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ACTIVATION AND DEACTIVATION OF GLASSY CARBON ELECTRODES

The Ohio State University

PH.D. 1985

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ACTIVATION AND DEACTIVATION OF GLASSY CARBON ELECTRODES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Ing-Feng Hu, M.S.

* * * * *

The Ohio State University

1985

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"Carbonaceous surfaces: modification, characterization, and uses for electrocatalysis", I.F. Hu, D.H. Karweik, S. Weng, and T. Kuwana, in "Catalyst Characterization Science", M.L. Deviney and J.L. Gland (Ed.), ACS Symposium series 288, Chapter 48.

"Vacuum heat-treatment for activation of glassy carbon electrodes", D. Fagan, I.F. Hu, and T. Kuwana, Anal. Chem., in press.

Major Field: Analytical Chemistry

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CHAPTER ONE

INTRODUCTION

In the last decade, solid electrodes (1,2) such as noble metal, carbon, and semiconductor electrodes have found numerous applications in the areas of electrochemical analysis (1-3), electrochemical synthesis (4), energy conversion (5), thermodynamic studies (6), and kinetic studies (6). However, an inherent problem in the use of solid electrodes is the degradation of the electrode surface (1). The surfaces of all solid electrodes are gradually deactivated by exposure to the atmosphere or to the working solution (7). Therefore, a surface preparation for activation of the electrode surface is required prior to the use of the electrode.

In general, a method of electrode activation should meet three criteria (8): (a) the production of a reproducible, and preferably known, surface area, (b) the creation of a maximum number of active sites on the surface, and (c) the minimization of contamination during the preparation step. Methods of surface preparation for platinum electrodes are well established and discussed at length by a number of authors (9-11). However, the surface preparation for glassy carbon, which is another popular electrode material, still remains a challenge to the electrochemist. This challenge gives rise to the motivation for the research described in this dissertation.

GENERAL OVERVIEW OF GLASSY CARBON

In 1962, starting from phenolic resins, Yamada and Sato (12) prepared a gas-impermeable carbon which they called glassy carbon. Although the details of glassy carbon (GC) fabrication have not been disclosed by the manufacturers and the original inventors, in principle, it is formed by means of carefully controlled heating of a premolded polymeric (e.g., phenol-formaldehyde) resin body under an inert atmosphere (13). Care must be taken that the polymeric substance does not pass into a liquid or tarry state immediately prior to carbonization because a product quite different from glassy carbon would then be obtained (14). The glassy carbon formed using this procedure has a random network structure of tangled graphite-like ribbon molecules (15) with a bond nature intermediate between sp^2 and sp^3 (15). This structure is illustrated in Fig. 1. Because of this random network structure, glassy carbon is anisotropic. The extent of anisotropy and graphitization (i.e., degree of sp^2 bonding character) are dependent on the heat-treatment temperature (HTT) during fabrication (15). As the HTT increases, glassy carbon becomes graphitized and isotropic. Commercially, the glassy carbons are often graded according to their highest heating temperature during the fabrication. For example, GC-10, GC-20, and GC-30 manufactured by Tokai Glassy Carbon Cooperation Company are made with HTT's of 1000°C, 2000°C, and 3000°C, respectively.

The physical and chemical properties of glassy carbon have been extensively studied (16-18) and can be found in the monograph of Jenkins and Kawamura (16). Some of the data are listed in Table 1. As shown in

Fig. 1. Schematic structural model for a glassy carbon (16)

Table 1. Properties of glassy carbon and graphite with the HHT of 1300°C (12)

	Glassy carbon	Graphite
Apparent density (g cm^{-3})	1.46-1.50	1.75-1.92
Hardness (Mohs)	4-5	45-55 (Shore)
Tensile (kg cm^{-2})	500-1000	400-500
Electrical resistivity (10^{-4} ohm cm)	35-50	9-11
Ash content (%)	0.1	0.2
Gas permeability ($\text{cm}^2 \text{ s}^{-1}$)	10^{-11} - 10^{-12}	10^{-4} - 10^{-6}
Thermal conductivity ($\text{kcal m}^{-1} \text{ h}^{-1} \text{ K}^{-1}$)	3-4	100-120
Coefficient of thermal expansion (10^{-6} K)	1.8-2.2	2.0-2.5
Total pore volume (%)	0.35	5
Oxidation resistance at 600°C ($\text{mg cm}^{-2} \text{ h}^{-1}$)	1	2.7

Table 1, glassy carbon has some outstanding features such as exceptionally low porosity, extremely low permeability to gases, high hardness and strength factors, inertness to a wide range of chemicals and reagents, non-wetting in contact with numerous metals and alloys, resistance to oxidation in atmosphere to 600°C, high purity, excellent wear resistance, and good thermal shock resistance. These features make glassy carbon a material of choice (16) for fabricating rocket nozzles , space shuttle protective layers , zone refining electrodes, capsules for the containment of nuclear fuel elements, high voltage linear accelerator components , spectrographic electrodes , and electrochemical electrodes.

The possibility of using glassy carbon as a working electrode was examined by Miller and Zittel in 1964 (19). The results showed that glassy carbon has high chemical inertness and a wide working potential window in aqueous and organic solvents. Table 2 lists the potential limits of glassy carbon electrodes in several aqueous electrolytes. Since this first test, glassy carbon has been widely used as a working electrode in numerous electrochemical applications (20). For instance, glassy carbon electrodes have been utilized in the studies of a variety of organic and inorganic electrode oxidations (20) which are not accessible at a mercury electrode. The growing interest in the Chemically Modified Electrode (CME) (21,22) since the mid-70's made glassy carbon even more attractive because the variety of functionalities on the glassy carbon allows one to derivatize various electrocatalytic species on the electrode surface. Depending on the

Table 2. Potential Limits of Glassy Carbon Electrodes (19)

Electrode area	Electrolyte	Potential limits* volt vs. SCE	
		Anodic	Cathodic
0.11 cm ²	0.1 M HNO ₃	1.25	-0.68
	0.1 M HCl	1.05	-0.80
	0.1 N H ₂ SO ₄	1.32	-0.80
	0.1 M HClO ₄	1.22	-0.88
	0.1 N H ₃ PO ₄	1.36	-0.80

* Potential limits are defined as the potentials at which the currents are 1.0 μ A at scan rate of 1.6 mV/s

surface treatment, functionalities such as carboxyls (23-26), quinones/hydroquinones (27-36), phenols (26,37,38), peroxides (39), aldehydes (40), ethers (40), esters (40), normal lactones (40), and α -lactones (40) can be created. For example, surface carboxyl functional groups can be produced by oxidizing the glassy carbon surface with KMnO_4 (41). It has also been suggested that surface carbon radicals (42,43) can be created if the carbon-carbon or carbon-oxygen bonds on the electrode surface are cleaved by means of heating (44) or mechanical polishing (45) under inert atmosphere or vacuum. Various surface treatments for the production of chemically modified glassy carbon electrodes have been summarized by Kuwana in a recent review article (46).

As described above, glassy carbon has an extremely rich surface chemistry. Because of this, glassy carbon is an attractive electrode for chemical modification. However, this feature also makes the production of a reproducible and active glassy carbon electrode very difficult. Variations in surface treatment procedures or conditions often change the state of the glassy carbon surface and consequently change the electrochemical response of the electrode. For example, the apparent heterogeneous rate constant of ferri-/ferro-cyanide redox reaction changes from ca. 10^{-3} (cm/s) for a glassy carbon polished on a polishing cloth to ca. 10^{-1} (cm/s) for a glassy carbon treated with chromic acid (47). Sometimes, significant change in electroactivity is observed even with the same preparation procedure (48) and the cause for this change is unknown. Another source which often causes the surface variation is the polishing method which has been widely adopted by

electrochemists for renewing glassy carbon surface. In general, the polishing is accomplished by physically pressing and circling glassy carbon on a polishing cloth or an optical flat dispersed with abrasives and wetted with distilled water. After polishing, the electrode is ultrasonically cleaned to remove the abrasives. The applied pressure, the circling speed, the polishing length, the frequency of wetting, the quality and quantity of abrasives, the polishing pad, the length of ultrasonication, and the air conditions during polishing are all variables which can cause the change on the electrode surface. Kuwana and coworkers have reported that the electrode activity toward the oxidations of ascorbic acid and several quinones decreases as the length of ultrasonication is increased (49,50). It has also been reported by Jordon et al. (51) that a high circling speed of polishing can produce a highly active electrode. It seems that any variation introduced during surface preparation can cause changes in the electrode surface. Because of the sensitivity of surface electroactivity to the preparation conditions and the poor understanding of the cause for surface deactivation and activation, it has been a frustrating experience for glassy carbon users to reproduce an active glassy carbon electrode.

Recently, in order to conquer this problem, tremendous efforts from many investigators have been made to develop methods for preparing an active and reproducible glassy carbon surface and several methods have been suggested. Generally, these methods begin with mechanical polishing to renew the electrode surface. Because the electrode activity is often low after polishing, post-treatment is then applied to activate the

electrode. Several recommended activation methods are: electrochemical oxidation and/or reduction (52-55), chemical oxidation (47), thermal treatment (56), radio-frequency plasma treatment (57,58), and in-situ laser radiation (59). Taylor and Humffray (47) have reported that the redox charge transfer rate of ferri-/ferrocyanide at a glassy carbon electrode increases two orders in magnitude when the electrode is chemically oxidized with chromic acid or concentrated sulfuric acid. Kuwana and Evans (57) have also demonstrated that the electrode activity for the oxidations of ascorbic acid and NADH is enhanced after the electrode is subjected to the radio-frequency plasma treatment. Parsons et al. (53), Engstrom et al. (54), and Rusling et al. (55) have also claimed that after anodizing the electrode at a potential above 1.3 V for more than 3 minutes, the electro-activity is improved for the reactions of ferri-/ferrocyanide, hydroquinone, catechol, hydrazine, and ascorbic acid, etc. Wightman and coworkers (56) have also observed that an electrode heated at 550 °C under low pressure has high activity for the reactions of several quinones and ascorbate. Recently, an ingenious method of in-situ activating the electrode surface by laser irradiation has also been developed by McCreery and Hershenhart (59).

Although the above methods can activate the glassy carbon electrode to some degree, they all create significant surface roughness (52-59) as indicated from the increase in the double layer charging current. As examples, the double layer charging current increases 10 times in magnitude when the electrode is chemically or electrochemically oxidized (47,54). About the same amount of increase in the charging current is also observed at the heat treated (56) or radio-frequency

plasma treated (57), or laser irradiated (59) glassy carbon electrodes. The large charging current makes the electrodes useless in the applications of trace electroanalysis and kinetic studies. A question also arises as to whether the surface roughness is responsible for the activity enhancement or just a coincidence. Several activation mechanisms have been proposed; they include: the increase of the "effective" electrode area due to roughening the surface (54), the increase of the surface functionalities which may be sites for the electron transfer (58) or proton transfer (60), and the removal of contaminants on the electrode surface (59,61). However, it has not been possible to verify these mechanisms because none of these activation methods developed so far can control the amount of surface functionalities, the degree of surface roughness, and the extent of surface cleanliness. The lack of knowledge of the activation and deactivation mechanism of the electrode surface makes it difficult to search for an optimum surface preparation method for the glassy carbon. Therefore, in order to devise a better surface preparation method, it is indispensable to acquire an understanding of the mechanism of activation and deactivation of the glassy carbon surface.

OBJECTIVES OF THIS STUDY

The object of this research is to understand the activation and deactivation mechanism of glassy carbon electrodes and then, based on this understanding, to devise a glassy carbon surface preparation method

which meets the three criteria mentioned at the beginning of this chapter. Chapter II starts with the study of the deactivation mechanism of glassy carbon electrodes. In this study, the apparent heterogeneous rate constant of the ferri-/ferro-cyanide redox reaction at a glassy carbon electrode is used as a probe to examine the activity of the electrode. The deactivation mechanism is then evaluated from the time dependence of the electrode activity under different experimental conditions. The results indicate that impurity contamination on the electrode surface is the major cause for the deactivation of glassy carbon electrode. For example, an electrode will be active if it is prepared by polishing under strictly clean conditions. The same electrode will be deactivated if any contamination occurs during the polishing steps. These studies also show, for the first time, that a properly prepared glassy carbon electrode can be as active as a clean platinum electrode for the electrode reaction of the ferri-/ferro-cyanide system.

Next, in Chapter II, causes for the activation of glassy carbon electrode are explored. Several possible factors are assessed such as removal of contaminants (61) from the surface, increase of the effective electrode area due to roughening of the surface (54), increase in surface functionalities which may act as electron transfer mediators (62,63), and exposure of fresh carbon defects (so-called edge carbon) (64) that may be sites for electron transfer. Examination of the glassy carbon surface roughness using scanning electron microscopy unveils the existence of a compact carbon microparticle layer on the polished glassy

carbon surface (65). Even after a long period of ultrasonication, this layer is still on the electrode surface. Although it has not been possible to determine the role of this layer in the electrode activity, it is self-evident that this microparticle layer increases the effective electrode area and consequently enhances the electrode activity. Next, the surface functionalities on the electrode surface are characterized. Two types of functionalities which are similar to 1,2-naphthoquinone and 13,14-picenedione are found on the surface (66). It is also observed that the electrode activity is proportional to the amount of surface functionalities. All the above observations seem to suggest that an increase of electrode activity resulting from polishing may be due to an increase of roughness and/or the amount of surface functionality. However, a further study of the electron transfer mechanism at glassy carbon using the electrode oxidation of ascorbic acid as a probe reveals that the most feasible path for the electron transfer is through the defect carbon sites on the glassy carbon surface. Based on those results, an activation mechanism is suggested. In this mechanism, electrode polishing roughens the electrode surface and consequently increases the amount of surface functionalities and defect carbon sites provided that no contamination occurs. The functionalities on the glassy carbon surface are not responsible for the increase in the electro-activity in the present case.

Rationalized from these above results, a high vacuum heat treatment procedure (67) for the activation of the glassy carbon surface is devised and discussed in Chapter III. This treatment was selected because of its potential for removing impurities and creating defect

carbon sites. A glassy carbon surface prepared using this method has high activity, low surface roughness, and low content of surface functionalities. These results, therefore, prove that the surface functionalities are not required for the activation of the glassy carbon.

In order to carry out the above studies, an electrochemical instrument, which can perform the tasks of cyclic voltammetry at fast scan rates, differential pulse voltammetry with adjustable sampling times, chronocoulometry, and convolution (semi-integration) of cyclic voltammetry, is required. Although it is possible to do all these tasks using the conventional analog instrument, which consists of a programmable function generator, a lock-in amplifier and a potentiostat in conjunction with a digital oscilloscope and an analog recorder, the instrument setup and data analysis procedures are tedious and time consuming. Also such a complete instrument would cost over \$10,000. A convenient solution to this instrumentation problem is to devise a computer controlled potentiostat. A personal microcomputer equipped with D/A and A/D converters can easily generate any wave function for the excitation signal, sample the output signal, process the data, display the result graphically, and save the data for further reference. In Chapter III, the software and hardware design of a computer controlled potentiostat using an Apple II microcomputer is discussed. This unit has the features of low cost (\$3,000), versatility, and user friendliness.

It is my hope that the results of this study will provide a

standard for the surface preparation of glassy carbon electrodes and that the developed computer controlled potentiostat will provide new applications and increase convenience for the user in electrochemical investigations.

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CHAPTER TWO

ACTIVATION AND DEACTIVATION OF GLASSY CARBON ELECTRODES

As described in chapter I, the development of surface treatment methods which create reproducible and active glassy carbon (GC) electrodes has been the goal of many investigators. To achieve this goal, a variety of electrode pre- and post-treatment methods and procedures has been suggested. Generally, these methods begin by polishing the electrode with successively smaller particles of alumina or diamond until a mirror-like finish is obtained, followed by ultrasonication in a water bath to remove the abraded carbon and polishing material. Additional steps, such as chemical (1), electrochemical (2-8), thermal (9) and radio frequency plasma (RFP) (10) treatments, as well as dispersion of metal oxide (MOx) particles (11-13) on the GC surface, have been employed to activate the electrode. Possible reasons for the activation caused by these activation treatments have been attributed to a) the removal of contaminants (5) from the surface, b) the increase in surface functional groups that may act as electron transfer mediators (6,14) or as proton transfer mediators (15) , c) the increase in the effective electrode area due to roughening of the surface, and d) the exposure of fresh carbon edges,

microparticles and defects that may be sites for electron transfer (16). In the case of the MO_x activation, items a), c), and d) appeared to be particularly pertinent. In addition, it was suggested that the MO_x particles could preferentially adsorb impurities and thereby protect the active sites of carbon (13). In order to develop possible modes for the electrode activation and to rationalize the corresponding activation mechanism, it is important to achieve a fundamental understanding of the physical, chemical and electrochemical nature of the glassy carbon surface. Since all surface treatments involves surface polishing, the understanding will be made on the polished glassy carbon surface in this study.

In general, electrode polishing is accomplished by physically pressing and circling glassy carbon on a polishing cloth or an optical flat dispersed with abrasives and wetted with distilled water. The polishing removes layers of carbon from the electrode surface and leaves carbon debris on the polishing pad. Recently, it was found in our laboratory that the polishing also disperses the abrasives onto the carbon surface (11) and compacts fine carbon debris onto the carbon surface (17). Surprisingly, some dispersed abrasives on the carbon surface significantly enhanced the electrochemical reversibility of some electrochemical reactions such as electrooxidation of ascorbic acid, p-aminophenol, quinhydrone, and catechol (11-13). This finding led to the exploration of a new type of modified electrode: the metal oxide dispersed electrode (MO_xE). If lengthy (> 10 minutes) ultrasonication is applied to the electrode after polishing, the dispersed abrasives can be removed and the electrode becomes inactive. To understand why and how

the electrode is deactivated requires a detailed examination of the effects of polishing and ultrasonication on the electrode surface. In the course of this examination, it was found that two variables appeared to have a significant effect on the activity of GC; one variable was the use of polishing cloths during the polishing procedure and the other variable was the minimization of possible sources of organic contaminants during the polishing procedure. For example, as previously reported by Engstrom and Strasser (5), whenever a polishing cloth was used, even as a base for polishing with an alumina slurry, the GCE was found inactive.

If care is taken to exclude sources of contamination, an active GCE can be prepared by polishing the surface with alumina on a glass plate to a mirror-like finish followed by a short period (< 10 minutes) of ultrasonication. A problem is, of course, to develop diagnostics which would indicate when an active GC electrode is produced, and to assess the level of that activity.

In this study, a procedure for creating an active electrode is developed. The electrode activity was assessed in terms of the heterogeneous electron transfer reversibility using ferri-/ferrocyanide and ascorbic acid as the probe redox systems. In addition, the mechanism of deactivation of the GC surface by impurity contamination was evaluated. Possible reasons for the activation of GCE via polishing, such as surface roughness and surface functionalities, were also studied. X-ray photoelectron spectroscopy (XPS) served to provide elemental ratios of carbon to oxygen. The XPS results correlated to the

presence of electroactive surface entities as identified by differential pulse voltammetry may serve as a means of assessing the reproducibility and activity of GC electrode. Scanning electron microscopy was used to examine the topography of the GCE surface and provided the information of a surface roughness. Electron transfer mechanism of the oxidation of ascorbic acid at a glassy carbon electrode was also used to examine the role of surface functionalities in the electrode activity.

EXPERIMENTAL SECTION

Chemicals: Reagent grade $K_3Fe(CN)_6$, L-ascorbic acid (J. T. Baker Chemical Co., Philipsburgh, NJ), KCl, K_2SO_4 , NaOH, and H_3PO_4 (Mallinckrodt Inc., Paris, KY) were used as received. All solutions were made with triply distilled water unless otherwise stated. The triply distilled water (3X-water) was prepared by distilling doubly distilled water from a dilute, alkaline permanganate solution. The doubly distilled water (2X-water) was prepared by taking laboratory distilled water and passing it through a Corning Model AG-B1 water purification system (an all quartz, low throughput still). All solutions were prepared fresh daily. The solutions for voltammetric experiments were purged with prepurified nitrogen for 20 min and were kept under a nitrogen atmosphere during the experiments.

Cleaning of Glassware: Unless otherwise stated, all glassware was cleaned in chromic acid and then thoroughly rinsed with 3X-water. It was stored in a drying oven at 150 °C.

Electrode Pretreatment: Glassy carbon plates (GC-20 grade, Tokai Electrode Mfg., Tokyo) and platinum foil were used as the working electrodes in the voltammetric experiments. The electrode surfaces were hand-polished successively with 600 grit (GCE only), 1.0, 0.3 and 0.05 μm alumina slurries to a mirror-like finish. The slurries were prepared from alumina powders (Buehler Ltd.) and 3X-water. Protective finger cots were worn during polishing and handling of the electrodes to prevent contamination from the hand. New finger cots were used each time the polishing abrasive was changed. The GCE's were polished on a glass plate which was cleaned by wiping it with tissue paper (Kimwipe) wetted with 2X-water. This wet-wipe was continued until no carbon or alumina debris was visible. The glass plate then was thoroughly rinsed with 3X-water. It was important to clean the plate between successive polishing steps. The Pt electrodes were polished on a nylon cloth (Buehler Ltd.). Details of polishing procedures are described below.

Polishing Procedures for GCE: The sequence of steps described below was developed after experimenting with several variations. Precleaning of glassware and the polishing glass plate was important. 3X-water was used throughout. The steps for preparing the activated GCE were as follows:

- (1) Polish the GCE with 600 grit alumina slurry to a rough finish.
- (2) Place the GCE in a beaker, cover it with water and then place the beaker in an ultrasonic bath. During the ultrasonication, the beaker was covered with a glass plate so that the water external to the beaker would not splash inadvertently into the beaker. The water in the beaker was changed frequently. The

ultrasonication time was 10 min. The electrode was thoroughly rinsed prior to each step.

- (3) Polish with 1.0 μm α -alumina slurry until the surface was visually smooth. If scratches were observed on the surface, repeat from step 1.
- (4) Repeat step 2.
- (5) Polish with 0.3 μm α -alumina slurry to a mirror-like surface.
- (6) Repeat step 2.
- (7) Polish with 0.05 μm γ -alumina slurry for ca. 5 min.
- (8) Repeat step 2.
- (9) Use electrode immediately. Drying the electrode with pre-purified air did not affect the activation.
- (10) Repeat step 1-9 if electrode deactivation is observed.

Preparation of Pt Electrode: For preparation of a Pt electrode begin with step 3 and proceed through steps 3-6 as described above for GCE. Steps 7-9 were as follows:

- (7) Flame the electrode in a Bunsen burner to a red glow and then quench the electrode via immediate immersion into a 70% perchloric acid solution.
- (8) Rinse the electrode thoroughly with 1.0 M H_2SO_4 and then insert into the electrochemical cell.
- (9) Cycle the potential of the Pt electrode between 1.35 and - 0.15 V vs. Ag/AgCl at a scan rate of 500 mV/s for 5 min in 1.0 M H_2SO_4 .

The Pt was considered as being activated if the cyclic voltammogram

exhibited the characteristic hydrogen adsorption and desorption fine structure and the oxide formation and removal profile (18). If the electrode was not activated, steps 7-9 were repeated.

Instrumentation and Cell. The electrochemical cell used is shown in Fig. 2. The body was Pyrex and the working electrode was press-fitted against a silicone O-ring (Fornier Rubber Co., Columbus, OH) which had an inner area of 0.083 cm^2 . The O-ring was soaked overnight in 3X-water and was dried in the oven before use. A silver/silver chloride (saturated KCl) electrode served as the reference electrode; all potentials reported herein are quoted with respect to this electrode. A double junction (Pt/cracked glass and porous Vycor) was used to prevent any leakage of AgCl from the reference into the working solution. A Pt foil, isolated by a frit, served as the auxiliary electrode. Cyclic voltammetry (CV) and potential step chronocoulometry were performed with an in-house constructed potentiostat with a conventional three electrode design. The voltammograms were recorded with a Houston (Houston Instruments, Co., Austin, TX) Model 2000 X-Y recorder equipped with a Y-t modulator or with a Tektronix 7613 storage oscilloscope or a digital oscilloscope. An Apple II+ microcomputer with an A-scope (Northwest Instrument System, Inc., Beaverton, OR) interface served as the digital oscilloscope. For the chronocoulometry experiments, a laboratory built pulse generator with a rise time of less than $10 \mu\text{s}$ was used to apply the potential step signal to the potentiostat. An RC operational amplifier integrator and Y-t recorder were triggered by the potential step signal. A Princeton Applied Research Model 174 polarographic analyzer was employed for differential

Fig. 2. Electrochemical cell: (A) Ag/AgCl electrode, (B) Pt/cracked glass, (c) Pt electrode, (D) porous Vycor, (E) capillary tube, (F) clamp, (G) copper for electrical contact to working electrode, (H) working electrode, (I) O-ring, (J) nitrogen gas inlet and outlet compartment.

pulse voltammetric analysis. The impedance measurements were performed with a Solartron TFA (Solartron Electronic Group Ltd., Farnborough Hampshire, England) Model 1174 frequency response analyzer. A computer controlled Physical Electronics (Eden Prairie, MN) Model 548 X-ray photoelectron spectrometer (19,20) provided elemental analysis of electrode surfaces. Some CV data and all the semi-integral CV's were also obtained using a computer-controlled potentiostat which will be discussed in Chapter III.

Evaluation of Heterogeneous Rate Constant for Ferri-/ferro-cyanide.

In this study the heterogeneous rate constant (k_s) of the ferri-/ferro-cyanide redox couple at a GCE was determined by cyclic voltammetry according to the method of Nicholson (21). The working solutions were 1.0 mM ferricyanide in 1.0 M KCl or 0.5 M K_2SO_4 . The following constants were assumed to apply in our system for the calculation of k_s for ferri-/ferro-cyanide: $D_O = 7.63 \times 10^{-6}$ cm²/s (22), $D_R = 6.32 \times 10^{-6}$ cm²/s (22), $\alpha = 0.5$, and $n = 1.0$. With these constants and the peak-peak separation (ΔE_p) of the cyclic voltammogram, k_s was calculated with the following equation (21): $k_s = 2.78 \times 10^{-2} \psi v^{1/2}$ (cm/s) where v is the CV scan rate and ψ was taken from a working curve (21) or from numerical data (23).

RESULTS AND DISCUSSION

As mentioned earlier, the GCE surface was renewed usually by polishing it with alumina slurry on a polishing cloth. Such an electrode pretreatment often resulted in an inactive electrode (5).

Therefore, a post-treatment to activate the electrode was necessary. Recently, during the investigation of the different modes of GCE activation, we found that an active electrode could be prepared without any post-treatment if care was taken to protect the electrode from contamination. The details of the procedure for the pretreatment have been described in the experimental section. Precleaning of the polishing glass plate before each polishing step was necessary. It was observed that residual carbon dust often remained on the glass plate after polishing; this carbon dust was carried through each successive polishing step if the glass plate was not intermittently cleaned. The transfer of this residual resulted in a failure to renew the electrode surface.

Activity of GCE. In order to examine the activity of a GCE, the redox system of ferri-/ferro-cyanide was utilized as a probe. This redox system was chosen because its heterogeneous electron transfer has been extensively studied (24-32) and was assumed to be a simple outer sphere reaction (31,32). Furthermore, the electron transfer rate of ferri-/ferro-cyanide at GCE has been shown to be very sensitive to the state of the GCE surface (1,5,7,9). For example, the heterogeneous rate constant for this reaction increased from 1×10^{-4} cm/s (1) to 2×10^{-2} cm/s (1) when a bare GCE (polished on a polishing cloth) was chemically oxidized. Even minor changes in the procedure for the electrode pretreatment, for example, polishing the GCE on a glass plate instead of a polishing cloth, can cause a significant change in the rate constant (5). The simplicity and sensitivity of this redox system make it ideal

as a probe for scrutinizing the state of GCE. Also, the adsorption and decomposition of ferri-/ferro-cyanide, reported to occur on Pt (33-35), was not evident on GC.

Typical cyclic voltammograms of ferri-/ferro-cyanide in 1 M KCl at an activated GCE are shown in Fig. 3. The solutions were prepared with 3X-water. The scan rate were varied from 30 to 100 mV/s. The separations (ΔE_p 's) between anodic and cathodic peaks were independent of scan rate and were constant at a value of 60 ± 1 mV, as expected for a reversible electron transfer reaction. These compare with ΔE_p 's of 90-150 mV at scan rate of 100 mV/s (9,13) for bare GCE (only polished on polishing cloth) and with Wightman and coworkers' (9) values of 70-80 mV at scan rate of 100 mV/s for GCE heat treated after polishing.

In order to assess the heterogeneous rate constant k_s for ferri-/ferro-cyanide, it was necessary in the present case to increase the scan rate to a value above 4 V/s. In these experiments the initial cyclic voltammogram was taken after the GCE had been in contact with the working solution for 10 min, during which the electrode potential was held at 0.5 V. The k_s values were calculated from experiments performed at five different scan rates ranging from 4 to 40 V/s. The iR drop between the working and reference electrodes was minimized by the use of a Luggin capillary and by the use of a GCE with area being less than 0.09 cm². The average k_s values with the active GCE's were 0.14 (± 0.01) and 0.12 (± 0.02) cm/s for the supporting electrolytes of 1 M KCl or 0.5 M K₂SO₄, respectively. These values compare to the previously reported ones of 10^{-3} to 10^{-4} cm/s for bare GCE (1,7,36), or of 10^{-2} to 10^{-3} cm/s for a chemically or electrochemically pretreated GCE (1,7), or

Fig. 3. Cyclic voltammograms of ferricyanide at GCE. Solution condition: 1 mM ferricyanide, 1 M KCl, and 3X-water. The scan rate for each of the 8 curves is (in order of decreasing peak current): 100, 90, 80, 70, 60, 50, 40, and 30 mV/s.

