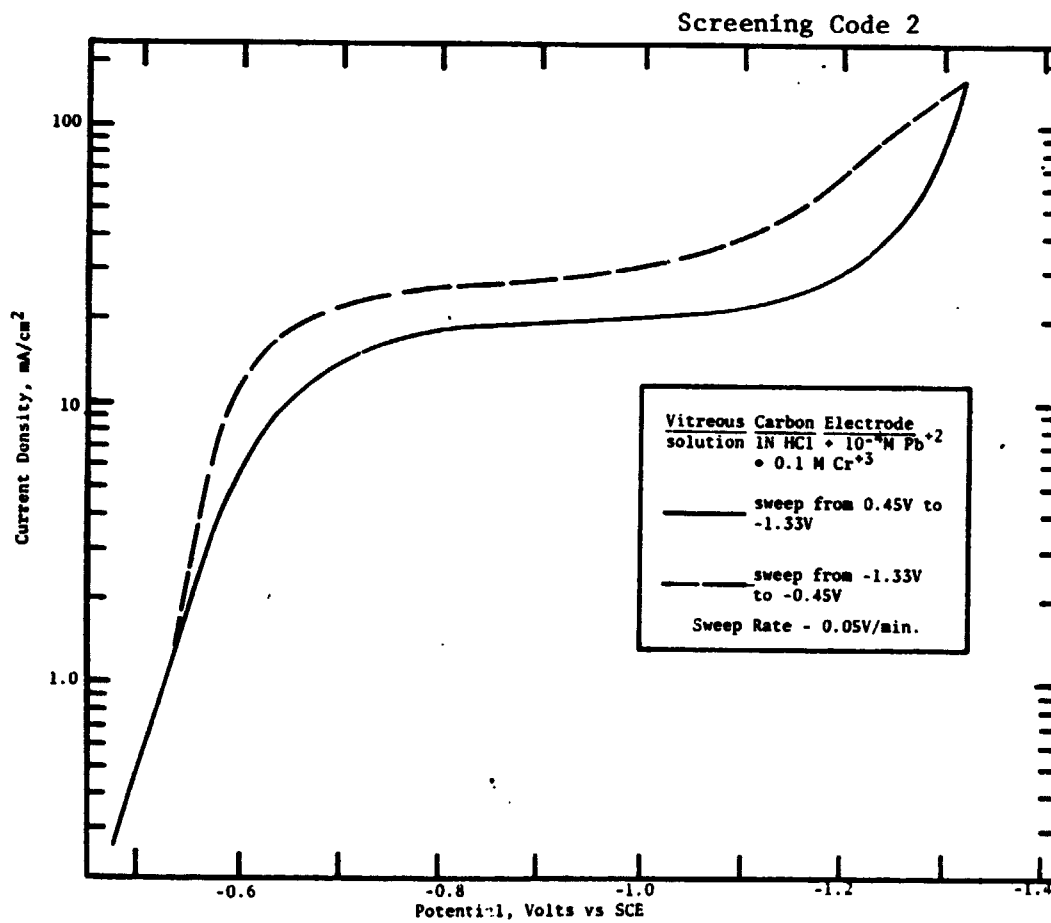


Figure IV-35

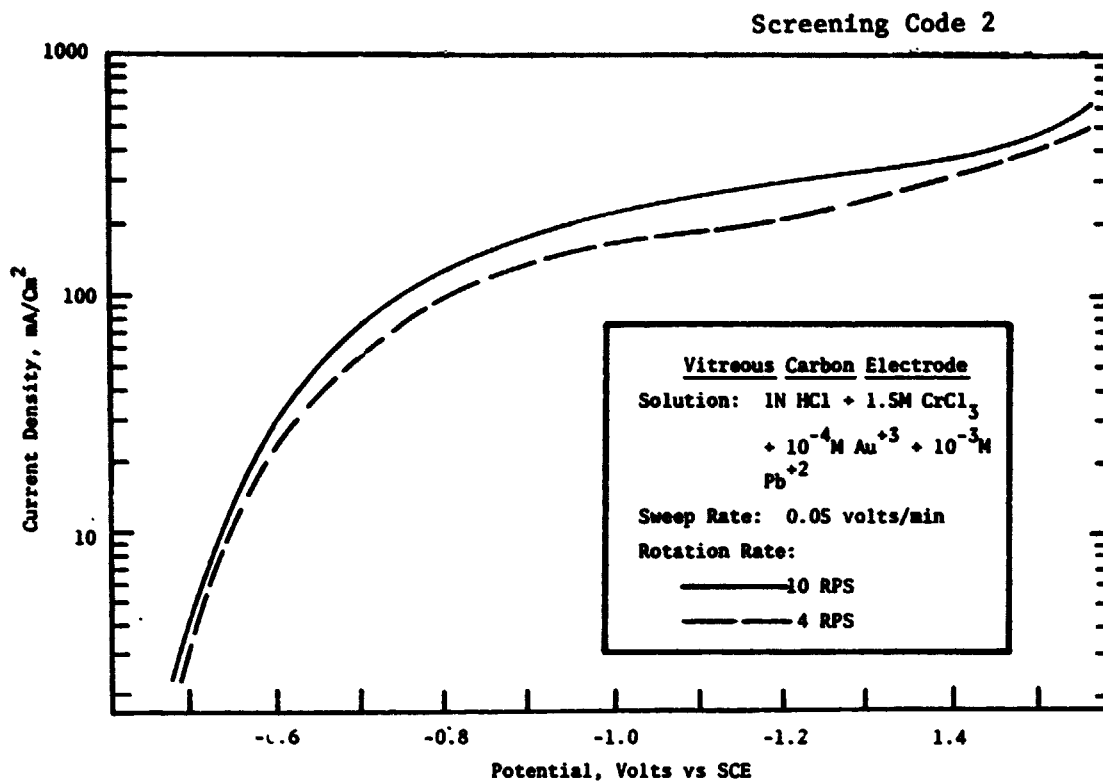


Figure IV-36

