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Application of electrocatalysis of anodic oxygen-transfer reactions: development of a coulometric method for the determination of chemical oxygen demand

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Application of electrocatalysis of anodic oxygen-transfer reactions:
Development of a coulometric method for the determination of chemical oxygen demand

by

Kimbell Lee Pamplin

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Analytical Chemistry
Major Professor: Dennis C. Johnson

Iowa State University
Ames, Iowa
1996

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This work is dedicated to

". . . our Lord Jesus Christ,

who gave Himself for our sins,

that He might deliver us from this present evil world,

according to the will of our God and Father,

to whom be glory forever and ever. Amen."

Galatians 1:3-5

TABLE OF CONTENTS

ACKNOWLEDGMENTS

My gratitude is first expressed to my wife, Galanell. She is a kind, gentle, and strong lady without whom my life would be empty. The song says it best:

It must have been cold there in my shadow, to never have sunshine on you face.
You were content to let me shine, that's your way, you always walked a step behind.
I was the one with all the glory, while you were the one with all the strength.
A beautiful face without a name for so long, and I never once heard you complain.
It might have appeared to go unnoticed, but I've got it all here in my heart.
I want you to know I know the truth, I would be nothing without you.
Did you ever know that you're my hero, you're everything I would like to be.
I could fly higher than an eagle, for you are the wind beneath my wings.
Thank you. Thank you. Thank God for you, the wind beneath my wings.[1]

For the encouragement that began at my birth and continues to this day, I thank my parents and family. My grandfather only completed the fourth grade. My grandmother, valedictorian in high school, declined an academic scholarship for college to help at home. These people were not "educated" and yet they valued education so much that they provided for most of my education. I owe them a debt that cannot be repaid.

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---

[1] Larry Henley and Jeff Silbar, *Beaches, The Original Soundtrack Recording,* sung by Bette Middler: Atlantic 81933.

me learn how to be a successful graduate student. Dr. Jisheng Ge, Dr. Mark Jensen, John Hoekstra, Matt Johll, Natasha Popovic, and Linda Houk all made the lab a great place to work. Jianren Feng's immense practical knowledge of electrochemistry was indispensable in my pursuit of my degree. To them all, I give my thanks.

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ABSTRACT

The goal of this research is the development of a method for the coulometric determination of chemical oxygen demand (COD). Several electrochemical mediator couples are considered including Fe(III/II), Ce(IV/III), Co(III/II), Mn(III/II), Tl(III/I), Mn(VII/II), and Cr(VI/III). Of these, the Cr(VI/III) pair is chosen as the best single mediator. A Bi(V)-doped PbO_2 anode is developed that can oxidize Cr(III) to Cr(VI) with virtually 100% current efficiency. The Bi(V)-doped PbO_2 electrode is optimized and characterized using scanning electron microscopy (SEM) studies of the electrode surface, cyclic voltammetry at a rotated disk electrode, and chronoamperometry. The most efficient anode contains Bi and Pb in a ratio of 0.4 Bi:Pb based on wavelength dispersive spectroscopy. The COD of several solutions containing organic compounds is determined by both an Environmental Protection Agency approved method and electrochemically with good agreement. A process is developed by which electrochemical recycling of the COD digestion solutions occurs during determination of COD. Simultaneous digestion of glucose and coulometric determination of glucose COD is achieved with good agreement between this and literature values.

CHAPTER 1. GENERAL INTRODUCTION

Background

Electrocatalysis

Electrocatalysis describes an electrochemical reaction meeting certain conditions.[1] First, the electrode must be the reaction site. Second, the electrode must survive unchanged during the reaction. When the electrode meets these two conditions, it serves as a catalyst for charge-transfer reactions. Anodic O-transfer reactions are oxidation reactions, and, therefore, charge-transfer reactions. Thus, the term "electrocatalysis" applies to anodic O-transfer reactions. Workers in this laboratory have devoted a great amount of effort to the electrocatalysis of anodic O-transfer reactions.[2]

Anodic O-Transfer Chemistry

Anodic O-transfer chemistry is a special class of electrochemistry occurring at the positively charged electrode, the anode. It differs from other electrochemistry in that while many electrochemical reactions only involve the transfer of electrons (*e.g.*, Equation [1]), O-transfer reactions require the transfer of oxygen atoms from the water molecules to another reactant. One compound exhibiting the latter behavior is dimethyl sulfoxide (DMSO). At an appropriate electrode, DMSO is oxidized to the sulfone ($DMSO_2$) in a process involving the transfer of two electrons and an oxygen atom (*i.e.*, Equation [2]).[3]

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad [1]$$

$$DMSO + H_2O \rightarrow DMSO_2 + 2H^+ + 2e^- \qquad [2]$$

Applications

Pulsed electrochemical detection

The general goals for the application of anodic O-transfer chemistry are widespread, but this research group focuses on two general areas. The first, pulsed electrochemical detection (PED),[4] finds application in detection schemes for liquid chromatography, capillary electrophoresis, and flow injection analysis. Electrodes used in this process are typically noble metals, for example AuO/Au.

Other electrochemical oxidations

The second general area of focus in this group concerns more extensive electrochemical oxidation of organic compounds. For the anode, applications in this category typically rely on a doped metal-oxide film electrode, such as a Bi-doped PbO_2 film deposited on a Au, Pt, or Ti substrate.

Extent of reaction

The second area can be subdivided based on extent of oxidation: partial or complete. Partial oxidation leads to applications in sensors[2h] and organic synthesis.[5] Complete oxidation of organic compounds to CO_2 is a useful method for destruction of hazardous organic waste.[6] This is typically known as *electrochemical incineration.*

Location of reaction

Another way to subdivide electrochemical oxidation of organic compounds is by the location of the organic compound during the reaction. Direct oxidation[7] describes the process when the organic compound must diffuse to the electrode and react at the electrode surface. However, often the organic compound is not electrochemically active. This means that even though the electrode potential is well above the thermodynamic threshold necessary for oxidation of the compound, little or no reaction is observed due to the extremely slow kinetics involved.[6] In this case, a mediator may oxidize the organic compound in a process called indirect oxidation.[6]

Chemical mediators. A mediator in this context is a chemical that may exist in at least two forms or states: the oxidized and reduced states. In the oxidized state, the mediator must be a strong oxidant, capable of oxidizing many compounds partially or completely. Equation [3] is an example of a reaction between a mediator in its oxidized

$$4Cr_2O_7^{2-} + C_6H_{12}O_6 + 32H^+ \rightarrow 8Cr^{3+} + 6CO_2 + 22H_2O \qquad [3]$$

state, $Cr_2O_7^{2-}$, and the organic compound glucose. In its reduced form, the mediator must be electrochemically active so that it can be regenerated at the electrode, as in Equation [4]. Figure 1 illustrates the mediation process.

$$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \qquad [4]$$

Oxygen transfer in Cr(III) oxidation. The reaction shown in Equation [4] is believed to be an O-transfer reaction because of the mechanistic pathway the reaction apparently follows. This reaction probably occurs via a mechanism in which O, as an adsorbed hydroxy radical $\cdot OH_{ads}$, is immobilized temporarily at the electrode surface. This labile species then reacts with the other reactant species to form the oxidized product. In the case of Equation [4], that product is $Cr_2O_7^{2-}$.

Electron transfer in Cr(III) oxidation. It should be noted, however, that the Cr(III) oxidation reaction can be written in such a way that no O atoms are transfered at all. Instead of a reaction in which O atoms are tranferred to the Cr^{3+} species, the oxidation of Cr^{3+} might simply involve transfers of electrons, protons, and water molecules away from two hydrated Cr^{3+} ions as in Equation [5]. This reaction would not

$$2[Cr(H_2O)_6]^{3+} \rightarrow Cr_2O_7^{2-} + 5H_2O + 14H^+ + 6e^- \qquad [5]$$

require the O-transfer mechanism described above. Work to address the question of these two possible pathways is being considered.

Oxygen Demand Analysis

The particular focus of this research is the use of anodic O-transfer chemistry to efficiently regenerate the oxidized form of a mediator for use in a chemical oxygen demand (COD) apparatus. Some background of the COD determination is appropriate.

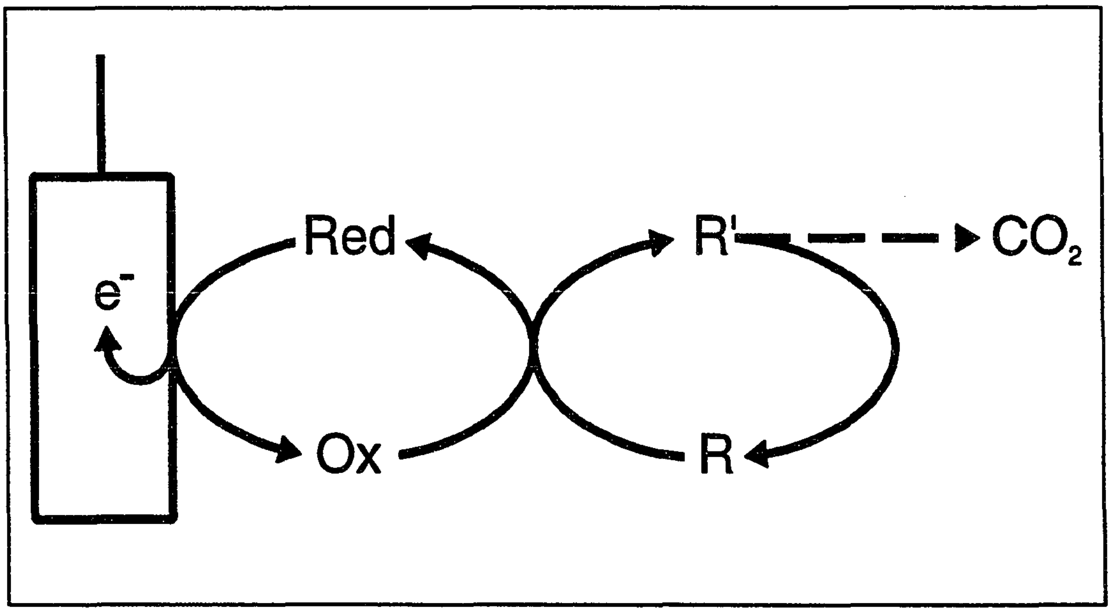

Figure 1. Mediated electrochemical oxidation. Ox/Red = Ce(IV/III), Mn(VII/II), Mn(III/II), Cr(VI/III), Co(III/II), etc.

Biological oxygen demand

Industrial effluents can significantly impact the well-being of the environment. These effluents can change the dissolved O concentration in natural bodies of water. Since the health of a natural water system depends on dissolved O, a decrease in dissolved O concentrations can have detrimental effects on the ecosystem. Effluents can be analyzed to determine their effect on dissolved O concentration using the biological oxygen demand (BOD) test. This test gives an accurate assessment of effluent's effect on the ecosystem, but it is time consuming, requiring days to complete.

Chemical oxygen demand

The COD test has one distinct advantage over the BOD test: the COD test is faster, requiring hours rather than days. In exchange for the speed, however, the COD test gives up some accuracy. Still, the determination of COD can result in a reasonable estimate of the BOD. The standard methods for the determination of COD use $Cr_2O_7^{2-}$ as a strong oxidizing agent to oxidize organics in a sample solution, ideally to CO_2. In the process, $Cr_2O_7^{2-}$ is reduced to Cr^{3+} that is subsequently determined using either a titrimetric or colorimetric procedure.[8] The $[Cr^{3+}]$ can then be related to the amount of O_2 that the sample would consume in an ecosystem. Two pitfalls of current COD methods are: (i) the expense of obtaining fresh dichromate solution and (ii) the expense and hazards of the disposal of waste dichromate, a carcinogen.

Coulometric determination of chemical oxygen demand

Development of a coulometric method to analyze COD samples is the focus of the fourth chapter. The goal of this method is the determination of COD while simultaneously regenerating the oxidant. This could eliminate the need for regular dichromate purchases and disposals associated with the COD test. In addition, the complete apparatus could be constructed in a small space, perhaps 10 dm^3 or less. This relatively small size would allow it to be easily portable and suitable for convenient field analysis and space travel.

Dissertation Organization

This dissertation is composed primarily of papers submitted to or accepted by journals. Each of these papers takes the form of a single chapter in this dissertation, those being chapters three and four. In addition to these papers, chapter two contains some supplementary work not submitted to a journal. Chapters one and five are a general introduction and general conclusions, respectively.

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CHAPTER 2. COMPARISON OF MEDIATOR CANDIDATES AS THE BASIS FOR A COULOMETRIC METHOD TO DETERMINE CHEMICAL OXYGEN DEMAND

Introduction

Chemical oxygen demand

The determination of chemical oxygen demand (COD) has been the subject of much research since its introduction several decades ago. The specific goals of these studies vary from more complete oxidation,[1] to elimination of interferences,[2] to speed and automation.[3] A requirement for fresh new chemicals with each analysis has remained constant through each of these studies. In addition to this requirement, the standard chemical oxidant currently used for the COD analysis in the United States is $Cr_2O_7^{2-}$, a carcinogen. That this chemical is hazardous and requires special disposal procedures adds to the total cost of the analysis. These requirements translate to a significant investment of money for each analysis.

In addition to the monetary aspect, the requirements of fresh chemicals for each analysis and disposal following each analysis make the possibility of on-site field analysis a rather bulky proposition. The weight and volume of materials required for repeated analysis make the possibility for routine analysis in space, *e.g.*, a mission to Mars, remote at best.

Coulometric chemical oxygen demand

Research described here is motivated by the goal of a self-contained reusable COD apparatus suitable for applications such as on-site field analysis and space travel. The apparatus should recycle the digestion solution so that fresh chemical oxidant is needed rarely. This goal may be achieved by an indirect coulometric method for determination of COD. While a direct method would be ideal and thermodynamically possible, kinetic limitations preclude this approach.

Mediator considerations

Oxidizing strength. For an indirect method, the choice of mediator is of central importance to the goal of automating the COD determination. Three criteria determine the effectiveness of a redox pair as a mediator for COD. The first requirement of a mediator is that it must be a powerful oxidizing agent in its oxidized state. It can be shown using thermodynamic data that virtually all organic compounds should be oxidized completely to CO_2 at potentials near 0 V *vs.* SCE or below. With this in mind, any oxidizer with a standard reduction potential near 1.0 V *vs.* SCE or larger should be more than sufficient as a COD oxidant.

Stability. The second requirement concerns the oxidant's ability to oxidize water. Any oxidant capable of driving this reaction with a significant rate would be unstable over the long term. More importantly, an oxidant capable of oxidizing water would be inefficient in transferring charge from the electrode and O to the organic analytes of interest.

Electrochemical activity. Third, the COD mediator must be anodically active in its reduced state. Furthermore, the coulometric determination of COD would be most accurate if the electrochemical oxidation of the mediator proceeds with 100% current efficiency. To achieve this, the potential at which the mediator is oxidized at the anode must be below the potential at which water is oxidized to form molecular oxygen (Equation [1]).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad [1]$$

Table 1 lists several strong oxidants with their reduction reactions and standard reduction potentials. Each of the redox pairs listed appear to have some promise with regard to meeting the three requirements listed above, and so deserve further scrutiny.

Possible mediators

Fe(III/II). Based on the criteria listed above, Fe(III/II) could be the ideal choice of mediator. Iron is cheap, non-toxic, already in the environment, and easily oxidized at common electrodes. Unfortunately, Fe(III) has been shown to be a poor oxidizer in some circumstances, *e.g.* in the mediated oxidation of ethylene glycol.[4] For this reason, the Fe(III/II) redox pair was not selected for further study.

Table 1. Standard reduction potentials[5] for various mediator redox pair candidates.

Mediator Reduction Reaction		E° (V vs. NHE)
$Co^{3+} + e^- \rightarrow Co^{2+}$		1.842
$Mn^{3+} + e^- \rightarrow Mn^{2+}$		1.51
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$		1.491
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	(1M H_2SO_4)	1.4430
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$		1.33
$Tl^{3+} + 2e^- \rightarrow Tl^+$		1.247
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	(1M H_2SO_4)	0.61

Ce(VI/III). Cerium (III) is also easily oxidized at common electrodes and is less hazardous than Cr(III/VI). In fact Ce(IV) has been proposed as a COD oxidant by Korenaga *et al.*[6] However, Ce(IV) does not compare well with Cr(VI) in the extent of oxidation achieved.[6] In addition, Ce(IV) is not stable over long periods of time due to self decomposition.[6] These disadvantages were sufficient to dismiss the Ce(IV/III) redox pair from this study.

Co(III/II). Cobalt(III) is a very strong oxidant. In fact, it is so strong that it is unstable with resepct to the oxidation of water. Cobalt(III) can be stabilized somewhat by dissolving it in sulfuric acid (≥ 3M) but it must be considered unstable over long periods of time. For this reason, the Co(III/II) redox pair was removed from consideration.

Mn(III/II) and Tl(III/I). The Mn(III/II) and Tl(III/I) may well prove to be excellent candidates for the purpose at hand, but much less is known about these systems than those of the more common oxidizers. For this reason, these may be investigated more extensively in future research. One certain disadvantage of the use Tl(III/II) redox pair is extreme toxicity of Tl.

Mn(VII/II) and Cr(VI/III). Both Mn(VII) and Cr(VI) are powerful oxidizing agents, as indicated by the large standard reduction potentials given in Table 1, and these compounds have been used frequently for oxidation of organic compounds.[7] In the United States, the standard method for determination of COD in organically polluted waters utilizes Cr(VI) with back titration of excess oxidant using a standard solution of Fe(II) or colorimetric determination of excess oxidant.[8] Since these two oxidizers are routinely used for COD determinations, they were chosen for further investigation.

Electrode choice

LaCourse *et al.*[9] first investigated the oxidation of Mn(II) to Mn(VII) at a Bi-doped PbO_2 electrode. They concluded that when Bi(III) was incorporated into the PbO_2 surface, the heterogeneous rate constant for the anodic oxidation of Mn(II) was increased by a factor greater than 25 times over that at Bi-free PbO_2. Yeo and Johnson[10] reported amperometric data that demonstrated Mn(II) can be oxidized to Mn(VII) at transport-limited rates at rotated Bi(V)-doped β-PbO_2 film electrodes in acidic media. Chang and Johnson[11] reported the catalyzed oxidation of Cr(III) to Cr(VI) at a PbO_2 upon addition of Bi(III) to the Cr(III) solution. Therefore, Bi(V)-doped PbO_2 electrodes were chosen for investigation in this research for anodic production of Mn(VII) and Cr(VI) in 1.0 M H_2SO_4. This chapter examines the possibility of Mn(VII) as an electrochemically generated mediator for COD analysis.

Experimental

Chemicals

All chemicals were analytical reagent grade from Fisher Scientific, Alfa Products, or Aldrich Chemicals. Water was distilled and purified further by passage through a NANOpure-II system (Barnstead).

Electrodes

A gold rotated disk electrode (RDE, 0.196 cm^2; Pine Instrument Co.) was used to obtain all voltametric data. A saturated calomel electrode (SCE, Fisher Scientific) provided the reference potential for all voltammetric experiments and all potential values are given *vs.* the SCE. The counter electrode was a coiled Pt wire (*ca.* 7 cm^2).

Deposition of Bi(V)-doped β-PbO_2 films followed procedures described previously.[11-12] These films, designated as "Bi-PbO_2/Au", were deposited on the Au RDE under quiescent conditions at 1.7 V in 1.0 M $HClO_4$ containing 10 mM $Pb(NO_3)_2$ and 0 to 20 mM $Bi(NO_3)_3 \bullet 5H_2O$ for up to 5 min.

The Bi-PbO_2 films were dissolved from the metal substrates by immersion for several minutes in a 50/50 mixture of glacial acetic acid and 30% hydrogen peroxide solution. The Au RDE was polished after removal of Bi-PbO_2 films using Buehler Microcloth with alumina slurries (1.0 µm, 0.3 µm, 0.05 µm; Buehler).

All Pb(II) and Bi(III) compounds are *toxic* substances. Therefore, waste solutions containing these metals were disposed according to accepted procedures.

Instrumentation

Voltammetric procedures have been described.[13] The Au RDE was used with a model MSRX rotator and speed controller (Pine) and a model RDE-4 bipotentiostat (Pine).