TABLE 3

Comparison of the literature data of the apparent heterogeneous rate constant of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ system with those of the present paper

Electrode/ holder	Solution condition	Polishing materials	Post-treatment	Kinetic parameter		Ref.
				$n\alpha$	$k_s/\text{cm s}^{-1}$	
GC-30S/ epoxy/ lucite	0.1 M phos ^a with 3X-water	4/0 emery paper, 0.3, 0.05 μm Al_2O_3 on wool cloth	electrochemical	0.23	4.7×10^{-3c}	36
				0.69	5.4×10^{-3d}	
GC-A/ epoxy/ glass tube	0.5 M K_2SO_4 with 3X-water	0.3 μm Al_2O_3 no details	chromic acid or conc. sulfuric acid	0.5	$\approx 10^{-4}$	1
				0.5	2.5×10^{-2}	
GC-EB3	0.5 M K_2SO_4 with 3X-water	grinding stone, emery paper, 5.0, 0.5, 0.05 μ Al_2O_3 on polishing cloth (polythene gloves were worn)	electrochemical		1.5×10^{-4}	7
Swansea-10					1.6×10^{-2}	
SIG-20					1.6×10^{-2}	
SIG-10 /lucite					1.1×10^{-2} 0.8×10^{-2}	
GC/teflon	0.5 M KNO_3 with BW ^b	400, 600 grit silicon carbide paper, 0.3 μ Al_2O_3 or Raybright gem polish on felt cloth	exposed to air for 1 h exposed to air for 5 h	0.72	9.6×10^{-4}	48
				0.635	2.0×10^{-3}	
				0.68	1.5×10^{-4}	
GC(tubular)/ epoxy	electrolysis 0.1 M phos ^a	polishing paper no details	electrochemical	0.201 0.198	1.3×10^{-3c} 1.4×10^{-3d}	37
GC-20	1.0 M KCl with 3X-water	600 grit, 1.0, 0.3, 0.05 μm Al_2O_3 on glass plate (finger cots were worn)		0.5	1.4×10^{-1}	present work
	0.5 M K_2SO_4 with 3X-water			0.5	1.2×10^{-1}	
GC-10 GC-20	0.5 M K_2SO_4 with 3X-water at pH 7.4	5.0, 0.3, 0.05 μm Al_2O_3 , Soxhlet extracted with toluene	heat at 520°C under 1 Torr and cool under atmosphere	$\Delta E_p = 90 \text{ mV}^e$ $\Delta E_p = 70-80 \text{ mV}^e$		9
GC-20	1.0 M KCl with 2X-water	1.0, 0.3, 0.05 μm Al_2O_3 on polishing cloth	MOx dispersion	$\Delta E_p = 150 \text{ mV}^e$ $\Delta E_p = 150 \text{ mV}^e$		13
Pt/Kel-F	0.5 M K_2SO_4	emery paper, Al_2O_3 on velvet cloth	conc. H_2SO_4	0.5	2×10^{-2}	26
Pt	0.5 M K_2SO_4 1.0 M KCl	melted into a small ball	hot nitric acid hot HCl , flame		1.3×10^{-1} 9×10^{-2}	103
Pt	1 M KCl	melted into a small ball	hot HClO_4	0.5	0.24	
Pt	1 M KCl	no details	flame aqua regia	0.5	2×10^{-1}	104
				0.5	1.0×10^{-2}	

^a Phos: phosphate buffer at pH 7.5.

^b BW: water prepared by Barnstead Nano-pure System.

^c Oxidation.

^d Reduction.

^e Scan rate: 100 mV/s.

of 0.2 to ca. 0.01 cm/s for Pt when K^+ was used as the cation in the supporting electrolyte (26-28,37,38). These k_s values at both GCE and Pt are summarized in Table 3. It is interesting to note that the k_s observed in this study was almost the same as that obtained for an active Pt electrode and was at least 10 times larger than those for a bare GCE or for a GCE activated using other methods.

The question, therefore, arose with regards to what was responsible for this k_s difference. A detailed comparison of the experimental conditions became necessary to answer this question. When the experimental conditions in Table 3 are examined, two possible factors leading to slower k_s 's are noted. One is the use of polishing cloths during the preparation of the GCE. The other is the mounting of the electrode in various kinds of sheathing or tubing. Most workers fitted a GCE in either a Teflon or plexiglass tube and polished it on a polishing cloth. Introduction of impurities from these holders (5) and from the polishing cloth (5) used during the polishing procedure has been confirmed by X-ray photoelectron spectroscopic analysis in our laboratory. Note that the k_s values for Pt may also vary with the electrode preparation procedures; e.g., $k_s = 0.2$ cm/s with flame treatment, compared to 0.02 cm/s with a nitric acid or electrochemical pretreatment (38).

Electrode Deactivation. For Pt, the adsorption of impurities at active sites of an electrode has been proposed as an explanation for the gradual retardation of the heterogeneous electron transfer rate (39-43) due to the loss of sites available for the adsorption/desorption of hydrogen. The time dependence of this active site loss has been assumed

to be related to the purity of the electrochemical system.

For GCE, it has not been possible to assess active sites by an electrochemical method related to a surface faradaic process. However, the level of activation may possibly be assessed by monitoring the k_s value of a redox couple such as ferri-/ferro-cyanide, if deactivation is directly related to the blockage of the surface activate sites by the adsorption of impurity.

Experiments, in which the k_s value of ferri-/ferro-cyanide at GCE and the extent of hydrogen adsorption/desorption were determined simultaneously, were conducted in 2X-water and with 3X-water solutions. The time dependent k_s and hydrogen adsorption data, as normalized to their initial values, are plotted in Fig. 4. In the case of Pt, the electrode was treated through steps 1-9 (see experimental section) and then subjected to additional potential cycling between 1.35 and -0.15 V for a period of 4 min in a 1 M H_2SO_4 solution made from 2X-water or 3X-water. At the end of this period, the area under the cyclic voltammogram in the region of hydrogen adsorption/desorption usually reached a maximum value corresponding to an electrochemical charge of 20.4 (± 0.60) μC and a calculated active area of 0.097 (± 0.003) cm^2 . CV scans were then taken at variable time intervals between the potential limits of 0.35 and -0.12 V at a scan rate of 50 mV/s. The normalized areas, assumed to be related to the electrode activity of Pt for 3X- and 2X-water, are plotted as a function of time in Fig. 4, curves a and b. The rate of activity loss for 2X-water is nearly twice that of 3X-water, indeed implicating impurities in deactivation.

Fig. 4. Time effect on the electrochemical activity of Pt electrode and GCE: time dependence of active area of Pt electrode in 1.0 M H_2SO_4 prepared with (curve a) 3X-water and (curve b) 2X-water; time dependence of apparent heterogeneous electron transfer rate of ferri-/ferrocyanide at GCE in ferri-/ferrocyanide solution prepared with (curve c) 3X-water and (curve d) 2X-water.

In the case of GCE, an initial CV scan was taken 4 min after the electrode was immersed in a 2X-water or 3X-water ferricyanide solution containing 1 M KCl. The electrode potential was held at +0.5 V during a "rest" period between successive CV scans. The k_s values were evaluated from the peak-to-peak separations of the cyclic voltammograms as previously described. For a ferricyanide solution prepared with 3X-water, the rate constant decreased slightly from an initial value of 0.177 (± 0.009) cm/s to 0.11 (± 0.007) cm/s in 15 min; for 2X-water, a larger decrease occurred, from 0.122 (± 0.006) cm/s to 0.063 (± 0.003) cm/s in the same time interval. These rate changes, normalized, are plotted in Fig. 4, curves c and d. The similarity between the pair of curves for Pt and GCE strongly suggests that the deactivation mechanism at Pt is the same as that for GCE.

Characterization of The GCE Surface. Some possible reasons for enhancement of the heterogeneous electron transfer rates at active GCE are: (a) surface cleanliness and lack of impurities which can adsorb on the surface and block active sites, as already discussed; (b) surface roughness which causes the effective electrode area for electron transfer to be greater than the geometric area; (c) the presence of surface functional groups that mediate electron transfer, and (d) surface energy states (44-47).

As indicated from the results of the above deactivation mechanism study, cleanliness is an important factor in the activation of the glassy carbon. Traces of silicon, calcium, fluorine, or different types of carbon has been detected on a GCE surface when Teflon and Kel-F holder are used during polishing (5,7,48). Therefore, an attempt was

made to examine the elemental species on an active electrode by using ESCA. A survey spectrum is shown in Figure 5. The spectrum shows that only carbon and oxygen are present on the electrode surface. No trace of aluminum from alumina or other elements were detected. Although this result does not exclude the presence of possible organic contaminants, it does indicate the absence of inorganic contaminants such as fluorine, silicon and calcium. Although the effect of these species to the electrochemistry has not been quantified, introduction of surface impurities, although often unintentional, should be avoided as much as possible.

The double layer capacity, C_{dl} , was used to assess the surface roughness of GCE. A sine wave signal with an amplitude of 10 mV at a frequency of 10 Hz was generated by a Solartron Model 1174 at an applied electrode potential of 0.27 V. A geometric electrode area of 0.090 cm^2 had been evaluated from chronocoulometric measurements for the reduction of ferricyanide in 1 M KCl. Based on this area, the C_{dl} of a GCE prepared with the procedures described in the experimental section was $20 \text{ } \mu\text{F}/\text{cm}^2$. This value is midway between the previously reported values of 15 (49) and $25 (1) \text{ } \mu\text{F}/\text{cm}^2$, both for a bare GCE. It appears that roughness may not be an important factor for the presently observed increase in the rate of electron transfer for ferri-/ferro-cyanide at GCE. However, gross increases in roughness can be produced when GCE's are treated chemically or electrochemically, as evidenced by capacitances as large as ca. $250 \text{ } \mu\text{F}/\text{cm}^2$ (1,50).

Fig. 5. X-ray photoelectron survey spectrum of an active GC surface. Recorded with a modified PHI Model 548 XPS/AES spectrometer with a 300 W Mg X-ray source and a base pressure of 3.0×10^{-10} Torr.

Next, an analysis of the GCE/electrolyte interface structure was made from an impedance plane plot of capacitance vs. resistance at various frequencies from 10 to 3000 Hz. Figure 6 shows typical impedance plane plot for an active GC prepared using the polishing procedure described in the experimental section. The measurement was performed in 1.0 M KCl electrolyte at an electrode potential of 0.27 V. This analysis showed that the cell resistance was independent of frequency when the frequency was in the range of 32 to 3000 Hz, and increased from 5 ohm to 8 ohm when the frequency decreased from 32 to 10 Hz. The double layer capacitance, C_{dl} , decreased from 20 to 18 $\mu\text{F}/\text{cm}^2$ when the frequency increased from 10 to 3000 Hz. These results indicated that the frequency response of the electrode interface structure was analogous to a capacitor and resistor in series, where the capacitor may be a composite of a double layer and a pseudo-capacitance (51) in parallel. The resistor was the uncompensated resistance between the reference and the working electrodes. A similar frequency response was previously reported for smooth Pt in 1 M KCl electrolyte (52). The behavior of the C_{dl} decay of GCE with the increase in the frequency has been observed by Yeager et al. (49) and Parsons et al. (50) and was attributed to surface faradaic processes (49) and to the semiconductor properties (44-47) of glassy carbon. The space charge of the semiconductor surface was suggested by Gerischer (46) for the dispersion of the capacitance. However, the presence of a very fine, thin layer of porous carbon dust may also be responsible since a similar frequency response may be obtained for an electrode with such a porous structure

Fig. 6. Impedance plane plot for an active GC in 1 M KCl solution at a potential of 0.27 V. The excitation signals were sine waves with an amplitude of 10 mV.

(49,53,54). The extent of the similarity is dependent on the structure of such a porous layer (54).

The possibility of the presence of a thin layer of carbon microparticles on GC surface was further explored by Kazee and Weisshaar (17) in our laboratory. In their investigation, a raw GC surface as received from the manufacture was examined using scanning electron microscopy (SEM). Pits and holes, which are due to gas-pockets formed near or at the surface during fabrication process, were observed on the raw GC surface (17). When the same electrode surface was polished and then examined by SEM, holes and pits which originally appeared on the raw surface, were only faintly visible in SEM micrographs as can be seen in Fig. 7a. There are two possible reasons for this disappearance of pits on the polished surface. One is the removal of pits by polishing. Another is the hiding of these holes by covering them with carbon microparticles which are created by polishing. To confirm the presence of this carbon microparticle layer, the polished GC surface was heated at 750°C under ambient air and then examined by SEM. The heat treatment was expected to remove the microparticle layer and expose underlying holes. As expected, caverns at the same position of those faintly seen on the freshly polished surface reappeared on the heated surface as shown in Fig. 7b. Grooves were also seen on the heated surface. Those grooves were probably created during polishing and were not visible to SEM when they were filled with carbon microparticles. From this SEM examination, it is evident that a finely divided carbon microparticle layer is compacted onto the glassy carbon surface during polishing.

Fig. 7. SEM micrographs of polished GC surfaces: (a) before heat treatment and (b) after heat treatment at 750 °C under ambient air.

A model of surface energy states (44-47) which is similar to that for a semiconductor has been proposed, in which the low density of energy states in the fermi-level is used to explain the inherently slower electron transfer rates at carbonaceous electrodes in comparison to those at metallic electrodes (47). However, the presence of a thin layer of carbon microparticles could result in an entirely different surface energy state (ie., the density and the energy level of electron orbitals on the surface) for a GC surface, and thus changes the electrode behavior. A carbonaceous electrode with a thin layer of carbon microparticles has been observed to be very chemically active (55-57).

Characterization of Surface Functionalities. The surface carbon radicals (58,63) created by cleaving carbon-carbon bonds during polishing are expected to be very active (64,65) and to react with oxygen and water to produce a variety of surface functional groups such as carboxyls (66-69), quinones/hydroquinones (70-79), phenols (69,80,81), peroxides (82), aldehydes (83), ethers (83), esters (83), normal lactones (83), and ϵ -lactones (83).

Of these functional groups, the quinoidal-like functionalities have been observed on a RF plasma treated GC surface (10) and have been proposed to be the electron transfer mediator for oxidation of ascorbic and NADH (3,6,14). Schreurs (79) has also proposed that the quinoidal-like functionalities on a rf-plasma treated GC surface are likely to be 1,4-naphthaquinone and 1,2-naphthaquinone. To examine these as well as other possibilities for the active GC created using the procedures in this study , differential pulse voltammetry (DPV), x-ray photoelectron

spectroscopy, chemical derivatization, and digital simulation were employed.

A typical result for DPV of an active GC surface is shown in Fig. 8, trace a. The DPV shows the presence of two redox couples with peak potentials of 0.25 V and 0.19 V (± 10 mV). Close correspondence was found between these two peaks at 0.25 and 0.19 V and the DPV electrochemistry of solution 1,2-naphthaquinone and 13,14-picenedione (84), respectively. The DPV wave for 1,2-naphthaquinone is shown in Fig. 8, trace b.

Further evidence for surface ortho-quinone groups was the derivatization that occurred when GCE's were refluxed with o-phenylenediamine in ethanol for 6 hr, followed by Soxhlet extraction for 1 hr. The reaction, suggested by Schreurs (79), forms phenazines (e.g., benzophenazine and dibenzophenazine). This was confirmed by the presence of DPV waves at potentials between -0.1 and -0.2 V at pH 2.0 and by the absence of the previously described waves at 0.19 and 0.25 V, as shown in Fig. 9. The XPS survey spectrum of a derivatized carbon surface in Fig. 10a shows the presence of C, N, and O as expected. The N 1s binding energy and the shape of the carbon peak indicate that the nitrogen is covalently bonded and is aromatic in character (85). This is supported by the high resolution spectra of the C 1s and N 1s regions which, shown in Fig. 10b, indicate the presence of different types of covalent carbon-heteroatom bonds (85) and aromatic N 1s binding energy position. The N 1s binding energy is quite unlike that of an amine which would be covalently bound (86). To confirm the nitrogen XPS peak

Fig. 8. Differential pulse voltammograms of freshly polished GCE in (curve a) 0.1 M phosphate buffer at pH 2.0 and (curve b) 0.1 M phosphate buffer with 1,2-naphthoquinone at pH 2.0. Pulse frequency is 2 Hz and amplitude is 10 mV; dc scan rate is 2 mV/s. $S = 10$ nA/mV (curve a) and 100 nA/mV (curve b).

Fig. 9. Differential pulse voltammogram of an o-phenylenediamine derivatized GCE in 0.1 M phosphate buffer at pH 2.0. Pulse frequency was 2 Hz with an amplitude 10 mV. The DC scan rate was 2 mV s^{-1} .

Fig. 10. X-ray photoelectron survey spectrum (a) of an o-phenylenediamine derivatized glassy carbon surface. High resolution C 1s and N 1s spectra of a derivatized surface (b) and surface which was derivatized following reduction with LiAlH_4 to destroy surface o-quinone functional groups (c). The spectra were signal averaged for 90 min (a) and 20 min (b and c) and smoothed prior to display.

corresponds to the surface phenazine complex, a blank was run by first reducing the surface with LiAlH_4 and then proceeding with the derivatization sequence. The results of the XPS scans of the C 1s and N 1s regions are shown in Fig. 10 c. The N 1s peak was not evident in the survey scan when recorded at the same signal to noise ratio as in Fig. 10a. The surface concentration of nitrogen was reduced to near the limit of detection. Quantitation at this signal to noise level is difficult. The reduction in signal level corresponds to a reduction of the nitrogen concentration to slightly less than 1.0 A/O for the blank. This trace of nitrogen probably results from an incomplete reduction of the surface quinone by the LiAlH_4 .

Digital simulation of the surface DPV waves (87-89) provides more evidence to support the presence of o-quinone on the GC surface. The surface waves were simulated to confirm the presence of a two electron charge transfer characteristic of quinones. It was assumed that the surface redox system was in Nernstian equilibrium before each pulse and that the current was kinetically controlled during the period of each pulse. The surface concentrations were calculated at each step using the Nernst equation and the current was calculated from the Butler-Volmer equation. Since no diffusion is involved, the current decay was assumed to follow the loss of the electroactive surface species. Since the surface reaction should be pseudo-first order, exponential decays of surface concentration and current were followed (87). The rate of decay was determined by the heterogeneous rate constant (87). The digital simulation program is listed in Appendix A. The resulting output for the simulation of two two-electron surface redox reactions with redox

potentials of 0.19 and 0.25 V respectively is shown in Figure 11b. Two simulated waves are well resolved and correspond very well with the experimental DPV waves, as shown in Figure 11a. A 2:1 concentration ratio was used to produce the simulation shown with the major peak resulting from slightly less than one monolayer as found experimentally. On the other hand, when a one-electron mechanism instead of a two-electron was used in the above simulation, the peaks of 0.19 V and 0.25 V were not resolvable as shown in Fig 11c. Although simulations can not produce conclusive proof of a mechanism, it does support the hypothesis of two-electron quinone surface electrochemistry.

Role of Surface Functionalities in The Electron Transfer Mechanism.

It has been known that several quinones are able to oxidize ascorbic acid rapidly (90). It was also observed by Evans and Kuwana (6) that the charge transfer rate for the oxidation of ascorbic acid at GCE is accelerated when the amount of the quinoidal-like functionalities on the GCE surface is increased by radio-frequency plasma treatment. Similar results have been obtained by other investigators (6,8) when a GCE was chemically or electrochemically oxidized in order to increase the surface quinone functionalities. Based on these results, it was suggested that the surface quinoidal-like functionalities might be the catalytic sites for the electron transfer in the oxidation of ascorbic acid at GCE. Indeed, this idea has been employed in the fabrication of 3,4-dihydroxybenzylamine modified GCE's (91,92) for the oxidation of NADH and ascorbic acid. Recently, Meyer et al. (15) reported that the surface functionalities may also promote the proton transfer for the

Fig. 11. Digital simulated differential pulse voltammograms of surface redox functionalities. (a) Experimental surface DPV waves, (b) digital simulated surface DPV waves with two two-electron redox reactions with the redox potentials at 0.19 and 0.25 V, (c) same as b except using one-electron instead of two-electron.

reactions of several quinones at GCE.

Although the surface quinone functionalities may be the sites for the electron transfer or proton transfer, it is not clear whether these functionalities or other possible sites such as defect carbon are responsible for the acceleration of the charge transfer rate observed in the present study. To answer this question, it requires an understanding of the kinetic mechanism of the electron transfer which occurs at the electrode.

In this study, the electro-oxidation of ascorbic acid was used as a probe to examine the electron transfer mechanism at the GC surface. The choice of this probe is based on the belief that the oxidation of ascorbic acid is an inner-sphere reaction which may be affected by the electrode surface functionalities (14). The mechanism of this reaction at the mercury electrode has been extensively studied by Ono et. al. (93), Perone et al. (94), and Ruiz et al. (95,96). Although the mechanism of this reaction at pH above 8 is still disputed (97), a mechanism proposed by Ruiz (95) for the reaction at pH below 8 is widely accepted (97). Fig. 12 illustrates the scheme of the mechanism. This mechanism involves a predissociation of a proton to give the monoanionic species followed by a 1 e^- , 1 H^+ oxidation of the monoanionic species to form the ascorbic acid radical anion, which then undergoes a second irreversible 1 e^- oxidation to dehydro-ascorbic acid (97). The latter species is rapidly protonated and then hydrated to yield the final product of 2,3-diketogulonic acid. The hydration rate at pH 7.2 is estimated by Perone (94) to be about $1.2 \times 10^3\text{ s}^{-1}$. Based on the above

Fig. 12. Proposed mechanism for the electrochemical oxidation of ascorbic acid in acid or neutral solution at mercury electrode (95).

mechanism, if one assumes that the proton transfer step is not the rate determinant step (rds), the rate constant for the overall reaction can be expressed (98) as:

$$k_{\text{obs}} = k_2 k_3 / (k_{-2} + k_3) \dots\dots (1)$$

where k_2 and k_{-2} are the forward and backward rate constants of the first oxidation step respectively, and k_3 is the standard rate constant for the second oxidation step. By replacing all the rate constants with potential-dependent rate constants and assuming the transfer coefficient $\alpha = 0.5$ for each electron transfer step, equation 1 becomes:

$$1/k(E_{\text{appl}}) = 1/(k^0_1 \exp(0.5F\Delta E_1/RT)) + 1/(k^*_2 \exp(1.5F\Delta E_{12}/RT)) \dots(2)$$

$$k^*_2 = k^0_2 \exp(0.5F(E^0_{12} - E^0_1)/RT) \dots(3)$$

where $k(E_{\text{appl}})$ is the apparent rate constant for the overall reaction at applied potential E_{appl} , k^0_1 and k^0_2 are the apparent rate constants for the first and second step respectively, ΔE_1 is $E_{\text{appl}} - E^0_1$, ΔE_{12} is $E_{\text{appl}} - E^0_{12}$, and E^0_{12} is the formal potential for the overall reaction. As indicated from equations 1 and 2, if the first electron transfer is the rds (i.e. $k_3 \gg k_{-2}$),

$$k(E_{\text{appl}}) = k^0_1 \exp(0.5F\Delta E_1/RT) \dots\dots (4)$$

and if the second electron transfer is the rds (i.e. $k_3 \ll k_{-2}$),

$$k(E_{app1}) = k_2^* \exp(1.5F\Delta E_{12}/RT) \dots (5)$$

As seen from equations 4 and 5, when the first electron oxidation is the rds, the apparent transfer coefficient is 0.5; when the second electron oxidation is the rds, the apparent transfer coefficient is 1.5. Therefore, by evaluating the apparent transfer coefficient, the rds for the oxidation of ascorbic acid can be determined. The apparent transfer coefficient, $\alpha_{apparent}$, can be obtained from the Tafel slope which is $(\beta_{apparent}/60)$ mV for a rds with one electron transfer (51). The value of the apparent transfer coefficient reported by Ruiz et al. (95) for the electro-oxidation of ascorbic acid at mercury electrode is ca. 1.4. This led Ruiz et al. to the conclusion that the rds for the oxidation of ascorbic acid is the second electron oxidation. However, it is important to note that the rds may change when the applied potential changes as indicated from equation 2. As the reaction is driven harder to the condition in which k_3 is larger than k_{-2} , the rds changes from the second oxidation step to the first oxidation step. In fact, this change of the rds with a change in potential was observed for the electro-oxidation of ascorbic acid at GCE in this study and will be discussed later.

It has been reported that the charge transfer rate for the electro-oxidation of ascorbic acid at a mercury electrode is quite rapid, as indicated from the 30 mV peak-to-peak separation between anodic and cathodic peaks of the cyclic voltammogram at a scan rate of 300 V/s

(94). However, the rate of this reaction at GCE was observed to be slow and was dependent on the state of the GC surface. Figure 13, trace a is a typical cyclic voltammogram obtained at an inactive GCE for the electro-oxidation of ascorbic acid at pH 2.0. The inactive GCE was prepared by polishing the electrode on a polishing cloth, followed by ultrasonication. The solution condition for the CV is 1.0 mM ascorbic acid in 0.1 M phosphate buffer adjusted with NaOH to pH 2.0. The anodic peak potential of this cyclic voltammogram is about 600 mV vs. Ag/AgCl (sat'd KCl) which is ca. 350 mV more positive than that obtained at mercury electrode (97). This indicates that the charge transfer rate of the oxidation of ascorbic acid at the inactive GCE is slower than that at mercury electrode. However, the rate of this reaction increases at an active GCE, as indicated from the anodic peak potential of 270 mV in the cyclic voltammogram shown in Figure 13, trace b. The active GC was prepared using the procedures described in the experimental section of this chapter. It is interesting to note that not only is the overpotential decreased by about 330 mV, but also the peak current is almost doubled as the electrode is activated. One of the possible reasons for this increase in the peak current may be the increase of the apparent transfer coefficient, since the peak current for the totally irreversible reaction is proportional to the square root of the apparent transfer coefficient (51). If this is the case, this implies that the rds of the oxidation of ascorbic acid is different for active and inactive GCE. The validity of this hypothesis will be assessed later.

Fig. 13. Cyclic voltammogram of the electro-oxidation of ascorbic acid at inactive GC (a) and at active GC (b). The solution condition is 0.1 mM ascorbic acid in 0.1 M phosphate buffer at pH 2.0.

As described before, it has been suggested that the quinone functionalities on GC surface may be the catalytic sites for oxidation of ascorbic acid and may be responsible for the increase of the GC electro-activity. In this study, it is also observed that an active GC surface has higher content of surface quinone functionalities than on an inactive GC surface. Therefore, attempts were made to determine whether surface quinones were responsible or coincident with the observed activation. Electrochemistry on the electrodes derivatized with *o*-phenylenediamine or deactivated via LiAlH_4 showed little evidence for activation with respect to the oxidation of ascorbic acid. However, the required chemical treatments of the electrodes surely contaminate the surface in addition to removing the functional groups. Therefore, these experiments do not distinguish between the possibilities of clean surface versus functional group activation. To resolve this issue, cyclic voltammograms corresponding to a scan rate of 100 mV/s were simulated (99) as simple, chemically irreversible electron transfer reactions without the inclusion of any catalysis via the *o*-quinone functionalities. The simulation program written in Fortran language is listed in Appendix B. A typical simulation result is shown in Fig. 14. For the simulation it is assumed that the electron transfer is completely irreversible and none of the products are electroactive. Literature values for the formal potential 250 mV vs. Ag/AgCl (sat'd KCl) (97) and the diffusion coefficient $D_0 = 5.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (6) were used in this simulation. The electrode area, determined from chronocoulometry, was 0.090 cm^2 to agree with the real CV. Although the

Fig. 14. Digital simulation for the CV of the electro-oxidation of ascorbic acid (dot line) and experimental CV (circles) at scan rate of 100 mV.

current following the potential reversal does not mimic the experimental CV exactly, there is a very close correspondence between the experimental (solid line) and simulated (circles) curves in Figure 14 when a value of 1.42 for the apparent transfer coefficient and a value of 1.0×10^{-2} for the apparent heterogeneous rate constant are used in the simulation. The kinetic data used here will be further confirmed experimentally in Chapter III. Although simulations do not provide conclusive proof, they do indicate that the surface functionalities may not be responsible for the increase of GCE activity in the present case and the surface cleanliness may be the most important factor. The result also indicated that some surface sites other than quinone functionalities are the most active sites for the electron transfer on the GC surface. However, this does not exclude the fact that quinone functionalities can mediate the electron transfer. Indeed, experimental evidence has shown that surface quinones may participate in the electron transfer. Evidence has come from the cyclic voltammograms for the oxidation of ascorbic acid at a partially active GC electrode, which can be produced occasionally by electrochemical oxidation or heat treatment (9) or by laser irradiation (100), or by deactivation of an active GC to some degree. A typical CV illustrating this is shown in Fig. 15. The CV is somewhat similar to that of an active GC, except that a broad peak appears posterior to the diffusional limited peak in the case of the partially active GC. Three possible mechanisms can be used to explain the occurrence of this followed-up peak. One of the possible mechanisms is that the electron transfer occurs at two type of active sites. If these two types of active sites have the distance of larger than square

Fig. 15. Cyclic voltammogram for the electro-oxidation of ascorbic acid at a partially active GC. The solution condition is 0.1 mM ascorbic acid in 0.1 M phosphate buffer at pH 2.0. The CV scan rate is 100 mV/s. The partially active GC was prepared by deactivating an active GC in the air for 20 min.

root of (diffusion coefficient $\times$ time), two diffusion peaks will occur (100). Another possible mechanism is that the rds of the reaction changes from the second oxidation step to the first oxidation step when the reaction is driven to the condition in which back rate of the first oxidation is slower than the forward rate of the second oxidation. The change of this rds causes a decrease in the apparent transfer coefficient from ca. 1.5 to ca. 0.5 for the reasons described before. When this decrease in the apparent transfer coefficient occurs, the rate of the diffusion is again higher than the rate of the electro-reaction and consequently another peak occurs. The third possible mechanism for this followed-up peak is that the electron transfer occurs through two pathways: one is via the most active site at a lower overpotential, and the other is via the surface quinone functionalities with a higher overpotential. At low overpotentials, the reaction occurs through the most active sites. However, at higher overpotentials, the surface functionalities start to mediate the electron transfer and control the rate of the reaction if the turn-over rate of this surface catalytic reaction is fast (14,92) or the most active sites are blocked by the reaction products. In this case, the apparent transfer coefficient is dependent on the turn-over rate of the surface catalytic reaction. Although more direct evidence is needed to support the latter mechanism, this mechanism can explain why the electrode activity enhancement is observed at a functionalized electrode surface and why some electrode reactions have the surface proton isotope effect as observed by Meyer et al. (15). It is difficult to explain the surface proton isotope effect and the fact that quinone functionalities mediate the electron transfer

using the mechanism in which surface functionalities are not involved in the electrode reaction.