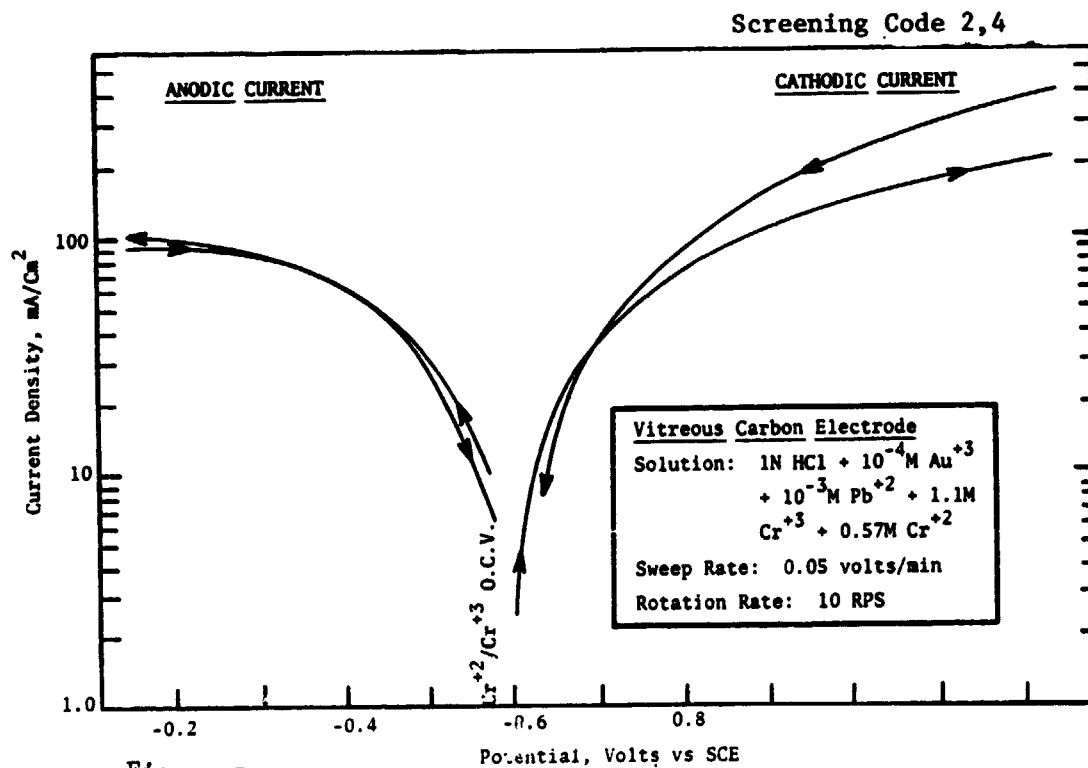


Figure IV-37

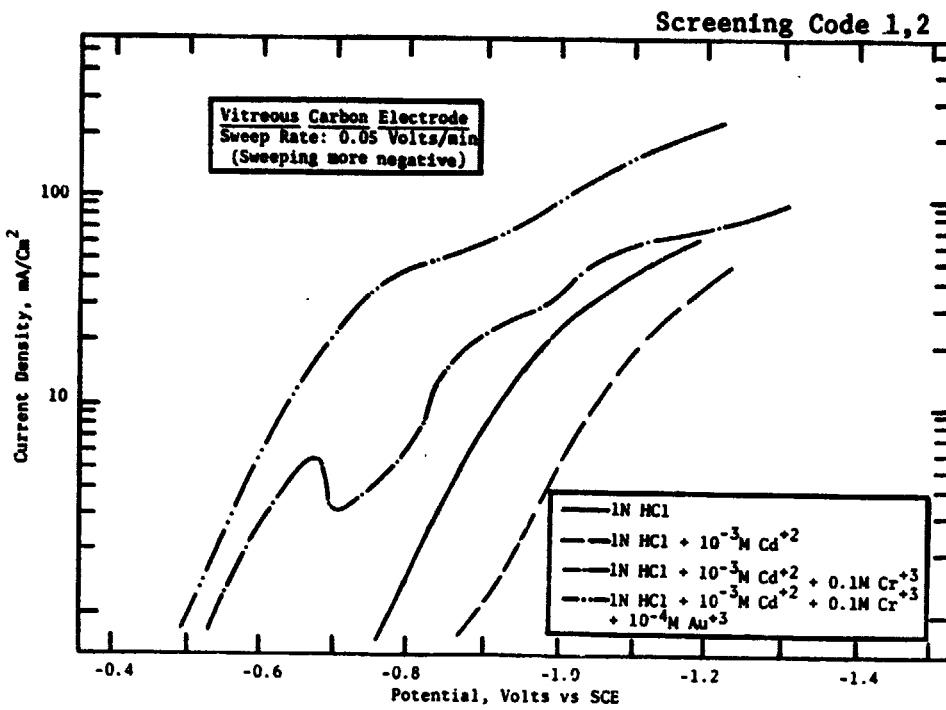


Figure IV-38