Results and Discussion

Voltammetric response of Mn(II)

Figure 1 contains current-potential (*i-E*) curves obtained by cyclic voltammetry at a Bi-PbO_2/Au RDE in 1.0 M H_2SO_4 with (curves B-D) and without (curve A) the presence of 10 mM Mn(II). This Bi-PbO_2 film was deposited from a solution containing [Bi(III)]/[Pb(II)] = 4 mM/10 mM, *i.e.*, Bi(V)/Pb(IV) = *ca.* 0.4 in the film. In the presence of Mn(II) (curve B), the anodic current far exceeds the residual current (curve A) as a

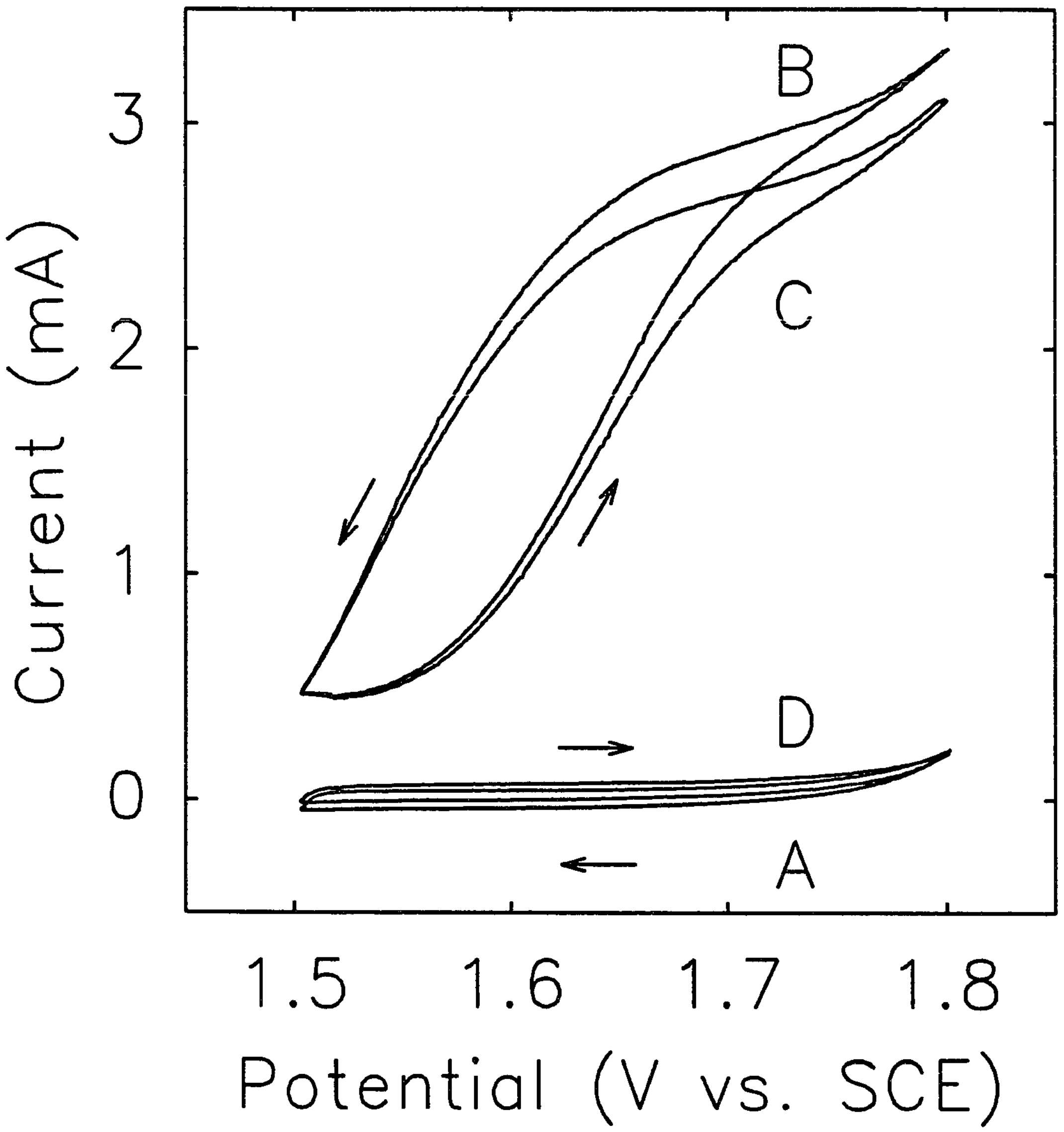

Figure 1. Cyclic voltammetric response for Mn(II) at a Bi-PbO$_2$/Au rotated disk electrode in 1.0 M H_2SO_4. Curves: (A) residual, (B - D) 10 mM Mn(II). Time: (B) 0 min, (C) 30 min, (D) 5.5 h. Electrodeposition of Bi-PbO$_2$: [Bi(III)]/[Pb(II)] = 4 mM/10 mM.

result of the oxidation of Mn(II). With continued application of the cyclic potential scan, the solution developed a purple color distinctly indicative of the presence of MnO_4^- and, in agreement with Yeo and Johnson,[10] this is concluded to be the product of Mn(II) oxidation at the Bi-PbO_2 electrode in this acidic medium. After 30 min of continuous scanning (curve C), the current is decreased by *ca.* 15% from its initial value (curve B). However, during this same time period, only 1% of the Mn(II) would be converted if the anodic current remained constant at the initial value (3 mA) shown in curve B for 1.7 V. Hence, the decrease in anodic response with time is a consequence of the partial deactivation of the electrode surface. After 5.5 h of repeated cyclic scans of the electrode potential, the anodic response (curve D) has returned nearly to the residual response (curve A). By this time, the solution no longer had the distinct MnO_4^- color and, instead, the dark brown color of MnO_2(s) was evident on the walls of the electrolysis cell. Visual examination of the electrode surface also revealed that its color had changed from the deep black color of Bi-PbO_2 to the brown color of MnO_2(s). Therefore, the loss of electrode activity demonstrated by curve D is concluded to be a consequence of the accumulation of the noncatalytic MnO_2(s) on the surface of the Bi-PbO_2 electrode.

Previous Mn(II) research

LaCourse *et al.*[9] also reported short lifetimes for the catalytic activity of the Bi-doped PbO_2 film electrodes when used in the anodic oxidation of Mn(II). During long term potentiostatic coulometric experiments, the Mn(II) solution quickly turned purple, characteristic of Mn(VII) production. However, "the current dropped off faster than would be predicted on the basis of electrolytic depletion of the reactant."[9] This loss in electrocatalytic activity was explained on the basis that fast electrocatalyzed O-transfer reactions deplete Bi(V) from the surface of the electrode: chemical corrosion. In addition, formation of MnO_2(s) within film pores seemed to cause instability in the film. Larew *et al.*[14] later speculated that MnO_2(s) formed at the electrode surface in LaCourse's experiments was due to an insufficiently catalyzed reaction. Chang[15] later showed that the lifetime of Bi-PbO_2 for Mn(II) oxidation could be extended nearly twofold if a small amount of Bi(III) was added to the solution containing Mn(II).

Thermodynamic considerations

Data presented in Figure 1 are apparently consistent with the conclusion that Mn(II) is oxidized at least partially to MnO_2(s), which then fouls and deactivates the electrode surface. It is now believed, however, that electrochemical oxidation of Mn(II) to MnO_2(s) at the electrode surface is virtually non-existant. Data presented here indicate that MnO_2(s) results only from the chemical reaction between Mn(II) and Mn(VII). This new conclusion is based on thermodynamic data and on the results of experiments aimed at testing this hypothesis.

The production of MnO_2(s) is predicted to occur by comproportionation in acidic mixtures of Mn(VII) and Mn(II), as indicated by:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+; \quad K_{eq} = 4.63\times10^{45} \qquad [2]$$

To test whether or not this reaction occurs at a significant rate, two solutions of 10 mM $KMnO_4$/1 M H_2SO_4 were prepared. In one of these solutions, Mn(II) was also present at a stoichiometric concentration of 15 mM. The solutions were gently stirred with a clean glass rod. The difference in color between solutions was instantly discernible. After about 5 min, the solution containing Mn(II) was dark brown, indicative of MnO_2(s) formation, while the Mn(II) free solution remained deep purple. Upon standing for several hours, most of the solid MnO_2 settled out on the bottom of the container, leaving a clearer solution above. The Mn(II)-free solution, however, remained deep purple in color.

It is believed that the potentiostatic coulometric experiment described by LaCourse *et al.*[9] amounted to titrating the Mn(II) with electrochemically generated Mn(VII). This "titration" however was incomplete due to the formation of the product, MnO_2(s), that deactivated the surface. This conclusion is consistent with previous data observed in this laboratory.

The consequence of this conclusion that Mn(II) in the presence of significant Mn(VII) forms MnO_2(s) is disastrous for the goal of using Mn(VII) as an electrochemically generated mediator. Any use of Mn(VII) as a mediator requires that it be present with Mn(II) in solution as mediation cycle occurs (see Chapter 1, Figure 1). Based on these results, no further consideration is being given to the anodic generation of Mn(VII) as the oxidation mediator in the indirect coulometric determination of COD.

Conclusions

Electrodes consisting of thin films of mixed bismuth(V)-lead(IV) oxides (Bi-PbO_2) have significantly greater activity for oxidation of Mn(II) to Mn(VII) in 1.0 M H_2SO_4 than electrodes consisting of pure PbO_2 films. However, this advantage only exists in the short term. As a significant concentration of Mn(VII) builds up, the predicted comproportionation reaction converts Mn(II) and Mn(VII) into insoluble MnO_2(s). This MnO_2(s) formation not only removes the intended mediator from solution, but it also coats the electrode with an inactive film, preventing further anodic activity.

Under certain conditions, *e.g.*, high anodic potential and PbO_2 electrode heavily doped with Bi, $C^S_{Mn(II)} = 0$ so the comproportionation reaction does not occur at the electrode surface.[16] This fact, however, does not solve the problem of the comproportionation reaction in solution, that effectively reduces the analytical concentration of Mn(VII/II) in solution to 0.

It is conceivable that Mn(VII) might still be used as a recyclable mediator if used in conjunction with a flow injection analysis apparatus. Perhaps mediator losses to MnO_2(s) could be held at insignificant levels if at one point Mn(II) is the stream is quantitatively converted to Mn(VII) and vice-versa at the digestion point. However, this possibility may not be worth the trouble in view of the many other effective COD procedures available.

Alternatively, it may be possible to use Mn(III/II) as a mediator if suitable conditions are found in which to electrogenerate Mn(III) efficiently. Some work in the electrogeneration of Mn(III) has been performed already with promising results.[17]

Acknowledgments

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CHAPTER 3. ELECTROCATALYSIS OF ANODIC OXYGEN-TRANSFER REACTIONS: OXIDATION OF Cr(III) TO Cr(VI) AT Bi(V)-DOPED PbO_2-FILM ELECTRODES

A paper accepted by the Journal of the Electrochemical Society[a]

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Abstract

Voltammetric and coulometric results are described for the electrocatalytic oxidation of Cr(III) to Cr(VI) at the mixed bismuth(V)-lead(IV) dioxide film electrodes (designated "Bi-PbO_2") that are electrodeposited from acidic solutions of Pb(II) containing Bi(III). A current efficiency of 99.2 % (σ = 1.1%, N = 12) is obtained for galvanostatic generation of Cr(VI) at a preconditioned Bi-PbO_2 film electrode. Preconditioning of the Bi-PbO_2 film merely involves the generation of Cr(VI) which, based on scanning electron micrographs, is concluded tentatively to achieve chemical stripping of non-catalytic portions of the Bi-PbO_2 films to produce films having greater electrocatalytic activity for the desired reaction. Electrochemical stripping of the Bi-PbO_2 electrode had a similar preconditioning effect. Based on wavelength dispersive spectroscopy, electrochemical stripping resulted in an increase in surface Bi concentration of 33% relative to Pb.

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Introduction

Much research in this laboratory has been directed to the electrocatalysis of anodic reactions that require the concomitant transfer of oxygen from H_2O to the oxidation product(s).[1-4] Our use of the term *electrocatalysis* is intended to imply involvement of specific surface sites within these anodic O-transfer mechanisms to increase the rate of the heterogeneous reactions. Compounds typically investigated include inorganic and organic substances that are not generally observed to be electrochemically active at the conventional anodes (Pt, Au, PbO_2 and C). Electrocatalytic activity has been substantially increased for various anodic O-transfer reactions at β-PbO_2 film electrodes that are heavily doped with various altervalent metallic ions. Anodic O-transfer mechanisms require the concomitant anodic discharge of H_2O to produce adsorbed hydroxyl radicals ($\cdot OH_{ads}$).[5] Therefore, the catalytic function of altervalent dopants in the doped metal oxide film electrodes is commonly attributed to a diminished overpotential for discharge of H_2O at the dopant sites. Furthermore, it is speculated that a moderately low surface coverage by dopant sites ($\theta < 0.5$) assures that the distance between $\cdot OH_{ads}$ species at adjacent dopant sites is sufficiently large to prevent them from combining to produce O_2, an undesirable side reaction that can diminish the current efficiency for the desired O-transfer reactions.

Publications have reported studies of the anodic oxidation of Cr(III) to Cr(VI) in the presence of various metallic cations[6-8] and organic compounds[9,10] using a wide variety of electrodes materials.[10-12] However, all reported values of the current efficiency for production of Cr(VI) are significantly below 100%.[13,14] This is the cause for needless expenditure of energy due to the evolution of O_2, a competing anodic reaction.

Chang and Johnson demonstrated that trace levels of Bi(III) (< *ca.* 10 µM) added to acidic solutions of dimethyl sulfoxide (DMSO) could result in significant electrocatalysis of DMSO oxidation to $DMSO_2$ at rotated PbO_2/Au electrodes.[4] This observation was attributed to the electrosorption of Bi(III) as Bi(V) on the pure PbO_2 surface. Chang and Johnson also observed that higher concentrations of Bi(III) (> *ca.* 10 µM) produced a momentary electrocatalytic activity followed by a loss of electrode activity.[4] This was explained by Larew *et al.* as the consequence of the formation of a monolayer of the electrosorbed Bi(V) which covered PbO_2 sites necessary for preadsorption of the DMSO.[15]

Research described here is motivated by the goal of automating the determination of ***chemical oxygen demand*** (COD) of polluted waters on the basis of an indirect coulometric procedure that utilizes an electrochemically generated oxidation mediator. Chromium(VI) is a powerful oxidizing agent, as indicated by the large standard reduction potential given by:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O;\ E^o_{Cr(VI/III)} = 1.33\ \text{V}\ vs.\ \text{NHE} \qquad [1]$$

and this compound has been used frequently for oxidation of organic compounds.[16] The standard method for determination of COD in organically polluted waters utilizes Cr(VI) with back titration of excess oxidant using a standard solution of Fe(II).[17]

Experimental

Chemicals

All chemicals were analytical reagent grade from Fisher Scientific, Alfa Products, or Aldrich Chemicals. Water was distilled and purified further by passage through a NANOpure-II system (Barnstead).

Electrodes

Deposition of Bi(V)-doped β-PbO_2 films followed procedures described previously.[15,18-20] These films, designated as "Bi-PbO_2/Au", were deposited on a gold rotated disk electrode (RDE, 0.196 cm^2; Pine Instrument Co.) under quiescent conditions at 1.7 V in 1.0 M $HClO_4$ containing 10 mM $Pb(NO_3)_2$ and 0 to 20 mM $Bi(NO_3)_3 \cdot 5H_2O$ for up to 5 min.

Deposition of films on the Pt gauze electrode (5-cm length, 4-cm diameter and ca. 126-cm^2 area, *ca.* 40 mesh woven from *ca.* 180-μm diameter wire) was achieved under potentiostatic (1.5 to 1.7 V, 5 to 20 min) or galvanostatic (50 mA for 15 to 20 min) conditions from 1 M HNO_3 or 1 M $HClO_4$ containing 0.5 M $Pb(NO_3)_2$ and 0.05 to 0.2 M $Bi(NO_3)_3 \cdot 5H_2O$. These films are designated as "Bi-PbO_2/Pt".

The Bi-PbO_2 films were dissolved from the metal substrates by immersion for several minutes in a 50/50 mixture of glacial acetic acid and 30% hydrogen peroxide solution. The Pt gauze electrode was frequently cathodized (500 mA for 10 min) which seemed to result in the best films. The Au RDE was polished after removal of Bi-PbO_2 films using Buehler Microcloth with alumina slurries (1.0 μm, 0.3 μm, 0.05 μm; Buehler).

All Pb(II) and Bi(III) compounds are *toxic* substances. Therefore, waste solutions containing these metals were disposed according to accepted procedures.

A saturated calomel electrode (SCE, Fisher Scientific) provided the reference potential for all voltammetric and potentiostatic coulometric experiments and all potential values are given *vs.* the SCE. The counter electrode was a coiled Pt wire (*ca.* 7 cm^2).

Instrumentation

Voltammetric procedures have been described.[3] The Au RDE was used with a model MSRX rotator and speed controller (Pine) and a model RDE-4 bipotentiostat (Pine). The cylindrical Pt gauze electrode was used with a coulometer, potentiostat, and power supply (Electrosynthesis Co., Inc.) for coulometric measurements. The scanning electron microscope (SEM) was a model JSM 840-A (JEOL).

Determination of current efficiency

The percent current efficiency ($\%_{eff}$) for conversion of Cr(III) to Cr(VI) was based on potentiometric titrations using 0.2 M $Fe(NH_4)_2(SO_4)_2{\bullet}6H_2O$ in 1.0 M H_2SO_4 standardized daily against reagent grade $K_2Cr_2O_7$. The Pt-gauze working electrode coated with designated films was placed in the central working chamber of a three-compartment cell. Reference and counter electrodes were placed in side-chambers separated from the working chamber by fritted glass disks (medium porosity). The working chamber was filled with 150 mL of 1.0 M H_2SO_4 containing 0.10 M $CrK(SO_4)_2{\cdot}12H_2O$ and the side chambers were filled with 1.0 M H_2SO_4. Oxidation of Cr(III) to Cr(VI) was performed galvanostatically at 100 mA, with magnetic stirring, and the total charge passed was monitored using the coulometer. The potentiostat was switched to "standby" when the charge reached *ca.* 400 C, *i.e.*, conversion of 10 % of the initial Cr(III), and the working electrode was raised above the level of the solution and rinsed with deionized water. The contents of all three chambers were quantitatively transferred to a beaker for titrimetric determination of Cr(VI). Values of $\%_{eff}$ were calculated as follows:

$$\%_{eff} \quad = \quad C_{Fe(II)}\, V_{Fe(II)}\, F\ 100\% \,/\, Q_{tot} \qquad [2]$$

where $C_{Fe(II)}$ and $V_{Fe(II)}$ are the concentration (mol L^{-1}) and volume (L) at the endpoint, respectively, of the titrant; Q_{tot} is the total charge passed (C); and F is the Faraday constant.

Results and Discussion

Voltammetric response of Cr(III)

Based on *i-E* curves (not shown) obtained at Au and Pt RDEs in 1.0 M H_2SO_4 with and without the presence of 10 mM Cr(III), it is readily apparent that, for both electrode materials, there is no significant change in voltammetric response that can be attributed to the oxidation of Cr(III).

Figure 1 contains the cyclic voltammetric curves obtained at a PbO_2/Au RDE (A,B) and Bi-PbO_2/Au RDE (C,D) in 1.0 M H_2SO_4 with (A,C) and without (B,D) the presence of 10 mM Cr(III). For both electrodes, anodic production of O_2 occurs at a significant rate for $E >$ *ca.* 1.75 V. Following the addition of Cr(III), very little increase in current is observed for the PbO_2/Au electrode (B); however, a significant increase in anodic current is observed at the Bi-PbO_2 electrode (C) in comparison to the residual response (D).

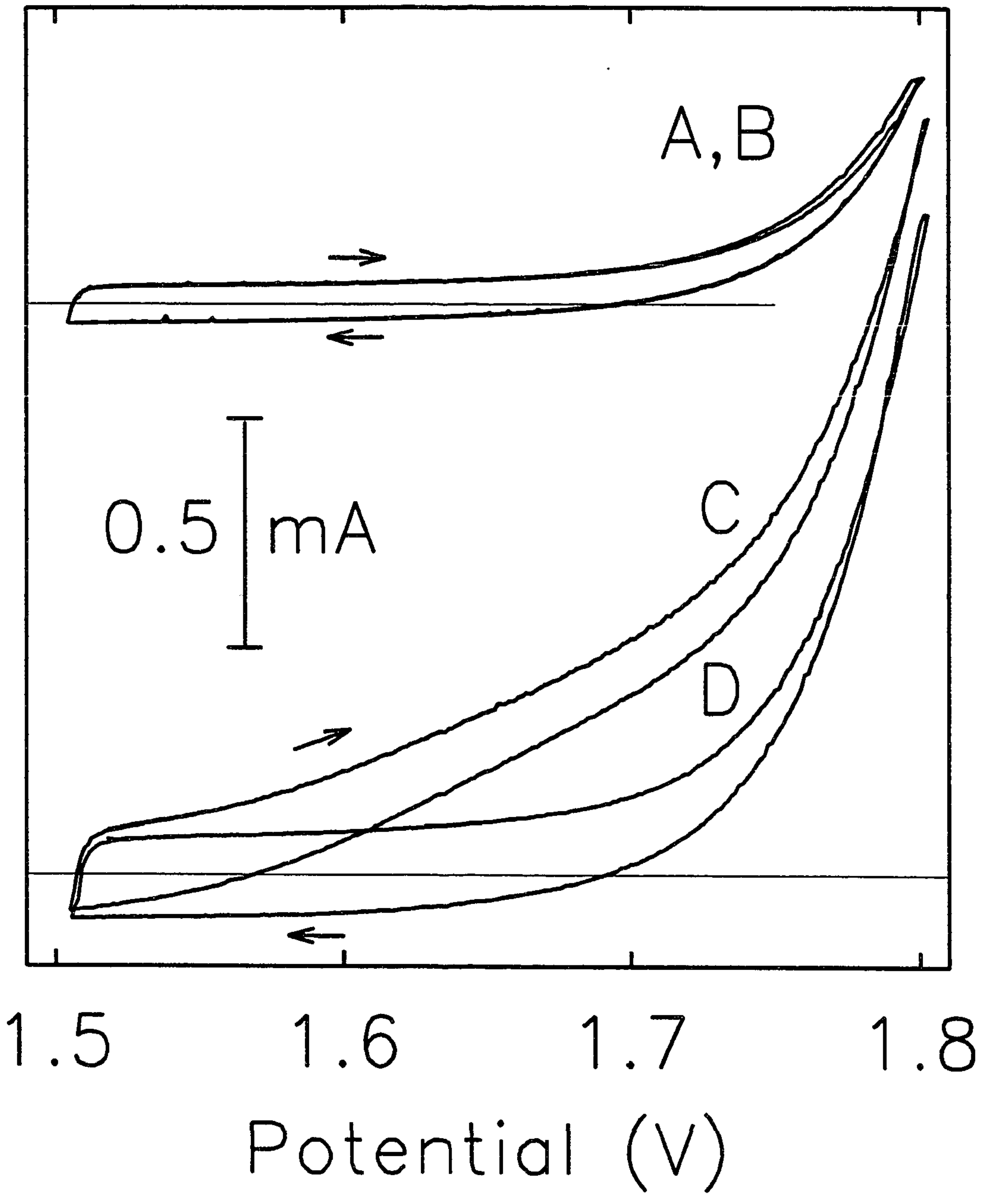

Figure 1. Cyclic voltammetric response of Cr(III) at rotated disk electrodes in 1.0 M H_2SO_4. Electrode: (A,B) PbO_2/Au, (C,D) Bi-PbO_2/Au. Concentration Cr(III) (mM): (A,C) 10, (B,D) 0. Scan rate: 20 mV s^{-1}. Rotation speed: 1600 rev min^{-1}. Electrodeposition of Bi-PbO_2: [Bi(III)]/[Pb(II)] = 4 mM/10 mM.

Variation in Bi(V) content of Bi-PbO$_2$ electrodes

Previous work has demonstrated that the ratio of Bi(V)/Pb(IV) in Bi-PbO$_2$ films is approximately equal to the ratio Bi(III)/Pb(II) in the corresponding solutions used for film deposition, provided [Bi(III)]/[Pb(II)] $\leq$ *ca.* 1.[21,22] Several different Bi-PbO$_2$ films were deposited on the Au RDE, by deposition from solutions containing 10 mM Pb(II) with a variable concentration of Bi(III), and their voltammetric response was recorded in 1.0 M H_2SO_4 containing 10 mM Cr(III). Figure 2 contains representative *i-E* curves recorded during the negative scan at four of these electrodes using a rotation speed of 1600 rev min^{-1}. In all cases, the anodic evolution of O_2 is obvious for $E > ca.$ 1.75 V. Curve D corresponds to the voltammetric response of the undoped PbO$_2$ electrode, *i.e.*, Bi(V)/Pb(IV) = 0, and this curve is virtually identical to the residual curve (not shown) obtained in the absence of Cr(III). Curves C, B and A were obtained at film electrodes corresponding to Bi(V)/Pb(IV) = 0.1, 0.3 and 0.4, respectively. No further increase in anodic current at 1.70 V was obtained for Bi(V)/Pb(IV) > 0.4. The current response in the region between 1.55 and 1.70 V is concluded to be the result of the oxidation of Cr(III) to Cr(VI). It is significant that a plateau current is not obtained for Cr(III) oxidation which is evidence for slow heterogeneous kinetics at the Bi-PbO$_2$ electrodes, *i.e.*, the reaction does not occur under purely transport-limited control at potential values for which O_2 evolution is minimal ($E > 1.75$ V). However, this fact does not preclude the possibility of 100% current efficiency for Cr(VI) production at $E < 1.75$ V.