In the above studies, the CV simulation has shown that the apparent transfer coefficient is 1.42 for the electro-oxidation of ascorbic acid at an active GC. It is also suggested, from the CV obtained at a partially active GC, that the apparent transfer coefficient changes at higher overpotentials. In order to confirm preliminary results, an attempt was made to determine the apparent transfer coefficient. The semi-integration technique (101) was used to evaluate the apparent transfer coefficient. This technique involves the semi-integral $(d^{-1/2}i(t)/dt^{-1/2})$ of the current in a CV with respect to time. The program used for the semi-integration is listed in Appendix C. The "G1" algorithm (102) was applied to this program. For a totally irreversible reaction, the relation between the semi-integral current, $I(t)$, and the potential, E , can be expressed as (51):

$$E = E^0' + (RT/\beta nF)\ln(D^{1/2}/k^0) + (RT/\beta nF)\ln[i(t)/(I_1 - I(t))] \dots (6)$$

where $i(t)$ is the current at the time t , $I(t)$ is the semi-integral current at time t , I_1 is the semi-integral diffusion limiting current, n is the number of electron in the rds, and β is the apparent transfer coefficient. As shown in equation 6, the apparent transfer coefficient can be evaluated from the slope of $\ln[i(t)/(I_1 - I(t))]$ vs. E . Figure 16, traces a, b and c show typical semi-integral CV's for the electro-oxidation of ascorbic acid at an active GC, a partially active GC, and

Fig. 16. Semi-integral CV for the electro-oxidation of ascorbic acid at (a) an active GC, (b) a partially active GC, and (c) an inactive GC. The scan rate for the CV is 100 mV/s. The solution condition is 1 mM ascorbic acid with 0.1 M phosphate buffer at pH 2.0. Background current is not corrected in these plots.

an inactive GC, respectively. The active GC was prepared using the polishing procedure described in the experimental section. The partially active GC was prepared by deactivating an active GC in the air for 20 min. It is important to note that the partially active electrode is not reproducible from experiment to experiment. The inactive GC was prepared by polishing the electrode on a polishing cloth, followed by ultrasonication. As can be seen from figure 16, trace a, there is no slope change in the rising portion of semi-integral current for the case of the active GC. This can be even clearly seen from the plot of $\ln[i(t)/(I_1-I(t))]$ vs. E as shown in Figure 17, trace a. The apparent transfer coefficient evaluated from this plot is ca. 1.4 ± 0.1 . This value corresponds very well with that used in the CV simulation and confirms that for an active GC the second electron transfer for the oxidation of ascorbic acid is the rds. In the case of the inactive GC, the slope change in the rising portion of semi-integral current is not evident from Figure 16, trace c and the apparent transfer coefficient evaluated the plot of $\ln[i(t)/(I_1-I(t))]$ vs. E , as shown in Figure 17, trace c, is 0.6 ± 0.2 . This value suggests that for an inactive GC the first oxidation step is the rds. This situation happens because, for an inactive GC, the apparent heterogeneous rate constant for both the first and the second oxidations are very low, and a higher overpotential is required to drive the reaction. At the high overpotential, the first oxidation step becomes the rds as rationalized from equation 2. In the case of the partially active GC, a change in the apparent transfer coefficient with respect to potential is indicated in Figure 16, trace b and Figure 17, trace b. The apparent transfer coefficient appears to

Fig. 17. Plot of $\ln[i(t)/(I_1 - I(t))]$ vs. E for (a) Figure 16, trace a, (b) Figure 16, trace b, and (c) Figure 16, trace c.

change from ca. 1.4 ± 0.1 to ca. 0.6. The reason for this change has been described earlier in this section.

Rationalized from the above results, a GC surface model with regard to the electron transfer is developed. In this surface model, there are three types of sites which are responsible for the electron transfer. The first type is the most active site (perhaps defect carbon). The second type is the surface electroactive functionality which has a lower activity than the first type. The third type is the least active site which may be the basal carbon (16) or sites blocked by contaminants. Based on this model, an electrode surface which has nothing but the most active site will have the highest electro-activity. However, one still can improve the electro-activity of a totally inactive electrode by functionalizing the electrode surface. In Chapter III, the validity of this surface model will be further pursued.

SUMMARY AND CONCLUSION

For the first time, heterogenous rates of ferri-/ferro-cyanide electron transfer, comparable to those obtained at Pt, have been obtained with carefully prepared ("activated"), clean glassy carbon electrodes. Using such rates to assess the "activity" of GCE's, it appears that the maintenance of clean conditions and avoidance of impurity introduction during GCE preparation and use is an important

factor in the extent of electrode activation. The results are consistent with the suggestion of Wightman and coworkers (9), and Engstrom and Strasser (5) regarding the function of heat-treatment and electrochemical pretreatment to the enhancement of GCE activity.

That GCE is deactivated by a mechanism similar to that with Pt is strongly suggested by the similarities of the ferri-/ferro-cyanide rate profiles with hydrogen adsorption-desorption curves at Pt in both 3X-water and 2X-water. This mechanism is assumed to be impurity adsorption and blockage of active sites. However, the deactivation rates of GCE compared to Pt will vary greatly depending on preparation procedures. There may be also some variation depending on the commercial source of the glassy carbon.

Mechanical polishing produces a layer of carbon microparticles on GC surface. Although this layer can enhance the GC activity, it is not responsible for the increase in the electrode activity observed in this study. Two electroactive functionalities were also found on the active glassy carbon surface and were assigned to 1,2-naphthaquinone and 1,3,4,6-tetrakis(hydroxymethyl)-2,5-dihydroxybenzene, as suggested from the data of chemical and electrochemical characterizations and the results of the DPV simulation. Although these surface functionalities can mediate the electron transfer, there are other sites more active than surface functionalities for the electron transfer on the GC surface since the oxidation of ascorbic acid occurs prior to mediation on an "active" electrode. The creation of these active sites is responsible for the increase in the GC electroactivity observed in this study. The question now is what are these active sites.

This question is explored in Chapter III.

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CHAPTER THREE

VACUUM HEAT-TREATMENT FOR ACTIVATION OF GLASSY CARBON ELECTRODES

In Chapter II, a model of a glassy carbon surface has been proposed with regard to the electron transfer. In this model, the electron transfer sites on a GC surface are categorized to three types. Each of these three types has different electro-activity with respect to one another. An electrode surface rich in the most active sites can be produced by polishing the electrode under strictly clean condition, as already demonstrated in Chapter II. By means of electrochemical oxidation (1-3) or chemical oxidation (4), the electrode surface can be functionalized with quinone groups which possesses a different electro-activity. If the electrode is contaminated, surface active sites will be blocked and rendered the inactive sites. To date, this model appears to explain the activation and deactivation phenomena observed at GC. However, two questions remain. What is the identity of the most active site and how can the sites be created without introducing surface functionalities, roughness and contaminants.

One possible active site is the defect carbon. To examine such a possibility, a vacuum heat treatment (VHT) method was devised.

this method was expected to remove surface contaminants and surface oxide functionalities to produce a surface of only carbon.

Wightman and coworkers (5,6) had previously activated GC via heat treatment (550 °C) at low (ca. millitorr) pressures. Although the extent of activation was reported to be independent of the heating duration, the background charging current increased considerably. This increase was probably due to surface roughening. Also, a possibility existed for the surface to react when the GC was exposed to ambient air prior to cooling.

To avoid such reactions, the method to be described involves the heating and cooling of GC under high vacuum ($< 2 \times 10^{-6}$ torr) where reactive gases are essentially absent. The results show that this method produces an activated electrode with substantially reduced concentration of surface functionalities and a low background capacitance.

With regards to a treatment method that controls the surface area and redox functionalities, what was needed initially was the development of analytical methods to probe the surface of GC. We found that differential pulse voltammetry (DPV), with the adjustment of sampling phase and time, allowed the monitoring of redox functionalities. The details of the theory of DPV with adjustable sampling time will be discussed later. The DPV data were correlated with X-ray photoelectron spectroscopy (XPS) results which gave the elemental ratios of oxygen to carbon. Scanning electron microscopy (SEM) and optical microscopy (OM) were also applied to obtain information regarding the surface topography of GC. Finally, the electron transfer mechanism at VHT surface was

assessed by examining the electro-oxidation of ascorbic acid at glassy carbon.

EXPERIMENTAL SECTION

Reagent grade potassium ferricyanide, ascorbic acid (J. T. Baker Chemical Co., Philipsburgh, NJ), KCl, NaOH, H_3PO_4 , and HNO_3 (Mallinckrodt Inc., Paris, KY) were used without further purification. All solutions were prepared daily with NANOpure water (Sybron Barnstead, Boston, MA). Glassware was cleaned in an isopropanol/KOH bath followed by immersion in 1 M H_2SO_4 and thoroughly rinsed in NANOpure water. All solutions used for electrochemical experiments were purged with prepurified nitrogen.

Glassy carbon samples were approximately 1.5 cm^2 pieces of Tokai GC-20 (Tokai Carbon Co., Ltd., Tokyo, Japan). The geometric area exposed to solution was $0.084 \pm 0.014 \text{ cm}^2$ (calculated from chronocoulometry). Electrodes were polished with 600 grit, 1.0 μm , 0.3 μm , and 0.05 μm alumina (Buehler Ltd., Lake Bluff, IL or Baikowski International, Charlotte, NC) slurries with NANOpure water on a ground glass plate followed by ultrasonication as previously described in Chapter II. The GC was then dried with prepurified nitrogen.

The heat treatment chamber was constructed in a standard 2-3/4 inch stainless steel UHV cross. A tungsten filament was wound around a quartz tube (1.6 mm i.d.) which was enclosed in a larger quartz tube (2.5 mm i.d.) to contain any evaporated tungsten. This assembly was

inserted into the UHV cross in a horizontal position. Electrical and thermocouple connections were made by a UHV feedthrough (Ceramaseal, Inc., New Lebanon Center, NY). High vacuum was established with a turbomolecular pump (Balzers, Hudson NH) after an initial rough pumping with a cryogenic sorption pump. The temperature was measured with a chromel-alumel thermocouple wire and a digital thermocouple gauge (Omega Engineering, Stamford, CT). For heat treatment, the GC sample was inserted into the smaller tube and heated by thermal radiation after evacuation to less than 2×10^{-6} torr. The temperature was maintained at 725 ± 25 °C for 10 minutes at a pressure between 2×10^{-6} and 8×10^{-6} torr. After heat treatment, the GC was allowed to cool to 35 °C before the chamber was filled with nitrogen and opened to the atmosphere.

Ferri-/ferro-cyanide and ascorbic acid were chosen as probes to determine the extent of surface activation. These two electrochemical systems have been used extensively for such evaluation as mentioned in Chapter II. Ferri-/ferro-cyanide is believed to undergo electron transfer via an outer-sphere mechanism (7) and exhibits an electron transfer rate that is slow at GC, unless the GC is activated prior to use (8). The electro-oxidation of ascorbic acid on the other hand, is chemically irreversible with electron transfer occurring via an inner-sphere mechanism. The electro-oxidation behavior of ascorbic acid is very sensitive to the surface state of the electrode (8) as previously described.

All electrochemical measurements were done with an in-house built three electrode potentiostat. The potentiostat was interfaced to an

Apple IIe computer using a 12 bit D/A and A/D interface card (Interactive Microware Inc., State College, PA). Synthesized excitation signals from this interface had the resolution of 0.48 mV. Software for cyclic voltammetry, chronocoulometry, and differential pulse voltammetry was written in machine language to provide optimal speed for instrumentation control, data acquisition, real time data display in the form of graph, and data analysis. In the CV mode, this unit can perform either single scan or multiscan (maximum scan number is 8) at a scan rate from 1 mV/s to 20 V/s with the resolution of 0.48 mV/step. This unit automatically scales the output data and display the cyclic voltammogram on the screen with the numerical data about the peak potential, peak current, peak area, and all the experimental parameters. Users may expand any portion of display to maximum sensitivity. In the DPV mode, this unit allows user to set the pulse frequency (0.5 Hz to 100 Hz), the pulse width, the pulse amplitude, the sampling time (minimum 50 μ s) , and the DC scan rate (maximum 1 V/s). The differetial pulse voltammogram is real-time displayed on the screen and automatically re-scaled to the maximum sensitivity at the end of the scan. Any portion of DPV display can also be expanded to maximum sensitivity. In the mode of chronocoulometry, this unit can perform single step or double step chronocoulometry with the highest time resolution of 50 μ s. Two thousand data points are taken for each step. Analog integrator is used to integrate the charge. The data are displayed in the form of "Anson plot" which is for the double step chronocoulometry. As any portion of data is selected for expansion, this

unit will also calculate the slope and the intercept of this part of data using the least square method. For all the operational modes, all the data can be saved in disk and can be plotted in a digital plotter or dot-matrix printer. The details of the software of this computer controlled potentiostat are listed in Appendix D.

The electrochemical cell and the reference electrode used in this study are the same as those used in Chapter II. All potentials are reported with respect to a Ag/AgCl (sat'd KCl) reference electrode.

Scanning electron micrographs were obtained with an ISI (Milpitas, CA) model SX-30 scanning electron microscope (SEM) using backscattered electrons and an acceleration voltage of 5 keV to enhance surface topography (9). X-ray photoelectron spectra were recorded with a Physical Electronics (Eden Prairie, MN) model 548 ESCA/Auger system with Mg $k\alpha$ radiation (10).

RESULTS AND DISCUSSION

Although GC electrodes have always been polished prior to use, an attempt was made to activate an "as received" sample of GC with VHT. Effect of VHT on the surface topography was examined using SEM. The SEM micrography of untreated surface typically showed holes, debris and imperfections (9) on the surface as can be seen in Figure 18a. The same surface after being subjected to VHT appeared to have no change on the surface topography, except the removal of some particulate matters as shown in Fig 18b. Next, the effect of VHT on the electrode activity was assessed using the probe of ferri-/ferro-cyanide redox system. Figure

a

b

Fig. 18. Scanning electron micrograph for a) "as received" GC surface, and b) after vacuum heat treatment.

Fig. 19. Cyclic voltammetric scans for "raw" (dashed line), polished (dotted line), and heat-treated (solid line) GC-20 in 1.0 mM ferricyanide. Electrolyte is 1.0 M KCl; reference electrode is Ag/AgCl with sat'd KCl; scan rate is 1.0 V/s, $i = 9.66 \mu\text{A}$.

19 compares the cyclic voltammograms of an "as received" (dashed line), an unpolished vacuum heat treated (solid line), and a freshly polished (dotted line) GC electrode in 1.0 mM $\text{Fe}(\text{CN})_6^{4-/3-}$. A ΔE_p of 300 mV for the untreated electrode (scan rate = 1 V/s) indicates that it is deactivated (exhibits slow charge transfer kinetics). After VHT, this value decreases to 75 mV which compares favorably with a polished electrode.

A polished GC electrode becomes deactivated after prolonged exposure to room air (8). This deactivation becomes evident by the increase in the ΔE_p for $\text{Fe}(\text{CN})_6^{4-/3-}$ or in the shift of the oxidative peak potential, E_{pa} , for ascorbic acid to more positive values. However, VHT reactivates the electrode so that ΔE_p 's of 60–65 mV and E_{pa} values of 285 mV can be achieved for these two reactants, respectively. Typical cyclic voltammograms for ascorbic acid are shown in Figures 20 and 21 to illustrate these observations. Figure 20 compares a polished, deactivated electrode (trace a) to an electrode after VHT (trace b). Figure 21 shows the CV scans for ascorbic acid after a deactivated GC electrode was heat treated at 520 °C (trace a), 650 °C (trace b) and 750 °C (trace c). Although a detailed temperature dependent study has not been completed, the trend suggests that a temperature in the order of 700–750 °C is necessary for optimal activation. It is interesting to note that the peak current at the active GC is larger than that at the inactive GC by a factor of ca. 2. This significant difference suggests that the kinetic parameter βn_a changes as the electrode is activated or deactivated. The reason for this apparent transfer coefficient change has been discussed in Chapter II. In order to evaluate apparent

Fig. 20. Cyclic voltammetric scans for a) polished, deactivated GC-20 and b) polished, deactivated, heat-treated GC-20 in 1.0 mM ascorbic acid. Electrolyte is 0.1 M phosphoric acid buffer adjusted to pH = 2.0 with NaOH, reference electrode is Ag/AgCl (sat'd KCl), scan rate is 0.1 V/s, $i = 6.33 \text{ uA}$.

Fig. 21. Temperature dependance of ascorbic acid oxidation on heat-treatment temperature; a) 520 °C, b) 650 °C, and c) 750 °C. Solution conditions same as in Figure 20; scan rate = 0.1 V/s.

transfer coefficient and assess the electron transfer mechanism in the case of the VHT surface, the semi-integral technique was used. Figure 22 shows a typical semi-integral CV obtained at a VHT electrode for the oxidation of ascorbic acid at pH 2.0. No change of the apparent transfer coefficient is evident from this semi-integral CV. The apparent transfer coefficient evaluated from the slope of $\ln[i(t)/(I_1 - I(t))]$ vs. E , as shown in Figure 23, is ca. 1.4 which is the same as that obtained at an active polished electrode. It is interesting to note that, because of the near zero background charging current at the VHT electrode, the semi-integral CV is very flat in the background region.

Both "as received" and polished/deactivated GC electrodes can be activated by VHT. The SEM photomicrographs show no significant alterations to the surface topography in contrast with heat treatment in air (9). Since no change in the macroscopic surface roughness could be observed by SEM, the roughness, assumed to be microscopic was evaluated by measuring the change in the capacitive charge by cyclic voltammetry and chronocoulometry.

Cyclic voltammetry experiments were run in phosphate buffer solution (pH = 2.0) to examine the electrochemical characteristics of electrode surface over a 0.9 volt potential range (-50 to 850 mV). Figure 24a shows the cyclic voltammogram for a polished electrode and Figure 24b for an electrode after VHT. The background charging current and the redox wave at ca. 250 mV, due to an ortho-quinone functionality (8) on the GC surface, become greatly diminished after VHT. However, in both cases the current increases considerably at potentials more

Fig. 22. Semi-integral CV for the oxidation of ascorbic acid at the VHT electrode. The solution condition is 1.0 mM ascorbic acid in 0.1 M phosphate buffer at pH 2.0. The CV scan rate is 100 mV/s. No background correction is taken.

Fig. 23. Plot of $\ln[i(t)/(I_1 - I(t))]$ vs. E for the semi-integral CV in Figure 22.

Fig. 24. Cyclic voltammetric scans for polished (trace a) and heat treated (trace b) GC-20. Solution conditions is 0.1 M phosphate buffer at pH 2.0; scan rate = 0.5 V/s.

positive than ca. 450 mV. The background charging current will continue to increase on successive scans if the positive potential limit is greater than this value.

To quantitate the change in the capacitive charge due to vacuum heat treatment, a chronocoulometric potential step method was used. In this method, successive square wave potential steps of 1 second duration were applied from an initial starting potential (E_i) of -50 mV to various final potentials (e.g., $E_f = -20, -10, 0, 10, 20, \dots$ to 450 mV, respectively). The charge Q vs. $t^{1/2}$ was plotted for each potential step and the extrapolated intercept on the Q axis (11) was assumed to be the total capacitive charge, Q_c , for that potential step. The electrolyte solution for the experiment was 0.1 M phosphate buffer in 0.1 M KCl at pH 2. After purging the solution with prepurified nitrogen, a nitrogen atmosphere was maintained in the cell during the experiment. The results of these chronocoulometry experiments are shown in Figure 25 with the inset showing an enlargement of the measured charge at small ΔE values.

For a freshly polished GC electrode, Q_c , is linear with potential in the E region of 0 to +80 mV and then increases non-linearly up to the arbitrary limit of +450 mV. The slope of the Q_c vs. ΔE plot in the linear region is 6.7 $\mu\text{C/V}$ with a standard deviation of 0.035 $\mu\text{C/V}$ for 7 runs with 2 different GC samples. This value of the slope corresponds to 74 $\mu\text{F/cm}^2$, when normalized to the geometric area of the electrode. If one assumes that the measured Q of 140 $\mu\text{F/cm}^2$, for final step potential of -50 to 450 mV, is a composite of double layer charge (non-faradaic) and faradaic charge due to surface functionalities (pseudo-

Fig. 25. Potential step chronocoulometric experiment for polished GC (trace a and inset trace a) and VHT GC (trace b and inset trace b). Solution: 0.1 M phosphate buffer with 0.1 M KCl at pH 2.0.

capacitance), then the difference of $66 \mu\text{F}/\text{cm}^2$ can be assigned to the latter source. Most of this charge appears in the potential region above 100 mV. The above calculation relies on the validity of the assumption that the double layer charge remains linear with potential at potentials greater than +80 mV.

If one repeats the chronocoulometric experiments with VHT GC electrodes, the measured Q_c values are much smaller as seen in curve b of Figure 25. The Q_c varies linearly with ΔE from 0 to 100 mV (see inset plot). The slope of this plot is $0.9 \mu\text{C}/\text{V}$ or $10 \mu\text{F}/\text{cm}^2$ compared to the value of $74 \mu\text{F}/\text{cm}^2$ for the polished GC electrode. Also, a Q_c of $17.6 \mu\text{F}/\text{cm}^2$ is obtained when the potential is stepped from -50 to 450 mV (a decrease by a factor of 8 from that of the polished case). The decrease in Q_c at higher potentials can be explained by the loss of surface functionalities upon heat treatment. However, the substantial decrease at low potentials, where it was assumed that the charge was due to only the double layer (non-faradaic), is surprising and difficult to explain. One possibility is that the surface microstructure of carbon is changing with VHT.

The polished and VHT GC surfaces were analyzed by XPS and the results are shown in Figure 26. The oxygen:carbon peak height ratio decreased from a value of 0.227 for the polished (trace A) to 0.060 for the VHT (trace B) electrode. The same GC sample (Tokai, grade GC-20) was taken through the XPS analysis after the polishing and then the heat treatment steps. The sample was briefly exposed to room air during the transfer from the VHT chamber to the XPS chamber which may account for

Fig. 26. X-ray photoelectron spectra of polished GC-20 before (trace a, O/C peak height ratio = 0.22) and after (trace b, O/C peak height ratio = 0.06) heat-treatment at 750 °C.

the presence of trace oxygen on the VHT results. When the VHT sample was stored under vacuum at 5×10^{-10} torr for 24 hr, the oxygen:carbon ratio decreased to 0.04. Proctor and Sherwood (12) had previously reported the removal of oxygen from carbon fiber surfaces via heating under high vacuum.

To confirm the removal of carbon-oxygen functionalities, DPV analysis was done on the GC prior to and after VHT. The DPV current was sampled 3.3 ms after the pulse and the dc background current measured 4.0 us before the pulse was subtracted. The differential pulse voltammograms are shown in Figure 27. Trace 27a is for a polished GC-20 sample. The electrolyte is phosphate buffer at pH 2.0 containing 0.1 M KCl. The peak at ca. 175 mV has been observed previously (8) and is assigned to an o-quinone functionality. The peak at 0.25 V previously observed is resolved in this typical DPV. The larger peak at ca. 700 mV has also been previously reported (13). Both peaks are greatly reduced in magnitude by VHT as seen in trace 27b. The small peak remaining at 350 mV is unidentified. It may be a polyaromatic larger than 1,2-naphthaquinone. Similar shifts to more positive potentials have been found on GC which had been chemically oxidized with chromic acid or potassium permanganate as shown in Figure 28. Trace 28a shows a typical surface DPV waves for a polished electrode. Two waves appears at the peak potentials of 0.19 and 0.25 V, respectively. However, when the electrode is oxidized with chromic acid, the potentials of two waves shift to ca. 0.4 V, as shown in Figure 28, trace b. It is also interesting to note that after chemical oxidation there is a tremendous increase in the amount of surface functionalities as indicated from the

Fig. 27. Differential pulse voltammetric curves for a) polished GC-20, and b) polished, heat-treated GC-20 in pH 2.0 phosphate buffer. DC scan rate = 2.0 mV/s, pulse amplitude = 10 mV, pulse width = 60 ms, pulse frequency = 2 Hz, sampling time = 3.3 ms after pulse. Reference electrode is Ag/AgCl.

Fig. 28. Differential pulse voltammograms for a) polished GC-20, and b) after oxidizing with chromic acid. Solution: 0.1 M phosphate buffer at pH 2.0. DPV was obtained using PAR 174 Polarographic Analyzer. DC scan rate = 2.0 mV/s, pulse frequency = 2 Hz, pulse amplitude = 10 mV.

peak height of the DPV waves.

Preliminary experiments currently underway suggest that activation, similar to VHT, can be accomplished by controlled heating and cooling of GC at ambient pressures in an inert atmosphere such as argon or nitrogen. Details of this study will be pursued in the future.

CONCLUSIONS

Vacuum heat treatment activates both "as received" and polished/deactivated GC electrodes for the redox reaction of ferri-/ferrocyanide and the oxidation of ascorbic acid. This treatment appears to remove most, if not all, of the surface redox functionalities as evidenced by the absence of DPV waves and of surface oxygen as observed by the extremely low oxygen:carbon ratio. It is my conclusion that redox functionalities, such as 1,4- and 1,2-dihydroquinones, are unnecessary for the rapid electro-oxidation of ascorbic acid. However, these surface functionalities still can mediate the electron transfer in the relatively higher overpotential range. This conclusion needs to be tested with other oxidations that occur at more positive potentials at which surface redox functionalities could participate in mediating electron transfers.

VHT is assumed to produce a "pristine" carbon surface which, in itself, is sufficient to provide active sites for electron transfer. It is speculated that the desorption of adsorbed materials occurs

initially, followed by the conversion of surface oxygen functionalities to carbon-carbon bonds, as the temperature rises during VHT. This conversion may be analogous to bond reorganization and annealing on metal surfaces when they are subjected to heating in an inert atmosphere. Further studies with thermal desorption mass spectrometry should help elucidate what is happening in terms of surface reactions during VHT.

In addition to increasing the electrochemical activity, VHT causes a dramatic lowering of the background double layer charge. This decrease of Q_{dl} is due to the removal of the surface redox species and to changes in the microscopic surface structure. The latter is evidenced by the concurrent lowering of Q_{dl} in the low potential region (-50 to $+30$ mV) where redox functionalities are assumed to be absent. Thus, it is concluded that activation, in the case of VHT, cannot be attributed to an increase in the effective surface area of the electrode, which may be the reason, in part, for the activation with the other surface treatment methods. The main reasons for activation are believed to be due to an increase in the active site density as the consequence of the removal of surface contaminants and the exposure of fresh carbon.

VHT is proposed as a method to prepare and activate glassy carbon, and perhaps other carbonaceous materials, as electrodes for many electroanalytical applications and for studies related to understanding fundamental properties of GC surfaces. However, it should be recognized that electrodes, such as ones studied herein, undergo continuous,

irreversible changes at relatively low positive potentials during usage. Reproducibility from laboratory-to-laboratory will rely eventually on the acceptance of one or two "standard" methods for carbon electrode treatment including certain application protocol.