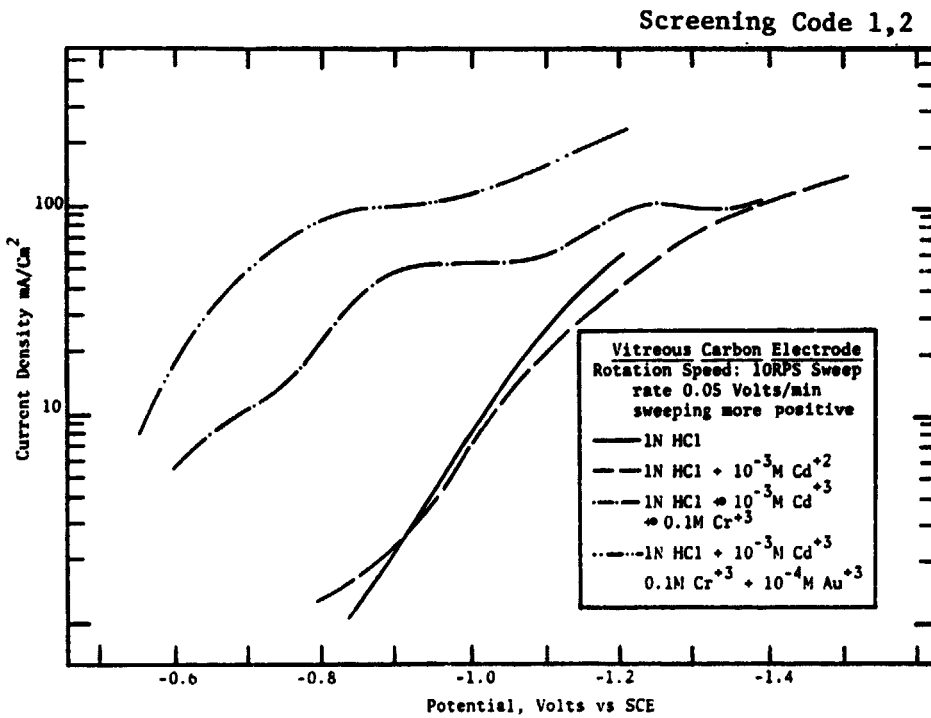


Figure IV-39

Screening Code 2,3,4

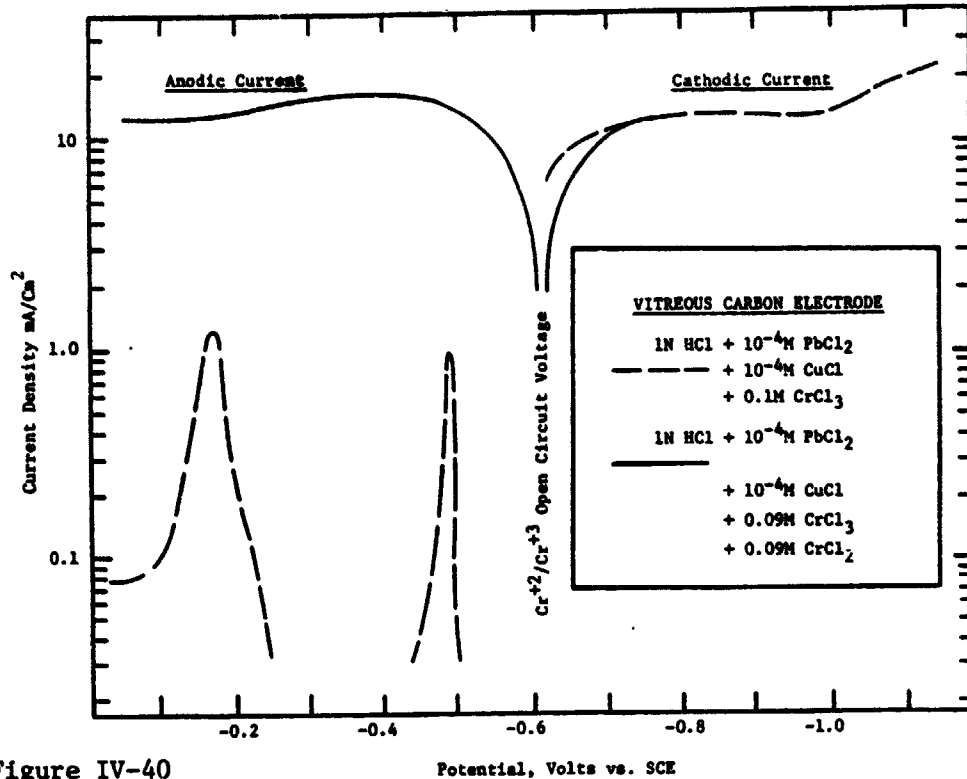