Figure 3 contains representative *i-E* curves recorded during the positive scan at two Bi-PbO$_2$/Au rotated disk electrodes using a rotation speed of 1600 rev min^{-1}. Curves A and B correspond to the voltammetric response at film electrodes with a ratio of

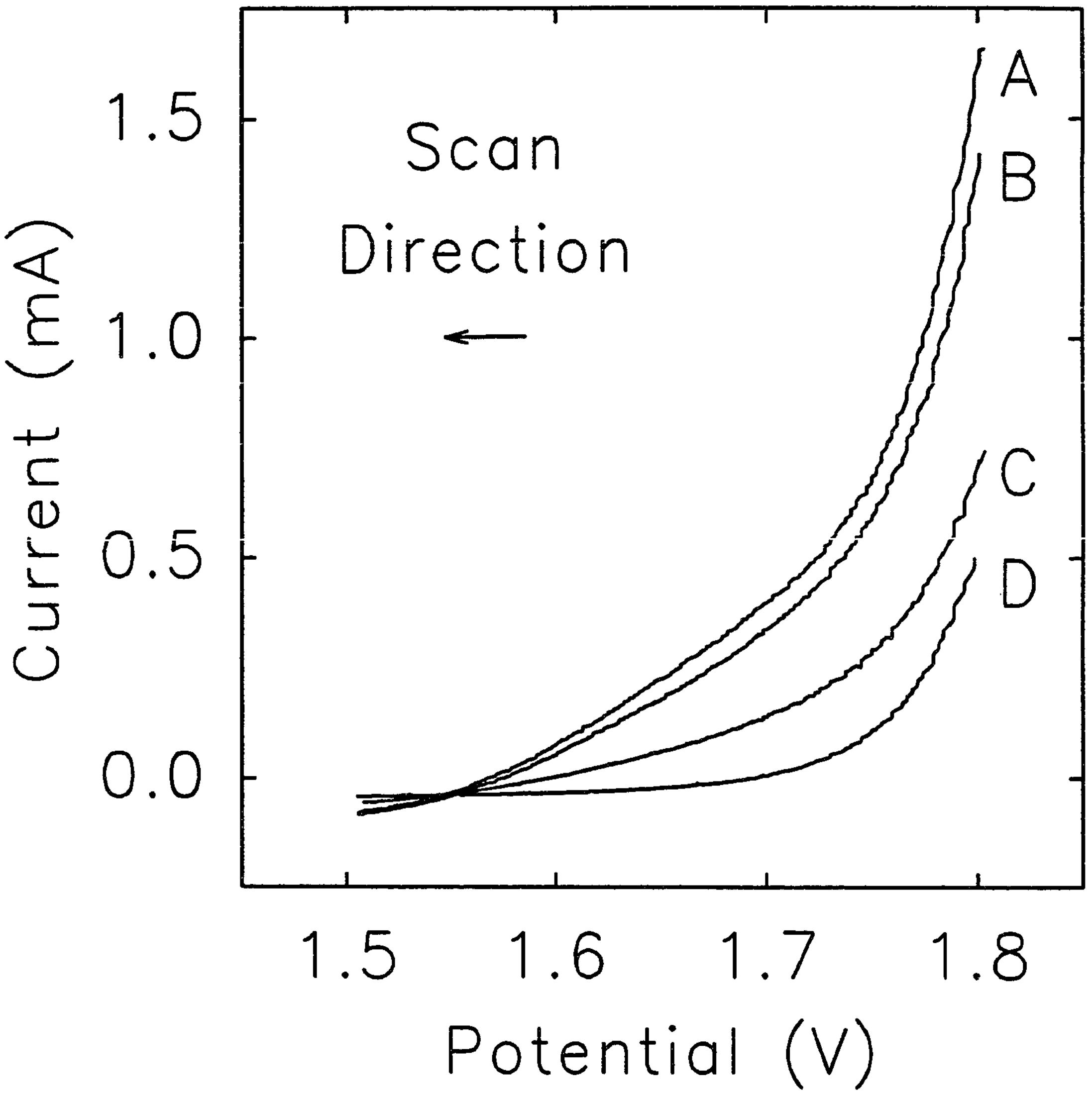

Figure 2. Voltammetric response (negative scan) for 10 mM Cr(III) at PbO_2/Au and Bi-PbO_2 rotated disk electrodes in 1.0 M H_2SO_4. Scan rate: 20 mV s^{-1}. Rotation speed: 1600 rev min^{-1}. [Bi(III)]/[Pb(II)] in electrodeposition of Bi-PbO_2 (mM/mM): (A) 4/10, (B) 3/10, (C) 1/10, (D) 0/10.

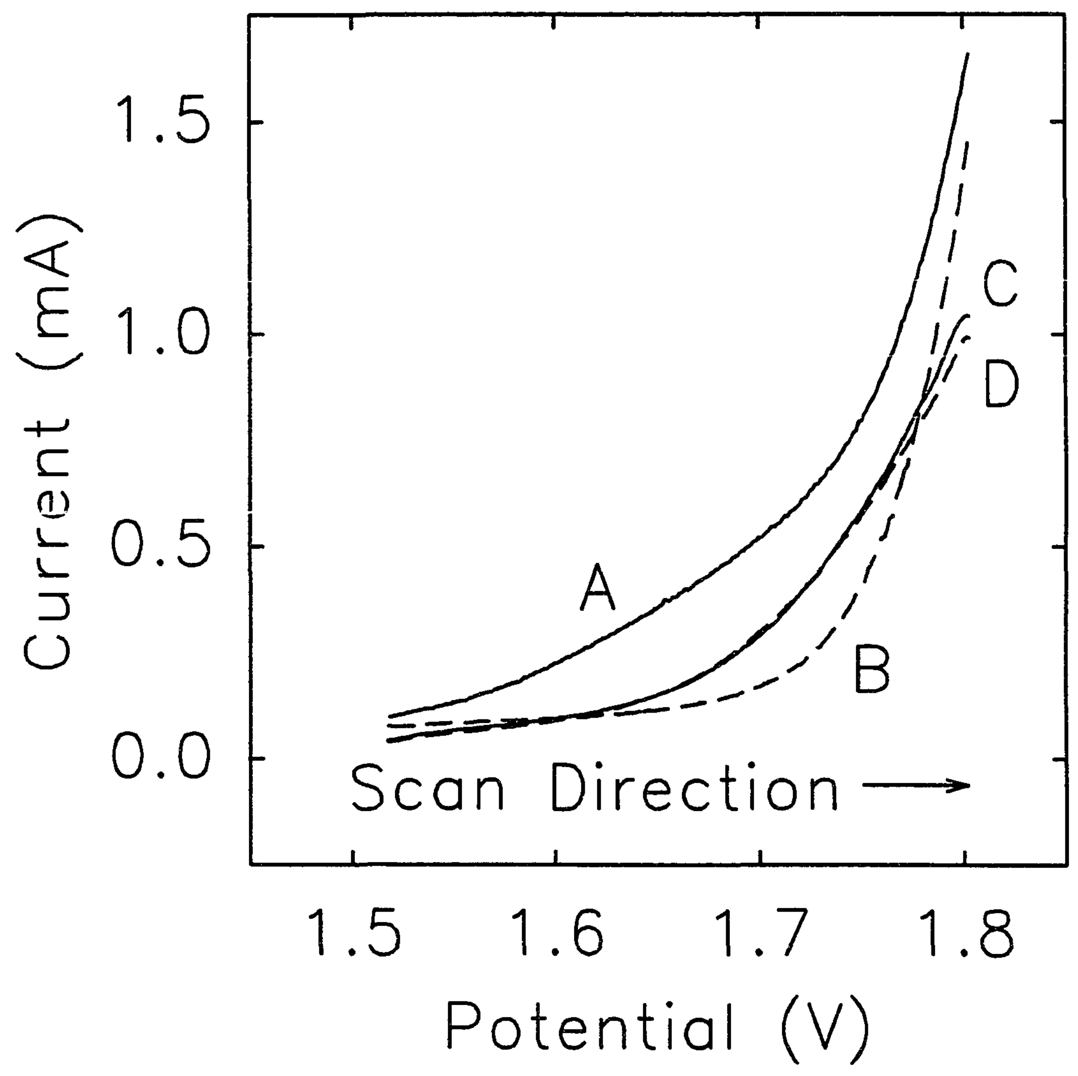

Figure 3. Voltammetric response (positive scan) for Cr(III) at Bi-PbO$_2$ rotated disk electrode in 1.0 M H_2SO_4. Concentration Cr(III) (mM): (A,C) 10, (B,D) 0. Scan rate: 20 mV s^{-1}. Rotation speed: 1600 rev min^{-1}. [Bi(III)]/[Pb(II)] in electrodeposition of Bi-PbO$_2$ (mM/mM): (A, B) 4/10, (C, D) 20/10.

Bi(V)/Pb(IV) = 0.4. Curves C and D correspond to the voltammetric response at film electrodes with a ratio of Bi(V)/Pb(IV) = 2.0. Curves A and C correspond to the voltammetric response at film electrodes in the presence of 10 mM Cr(III). Curves B and D correspond to the voltammetric response at film electrodes in only the supporting electrolyte (1 M H_2SO_4). At the higher Bi(V)/Pb(IV) ratio, the voltammetric response in the presence of Cr(III) is essentially the same as that of the residual. It is also significant to note the lower oxygen-evolution overpotential for the residual curve of the higher Bi(V)/Pb(IV) ratio, Curve D. Explanation of the data involves the increased surface concentration of active Bi sites. As the concentration of surface Bi sites increases, the distance between these sites decreases. When Bi sites are close enough, $\cdot OH_{ads}$ generated at those sites may react to form molecular oxygen[23] as in Equation [3]. Data in

$$2\cdot OH_{ads} \rightarrow O_2 + 2H^+ + 2e^- \qquad [3]$$

Figure 3 are in agreement with Larew *et al.* who found that the maximum electrode activity resulted from a surface containing 0.5 monolayer of electrosorbed Bi(V), *i.e.* Bi(V)/Pb(IV) = *ca.* 1.[15] The lack of activity for Cr(III) oxidation in Curve C is explained by the complexity of the reaction. Oxidation of Cr(III) to $Cr_2O_7^{2-}$ involves at least nine atoms. It is reasonable to assume that a reaction involving so many atoms requires several steps. It is also reasonable to assume that the Cr species may require adsorption in order to complete this multi-step surface-catalyzed mechanism. In this case, if the Cr species only adsorb at Pb sites, a surface filled with Bi sites such as that used to obtain data in Curve C should not show any activity for Cr(III) oxidation.

Electrocatalytic effect of electrosorbed Bi(V)

Figure 4 contains current-time (*i*-*t*) curves obtained at the PbO_2/Au RDE in 1.0 M $HClO_4$ containing 10 mM $CrK(SO_4)_2$ as a function of added Bi(III), in the manner of Chang and Johnson.[4] Mixing of the solution following each addition of Bi(III) was achieved quickly (< 10 s) by the action of the rotated electrode (400 rev min^{-1}). After the brief mixing period, the *i*-*t* curves were recorded following a potential step from 1.4 V to 1.7 V to achieve electrosorption of Bi(III) as Bi(V). After 800 s, the potential was returned to 1.4 V to cause cathodic desorption of the adsorbed Bi(V).[4] This process was repeated for each incremental addition of Bi(III). The chronoamperometric curves in Figure 4 demonstrate that, for incremental increases in Bi(III) concentration (A to F), the anodic current for Cr(III) oxidation quickly rises to a constant value reaching a maximum for 6 μM Bi(III) (F). For Bi(III) concentration increasing above 6 μM (G to J), the current decreased from its maximum value. This declining response observed for increasing Bi(III) concentration is virtually identical to that observed by Larew *et al.* for the oxidation of DMSO.[15] Similar to the data in Figure 3, the data in Figure 4 can be explained by the increasing surface concentration of Bi(V) sites. Here, active Bi(V) sites are not due to the incorporation of Bi(V) in the PbO_2 lattice during deposition, but rather they are the result of Bi(V) electrosorption on the PbO_2 electrode surface. At an anodic potential of 1.7 V in these conditions, Bi(III) ions are electrosorbed to the PbO_2 surface as Bi(V). As the fractional monolayer of electrosorbed Bi(V) increases, activity also increases to a point. As in Figure 3, when the surface coverage exceeds a certain fractional monolayer, activity decreases. It is believed that in the case of electrosorption, the equilibrium fractional monolayer changes as the concentration of Bi(III) in the bulk

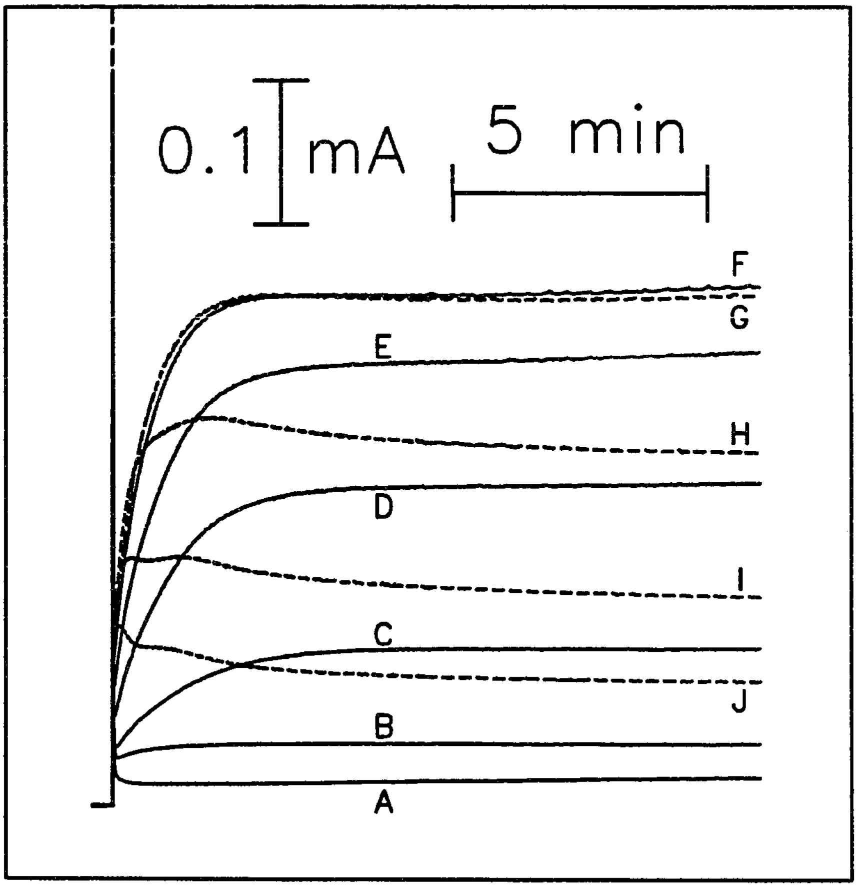

Figure 4. Chronoamperometric response for 10 mM Cr(III) at a PbO_2/Au rotated disk electrode in 1.0 M $HClO_4$ as a function of added Bi(III). Rotation speed: 400 rev min^{-1}. Potential step: 1.4 V to 1.7 V at zero time. Concentration Bi(III) (µM): (A) 0, (B) 1, (C) 2, (D) 3, (E) 4, (F) 6, (G) 8, (H) 16, (I) 32, (J) 64.

solution changes. This belief is based on the assumption that an equilibrium is established between the rates of electrosorbtion k_1 and desorbtion k_{-1} of Bi(V) at the electrode surface, and that this equilibrium is influenced by the concentration of Bi(III) in the bulk solution (see Equation [4]).

$$\mathrm{Bi(III)_{aq}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Bi(V)_{ads}} + 2e^- \qquad [4]$$

Effect of electrochemical stripping of Bi-PbO$_2$ film

Chang and Johnson[21] reported that an ultra-thin film of Bi-PbO$_2$ remains at Au electrodes following the cathodic stripping of a majority of the film. Furthermore, they reported that the ultra-thin film has an activity for oxidation of DMSO to DMSO$_2$ that is significantly greater than that observed for the original thick film.

The voltammetric response at the Au RDE covered by a thick, opaque Bi-PbO$_2$ film was obtained in 1.0 M H_2SO_4 with and without the presence of 10 mM Cr(III) as a function of the potentiostatic pretreatment of the electrode at increasingly negative potentials. Figure 5 contains *i-E* curves obtained at the intact Bi-PbO$_2$ film in the presence of Cr(III) (D) in comparison to the residual response (E). Curves E and D were obtained by voltammetric scans from a potential of 1.5 V, which is not sufficient to bring about cathodic dissolution of any portion of the Bi-PbO$_2$ film. The Bi-PbO$_2$ then was progressively stripped from the Au surface by application of increasingly negative values of potentials (5 - 45 s). Following each pretreatment, the electrode surface was rinsed and the *i-E* curves recorded during a positive scan from 1.5 V in the absence and presence of 10 mM Cr(III). Curves C, B and A correspond to Cr(III) response following pretreatment at 1.4, 1.2 and 1.1 V, respectively. For this electrode, the high activity demonstrated by

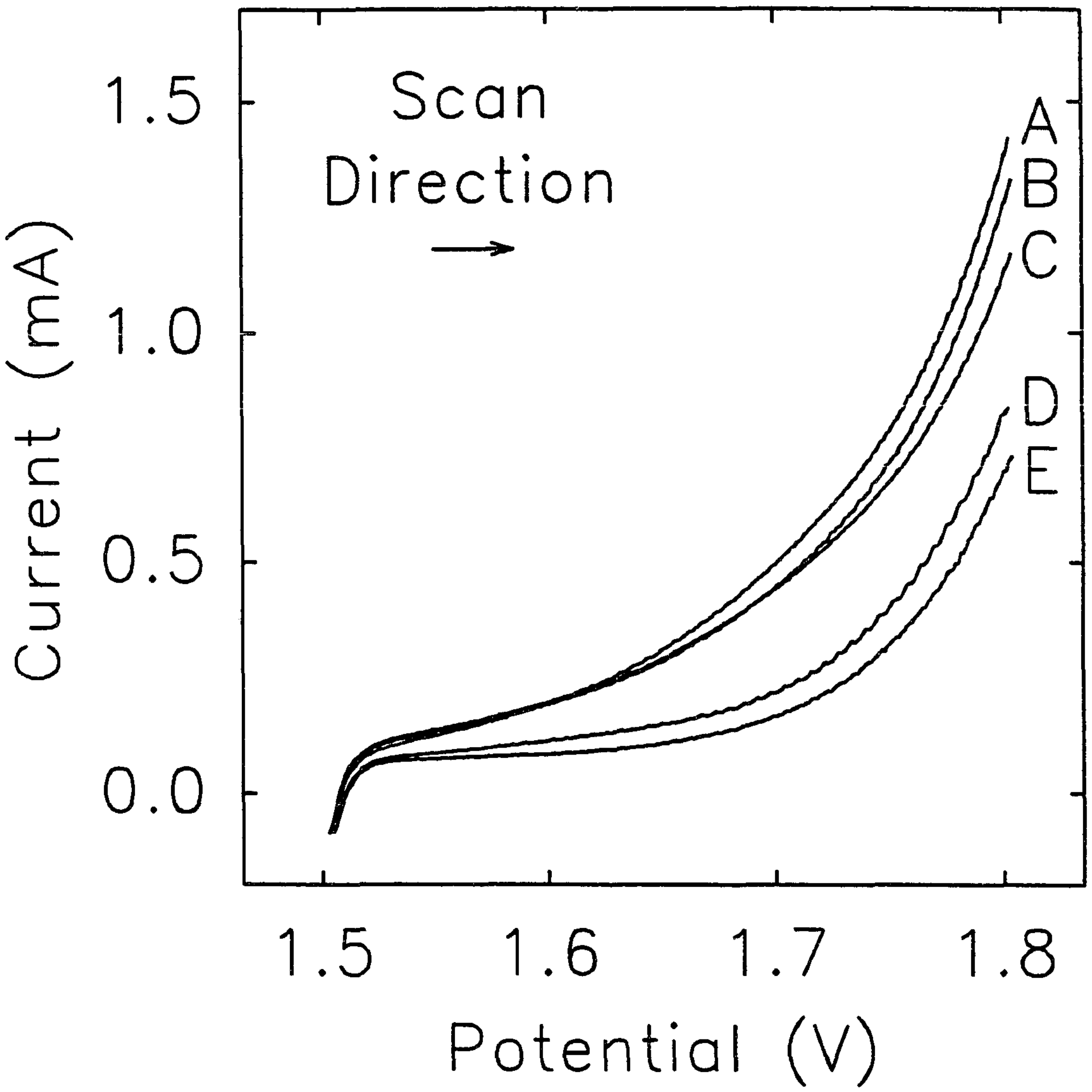

Figure 5. Voltammetric response (positive scan) of Cr(III) at cathodically stripped and unstripped Bi-PbO_2/Au rotated disk electrodes in 1.0 M H_2SO_4. Concentration Cr(III) (mM): (A - D) 10, (E) 0. Potential of cathodic stripping (V): (A) 1.10, (B) 1.20, (C) 1.40 V, (D,E) unstripped films. Scan rate: 40 mV s^{-1}. Rotation speed: 1600 rev min^{-1}. Electrodeposition of Bi-PbO_2: [Bi(III)]/[Pb(II)] = 4 mM/10 mM.

curve A for oxidation of Cr(III) is sufficient evidence that a catalytic film remains on the Au surface that has electrocatalytic properties superior to that of the thicker unstripped Bi-PbO_2 films. Voltammetric curves obtained following pretreatment at potential values ≤ 1.0 V (not shown) demonstrated a severe decline of electrode activity for Cr(III) oxidation. All residual curves were virtually identical to that given by curve E in Figure 5. Therefore, changes in Cr(III) response shown in Figure 5 are not a consequence of changes in charging current or the rate of O_2 evolution.