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APPENDIX A

This appendix lists the computer program, SIMDPV, used for simulating differential pulse voltammograms of surface functionalities.

```

1.      //      JOB
2.      //SIMDPP EXEC PLOTV
3.      //GO.SOURCE DD *
10.          DIMENSION CPLOT(2,4000),EPLOT(2,4000)
20.          DIMENSION NC(2), EZERO(4), PZERO(4)
30.          DATA NC/1,2/
40.      C
50.      C      INPUT PARAMETERS
60.      C
70.          READ(5,*)EZERO(1)
80.          WRITE(6,12)EZERO(1)
90.          12 FORMAT('OE ZERO OF SPECIES 1: ',T50,F8.4)
100.         READ(5,*)EZERO(2)
110.         WRITE(6,14)EZERO(2)
120.         14 FORMAT('OE ZERO OF SPECIES 2: ',T50,F8.4)
130.         READ(5,*)EINIT
140.         WRITE(6,10)EINIT
150.         10 FORMAT('OINITIAL POTENTIAL: ',T50,F8.4)
160.         READ(5,*)EFINAL
170.         WRITE(6,20)EFINAL
180.         20 FORMAT('OFINAL POTENTIAL: ',T50,F8.4)
190.         READ(5,*)ALPHA
200.         WRITE(6,30)ALPHA
210.         30 FORMAT('OALPHA: ',T50,F8.4)
220.         READ(5,*)RATHS
230.         WRITE(6,40)RATHS
240.         40 FORMAT('OHETEROGENEOUS RATE CONSTANT: ',T50,E14.6)
250.         READ(5,*)CONC1
260.         WRITE(6,50)CONC1
270.         50 FORMAT('OSURFACE COVERAGE OF SPECIES 1: ',T50,E14.6)
280.         READ(5,*)CONC2
290.         WRITE(6,60)CONC2
300.         60 FORMAT('OSURFACE COVERAGE OF SPECIES 2: ',T50,E14.6)
310.         READ(5,*)AREA
320.         WRITE(6,70)AREA
330.         70 FORMAT('OELECTRODE AREA: ',T50,E14.6)
340.         READ(5,*)ACFQ
350.         WRITE(6,80)ACFQ
360.         80 FORMAT('OAC FREQUENCY: ',T50,F8.4)
370.         READ(5,*)DCSR
380.         WRITE(6,90)DCSR
390.         90 FORMAT('ODC SCAN RATE: ',T50,F8.4)
400.         READ(5,*)ACAM
410.         WRITE(6,100)ACAM
420.         100 FORMAT('OAC AMPLITUDE: ',T50,F8.4)
430.         READ(5,*)PULT
440.         WRITE(6,110)PULT
450.         110 FORMAT('OPULSE DURATION: ',T50,E14.6)
460.         READ(5,*)SAMPT
480.         WRITE(6,120)SAMPT
490.         120 FORMAT('OSAMPLING AT TIME: ',T50,E14.6)
500.      C

```

```

530.          PINIT=EINIT/25.69
540.          PFINAL=EFINAL/25.69
550.          ER=ABS(EINIT-EFINAL)
560.          PR=ER/25.69
570.          ACTQ=1.0/ACFQ
580.          ACPM=ACAM/25.69
590.          SR=DCSR/25.69
600.          DO 520 I=1,2
610.             PZERO(1)=EZERO(1)/25.69
620.             PZERO(2)=EZERO(2)/25.69
640.             A1=EXP(NC(I)*(PZERO(1)-PINIT))
650.             A2=1.0-A1
660.             B1=EXP(NC(I)*(PZERO(2)-PINIT))
670.             B2=1.0-B1
680.             DCDV=ACTQ*SR
690.             ACDV=PULT*SR
700.             DV=DCDV+ACDV
710.             DT=PULT+ACTQ
720.             TT=PR/SR
730.             ITT=TT/DT+0.5
740.             AL=-1.0*ALPHA
750.             BETA=1.0-ALPHA
760.             EXC1=NC(I)*9.64846E13*AREA*RATHS*CONC1
770.             EXC2=NC(I)*9.64846E13*AREA*RATHS*CONC2
780.             CMAX=0.0
790.             UP=PINIT
800.             DO 520 K=1,ITT
810.                X1=NC(I)*(UP+ACPM-PZERO(1))
820.                X2=NC(I)*(UP+ACPM-PZERO(2))
830.                CUR1=EXC1*(A2=EXP(AL*X1)-A1=EXP(BETA*X1))
840.                CUR2=EXC2*(B2=EXP(AL*X2)-B1=EXP(BETA*X2))
850.                EPLOT(I,K)=UP=0.02569
860.                CPLOT(I,K)=ABS(CUR1+CUR2)
870.                UP=UP+DV
880.                A1=EXP(NC(I)*(PZERO(1)-UP))/(1+EXP(NC(I)*(PZERO(1)-UP)))
890.                B1=EXP(NC(I)*(PZERO(2)-UP))/(1+EXP(NC(I)*(PZERO(2)-UP)))
900.                A2=1.0-A1
910.                B2=1.0-B1
920.                IF (CPLOT(I,K) .GT. CMAX) CMAX=CPLOT(I,K)
930.                520 CONTINUE
930.5          DO 530 L=1,2
931.             DO 530 I=1,ITT,4
932.                WRITE(6,370)EPLOT(L,I),CPLOT(L,I)
933.                370 FORMAT(' ',E14.6,T30,E14.6)
934.                530 CONTINUE
940.                CALL PLOTS
950.                CALL PLOT(1.,1.,-3)
960.                DVX=0.1
970.                DYY=CMAX/8.0
980.                CALL AXIS(0.,0., 'POTENTIAL (V)',-13.6,0.0,0.0,0.0,DVX)
990.                CALL AXIS(0.,0., 'CURRENT (NANOAMP)',17.8,0.0,90.0,0.0,DVY)
1000.            CALL NEWPEN(3)

```

```
1010.      COEF2=10.0
1020.      COEF4=8.0/CMAX
1030.      DO 600 M=1,2
1040.      NK=3
1050.      DO 600 I=1,ITT
1060.      IF (I .GT. 1) NK=2
1070.      X=EPL0T(M,I)*COEF2
1080.      Y=CPL0T(M,I)*COEF4
1090.      CALL PLOT(X,Y,NK)
1100.      600 CONTINUE
1110.      CALL PLOT(0.,0.,999)
1120.      STOP
1130.      END
```


APPENDIX B

This appendix lists the computer program, SIMAA, used for simulating cyclic voltammograms of a totally irreversible electro-reaction.

```

1.      //      JOB ,
1.5     // TIME=20
2.      /*JOBPARM  LINES=500000
3.      //SIMAA   EXEC PLOTV,TIME=20
4.      //GO.SOURCE DD *
5.          DIMENSION EPLOT(4,2000),CPLOT(4,2000)
6.          DIMENSION AA(5000),SCRAT(4),KK(4)
7.          DATA SCRAT/50.0,100.0,150.0,200.0/
8.          READ (5,*) EZERO
9.          WRITE (6,10) EZERO
10.         10 FORMAT ('OREDOX POTENTIAL: ',T50,F8.4)
11.         READ(5,*)CONC
12.         WRITE(6,11)CONC
13.         11 FORMAT('OCONCENTRATION: ',T50,E16.4)
14.         READ(5,*) DIFF
15.         WRITE(6,20) DIFF
16.         20 FORMAT('ODIFFUSION COFFECIENT: ',T50,E14.6)
17.         READ(5,*) RATHS
18.         WRITE(6,30)RATHS
19.         30 FORMAT('OHETEROGENEOUS RATE CONSTANT: ',T50,E14.6)
20.         READ (5,*)AREA
21.         WRITE(6,22)AREA
22.         22 FORMAT('OELECTRODE AREA: ',T50,F8.4)
23.         READ (5,*) EINIT
24.         WRITE (6,40)EINIT
25.         40 FORMAT('OINITIAL POTENTIAL: ',T50,F8.4)
26.         READ (5,*) EFINAL
27.         WRITE (6,50)EFINAL
28.         50 FORMAT('OFINAL POTENTIAL: ',T50,F8.4)
29.         READ(5,*)DEOBS
30.         WRITE(6,60)DEOBS
31.         60 FORMAT('OPOTENTIAL INTERVAL FOR PLOT: ',T50,F8.4)
32.         70 FORMAT('OSCAN RATE: ',T50,F8.4)
33.         READ(5,*)ALPHA
34.         WRITE(6,80)ALPHA
35.         80 FORMAT('OALPHA: ',T50,F8.4)
36.         READ (5,*)XLA
37.         WRITE(6,72)XLA
38.         72 FORMAT('OLAMDA: ',T50,F8.4)
39.         READ (5,*) TSTEP
40.         WRITE(6,90)TSTEP
41.         90 FORMAT('OITERATION TIME STEP/25.69 MV: ',T50,E14.6)
42.         DO 123 IG=1,4
43.         123 KK(IG)=0
44.         DO 220 IY=2,2
45.         SR=SCRAT(IY)
46.         WRITE(6,70)SR
47.         C      PARAMETER CALCULATION
48.         PINIT=EINIT/25.69
49.         PFINAL=EFINAL/25.69
50.         PZERO=EZERO/25.69
51.         PSR=SR/25.69

```

```

52.      ER=ABS(EFINAL-EINIT)
53.      PR=ER/25.69
54.      TT=ER/SR
55.      DT=TT/TSTEP
56.      PS=PR/TSTEP
57.      DX=SQRT(DT/XLA)
58.      XL=10.0*SQRT(TT)
59.      NX=(XL/DX)+1
60.      IF(NX .GT. TSTEP) NX=TSTEP
61.      OT=DEOBS/SR
62.      IO=OT/DT
63.      CO=1.0
64.      MM=0
65.      COEF=2*9.64846E7*AREA*CONC
66.      DO 100 I=1,NX
67. 100  AA(I)=1.0
68.      OW=(DX*RATHS)/SQRT(DIFF)
69.      BETA=1.0-ALPHA
70.      UP=PINIT
71.      ISTEP=TSTEP
72.      PS=-PS
73.      DO 200 IC=1,2
74.      PS=-PS
75.      DO 200 IT=1,ISTEP
76.      NZ=6.0*SQRT(XLA*IT)+3
77.      IF (NZ .GT. NX) NZ=NX
78.      X1=UP+UP-PZERO-PZERO
79.      CU=CO*RATHS*EXP(X1*BETA)
80.      CO=AA(1)/(OW*EXP(BETA*X1)+1)
81.      U1=CO
82.      U2=AA(1)
83.      DO 300 IX=1,NZ
84.      U3=AA(IX+1)
85.      AA(IX)=U2+XLA*(U1-U2-U2+U3)
86.      U1=U2
87.      U2=U3
88. 300  CONTINUE
89.      MM=MM+1
90.      IF (MM .LT. IO) GOTO 200
91.      MM=0
92.      KK(IY)=KK(IY)+1
93.      EPLOT(IY,KK(IY))=UP*0.02569
94.      CPLOT(IY,KK(IY))=CU*COEF
95. 200  UP=UP+PS
96.      IDU=KK(IY)
97.      DO 500 I=1,IDU
98.      WRITE(6,120) EPLOT(IY,I),CPLOT(IY,I)
99. 120  FORMAT(' ',E14.6,T20,E14.6)
100. 500  CONTINUE
101. 220  CONTINUE
102.      CALL PLOTS(0,0,0)
103.      CALL PLOT(1.,1.,-3)
104.      TEINIT=EINIT/1000.0
105.      DVX=0.1

```

```
106.      DVY=10.0
107.      CALL NEWPEN(3)
108.      CALL AXIS(0.,0., 'POTENTIAL (V)', -13,6.0,0.0,0.0, DVX)
109.      CALL AXIS(0.,0., 'CURRENT (MICROAMP)', 18,8.0,90.0,0.0, DVY)
110.      COEF2=10.0
111.      COEF3=0.0
112.      COEF4=0.1
113.      DO 600 II=2,2
114.      NK=3
115.      IDU=KK(II)
116.      DO 600 I=1, IDU
117.      IF(I .GT. 1) NK=2
118.      X=EPLLOT(II,I)*COEF2-COEF3
119.      Y=CPLLOT(II,I)*COEF4
120.      CALL PLOT(X,Y,NK)
121. 600 CONTINUE
122.      CALL PLOT(0.,0.,999)
123.      STOP
124.      END
```

APPENDIX C

This appendix lists the computer program, SEMI-INTEG, used for semi-integrating a cyclic voltammogram.

```

*****
*                                     *
*      File: SEMI-INTEG              *
*                                     *
*      Written by Ing-Feng Hu        *
*                                     *
*****
*
*
*****
*                                     *
*      This program semi-integrates  *
*      CV data obtained by the computer- *
*      controlled potentiostat       *
*                                     *
*****

```

```

20 HIMEM: - 27392
30 D$ = CHR$ (4)
40 PRINT D$;"CATALOG,D2"
50 INPUT "FILE NAME: ";F$
60 PRINT D$;"OPEN "F$";,D2"
70 PRINT D$;"READ";F$
80 INPUT DA$: INPUT CT: INPUT SR: INPUT SF: INPUT DU$
90 INPUT EI: INPUT ES
91 PRINT D$;"CLOSE"
95 DT = 2000. / (4096 * SR):NT = INT (4096 * ABS (EI - ES) / 2000.)
96 DIM C1(2500)
100 PRINT D$;"BLOAD "DU$";,A$3000,D2"
102 SF = 2000. / (4096 * SF):SV = 2048 * SF
103 FOR I = 1 TO NT
104 R1 = 12286 + I * 2
105 C1(I) = (256 * PEEK (R1) + PEEK (R1 + 1)) * SF - SV
106 NEXT
112 DIM C2(270),G(2500)
151 G(1) = 1:G(0) = 1
152 FOR I = 1 TO NT
153 G(I) = G(I - 1) * (1 - 0.5 / I)
154 NEXT
155 M = 0
160 FOR K = 1 TO NT
165 M = M + 1
170 FOR J = 1 TO K
210 C2(M) = C2(M) + G(K - J) * C1(J)
220 NEXT J
230 C2(M) = C2(M) * SQR (DT)
235 PRINT "C2("M")="C2(M)
240 NEXT K
242 UX = C2(1):UI = C2(1)
243 FOR I = 1 TO NT

```

```

244 IF C2(I) > UX THEN UX = C2(I)
245 IF C2(I) < UI THEN UI = C2(I)
246 NEXT
247 M = 0
251 F$ = "CONV-" + DU$
260 PRINT D$;"OPEN "F$";D2"
270 PRINT D$;"WRITE "F$""
275 PRINT NT: PRINT EI: PRINT ES: PRINT SR: PRINT UX: PRINT UI
280 FOR I = 1 TO NT
300 PRINT C2(I)
310 NEXT
320 PRINT D$;"CLOSE"
322 F$ = "LOG-" + DU$
323 M = 0
324 FOR I = 1 TO NT
325 M = M + 1: IF UX = C2(M) THEN 327
326 C1(M) = LOG ( ABS (C1(I) / (UX - C2(M)))): NEXT
327 UX = C1(1):UI = C1(1)
328 FOR I = 1 TO M - 1
329 IF C1(I) > UX THEN UX = C1(I)
330 IF C1(I) < UI THEN UI = C1(I)
331 NEXT
332 PRINT D$;"OPEN "F$""
333 PRINT D$;"WRITE "F$""
334 PRINT NT : PRINT M - 1: PRINT EI: PRINT ES: PRINT SR
    : PRINT UX: PRINT UI
335 FOR I = 1 TO M - 1
336 PRINT C1(I)
337 NEXT
338 PRINT D$;"CLOSE"
339 HOME : TEXT : PRINT
340 INPUT "RUN HPLOT-SEMI ?";DU$
350 IF DU$ < > "Y" THEN 360
355 PRINT D$;"RUN HPLOT-SEMI,D1"
360 PRINT D$;"RUN HELLO,D1"

```

APPENDIX D

This appendix lists the computer programs of the computer-controlled potentiostat.

Program 1

Program, CV, used to supervise cyclic voltammetric experiments, processing data, and display cyclic voltammograms.

```

1 *****
2 *
3 *          CYCLIC VOLTAMMETRY PROGRAM
4 *          WRITTEN BY ING-FENG HU
5 *          1st VERSION - OCT 20, 1984
6 *          LATEST VERSION -MAR 12, 1985
7 *          THIS VERSION IS FOR 128K MEMORY
8 *          AND MULTISCANNIG CV
9 *
12 *
13 *****
14 *
15 *
16 *
17 *
18 *
19 *****
20 *
21 *          TEXT FILE NAME: T.FASTCV
22 *          B TEXT FILE NAME: FASTCV.S
23 *          OBJ FILE NAME: FASTCV
24 *
25 *          PROGRAM START AT $9050 (-28592)
26 *          CALL -28592
27 *
28 *          BEFORE CALL THIS ROUTINE
29 *          SET UP THE FOLLOWING PARAMETERS
30 *          FROM MAIN BASIC PROGRAM
31 *          $1C: POKE 28,INITIAL POTENTIAL (LOW BYTE)
32 *          $1D: POKE 29,INITIAL POTENTIAL (HIGH BYTE)
33 *          $9040: POKE -28608, SWITCH POTENTIAL (L.B)
34 *          $9041: POKE -28607, SWITCH POTENTIAL (H.B)
35 *
36 *          $9007: POKE -28665, INITIAL SCAN DIRECTION
37 *                  1 FOR ANODIC, 0 FOR CATHODIC SCAN
38 *
39 *          $903D: POKE -28611, SCAN RATE (L.B)
40 *          $903E: POKE -28610, SCAN RATE (H.B)
41 *          SCAN RATE IS CONTROLLED BY
42 *          A REAL TIME CLOCK WITH 1 uS RESOLUTION
43 *
44 *****
45 *
46 *
47 *
48 *
49 *          ORG $9050          ;Program start from -28592
50 *          OBJ $9050          ;
51 *
52 *
53 INITPL EQU $1C          ;Initial potential (L.B) is here

```

54	INITPH	EQU	\$1D	;	(H.B) here
55	INITVL	EQU	\$9000	;	Another place for init E (L.B)
56	INITVH	EQU	\$9001	;	(H.B)
57	SW1L	EQU	\$8F00	;	1st switch E
58	SW1H	EQU	\$8F01	;	
59	SW2L	EQU	\$8F02	;	2nd switch E
60	SW2H	EQU	\$8F03	;	
61	SW3L	EQU	\$8F04	;	3rd switch E
62	SW3H	EQU	\$8F05	;	
63	SW4L	EQU	\$8F06	;	4th switch E
64	SW4H	EQU	\$8F07	;	
65	SW5L	EQU	\$8F08	;	5th switch E
66	SW5H	EQU	\$8F09	;	
67	SW6L	EQU	\$8FOA	;	6th switch E
68	SW6H	EQU	\$8FOB	;	
69	SW7L	EQU	\$8FOC	;	7th switch E
70	SW7H	EQU	\$8FOD	;	
71	SW8L	EQU	\$8FOE	;	8th switch E
72	SW8H	EQU	\$8FOF	;	
73	SWADRL	EQU	\$EC	;	Idex switch E addr.
74	SWADRH	EQU	\$ED	;	
75	TSWCT	EQU	\$8F22	;	Save scan no. to restore
76	SWPL	EQU	\$9040	;	Current switch E
77	SWPH	EQU	\$9041	;	
78	STADL	EQU	\$A	;	Start addr. (L.B) of CV E table
79	STADH	EQU	\$B	;	(H.B)....
80	TSTADL	EQU	\$900A	;	start addr. (L.B) for CV E table
81	TSTADH	EQU	\$900B	;	(H.B).....
82	LSADL	EQU	\$9045	;	End addr. (L.B) for CV E table
83	LSADH	EQU	\$9046	;	(H.B).....
84	DRCT	EQU	\$9007	;	Init scan direction 0-cathodic
85				;	1-anodic scan
86	SWCT	EQU	\$9004	;	2-Init scan, 1-rev. scan, 0-end
87	ENDCT	EQU	\$9008	;	1-Init scan, 0-rev. scan
88	XMINL	EQU	\$9016	;	(L.B) for cathodic peak E
89	XMINH	EQU	\$9017	;	(H.B).....
90	XMAXL	EQU	\$9014	;	(L.B) of anodic peak E
91	XMAXH	EQU	\$9015	;	(H.B)
92	YMINL	EQU	\$9012	;	(L.B) for cathodic peak I
93	YMINH	EQU	\$9013	;	(H.B)
94	YMAXL	EQU	\$9010	;	(L.B) of anodic peak I
95	YMAXH	EQU	\$9011	;	(H.B)
96	YRANGL	EQU	\$9018	;	(L.B) of I peak to peak
97	YRANGH	EQU	\$9019	;	(H.B)
98	XRANGL	EQU	\$901A	;	(L.B) of scan E range
99	XRANGH	EQU	\$901B	;	(H.B)
100	XSCALL	EQU	\$901C	;	(L.B) of E plot scaling factor
101	XSCALM	EQU	\$901D	;	(M.B)
102	XSCALH	EQU	\$901E	;	(H.B)
103	YSCALL	EQU	\$9020	;	(L.B) of I plot scale factor
104	YSCALM	EQU	\$9021	;	(M.B)