Figure IV-40

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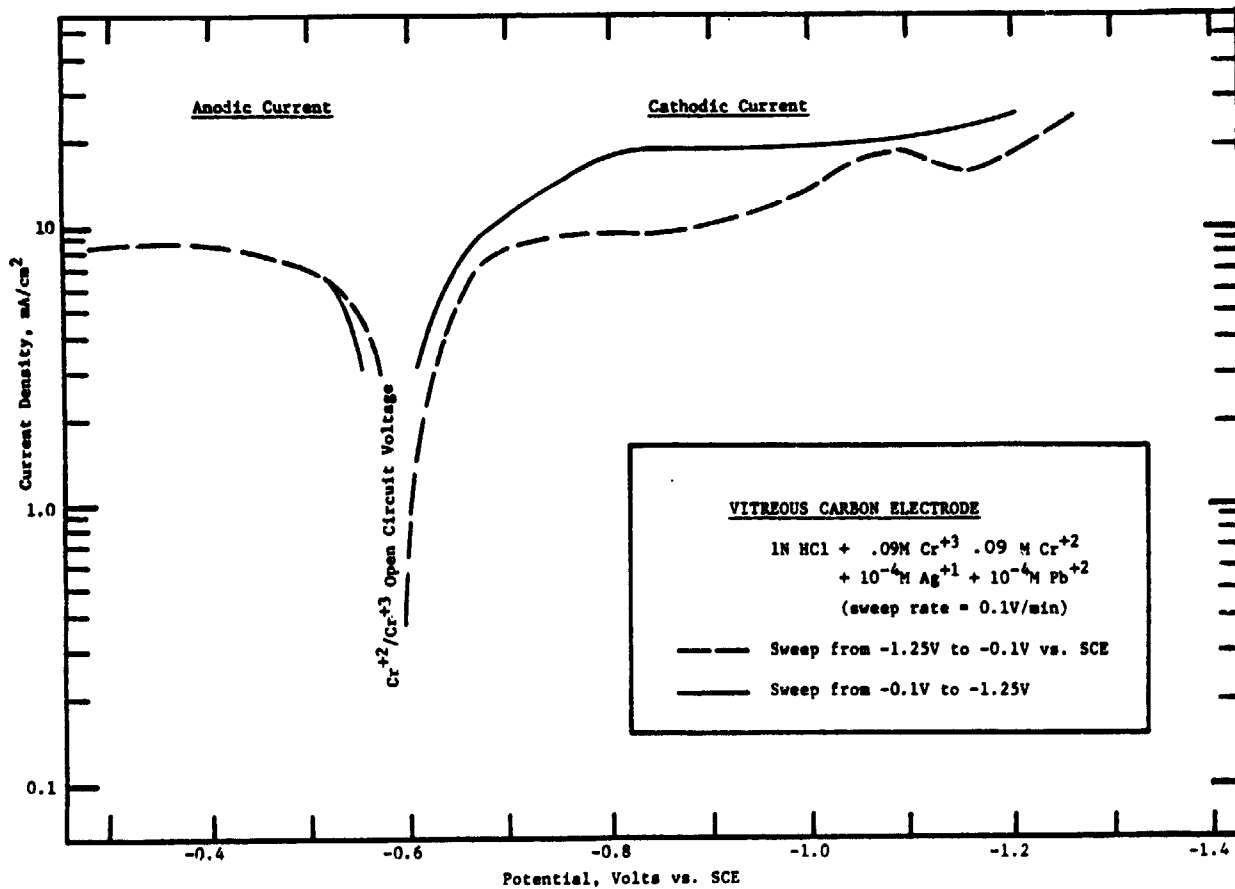