Constant current coulometry

Constant current coulometry was used to determine the current efficiency ($\%_{eff}$) for oxidation of Cr(III) to Cr(VI) at PbO_2/Pt and Bi-PbO_2/Pt gauze electrodes. Nine determinations of $\%_{eff}$, calculated according to Equation [3], were completed for the PbO_2/Pt electrode and the individual results are plotted in Figure 6, curve A (○). The average $\%_{eff}$ for the PbO_2/Pt is 81.2% with a standard deviation equal to 7.2%. It is obvious from these results that Cr(VI) cannot be generated with 100 % current efficiency at the PbO_2/Pt electrode. Eighteen determinations of $\%_{eff}$ were completed for the Bi-PbO_2/Pt electrode and these results are plotted in Figure 6, curve B (●). Initial values of $\%_{eff}$ for this electrode were significantly below 100 %. However, the apparent electrocatalytic activity of the Bi-PbO_2/Pt electrode increased with use and the average $\%_{eff}$ is 99.2% for the last 12 determinations with a standard deviation of 1.1%.

A possible explanation for the increased efficiency for Cr(VI) generation at the Bi-PbO_2/Pt electrode is the slow chemical stripping of inactive regions of the Bi-PbO_2 film to produce a more active film such as demonstrated by data in Figure 5 (curves A - C). The

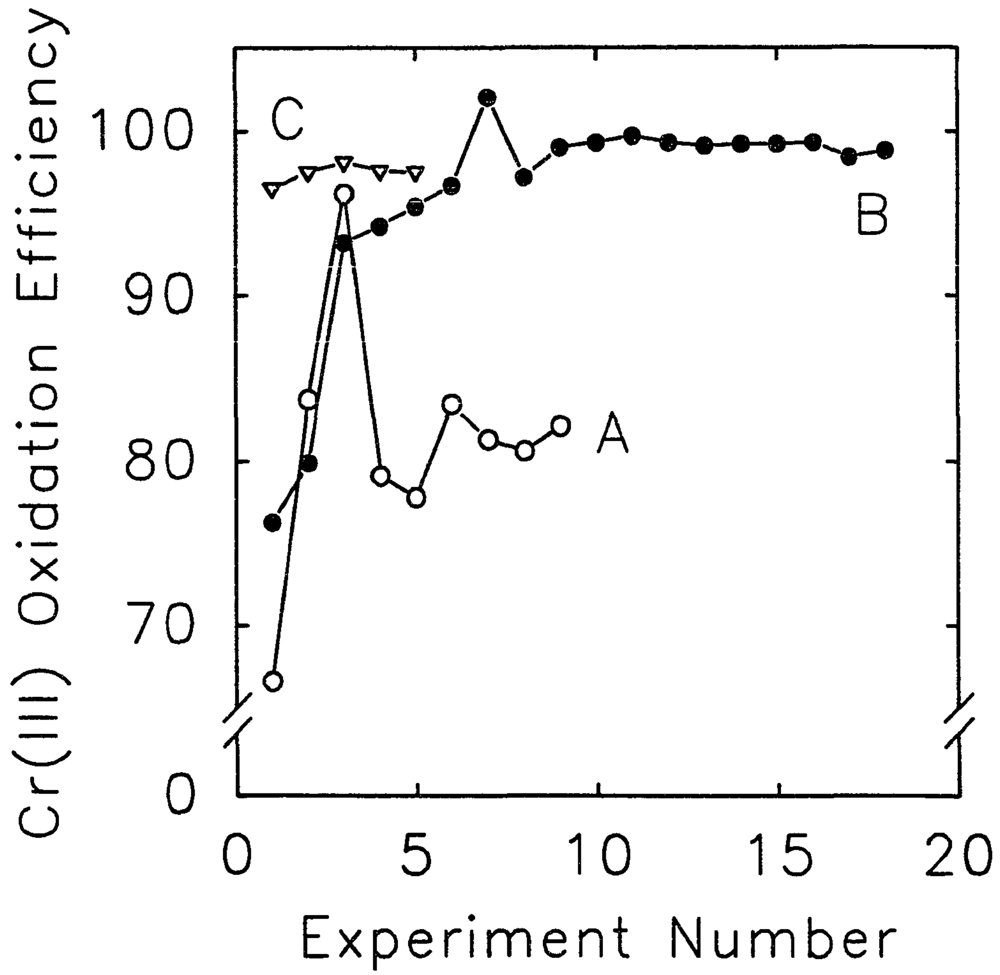

Figure 6. Oxidation efficiency for oxidation of Cr(III) at PbO_2/Pt (○) and Bi-PbO_2/Pt (●,▿) in 1.0 M H_2SO_4 containing 0.1 M $CrK(SO_4)_2$. [Bi(III)]/[Pb(II)] in deposition solution (M/M): (○) 0/0.5, (●,▿) 0.05/0.5. Constant anodic current: 100 mA. Data points represented with a "▿" were obtained after electrochemical stripping at 0.7 V for 30 s in deposition solution.

value $E^\circ_{Pb(IV/II)}$ = 1.46 V *vs.* NHE is larger than $E^\circ_{Cr(VI/III)}$ = 1.33 V *vs.* NHE and, therefore, PbO_2 is thermodynamically capable of oxidizing Cr(III) to Cr(VI). Thermodynamic data are not available for Bi-PbO_2; however, we will assume for this consideration that the corresponding E° is comparable to the value for the Pb(IV/II) redox couple. Therefore, under galvanostatic conditions for which the concentration of Cr(III) at the electrode surface is not suppressed to zero, it is conceivable that the bulk of the Bi-PbO_2 film is chemically stripped by reaction with Cr(III). Experimental evidence supporting this speculation is the observation that Bi-PbO_2 films at open circuit potential in 1.0 M H_2SO_4 were dissolved after addition of Cr(III).

To test the hypothesis concerning chemical stripping of less active Bi-PbO_2 regions, a Bi-PbO_2/Pt gauze electrode was made by electrodeposition from a solution containing 0.5 M $Pb(NO_3)_2$ and 0.05 M $Bi(NO_3)_3$ in a 1 M HNO_3 supporting electrolyte for 5 min at 1.7 V. Following deposition, electrochemical stripping was achieved by changing the potential to 0.7 V for 30 s. The electrode remained black following the electrochemical stripping step. Using this electrochemically stripped electrode, Cr(VI) was generated as described above, and the resulting solution was titrated with Fe(II) to determine the current efficiency. Five runs were completed using this electrode, and these data are shown in Figure 6, curve C (▿). The current efficiency for these five runs averaged 97.4 % with a 0.5% standard deviation. Since this electrode required no preconditioning other than the electrochemical stripping, it is believed that these data support the conclusion offered above that chemical stripping of inactive regions of the Bi-PbO_2 reveals a more active film.

Based on data in Figure 6, it is apparent that this chemical means for production of

Cr(VI) by reaction of Cr(III) with PbO_2 does not occur at a significant rate in comparison to the anodic process. Danilov and Velichenko suggest that the rate of chemical oxidation of Cr(III) by PbO_2 is between two and three orders of magnitude lower than the corresponding electrochemical process at PbO_2 anodes.[24] It should also be noted that under proper conditions the electrode is quite stable. A single deposition of Bi-PbO_2/Pt was used for all eighteen runs with no further preparation or regeneration. This translates to nearly twenty hours of electrolysis with no ill effects. In another experiment, a similarly prepared electrode was used continuously for 265 hours with no observed decrease in activity.

Scanning electron microscopy

To further investigate the cause of the increased efficiency observed after preconditioning, a platinum foil electrode (area = 4 cm^2) was coated with a Bi-PbO_2 film from a 1 M HNO_3 solution containing 0.5 M $Pb(NO_3)_2$ and 0.05 M $Bi(NO_3)_3 \cdot 5H_2O$. After a deposition step of 7 min at 1.7 V, the electrode was removed, rinsed with deionized water, and allowed to dry. The electrode was then positioned in the same solution such that half of the electrode was submerged. The potential was maintained at 0.7 V for 30 s. Following this stripping step, the electrode was again rinsed and allowed to dry. At this point, the portion of the surface that had been electrochemically stripped bore a slightly different shade, easily observable by the naked eye. Scanning electron microscopy and wavelength dispersive spectroscopy were performed on both the stripped and unstripped portion of the electrode. Micrographs of the unstripped (Figures 7A and 7C) and stripped (Figures 7B and 7D) surfaces show a distinct result of the stripping. Figures 7C and 7D

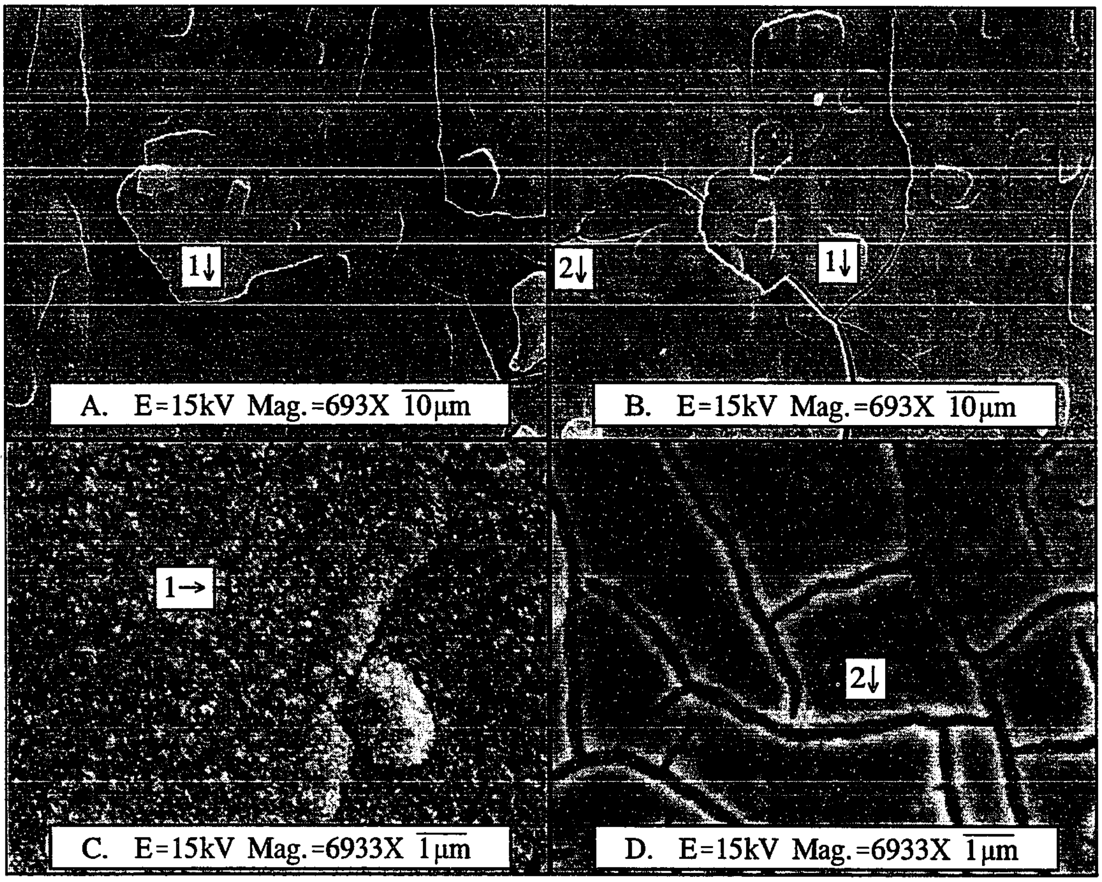

Figure 7. Scanning electron micrographs of Bi-PbO_2/Pt foil before (A, C) and after (B, D) a 30 s electrochemical stripping period at 0.7 V in 1.0 M $HClO_4$ containing 0.5 M $Pb(NO_3)_2$ and 0.05 M $Bi(NO_3)_3{\cdot}5H_2O$.

are at ten times the magnification of that shown in Figures 7A and 7B. In Figure 7 (A - D), two kinds of cracks in the film are observed. It is believed that the dominant cracks shown in Figures 7A, 7B and 7C are the result of vacuum stress during the SEM analysis in which water in the film-substrate interface is removed, causing the film to peel away. Examples of these cracks are marked with a "1". Smaller scale cracks, marked with a "2", appear only in the regions exposed to electrochemical stripping, Figures 7B and 7D. Based on previous results, the presence of smaller cracks in the micrographs is most probably due to the electrochemical stripping. Possible changes in the PbO_2 lattice,[4,21,25] such as possible surface segregation, is indicated by the EDS results in Table 1. It is significant that these data clearly show an increase in the surface concentration of Bi relative to Pb after the stripping step. The increase in efficiency illustrated in Figure 6 is believed to be caused by an increase in the Bi/Pb ratio on the surface of the electrode similar to the increase shown in Table 1. Future studies will seek to obtain structural information for the ultra-thin films of Bi-PbO_2.

Voltammetric response of Mn(II)

The anodic oxidation of Mn(II) to Mn(VII) also was investigated as a basis for mediation of oxidation reactions because of the oxidizing power of Mn(VII) in acidic media, as indicated by:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O; \quad E^o_{Mn(VII/II)} = 1.51 \text{ V } vs. \text{ NHE} \qquad [5]$$

Yeo and Johnson[1] reported amperometric data that demonstrated Mn(II) can be oxidized to Mn(VII) at transport-limited rates at rotated Bi(V)-doped β-PbO_2 film electrodes in acidic media. The anodic generation of Mn(VII) was examined in the present study to

Table 1. Results of wavelength dispersive spectroscopy at an unstripped and electrochemically stripped Bi-PbO_2/Pt foil electrode.[a]

	Counts / Unstripped Portion of Electrode	Counts / Electrochemically Stripped Portion of Electrode
Pb-Mα peak (5.29Å)	793	666
Bi-Mα peak (5.12Å)	383	429
Ratio Bi/Pb	0.483	0.644
Increase in ratio after stripping	33%	

[a] Deposited from a solution containing 0.5 M $Pb(NO_3)_2$, 0.05 M $Bi(NO_3)_3 \cdot 5H_2O$, and 1 M $HClO_4$ at 1.7 V for 5 min. Electrochemical stripping was achieved at 0.7 V for 30 s in the same solution.

investigate its use in place of Cr(VI). However, following a brief period of activity, accompanied by the appearance of purple MnO_4^-, the electrode current decayed to the background value. This decay was accompanied by accumulation of a black film of MnO_2(s) on the electrode surface and the cell walls. The production of MnO_2(s) is predicted to occur by comproportionation in acidic mixtures of Mn(VII) and Mn(II), as indicated by:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+; \; K_{eq} = 4.6\times10^{45} \qquad [6]$$

Based on these results, it is concluded that the electrogeneration of Mn(VII) cannot be successful as the basis for homogeneously mediated anodic oxidations of organic materials.

Conclusions

Electrodes consisting of thin films of mixed bismuth(V)-lead(IV) oxides (Bi-PbO_2) have significantly greater activity for oxidation of Cr(III) to Cr(VI) in 1.0 M H_2SO_4 than electrodes consisting of pure PbO_2 films. The activity of thick Bi-PbO_2 films applied for Cr(VI) production actually increases during use and Cr(VI) can be generated with virtually 100% current efficiency at the preconditioned Bi-PbO_2. The preconditioning process is concluded tentatively to correspond to chemical stripping of those regions of the Bi-PbO_2 film characterized by low catalytic activity to leave behind a film having uniformly high activity. This conclusion is supported by voltammetric data reported by Chang and Johnson[21] demonstrating that the peak potential for voltammetric dissolution of Bi-PbO_2 films (negative scan) is shifted by a significant amount to increasingly negative values as the Bi(V)/Pb(IV) ratio in the film is increased. If these peak potentials can be correlated to thermodynamic E° values for the corresponding redox couples, then the susceptibility of Bi-PbO_2 to chemical stripping in the presence of Cr(III) will decrease as the Bi(V)/Pb(IV) ratio increases. There is also the possibility that this data reflect a kinetic rather than thermodynamic dependence on Bi(V) content. In this case as well, however, the result is the same, *i.e.*, the susceptibility of Bi-PbO_2 to chemical stripping in the presence of Cr(III) decreases as the Bi(V)/Pb(IV) ratio increases. Therefore, if Bi-PbO_2 films do not have a constant Bi(V)/Pb(IV) throughout, then chemical stripping will selectively remove regions of the films containing low values of Bi(V)/Pb(IV), *i.e.*, low catalytic activity, while leaving behind those portions of the film with high Bi(V)/Pb(IV), *i.e.*, high catalytic activity.

It is expected also that Bi-PbO_2 electrodes can have significance in a variety of other electrochemical industries that rely on the use of Cr(VI) to achieve homogeneous oxidation processes.[14,26] Examples include the oxidation of organic compounds, such as anthracene and montan wax, regeneration of chromium electroplating solutions and chromic acid baths, and refining chromium ores.[14,26] Indirect electrolytic oxidations with anodically-generated oxidation mediators eliminates the need to purchase costly oxidation reagents and, furthermore, minimizes the concern for costly disposal practices required for large quantities of the reduced form of oxidation reagents. Additional applications can include a coulometric version of the chemical-oxygen-demand test and the oxidative degradation of toxic organic wastes by an electrolytic process we refer to as *indirect electrochemical incineration.*

Acknowledgements

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CHAPTER 4. DEVELOPMENT OF A COULOMETRIC METHOD FOR THE DETERMINATION OF CHEMICAL OXYGEN DEMAND THAT RECYCLES $Cr_2O_7^{2-}$

A paper to be submitted to Analytical Chemistry

Kim L. Pamplin and Dennis C. Johnson

Abstract

A coulometric determination of chemical oxygen demand (COD) is developed in which Cr(III) is determined using constant-potential exhaustive electrolysis. The Cr(VI) electrochemically generated during the Cr(III) determination is reused as the oxidant in subsequent coulometric COD determinations. Results obtained using the coulometric COD determination for 10 compounds averaged 106.7% (standard deviation s = 7.9%, N = 40) of the theoretical values predicted based on complete oxidation to CO_2. For two test compounds, potassium hydrogen phthalate (KHP) and glucose, the digestion solutions were reused in numerous consecutive determinations without any observed adverse effects. Over the 10 KHP and 11 glucose experiments, recovery averaged 103.8% (s = 6.0%) and 100.2% (s = 4.2%), respectively. Preliminary results are reported for the simultaneous digestion and coulometric determination of COD for glucose. In five determinations using this method, COD averaged 92.6% (s = 3.6%) of values predicted based on complete oxidation to CO_2.

Introduction

The determination of chemical oxygen demand (COD) serves as an important test of water quality throughout the world. The COD results are used to estimate biological oxygen demand, a key parameter since the ultimate goal is often to estimate the effect of effluents on natural aquatic ecosystems. The COD determination requires a strong chemical oxidizing agent that oxidizes most organic components in a sample. In the ideal case, the organic oxidation is complete, producing CO_2. COD determination also requires a method of determining the amount of oxidizing agent consumed. This is commonly achieved by titrimetric or colorimetric means.[1]

Much research over the past several decades has been devoted to developing and improving the procedure for determination of COD. Improvements have come in the pursuit of more complete oxidation,[2] elimination of interferences[3], and speed and automation.[4] Another possibility that deserves investigation is an electrochemical method of COD determination.

A direct electrochemical determination of COD would be most useful, in that the only reagent necessary for the determination would be the electron. In fact, based on thermodynamic calculations, virtually all organic compounds should be oxidized completely to CO_2 at potentials well within the limits available in aqueous solutions. Unfortunately, for the vast majority of organic compounds, kinetic limitations preclude any significant oxidation at an electrode below the potential limit set by solvent breakdown.

Since a direct electrochemical determination of COD may not be possible using current technology, an indirect electrochemical method is worth investigation. Indirect electrochemical oxidation of organic compounds has received much attention, primarily due to its potential use as a waste treatment method[5] and for organic synthesis.[6]

Figure 1 illustrates indirect electrochemical oxidation. In this process, a strong oxidant, commonly called a mediator, reacts with and oxidizes an organic analyte, thereby generating the reduced form of the mediator and an oxidized form of the organic analyte. The reduced form of the mediator then returns to the anode by convective-diffusional transport where it is oxidized. In its oxidized state, it can again diffuse into the bulk solution and continue the oxidation process. Several cycles through this process may be necessary for the organic compound to reach its ultimate oxidation state.

The Cr(VI/III) redox couple (see Equation [1]) is well suited for such an

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O;\ E^{\circ}_{Cr(VI/III)}=1.33\text{V vs. NHE} \qquad [1]$$

application. Chromium(VI) in the form of dichromate is the oxidizing agent used in the determination of COD in much of the Western world.[4c,7] In the U.S., the Environmental Protection Agency (EPA) specifies methods for the determination of COD using Cr(VI).[8] The electrochemical generation of Cr(VI) from Cr(III) has been well documented and studied for many years.[6a,9] The major shortcoming of this electrochemistry is the fact that

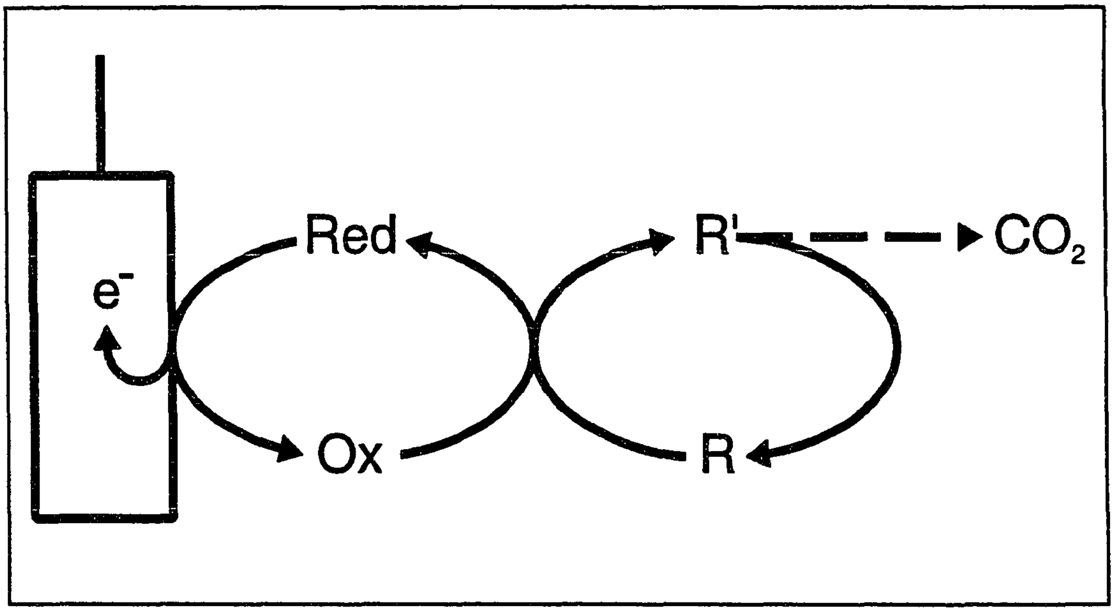

Figure 1. Indirect electrochemical oxidation.