105	YSCALH	EQU	\$9022	; (H.B)
106	DIVL	EQU	\$9023	; DIVL, DIVM AND DIVH are 3-byte
107	DIVM	EQU	\$9024	; of divisor for I (190/YRANGE),
108	DIVH	EQU	\$9025	; E (250/XRANGE) division
109	QUTNL	EQU	\$9026	; QUTNL, QUTNM AND QUTNH-3 bytes
110	QUTNM	EQU	\$9027	; of dividend and replaced by
111	QUTNH	EQU	\$9028	; Quotient after division
112	TAD1	EQU	\$9029	; Place for temporary data (L.B)
113	TAD2	EQU	\$902A	; Place for temporary data (H.B)
114	REML	EQU	\$902B	; (L.B) of remainder in division
115	REMM	EQU	\$902C	; (M.B)
116	REMH	EQU	\$902D	; (H.B)
117	TEXT	EQU	\$FB2F	; ROM text routine
118	HOME	EQU	\$FB60	; ROM home routine
119	STROBE	EQU	\$C010	; ROM key strobe flag
120	GR	EQU	\$C050	; Text mode off switch
121	HGR	EQU	\$C057	; HGR mode on switch
122	HGR1	EQU	\$C054	; Page 2 off switch
123	HPAGE	EQU	\$E6	; HGR page 1 or 2
124	HPLOT	EQU	\$F457	; ROM HGR plot routine
125	SETCOL	EQU	\$F6F0	; Color switch
126	HCLR	EQU	\$F3F2	; ROM HGR clear routine
127	FULSCR	EQU	\$C052	; Full screen switch
128	PLDT1	EQU	\$902E	; PLDT1 to PLDT5 are the product
129	PLDT2	EQU	\$902F	; of 2 bytes multiplicants (I or E)
130	PLDT3	EQU	\$9030	; times 3 bytes multiplier (scaling
131	PLDT4	EQU	\$9031	; factor)
132	PLDT5	EQU	\$9032	;
133	XPLDTL	EQU	\$9033	; (L.B) of scaled E for plot
134	XPLDTH	EQU	\$9034	; (H.B)
135	YPLDT	EQU	\$9035	; (L.B) of scaled I for plot
136	MULTL	EQU	\$9036	; (L.B) of multiplier
137	MULTM	EQU	\$9037	; (M.B)
138	MULTH	EQU	\$9038	; (H.B)
139	XLEL	EQU	\$9039	; (L.B) of low E of CV scan
140	XLEH	EQU	\$903A	; (H.B)
141	XHEL	EQU	\$903B	; (L.B) of high E of CV scan
142	XHEH	EQU	\$903C	; (H.B)
143	BASE1	EQU	\$C200	; Addr. of DA out
144	FREQ1	EQU	\$903D	; (L.B) of count in CLOCK
145	FREQH	EQU	\$903E	; (H.B)
146	CHGAIN	EQU	\$903F	; 16*AD gain code + channel no.
147	AD1	EQU	\$C0D0	; STA AD1 to init. AD conversion
148				; LDA AD1 to get L.B AD
149	AD2	EQU	\$C0D1	; LDA AD2 to get H.B AD
150	AUXRD	EQU	\$C003	; Read auxiliary memory
151	MAINRD	EQU	\$C002	; Read main memory
152	AUXWRT	EQU	\$C005	; Write auxiliary memory
153	MAINWRT	EQU	\$C004	; Write main memory
154	AUXMOVE	EQU	\$C311	; Move data between aux and main
155	AIL	EQU	\$3C	; Source start addr. (L.B)

```

156 A1H      EQU  $3D      ;                      (H.B)
157 A2L      EQU  $3E      ;Source end addr. (L.B)
158 A2H      EQU  $3F      ;                      (H.B)
159 A4L      EQU  $42      ;Destination start addr. (L.B)
160 A4H      EQU  $43      ;                      (H.B)
161 *
162 *
163 *
164 *
165 *
166 *****
167 *
168 *      CVTAB subroutine creates CV E table
169 *      CV E TABLE block start from $6000
170 *      L.B data first and followed with H.B data
171 *
172 *      END addr. of table block is dependent on
173 *      the CV scan range
174 *      End of table can not exceed $88FF
175 *
176 *****
177 *
178 *
179 *
180 *
9050: A5 1C      181  CVTAB  LDA  INITPL
9052: 8D 00 90   182          STA  INITVL
9055: A5 1D      183          LDA  INITPH
9057: 8D 01 90   184          STA  INITVH
905A: A9 8F      185          LDA  #$8F      ;Store switch addr.
905C: 85 ED      186          STA  SWADRH      ;
905E: A9 00      187          LDA  #$0      ;
9060: 85 EC      188          STA  SWADRL      ;
9062: AD 04 90   189          LDA  SWCT
9065: 8D 22 8F   190          STA  TSWCT
9068: A2 00      191          LDX  #$00
906A: A1 EC      192          LDA  (SWADRL,X) ;Get 1st switch E
906C: 8D 40 90   193          STA  SWPL      ;
906F: E6 EC      194          INC  SWADRL      ;Increment addr.
9071: A1 EC      195          LDA  (SWADRL,X) ;
9073: 8D 41 90   196          STA  SWPH      ;
9076: E6 EC      197          INC  SWADRL      ;
9078: A9 00      198          LDA  #$00      ;Set table start addr. at
907A: 85 0A      199          STA  STADL      ;$4000
907C: 8D 0A 90   200          STA  TSTADL
907F: A9 40      201          LDA  #$40
9081: 85 0B      202          STA  STADH
9083: 8D 0B 90   203          STA  TSTADH
9086: A9 00      204  DIR    LDA  #$00      ;init scan direction ?
9088: CD 07 90   205          CMP  DRCT      ;0 for cathodic scan
908B: F0 03      206          BEQ  FETCL      ;1 for anodic scan

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908D: 4C FD 90	207		JMP	ANODE	;creat init. anod scan E
9090: A5 1C	208	FETCL	LDA	INITPL	;creat cathodic scan E
9092: 8D 05 C0	209		STA	AUXWRT	;write to aux. memory
9095: 81 0A	210		STA	(STADL,X)	;Low byte first
9097: 8D 04 C0	211		STA	MAINWRT	;Go back to write main
909A: E6 0A	212		INC	STADL	;Increase table addr.
909C: D0 02	213		BNE	FETCH	;change H.B addr. ?
909E: E6 0B	214		INC	STADH	;yes, increase H.B addr.
90A0: A5 1D	215	FETCH	LDA	INITPH	;no, store high byte E
90A2: 8D 05 C0	216		STA	AUXWRT	;Write to aux. memory
90A5: 81 0A	217		STA	(STADL,X)	
90A7: 8D 04 C0	218		STA	MAINWRT	;Go back to write main
90AA: E6 0A	219		INC	STADL	;Increase table addr.
90AC: D0 02	220		BNE	INCV	;change H.B addr. ?
90AE: E6 0B	221		INC	STADH	;yes, then increase
90B0: E6 1C	222	INCV	INC	INITPL	;no, then increase E
90B2: D0 02	223		BNE	CBR	;increase H.B E ?
90B4: E6 1D	224		INC	INITPH	;yes, then increase
90B6: A5 1C	225	CBR	LDA	INITPL	;is the foward scan ?
90B8: CD 40 90	226		CMP	SWPL	;switch, this scan end E
90BB: D0 D3	227		BNE	FETCL	;If scan end E reached
90BD: A5 1D	228		LDA	INITPH	;no, back to FETCL
90BF: CD 41 90	229		CMP	SWPH	;continue scan E table
90C2: D0 CC	230		BNE	FETCL	;
90C4: A5 1C	231		LDA	INITPL	;indicate next scan rev
90C6: 8D 05 C0	232		STA	AUXWRT	;Write to aux. memory
90C9: 81 0A	233		STA	(STADL,X)	;finish end E in table
90CB: 8D 04 C0	234		STA	MAINWRT	;Go back to main
90CE: E6 0A	235		INC	STADL	
90D0: D0 02	236		BNE	FETCF	
90D2: E6 0B	237		INC	STADH	
90D4: A5 1D	238	FETCF	LDA	INITPH	
90D6: 8D 05 C0	239		STA	AUXWRT	;Write to aux.
90D9: 81 0A	240		STA	(STADL,X)	
90DB: 8D 04 C0	241		STA	MAINWRT	;Go back to main
90DE: E6 0A	242		INC	STADL	
90E0: D0 02	243		BNE	CBRX	
90E2: E6 0B	244		INC	STADH	
90E4: CE 04 90	245	CBRX	DEC	SWCT	;how many scans left
90E7: FO 11	246		BEQ	JOUT	;No, then out
90E9: A1 EC	247		LDA	(SWADRL,X)	;Get next switch E
90EB: 8D 40 90	248		STA	SWPL	;
90EE: E6 EC	249		INC	SWADRL	;
90F0: A1 EC	250		LDA	(SWADRL,X)	;
90F2: 8D 41 90	251		STA	SWPH	;
90F5: E6 EC	252		INC	SWADRL	
90F7: 4C FD 90	253		JMP	ANODE	;
90FA: 4C 6F 91	254	JOUT	JMP	OUT	;
90FD: A5 1C	255	ANODE	LDA	INITPL	;Set anodic scan table
90FF: 8D 05 C0	256		STA	AUXWRT	;Write to aux.
9102: 81 0A	257		STA	(STADL,X)	

9104:	8D 04 C0	258		STA	MAINWRT	;Go back to main
9107:	E6 0A	259		INC	STADL	
9109:	D0 02	260		BNE	ANODH	
910B:	E6 0B	261		INC	STADH	
910D:	A5 1D	262	ANODH	LDA	INITPH	
910F:	8D 05 C0	263		STA	AUXWRT	;To aux.
9112:	81 0A	264		STA	(STADL,X)	
9114:	8D 04 C0	265		STA	MAINWRT	;Go back to main
9117:	E6 0A	266		INC	STADL	
9119:	D0 02	267		BNE	DECV	
911B:	E6 0B	268		INC	STADH	
911D:	A4 1C	269	DECV	LDY	INITPL	
911F:	88	270		DEY		
9120:	84 1C	271		STY	INITPL	
9122:	C0 FF	272		CPY	#\$FF	
9124:	D0 05	273		BNE	ABR	
9126:	A4 1D	274		LDY	INITPH	
9128:	88	275		DEY		
9129:	84 1D	276		STY	INITPH	
912B:	A5 1C	277	ABR	LDA	INITPL	;for. scan switch E is
912D:	CD 40 90	278		CMP	SWPL	;the end E of this scan
9130:	D0 CB	279		BNE	ANODE	;Compare with current E
9132:	A5 1D	280		LDA	INITPH	;to see if reach the end
9134:	CD 41 90	281		CMP	SWPH	;no, back to continue
9137:	D0 C4	282		BNE	ANODE	;the scan table
9139:	A5 1C	283		LDA	INITPL	;indicate next scan is
913B:	8D 05 C0	284		STA	AUXWRT	;Write to aux.
913E:	81 0A	285		STA	(STADL,X)	;the rev. scan
9140:	8D 04 C0	286		STA	MAINWRT	;Go back to main
9143:	E6 0A	287		INC	STADL	;and finished the last
9145:	D0 02	288		BNE	ANOD1	
9147:	E6 0B	289		INC	STADH	
9149:	A5 1D	290	ANOD1	LDA	INITPH	
914B:	8D 05 C0	291		STA	AUXWRT	;Write to aux.
914E:	81 0A	292		STA	(STADL,X)	
9150:	8D 04 C0	293		STA	MAINWRT	;Back to main
9153:	E6 0A	294		INC	STADL	
9155:	D0 02	295		BNE	ABRX	
9157:	E6 0B	296		INC	STADH	
9159:	CE 04 90	297	ABRX	DEC	SWCT	;the last ?
915C:	F0 11	298		BEQ	OUT	;yes, OUT for RTS
915E:	A1 EC	299		LDA	(SWADRL,X)	;Get next switch E
9160:	8D 40 90	300		STA	SWPL	;
9163:	E6 EC	301		INC	SWADRL	;
9165:	A1 EC	302		LDA	(SWADRL,X)	;
9167:	8D 41 90	303		STA	SWPH	;
916A:	E6 EC	304		INC	SWADRL	;
916C:	4C 90 90	305		JMP	FETCL	;no, goto cathodic scan
916F:	A4 0A	306	OUT	LDY	STADL	;Restore all the parameters
9171:	8C 45 90	307		STY	LSADL	;Start table addr. restored
9174:	A4 0B	308		LDY	STADH	

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9176: 8C 46 90 309      STY  LSADH
9179: AD 0A 90 310      LDA  TSTADL
917C: 85 0A 311        STA  STADL
917E: AD 0B 90 312      LDA  TSTADH
9181: 85 0B 313        STA  STADH
9183: AD 22 8F 314      LDA  TSWCT      ;Restore scan no.
9186: 8D 04 90 315      STA  SWCT      ;
9189: AD 00 90 316      LDA  INITVL     ;Restore init. E
918C: 85 1C 317        STA  INITPL     ;
918E: AD 01 90 318      LDA  INITVH     ;
9191: 85 1D 319        STA  INITPH     ;
9193: A9 8F 320        LDA  #$8F      ;Initialize the DA
9195: 8D 02 C2 321      STA  BASE1+$2
9198: A9 FF 322        LDA  #$FF
919A: 8D 03 C2 323      STA  BASE1+$3
919D: AD 3D 90 324      LDA  FREQL     ;Set count of CLOCK
91A0: 8D 04 C2 325      STA  BASE1+$4
91A3: AD 3E 90 326      LDA  FREQH
91A6: 8D 05 C2 327      STA  BASE1+$5
91A9: A9 E0 328        LDA  #$E0
91AB: 8D 0B C2 329      STA  BASE1+$B
91AE: A9 8A 330        LDA  #$8A
91B0: 8D 0C C2 331      STA  BASE1+$0C
91B3: A5 1D 332        LDA  INITPH     ;Set potentiostat at
91B5: 8D 00 C2 333      STA  BASE1     ;initial potential
91B8: A5 1C 334        LDA  INITPL
91BA: 8D 01 C2 335      STA  BASE1+$01
91BD: 60 336          RTS
337 *
338 *
339 *
340 *
341 *****
342 *
343 *      STARTAD INITIALIZE DA AND AD      *
344 *      OUTPUT SCAN POTENTIAL            *
345 *      AND SAMPLE CURRENT                *
346 *      STORE CURRENT DATA STARTING      *
347 *      FROM $6000, H.B FIRST AND THEN    *
348 *      L.B NEXT                          *
349 *      SCAN AND SAMPLING RATE ARE        *
350 *      CONTROLLED BY THE CLOCK            *
351 *      INTERRUPT                          *
352 *
353 *****
354 *
355 *
356 *
91BE: A5 0A 357 STARTAD LDA  STADL      ;Start addr. for move
91C0: 85 3C 358      STA  A1L
91C2: 85 42 359      STA  A4L

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91C4:	A5 0B	360		LDA	STADH	
91C6:	85 3D	361		STA	A1H	
91C8:	85 43	362		STA	A4H	
91CA:	AD 45 90	363		LDA	LSADL	;End addr.
91CD:	85 3E	364		STA	A2L	
91CF:	AD 46 90	365		LDA	LSADH	
91D2:	85 3F	366		STA	A2H	
91D4:	18	367		CLC		
91D5:	20 11 C3	368		JSR	AUXMOVE	;Move from aux. to main
91D8:	A9 91	369		LDA	#>INTERS	;Set the addr. of
91DA:	8D FE 03	370		STA	\$3FE	;inter. service routine
91DD:	A9 EC	371		LDA	#<INTERS	;L.B addr. in \$3FE
91DF:	8D FF 03	372		STA	\$3FF	;H.B addr. in \$3FF
91E2:	78	373		SEI		;NO interruption now
91E3:	A9 C0	374		LDA	#\$C0	;Start clock interrupt
91E5:	8D 0E C2	375		STA	BASE1+\$0E	
91E8:	A0 01	376		LDY	#\$1	
91EA:	A2 00	377		LDX	#\$0	
91EC:	AD 0D C2	378	INTERS	LDA	BASE1+\$D	;Check interrupt flag
91EF:	29 40	379		AND	#\$40	;to see if it needs
91F1:	F0 38	380		BEQ	EXIT2	;service or not
91F3:	AD 04 C2	381		LDA	BASE1+\$04	;yes, clear inter. flag
91F6:	AD 3F 90	382		LDA	CHGAIN	;Init. AD conversion
91F9:	8D D0 C0	383		STA	AD1	
91FC:	A5 0A	384		LDA	STADL	;While conversion check
91FE:	38	385		SEC		;CV scan completed ?
91FF:	ED 45 90	386		SBC	LSADL	
9202:	A5 0B	387		LDA	STADH	
9204:	ED 46 90	388		SBC	LSADH	
9207:	B0 25	389		BCS	CHECK	;yes, check out for RTS
9209:	B1 0A	390		LDA	(STADL),Y	;no, then output scan E
920B:	8D 00 C2	391		STA	BASE1	
920E:	A1 0A	392		LDA	(STADL,X)	
9210:	8D 01 C2	393		STA	BASE1+\$1	
9213:	AD D1 C0	394		LDA	AD2	;Get H.B AD
9216:	29 0F	395		AND	#\$0F	;mask 4 high bits
9218:	81 0A	396		STA	(STADL,X)	;store the data
921A:	E6 0A	397		INC	STADL	
921C:	D0 02	398		BNE	STEP2	
921E:	E6 0B	399		INC	STADH	
9220:	AD D0 C0	400	STEP2	LDA	AD1	;Get L.B AD
9223:	81 0A	401		STA	(STADL,X)	;Store it
9225:	E6 0A	402		INC	STADL	
9227:	D0 02	403		BNE	EXIT2	
9229:	E6 0B	404		INC	STADH	
922B:	4C EC 91	405	EXIT2	JMP	INTERS	
922E:	A9 00	406	CHECK	LDA	#\$0	;Restore parameters and
9230:	8D 0E C2	407		STA	BASE1+\$E	;Stop clock interrupt
9233:	A9 65	408		LDA	#\$65	
9235:	8D FE 03	409		STA	\$3FE	;Restore monitor inter.
9238:	A9 FF	410		LDA	#\$FF	;service routine addr.

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923A: 8D FF 03 411      STA  $3FF      ;
923D: AD 0A 90 412      LDA  TSTADL
9240: 85 0A      413      STA  STADL
9242: AD 0B 90 414      LDA  TSTADH
9245: 85 0B      415      STA  STADH
416 *
417 *
418 *
419 *
420 *****
421 * *
422 *      PEAK ANODIC AND CATHODIC E, I *
423 *      MAX I AND E IS FOR ANODIC PEAK *
424 *      MIN I AND E IS FOR CATHODIC PEAK *
425 * *
426 *      AFTER MAX AND MIN ARE PEAKED *
427 *      PLOT SCALE FACTOR IS CALCULATED *
428 *      BY TRIPLE PRECISION DIVISION ROUTINE *
429 * *
430 *****
431 *
432 *
433 *
434 *
9247: A2 00      435      LDX  #$00
9249: A9 00      436      LDA  #$00
924B: 8D 10 90 437      STA  YMAXL
924E: A9 00      438      LDA  #$00
9250: 8D 11 90 439      STA  YMAXH
9253: A9 FF      440      LDA  #$FF
9255: 8D 12 90 441      STA  YMINL
9258: A9 FF      442      LDA  #$FF
925A: 8D 13 90 443      STA  YMINH
925D: A0 01      444      PEAK  LDY  #$01
925F: B1 0A      445      LDA  (STADL),Y
9261: 38      446      SEC      ;See if current I larger
9262: ED 10 90 447      SBC  YMAXL      ;than YMAX
9265: A1 0A      448      LDA  (STADL,X) ;if yes, goto MAX to
9267: ED 11 90 449      SBC  YMAXH      ;replace YMAX and store
926A: B0 1C      450      BCS  MAX1      ;correspondent E
926C: B1 0A      451      POUT  LDA  (STADL),Y ;See if current I less
926E: 38      452      SEC      ;than YMIN
926F: ED 12 90 453      SBC  YMINL      ;yes, goto MIN to
9272: A1 0A      454      LDA  (STADL,X) ;replace YMIN and store
9274: ED 13 90 455      SBC  YMINH      ;correspondent E
9277: 90 12      456      BCC  MIN1      ;
9279: E6 0A      457      POUT1 INC  STADL      ;Increase the addr. of
927B: D0 02      458      BNE  ADD2      ;
927D: E6 0B      459      INC  STADH      ;
927F: E6 0A      460      ADD2  INC  STADL      ;
9281: D0 0B      461      BNE  PEND

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9283:	E6	OB	462	INC	STADH	
9285:	4C	8E	92 463	JMP	PEND	;end of data ?
9288:	4C	28	93 464	JMP	MAX	
928B:	4C	45	93 465	JMP	MIN	
928E:	A4	OB	466	LDY	STADH	
9290:	CC	46	90 467	CPY	LSADH	
9293:	D0	C8	468	BNE	PEAK	;no, continue peaking
9295:	A4	OA	469	LDY	STADL	
9297:	CC	45	90 470	CPY	LSADL	
929A:	D0	C1	471	BNE	PEAK	
929C:	AD	OA	90 472	LDA	TSTADL	;yes, restore parameters
929F:	85	OA	473	STA	STADL	
92A1:	AD	OB	90 474	LDA	TSTADH	
92A4:	85	OB	475	STA	STADH	
92A6:	AD	10	90 476	LDA	YMAXL	;and cal. the plot scale
92A9:	38		477	SEC		;factor
92AA:	ED	12	90 478	SBC	YMINL	;Get y-axis full range
92AD:	8D	18	90 479	STA	YRANGL	;
92B0:	8D	23	90 480	STA	DIVL	;and as a divisor
92B3:	AD	11	90 481	LDA	YMAXH	
92B6:	ED	13	90 482	SBC	YMINH	
92B9:	8D	19	90 483	STA	YRANGH	
92BC:	8D	24	90 484	STA	DIVM	
92BF:	A9	00	485	LDA	#\$00	
92C1:	8D	25	90 486	STA	DIVH	
92C4:	A9	A0	487	LDA	#\$A0	;0-160 on HGR y-axis
92C6:	8D	28	90 488	STA	QUTNH	;Let it as dividend
92C9:	A9	00	489	LDA	#\$00	
92CB:	8D	27	90 490	STA	QUTNM	
92CE:	8D	26	90 491	STA	QUTNL	
92D1:	20	62	93 492	JSR	DIV24	;Now, get (160/YRANGE)
92D4:	AD	28	90 493	LDA	QUTNH	;
92D7:	8D	22	90 494	STA	YSCALH	
92DA:	AD	27	90 495	LDA	QUTNM	
92DD:	8D	21	90 496	STA	YSCALM	
92E0:	AD	26	90 497	LDA	QUTNL	
92E3:	8D	20	90 498	STA	YSCALL	
92E6:	AD	3B	90 499	LDA	XHEL	;Calculate XRANGE
92E9:	38		500	SEC		
92EA:	ED	39	90 501	SBC	XLEL	
92ED:	8D	1A	90 502	STA	XRANGL	
92F0:	8D	23	90 503	STA	DIVL	;as a divisor
92F3:	AD	3C	90 504	LDA	XHEH	
92F6:	ED	3A	90 505	SBC	XLEH	
92F9:	8D	1B	90 506	STA	XRANGH	
92FC:	8D	24	90 507	STA	DIVM	
92FF:	A9	00	508	LDA	#\$00	
9301:	8D	25	90 509	STA	DIVH	
9304:	8D	26	90 510	STA	QUTNL	
9307:	8D	27	90 511	STA	QUTNM	
930A:	A9	FA	512	LDA	#\$FA	;HGR x-axis from 0-250

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930C: 8D 28 90 513      STA  QUTNH      ;as a dividend
930F: 20 62 93 514      JSR  DIV24      ;Calculate (250/XRANGE)
9312: AD 28 90 515      LDA  QUTNH
9315: 8D 1E 90 516      STA  XSCALH
9318: AD 27 90 517      LDA  QUTNM
931B: 8D 1D 90 518      STA  XSCALM
931E: AD 26 90 519      LDA  QUTNL
9321: 8D 1C 90 520      STA  XSCALL
9324: 20 B2 93 521      JSR  PLOTVC      ;Jump HGR plot routine
9327: 60               522      RTS      ;After plot, back basic
                               523
                               524
9328: A1 0A           525      MAX      LDA  (STADL,X)
932A: 8D 11 90 526      STA  YMAXH
932D: B1 0A           527      LDA  (STADL),Y
932F: 8D 10 90 528      STA  YMAXL
9332: 8D 03 C0 529      STA  AUXRD
9335: B1 0A           530      LDA  (STADL),Y
9337: 8D 15 90 531      STA  XMAXH
933A: A1 0A           532      LDA  (STADL,X)
933C: 8D 02 C0 533      STA  MAINRD
933F: 8D 14 90 534      STA  XMAXL
9342: 4C 6C 92 535      JMP  POUT
9345: A1 0A           536      MIN      LDA  (STADL,X)
9347: 8D 13 90 537      STA  YMINH
934A: B1 0A           538      LDA  (STADL),Y
934C: 8D 12 90 539      STA  YMINL
934F: 8D 03 C0 540      STA  AUXRD
9352: B1 0A           541      LDA  (STADL),Y
9354: 8D 17 90 542      STA  XMINH
9357: A1 0A           543      LDA  (STADL,X)
9359: 8D 02 C0 544      STA  MAINRD
935C: 8D 16 90 545      STA  XMINL
935F: 4C 79 92 546      JMP  POUT1
                               547      *
                               548      *
                               549      *
550      *****
551      *
552      *      TRIPLE PRECISION DIVISION ROUTINE      *
553      *      FOR CALCULATE PLOT SCALE FACTOR      *
554      *      OF I AND E      *
555      *
556      *****
557      *
558      *
9362: A9 00           559      DIV24      LDA  #$00      ;Clear remainder
9364: 8D 2B 90 560      STA  REML
9367: 8D 2C 90 561      STA  REMM
936A: 8D 2D 90 562      STA  REMH
936D: A2 18           563      LDX  #$18      ;dividend bit count 24

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936F: 0E 26 90 564 NXTBT ASL QUTNL ;Shift dividend/Quot. left
9372: 2E 27 90 565 ROL QUTNM
9375: 2E 28 90 566 ROL QUTNH
9378: 2E 2B 90 567 ROL REML ;partial dividend left
937B: 2E 2C 90 568 ROL REMM
937E: 2E 2D 90 569 ROL REMH
9381: AD 2B 90 570 LDA REML ;Subtract low bytes
9384: 38 571 SEC
9385: ED 23 90 572 SBC DIVL
9388: 8D 29 90 573 STA TAD1 ;Save low bytes
938B: AD 2C 90 574 LDA REMM ;Subtr. next high bytes
938E: ED 24 90 575 SBC DIVM
9391: 8D 2A 90 576 STA TAD2 ;Save it
9394: AD 2D 90 577 LDA REMH ;Subtr. most high bytes
9397: ED 25 90 578 SBC DIVH
939A: 90 12 579 BCC CNTDN ;Divisor>Dividend ?
939C: EE 26 90 580 INC QUTNL ;No, set bit in quot.
939F: 8D 2D 90 581 STA REMH ;and return subtra.
93A2: AD 2A 90 582 LDA TAD2 ;as the new remainder
93A5: 8D 2C 90 583 STA REMM
93A8: AD 29 90 584 LDA TAD1
93AB: 8D 2B 90 585 STA REML
93AE: CA 586 CNTDN DEX ;Decrement bit count
93AF: DO BE 587 BNE NXTBT ;Loop until 24 bits
93B1: 60 588 RTS

589 *
590 *
591 *
592 *
593 *
594 *****
595 * *
596 * HGR PLOT ROUTINE *
597 * PLOT THE DATA IN 250*160 HGR1 *
598 * BOTTOM 4 LINES FOR HGR TEXT *
599 * Y-AXIS IS CURRENT, UP-CATHODIC *
600 * DOWN-ANODIC *
601 * X-AXIS IS POTENTIAL, LEFT-ANODIC *
602 * RIGHT-CATHODIC *
603 * *
604 *****
605 *
606 *
607 *
93B2: A2 03 608 PLOTVCV LDX #$3 ;Set color=white
93B4: 20 F0 F6 609 JSR SETCOL
93B7: A9 20 610 LDA #$20 ;Set display page 1
93B9: 85 E6 611 STA HPAGE
93BB: 8D 57 C0 612 STA HGR ;Turn on HGR mode
93BE: 8D 52 C0 613 STA FULSCR ;Set HGR fullscreen
93C1: 8D 50 C0 614 STA GR ;Turn off text mode

```

93C4:	A0 01	615	NEXPL	LDY	#\$01	
93C6:	A2 00	616		LDX	#\$00	
93C8:	B1 0A	617		LDA	(STADL),Y	;Get I data
93CA:	38	618		SEC		
93CB:	ED 12 90	619		SBC	YMINL	;Subtract bias
93CE:	8D 29 90	620		STA	TAD1	;Save it
93D1:	A1 0A	621		LDA	(STADL,X)	
93D3:	ED 13 90	622		SBC	YMINH	
93D6:	8D 2A 90	623		STA	TAD2	
93D9:	AD 20 90	624		LDA	YSCALL	;Get I scale factor
93DC:	8D 36 90	625		STA	MULTL	;as a multiplier
93DF:	AD 21 90	626		LDA	YSCALM	
93E2:	8D 37 90	627		STA	MULTM	
93E5:	AD 22 90	628		LDA	YSCALH	
93E8:	8D 38 90	629		STA	MULTH	
93EB:	20 6E 94	630		JSR	MLT24	;Calculate plot value
93EE:	A9 A0	631		LDA	#\$A0	;Reverse value to let
93F0:	38	632		SEC		;cath. up, anod. down
93F1:	ED 30 90	633		SBC	PLDT3	;
93F4:	8D 35 90	634		STA	YPLDT	;
93F7:	8D 03 C0	635		STA	AUXRD	;Read from aux.
93FA:	A1 0A	636		LDA	(STADL,X)	;Get E data
93FC:	8D 02 C0	637		STA	MAINRD	;Back to main
93FF:	38	638		SEC		;Subtract bias
9400:	ED 39 90	639		SBC	XLEL	
9403:	8D 29 90	640		STA	TAD1	;as a multiplicant
9406:	8D 03 C0	641		STA	AUXRD	
9409:	B1 0A	642		LDA	(STADL),Y	
940B:	8D 02 C0	643		STA	MAINRD	
940E:	ED 3A 90	644		SBC	XLEH	
9411:	8D 2A 90	645		STA	TAD2	
9414:	AD 1C 90	646		LDA	XSCALL	;Get E scale factor
9417:	8D 36 90	647		STA	MULTL	;as a multiplier
941A:	AD 1D 90	648		LDA	XSCALM	
941D:	8D 37 90	649		STA	MULTM	
9420:	AD 1E 90	650		LDA	XSCALH	
9423:	8D 38 90	651		STA	MULTH	
9426:	20 6E 94	652		JSR	MLT24	;Calc. E plot value
9429:	AD 30 90	653		LDA	PLDT3	;plot start from 10-260
942C:	18	654		CLC		
942D:	69 0A	655		ADC	#\$0A	
942F:	8D 33 90	656		STA	XPLDTL	
9432:	A9 00	657		LDA	#\$00	
9434:	69 00	658		ADC	#\$00	
9436:	8D 34 90	659		STA	XPLDTH	
9439:	AE 33 90	660		LDX	XPLDTL	;x-plot value to x-reg.
943C:	AC 34 90	661		LDY	XPLDTH	;H.B in y-reg.
943F:	AD 35 90	662		LDA	YPLDT	;y-plot value to A-reg.
9442:	20 57 F4	663		JSR	HPLOT	;and goto ROM HPLOT
9445:	A2 08	664		LDX	#\$08	;Plot increment count
9447:	E6 0A	665	ADINC	INC	STADL	;each 4 point plotted

```

9449: D0 02      666      BNE  NEXINC
944B: E6 0B      667      INC  STADH
944D: CA        668  NEXINC  DEX
944E: D0 F7      669      BNE  ADINC      ;Loop until 4th point
9450: A5 0A      670      LDA  STADL      ;end of data ?
9452: 38         671      SEC
9453: ED 45 90   672      SBC  LSADL
9456: A5 0B      673      LDA  STADH
9458: ED 46 90   674      SBC  LSADH
945B: 90 03      675      BCC  JNEXPL
945D: 4C 63 94   676      JMP  PLOUT
9460: 4C C4 93   677  JNEXPL  JMP  NEXPL
9463: AD 0A 90   678  PLOUT   LDA  TSTADL
9466: 85 0A      679      STA  STADL
9468: AD 0B 90   680      LDA  TSTADH
946B: 85 0B      681      STA  STADH
946D: 60         682      RTS
683      *
684      *
685      *
686      *
687      *
688      *****
689      *
690      *      TRIPLE PRECISION MULTIPLY ROUTINE      *
691      *      (TAD1,TAD2)-MULTIPLICANT                  *
692      *      (MULTL,MULTM,MULTH)-MULTIPLIER              *
693      *      (PLDT5,PLDT4,PLDT3,PLDT2,PLDT1)-          *
694      *      PRODUCT                                      *
695      *
696      *****
697      *
698      *
946E: A9 00      699  MLT24   LDA  #$00      ;Clear product
9470: 8D 2E 90   700      STA  PLDT1
9473: 8D 2F 90   701      STA  PLDT2
9476: 8D 30 90   702      STA  PLDT3
9479: 8D 31 90   703      STA  PLDT4
947C: 8D 32 90   704      STA  PLDT5
947F: A2 10      705      LDX  #$10      ;Multiplier count = 16
9481: 4E 2A 90   706  NEXMBT  LSR  TAD2      ;Shift multiplier right
9484: 6E 29 90   707      ROR  TAD1
9487: 90 19      708      BCC  ALIGN      ;Multiplier =1 ?
9489: AD 30 90   709      LDA  PLDT3      ;Yes, fetch new PLDT
948C: 18         710      CLC
948D: 6D 36 90   711      ADC  MULTL
9490: 8D 30 90   712      STA  PLDT3
9493: AD 31 90   713      LDA  PLDT4
9496: 6D 37 90   714      ADC  MULTM
9499: 8D 31 90   715      STA  PLDT4
949C: AD 32 90   716      LDA  PLDT5

```

949F:	6D 38 90	717	ADC	MULTH	
94A2:	6A	718	ALIGN	ROR	A ;Rot. 5-bytes PLDT right
94A3:	8D 32 90	719		STA	PLDT5
94A6:	6E 31 90	720		ROR	PLDT4
94A9:	6E 30 90	721		ROR	PLDT3
94AC:	6E 2F 90	722		ROR	PLDT2
94AF:	6E 2E 90	723		ROR	PLDT1
94B2:	CA	724		DEX	;Decrement bit count
94B3:	D0 CC	725		BNE	NEXMBT ;Loop until 16 bit done
94B5:	60	726		RTS	

--End assembly, 1126 bytes, Errors: 0

Program 2

Program, DPV, used to supervise differential pulse voltammetric experiments, process data, and display differential pulse voltammograms.

```

1 *****
2 *
3 *      SQUARE WAVE STEP DIFFERENTIAL PULSE      *
4 *      VOLTAMMETRY PROGRAM                      *
5 *      WRITTEN BY ING-FENG HU                   *
6 *      1st VERSION - APRIL 20, 1985             *
7 *
11 *****
12 *
13 *
14 *
15          ORG  $8BA0          ;Prog. start from
16          OBJ  $8BA0          ;$8BA0 = -29792
17 *
18 *
19 INITPL    EQU  $8B00          ;Init. E at -29952
20 INITPH    EQU  $8B01          ; -29951
21 INITVL    EQU  $8B02          ; -29950
22 INITVH    EQU  $8B03          ; -29949
23 PAL       EQU  $8B04          ;Pulse ampl. at -29948
24 PAH       EQU  $8B05          ; -29947
25 STADL     EQU  $A             ;Data start addr.
26 STADH     EQU  $B             ;
27 TSTADL    EQU  $8B06          ; -29946,-29945
28 TSTADH    EQU  $8B07          ;
29 LSADL     EQU  $8B08          ; -29944,-29943
30 LSADH     EQU  $8B09          ;
31 DRCT      EQU  $8B0A          ;scan dir. at -29942
32 DBADL     EQU  $EC            ;Data start addr.
33 DBADH     EQU  $ED            ;236,237
34 FDBADL    EQU  $8B0B          ;Last data at -29941
35 FDBADH    EQU  $8B0C          ; -29940
36 YMAXL     EQU  $8B0D          ;Y max. at -29939
37 YMAXH     EQU  $8B0E          ; -29938
38 YMINL     EQU  $8B0F          ;Y min. at -29937
39 YMINH     EQU  $8B10          ; -29936
40 DAL       EQU  $8B11          ;DA data -29935
41 DAH       EQU  $8B12          ; -29934
42 DOUTL     EQU  $8B13          ;AD data
43 DOUTH     EQU  $8B14          ; -29933,-39932
44 PLL       EQU  $8B15          ;Back pulse ampl.
45 PLH       EQU  $8B16          ; -29931,-29930
46 PSCTL     EQU  $8B17          ;Pulse count
47 PSCTH     EQU  $8B18          ; -29929,-29928
48 TSL       EQU  $8B19          ;Pulse out count
49 TSH       EQU  $8B1A          ; -29927,-29926
50 SAML      EQU  $8B1B          ;Sampling count
51 SAMH      EQU  $8B1C          ; -29925,-29924
52 BKL       EQU  $8B1D          ;Pulse back count
53 BKH       EQU  $8B1E          ; -29923,-29922
54 BDL       EQU  $8B1F          ;Background data