Figure IV-41



Screening Code 1,2

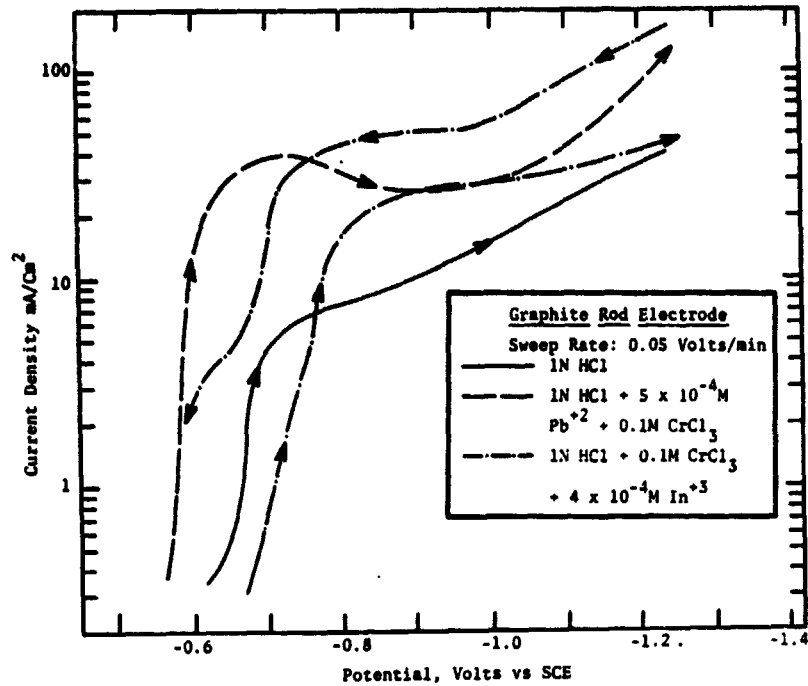


Figure IV-42

Screening Code 2,4

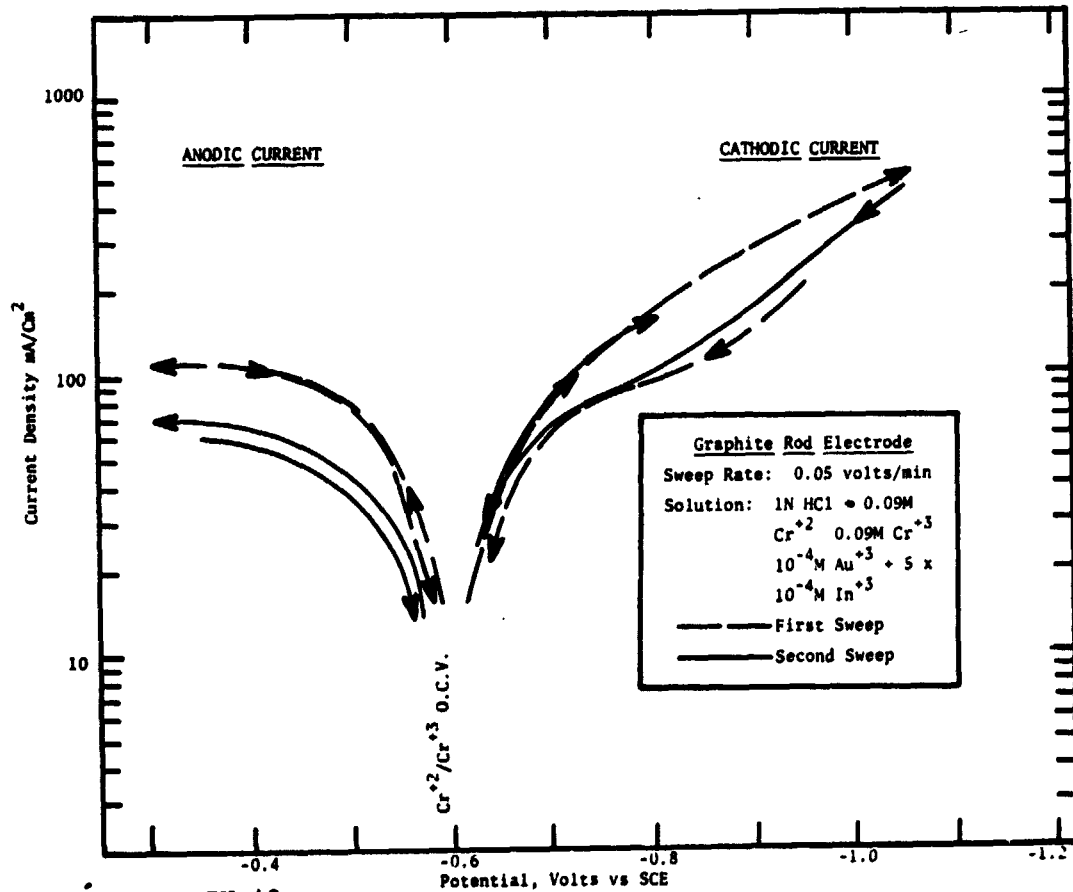


Figure IV-43

Screening Codes 2, 4

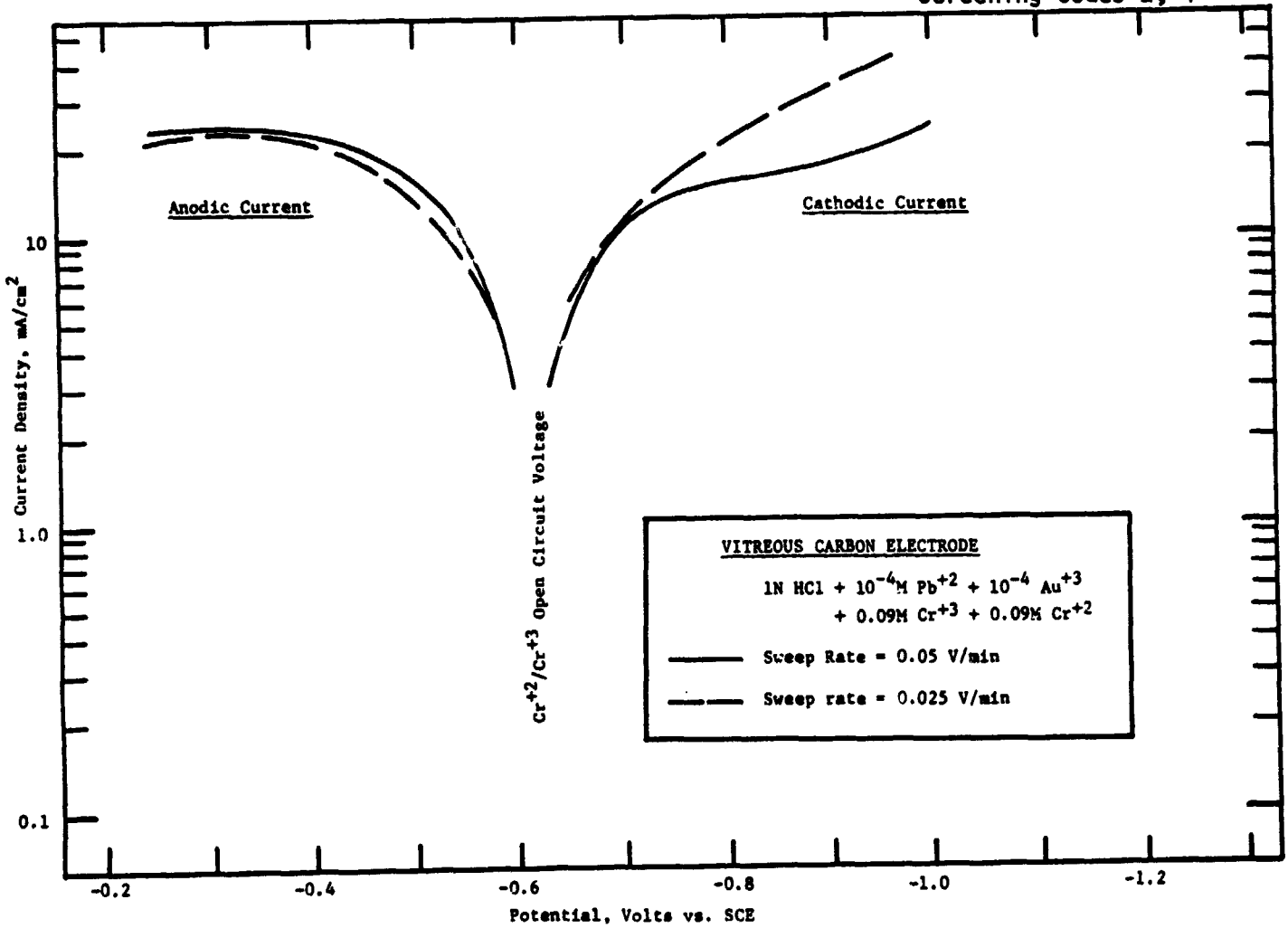


Figure IV-44

## V. EVALUATION OF DISSOLVED ORGANIC COMPOUNDS AS HYDROGEN EVOLUTION INHIBITORS

### A. Introduction

Five organic compounds mentioned by Vetter<sup>(6)</sup> as hydrogen evolution inhibitors were tested with the objective of thereby increasing the number of suitable electrocatalysts. The organic inhibitors considered were thiourea, palmitic acid, cetyl alcohol, hexanol and n-propanol.

### B. Experimental Results

The first material to be tested was thiourea. Solutions of  $10^{-x}$  M thiourea ( $x = 1, 2, 3, 4, 5$ ) in 1N HCl were prepared. As shown in Figure V-1, concentrations above  $10^{-4}$  M enhanced hydrogen evolution. Solutions containing  $10^{-4}$  and  $10^{-5}$  M thiourea in 1N HCl and 0.1M  $\text{CrCl}_3$  were tested. The addition of thiourea at these levels had virtually no effect on the gold electrode.

The work reported in the literature on palmitic acid was performed in 6N HCl. In attempting to prepare a  $10^{-3}$  M solution, we found palmitic acid (as in the case with most aliphatic carboxylic acids) to be virtually insoluble. Upon testing the solution, which was less than  $10^{-3}$  M palmitic acid, we found that hydrogen evolution was only slightly enhanced as shown in Figure V-2.