Cr(III) oxidation requires a potential equal to or greater than the O_2-evolution overpotential. The result is a competing reaction that prohibits efficient generation of Cr(VI). The acquisition of quantitative data for indirect electrochemical oxidation from the oxidation of Cr(III) requires an efficient electrode reaction. That is, quantitative data cannot be obtained practically if a competing reaction, *e.g.* discharge of water to form molecular oxygen (Equation [2]), proceeds at a significant rate. Since O_2-evolution

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad [2]$$

current increases exponentially with potential, small fluctuations in electrode potential result in large fluctuations in current. In addition, gaseous O_2 bubbles produced at the electrode continuously vary the effective electrode surface area and thus the current. This makes the quantitative measurement of the Cr(III) oxidation impractical if not impossible at a normal PbO_2 electrode. However, recent studies in this laboratory have shown that Cr(VI) can be generated at >99% efficiency at a Bi(V)-doped PbO_2 (designated Bi-PbO_2) film electrode,[10] making indirect electrochemical determination of COD a possibility.

While a potentiometric or amperometric COD determination might be designed simply to determine the Cr(III) or Cr(VI) concentration following digestion, it is hard to imagine that these would compete well with established procedures. However, exhaustive electrolysis offers a significant advantage. Exhaustive electrolysis of spent COD solutions serves two major functions: (i) the Cr(III) concentration is determined, and (ii) the Cr(VI) is regenerated from the otherwise "waste" COD solution.

Controlled potential coulometry can be used to determine the concentration of an electroactive reactant. This technique is discussed in depth by Bard and Santhanam.[11] In the limiting current region, the electrochemical reaction that converts the reduced reactant

(R) to the oxidized product (O) behaves like a first-order homogeneous reaction in which p_o represents the rate constant. The variable p_o can also be considered a cell constant (see Equation [3]; A = electrode area, D = diffusion coefficient, V = solution volume, δ =

$$p_o = ADV^{-1}\delta^{-1} \qquad [3]$$

diffusion layer thickness). Using controlled potential coulometry under these conditions, current i is related to time t and initial current i_o by Equation [4].[11,12] Taking the natural

$$i = i_o e^{-p_o t} \qquad [4]$$

logarithm of both sides results in Equation [5]. Based on Equation [5], a plot of ln$i$ *vs.* t

$$\ln i = \ln i_o + (-p_o)t \qquad [5]$$

results in a straight line with slope $-p_o$ and intercept lni_o. Linear regression techniques applied to plots of ln$i$ *vs.* t give an intercept b = ln$i_{o,r}$, that is an approximate value of lni_o, and a slope $m = -p_{o,r}$, that is an approximate value for $-p_o$. Equation [6] relates i_o to the

$$i_o = nFVp_oC_{o,R} \qquad [6]$$

initial bulk concentration of R ($C_{o,R}$) where n and F have their usual electrochemical significance.

During the digestion period of a normal COD experiment, organic compounds are oxidized while some Cr(VI) is reduced to Cr(III). The Cr(III) concentration can be directly related to the amount of oxygen that would be consumed by the organic compounds if allowed to react naturally in the environment. To determine COD electrochemically, the initial concentration of Cr(III) following digestion $C_{o,Cr(III)}$ can be converted to total charge Q_{tot} using Equation [7]. Equation [8] results from rearranging

$$Q_{tot} = C_{o,Cr(III)}nVF \qquad [7]$$

$$Q_{tot} = i_o p_o^{-1} \qquad [8]$$

Equation [6] and substituting for $C_{o,Cr(III)}$ in Equation [7]. Substituting the linear regression results into Equation [8] produces Equation [9]. It is significant to note that Q_{tot} and all

$$Q_{tot} = p_{o,r}^{-1} e^{(\ln i_{o,r})} \qquad [9]$$

subsequent values that depend on Q_{tot} are independent of the analytical concentration of Cr (Cr(VI) + Cr(III)), D, V, A, and δ, so long as these are constant throughout the determination period. This method of calculating Q_{tot} will be referred to as the "regression" method.

An alternative numerical method of estimating Q_{tot} is represented by Equations [10-11]. Using this

$$Q_{sum} = \sum_{j=0}^{\infty} (i \bullet \Delta t)_j \qquad [10]$$

$$\lim_{\Delta t \to 0} Q_{sum} = Q_{tot} \qquad [11]$$

method, charge calculated at each Δt is summed over the entire data set. This method of calculating Q_{tot} will be referred to as the "summation" method.

Even though the Bi-PbO$_2$ film electrode can be very efficient in oxidizing Cr(III), an exhaustive electrolysis under constant potential conditions means that by nature, any background current i_{bkg}, even if insignificant compared to i_o, may contribute significantly to Q_{tot} due to the length of time required for the experiment and rapid decrease in current from i_o. For this reason, the charge Q_{bkg} due to i_{bkg} must be estimated and subtracted from Q_{tot}. Equation [12] is used to estimate Q_{bkg} for the regression method. For the summation

$$Q_{bkg} = i_{bkg}(t_f - t_o) \qquad [12]$$

method of calculating Q_{tot}, Q_{bkg} is determined according to Equation [13]. The actual

$$Q_{bkg} = i_{bkg} t_f \qquad [13]$$

charge Q_{act} is easily determined from the difference between Q_{tot} and Q_{bkg}. Chemical oxygen demand is determined according to Equation [14] in which *FW* is formula weight

$$\frac{mg\ O_2}{L}\ COD = \frac{Q_{act}}{nF}\frac{mol\ O_2}{mol\ Cr(III)}\frac{FW_{O_2}}{V_s} \qquad [14]$$

and V_s is the sample volume added to the digestion solution.

Experimental

Chemicals

All chemicals were analytical reagent grade from Fisher Scientific, Alfa Products, or Aldrich Chemicals. Water was distilled and purified further by passage through a NANOpure-II system (Barnstead). All Pb(II), Bi(III), Cr(VI), Ag, and Hg compounds are considered *hazardous* substances. Therefore, waste solutions containing these metals were disposed according to accepted procedures. The COD digestion solutions were either purchased premixed (Hach Co.) or prepared according to Jirka and Carter[4a] except as noted with no significant difference in performance observed.

Electrodes

Bismuth-doped PbO_2 working electrodes were made by electrodeposition on a substrate from 0.5 M $Pb(NO_3)_2$/0.2 M $Bi(NO_3)_3 \cdot 5H_2O$/1 M $HClO_4$, as described previously.[10] A cylindrical Pt gauze electrode (5-cm length, 4-cm diameter and ca. 126-cm^2 area) and a Pt wire electrode (*ca.* 7 cm^2) served as substrates for the Bi-PbO_2 films. A saturated calomel electrode (SCE, Fisher Scientific) provided the reference potential for all experiments and all potential values are given *vs.* the SCE. The counter electrode (CE) was either a coiled Pt wire (*ca.* 7 cm^2) or a Pt wire-and-gauze assembly (*ca.* 1 cm^2).

Instrumentation

A model RDE-4 bipotentiostat (Pine) was used for coulometric determination of COD with the wire electrode. A coulometer, potentiostat, and power supply (Electrosynthesis Co., Inc.) were used for coulometric determination of COD in conjunction with the Pt gauze electrode. Computer data acquisition was achieved using a 486-based PC, data acquisition software (ASYST 4.0, ASYST Software Technologies, Inc, Rochester, NY) and hardware (DAS-16 analog-digital interface, MetraByte Corp., Taunton MA). Some data were acquired using a strip chart recorder.

Chemical oxygen demand

For comparison, COD was determined for all test solutions using an EPA approved method described elsewhere.[4a,13] This method requires two hours of digestion in a capped test tube at 150° C followed by colorimetric determination of Cr^{3+} or $Cr_2O_7^{2-}$, depending on the O demand.

Coulometric determination of COD

The digestion method for the coulometric COD procedure was identical to the EPA method described above. The difference between the coulometric and normal COD procedures is in the determination of Cr^{3+} concentration. Following digestion, the solution ($V \approx 5$ mL) was quantitatively transferred to the central chamber (total capacity of *ca.* 20 mL) of a three-chambered electrochemical cell with the wire WE. Each of the other two chambers contained 1 M H_2SO_4 and either a SCE or a CE. The two side chambers were separated from the central chamber by medium porosity fritted glass disks.

Computer data acquisition commenced when the WE, energized at 1.6 V, was immersed in the stirred solution. To verify that the reaction was complete, data were acquired for 10^4 s, sufficient for a steady baseline to develop.

Coulometric determination of COD using recycled digestion solution

Experiments using recycled digestion solutions from the coulometric determination of COD were performed in 1.5 oz. (44 mL) round wide-mouth glass bottles (similar to Qorpak No. 7939) with black phenolic caps (similar to Qorpak No. 5017, 43mm-400) and Teflon disc liners (1.733" (44.02 mm) dia., similar to Qorpak No. 5Y45QYD but manufactured at the Chemistry Department Machine Shop, Iowa State University, Ames, IA). The CE was isolated from the COD solution by a glass tube with a fritted glass disk at one end (Ace Glass Inc., Cat. 7209-10). The SCE reference was isolated from the solution by a Luggin capillary filled with 1 M H_2SO_4. This was used both to minimize the amount of Cl^- reaching the electrochemical cell from the SCE and to minimize the size of components within the small glass bottle that served as an electrochemical cell.

Into the 1.5 oz. bottle was placed 6.00 mL of digestion solution made according to Jirka and Carter[4a], 1.00 to 4.00 mL of sample solution, and a PTFE coated magnetic stirring bar (0.5" x 0.125"). The capped bottle was placed in a 150°C oven for 2 h, removed, cooled, and opened, and placed on a magnetic stirrer. It should be noted that the combined sample and digestion solution was always ≥50% concentrated H_2SO_4 so that the boiling point would always be ≥150°C. The WE, the tip of the glass tube containing the CE, and the tip of the Luggin capillary were immersed in the solution. Prior to immersion, the working electrode was energized at a constant potential of 1.6 V.

Computer data acquisition commenced when the WE was immersed. Following electrolysis, water was removed from the solution by evaporation in the 150°C oven for 1 h.

Simultaneous digestion and coulometric determination of COD with solution recycling

The electrochemical cell

Determination of COD during digestion was achieved using a jacketed four-chambered Pyrex electrochemical cell (Chemistry Department Glass Shop, Iowa State University, Ames, IA). The cell was heated using a circulator (Brinkman Lauda RM-6 Refrigerating Circulator) to a constant temperature of 60 - 80°C ± 0.1°C. The four chambers of the cell were arranged with a large central chamber (vol. ≈ 250 mL) and three smaller side chambers each separated from the central chamber by a 20 mm dia. fine fritted glass disk. Two Pt wire CE's, at the same potential, were placed in opposite side chambers. A SCE reference was placed in the third side chamber. The central chamber contained the a Bi-PbO_2/Pt gauze WE and a magnetic stirring bar. The opening of the central chamber was a standard taper 50/50 ground glass joint. This joint was used to attach a reflux condenser via a specially made adapter. The adapter had a small hole through which a Pt wire connected the WE and the potentiostat.

Procedure

All chambers of the cell were charged with 1 M H_2SO_4, including 150 mL in the central chamber. To the central chamber was added 4.4 g $K_2Cr_2O_7$. The WE was held at a constant potential of 1.6 V. At time $t = 0$, *ca.* 0.1 g glucose, weighed accurately, was added to the central chamber and the condenser was replaced. Data were collected for 12-24 h or until a steady baseline was reestablished. Subsequent experiments required only the addition of more glucose. Electrodes and digestion solution were all reused in several experiments.

Results and Discussion

Coulometric determination of COD

Figure 2 contains data from a typical run plotted as $\ln i$ *vs.* t where i is given in A. The data are treated by using linear regression to determine the best fit to the theoretically straight line from time $t = 0$ until a constant background is reached. Linear regression techniques are applied beginning with the first 20 data points and increasing progressively throughout the data set. The fit with the highest correlation coefficient (R^2) is taken as the best fit for the line. An iterative process is used to determine i_{bkg}. First, the current values from an arbitrary number of points at the end of the data set are averaged, and this average value is assigned to i_{bkg}. The line $\ln i = \ln i_{bkg}$ is constructed, and the time t_{bkg} at the intersection of $\ln i = \ln i_{bkg}$ and $\ln i = -p_o t + \ln i_o$ is determined according to Equation [15]. A new average is determined consisting of the points from t_{bkg} through the end of the set. A new t_{bkg} is determined, and so on until a new i_{bkg} does not change the number of data points averaged.

$$t_{bkg} = (\ln i_o - \ln i_{bkg})p_o^{-1} \qquad [15]$$

Table 1 gives results of several determinations of COD using both an EPA approved colorimetric method and the coulometric method. These two methods were

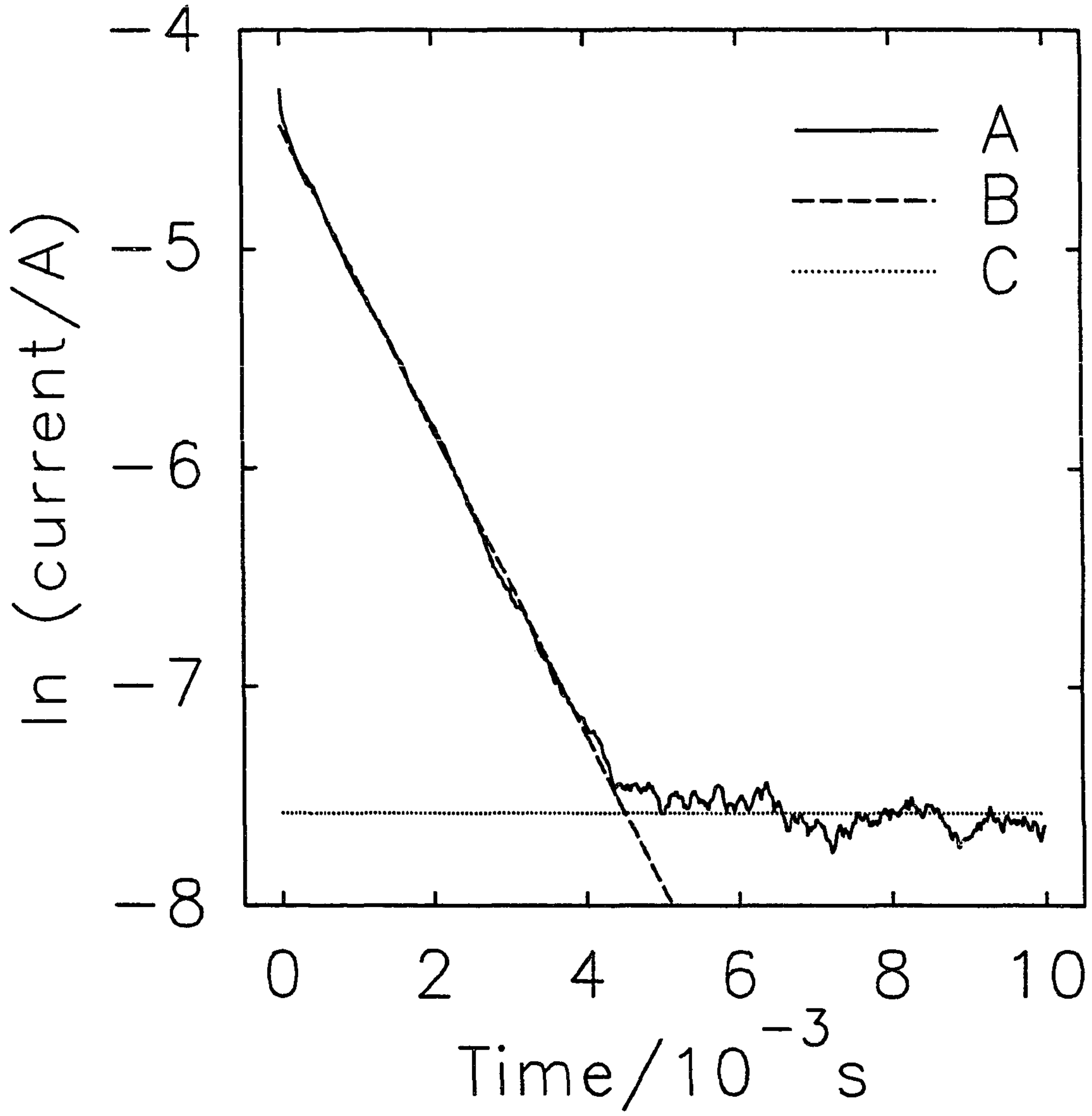

Figure 2. Coulometric determination of chemical oxygen demand of acetaldehyde.

A. Experimental data obtained using constant-potential (1.6V) coulometry of Cr(III) at Bi-PbO$_2$ in a COD digestion solution.

B. Linear regression of experimental data from t_o though $t \approx 4000$ s: y = -6.9 X 10^{-4} x - 4.44, R^2=0.9986

C. Average of data from $t \approx 4500$ s through t = 10000 s: y = -7.58.

Coulometric COD/Normal COD = 1.04

Table 1. Comparison of normal and coulometric methods for determination of COD.[a]

Method	EPA Approved			Constant Potential Coulometry		
Compound	Average	SD[b]	N[c]	Average	SD[b]	N[c]
KHP	101.4%	1.4%	5	105.9%	4.6%	3
Glucose	100.1	2.4	5	113.8	10.7	4
Maltose	101.9	2.4	5	112.6	5.6	4
Oxalic Acid	87.1	0.8	5	95.4	4.4	4
Glyoxylic Acid	105.4	2.3	5	108.6	6.6	4
Ethylene Glycol	102.5	0.6	5	109.8	6.5	4
Acetaldehyde	117.1	0.4	3	112.2	9.8	6
Ethanol	91.9	2.9	5	106.0	6.3	5
Phenol	100.9	2.8	5	98.9	1.6	3
Acetic Acid	102.3	2.5	5	103.9	3.4	3
Average	101.0		48	106.7		40
SD[b]	2.3			7.9		

[a] Values given are percent of theoretical assuming complete conversion to CO_2
[b] SD = standard deviation
[c] N = number of observations

compared by evaluating ten different compounds including two standard test compounds,[1,14] potassium hydrogen phthalate (KHP) and glucose. The coulometric results are in good agreement with the EPA approved method. The coulometry-based COD data listed in Table 1 were calculated using the regression method described in Equations [4-9].

Table 2. Comparison of an EPA approved method[a] for determination of COD[b] with a coulometric method that uses recycled digestion solution.

Method	EPA Approved		Constant Potential Coulometry			
Basis	Absorbance		Regression[c]		Summation[d]	
Compound	KHP	Glucose	KHP	Glucose	KHP	Glucose
Mean	101.4%	100.1	103.8	100.2	82.8	82.2
SD[e]	1.4%	2.4	6.0	4.2	16.6	13.1
N[f]	5	5	10	11	10	11

[a] Hach colorimetric method[13]
[b] Values given as a percent of theoretical assuming complete conversion to CO_2
[c] $Q_{tot} = -m^{-1} e^{b}$; m = slope and b = intercept of ln$i$ *vs.* t plot
[d] $Q_{tot} = \Sigma(i_j \Delta t_j)$; j = datum index; Q_{tot} evaluated over all data
[e] SD = standard deviation
[f] N = number of observations

Coulometric determination of COD with chemical recycling

Two test compounds, KHP and glucose, were used to evaluate this method. Data for these experiments are presented in Table 2.

For these experiments, results from both the regression and summation methods of data treatment are shown. The regression method is a significantly better method for evaluating this data. One possible explanation for the discrepancy between the two evaluation techniques is that the regression method in theory evaluates from $t = 0$ to $t = \infty$, while the summation method can only evaluate the data for the length of time the data are gathered. Another possible explanation is that the summation method relies more on the approximation of i_{bkg} than does the regression method. While a small error in i_{bkg} certainly affects Q_{tot} for both methods, in the summation method this effect is magnified since Q_{bkg} is calculated for the complete experiment in the summation method. Finally, The regression method is based on data obtained during the initial part of the electrolysis for which *i* is determined with highest accuracy, while the summation method is strongly influenced by *i* at large time which have high uncertainties.

Statistical tests are used to compare the significance of the difference in mean and the significance of the difference in precision for two sets of data.[15] Based on these tests (see Table 3), there is no significant difference between the mean COD values obtained using the EPA method and the regression method for either KHP or glucose. Also, there is no significant difference between the precision of the EPA and coulometric methods for glucose. The test indicates a significant difference in precision between the EPA and coulometric methods for KHP. It is believed that more experience with this method

Table 3. Statistical comparison[15] of precision and accuracy for EPA approved and coulometric methods of COD determination.

	KHP	Glucose
Pooled standard deviation[a]	5.05	3.77
Significant difference[b]	11.7	8.4
Observed difference[c]	2.4	0.1
F_{cr}, 90% confidence level[d]	6	6
F_{obs}[e]	18.4	3.1

[a] Calculated from data in Table 2, absorbance and regression methods

[b] Based on 99.9% confidence limit. Differences in standard deviation below this value are considered insignificant.

[c] From Table 2, absorbance and regression methods

[d] Critical value of F at the 90% confidence level. Values of F_{obs} below F_{cr} indicate insignificant differences in precision.

[e] Values of F calculated from observed data in Table 2

would increase the precision of the coulometric method, such that there would be no significant difference in the precision obtained between the two methods.

These experiments were performed in on samples within 500 - 1500 mg L^{-1} COD range, though no attempt was made to establish limits of detection.

Electrode lifetime

While the data shown here only represent 60 h of electrode use, previous experiments in this laboratory under similar conditions indicated that an electrode in use continuously for 265 h showed no apparent decrease in activity.[10]

Simultaneous digestion and coulometric determination of COD with solution recycling

An initial attempt at the simultaneous digestion and coulometric determination of COD using solution recycling was made. In five runs, the average COD for glucose was 92.6% of theory assuming complete oxidation, with a standard deviation of 3.6%. This compares well with a literature value of 92% and a standard deviation of 8.2%.[14] There are several possible reasons for the incomplete oxidation. The digestion occurred in an open cell rather than a sealed container. Even though a condenser was placed at the opening of the cell, volatile products of the digestion process may have escaped, resulting in a lower actual yield. A second possible explanation for the lower results is the mild digestion conditions. In these experiments, neither Ag (used as a catalyst) nor Hg was included in the reactor, and the acid concentration was only 1 M, significantly lower than other determinations. In addition, the temperature was significantly below reflux temperature. Finally, since the determination of Cr(III) (and COD) occurred during the digestion, data could not be analyzed according to the regression method. In this case Q_{tot} was obtained from a coulometer in series with the CE. An approximate value for Q_{bkg} was calculated according to Equation [16]. A value for i_{bkg} was calculated from the

$$Q_{bkg} = i_{bkg} t_f \qquad [16]$$

average of i immediately before addition of glucose and i at the conclusion of the experiment. Due to the duration of these experiments, a small error in estimating i_{bkg} could result in significant error in calculation of Q_{actr}, upon which the COD values were based.