```

55	BDH	EQU	\$8B20	; -29921, -29920
56	XRANGL	EQU	\$8B21	; X range
57	XRANGH	EQU	\$8B22	; -29919, -29918
58	XSCALL	EQU	\$8B23	; X scale
59	XSCALM	EQU	\$8B24	; -29917, -29916
60	XSCALH	EQU	\$8B25	; and -29915
61	XRANGL2	EQU	\$8B26	; 2nd X range
62	XRANGH2	EQU	\$8B27	; -29914, -29913
63	XSCALL2	EQU	\$8B28	; 2nd x scale
64	XSCALM2	EQU	\$8B29	; -29912, -29911
65	XSCALH2	EQU	\$8B2A	; and -29910
66	DIVL	EQU	\$8B2B	; Divisor
67	DIVM	EQU	\$8B2C	; -29909, -29908
68	DIVH	EQU	\$8B2D	; and -29907
69	QUTNL	EQU	\$8B2E	; Dividend and Quotient
70	QUTNM	EQU	\$8B2F	; -29906, -29905
71	QUTNH	EQU	\$8B30	; and -29904
72	TAD1	EQU	\$8B31	; Temporary data
73	TAD2	EQU	\$8B32	; -29903, -29902
74	REML	EQU	\$8B33	; Remainder
75	REMM	EQU	\$8B34	; -29901, -29900
76	REMH	EQU	\$8B35	; and -29899
77	TEXT	EQU	\$FB2F	
78	HOME	EQU	\$FB60	
79	STROBE	EQU	\$C010	
80	GR	EQU	\$C050	
81	HGR	EQU	\$C057	
82	HGR1	EQU	\$C054	
83	HPAGE	EQU	\$E6	
84	HPLLOT	EQU	\$F457	
85	LPLOT	EQU	\$F53A	
86	SETCOL	EQU	\$F6F0	
87	HCLR	EQU	\$F3F2	
88	FULSCR	EQU	\$C052	
89	PLDT1	EQU	\$8B36	; Product
90	PLDT2	EQU	\$8B37	; -29898, -29897
91	PLDT3	EQU	\$8B38	; -29896, -29895, -29894
92	PLDT4	EQU	\$8B39	;
93	PLDT5	EQU	\$8B3A	;
94	XPLDTL	EQU	\$8B3B	; X-plot value
95	XPLDTH	EQU	\$8B3C	; -29893, -29892
96	YPLDT	EQU	\$8B3D	; Y-plot value -29891
97	MULTL	EQU	\$8B3E	; Multiplier
98	MULTM	EQU	\$8B3F	; -29890, -29889, -29888
99	MULTH	EQU	\$8B40	
100	ADL	EQU	\$8B41	; Sampled data
101	ADH	EQU	\$8B42	; -29887, -29886
102	XHEL	EQU	\$8B43	; X-pulse no.
103	XHEH	EQU	\$8B44	; -29885, -29884
104	XHEL2	EQU	\$8B45	; 2nd pulse no.
105	XHEH2	EQU	\$8B46	; -29883, -29882

```

106 BASE1 EQU $C200
107 BIASL EQU $8B47 ;Baseline
108 BIASH EQU $8B48 ; -29881,-29880
109 CHGAIN EQU $8B49 ;AD chennel+gaine -29879
110 AD1 EQU $C0D0 ;
111 AD2 EQU $C0D1 ;
112 FLAG EQU $8B4C ;Plot flag -29876
113 DOUTL1 EQU $8B4D ;Store data
114 DOUTH1 EQU $8B4E ; -29875,-29874
115 DOUTL5 EQU $8B4F ; -29873,-29872
116 DOUTH5 EQU $8B50
117 SCCT EQU $8B51 ;Sensitive count -29871
118 BIASL2 EQU $8B53 ;2nd biasline
119 BIASH2 EQU $8B54 ; -29869,-29868
120 PRCTL EQU $8B55 ;Data proc. count
121 PRCTH EQU $8B56 ; -29867,-29866
122 FLAG2 EQU $8B57 ;Plot count -29865
123 DOUTL2 EQU $8B58 ;Store data
124 DOUTH2 EQU $8B59 ; -29864,-29863
125 DOUTL3 EQU $8B5A ; -29862,-29861
126 DOUTH3 EQU $8B5B
127 FLAG3 EQU $8B5C ;HLINE count -29860
128 FLAG7 EQU $8B5D ;Move aux. flag -29859
129 AUXMOVE EQU $C311 ;Move data aux <-> main
130 ;CLC: aux -> main
131 ;SEC: main ->aux.
132 A1L EQU $3C ;Source data start addr.
133 A1H EQU $3D ;
134 A2L EQU $3E ;Source data end addr.
135 A2H EQU $3F ;
136 A4L EQU $42 ;Destination start addr.
137 A4H EQU $43 ;
138 FLAG5 EQU $8B5F
139 YRANGL EQU $8B60 ; -29857
140 YRANGH EQU $8B61 ; -29856
141 YSCALL EQU $8B62 ; -29855,-29854,-29853
142 YSCALM EQU $8B63 ;
143 YSCALH EQU $8B64 ;
144 PLCTL EQU $8B65 ;Plot count
145 PLCTH EQU $8B66 ;
146 FLAG8 EQU $8B67 ;1st cycle flag
147 FRAME EQU $8900 ;Frame plot routine
148 ;
149 ;
150 ;
151 ;
152 ;
8BA0: AD 00 8B 153 CVTAB LDA INITPL ;Get init. E
8BA3: 8D 02 8B 154 STA INITVL ;
8BA6: AD 01 8B 155 LDA INITPH ;
8BA9: 8D 03 8B 156 STA INITVH ;

```

8BAC:	A9 00	157		LDA	#\$0	;Store init. data addr.
8BAE:	85 EC	158		STA	DBADL	;\$4000
8BB0:	A9 40	159		LDA	#\$40	;
8BB2:	85 ED	160		STA	DBADH	;
8BB4:	A9 00	161	DIR	LDA	#\$00	;Decide scan direction
8BB6:	CD 0A 8B	162		CMP	DRCT	;0=cathod
8BB9:	FO 15	163		BEQ	JFETCL	;1=anodic scan
8BBB:	AD 21 8B	164		LDA	XRANGL	;Init. X-coord. value
8BBE:	8D 43 8B	165		STA	XHEL	;for anodic scan
8BC1:	8D 45 8B	166		STA	XHEL2	
8BC4:	AD 22 8B	167		LDA	XRANGH	;max. pulse no. is
8BC7:	8D 44 8B	168		STA	XHEH	;the init. value
8BCA:	8D 46 8B	169		STA	XHEH2	
8BCD:	4C E0 8B	170		JMP	OUT	;RTS
8BD0:	A9 00	171	JFETCL	LDA	#\$0	;for cathodic scan
8BD2:	8D 43 8B	172		STA	XHEL	;0 is the init. value
8BD5:	8D 45 8B	173		STA	XHEL2	
8BD8:	A9 00	174		LDA	#\$0	;i.e ->
8BDA:	8D 44 8B	175		STA	XHEH	
8BDD:	8D 46 8B	176		STA	XHEH2	
8BE0:	A9 8F	177	OUT	LDA	#\$8F	;Initilize DA
8BE2:	8D 02 C2	178		STA	BASE1+\$2	;
8BE5:	A9 FF	179		LDA	#\$FF	;
8BE7:	8D 03 C2	180		STA	BASE1+\$3	;
8BEA:	A9 E0	181		LDA	#\$E0	;
8BEC:	8D 0B C2	182		STA	BASE1+\$B	;
8BEF:	A9 8A	183		LDA	#\$8A	;
8BF1:	8D 0C C2	184		STA	BASE1+\$0C	;
8BF4:	AD 03 8B	185		LDA	INITVH	;and set init. E
8BF7:	8D 00 C2	186		STA	BASE1	
8BFA:	AD 02 8B	187		LDA	INITVL	
8BFD:	8D 01 C2	188		STA	BASE1+\$01	
8C00:	AD 21 8B	189		LDA	XRANGL	;Calculate the plot
8C03:	8D 2B 8B	190		STA	DIVL	;scale for X-axis
8C06:	AD 22 8B	191		LDA	XRANGH	;scale = 250/XRANG
8C09:	8D 2C 8B	192		STA	DIVM	
8C0C:	A9 00	193		LDA	#\$0	
8C0E:	8D 2D 8B	194		STA	DIVH	
8C11:	8D 2E 8B	195		STA	QUTNL	
8C14:	8D 2F 8B	196		STA	QUTNM	
8C17:	A9 FA	197		LDA	#\$FA	;#250,00,00
8C19:	8D 30 8B	198		STA	QUTNH	
8C1C:	20 80 92	199		JSR	DIV24	
8C1F:	AD 30 8B	200		LDA	QUTNH	
8C22:	8D 25 8B	201		STA	XSCALH	;Store x-scale
8C25:	AD 2F 8B	202		LDA	QUTNM	
8C28:	8D 24 8B	203		STA	XSCALM	
8C2B:	AD 2E 8B	204		LDA	QUTNL	
8C2E:	8D 23 8B	205		STA	XSCALL	
8C31:	A9 00	206		LDA	#\$0	;Clear flag and
8C33:	8D 17 8B	207		STA	PSCTL	;counter

8C36:	8D 18 8B	208	STA	PSCTH	;pulse counter
8C39:	8D 4D 8B	209	STA	DOUTL1	;Sampling data
8C3C:	8D 4E 8B	210	STA	DOUTH1	
8C3F:	38	211	SEC		
8C40:	AD 19 8B	212	LDA	TSL	;6 countes before
8C43:	E9 06	213	SBC	#\$6	;pulse up,
8C45:	8D 55 8B	214	STA	PRCTL	;start to procced
8C48:	AD 1A 8B	215	LDA	TSH	;data.
8C4B:	E9 00	216	SBC	#\$0	
8C4D:	8D 56 8B	217	STA	PRCTH	
8C50:	38	218	SEC		
8C51:	AD 19 8B	219	LDA	TSL	;4 counts before
8C54:	E9 04	220	SBC	#\$4	;pulse up,
8C56:	8D 65 8B	221	STA	PLCTL	;start to plot
8C59:	AD 1A 8B	222	LDA	TSH	;data
8C5C:	E9 00	223	SBC	#\$0	;
8C5E:	8D 66 8B	224	STA	PLCTH	;
8C61:	60	225	RTS		
		226			;
		227			;
		228			;
		229			;
		230			;
		231			;
8C62:	A9 8F	232	STARTAD	LDA	#\$8F
8C64:	8D 02 C2	233		STA	BASE1+\$2
8C67:	A9 FF	234		LDA	#\$FF
8C69:	8D 03 C2	235		STA	BASE1+\$3
8C6C:	A9 00	236		LDA	#\$0
8C6E:	8D 04 C2	237		STA	BASE1+\$4
8C71:	A9 02	238		LDA	#\$2
8C73:	8D 05 C2	239		STA	BASE1+\$5
8C76:	A9 E0	240		LDA	#\$E0
8C78:	8D 0B C2	241		STA	BASE1+\$B
8C7B:	A9 8A	242		LDA	#\$8A
8C7D:	8D 0C C2	243		STA	BASE1+\$C
8C80:	A9 00	244		LDA	#\$0
8C82:	85 0A	245		STA	STADL
8C84:	8D 06 8B	246		STA	TSTADL
8C87:	A9 40	247		LDA	#\$40
8C89:	85 0B	248		STA	STADH
8C8B:	8D 07 8B	249		STA	TSTADH
8C8E:	AD 0B 8B	250		LDA	FDBADL
8C91:	8D 08 8B	251		STA	LSADL
8C94:	AD 0C 8B	252		LDA	FDBADH
8C97:	8D 09 8B	253		STA	LSADH
8C9A:	AD 43 8B	254		LDA	XHEL
8C9D:	8D 45 8B	255		STA	XHEL2
8CA0:	AD 44 8B	256		LDA	XHEH
8CA3:	8D 46 8B	257		STA	XHEH2
8CA6:	AD 21 8B	258		LDA	XRANGL

;Set data start addr.
;for final plot

;Data final addr.
;for final plot

8CA9:	8D 26 8B	259		STA	XRANGL2	
8CAC:	AD 22 8B	260		LDA	XRANGH	
8CAF:	8D 27 8B	261		STA	XRANGH2	
8CB2:	AD 0A 8B	262		LDA	DRCT	;Give the 1st pulse
8CB5:	C9 00	263		CMP	#\$0	;anodic or cathodic
8CB7:	F0 18	264		BEQ	CDO	;scan
8CB9:	AD 02 8B	265		LDA	INITVL	;anodic scan
8CBC:	38	266		SEC		
8CBD:	ED 04 8B	267		SBC	PAL	
8CC0:	48	268		PHA		
8CC1:	AD 03 8B	269		LDA	INITVH	
8CC4:	ED 05 8B	270		SBC	PAH	
8CC7:	8D 00 C2	271		STA	BASE1	
8CCA:	68	272		PLA		
8CCB:	8D 01 C2	273		STA	BASE1+\$1	
8CCE:	4C E6 8C	274		JMP	CDOC	
8CD1:	AD 02 8B	275	CDO	LDA	INITVL	;cathodic scan
8CD4:	18	276		CLC		
8CD5:	6D 04 8B	277		ADC	PAL	
8CD8:	48	278		PHA		
8CD9:	AD 03 8B	279		LDA	INITVH	
8CDC:	6D 05 8B	280		ADC	PAH	
8CDF:	8D 00 C2	281		STA	BASE1	
8CE2:	68	282		PLA		
8CE3:	8D 01 C2	283		STA	BASE1+\$1	
8CE6:	AD 03 8B	284	CDOC	LDA	INITVH	;Store init. E for
8CE9:	8D 12 8B	285		STA	DAH	;DA output
8CEC:	8D 00 C2	286		STA	BASE1	
8CEF:	AD 02 8B	287		LDA	INITVL	
8CF2:	8D 11 8B	288		STA	DAL	
8CF5:	8D 01 C2	289		STA	BASE1+\$1	
8CF8:	A9 04	290		LDA	#\$4	;Set un-plot flag
8CFA:	8D 57 8B	291		STA	FLAG2	;for first 3 data
8CFD:	8D 4C 8B	292		STA	FLAG	;use for baseline
8D00:	A9 01	293		LDA	#\$1	;HPlot flag,
8D02:	8D 5C 8B	294		STA	FLAG3	;first plot point
8D05:	A9 00	295		LDA	#\$0	;Clear baseline
8D07:	8D 47 8B	296		STA	BIASL	
8D0A:	8D 48 8B	297		STA	BIASH	
8D0D:	8D 54 8B	298		STA	BIASH2	
8D10:	8D 53 8B	299		STA	BIASL2	
8D13:	8D 51 8B	300		STA	SCCT	;Sensitivity count
8D16:	8D 10 C0	301		STA	\$C010	;Clear key strobe
8D19:	8D 5F 8B	302		STA	FLAG5	
8D1C:	A9 8E	303		LDA	#>INTERS	
8D1E:	8D FE 03	304		STA	\$3FE	
8D21:	A9 AE	305		LDA	#<INTERS	
8D23:	8D FF 03	306		STA	\$3FF	
8D26:	A9 C0	307		LDA	#\$C0	;Set clock at
8D28:	8D 0E C2	308		STA	BASE1+\$E	;1 interrupt/1 ms
8D2B:	78	309		SEI		

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8D2C: A5 EC      310 CHECKEND LDA DBADL      ;Check data end
8D2E: 38         311 SEC                      ;
8D2F: ED 0B 8B   312 SBC FDBADL
8D32: A5 ED      313 LDA DBADH
8D34: ED 0C 8B   314 SBC FDBADH
8D37: B0 32      315 BCS END2              ;yes, RTS
8D39: AD 00 C0   316 LDA $C000            ;Any key pressed ?
8D3C: 10 2A      317 BPL CLINT2          ;no, then check interrupt
8D3E: A2 01      318 LDX #$1             ;yes, check which key
8D40: 8E 5C 8B   319 STX FLAG3          ;and set HPL0T flag
8D43: C9 88      320 CMP #$88              ;-> KEY
8D45: F0 47      321 BEQ UP              ;baseline up
8D47: C9 95      322 CMP #$95              ;<- KEY
8D49: F0 2C      323 BEQ DOWN            ;baseline down
8D4B: C9 AC      324 CMP #$AC              ;> KEY
8D4D: F0 77      325 BEQ FUP             ;baseline up fast
8D4F: C9 C4      326 CMP #$C4              ;< KEY
8D51: F0 5C      327 BEQ FDOWN          ;baseline down fast
8D53: C9 AE      328 CMP #$AE              ;D KEY
8D55: F0 17      329 BEQ DESC2           ;reduce 0.75
8D57: C9 C9      330 CMP #$C9              ;I KEY
8D59: F0 16      331 BEQ INSC2           ;enlarge 0.75
8D5B: C9 DA      332 CMP #$DA              ;Z KEY
8D5D: F0 15      333 BEQ ZBIAS2          ;back to orig. baseline
8D5F: C9 9B      334 CMP #$9B              ;ESC KEY
8D61: F0 08      335 BEQ END2              ;stop scan
8D63: A2 00      336 LDX #$0              ;no key pressed
8D65: 8E 5C 8B   337 STX FLAG3          ;reset plot to HLINE
8D68: 4C AE 8E   338 CLINT2 JMP INTERS      ;to inter. sev. routine
8D6B: 4C 0B 8E   339 END2 JMP END          ;RTS routine
8D6E: 4C E7 8D   340 DESC2 JMP DESC        ;low baseline
8D71: 4C F0 8D   341 INSC2 JMP INSC         ;
8D74: 4C F9 8D   342 ZBIAS2 JMP ZBIAS        ;
8D77: 18         343 DOWN CLC              ;
8D78: AD 47 8B   344 LDA BIASL
8D7B: 69 01      345 ADC #$1
8D7D: 8D 47 8B   346 STA BIASL
8D80: AD 48 8B   347 LDA BIASH
8D83: 69 00      348 ADC #$0
8D85: 8D 48 8B   349 STA BIASH
8D88: 8D 10 C0   350 STA $C010          ;Clear key strobe
8D8B: 4C AE 8E   351 JMP INTERS        ;Check interrupt
8D8E: 38         352 UP SEC              ;Increase baseline by 1
8D8F: AD 47 8B   353 LDA BIASL
8D92: E9 01      354 SBC #$1
8D94: 8D 47 8B   355 STA BIASL
8D97: AD 48 8B   356 LDA BIASH
8D9A: E9 00      357 SBC #$0
8D9C: 8D 48 8B   358 STA BIASH
8D9F: B0 08      359 BCS UPOUT          ;out of scale ?
8DA1: A9 00      360 LDA #$0            ;yes, set baseline

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8DA3:	8D 47 8B	361		STA	BIASL	;to zero
8DA6:	8D 48 8B	362		STA	BIASH	
8DA9:	8D 10 C0	363	UPOUT	STA	\$C010	;no, clear key strobe
8DAC:	4C AE 8E	364		JMP	INTERS	;check interrupt
8DAF:	18	365	FDOWN	CLC		;Dec. baseline by 10
8DB0:	AD 47 8B	366		LDA	BIASL	
8DB3:	69 0A	367		ADC	#\$A	
8DB5:	8D 47 8B	368		STA	BIASL	
8DB8:	AD 48 8B	369		LDA	BIASH	
8DBB:	69 00	370		ADC	#\$0	
8DBD:	8D 48 8B	371		STA	BIASH	
8DC0:	8D 10 C0	372		STA	\$C010	;Clear key strobe
8DC3:	4C AE 8E	373		JMP	INTERS	;Check interrupt
8DC6:	38	374	FUP	SEC		;Inc. baseline by 10
8DC7:	AD 47 8B	375		LDA	BIASL	
8DCA:	E9 0A	376		SBC	#\$A	
8DCC:	8D 47 8B	377		STA	BIASL	
8DCF:	AD 48 8B	378		LDA	BIASH	
8DD2:	E9 00	379		SBC	#\$0	
8DD4:	8D 48 8B	380		STA	BIASH	
8DD7:	B0 08	381		BCS	FUPOUT	;out of scale ?
8DD9:	A9 00	382		LDA	#\$0	;yes, set baseline to
8ddb:	8D 48 8B	383		STA	BIASH	;zero
8DDE:	8D 47 8B	384		STA	BIASL	
8DE1:	8D 10 C0	385	FUPOUT	STA	\$C010	;Clear key strobe
8DE4:	4C AE 8E	386		JMP	INTERS	;Interrupt ?
8DE7:	EE 51 8B	387	DESC	INC	SCCT	;Dec. sensitivity
8DEA:	8D 10 C0	388		STA	\$C010	;Clear key strobe
8DED:	4C AE 8E	389		JMP	INTERS	;Interrupt ?
8DF0:	CE 51 8B	390	INSC	DEC	SCCT	;Inc. sensitivity
8DF3:	8D 10 C0	391		STA	\$C010	;Clear key strobe
8DF6:	4C AE 8E	392		JMP	INTERS	;Interrupt ?
8DF9:	AD 53 8B	393	ZBIAS	LDA	BIASL2	;Restore init. baseline
8DFC:	8D 47 8B	394		STA	BIASL	
8DFF:	AD 54 8B	395		LDA	BIASH2	
8E02:	8D 48 8B	396		STA	BIASH	
8E05:	8D 10 C0	397		STA	\$C010	;Clear key strobe
8E08:	4C AE 8E	398		JMP	INTERS	;Interrupt ?
8EOB:	AD 03 8B	399	END	LDA	INITVH	;Restore parameters
8EOE:	8D 00 C2	400		STA	BASE1	;peak data and
8E11:	AD 02 8B	401		LDA	INITVL	;RTS
8E14:	8D 01 C2	402		STA	BASE1+\$1	
8E17:	A9 00	403		LDA	#\$0	
8E19:	8D 0E C2	404		STA	BASE1+\$E	
8E1C:	A9 65	405		LDA	#\$65	
8E1E:	8D FE 03	406		STA	\$3FE	
8E21:	A9 FF	407		LDA	#\$FF	
8E23:	8D FF 03	408		STA	\$3FF	
8E26:	8D 10 C0	409		STA	\$C010	
8E29:	A9 00	410		LDA	#\$0	
8E2B:	85 EC	411		STA	DBADL	

8E2D:	A9 40	412		LDA	#\$40	
8E2F:	85 ED	413		STA	DBADH	
8E31:	A9 01	414	SPEAK	LDA	#\$1	;Restore HLINE flage
8E33:	8D 5C 8B	415		STA	FLAG3	
8E36:	A2 00	416		LDX	#\$0	
8E38:	A9 00	417		LDA	#\$0	
8E3A:	8D 0D 8B	418		STA	YMAXL	
8E3D:	8D 0E 8B	419		STA	YMAXH	
8E40:	A9 FF	420		LDA	#\$FF	
8E42:	8D 0F 8B	421		STA	YMINL	
8E45:	8D 10 8B	422		STA	YMINH	
8E48:	A0 01	423	PEAK	LDY	#\$01	;Peak data
8E4A:	A1 0A	424		LDA	(STADL,X)	;get data
8E4C:	38	425		SEC		;> YMAX ?
8E4D:	ED 0D 8B	426		SBC	YMAXL	
8E50:	B1 0A	427		LDA	(STADL),Y	
8E52:	ED 0E 8B	428		SBC	YMAXH	
8E55:	B0 1C	429		BCS	MAX1	;yes. YMAX=data
8E57:	A1 0A	430	POUT	LDA	(STADL,X)	;
8E59:	38	431		SEC		;< YMIN ?
8E5A:	ED 0F 8B	432		SBC	YMINL	
8E5D:	B1 0A	433		LDA	(STADL),Y	
8E5F:	ED 10 8B	434		SBC	YMINH	
8E62:	90 12	435		BCC	MIN1	;yes. YMIN=data
8E64:	E6 0A	436	POUT1	INC	STADL	;Inc. data addr.
8E66:	D0 02	437		BNE	ADD2	
8E68:	E6 0B	438		INC	STADH	
8E6A:	E6 0A	439	ADD2	INC	STADL	
8E6C:	D0 0B	440		BNE	PEND	
8E6E:	E6 0B	441		INC	STADH	
8E70:	4C 79 8E	442		JMP	PEND	
8E73:	4C 94 8E	443	MAX1	JMP	MAX	
8E76:	4C A1 8E	444	MIN1	JMP	MIN	
8E79:	A4 0B	445	PEND	LDY	STADH	;Data end ?
8E7B:	CC 09 8B	446		CPY	LSADH	
8E7E:	D0 C8	447		BNE	PEAK	;no. loop peak
8E80:	A4 0A	448		LDY	STADL	
8E82:	CC 08 8B	449		CPY	LSADL	
8E85:	D0 C1	450		BNE	PEAK	;no. loop peak
8E87:	AD 06 8B	451		LDA	TSTADL	
8E8A:	85 0A	452		STA	STADL	
8E8C:	AD 07 8B	453		LDA	TSTADH	
8E8F:	85 0B	454		STA	STADH	
8E91:	4C 30 93	455		JMP	RELOT	;Rescale data and plot
8E94:	A1 0A	456	MAX	LDA	(STADL,X)	;Replace YMAX=data
8E96:	8D 0D 8B	457		STA	YMAXL	
8E99:	B1 0A	458		LDA	(STADL),Y	
8E9B:	8D 0E 8B	459		STA	YMAXH	
8E9E:	4C 57 8E	460		JMP	POUT	;Check min.
8EA1:	A1 0A	461	MIN	LDA	(STADL,X)	;Replace YMIN=data
8EA3:	8D 0F 8B	462		STA	YMINL	

8EA6:	B1 0A	463		LDA	(STADL),Y	
8EA8:	8D 10 8B	464		STA	YMINH	
8EAB:	4C 64 8E	465		JMP	POUT1	;Inc. data addr.
8EAE:	AD 0D C2	466	INTERS	LDA	BASE1+\$D	;Interrupt ?
8EB1:	29 40	467		AND	#\$40	
8EB3:	FO 5B	468		BEQ	EXIT	;no. exit
8EB5:	AD 04 C2	469		LDA	BASE1+\$4	;yes. clear inter. flag
8EB8:	EE 17 8B	470	GO1	INC	PSCTL	;Inc. pulse count
8EBB:	DO 03	471		BNE	MED3	
8EBD:	EE 18 8B	472		INC	PSCTH	
8ECO:	AD 17 8B	473	MED3	LDA	PSCTL	;Proc. data
8EC3:	CD 55 8B	474		CMP	PRCTL	;
8EC6:	DO 08	475		BNE	MEDPLT	;no.
8EC8:	AD 18 8B	476		LDA	PSCTH	;
8ECB:	CD 56 8B	477		CMP	PRCTH	;
8ECE:	FO 4C	478		BEQ	DPROC	;yes.
8ED0:	AD 17 8B	479	MEDPLT	LDA	PSCTL	;Plot data
8ED3:	CD 65 8B	480		CMP	PLCTL	;
8ED6:	DO 08	481		BNE	MED	;no.
8ED8:	AD 18 8B	482		LDA	PSCTH	;
8EDB:	CD 66 8B	483		CMP	PLCTH	;
8EDE:	FO 3F	484		BEQ	MPLDAT	;yes
8EE0:	AD 17 8B	485	MED	LDA	PSCTL	;generate pulse ?
8EE3:	CD 19 8B	486		CMP	TSL	
8EE6:	DO 08	487		BNE	PSTEP	;no.
8EE8:	AD 18 8B	488		LDA	PSCTH	
8EEB:	CD 1A 8B	489		CMP	TSH	
8EEE:	FO 23	490		BEQ	BGDSAM	;yes. generate it
8EF0:	AD 17 8B	491	PSTEP	LDA	PSCTL	;Stop pulse ?
8EF3:	CD 1D 8B	492		CMP	BKL	
8EF6:	DO 08	493		BNE	MED2	;no.
8EF8:	AD 18 8B	494		LDA	PSCTH	
8EFB:	CD 1E 8B	495		CMP	BKH	
8EFE:	FO 19	496		BEQ	PBK	;yes. pulse down
8F00:	AD 17 8B	497	MED2	LDA	PSCTL	;Sampling data ?
8F03:	CD 1B 8B	498		CMP	SAML	
8F06:	DO 08	499		BNE	EXIT	;no.
8F08:	AD 18 8B	500		LDA	PSCTH	
8F0B:	CD 1C 8B	501		CMP	SAMH	
8FOE:	FO 06	502		BEQ	SSAM	;yes. sample it
8F10:	4C 2C 8D	503	EXIT	JMP	CHECKEND	;End scan ?
		504	*			
		505	*			
		506	*			
8F13:	4C 22 8F	507	BGDSAM	JMP	BGSAM	
8F16:	4C 82 8F	508	SSAM	JMP	SAMS	
8F19:	4C 97 91	509	PBK	JMP	PBKS	
8F1C:	4C DB 8F	510	DPROC	JMP	SDPROC	
8F1F:	4C E1 91	511	MPLDAT	JMP	PLOT	
		512	*			
		513	*			

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514 *
515 *
516 *
517 *
518 *
519 *
520 *
521 *
522 *
523 *
524 *
8F22: AD 49 8B 525 BGSAM LDA CHGAIN ;Start background sample
8F25: 8D D0 CO 526 STA AD1 ;and generate pulse
8F28: 48 527 PHA
8F29: 68 528 PLA
8F2A: 48 529 PHA
8F2B: 68 530 PLA
8F2C: 48 531 PHA
8F2D: 68 532 PLA
8F2E: 48 533 PHA
8F2F: 68 534 PLA
8F30: 48 535 PHA
8F31: 68 536 PLA
8F32: AD D1 CO 537 LDA AD2
8F35: 29 0F 538 AND #$F
8F37: 8D 20 8B 539 STA BDH ;Save background
8F3A: 48 540 PHA
8F3B: 68 541 PLA
8F3C: 48 542 PHA
8F3D: 68 543 PLA
8F3E: AD D0 CO 544 LDA AD1
8F41: 8D 1F 8B 545 STA BDL
8F44: AD 0A 8B 546 LDA DRCT ;+ or - pulse
8F47: C9 01 547 CMP #$1
8F49: F0 16 548 BEQ ANODE
8F4B: 18 549 CATHOD CLC ;- pulse
8F4C: AD 11 8B 550 LDA DAL ;Get pulse hight
8F4F: 6D 04 8B 551 ADC PAL
8F52: 8D 11 8B 552 STA DAL
8F55: AD 12 8B 553 LDA DAH
8F58: 6D 05 8B 554 ADC PAH
8F5B: 8D 12 8B 555 STA DAH
8F5E: 4C 73 8F 556 JMP SHOUT
8F61: 38 557 ANODE SEC ;+ pulse
8F62: AD 11 8B 558 LDA DAL
8F65: ED 04 8B 559 SBC PAL
8F68: 8D 11 8B 560 STA DAL
8F6B: AD 12 8B 561 LDA DAH
8F6E: E9 00 562 SBC #$0
8F70: 8D 12 8B 563 STA DAH
8F73: AD 12 8B 564 SHOUT LDA DAH ;Output pulse