We attempted to study the effect of cetyl alcohol addition to a solution of 0.1M  $\text{CrCl}_3$  in 1N HCl containing  $\text{PbCl}_2$  and  $\text{AuCl}_3$ . The purpose was to see if the onset of  $\text{H}_2$  evolution on the gold-lead plated electrode would be altered by the presence of the cetyl alcohol. We found that cetyl alcohol did not measurably dissolve. Consequently, the current-potential curves showed no discernible change. The cited use of this inhibitor was in 6N HCl, and we suspect that a stronger acid than we employed is required to solubilize cetyl alcohol.

A similar experiment was conducted with hexanol as was performed with cetyl alcohol. The solubility of hexanol also appears to be quite low. When  $\sim 10^{-4}$  M hexanol was added, no effect on  $\text{H}_2$  evolution was observed.  $10^{-3}$  M hexanol also did not show any effect. Upon addition to the cell of an amount of hexanol which would exceed its solubility, it was noted that the electrode appeared to be

poisoned, and the chromic ion reaction was suppressed.

Finally, an experiment was performed to determine whether the addition of n-propanol would have any effect on the hydrogen evolution characteristics of a carbon electrode plated with gold and lead and acting as a catalyst for chromic ion reduction. Linear potential sweeps were applied at a rate of 100 mV/min and limiting currents were observed. The solutions that were tested were 1N HCl +  $10^{-4}$  M  $Pb^{2+}$  +  $10^{-4}$  M  $Au^{3+}$  + 0.1M  $Cr^{3+}$  and the same solution with additions of  $10^{-4}$  M n-propanol and  $10^{-2}$  M n-propanol. We did not observe any change in the hydrogen evolution characteristics of the electrode with the addition of n-propanol. With this experiment the solution used was freshly prepared, and there did seem to be a problem with plating occurring. We have noticed this before with plating solutions and feel that more investigation into plating could be quite beneficial for future study.

#### C. Recommendations

Based on the work done so far, a useful hydrogen evolution inhibitor has yet to be identified.