Conclusions

Chemical oxygen demand can be determined for several compounds using a coulometric procedure in which the digestion solution is regenerated and reused. Time required for digestion is the same in the coulometric procedure as in EPA approved procedures. However, in these experiments, analysis times of the digestion solution are significantly longer than those for conventional methods. This analysis time can be decreased by varying parameters such as the digestion solution volume, electrode area, and current density, so that the total analysis time for the coulometric determination of COD might compare with other methods. Electrochemical analysis on a submicroliter scale is routine,[16] so it is certainly conceivable that COD determination could be made electrochemically on a much smaller scale than what is shown here.

A COD determination that reuses the same digestion solution could be of significant value in field analysis. This method could even find application in long term manned space flight. In this situation, water recycling, and hence water treatment and analysis, may be necessary. A small scale COD apparatus that functions without requiring the addition of more chemicals and without the generation of excess waste (e.g. spent COD digestion solution) could be a significant benefit.

Coulometric determination of COD with simultaneous digestion of solution appears to be possible. However, more investigation is necessary to optimize conditions of the digestion/determination process and data analysis before this can be used routinely.

As a whole, the coulometric determinations of COD illustrated here represent a first step. Further study is needed to show application to a more diverse sampling of compounds and matrices. For example, matrices with inorganic electroactive species that would not be oxidized in a normal COD determination might be oxidized directly at an electrode. Future investigations will seek to address such challenges.

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CHAPTER 5. GENERAL CONCLUSIONS

Mediator Choice

Though there are several redox couples that meet initial standards for consideration as a mediator in a coulometric method for determination of COD. Upon further consideration, mediators whose oxidized forms are widely used in determination of COD, Mn(VII/II) and Cr(VI/III), appear to be the best choices for more extensive study at this time. However, other candidates may be useful if suitable conditions can be found for their generation and reaction.

It was found that, as predicted, the Mn(VII/II) redox couple, does not work well as an electrochemically generated mediator. This is due to the comproportionation reaction between Mn(II) and Mn(VII) resulting in insoluble MnO_2. For this reason, Cr(VI/III) was chosen for the mediator.

Electrode for Cr(III) Oxidation

Chromium(VI) has been used as a strong oxidizer for decades. Lead dioxide electrodes have been used to generate Cr(VI) for decades, also. An electrode at which the Cr(III) oxidation proceeds efficiently would allow these two Cr reactions to be combined in a coulometric method for the determination of COD. This research has shown that thin-film Bi-PbO_2 electrodes have significantly greater activity for the oxidation of Cr(III) in 1 M H_2SO_4 than pure PbO_2 electrodes. Efficiency for the generation of Cr(VI) at the Bi-PbO_2 reached virtually 100% during electrode preconditioning. The preconditioning process involves mild chemical or electrochemical stripping to reveal a more active surface that SEM studies showed was higher in Bi:Pb ratio than the initial surface. This electrode can be applied to the efficient generation of Cr(VI) for industrial processes, for a coulometric determination of COD, and for indirect electrochemical incineration.

Application of Cr(III) Oxidation

Preliminary application of anodic oxidation of Cr(III) is shown in the coulometric method for the determination of COD. COD of several compounds is determined coulometrically with results that are in good agreement with those from accepted methods. Since Cr(VI) is regenerated in the coulometric determination of COD, it makes sense to recycle the digestion solution. COD is determined coulometrically several times using KHP and glucose as standard test compounds, with statistically the same results as from an accepted method. Simultaneous digestion and coulometric determination of COD was achieved using glucose as a test compound, with good agreement between COD values from experimental and accepted methods of determination.

The coulometric method of determination of COD may be appropriate in field analysis and long-term manned space travel, in which a self-contained, light-weight, low-maintainence determination of water quality is needed.

APPENDIX: STANDARD OPERATING PROCEDURE FOR PC-CONTROLLED ELECTROCHEMISTRY EXPERIMENTS

Background

This appendix contains the programs used with ASYST 4.0 for collection of electrochemical data and instructions for their use. These programs all have their roots in a program called MCV.JOE, written by Joe Vitt.[1] There were three significant changes in programming philosophy that led to the modifications incorporated into these programs. The first change concerns the amount of code in memory at any given point. The philosophy illustrated by Vitt's technique was that all code that might be used should be loaded once and stay in memory throughout the session. The advantages of this approach include quicker response to individual tasks once the code is loaded. The disadvantages include longer startup times and less available RAM. The programs listed here are different in that a single core program (MAIN.KIM) is the only code loaded at the start. This program includes the bare essentials of routine operation, but many of the lesser used individual tasks are not included. Instead, code for secondary tasks is located in subroutines, separate files that are loaded by MAIN.KIM as necessary and then deleted. This frees up memory and speeds the initial loading process. The disadvantage is that the code for each task not located in MAIN.KIM must be loaded each time it is used. Fortunately, these subroutines are all very short so the loading time on my computer (486-based PC clone, 40 MHz, 8 Mbytes RAM) is very reasonable, less than three seconds.

A second departure from the Vitt legacy concerns the RAM storage of data. Vitt's programs generally allowed the operator to obtain and store data for 15 cyclic voltammograms in RAM before being forced to save some to disk. To do this, he used

15 separate 1 X 500-point arrays for the potential data and an identical set for the current data, 30 arrays in all. MAIN.KIM replaces those 30 arrays with a single 15 X 1005-point array. This includes 15 X 500 for potential data, 15 X 500 for current data, and 15 X 5 for identification purposes, *e.g.* data set number, color number, etc. This requires slightly less memory for the arrays and 29 fewer lines of code to create (and load).

Finally, to accompany the new single array described above, a single set of data handling commands replaced Vitt's set of 15 commands for each operation. For example, to plot a cyclic voltammogram on the computer screen, Vitt had 15 different commands: PLOTCV1, PLOTCV2, PLOTCV3, . . . , PLOTCV15. This pattern was repeated for the commands SHOWCV*x*, SAVECV*x*, RETRIEVECV*x*, and various others. Each set of these 15 commands was replaced in MAIN.KIM and associated programs with single commands PLOTCV, SHOWCV, SAVECV, etc. that each subsequently prompts the operator for a data set number (1-15). Most of these commands were then incorporated into the function keys to reduce keystrokes.

It should be noted that Vitt's programs worked exceptionally well for him and others in this group. In fact, those programs are still in use in one form or another on nearly every computer in this group. Each member of this group that has followed Vitt has benefitted from his initial work with ASYST. Consequently, this text is not meant as a critique of his work, but rather an explanation of the different approaches represented.

Standard Operating Procedure

The following instructions are not intended to duplicate the initiation to ASYST that can be acquired in the various ASYST manuals. Anyone unfamiliar with ASYST should first take some time to understand the basic principles in ASYST before trying to operate MAIN.KIM and its associated programs. This is designed to help guide the knowledgeable ASYST user through these programs.

Perhaps the best way to explain MAIN.KIM and its associated programs is in the form a glossary of commands with associated explanations. Following the glossary, full text of the programs is included. All commands listed require that ASYST has been loaded and MAIN.KIM has been loaded within ASYST. To load ASYST on my computer, simply type "as" at the "C:\>" prompt. This executes a batch file that loads ASYST 4.0 in the configuration I used. Once in ASYST, "kp" loads the program MAIN.KIM.

Glossary

ND	Shortcut to the ASYST command NORMAL.DISPLAY.
OUT	Sets the output voltage from the D/A board. This requires a number between -5 and 4.999 on the number stack.
COLOUR	Sets the plotting color on screen to a color unique for each particular data set.
LABEL1	Enscribes time and date stamps on plots. Also puts numbers 1-15 on the plot, each in its unique color. This helps identify individual data sets by their color in a plot of many on the screen.
CVLABEL.X	Labels the x-axis as "Potential/V".
CVLABEL.Y	Labels the y-axis as "Current/mA".
CVLABELS	Executes CVLABLE.X, CVLABEL.Y, and LABEL1 commands.

XAP	Displays the graphics screen with the parameters set by F1.
SC	Acquires data in oscilloscope fashion: real time plot to the screen that does not end until the user hits any key. Requires the screen to be in graphics mode with an appropriately scaled graph. See XAP, F1.
PARAMENU	Loads PARAMENU.KIM. Allows operator to set parameters for acquiring and plotting data.
RUNSUB	Loads and executes the data acquisition subroutines.
BIG2SMALL	Extracts individual data set from large 15 X 1005 array (CVS) and places it in two 1 X 500 arrays (POTS and CURRS) for plotting and saving operations.
CONVERTS	Executes BIG2SMALL for an individual data set designated by the user.
PLOT	Redraws the graphics display with parameters appropriate for the individual data set designated by the user.
SHEW	Plots the individual data set designated by the user on top of whatever graph and data are already on the screen.
KLSUB	Executes subroutines that acquire data for Koutecky-Levich plots using rotation rates from 4900 to 88 rpm.
KLTREAT	Executes subroutines that take the maximum of each current array and saves it with its corresponding rpm data in Lotus 123 format. Appropriate for CVs with peaks, *e.g.* glucose.
SAVE123	Saves an individual data set in the Lotus 123 format.

SAVEASY	Saves an individual data set in the ASYST format.
RECALL	Retrieves data files saved in ASYST format.
COTTRELL.SUB	Executes subroutines that acquire chronoamperometric (current-time) data.
YAP	Replots the current or previous graph using the same parameters without the data.
SETUPSCREEN	Plots a graph using XAP. Also sets the text window REG and graphics window outlines.
OSRESET	Replots the current graph following printing.
SET	Shortcut to SETUPSCREEN
RESET	Unmarks individual data sets that have been "marked" for printing.
OS.PLOT	Allows user to plot a graph according to specific parameters supplied in ZX. Overrides ASYST default setting that draws graphs only using "nice round numbers".
ZX	Executes RESET and OS.PLOT. Requires minimum and maximum values for x- and y-axes to be on the number stack.
OS	Allows user to plot the CV with an offset along the y-axis. Requires values for the offset and CV# on the number stack.
OSBIG	Plots all CVs 1-14 using offset values previously specified.
OSBG	Same as OSBIG but includes CV #15.
BIG	Replots the graph using the entire screen for printing. No text window appears, which makes the size of the graph larger on the printout.

DOIT	Sends the contents of the screen graphically to the printer, then clears the screen and lists all experimental conditions, which then go to the printer also.
OS.ALL	Prints CVs that have been offset on full screen using BIG, DOIT.
F1	Executes PARAMENU
F2	Executes KLSUB
F3	Executes RUNSUB
F4	Executes PLOT
F5	Executes SHEW
F6	Executes OS.ALL
F7	Executes SAVE123
F8	Executes SAVEASY
F9	Executes RECALL
F10	Executes COTTRELL.SUB

Programs

C:\APPLICAT\ASYST\THEMENU\MAIN.KIM

```
echo.off : alpha ." Kim" ; install alpha in prompt.xeq
\ *************************** COLUMN 1 : WHICH ROW IS THIS?
\ *************************** COLUMN 2 : IS A CV IN THIS COLUMN? 1 Y/0 N
\ *************************** COLUMN 3 : IS IT OFFSET?
\ *************************** COLUMN 4 : WHAT IS THE OFFSET?
\ *************************** COLUMN 5 : WHAT COLOR?
INTEGER SCALAR YOU  : ND NORMAL.DISPLAY ; ND DASH16
REAL DIM[ 15 , 1005 ] ARRAY CVS  REAL DIM[ 500 ] ARRAY POTS
REAL DIM[ 500 ] ARRAY CURRS 0 CVS := REAL SCALAR UPLIM
REAL SCALAR LOWLIM          \ DEFINITION OF SOME VARIABLES AND
REAL SCALAR VOLTRANGE       \ DIMENSIONING ARRAYS AND SETTING TO 0
```

```
REAL SCALAR CURR.SET REAL SCALAR ACQRATE REAL SCALAR RATE
REAL SCALAR START INTEGER SCALAR CV#
INTEGER SCALAR DIGSTART
INTEGER SCALAR DIM1
INTEGER DIM[ 10 ] ARRAY POT.BUFFER
DEF.PALETTE CREATE.COPY NEW.PALETTE
52 NEW.PALETTE [ 5 ] := 53 NEW.PALETTE [ 6 ] := 6 NEW.PALETTE [ 7 ] :=
47 NEW.PALETTE [ 9 ] := 46 NEW.PALETTE [ 10 ] :=
0 NEW.PALETTE [ 2 ] := 1 NEW.PALETTE [ 1 ] :=

LOAD SCALE.KIM
1 1 D/A.TEMPLATE ROTATION
: OUT ROTATION D/A.INIT 0 5 D/A.SCALE D/A.OUT ;
0 OUT

: COLOUR \ ******************** USE COLOR #
  CVS [ CV# , 5 ] COLOR
;

: LABEL1 .4 .97 POSITION "TIME LABEL
.2 .97 POSITION "DATE LABEL
16 1 DO
   16 I - CV# := COLOUR
   NORMAL.COORDS
   .96 .95 I .05 * - POSITION
   16 I - "." LABEL 14 COLOR
LOOP ;

: CVLABEL.X .5 .05 POSITION " POTENTIAL/V" CENTERED.LABEL ;

: CVLABEL.Y 90 LABEL.DIR 90 CHAR.DIR
0 .5 POSITION " CURRENT/mA" CENTERED.LABEL 0 LABEL.DIR 0 CHAR.DIR ;

: CVLABELS 14 COLOR NORMAL.COORDS LABEL1 CVLABEL.X CVLABEL.Y
   0 0 POSITION WORLD.COORDS CURSOR.OFF ;

: XAP VUPORT.CLEAR
CURR.SET 5 * NEG CURR.SET 5 * VERTICAL WORLD.SET
LOWLIM UPLIM HORIZONTAL WORLD.SET
AXIS.DEFAULTS XY.AXIS.PLOT CVLABELS
;

: SC LOAD THEMENU\SCOPE.KIM ;

\ **********************F1--PARAMETERS MENU************************
```

```
1.8 UPLIM :=  \ SETTING INITIAL VALUES ACTIVE UPON LOADING MCV.JOE
1.5 LOWLIM :=
40.0 RATE :=
1.0 CURR.SET :=
lowlim 0.02 + START :=
500 DIM1 :=
: PARAMENU
    LOAD THEMENU\PARAMENU.KIM
    LOAD CY.KIM
;

\ ******************ACQUISITION OF THE DATA******************
: RUNSUB
    LOAD THEMENU\DATAQUIS.KIM
    LOAD STARS.KIM
;

\ ************************** SET PARAMETERS IN COLUMNS 1-5
CVS SUB[ 1 , 15 , 1 ; 1 , 1 , 1 ] []RAMP \ ***** SET CV#
15 1 CVS SUB[ 1 , 15 , 1 ; 5 , 1 , 1 ] []FILL \ ***** SET COLOR
: BIG2SMALL \ **** SUBROUTINE THAT TAKES DATA FROM LARGE 15X1010
ARRAY
   CVS XSECT[ CV# , ! ] DUP
   SUB[ 6 , 500 ,  1 ] POTS :=
   SUB[ 506 , 500 , 1 ] CURRS :=
;
: CONVERTS \ *************** 2 D ARRAY > 1 D ARRAY
   ." which CV? "
   #INPUT CR ." OK "
   CV# := BIG2SMALL
;
: PLOT \ ************************** PLOT COMMAND
   ." Plot " CONVERTS
   COLOUR
   HORIZONTAL AXIS.FIT.ON LABEL.SCALE.ON
   VERTICAL AXIS.FIT.ON LABEL.SCALE.ON
   POTS CURRS XY.AUTO.PLOT CVLABELS 14 COLOR OUTLINE
   LOAD CY.KIM
   \ 0 0 POSITION
;
: SHEW \ ************************** SHOW CVS ON CURRENT AXES
   ." Show " CONVERTS
   COLOUR
   POTS CURRS XY.DATA.PLOT CURSOR.OFF \ 0 0 POSITION
;
```

```
\ ****THIS CONTROLS THE ROTATOR, COLLECTS DATA FOR # OF CVS***
: KLSUB
   LOAD THEMENU\KL_EXPNT.KIM
;
40 STRING FILENAME.WK?
REAL DIM[ 14 ] ARRAY KLDATA
INTEGER SCALAR COLUMN#
: KLTREAT  \ ************* TAKES THE MAX OF EACH CV AND SAVES IT W/
RPM ******
   LOAD THEMENU\KL_DATA.KIM \ ******** IN LOTUS *********************
;

\ *******F7==SAVE DATA TO A LOTUS WORKSHEET FILE********************
: SAVE123
      LOAD THEMENU\123STORE.KIM
;

\*****************F8==STORE CV TO ASYST FORMATTED DATA FILE*********
: SAVEASY
      LOAD THEMENU\ASYSTORE.KIM
;

\ *********F9==THIS SHOULD RETRIEVE OLD ASYST DATA FILES************
\ *****************AND PUTS THEM IN CHOSEN CV, 1-15*********************
: RECALL
      LOAD THEMENU\RETRIEVE.KIM
;

\ *********F10==THIS SHOULD RUN COTTRELL EXPERIMENTS ***************
\ *************AND PUT  THEM IN CHOSEN CV, 1-15*********************
: COTTRELL.SUB
      LOAD THEMENU\CHRONO.KIM
;
\ ******************************************************************
1 1 4 78 WINDOW REG
: YAP VUPORT.CLEAR
XY.AXIS.PLOT CVLABELS
;
: SETUPSCREEN
  0 0 VUPORT.ORIG 1 .8 VUPORT.SIZE 0 VUPORT.COLOR
  GRAPHICS.DISPLAY
  XAP
  NEW.PALETTE GRAPHICS.PALETTE
  REG {BORDER}
  OUTLINE
```

```
;
: OSRESET
  0 0 VUPORT.ORIG 1 .8 VUPORT.SIZE 0 VUPORT.COLOR
  GRAPHICS.DISPLAY
  YAP OUTLINE
  NEW.PALETTE GRAPHICS.PALETTE
  REG {BORDER}
;
: set setupscreen ;

\ offset
: RESET \ 16 1 DO
  \ 0 CVS [ I , 3 ] := 0 CVS [ I , 4 ] :=
  0 CVS SUB[ 1 , 15 , 1 ; 3 , 2 , 1 ] := ;
  \ LOOP ;
REAL SCALAR X1 REAL SCALAR X2 REAL SCALAR Y1 REAL SCALAR Y2
: OS.PLOT
  VERTICAL AXIS.FIT.OFF LABEL.SCALE.OFF Y1 Y2 WORLD.SET
  HORIZONTAL AXIS.FIT.OFF LABEL.SCALE.OFF X1 X2 WORLD.SET
  VUPORT.CLEAR XY.AXIS.PLOT CVLABELS OUTLINE ;
: ZX Y2 := Y1 := X2 := X1 :=  RESET OS.PLOT ;

REAL SCALAR OS#

: OS \ ***** ALLOWS ONE TO MOVE THE CV UP OR DOWN BY TYPING A
VALUE FOR
    \ ***** THE CV#, A VALUE FOR THE AMOUNT OF OFFSET, AND "OS"
    \ ***** EXAMPLE: OFFSET CV1 BY -.2 >>>  1 -.2 OS [CR]
  OS# := CV# :=
  OS# CVS [ CV# , 4 ] :=
  BIG2SMALL COLOUR
  POTS CURRS OS# + XY.DATA.PLOT
  1 CVS [ CV# , 3 ] :=
  \ 0 0 POSITION
;

: OSBIG 15 1 DO I 0 OS LOOP ; \ ***** SHOWS CVS 1-14 W/ 0 OFFSET

: OSBG OSBIG 15 0 OS ;          \ ***** SHOWS CVS 1-15 W/ 0 OFFSET

: BIG 0 0 VUPORT.ORIG 1 1 VUPORT.SIZE VUPORT.CLEAR CVLABELS OUTLINE
;

: DOIT SCREEN.PRINT LOAD THEMENU\CONDITNS.KIM GRAPHICS.DISPLAY
OSRESET ;
```

```
: OS.ALL \ ***** THIS PRINTS ALL CVS WHICH HAVE BEEN OFFSET ON A
FULL SCREEN
  BIG XY.AXIS.PLOT
    16 1 DO
      CVS [ I , 3 ] 1 = IF
      CVS [ I , 4 ] OS# := I CV# :=
      BIG2SMALL COLOUR POTS CURRS OS# + XY.DATA.PLOT
    THEN
  LOOP DOIT
  16 1 DO
    CVS [ I , 3 ] 1 = IF
      CVS [ I , 4 ] OS# := I CV# :=
      BIG2SMALL COLOUR POTS CURRS OS# + XY.DATA.PLOT
    THEN
  LOOP
;

\ ************************ASSIGN FUNCTION KEYS*******************
F1 FUNCTION.KEY.DOES PARAMENU
F2 FUNCTION.KEY.DOES KLSUB
F3 FUNCTION.KEY.DOES RUNSUB
F4 FUNCTION.KEY.DOES PLOT
F5 FUNCTION.KEY.DOES SHEW
F6 FUNCTION.KEY.DOES OS.ALL
F7 FUNCTION.KEY.DOES SAVE123
F8 FUNCTION.KEY.DOES SAVEASY
F9 FUNCTION.KEY.DOES RECALL
F10 FUNCTION.KEY.DOES COTTRELL.SUB

SETUPSCREEN

LOAD 1812.KIM
```

C:\APPLICAT\ASYST\THEMENU\PARAMENU.KIM

```
SCALAR IT
MENU PARAMETERS.MENU
    PARAMETERS.MENU
    " PARAMETERS MENU" MENU.TITLE
    MENU.blow.UP
    MENU.NO.PROTECT
1 1 5 78 MENU.SHAPE
1 1 " LOWLIM(VOLTS)" MENU.ITEM{ LOWLIM }
```

```
3 1 " UPLIM(VOLTS)" MENU.ITEM{ UPLIM }
1 25 " SCANRATE(mV/SEC)" MENU.ITEM{ RATE }
3 25 " START POT(VOLTS)" MENU.ITEM{ START }
1 55 " CURRSET(mA/V)" MENU.ITEM{ CURR.SET }
MENU.END
: CALCULATE.TIME \ CALCULATE THE TIME BETWEEN DATA POINTS
UPLIM LOWLIM - VOLTRANGE :=
VOLTRANGE 2. * RATE / 1000 * DIM1 / 1000 * ACQRATE :=
   \ 2 * GIVES TOTAL # OF VOLTS
   \ RATE / GIVES TOTAL NUMBER OF SEC TO ACQUIRE DATA
   \ 1000 * CONVERTS mV TO VOLTS
   \ 1000 * GIVES TOTAL NUMBER OF mSEC TO ACQUIRE DATA
   \ DIM1 / GIVES NUMBER OF mSEC PER DATA POINT
   \ CONVERT START TO DIGITAL VALUE
START 5 + 4096. * 10. / DIGSTART :=
;
CALCULATE.TIME      \ MAKES DEFAULT PARAMETERS ACTIVE SO CV
                    \ CAN BE OBTAINED UPON LOADING PROGRAM
                    \ WITHOUT FIRST USING F1 MENU.
: SET.PARAMETERS.MENU
SCREEN.CLEAR
PARAMETERS.MENU MENU.EXECUTE
LOWLIM 0.02 + START :=
CALCULATE.TIME        \ MAKES NEW PARAMETERS ACTIVE UPON EXITING
CR ." The current start potential is " START . ."  V."
CR ." Type F3 to run a CV."
CR PROMPT.XEQ SPACE ;
set.parameters.menu
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\ROTARATE.KIM