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8F76:	8D 00 C2	565		STA	BASE1	
8F79:	AD 11 8B	566		LDA	DAL	
8F7C:	8D 01 C2	567		STA	BASE1+\$1	
8F7F:	4C AE 8E	568		JMP	INTERS	;Interrupt ?
		569	*			
		570	*			
		571	*			
		572	*			
		573	*			
		574	*			
		575	*			
8F82:	AD 49 8B	576	SAMS	LDA	CHGAIN	;Sampling data
8F85:	8D D0 C0	577		STA	AD1	
8F88:	48	578		PHA		
8F89:	68	579		PLA		
8F8A:	48	580		PHA		
8F8B:	68	581		PLA		
8F8C:	48	582		PHA		
8F8D:	68	583		PLA		
8F8E:	48	584		PHA		
8F8F:	68	585		PLA		
8F90:	48	586		PHA		
8F91:	68	587		PLA		
8F92:	AD D1 C0	588		LDA	AD2	
8F95:	29 0F	589		AND	#\$F	
8F97:	8D 42 8B	590		STA	ADH	;Save data
8F9A:	48	591		PHA		
8F9B:	68	592		PLA		
8F9C:	48	593		PHA		
8F9D:	68	594		PLA		
8F9E:	AD D0 C0	595		LDA	AD1	
8FA1:	8D 41 8B	596		STA	ADL	
8FA4:	38	597		SEC		;Substract background
8FA5:	ED 1F 8B	598		SBC	BDL	
8FA8:	8D 13 8B	599		STA	DOUTL	
8FAB:	AD 42 8B	600		LDA	ADH	
8FAE:	ED 20 8B	601		SBC	BDH	
8FB1:	90 06	602		BCC	INVR	;Always take positive
8FB3:	8D 14 8B	603		STA	DOUTH	
8FB6:	4C CC 8F	604		JMP	EXIT11	
8FB9:	38	605	INVR	SEC		
8FBA:	AD 1F 8B	606		LDA	BDL	
8FBD:	ED 41 8B	607		SBC	ADL	
8FC0:	8D 13 8B	608		STA	DOUTL	
8FC3:	AD 20 8B	609		LDA	BDH	
8FC6:	ED 42 8B	610		SBC	ADH	
8FC9:	8D 14 8B	611		STA	DOUTH	
8FCC:	AD 13 8B	612	EXIT11	LDA	DOUTL	
8FCF:	8D 4D 8B	613		STA	DOUTL1	;Save it for averaging
8FD2:	AD 14 8B	614		LDA	DOUTH	
8FD5:	8D 4E 8B	615		STA	DOUTH1	

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8FD8: 4C AE 8E 616      JMP  INTERS      ;Interrupt ?
        617      *
        618      *
8FDB:  AD 4C 8B 619      SDPROC  LDA  FLAG      ;First 3 data ?
8FDE:  C9 00      620      CMP  #$0      ;no. treat, plot data
8FEO:  FO 15      621      BEQ  PCC4
8FE2:  AD 57 8B 622      LDA  FLAG2     ;First 3 data
8FE5:  C9 03      623      CMP  #$3      ;1st one ?
8FE7:  FO 11      624      BEQ  BPC3      ;yes.
8FE9:  C9 02      625      CMP  #$2      ;2nd one ?
8FEB:  FO 1F      626      BEQ  BPC2      ;yes
8FED:  C9 01      627      CMP  #$1      ;3rd one ?
8FEF:  FO 2D      628      BEQ  BPC1      ;yes.
8FF1:  CE 57 8B 629      DEC  FLAG2
8FF4:  4C AE 8E 630      JMP  INTERS
8FF7:  4C A9 90 631      PCC4    JMP  PCC
8FFA:  AD 4D 8B 632      BPC3    LDA  DOUTL1    ;Put 1st on to
8FFD:  8D 5A 8B 633      STA  DOUTL3    ;DOUT3
9000:  AD 4E 8B 634      LDA  DOUTH1
9003:  8D 5B 8B 635      STA  DOUTH3
9006:  CE 57 8B 636      DEC  FLAG2    ;Dec. flag2
9009:  4C AE 8E 637      JMP  INTERS    ;Interrupt ?
900C:  AD 4D 8B 638      BPC2    LDA  DOUTL1    ;Put 2nd one to
900F:  8D 58 8B 639      STA  DOUTL2    ;DOUT2
9012:  AD 4E 8B 640      LDA  DOUTH1
9015:  8D 59 8B 641      STA  DOUTH2
9018:  CE 57 8B 642      DEC  FLAG2    ;Dec. flag2
901B:  4C AE 8E 643      JMP  INTERS    ;Interrupt ?
901E:  AD 4D 8B 644      BPC1    LDA  DOUTL1    ;(3rd+2nd+1st)/3
9021:  18      645      CLC      ;= BIAS
9022:  6D 5A 8B 646      ADC  DOUTL3
9025:  8D 47 8B 647      STA  BIASL
9028:  AD 4E 8B 648      LDA  DOUTH1
902B:  6D 5B 8B 649      ADC  DOUTH3
902E:  4A      650      LSR  A      ;Divide by 2
902F:  8D 48 8B 651      STA  BIASH
9032:  6E 47 8B 652      ROR  BIASL
9035:  AD 47 8B 653      LDA  BIASL
9038:  18      654      CLC
9039:  6D 58 8B 655      ADC  DOUTL2
903C:  8D 47 8B 656      STA  BIASL
903F:  AD 48 8B 657      LDA  BIASH
9042:  6D 59 8B 658      ADC  DOUTH2
9045:  4A      659      LSR  A      ;Divide by 2
9046:  8D 48 8B 660      STA  BIASH
9049:  6E 47 8B 661      ROR  BIASL
904C:  A2 00      662      LDX  #$0
904E:  A0 01      663      LDY  #$1
9050:  AD 47 8B 664      LDA  BIASL
9053:  81 EC      665      STA  (DBADL,X)
9055:  AD 48 8B 666      LDA  BIASH

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9058:	91 EC	667	STA	(DBADL),Y	
905A:	18	668	CLC		
905B:	A5 EC	669	LDA	DBADL	
905D:	69 02	670	ADC	#\$2	
905F:	85 EC	671	STA	DBADL	
9061:	A5 ED	672	LDA	DBADH	
9063:	69 00	673	ADC	#\$0	
9065:	85 ED	674	STA	DBADH	
9067:	AD 47 8B	675	LDA	BIASL	
906A:	38	676	SEC		;Bias up #20
906B:	E9 14	677	SBC	#\$14	
906D:	8D 47 8B	678	STA	BIASL	
9070:	8D 53 8B	679	STA	BIASL2	
9073:	AD 48 8B	680	LDA	BIASH	
9076:	E9 00	681	SBC	#\$0	
9078:	8D 48 8B	682	STA	BIASH	
907B:	8D 54 8B	683	STA	BIASH2	
907E:	B0 0E	684	BCS	BIASOUT	
9080:	A9 00	685	LDA	#\$0	
9082:	8D 47 8B	686	STA	BIASL	
9085:	8D 48 8B	687	STA	BIASH	
9088:	8D 54 8B	688	STA	BIASH2	
908B:	8D 53 8B	689	STA	BIASL2	
908E:	AD 58 8B	690	BIASOUT LDA	DOUTL2	;Replace 2->3
9091:	8D 5A 8B	691	STA	DOUTL3	;
9094:	AD 59 8B	692	LDA	DOUTH2	;
9097:	8D 5B 8B	693	STA	DOUTH3	
909A:	AD 4D 8B	694	LDA	DOUTL1	;and 1->2
909D:	8D 58 8B	695	STA	DOUTL2	
90A0:	AD 4E 8B	696	LDA	DOUTH1	
90A3:	8D 59 8B	697	STA	DOUTH2	
90A6:	4C AE 8E	698	JMP	INTERS	
90A9:	AD 4D 8B	699	PCC ' LDA	DOUTL1	;data (1+2*2+3)/3
90AC:	18	700	CLC		
90AD:	6D 5A 8B	701	ADC	DOUTL3	
90B0:	8D 4F 8B	702	STA	DOUTL5	
90B3:	AD 4E 8B	703	LDA	DOUTH1	
90B6:	6D 5B 8B	704	ADC	DOUTH3	
90B9:	4A	705	LSR	A	;Divide by 2
90BA:	8D 50 8B	706	STA	DOUTH5	
90BD:	6E 4F 8B	707	ROR	DOUTL5	
90C0:	AD 4F 8B	708	LDA	DOUTL5	
90C3:	18	709	CLC		
90C4:	6D 58 8B	710	ADC	DOUTL2	
90C7:	8D 4F 8B	711	STA	DOUTL5	
90CA:	AD 50 8B	712	LDA	DOUTH5	
90CD:	6D 59 8B	713	ADC	DOUTH2	
90D0:	4A	714	LSR	A	;Divide by 2
90D1:	8D 50 8B	715	STA	DOUTH5	
90D4:	6E 4F 8B	716	ROR	DOUTL5	
90D7:	AD 58 8B	717	LDA	DOUTL2	

90DA:	8D 5A 8B	718	STA	DOUTL3	
90DD:	AD 59 8B	719	LDA	DOUTH2	
90EO:	8D 5B 8B	720	STA	DOUTH3	
90E3:	AD 4D 8B	721	LDA	DOUTL1	
90E6:	8D 58 8B	722	STA	DOUTL2	
90E9:	AD 4E 8B	723	LDA	DOUTH1	
90EC:	8D 59 8B	724	STA	DOUTH2	
90EF:	A2 00	725	LDX	#\$0	
90F1:	A0 01	726	LDY	#\$1	
90F3:	AD 4F 8B	727	LDA	DOUTL5	
90F6:	81 EC	728	STA	(DBADL,X)	
90F8:	AD 50 8B	729	LDA	DOUTH5	
90FB:	91 EC	730	STA	(DBADL),Y	
90FD:	18	731	CLC		
90FE:	A5 EC	732	LDA	DBADL	
9100:	69 02	733	ADC	#\$2	
9102:	85 EC	734	STA	DBADL	
9104:	A5 ED	735	LDA	DBADH	
9106:	69 00	736	ADC	#\$0	
9108:	85 ED	737	STA	DBADH	
910A:	AD 4F 8B	738	LDA	DOUTL5	
910D:	38	739	SEC		
910E:	ED 47 8B	740	SBC	BIASL	
9111:	8D 31 8B	741	STA	TAD1	
9114:	AD 50 8B	742	LDA	DOUTH5	
9117:	ED 48 8B	743	SBC	BIASH	
911A:	90 0C	744	BCC	REV11	
911C:	8D 50 8B	745	STA	DOUTH5	
911F:	AD 31 8B	746	LDA	TAD1	
9122:	8D 4F 8B	747	STA	DOUTL5	
9125:	4C 3B 91	748	JMP	PCC1	
9128:	AD 47 8B	749	LDA	BIASL	
912B:	38	750	SEC		
912C:	ED 4F 8B	751	SBC	DOUTL5	
912F:	8D 4F 8B	752	STA	DOUTL5	
9132:	AD 48 8B	753	LDA	BIASH	
9135:	ED 50 8B	754	SBC	DOUTH5	
9138:	8D 50 8B	755	STA	DOUTH5	
913B:	AE 51 8B	756	LDX	SCCT	;lower data
913E:	EO 00	757	CPX	#\$0	
9140:	FO 07	758	BEQ	HSCALE	;no.
9142:	20 67 91	759	JSR	PARTDIV	;yes. data*3/4
9145:	CA	760	DEX		
9146:	4C 3E 91	761	JMP	LOOP3	;Loop to data in scale
9149:	38	762	SEC		
914A:	AD 4F 8B	763	LDA	DOUTL5	
914D:	E9 A0	764	SBC	#\$A0	;If data > 160
914F:	AD 50 8B	765	LDA	DOUTH5	
9152:	E9 00	766	SBC	#\$0	
9154:	90 0E	767	BCC	REXIT	
9156:	EE 51 8B	768	INC	SCCT	


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9159: 20 67 91 769      JSR  PARTDIV
915C: A9 01 770      LDA  #$1
915E: 8D 5C 8B 771      STA  FLAG3
9161: 4C 49 91 772      JMP  HSCALE
9164: 4C AE 8E 773  REXIT JMP  INTERS
774
775
776
9167: 8A 777  PARTDIV TXA
9168: 48 778      PHA
9169: 4E 50 8B 779      LSR  DOUTH5      ;Data * 3/4
916C: 6E 4F 8B 780      ROR  DOUTL5      ;Divide by 2
916F: AD 4F 8B 781      LDA  DOUTL5
9172: 8D 31 8B 782      STA  TAD1
9175: AD 50 8B 783      LDA  DOUTH5
9178: 8D 32 8B 784      STA  TAD2
917B: 4E 50 8B 785      LSR  DOUTH5      ;Divide by 2 again
917E: 6E 4F 8B 786      ROR  DOUTL5      ;to get data/4
9181: AD 4F 8B 787      LDA  DOUTL5
9184: 18 788      CLC      ;Data/2+data/4=data*3/4
9185: 6D 31 8B 789      ADC  TAD1
9188: 8D 4F 8B 790      STA  DOUTL5
918B: AD 50 8B 791      LDA  DOUTH5
918E: 6D 32 8B 792      ADC  TAD2
9191: 8D 50 8B 793      STA  DOUTH5
9194: 68 794      PLA
9195: AA 795      TAX
9196: 60 796      RTS
797  *
798  *
9197: AD 0A 8B 799  PBKS  LDA  DRCT      ;Pulse down
919A: C9 01 800      CMP  #$1      ;direction
919C: FO 16 801      BEQ  ANODE2
919E: 38 802  CATHOD2 SEC      ;Cathodic scan
919F: AD 11 8B 803      LDA  DAL      ;dec. DA value
91A2: ED 15 8B 804      SBC  PLL
91A5: 8D 11 8B 805      STA  DAL
91A8: AD 12 8B 806      LDA  DAH
91AB: ED 16 8B 807      SBC  PLH
91AE: 8D 12 8B 808      STA  DAH
91B1: 4C C7 91 809      JMP  SHOUT2
91B4: 18 810  ANODE2 CLC      ;Anodic scan
91B5: AD 11 8B 811      LDA  DAL      ;inc. DA value
91B8: 6D 15 8B 812      ADC  PLL
91BB: 8D 11 8B 813      STA  DAL
91BE: AD 12 8B 814      LDA  DAH
91C1: 6D 16 8B 815      ADC  PLH
91C4: 8D 12 8B 816      STA  DAH
91C7: AD 12 8B 817  SHOUT2 LDA  DAH
91CA: 8D 00 C2 818      STA  BASE1
91CD: AD 11 8B 819      LDA  DAL

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91D0: 8D 01 C2 820 STA BASE1+$1
91D3: A9 00 821 LDA #$0 ;Reset pulse count
91D5: 8D 17 8B 822 STA PSCTL
91D8: 8D 18 8B 823 STA PSCTH
91DB: 8D 5F 8B 824 STA FLAG5 ;and flag5 count
91DE: 4C AE 8E 825 JMP INTERS
      826 *
      827 *
      828 *
      829 *
      830 *
      831 *
91E1: AD 0A 8B 832 PLOT LDA DRCT ;Start to plot data
91E4: C9 00 833 CMP #$0 ;X-direction
91E6: D0 0B 834 BNE MED20 ;Dec. x-direction
91E8: EE 43 8B 835 INC XHEL ;Inc. x-direction
91EB: D0 27 836 BNE MED21
91ED: EE 44 8B 837 INC XHEH
91F0: 4C 14 92 838 JMP MED21
91F3: AD 43 8B 839 MED20 LDA XHEL ;Dec. x-value
91F6: 38 840 SEC
91F7: E9 01 841 SBC #$1
91F9: 8D 43 8B 842 STA XHEL
91FC: AD 44 8B 843 LDA XHEH
91FF: E9 00 844 SBC #$0
9201: 90 06 845 BCC GO41 ;Dont less than 0
9203: 8D 44 8B 846 STA XHEH
9206: 4C 14 92 847 JMP MED21
9209: A9 00 848 GO41 LDA #$0 ;if less than 0
920B: 8D 43 8B 849 STA XHEL ;set it to 0
920E: 8D 44 8B 850 STA XHEH
9211: 8D 44 8B 851 STA XHEH
9214: AD 4C 8B 852 MED21 LDA FLAG ;First 3 points
9217: C9 00 853 CMP #$0 ;no plot
9219: F0 06 854 BEQ XPLOT
921B: CE 4C 8B 855 DEC FLAG
921E: 4C 75 92 856 JMP FORD
9221: AD 43 8B 857 XPLOT LDA XHEL ;Get x value
9224: 8D 31 8B 858 STA TAD1 ;and time plot scale
9227: AD 44 8B 859 LDA XHEH
922A: 8D 32 8B 860 STA TAD2
922D: AD 23 8B 861 LDA XSCALL
9230: 8D 3E 8B 862 STA MULTL
9233: AD 24 8B 863 LDA XSCALM
9236: 8D 3F 8B 864 STA MULTM
9239: AD 25 8B 865 LDA XSCALH
923C: 8D 40 8B 866 STA MULTH
923F: 20 D0 92 867 JSR MLT24
9242: AD 38 8B 868 LDA PLDT3
9245: 18 869 CLC
9246: 69 0A 870 ADC #$A ;Plot x 10->260

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9248: 48      871      PHA      ;Save in stack
9249: A9 00    872      LDA      #$0
924B: 69 00    873      ADC      #$0
924D: 48      874      PHA      ;Save in stack
924E: AD 5C 8B 875      LDA      FLAG3 ;HPLOT or HLINE ?
9251: C9 00    876      CMP      #$0
9253: F0 13    877      BEQ      HLINE
9255: CE 5C 8B 878      DEC      FLAG3
9258: 68      879      PLA      ;Pull H.B from stack
9259: A8      880      TAY      ;Put into Y-REG.
925A: 68      881      PLA      ;Pull L.B from stack
925B: AA      882      TAX      ;Put into X-REG.
925C: A9 A0    883      LDA      #$A0 ;Inv. Y
925E: 38      884      SEC
925F: ED 4F 8B 885      SBC      DOUTL5
9262: 20 57 F4 886      JSR      HPLOT
9265: 4C 75 92 887      JMP      FORD
9268: A9 A0    888      LDA      #$A0 ;Inv. Y
926A: 38      889      SEC
926B: ED 4F 8B 890      SBC      DOUTL5
926E: A8      891      TAY      ;Put y to Y-REG.
926F: 68      892      PLA      ;Pull H.B from stack
9270: AA      893      TAX      ;put into X-REG.
9271: 68      894      PLA      ;Pull L.B from stack
9272: 20 3A F5 895      JSR      LPLOT ;HLINE plot
9275: A9 00    896      LDA      #$0
9277: 8D 4D 8B 897      STA      DOUTL1 ;Clear data
927A: 8D 4E 8B 898      STA      DOUTH1
927D: 4C 2C 8D 899      JMP      CHECKEND ;Data end ?
900
901
902
903
904
905      ; TRIPLE PRECISION DIVISION FOR SCALING X AND Y
906
907
908
9280: A9 00    909      DIV24    LDA      #$00 ;Clear remainder
9282: 8D 33 8B 910      STA      REML
9285: 8D 34 8B 911      STA      REMM
9288: 8D 35 8B 912      STA      REMH
928B: A2 18    913      LDX      #$18 ;24 dividend bit count
928D: 0E 2E 8B 914      NXTBT    ASL      QUTNL ;dividend/Quot. left
9290: 2E 2F 8B 915      ROL      QUTNM
9293: 2E 30 8B 916      ROL      QUTNH
9296: 2E 33 8B 917      ROL      REML ;partial dividend left
9299: 2E 34 8B 918      ROL      REMM
929C: 2E 35 8B 919      ROL      REMH
929F: AD 33 8B 920      LDA      REML ;Subtract low bytes
92A2: 38      921      SEC

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92A3:	ED	2B	8B	922		SBC	DIVL	
92A6:	8D	31	8B	923		STA	TAD1	;Save low bytes
92A9:	AD	34	8B	924		LDA	REMM	;Subtra. next high byte
92AC:	ED	2C	8B	925		SBC	DIVM	;
92AF:	8D	32	8B	926		STA	TAD2	;Save it
92B2:	AD	35	8B	927		LDA	REMH	;Subtra. most high byte
92B5:	ED	2D	8B	928		SBC	DIVH	
92B8:	90	12		929		BCC	CNTDN	;Divisor > Dividend ?
92BA:	EE	2E	8B	930		INC	QUTNL	;no. set bit in Quot.
92BD:	8D	35	8B	931		STA	REMH	;return subtraction
92C0:	AD	32	8B	932		LDA	TAD2	;as the new remainder
92C3:	8D	34	8B	933		STA	REMM	
92C6:	AD	31	8B	934		LDA	TAD1	
92C9:	8D	33	8B	935		STA	REML	
92CC:	CA			936	CNTDN	DEX		;Dec. bit count
92CD:	DO	BE		937		BNE	NXTBT	;loop until 24 bits done
92CF:	60			938		RTS		
				939				;
				940				;
				941				;
				942				;
				943				;
				944				;
				945				;
				946				;
				947				;
				948				;
				949				;
				950				;
92D0:	A9	00		950	MLT24	LDA	#\$00	;Clear product
92D2:	8D	36	8B	951		STA	PLDT1	
92D5:	8D	37	8B	952		STA	PLDT2	
92D8:	8D	38	8B	953		STA	PLDT3	
92DB:	8D	39	8B	954		STA	PLDT4	
92DE:	8D	3A	8B	955		STA	PLDT5	
92E1:	A2	0C		956		LDX	#\$C	;Multiplier count = 12
92E3:	4E	32	8B	957	NEXMBT	LSR	TAD2	;Shift multiplier right
92E6:	6E	31	8B	958		ROR	TAD1	
92E9:	90	19		959		BCC	ALIGN	;Multiplier = 1 ?
92EB:	AD	38	8B	960		LDA	PLDT3	;yes. fetch new PLDT
92EE:	18			961		CLC		
92EF:	6D	3E	8B	962		ADC	MULTL	
92F2:	8D	38	8B	963		STA	PLDT3	
92F5:	AD	39	8B	964		LDA	PLDT4	
92F8:	6D	3F	8B	965		ADC	MULTM	
92FB:	8D	39	8B	966		STA	PLDT4	
92FE:	AD	3A	8B	967		LDA	PLDT5	
9301:	6D	40	8B	968		ADC	MULTH	
9304:	6A			969	ALIGN	ROR	A	;Rot 5-bytes PLDT right
9305:	8D	3A	8B	970		STA	PLDT5	
9308:	6E	39	8B	971		ROR	PLDT4	
930B:	6E	38	8B	972		ROR	PLDT3	

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930E: 6E 37 8B 973      ROR  PLDT2
9311: 6E 36 8B 974      ROR  PLDT1
9314: CA 975            DEX          ;Dec. bit count
9315: DO CC 976          BNE  NEXMBT   ;Loop until 12 bit done
9317: 4E 39 8B 977      LSR  PLDT4   ;another 4 bits to go
931A: 6E 38 8B 978      ROR  PLDT3   ;Total bit = 16 bits
931D: 4E 39 8B 979      LSR  PLDT4   ;this way to save time
9320: 6E 38 8B 980      ROR  PLDT3
9323: 4E 39 8B 981      LSR  PLDT4
9326: 6E 38 8B 982      ROR  PLDT3
9329: 4E 39 8B 983      LSR  PLDT4
932C: 6E 38 8B 984      ROR  PLDT3
932F: 60 985            RTS
986 *
987 *
988 *
989 *
990 *
991 *
9330: AD 0D 8B 992  REPLOTLDA  YMAXL   ;Get y-axis full range
9333: 38 993            SEC
9334: ED 0F 8B 994      SBC  YMINL   ;
9337: 8D 60 8B 995      STA  YRANGL   ;
933A: 8D 2B 8B 996      STA  DIVL    ;
933D: AD 0E 8B 997      LDA  YMAXH   ;
9340: ED 10 8B 998      SBC  YMINH   ;
9343: 8D 61 8B 999      STA  YRANGH   ;
9346: 8D 2C 8B 1000     STA  DIVM    ;
9349: A9 00 1001        LDA  #$0
934B: 8D 2D 8B 1002     STA  DIVH    ;
934E: A9 A0 1003        LDA  #$A0    ;0-160 on the HGR y-axis
9350: 8D 30 8B 1004     STA  QUTNH   ;
9353: A9 00 1005        LDA  #$0
9355: 8D 2F 8B 1006     STA  QUTNM   ;
9358: 8D 2E 8B 1007     STA  QUTNL   ;
935B: 20 80 92 1008     JSR  DIV24   ;Get (160/YRANG)
935E: AD 30 8B 1009     LDA  QUTNH   ;
9361: 8D 64 8B 1010     STA  YSCALH   ;
9364: AD 2F 8B 1011     LDA  QUTNM   ;
9367: 8D 63 8B 1012     STA  YSCALM   ;
936A: AD 2E 8B 1013     LDA  QUTNL   ;
936D: 8D 62 8B 1014     STA  YSCALL   ;
9370: AD 26 8B 1015     LDA  XRANGL2  ;Get X-RANGE
9373: 8D 2B 8B 1016     STA  DIVL    ;
9376: AD 27 8B 1017     LDA  XRANGH2  ;
9379: 8D 2C 8B 1018     STA  DIVM    ;
937C: A9 00 1019        LDA  #$0
937E: 8D 2D 8B 1020     STA  DIVH    ;
9381: 8D 2E 8B 1021     STA  QUTNL   ;
9384: 8D 2F 8B 1022     STA  QUTNM   ;
9387: A9 FA 1023        LDA  #$FA    ;

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9389:	8D 30 8B	1024	STA	QUTNH	;
938C:	20 80 92	1025	JSR	DIV24	;Get (250/XRANGE)
938F:	AD 30 8B	1026	LDA	QUTNH	;
9392:	8D 2A 8B	1027	STA	XSCALH2	;
9395:	AD 2F 8B	1028	LDA	QUTNM	;
9398:	8D 29 8B	1029	STA	XSCALM2	;
939B:	AD 2E 8B	1030	LDA	QUTNL	;
939E:	8D 28 8B	1031	STA	XSCALL2	;
93A1:	A2 03	1032	LDX	#\$3	;Set color=white
93A3:	20 F0 F6	1033	JSR	SETCOL	;
93A6:	A9 20	1034	LDA	#\$20	;Set HGR page 1
93A8:	85 E6	1035	STA	HPAGE	;
93AA:	8D 57 C0	1036	STA	HGR	;Turn on HGR mode
93AD:	8D 52 C0	1037	STA	FULSCR	;Set fullscreen
93B0:	20 F2 F3	1038	JSR	HCLR	;Clear screen
93B3:	8D 50 C0	1039	STA	GR	;Turn off text mode
93B6:	20 00 89	1040	JSR	FRAME	;Draw frame
93B9:	A0 01	1041 NEXPL	LDY	#\$1	;
93BB:	A2 00	1042	LDX	#\$0	;
93BD:	A1 0A	1043	LDA	(STADL,X)	;
93BF:	38	1044	SEC		;
93C0:	ED 0F 8B	1045	SBC	YMINL	;Subtract bias
93C3:	8D 31 8B	1046	STA	TAD1	;Save it for mult.
93C6:	B1 0A	1047	LDA	(STADL),Y	;
93C8:	ED 10 8B	1048	SBC	YMINH	;
93CB:	8D 32 8B	1049	STA	TAD2	;
93CE:	AD 62 8B	1050	LDA	YSCALL	;
93D1:	8D 3E 8B	1051	STA	MULTL	;
93D4:	AD 63 8B	1052	LDA	YSCALM	;
93D7:	8D 3F 8B	1053	STA	MULTM	;
93DA:	AD 64 8B	1054	LDA	YSCALH	;
93DD:	8D 40 8B	1055	STA	MULTH	;
93E0:	20 D0 92	1056	JSR	MLT24	;
93E3:	A9 A0	1057	LDA	#\$A0	;
93E5:	38	1058	SEC		;Inv. y-axis
93E6:	ED 38 8B	1059	SBC	PLDT3	;
93E9:	8D 3D 8B	1060	STA	YPLDT	;
93EC:	AD 0A 8B	1061	LDA	DRCT	;
93EF:	C9 00	1062	CMP	#\$0	;
93F1:	F0 14	1063	BEQ	CAPLOT	;Cathodic scan
93F3:	AD 45 8B	1064	LDA	XHEL2	;Anodic scan <-
93F6:	38	1065	SEC		;
93F7:	E9 01	1066	SBC	#\$1	;
93F9:	8D 45 8B	1067	STA	XHEL2	;
93FC:	AD 46 8B	1068	LDA	XHEH2	;
93FF:	E9 00	1069	SBC	#\$0	;
9401:	8D 46 8B	1070	STA	XHEH2	;
9404:	4C 0F 94	1071	JMP	RXSCAL	;
9407:	EE 45 8B	1072 CAPLOT	INC	XHEL2	;
940A:	D0 03	1073	BNE	RXSCAL	;
940C:	EE 46 8B	1074	INC	XHEH2	;

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940F: AD 45 8B 1075 RXSCAL LDA XHEL2 ;
9412: 8D 31 8B 1076 STA TAD1 ;
9415: AD 46 8B 1077 LDA XHEH2 ;
9418: 8D 32 8B 1078 STA TAD2 ;
941B: AD 28 8B 1079 LDA XSCALL2 ;
941E: 8D 3E 8B 1080 STA MULTL ;
9421: AD 29 8B 1081 LDA XSCALM2 ;
9424: 8D 3F 8B 1082 STA MULTM ;
9427: AD 2A 8B 1083 LDA XSCALH2 ;
942A: 8D 40 8B 1084 STA MULTH ;
942D: 20 D0 92 1085 JSR MLT24 ;
9430: AD 38 8B 1086 LDA PLDT3 ;
9433: 18 1087 CLC ;
9434: 69 0A 1088 ADC #$A ;
9436: 8D 3B 8B 1089 STA XPLDTL ;
9439: A9 00 1090 LDA #$0
943B: 69 00 1091 ADC #$0
943D: 8D 3C 8B 1092 STA XPLDTH ;
9440: AD 5C 8B 1093 LDA FLAG3 ;HPlot or HLINE ?
9443: C9 00 1094 CMP #$0 ;
9445: F0 12 1095 BEQ RHLINE ;HLINE
9447: AE 3B 8B 1096 RHPlot LDX XPLDTL ;X-plot value in X,Y-REG
944A: AC 3C 8B 1097 LDY XPLDTH ;
944D: AD 3D 8B 1098 LDA YPLDT ;Y-plot value in A-REG.
9450: 20 57 F4 1099 JSR HPlot ;
9453: CE 5C 8B 1100 DEC FLAG3 ;
9456: 4C 65 94 1101 JMP REND ;Data end ?
9459: AC 3D 8B 1102 RHLINE LDY YPLDT ;Y-plot value in Y-REG
945C: AD 3B 8B 1103 LDA XPLDTL ;X-plot value in A,X-REG
945F: AE 3C 8B 1104 LDX XPLDTH ;
9462: 20 3A F5 1105 JSR LPlot ;
9465: E6 0A 1106 REND INC STADL ;
9467: D0 02 1107 BNE RNEXINC ;
9469: E6 0B 1108 INC STADH ;
946B: E6 0A 1109 RNEXINC INC STADL ;
946D: D0 02 1110 BNE RCHECK ;Check data end ?
946F: E6 0B 1111 INC STADH ;
9471: A5 0A 1112 RCHECK LDA STADL ;
9473: 38 1113 SEC ;
9474: ED 08 8B 1114 SBC LSADL ;
9477: A5 0B 1115 LDA STADH ;
9479: ED 09 8B 1116 SBC LSADH ;
947C: 90 06 1117 BCC JNEXPL ;
947E: A9 01 1118 LDA #$1
9480: 8D 5C 8B 1119 STA FLAG3
9483: 60 1120 RTS
9484: 4C B9 93 1121 JNEXPL JMP NEXPL
9487: A9 00 1122 TOAUX LDA #$0
9489: 85 3C 1123 STA A1L
948B: A9 20 1124 LDA #$20
948D: 85 3D 1125 STA A1H

```

948F:	A9 00	1126	LDA	#\$0	
9491:	85 3E	1127	STA	A2L	
9493:	85 42	1128	STA	A4L	
9495:	A9 40	1129	LDA	#\$40	
9497:	85 3F	1130	STA	A2H	
9499:	85 43	1131	STA	A4H	
949B:	38	1132	SEC		
949C:	20 11 C3	1133	JSR	AUXMOVE	;Move HGR pg.1 to AUX
949F:	60	1134	RTS		
94A0:	A9 00	1135	LDA	#\$0	TOMAIN
94A2:	85 42	1136	STA	A4L	
94A4:	A9 20	1137	LDA	#\$20	
94A6:	85 43	1138	STA	A4H	
94A8:	A9 00	1139	LDA	#\$0	
94AA:	85 3E	1140	STA	A2L	
94AC:	85 3C	1141	STA	A1L	
94AE:	A9 60	1142	LDA	#\$60	
94B0:	85 3F	1143	STA	A2H	
94B2:	A9 40	1144	LDA	#\$40	
94B4:	85 3D	1145	STA	A1H	
94B6:	18	1146	CLC		
94B7:	20 11 C3	1147	JSR	AUXMOVE	;Move HGR pg.1 to main
94BA:	60	1148	RTS		

—End assembly, 2331 bytes, Errors: 0

Program 3

Program, COUL, used to supervise double step chronocoulometric experiments, process data, and display "Anson plot".