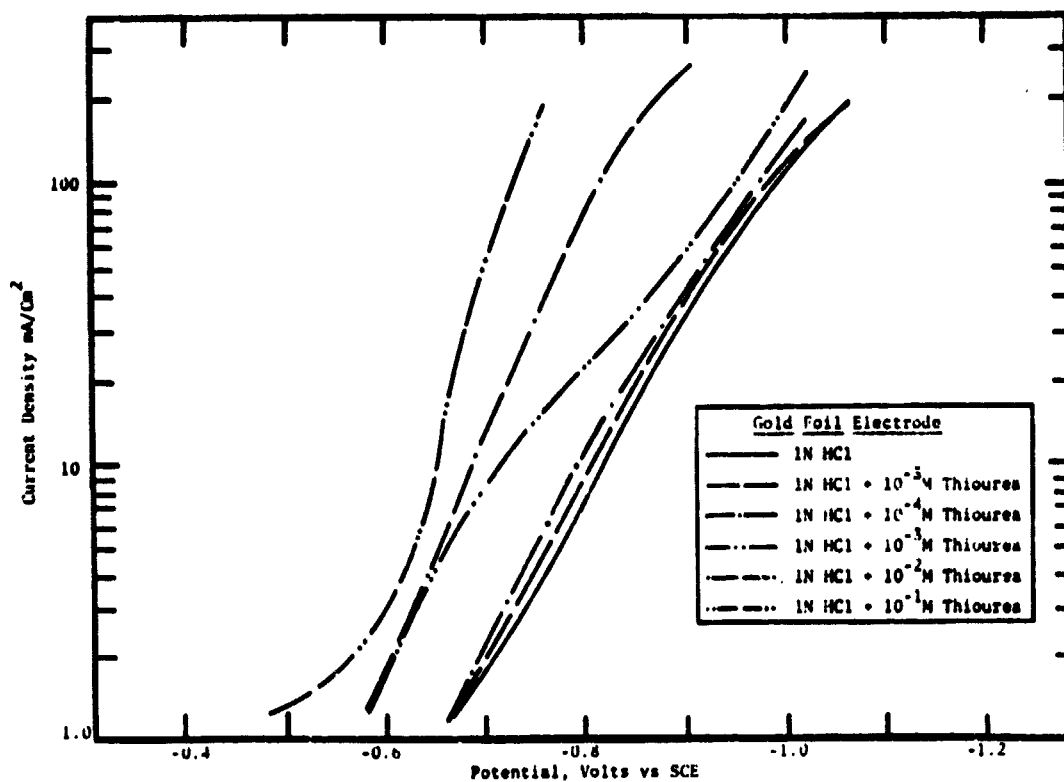


Figure V 1

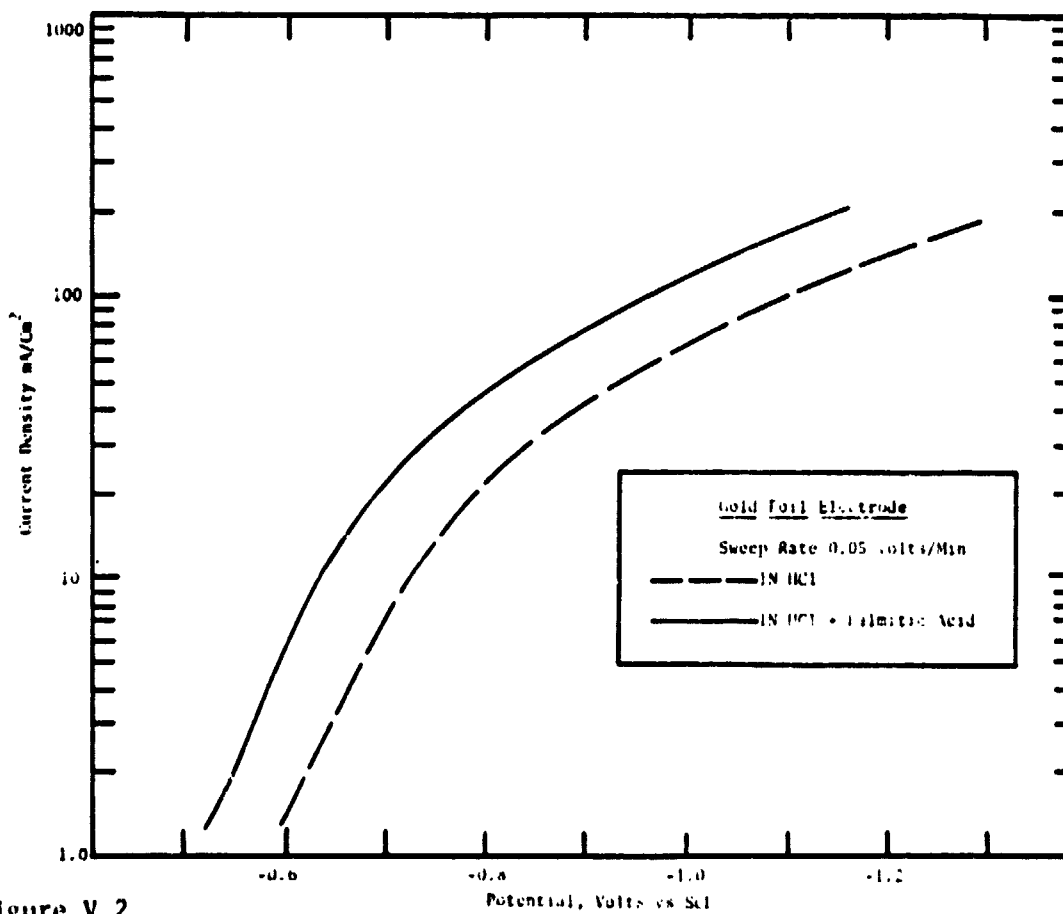


Figure V 2

VI. PRELIMINARY COST ANALYSIS OF CHROMIUM CHEMICALS

A. Discussion

Some preliminary cost information was obtained under this contract. The results are presented in Table I. The (dollar per pound) price of large lots of the various chromium chemicals listed was obtained from Chemical Marketing Reporter. The price of chromium metal was quoted by Union Carbide Corp., Metals Div., Marietta, Ohio. The prices were converted to the units dollar per pound of chromium in order to facilitate comparisons.

TABLE VI-1

COST OF COMMON CHROMIUM COMPOUNDS  
(large quantities)

	<u>\$/lb</u>	<u>\$/lb Cr</u>
Potassium Chromate $K_2CrO_4$ (194.2)	.57	1.90
Potassium Dichromate $K_2Cr_2O_7$ (294.19)	.48	1.36
Potassium Chromium Sulfate $KCr(SO_4)_2 \cdot 12H_2O$ (499.41) Potash Chromium Alum	.24	2.79
Sodium Chromate $Na_2CrO_4$ (252.05) Tetrahydrate	.32	1.55
(161.97) Anhydrous	.39-.43	1.21-1.34
Sodium Dichromate $Na_2Cr_2O_7 \cdot 2H_2O$ (298)	.37	1.06
Ammonium Dichromate $(NH_4)_2Cr_2O_7$ (252.06)	.78	1.89
<b>Lead Compounds:</b>		
Chrome Yellow $PbCrO_4$ (323.18)	.83	5.16
Chrome Orange $Pb_2(OH)_2 \cdot CrO_4$ (564.39)	.83-.89	9.01-9.66
Chrome Green $Fe_4(Fe(CN)_6) \cdot PbCrO_4$ (758)	1.36	19.83
Chromium Fluoride $CrF_3$ (108.99)	.81	1.70
Chromium Oxide Green $Cr_2O_3$ (151.99)	2.10	6.14
Zinc Chromate $ZnCrO_4$ (233.36)	1.00	4.49
Chromium Cr (52.00)	2.99	2.99

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