```
SCALAR IT
LOAD THEMENU\ROTARATE.KIM
: CVMAX
  15 1 DO
    I CV# := BIG2SMALL
    CURRS []MAX
    KLDATA [ I ] :=
  LOOP
;
: KL123
  CR ." Write to which file? " "INPUT FILENAME.WK? ":=
```

```
  CR ." Is this a new file? "
  KEY 89 = IF
    ." Y ... WORKING"
    FILENAME.WK? DEFER> 123FILE.CREATE
    FILENAME.WK? DEFER> 123FILE.OPEN
    1 1 123WRITE.DOWN ROTRATE ARRAY>123FILE
    ELSE FILENAME.WK? DEFER> 123FILE.OPEN
    THEN
  CR ." Write to which column? " #INPUT COLUMN# :=
  1 COLUMN# 123WRITE.DOWN KLDATA ARRAY>123FILE
  123FILE.CLOSE CR ." Operation complete. "
;
CVMAX KL123
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\ROTARATE.KIM

```
REAL DIM[ 14 ] ARRAY ROTRATE
  88 ROTRATE [ 14 ] :=
 100 ROTRATE [ 13 ] :=  \ CAN CHANGE THESE VALUES TO WHATEVER
 131 ROTRATE [ 12 ] :=
 166 ROTRATE [ 11 ] :=  \ ROTATION RATES ARE DESIRED, IN RPMs
 217 ROTRATE [ 10 ] :=
 295 ROTRATE [ 9 ] :=
 400 ROTRATE [ 8 ] :=
 663 ROTRATE [ 7 ] :=
 900 ROTRATE [ 6 ] :=
1179 ROTRATE [ 5 ] :=
1600 ROTRATE [ 4 ] :=
2500 ROTRATE [ 3 ] :=
3600 ROTRATE [ 2 ] :=
4900 ROTRATE [ 1 ] :=
```

C:\APPLICAT\ASYST\THEMENU\CHRONO.KIM

```
ECHO.OFF ND
REAL SCALAR IT 1 IT :=
DP.REAL SCALAR DIV
DP.REAL SCALAR DIVE
DP.REAL SCALAR DIVE1
REAL SCALAR OXPOT
```

```
REAL SCALAR CURR.MAX
INTEGER SCALAR COUNT2
DP.INTEGER SCALAR COUNT1
INTEGER SCALAR COUNT
INTEGER SCALAR TEST
INTEGER DIM[ 500 ] ARRAY DATA.BUFFER

0 POTS :=   0 currs :=  .1 DIVE :=  0 div :=    0 CURR.SET :=   0 dive1 :=
0 COUNT2 := 0 count1 := 0 count :=  0 test :=   0 CURR.MAX := \ 0 RALPH :=
\ 0 SAM :=
CR ." WHICH RUN IS THIS?"
       CR #INPUT
       CV# :=
CR ." INPUT THE CURRENT SETTING IN THE RDE4, IN mA PER VOLT"
       CR #INPUT
       CURR.SET :=
CR ." INPUT THE POTENTIAL AT WHICH YOU WISH TO OXIDIZE."
       CR #INPUT
       OXPOT := OXPOT .
45 DIV := 1 COUNT :=
CR ." INPUT THE WINDOW CURRENT IN uA" CR
       #INPUT
       CURR.MAX := CURR.MAX .

DOTTED GRAPHICS.DISPLAY REG
NEW.PALETTE GRAPHICS.PALETTE VUPORT.CLEAR {BORDER}
VERTICAL WORLD.COORDS -2 3 \ curr.set -1 * CURR.SET 5. *
WORLD.SET     12 10 axis.divisions
HORIZONTAL WORLD.COORDS -1 5 WORLD.SET XY.AXIS.PLOT OUTLINE
1 COLOR
CR ." Hit any key thrice to conclude the experiment."
   \ CALCULATE TIME BETWEEN DATA POINTS, IN SECONDS
DIV 1000 / DIVE1 :=
   \ DEFINE WORD TO TAKE DATA
1 1 A/D.TEMPLATE CHRON.TEMPLATE
.02 CONVERSION.DELAY
DATA.BUFFER TEMPLATE.BUFFER
: CHRONO                   \ DEFINE A WORD TO TAKE DATA
   CHRON.TEMPLATE A/D.INIT
 1 COUNT1 :=
 DIV SYNC.PERIOD           \ SET THE TIME BETWEEN DATA POINTS
   BEGIN
   A/D.IN>ARRAY                     \ * MAKE A READING
\  DIVE RALPH + SAM :=
   DIVE LOG                         \ ***** PLOT POINT
```

```
   DATA.BUFFER [ COUNT1 ] 409.5 / 5. - CURR.SET *  ABS LOG
   DRAW.TO       \ ********************V*V*V TAKE THIS DATA? V V V V
   count 1 > if    \ ***** Forces program to take the first data point ******
                   \ ***** Is the current datum significantly different than the last
                   \ ***** point that was saved or has the operator terminated the run?
      DATA.BUFFER [ COUNT1 ]
      CURRS [ COUNT 1 - ] - ABS CURR.SET CURR.MAX / >
      TEST 2 = OR
      IF
      DIVE POTS [ COUNT ] := \ ***** WHAT TIME IS THE DATA TAKEN?
      DATA.BUFFER [ COUNT1 ] CURRS [ COUNT ] := \ ***** Save the data
      COUNT 1 + COUNT :=  15 COUNT 50 / - COLOR  \ ***** Advance the count,
      then            \ ***** Change the color every 50 points saved.
   else
      DIVE POTS [ COUNT ] := \ ***** WHAT TIME IS THE DATA TAKEN?
      DATA.BUFFER [ COUNT1 ] CURRS [ COUNT ] :=
      count 1 + count :=
      1 test := \ ***** inserted due to problems w/ graphing
      15 COUNT 50 / - COLOR
      ROTATION D/A.INIT
      OXPOT OUT \ ***** After the first point, go to oxidizing potential.
      CHRON.TEMPLATE A/D.INIT
   then
   DIVE DIVE1 + DIVE :=    \ MOVE CLOCK TO NEXT POSITION
   1 COUNT1 + COUNT1 :=    \ ADVANCE COUNT TO NEXT ARRAY POSITION
   COUNT1 501 =
   COUNT 501 = OR IF       \ IF CURRS  IS FULL, STOP. OTHERWISE CONTINUE
   1 TEST := THEN
   ?BUFFER.FULL IF        \ If buffer is full, exit this loop
   1 TEST := THEN
   TEST 1 =             \ Test statement.  If true, exits loop.
   SYNCHRONIZE
   UNTIL
;

: ?DONE                 \ DEFINE A WORD TO SEE IF EXPERIMENT IS OVER
      PAUSE             \ HAS A KEY BEEN PRESSED?
      ?KEY IF           \ HAS A KEY BEEN PRESSED A THIRD TIME?
      2 TEST := ELSE     \ <---- STOP
      0 TEST := THEN     \ <---- CONTINUE
;

: CONVERT  \ CHANGES DATA TO MEANINGFUL UNITS AND STORES IN
CURRS
      CURRS 4095. / 10. * 5. - CURR.SET * CURRS :=
```

```
    POTS CVS SUB[ CV# , 1 , 1 ; 6 , 500 , 1 ] := \ DUMP TO BIG ARRAY
    CURRS CVS SUB[ CV# , 1 , 1 ; 506 , 500 , 1 ] :=
;

\ DEFINE A WORD THAT WILL RUN THE EXPERIMENT,
\ AND CONVERT IT TO REAL UNITS
: RUN
    CURSOR.OFF
    .1 DIVE :=
    BEGIN           \ START CONDITIONAL DATA AQUIS. LOOP
        CHRONO  \ GET DATA FOR 2ND HALF OF ARRAY
        ?done
        COUNT COUNT2 = IF   \ NEW DATA TAKEN DURING LAST
CYCLE?(500PTS)
           DIV 50 + DIV :=   \ INCREASE TIME BTWN SAMPLING
           DIV 1000 / DIVE1 := \ ADJUST PLOTTING CLOCK
           DIV SYNC.PERIOD     \ FINAL ADJUSTMENTS TO CLOCK
           DIVE DIVE1 + DIVE :=  \ ADVANCE CLOCK
           SYNCHRONIZE ELSE
        COUNT COUNT2 := THEN
        count 501 =  IF
           1 TEST :=  THEN
        TEST 1 =   \ EXIT LOOP IF DONE
        TEST 0 = IF DIVE DIVE1 + DIVE := SYNCHRONIZE THEN
    UNTIL
    CONVERT \ CHANGE TO MEANINGFUL UNITS & STORE IN CURRS
;

ROTATION D/A.INIT

RUN
LOAD CHARGE!.KIM CR ." FINISHED" CR
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\POLISH.KIM

```
SCALAR IT
\ This program was written to simply beep at appropriate times to aid me in
\ polishing my electrode.  It will give me 20 seconds after I start it and then
\ beep, telling me to begin.  It will then beep again telling me to stop.  It
\ will then allow me 20 seconds to rinse the electrode before beeping again
\ to signal me to start on the second polishing phase.  This continues through
\ the four phases but can be stopped at any time.
```

```
19000 MSEC.DELAY \ Go to the polishing station.
500 880 TUNE 500 MSEC.DELAY 500 880 TUNE
119500 MSEC.DELAY \ Polish: 1.0 um alumina.
500 440 TUNE
19500 MSEC.DELAY  \ Rinse.
500 880 TUNE 500 MSEC.DELAY 500 880 TUNE
120500 MSEC.DELAY \ Polish: 0.3 um alumina.
500 440 TUNE
19500 MSEC.DELAY  \ Rinse.
500 880 TUNE 500 MSEC.DELAY 500 880 TUNE
120500 MSEC.DELAY \ Polish: 0.05 um alumina.
500 440 TUNE
19500 MSEC.DELAY  \ Rinse.
500 880 TUNE 500 MSEC.DELAY 500 880 TUNE
120500 MSEC.DELAY \ Polish: cloth only.
500 440 TUNE
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\ASSTO123.KIM

```
SCALAR ASSTO123
\ ***** Name: ASSTO123.KIM
\ ***** Created: 06 SEP 94 by Kim Pamplin
\ ***** This file is designed to save the 15 cvs currently in memory and save
\ ***** them in a Lotus 1-2-3 format.  The new WK1 worksheet will have
\ ***** potentials saved in odd numbered columns and currents saved in even
\ ***** numbered columns.  The worksheet will be 30 by 500.  This leaves only
\ ***** one cv that must be saved manually if you have 8 pairs.

: SAVE'EM
  CR ." Write to which file? " "INPUT FILENAME.WK? ":=
  CR ." Is this a new file? "
  KEY 89 = IF
    ." Y ... WORKING"
    FILENAME.WK? DEFER> 123FILE.CREATE
    FILENAME.WK? DEFER> 123FILE.OPEN
    ELSE FILENAME.WK? DEFER> 123FILE.OPEN
    THEN
  CR ." Begin with which column? " #INPUT COLUMN# :=
  16 1 DO
    I CV# := BIG2SMALL
    1 I 2 * 2 - COLUMN# + 123WRITE.DOWN POTS ARRAY>123FILE
    1 I 2 * 1 - COLUMN# + 123WRITE.DOWN CURRS ARRAY>123FILE
```

```
  LOOP
  123FILE.CLOSE CR ." Operation complete. "
;

SAVE'EM
FORGET ASSTO123
```

C:\APPLICAT\ASYST\THEMENU\POTFIX.KIM

```
SCALAR POTFIX \ DEFINITION USED TO CLEAR POTFIX FROM MEMORY

   \ ***** Name: POTFIX.KIM
   \ ***** Created: 30 AUG 94 by Kim Pamplin
   \ ***** Purpose: This file is designed to alter cv data so that the huge
   \ *****          spikes found in the triangular potenial wave are
   \ *****          eliminated.

   \ ***** Part I: Definition of variables
REAL DIM[ 500 ] ARRAY POT# \ ***** The x array (POTS is the y array)
REAL DIM[ 2 ] ARRAY MB1 \ ***** Used for the slope and intercept of a portion
REAL DIM[ 2 ] ARRAY MB2 \ ***** of the line.
REAL SCALAR RATIO \ ***** Used to store the ratio of the slopes of two portions
         \ ***** of the pots vs pot# waveform.
POT# []RAMP \ ***** Fill the array with integers 1 to 500
LOAD.OVERLAY MATFIT.SOV

   \ ***** Part II: Find the spikes
: POT.FIX.IT \ Define a word to do the work.
477 14 DO  \ ***** This skips analysis of first and last 13 points.
POT# SUB[ I 13 - , 10 , 1 ] POTS SUB[ I 13 - , 10 , 1 ] 1 \ ***** Places the
   \ ***** coordinates for ten points of a line and the degree of polynomial
   \ ***** (1) on the number stack in preparation for the next operation
   LEASTSQ.POLY.FIT \ ***** Finds the slope and intercept of the above line
   MB1 := \ ***** Places the slope/intercept in an array
   POT# SUB[ I 3 + , 10 , 1 ] POTS SUB[ I 3 + , 10 , 1 ] 1 \ ***** Places the
   \ ***** coordinates for ten points of a line and the degree of polynomial
   \ ***** (1) on the number stack in preparation for the next operation
   LEASTSQ.POLY.FIT \ ***** Finds the slope and intercept of the above line
   MB2 := \ ***** Places the slope/intercept in an array
   MB1 [ 1 ] MB2 [ 1 ] / RATIO := \ ***** Takes the ratio of the two slopes
   RATIO 1 - ABS 0.25 < IF
      POT# [ I ] MB1 [ 1 ] * MB1 [ 2 ] + POTS [ I ] - ABS VOLTRANGE 100 / > IF
         POTS [ I ] CURRS [ I ] POSITION CURSOR.ON
```

```
      POT# [ I ] MB1 [ 1 ] * MB1 [ 2 ] + POTS [ I ] :=
    THEN
  THEN
LOOP
;
pot.fix.it
forget potfix
```

C:\APPLICAT\ASYST\THEMENU\KL_EXPNT.KIM

```
SCALAR IT
\ ****THIS CONTROLS THE ROTATOR, COLLECTS DATA FOR # OF CVS***
LOAD THEMENU\RGSUB.KIM
LOAD THEMENU\ROTARATE.KIM
 1 1 D/A.TEMPLATE ROTATION
 ROTATION D/A.INIT
\ : OUT 0 5 D/A.SCALE D/A.OUT ;
\ 1.6 OUT
 rotrate 1000 / rotrate :=
: ROTSHOW BIG2SMALL COLOUR POTS CURRS XY.DATA.PLOT
    ROTRATE [ I ] 1000 * FIX . ;
: ROTATOR2 CR
    ." Rotation rates completed:" CR
    15 1 do
      rotrate [ i ] out i runguts
      100 10 2 log 12 / i * 440 log + ** tune ROTSHOW
    loop 0 out 500 10 2 log 12 / 440 log + ** tune
;
: ROTATOR CR
    ." Levich experiment in progress, please wait."
    ROTATOR2
    CR
    ." Levich experiment completed."
    CR PROMPT.XEQ SPACE
;
ROTATOR
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\DATAQUIS.KIM

```
SCALAR IT
```

```
\ ************************************************************
\ ******************ACQUISITION OF THE DATA******************
LOAD THEMENU\RGSUB.KIM
: RUNCV
  CR ." Run which CV# ? "
  #INPUT CR
  RUNGUTS
  LOAD THEMENU\SMOOTHER.KIM
  ." Now what? " CR
;
RUNCV
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\ASYSTORE.KIM

```
SCALAR IT
\ **********************************************************************

\ ************F8==STORE CV TO ASYST FORMATTED DATA FILE*********
LOAD THEMENU\FILENAME.KIM
\ CREATE A FILE TEMPLATE
: storage    \ file template is erased whenever an error occurs
    FILE.TEMPLATE      \ so i recreate the file template every time
    REAL DIM[ DIM1 ] SUBFILE
    2 TIMES
    END
    FILENAME DEFER> FILE.CREATE
    FILENAME DEFER> FILE.OPEN
;
: STORE.CV
    storage
    BIG2SMALL
    1 SUBFILE POTS ARRAY>FILE
    2 SUBFILE CURRS ARRAY>FILE
    FILE.CLOSE
;

MENU STORE.ASYST.MENU
    STORE.ASYST.MENU
    " ASYST DATA FILE STORAGE MENU" MENU.TITLE
    MENU.blow.up
    1 40 4 78 MENU.SHAPE
    1 2 " CV#" MENU.ITEM{ CV# }
```

```
    2 2 " FILENAME" MENU.ITEM{ FILENAME }
    1 28 " STORE" MENU.ITEM{ STORE.CV }
MENU.END
: STORE.ASYST
    SCREEN.CLEAR
    STORE.ASYST.MENU MENU.EXECUTE
    CR PROMPT.XEQ SPACE
;
STORE.ASYST
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\RETRIEVE.KIM

```
SCALAR IT
\ *********************************************************************
\ *********F9==THIS SHOULD RETRIEVE OLD ASYST DATA FILES************
\ **************AND PUTS THEM IN CHOSEN CV, 1-15**********************
LOAD THEMENU\FILENAME.KIM
: GET.CV
    FILENAME DEFER> FILE.OPEN
    1 SUBFILE CVS SUB[ CV# , 1 , 1 ; 6 , 500 , 1 ] FILE>ARRAY
    2 SUBFILE CVS SUB[ CV# , 1 , 1 ; 506 , 500 , 1 ] FILE>ARRAY
    FILE.CLOSE
;

MENU GET.ASYST.MENU
    GET.ASYST.MENU
    " ASYST DATA FILE RETRIEVAL MENU" MENU.TITLE
    MENU.PULL.DOWN
    1 40 4 78 MENU.SHAPE
    1 2 " CV#" MENU.ITEM{ CV# }
    2 2 " FILENAME" MENU.ITEM{ FILENAME }
    1 25 " RETRIEVE" MENU.ITEM{ GET.CV }
MENU.END
: GET.ASYST
    SCREEN.CLEAR
    GET.ASYST.MENU MENU.EXECUTE
    CR PROMPT.XEQ SPACE
;
GET.ASYST
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\RGSUB.KIM

```
5 string potsy
5 string ralph
5 string cursy " 1.00" cursy ":=
\ ************************************************************
\ ******************ACQUISITION OF THE DATA******************
\ DEFINE THE TEMPLATE FOR DATA ACQUISITION
   INTEGER DIM[ 5000 , 2 ] ARRAY DATA.BUFFER \ 10 * following DIM1
1 2 A/D.TEMPLATE CV.TEMPLATE
.02 CONVERSION.DELAY
DATA.BUFFER TEMPLATE.BUFFER
: CV   \ DEFINE WORD TO TAKE DATA
   CV.TEMPLATE A/D.INIT
   ACQRATE SYNC.PERIOD
   DIM1 0 DO        \ TAKES DATA IN GROUPS OF TEN
       WORLD.COORDS
       SYNCHRONIZE    \ EACH GROUP OF TEN IS ACQUIRED AS FAST AS
       11 1 DO A/D.IN>ARRAY LOOP \ POSSIBLE
       DATA.BUFFER [ I 10 * 5 + , 2 ] 4096. / 10 * 5 -
       DUP "." ralph ":=
       DATA.BUFFER [ I 10 * 5 + , 1 ] 4096. / 10 * 5 - CURR.SET *
       DUP "."
       COLOUR
       DRAW.TO
       ralph cursy "= if
         "drop
         else
         normal.coords
         0 color
         .63 .97 position
         potsy label
         .78 .97 position
         cursy label
         14 color
         potsy ":=
         ralph cursy ":=
         .63 .97 position
         potsy label
         .78 .97 position
         cursy label
       then
   LOOP SOLID
   normal.coords
```

```
  0 color
  .63 .97 position
  potsy label
  .78 .97 position
  cursy label
  colour world.coords
;
INTEGER SCALAR L
: AVERAGE
   500 0 DO I L :=
     0
     11 1 DO
        DATA.BUFFER [ L 10 * I + , 1 ] +
     LOOP
     10 / CURRS [ L 1 + ] :=
     0
     11 1 DO
        DATA.BUFFER [ L 10 * I + , 2 ] +
     LOOP
     10 / POTS [ L 1 + ] :=
   LOOP
;
\ READ POT UNTIL IS > START
2 2 A/D.TEMPLATE POT.TEMPLATE
: READPOT
14 COLOR NORMAL.COORDS .6 .97 POSITION " i=" LABEL
.75 .97 POSITION " E=" label WORLD.COORDS COLOUR
DOTTED CURSOR.OFF
POT.TEMPLATE A/D.INIT
2 1 DO   \ USED THIS NESTED STRUCTURE WITH THE WAIT TIME
11 1 DO
 BEGIN   \ BECAUSE WAS STILL HAVING TROUBLE GETTING IT TO
   11 1 DO  \ ALWAYS START ON POSITIVE SCAN AT SAME POTENTIAL
   A/D.IN
   POT.BUFFER [ I ] :=
   LOOP
 POT.BUFFER MEAN 4096. / 10. * 5 - "." ralph ":=
 ralph cursy "= if else
 normal.coords
 0 color
 .78 .97 position
 cursy label
 14 color
 ralph cursy ":=
 .78 .97 position
```

```
 cursy label  then
 POT.BUFFER MEAN DIGSTART <
 UNTIL
LOOP 20 MSEC.DELAY LOOP
BEGIN
 11 1 DO A/D.IN POT.BUFFER [ I ] :=
   LOOP
 POT.BUFFER MEAN DIGSTART >
UNTIL
CV
;
\ DEFINE A WORD THAT WILL CONVERT DATA TO MEANINGFUL UNITS
: CONVERT
POTS 4095. / 10. * 5 - POTS :=
CURRS 4095. / 10. * 5 - CURR.SET * CURRS :=
;
\ DEFINE A WORD THAT WILL RUN THE EXPERIMENT, SEPARATE THE DATA,
\ AND CONVERT IT TO REAL UNITS
: RUNGUTS
  CV# := COLOUR READPOT AVERAGE CONVERT
\  POTS [ 2 ] POTS [ 1 ] := CURRS [ 2 ] CURRS [ 1 ] :=
  501 1 DO \ **************** DUMP TO BIG ARRAY
     POTS [ I ] CVS [ CV# , I 5 + ] :=
     CURRS [ I ] CVS [ CV# , I 505 + ] :=
  LOOP
;
```

C:\APPLICAT\ASYST\THEMENU\WARMUP.KIM

```
: GYRATE
1601 1 DO
I 1000. / OUT
10 MSEC.DELAY
LOOP
;
GYRATE
FORGET GYRATE
```

C:\APPLICAT\ASYST\THEMENU\SCOPE.KIM

```
REAL SCALAR IT
REAL SCALAR LBJ
REAL SCALAR JFK
REAL SCALAR FDR
REAL SCALAR RWR
REAL SCALAR POTMAX
REAL SCALAR POTMIN
REAL SCALAR POTRAN
REAL SCALAR MEDIAN
CR ." Enter the horizontal full scale multiplier (1 = 17 s)  " \ #INPUT
1. 10000. * IT :=
CR ." Enter the sampling time delay (ms)  " \ #INPUT
50. RWR :=
CR ." Enter the maximum potential (V)  "  #INPUT
POTMAX :=
POTMAX .
CR ." Enter the minumum potential (V)  " #INPUT
POTMIN :=
POTMIN . PAUSE
POTMAX POTMIN - POTRAN :=
POTRAN . PAUSE
POTRAN 10. / JFK :=
JFK .  PAUSE
POTRAN 2. / POTMIN + MEDIAN := MEDIAN . PAUSE
MEDIAN 5. + POTRAN / NEG .5 + FDR :=  FDR . PAUSE
REAL DIM[ IT 3 + ] ARRAY DATA.BUFFER
VUPORT.CLEAR
NORMAL.COORDS
.05 .05 AXIS.ORIG
.9 .9 AXIS.SIZE
.05 .05 AXIS.POINT
VERTICAL 0. 1. WORLD.SET GRID.OFF NO.LABELS
HORIZONTAL 0. 1. WORLD.SET GRID.OFF NO.LABELS
OUTLINE
XY.AXIS.PLOT

CURSOR.OFF
1 1 A/D.TEMPLATE CV.TEMPLATE
: SCOPEIT
CV.TEMPLATE A/D.INIT
A/D.IN 4096. / JFK / FDR + DATA.BUFFER :=
BEGIN
```

```
  IT 3 + 2 DO
    I 2 - LBJ :=
    IT 2 + I = I 2 = OR IF ELSE
      0 COLOR
      LBJ IT / DATA.BUFFER [ I ] POSITION
      LBJ 1 + IT / DATA.BUFFER [ I 1 + ]
      DRAW.TO
      14 COLOR
    THEN
    A/D.IN 4096. / JFK / FDR +
    2 I = IT 2 + I = OR IF
      DATA.BUFFER [ I ] :=
      ELSE
      LBJ 1 - IT / DATA.BUFFER [ I 1 - ] POSITION
      DUP DATA.BUFFER [ I ] :=
      LBJ IT / SWAP
      DRAW.TO
    THEN
  RWR MSEC.DELAY
  LOOP
  PAUSE ?KEY IF
    TRUE
  ELSE
    FALSE
  THEN
UNTIL
;
SCOPEIT
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\CONDITNS.KIM

```
ECHO.OFF
SCALAR IT
LOAD THEMENU\FILENAME.KIM
SCALAR PB 10 PB :=
SCALAR BI  4 BI :=
SCALAR ANALYTE 10 ANALYTE :=
6 STRING ANAL.CMPD " Cr" ANAL.CMPD ":=
SCALAR DEP.ELECTROLYTE 1 DEP.ELECTROLYTE :=
6 STRING DEP.ELEC.TYPE " HClO4" DEP.ELEC.TYPE ":=
REAL SCALAR DEP.I/V/PHI 1.7 DEP.I/V/PHI :=
6 STRING DEP.UNITS " V" DEP.UNITS ":=
```

```
INTEGER SCALAR DEP.ROTATION.RATE 0 DEP.ROTATION.RATE :=
SCALAR T/C 1 T/C :=
6 STRING T/C.UNITS " s" T/C.UNITS ":=
SCALAR OX.ELECTROLYTE 1 OX.ELECTROLYTE :=
6 STRING OX.ELEC.TYPE " H2SO4" OX.ELEC.TYPE ":=
INTEGER SCALAR OX.I/V/PHI 40 OX.I/V/PHI :=
6 STRING OX.UNITS " mV/s" OX.UNITS ":=
INTEGER SCALAR OX.ROTATION.RATE 1600 OX.ROTATION.RATE :=
MENU CONDITIONS.MENU
    CONDITIONS.MENU
    " Conditions Menu" MENU.TITLE
    MENU.BLOW.UP
    MENU.NO.PROTECT
1 1 5 78 MENU.SHAPE
0 1 " Filename" MENU.ITEM{ FILENAME }
1 1 " [Pb]/mM" MENU.ITEM{ PB }
1 21 " [Bi]/mM" MENU.ITEM{ BI }
1 41 " Analyte/mM" MENU.ITEM{ ANALYTE }
1 61 " Analyte" MENU.ITEM{ ANAL.CMPD }
2 1 " Dep Elec/M" MENU.ITEM{ DEP.ELECTROLYTE }
2 21 "NULL MENU.ITEM{ DEP.ELEC.TYPE }
2 41 " Anal Elec/M" MENU.ITEM{ OX.ELECTROLYTE }
2 61 "NULL MENU.ITEM{ OX.ELEC.TYPE }
3 1 " I/V/PHI" MENU.ITEM{ DEP.I/V/PHI }
3 21 " Dep units" MENU.ITEM{ DEP.UNITS }
3 41 " I/V/PHI" MENU.ITEM{ OX.I/V/PHI }
3 61 " Ox units" MENU.ITEM{ OX.UNITS }
4 1 " D rpm" MENU.ITEM{ DEP.ROTATION.RATE }
4 21 " D T/C" MENU.ITEM{ T/C }
4 41 "NULL MENU.ITEM{ T/C.UNITS }
4 61 " O rpm" MENU.ITEM{ OX.ROTATION.RATE }
MENU.END
: SET.CONDS
   CONDITIONS.MENU MENU.EXECUTE
;
SET.CONDS
ND
."     Deposition Conditions          Analyte Conditions" CR
."     [Pb] =" PB . ." mM  [Bi] =" BI . ." mM       [" ANAL.CMPD "TYPE
." ] = " ANALYTE . ." mM" CR
."     Electrolyte: " DEP.ELECTROLYTE . ." M " DEP.ELEC.TYPE "TYPE
."        Electrolyte: " OX.ELECTROLYTE . ." M " OX.ELEC.TYPE "TYPE CR
."     I/V/PHI = " DEP.I/V/PHI . DEP.UNITS "TYPE
."          I/V/PHI = " OX.I/V/PHI . OX.UNITS "TYPE CR
."     Rotation Rate = " DEP.ROTATION.RATE . ."  rpm"
```

```
."        Rotation Rate = " OX.ROTATION.RATE . ." rpm" CR
."     t/Q = " T/C . T/C.UNITS "TYPE
."               " FILENAME "TYPE
SCREEN.PRINT(DOS)

FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\SMOOTHER.KIM

```
ECHO.OFF
SCALAR IT
\ This program is designed to remove bit noise from the potential array for
\ cvs taken over a small potential range.  Bit noise is observed in the
\ potential array when the resolution of the data aquisition board is
\ significant (nearly as big as or bigger than each potential step is supposed
\ to be) compared to the desired potential step for each datum.
\ This program will use linear regression on each line segment of the
\ triangular potential waveform.  Based on the linear regression, it will
\ calculate the maximum and minimum potentials and then connect them to each
\ other and the beginning and ending potentials with linear potential sweeps.
\ I firmly believe that this will result in an array which is closer to the
\ waveform produced by the potentiostat than that recorded by the computer.
\ Kim Pamplin 11 NOV 94

\ As amended, this program will determine whether the cv starts on a negative
\ or positive scan.  Without this, the program only worked on cvs which start
\ on the positive scan.  Once it determines the scan direction, it can smooth
\ the potential wave with the appropriate subroutine, one for going up first,
\ the other for going down first.
\ KIM PAMPLIN 25 MAY 95

\ As further amended, this program will now plot the raw data and then smooth
\ the potential data as before, but now it will also smooth the current data
\ in three segments divided at the potential sweep direction shifts.

\ PLOT THE RAW DATA IN BLACK
1 COLOR POTS CURRS XY.DATA.PLOT

\ DEFINE VARIABLES
REAL DIM[ 1 ] ARRAY DUM \ DUMMY VARIABLE USED TO PUT DATA IN A
SCALAR
REAL SCALAR XP \ MAxIMUM pOTENTIAL
REAL SCALAR XPI \ MAxIMUM pOTENTIAL iNDEX
```

```
REAL SCALAR NP \ MInIMUM pOTENTIAL
REAL SCALAR NPI \ MInIMUM pOTENTIAL iNDEX
REAL DIM[ 2 ] ARRAY FIT \ TO STORE SLOPES AND INTERCEPTS

\ DETERMINE THE MAX AND MIN POTENTIALS
\  LOAD THE APPROPRIATE WORDS
LOAD.OVERLAY WAVEOPS.SOV
\  SET THE NUMBER OF OPTIMA TO BE FOUND
1 SET.#.OPTIMA
\  SET THE NUMBER OF POINTS USED IN FINDING LOCAL OPTIMA
21 SET.#.POINTS
\  GET MAXIMUM, MINIMUM OF THE MOST RECENTLY PLOTTED OR SHOWN
ARRAY
POTS LOCAL.MAXIMA
POTS LOCAL.MINIMA
\  PLACE THEM IN THEIR SCALARS
DUM := DUM [ 1 ] NP :=
DUM := DUM [ 1 ] NPI :=
DUM := DUM [ 1 ] XP :=
DUM := DUM [ 1 ] XPI :=

\ Determine the initial sweep direction.  If the minimum (np) comes before the
\ maximum (xp), then the initial sweep direction must be negative.  So, the
\ question is: is the minimum potential index smaller than the maximum potent-
\ ial index?
: EXECUTE
NPI XPI < IF \
****************************************************************
   \ IF INITIAL SWEEP DIRECTION IS NEGATIVE, THIS CODE WILL EXECUTE.

\ DETERMINE THE SLOPE FROM START TO MIN
\ CR ." In which CV# do you wish the results to be placed?"
\ CVS SUB[ CV# , 1 , 1 ; 506 , 500 , 1 ] \ TRANSFERS CURRENT DATA TO ...
\ #INPUT
\ CV# :=
\ CVS SUB[ CV# , 1 , 1 ; 506 , 500 , 1 ] := \ ... THE NEW CV# ARRAY
LOAD.OVERLAY MATFIT.SOV
CURRS []RAMP \ USED AS X AXIS IN POTENTIAL WAVEFORM
CURRS SUB[ 1 , NPI , 1 ]
POTS SUB[ 1 , NPI , 1 ]
1 LEASTSQ.POLY.FIT \ THIS REQUIRES X AND Y ARRAYS AND POLYNOMIAL
ORDER ON STACK
FIT := \ THE PUTS THE SLOPE AND INTERCEPT IN THE ARRAY "FIT"
\  CALCULATE THE REAL MINIMUM POTENTIAL
FIT [ 2 ] \ REAL BEGINNING POTENTIAL
```

```
FIT [ 1 ] NPI * FIT [ 2 ] + \ REAL MIN POTENTIAL
CVS SUB[ CV# , 1 , 1 ; 6 , NPI , 1 ] \ PORTION OF ARRAY TO BE FITTED
[]FILL \ REPLACES ABOVE PORTION OF ARRAY WITH LINEAR RAMP
BETWEEN REAL
   \ BEGINNING AND MIN POTENTIALS

\ DETERMINE THE SLOPE FROM MIN TO MAX
CURRS SUB[ NPI , XPI NPI - 1 + , 1 ]
POTS SUB[ NPI , XPI NPI - 1 + , 1 ]
1 LEASTSQ.POLY.FIT \ This requires x and y arrays and polynomial order on stack
FIT := \ THE PUTS THE SLOPE AND INTERCEPT IN THE ARRAY "FIT"
\   CALCULATE THE REAL MINIMUM POTENTIAL
CVS [ CV# , NPI 5 + ] \ REAL MIN POTENTIAL
FIT [ 1 ] XPI * FIT [ 2 ] + \ REAL MAX POTENTIAL
CVS SUB[ CV# , 1 , 1 ; NPI 5 + , XPI NPI - 1 + , 1 ] \ Fitted portion of array
[]FILL \ replaces above portion of array with linear ramp between real
   \ BEGINNING AND MAX POTENTIALS

\ DETERMINE THE SLOPE FROM MAX TO END
CURRS SUB[ XPI , 501 XPI - , 1 ]
POTS SUB[ XPI , 501 XPI - , 1 ]
1 LEASTSQ.POLY.FIT \ This requires x and y arrays and polynomial order on stack
FIT := \ THE PUTS THE SLOPE AND INTERCEPT IN THE ARRAY "FIT"
\   CALCULATE THE REAL MINIMUM POTENTIAL
CVS [ CV# , XPI 5 + ] \ REAL MIN POTENTIAL
FIT [ 1 ] 500 * FIT [ 2 ] + \ REAL END POTENTIAL
CVS SUB[ CV# , 1 , 1 ; XPI 5 + , 501 XPI - , 1 ] \ FITTED PORTION OF ARRAY
[]FILL \ Replaces above portion of array with linear ramp between real
   \ BEGINNING AND MAX POTENTIALS

ELSE

\ ************************************************************************

\ IF THE INITIAL SWEEP DIRECTION IS POSITIVE, THIS CODE WILL EXECUTE.

\ DETERMINE THE SLOPE FROM START TO MAX
\ CR ." In which CV# do you wish the results to be placed?"
\ CVS SUB[ CV# , 1 , 1 ; 506 , 500 , 1 ] \ TRANSFERS CURRENT DATA TO ...
\ #INPUT
\ CV# :=
\ CVS SUB[ CV# , 1 , 1 ; 506 , 500 , 1 ] := \ ... THE NEW CV# ARRAY
LOAD.OVERLAY MATFIT.SOV
CURRS []RAMP \ USED AS X AXIS IN POTENTIAL WAVEFORM
CURRS SUB[ 1 , XPI , 1 ]
```

```
POTS SUB[ 1 , XPI , 1 ]
1 LEASTSQ.POLY.FIT \ THIS REQUIRES X AND Y ARRAYS AND POLYNOMIAL
ORDER ON STACK
FIT := \ THE PUTS THE SLOPE AND INTERCEPT IN THE ARRAY "FIT"
\   CALCULATE THE REAL MAXIMUM POTENTIAL
FIT [ 2 ] \ REAL BEGINNING POTENTIAL
FIT [ 1 ] XPI * FIT [ 2 ] + \ REAL MAX POTENTIAL
CVS SUB[ CV# , 1 , 1 ; 6 , XPI , 1 ] \ Portion of array to be fitted
[]FILL \ replaces above portion of array with linear ramp between real
   \ beginning and max potentials

\ DETERMINE THE SLOPE FROM MAX TO MIN
CURRS SUB[ XPI , NPI XPI - 1 + , 1 ]
POTS SUB[ XPI , NPI XPI - 1 + , 1 ]
1 LEASTSQ.POLY.FIT \ This requires x and y arrays and polynomial order on stack
FIT := \ THE PUTS THE SLOPE AND INTERCEPT IN THE ARRAY "FIT"
\   CALCULATE THE REAL MINIMUM POTENTIAL
CVS [ CV# , XPI 5 + ] \ REAL MAX POTENTIAL
FIT [ 1 ] NPI * FIT [ 2 ] + \ REAL MIN POTENTIAL
CVS SUB[ CV# , 1 , 1 ; XPI 5 + , NPI XPI - 1 + , 1 ] \ FITTED PORTION OF ARRAY
[]FILL \ REPLACES ABOVE PORTION OF ARRAY WITH LINEAR RAMP
BETWEEN REAL
   \ BEGINNING AND MAX POTENTIALS

\ DETERMINE THE SLOPE FROM MIN TO END
CURRS SUB[ NPI , 501 NPI - , 1 ]
POTS SUB[ NPI , 501 NPI - , 1 ]
1 LEASTSQ.POLY.FIT \ THIS REQUIRES X AND Y ARRAYS AND POLYNOMIAL
ORDER ON STACK
FIT := \ THE PUTS THE SLOPE AND INTERCEPT IN THE ARRAY "FIT"
\   CALCULATE THE REAL MINIMUM POTENTIAL
CVS [ CV# , NPI 5 + ] \ REAL MIN POTENTIAL
FIT [ 1 ] 500 * FIT [ 2 ] + \ REAL END POTENTIAL
CVS SUB[ CV# , 1 , 1 ; NPI 5 + , 501 NPI - , 1 ] \ Fitted portion of array
[]FILL \ replaces above portion of array with linear ramp between real
   \ beginning and max potentials

\ SMOOTH THE CURRENT ARRAY
\ LOAD THE NECESSARY WORDS
LOAD.OVERLAY WAVEOPS.SOV
CVS XSECT[ CV# , ! ] SUB[ 506 , XPI , 1 ]
SMOOTH
CVS XSECT[ CV# , ! ] SUB[ 506 , XPI , 1 ]
:=
CVS XSECT[ CV# , ! ] SUB[ 506 XPI + , NPI XPI - 1 + , 1 ]
```

```
SMOOTH
CVS XSECT[ CV# , ! ] SUB[ 506 XPI + , NPI XPI - 1 + , 1 ]
:=
\ CVS XSECT[ CV# , ! ] SUB[ 506 NPI + , 500 NPI - , 1 ]
\ SMOOTH
\ CVS XSECT[ CV# , ! ] SUB[ 506 NPI + , 500 NPI - , 1 ]
\ :=

THEN
BIG2SMALL COLOUR POTS CURRS XY.DATA.PLOT CURSOR.OFF
;
EXECUTE
FORGET IT
```

C:\APPLICAT\ASYST\THEMENU\123STORE.KIM

```
SCALAR IT

\ *******F7==SAVE DATA TO A LOTUS WORKSHEET FILE********************
LOAD THEMENU\FILENAME.KIM
: STORAGE.123
    FILENAME.WK? DEFER> 123FILE.CREATE
    FILENAME.WK? DEFER> 123FILE.OPEN
;
: STORE.123 STORAGE.123
    1 1 123WRITE.DOWN CVS SUB[ CV# , 1 , 1 ; 6 , 500 , 1 ] ARRAY>123FILE
    1 2 123WRITE.DOWN CVS SUB[ CV# , 1 , 1 ; 506 , 500 , 1 ] ARRAY>123FILE
    123FILE.CLOSE
;

MENU STORE.123.MENU
    STORE.123.MENU
    " LOTUS DATA FILE STORAGE MENU" MENU.TITLE
    MENU.blow.up
    1 36 4 78 MENU.SHAPE
    1 2 " CV#" MENU.ITEM{ CV# }
    2 2 " FILENAME.WK?" MENU.ITEM{ FILENAME.WK? }
    1 32 " STORE" MENU.ITEM{ STORE.123 }
MENU.END

: STORES.123
    SCREEN.CLEAR
    STORE.123.MENU MENU.EXECUTE
```

```
    CR PROMPT.XEQ SPACE
;

STORES.123
FORGET IT


C:\APPLICAT\ASYST\THEMENU\FILENAME.KIM


\ ***********************************************************************

\ ************COMPILE FILENAME USING DATE AND TIME**************
 2 STRING YR
 2 STRING MO
 2 STRING DY
 2 STRING HR
 2 STRING MN
 4 STRING YRMO
 4 STRING DYHR
 4 STRING TAIL
 6 STRING DYHRMN
10 STRING DYHRMNTAIL
40 STRING FILENAM
40 STRING FILENAME
40 STRING FILENAME.WK?
REAL SCALAR REALWEEKS
INTEGER SCALAR INTWEEKS
INTEGER SCALAR MONTH#
"DATE 2 "RIGHT YR ":=    \ DATE MO/DY/YR    TIME  HR:MN:SC.HN
"DATE 2 "LEFT MO ":=     \      12345678          12345678901
"DATE 4 2 "SUB DY ":=
"TIME 2 "LEFT HR ":=
"TIME 4 2 "SUB MN ":=
YR MO "CAT YRMO ":=
" C:\RES\DATA\" FILENAM ":=
FILENAM YRMO "CAT FILENAM ":=
FILENAM " \" "CAT FILENAM ":=
DY HR "CAT DYHR ":=
DYHR MN "CAT DYHRMN ":=
YR 32 "NUMBER 95. - 365. *  \ Convert year to #, sub 95 from, convert to days
: GOMO MO 32 "NUMBER CASE
    1 OF 0 MONTH# := ENDOF
    2 OF 31 MONTH# := ENDOF
    3 OF 60 MONTH# := ENDOF
```

```
   4 OF 91 MONTH# := ENDOF
   5 OF 121 MONTH# := ENDOF
   6 OF 152 MONTH# := ENDOF
   7 OF 182 MONTH# := ENDOF
   8 OF 213 MONTH# := ENDOF
   9 OF 244 MONTH# := ENDOF
   10 OF 274 MONTH# := ENDOF
   11 OF 305 MONTH# := ENDOF
   12 OF 335 MONTH# := ENDOF
   0 MONTH# := ENDCASE
;
GOMO
MONTH# +
DY 32 "NUMBER + 7 / REALWEEKS :=
REALWEEKS INTWEEKS :=
: GO REALWEEKS INTWEEKS < IF INTWEEKS 1 - INTWEEKS := THEN
REALWEEKS INTWEEKS - 7 * INTWEEKS := INTWEEKS CASE
   1 OF " .SUN" TAIL ":= ENDOF
   2 OF " .MON" TAIL ":= ENDOF
   3 OF " .TUE" TAIL ":= ENDOF
   4 OF " .WED" TAIL ":= ENDOF
   5 OF " .THU" TAIL ":= ENDOF
   6 OF " .FRI" TAIL ":= ENDOF
   7 OF " .SAT" TAIL ":= ENDOF
   " .NUN" TAIL ":=
ENDCASE ; GO
DYHRMN TAIL "CAT DYHRMNTAIL ":=
FILENAM DYHRMNTAIL "CAT FILENAME ":=
" .WK1" TAIL ":=
DYHRMN TAIL "CAT DYHRMNTAIL ":=
FILENAM DYHRMNTAIL "CAT FILENAME.WK? ":=
```

References

1. Joe Vitt, Ph.D. Disserttation, Iowa State University, Ames, Iowa (1991).