```

*****
*                                     *
*      File: COUL                     *
*                                     *
*      Written by Ing-Feng Hu         *
*                                     *
*****

```

This program supervises double potential
step chronocoulometric experiments and
displays "Anson Plot"

```

1          ORG  $9050
2          OBJ  $9050
3
4          ;
5          ;
6          ;
7          ;
8          ;
9          ;
10         ;
11  INITPL  EQU  $9042
12  INITPH  EQU  $9043
13  INITVL  EQU  $9000
14  INITVH  EQU  $9001
15  SWPL    EQU  $9040
16  SWPH    EQU  $9041
17  STADL   EQU  $A
18  STADH   EQU  $B
19  TSTADL  EQU  $900A
20  TSTADH  EQU  $900B
21  LSADL   EQU  $9045
22  LSADH   EQU  $9046
23  MSADL   EQU  $9047
24  MSADH   EQU  $9048
25  DIR     EQU  $9049
26  XMINL   EQU  $9016
27  XMINH   EQU  $9017
28  XMAXL   EQU  $9014
29  XMAXH   EQU  $9015
30  YMINL   EQU  $9012
31  YMINH   EQU  $9013
32  YMAXL   EQU  $9010
33  YMAXH   EQU  $9011
34  DBADL   EQU  $EC
35  DBADH   EQU  $ED

```

36	TDBADL	EQU	\$900C
37	TDBADH	EQU	\$900D
38	FDBADL	EQU	\$900E
39	FDBADH	EQU	\$900F
40	YRANGL	EQU	\$9018
41	YRANGH	EQU	\$9019
42	XRANGL	EQU	\$901A
43	XRANGH	EQU	\$901B
44	XSCALL	EQU	\$901C
45	XSCALM	EQU	\$901D
46	XSCALH	EQU	\$901E
47	YSCALL	EQU	\$9020
48	YSCALM	EQU	\$9021
49	YSCALH	EQU	\$9022
50	DIVL	EQU	\$9023
51	DIVM	EQU	\$9024
52	DIVH	EQU	\$9025
53	QUTNL	EQU	\$9026
54	QUTNM	EQU	\$9027
55	QUTNH	EQU	\$9028
56	TAD1	EQU	\$9029
57	TAD2	EQU	\$902A
58	REML	EQU	\$902B
59	REMM	EQU	\$902C
60	REMH	EQU	\$902D
61	TEXT	EQU	\$FB2F
62	HOME	EQU	\$FB60
63	STROBE	EQU	\$C010
64	GR	EQU	\$C050
65	HGR	EQU	\$C057
66	HGR1	EQU	\$C054
67	HPAGE	EQU	\$E6
68	HPLOT	EQU	\$F457
69	SETCOL	EQU	\$F6F0
70	HCLR	EQU	\$F3F2
71	FULSCR	EQU	\$C052
72	PLDT1	EQU	\$902E
73	PLDT2	EQU	\$902F
74	PLDT3	EQU	\$9030
75	PLDT4	EQU	\$9031
76	PLDT5	EQU	\$9032
77	XPLDTL	EQU	\$9033
78	XPLDTH	EQU	\$9034
79	YPLDT	EQU	\$9035
80	MULTL	EQU	\$9036
81	MULTM	EQU	\$9037
82	MULTH	EQU	\$9038
83	XLEL	EQU	\$9039
84	XLEH	EQU	\$903A
85	XHEL	EQU	\$903B
86	XHEH	EQU	\$903C

```

      87  BASE1    EQU  $C200
      88  FREQL   EQU  $903D
      89  FREQH   EQU  $903E
      90  CHGAIN  EQU  $903F
      91  AD1     EQU  $CODO
      92  AD2     EQU  $COD1
      93
      94
      95
      96
      97
      98
9050: AD 42 90 99  INITSET  LDA  INITPL
9053: 8D 00 90 100         STA  INITVL
9056: AD 43 90 101         LDA  INITPH
9059: 8D 01 90 102         STA  INITVH
905C: A9 00          103         LDA  #$0
905E: 8D 39 90 104         STA  XLEL
9061: 8D 3A 90 105         STA  XLEH
9064: A9 00          106         LDA  #$00
9066: 85 0A          107         STA  STADL
9068: 8D 0A 90 108         STA  TSTADL
906B: A9 40          109         LDA  #$40
906D: 85 0B          110         STA  STADH
906F: 8D 0B 90 111         STA  TSTADH
9072: A9 42          112         LDA  #$42
9074: 8D 45 90 113         STA  LSADL
9077: A9 5F          114         LDA  #$5F
9079: 8D 46 90 115         STA  LSADH
907C: A9 A2          116         LDA  #$A2
907E: 8D 47 90 117         STA  MSADL
9081: A9 4F          118         LDA  #$4F
9083: 8D 48 90 119         STA  MSADH
9086: A9 00          120         LDA  #$0
9088: 8D 49 90 121         STA  DIR
908B: A9 00          122         LDA  #$00
908D: 85 EC          123         STA  DBADL
908F: 8D 0C 90 124         STA  TDBADL
9092: A9 70          125         LDA  #$70
9094: 85 ED          126         STA  DBADH
9096: 8D 0D 90 127         STA  TDBADH
9099: A9 8F          128         LDA  #$8F
909B: 8D 02 C2 129         STA  BASE1+$2
909E: A9 FF          130         LDA  #$FF
90A0: 8D 03 C2 131         STA  BASE1+$3
90A3: AD 3D 90 132         LDA  FREQL
90A6: 8D 04 C2 133         STA  BASE1+$4
90A9: AD 3E 90 134         LDA  FREQH
90AC: 8D 05 C2 135         STA  BASE1+$5
90AF: A9 E0          136         LDA  #$E0
90B1: 8D 0B C2 137         STA  BASE1+$B

```

```

90B4: A9 8A      138      LDA  #$8A
90B6: 8D 0C C2   139      STA  BASE1+$C
90B9: AD 43 90   140      LDA  INITPH
90BC: 8D 00 C2   141      STA  BASE1
90BF: AD 42 90   142      LDA  INITPL
90C2: 8D 01 C2   143      STA  BASE1+$1
90C5: 60         144      RTS
                        145      ;
                        146      ;
                        147      ;
                        148      ;
90C6: AD 3F 90   149  STARTAD LDA  CHGAIN
90C9: 8D D0 C0   150      STA  AD1
90CC: A2 00      151      LDX  #$0
90CE: EA         152      NOP
90CF: EA         153      NOP
90D0: EA         154      NOP
90D1: AD D1 C0   155      LDA  AD2
90D4: 29 0F      156      AND  #$F
90D6: 81 0A      157      STA  (STADL,X)
90D8: E6 0A      158      INC  STADL
90DA: D0 02      159      BNE  EXTRA
90DC: E6 0B      160      INC  STADH
90DE: AD D0 C0   161  EXTRA  LDA  AD1
90E1: 81 0A      162      STA  (STADL,X)
90E3: E6 0A      163      INC  STADL
90E5: D0 02      164      BNE  EXTRA2
90E7: E6 0B      165      INC  STADH
90E9: A9 8F      166  EXTRA2  LDA  #$8F
90EB: 8D 02 C2   167      STA  BASE1+$02
90EE: A9 FF      168      LDA  #$FF
90F0: 8D 03 C2   169      STA  BASE1+$3
90F3: AD 3D 90   170      LDA  FREQL
90F6: 8D 04 C2   171      STA  BASE1+$4
90F9: AD 3E 90   172      LDA  FREQH
90FC: 8D 05 C2   173      STA  BASE1+$5
90FF: A9 E0      174      LDA  #$E0
9101: 8D 0B C2   175      STA  BASE1+$B
9104: A9 8A      176      LDA  #$8A
9106: 8D 0C C2   177      STA  BASE1+$C
9109: AD 41 90   178      LDA  SWPH
910C: 8D 00 C2   179      STA  BASE1
910F: AD 40 90   180      LDA  SWPL
9112: 8D 01 C2   181      STA  BASE1+$1
9115: A9 C0      182      LDA  #$C0
9117: 8D 0E C2   183      STA  BASE1+$E
911A: AD 49 90   184  CHECK  LDA  DIR
911D: C9 00      185      CMP  #$0
911F: D0 22      186      BNE  LSCMP
9121: A5 0A      187      LDA  STADL
9123: CD 47 90   188      CMP  MSADL

```

9126:	D0 49	189	BNE	INTERS
9128:	A5 0B	190	LDA	STADH
912A:	CD 48 90	191	CMP	MSADH
912D:	D0 42	192	BNE	INTERS
912F:	A9 01	193	LDA	#\$1
9131:	8D 49 90	194	STA	DIR
9134:	AD 43 90	195	LDA	INITPH
9137:	8D 00 C2	196	STA	BASE1
913A:	AD 42 90	197	LDA	INITPL
913D:	8D 01 C2	198	STA	BASE1+\$1
9140:	4C 71 91	199	JMP	INTERS
9143:	A5 0A	200	LSCMP	LDA STADL
9145:	38	201		SEC
9146:	ED 45 90	202		SBC LSADL
9149:	A5 0B	203		LDA STADH
914B:	ED 46 90	204		SBC LSADH
914E:	90 21	205		BCC INTERS
9150:	A9 00	206		LDA #\$00
9152:	8D 0E C2	207		STA BASE1+\$E
9155:	A9 65	208		LDA #\$65
9157:	8D FE 03	209		STA \$3FE
915A:	A9 FF	210		LDA #\$FF
915C:	8D FF 03	211		STA \$3FF
915F:	AD 0A 90	212		LDA TSTADL
9162:	85 0A	213		STA STADL
9164:	AD 0B 90	214		LDA TSTADH
9167:	85 0B	215		STA STADH
9169:	A9 00	216		LDA #\$0
916B:	8D 49 90	217		STA DIR
916E:	4C B4 91	218		JMP PEAK1
9171:	AD 0D C2	219	INTERS	LDA BASE1+\$0D
9174:	29 40	220		AND #\$40
9176:	FO 39	221		BEQ EXIT2
9178:	AD 3F 90	222		LDA CHGAIN
917B:	8D D0 C0	223		STA AD1
917E:	A4 0A	224		LDY STADL
9180:	AD 04 C2	225		LDA BASE1+\$04
9183:	A2 00	226		LDX #\$0
9185:	A4 0A	227		LDY STADL
9187:	48	228		PHA
9188:	68	229		PLA
9189:	48	230		PHA
918A:	68	231		PLA
918B:	48	232		PHA
918C:	68	233		PLA
918D:	48	234		PHA
918E:	68	235		PLA
918F:	AD D1 C0	236		LDA AD2
9192:	29 0F	237		AND #\$0F
9194:	81 0A	238		STA (STADL,X)
9196:	C8	239		INY

9197:	84	0A	240		STY	STADL
9199:	D0	05	241		BNE	STEP2
919B:	A4	0B	242		LDY	STADH
919D:	C8		243		INY	
919E:	84	0B	244		STY	STADH
91A0:	AD	D0	245	STEP2	LDA	AD1
91A3:	81	0A	246		STA	(STADL,X)
91A5:	A4	0A	247		LDY	STADL
91A7:	C8		248		INY	
91A8:	84	0A	249		STY	STADL
91AA:	D0	05	250		BNE	EXIT2
91AC:	A4	0B	251		LDY	STADH
91AE:	C8		252		INY	
91AF:	84	0B	253		STY	STADH
91B1:	4C	1A	254	EXIT2	JMP	CHECK
			255			
			256			
			257			
			258			
			259			
			260			
			261			
			262			
91B4:	A2	00	263	PEAK1	LDX	#\$00
91B6:	A9	00	264		LDA	#\$00
91B8:	8D	10	265		STA	YMAXL
91BB:	A9	00	266		LDA	#\$00
91BD:	8D	11	267		STA	YMAXH
91C0:	A9	FF	268		LDA	#\$FF
91C2:	8D	12	269		STA	YMINL
91C5:	8D	13	270		STA	YMINH
91C8:	A0	01	271	PEAK	LDY	#\$1
91CA:	B1	0A	272		LDA	(STADL),Y
91CC:	38		273		SEC	
91CD:	ED	10	274		SBC	YMAXL
91D0:	A1	0A	275		LDA	(STADL,X)
91D2:	ED	11	276		SBC	YMAXH
91D5:	B0	26	277		BCS	MAX1
91D7:	B1	0A	278	POUT	LDA	(STADL),Y
91D9:	38		279		SEC	
91DA:	ED	12	280		SBC	YMINL
91DD:	A1	0A	281		LDA	(STADL,X)
91DF:	ED	13	282		SBC	YMINH
91E2:	90	1C	283		BCC	MIN1
91E4:	A4	0A	284		LDY	STADL
91E6:	C8		285		INY	
91E7:	84	0A	286		STY	STADL
91E9:	D0	03	287		BNE	ADD2
91EB:	A4	0B	288		LDY	STADH
91ED:	C8		289		INY	
91EE:	A4	0A	290	ADD2	LDY	STADL

91F0: C8	291		INY
91F1: 84 0A	292		STY STADL
91F3: D0 0E	293		BNE PEND
91F5: A4 0B	294		LDY STADH
91F7: C8	295		INY
91F8: 84 0B	296		STY STADH
91FA: 4C 03 92	297		JMP PEND
91FD: 4C 9D 92	298	MAX1	JMP MAX
9200: 4C AA 92	299	MIN1	JMP MIN
9203: A4 0B	300	PEND	LDY STADH
9205: CC 46 90	301		CPY LSADH
9208: D0 BE	302		BNE PEAK
920A: A4 0A	303		LDY STADL
920C: CC 45 90	304		CPY LSADL
920F: D0 B7	305		BNE PEAK
9211: AD 0A 90	306		LDA TSTADL
9214: 85 0A	307		STA STADL
9216: AD 0B 90	308		LDA TSTADH
9219: 85 0B	309		STA STADH
921B: AD 10 90	310		LDA YMAXL
921E: 38	311		SEC
921F: ED 12 90	312		SBC YMINL
9222: 8D 18 90	313		STA YRANGL
9225: 8D 23 90	314		STA DIVL
9228: AD 11 90	315		LDA YMAXH
922B: ED 13 90	316		SBC YMINH
922E: 8D 19 90	317		STA YRANGH
9231: 8D 24 90	318		STA DIVM
9234: A9 00	319		LDA #\$00
9236: 8D 25 90	320		STA DIVH
9239: A9 BE	321		LDA #\$BE
923B: 8D 28 90	322		STA QUTNH
923E: A9 00	323		LDA #\$0
9240: 8D 27 90	324		STA QUTNM
9243: 8D 26 90	325		STA QUTNL
9246: 20 B7 92	326		JSR DIV24
9249: AD 28 90	327		LDA QUTNH
924C: 8D 22 90	328		STA YSCALH
924F: AD 27 90	329		LDA QUTNM
9252: 8D 21 90	330		STA YSCALM
9255: AD 26 90	331		LDA QUTNL
9258: 8D 20 90	332		STA YSCALL
925B: AD 3B 90	333		LDA XHEL
925E: 38	334		SEC
925F: ED 39 90	335		SBC XLEL
9262: 8D 1A 90	336		STA XRANGL
9265: 8D 23 90	337		STA DIVL
9268: AD 3C 90	338		LDA XHEH
926B: ED 3A 90	339		SBC XLEH
926E: 8D 1B 90	340		STA XRANGH
9271: 8D 24 90	341		STA DIVM

9274:	A9 00	342		LDA	#\$00	
9276:	8D 25 90	343		STA	DIVH	
9279:	8D 26 90	344		STA	QUTNL	
927C:	8D 27 90	345		STA	QUTNM	
927F:	A9 FA	346		LDA	#\$FA	
9281:	8D 28 90	347		STA	QUTNH	
9284:	20 B7 92	348		JSR	DIV24	
9287:	AD 28 90	349		LDA	QUTNH	
928A:	8D 1E 90	350		STA	XSCALH	
928D:	AD 27 90	351		LDA	QUTNM	
9290:	8D 1D 90	352		STA	XSCALM	
9293:	AD 26 90	353		LDA	QUTNL	
9296:	8D 1C 90	354		STA	XSCALL	
9299:	20 07 93	355		JSR	PLOTVCV	
929C:	60	356		RTS		
		357				;
		358				;
		359				;
		360				;
		361				;
		362				;
929D:	A1 0A	363	MAX	LDA	(STADL,X)	
929F:	8D 11 90	364		STA	YMAXH	
92A2:	B1 0A	365		LDA	(STADL),Y	
92A4:	8D 10 90	366		STA	YMAXL	
92A7:	4C D7 91	367		JMP	POUT	
92AA:	A1 0A	368	MIN	LDA	(STADL,X)	
92AC:	8D 13 90	369		STA	YMINH	
92AF:	B1 0A	370		LDA	(STADL),Y	
92B1:	8D 12 90	371		STA	YMINL	
92B4:	4C D7 91	372		JMP	POUT	
		373				;
		374				;
		375				;
		376				;
		377				;
		378				;
		379				;
		380				;
		381				;
		382				;
92B7:	A9 00	383	DIV24	LDA	#\$00	
92B9:	8D 2B 90	384		STA	REML	
92BC:	8D 2C 90	385		STA	REMM	
92BF:	8D 2D 90	386		STA	REMH	
92C2:	A2 18	387		LDX	#\$18	
92C4:	0E 26 90	388	NXTBT	ASL	QUTNL	
92C7:	2E 27 90	389		ROL	QUTNM	
92CA:	2E 28 90	390		ROL	QUTNH	
92CD:	2E 2B 90	391		ROL	REML	
92D0:	2E 2C 90	392		ROL	REMM	

92D3:	2E 2D 90	393		ROL	REMH
92D6:	AD 2B 90	394		LDA	REML
92D9:	38	395		SEC	
92DA:	ED 23 90	396		SBC	DIVL
92DD:	8D 29 90	397		STA	TAD1
92E0:	AD 2C 90	398		LDA	REMM
92E3:	ED 24 90	399		SBC	DIVM
92E6:	8D 2A 90	400		STA	TAD2
92E9:	AD 2D 90	401		LDA	REMH
92EC:	ED 25 90	402		SBC	DIVH
92EF:	90 12	403		BCC	CNTDN
92F1:	EE 26 90	404		INC	QUTNL
92F4:	8D 2D 90	405		STA	REMH
92F7:	AD 2A 90	406		LDA	TAD2
92FA:	8D 2C 90	407		STA	REMM
92FD:	AD 29 90	408		LDA	TAD1
9300:	8D 2B 90	409		STA	REML
9303:	CA	410	CNTDN	DEX	
9304:	D0 BE	411		BNE	NXTBT
9306:	60	412		RTS	
		413			;
		414			;
		415			;
		416			;
		417			;
		418			;
		419			;
		420			;
		421			;
		422			;
9307:	A2 03	423	PLOTCV	LDX	#\$3
9309:	20 F0 F6	424		JSR	SETCOL
930C:	A9 20	425		LDA	#\$20
930E:	85 E6	426		STA	HPAGE
9310:	8D 57 C0	427		STA	HGR
9313:	8D 52 C0	428		STA	FULSCR
9316:	8D 50 C0	429		STA	GR
9319:	A0 01	430	NEXPL	LDY	#\$1
931B:	A2 00	431		LDX	#\$0
931D:	B1 0A	432		LDA	(STADL),Y
931F:	38	433		SEC	
9320:	ED 12 90	434		SBC	YMINL
9323:	8D 29 90	435		STA	TAD1
9326:	A1 0A	436		LDA	(STADL,X)
9328:	ED 13 90	437		SBC	YMINH
932B:	8D 2A 90	438		STA	TAD2
932E:	AD 20 90	439		LDA	YSCALL
9331:	8D 36 90	440		STA	MULTL
9334:	AD 21 90	441		LDA	YSCALM
9337:	8D 37 90	442		STA	MULTM
933A:	AD 22 90	443		LDA	YSCALH

933D:	8D 38 90	444		STA	MULTH
9340:	20 08 94	445		JSR	MLT24
9343:	AD 30 90	446		LDA	PLDT3
9346:	8D 35 90	447		STA	YPLDT
9349:	A1 EC	448		LDA	(DBADL,X)
934B:	38	449		SEC	
934C:	ED 39 90	450		SBC	XLEL
934F:	8D 29 90	451		STA	TAD1
9352:	B1 EC	452		LDA	(DBADL),Y
9354:	ED 3A 90	453		SBC	XLEH
9357:	8D 2A 90	454		STA	TAD2
935A:	AD 1C 90	455		LDA	XSCALL
935D:	8D 36 90	456		STA	MULTL
9360:	AD 1D 90	457		LDA	XSCALM
9363:	8D 37 90	458		STA	MULTM
9366:	AD 1E 90	459		LDA	XSCALH
9369:	8D 38 90	460		STA	MULTH
936C:	20 08 94	461		JSR	MLT24
936F:	AD 30 90	462		LDA	PLDT3
9372:	8D 33 90	463		STA	XPLDTL
9375:	A9 00	464		LDA	#\$00
9377:	8D 34 90	465		STA	XPLDTH
937A:	AE 33 90	466		LDX	XPLDTL
937D:	AC 34 90	467		LDY	XPLDTH
9380:	AD 35 90	468		LDA	YPLDT
9383:	20 57 F4	469		JSR	HPLOT
9386:	A4 EC	470		LDY	DBADL
9388:	C8	471		INY	
9389:	84 EC	472		STY	DBADL
938B:	D0 05	473		BNE	NE2
938D:	A4 ED	474		LDY	DBADH
938F:	C8	475		INY	
9390:	84 ED	476		STY	DBADH
9392:	A4 EC	477	NE2	LDY	DBADL
9394:	C8	478		INY	
9395:	84 EC	479		STY	DBADL
9397:	D0 05	480		BNE	ADINC
9399:	A4 ED	481		LDY	DBADH
939B:	C8	482		INY	
939C:	84 ED	483		STY	DBADH
939E:	A4 0A	484	ADINC	LDY	STADL
93A0:	C8	485		INY	
93A1:	84 0A	486		STY	STADL
93A3:	D0 05	487		BNE	NEXINC
93A5:	A4 0B	488		LDY	STADH
93A7:	C8	489		INY	
93A8:	84 0B	490		STY	STADH
93AA:	A4 0A	491	NEXINC	LDY	STADL
93AC:	C8	492		INY	
93AD:	84 0A	493		STY	STADL
93AF:	D0 05	494		BNE	MCOMP

93B1:	A4 0B	495		LDY	STADH
93B3:	C8	496		INY	
93B4:	84 0B	497		STY	STADH
93B6:	AD 49 90	498	MCOMP	LDA	DIR
93B9:	C9 00	499		CMP	#\$0
93BB:	D0 1E	500		BNE	COMP
93BD:	A5 0A	501		LDA	STADL
93BF:	CD 47 90	502		CMP	MSADL
93C2:	D0 27	503		BNE	JNEXPL
93C4:	A5 0B	504		LDA	STADH
93C6:	CD 48 90	505		CMP	MSADH
93C9:	D0 20	506		BNE	JNEXPL
93CB:	A9 01	507		LDA	#\$1
93CD:	8D 49 90	508		STA	DIR
93D0:	A9 70	509		LDA	#\$70
93D2:	85 ED	510		STA	DBADH
93D4:	A9 00	511		LDA	#\$0
93D6:	85 EC	512		STA	DBADL
93D8:	4C EB 93	513		JMP	JNEXPL
93DB:	A5 0A	514	COMP	LDA	STADL
93DD:	38	515		SEC	
93DE:	ED 45 90	516		SBC	LSADL
93E1:	A5 0B	517		LDA	STADH
93E3:	ED 46 90	518		SBC	LSADH
93E6:	90 03	519		BCC	JNEXPL
93E8:	4C EE 93	520		JMP	PLOUT
93EB:	4C 19 93	521	JNEXPL	JMP	NEXPL
93EE:	AD 0A 90	522	PLOUT	LDA	TSTADL
93F1:	85 0A	523		STA	STADL
93F3:	AD 0B 90	524		LDA	TSTADH
93F6:	85 0B	525		STA	STADH
93F8:	AD 0C 90	526		LDA	TDBADL
93FB:	85 EC	527		STA	DBADL
93FD:	AD 0D 90	528		LDA	TDBADH
9400:	85 ED	529		STA	DBADH
9402:	A9 00	530		LDA	#\$0
9404:	8D 49 90	531		STA	DIR
9407:	60	532		RTS	
		533			;
		534			;
		535			;
		536			;
		537			;
		538			;
		539			;
		540			;
		541			;
		542			;
9408:	A9 00	543	MLT24	LDA	#\$00
940A:	8D 2E 90	544		STA	PLDT1
940D:	8D 2F 90	545		STA	PLDT2

9410:	8D 30 90	546		STA	PLDT3
9413:	8D 31 90	547		STA	PLDT4
9416:	8D 32 90	548		STA	PLDT5
9419:	A2 10	549		LDX	#\$10
941B:	4E 2A 90	550	NEXMBT	LSR	TAD2
941E:	6E 29 90	551		ROR	TAD1
9421:	90 19	552		BCC	ALIGN
9423:	AD 30 90	553		LDA	PLDT3
9426:	18	554		CLC	
9427:	6D 36 90	555		ADC	MULTL
942A:	8D 30 90	556		STA	PLDT3
942D:	AD 31 90	557		LDA	PLDT4
9430:	6D 37 90	558		ADC	MULTM
9433:	8D 31 90	559		STA	PLDT4
9436:	AD 32 90	560		LDA	PLDT5
9439:	6D 38 90	561		ADC	MULTH
943C:	6A	562	ALIGN	ROR	A
943D:	8D 32 90	563		STA	PLDT5
9440:	6E 31 90	564		ROR	PLDT4
9443:	6E 30 90	565		ROR	PLDT3
9446:	6E 2F 90	566		ROR	PLDT2
9449:	6E 2E 90	567		ROR	PLDT1
944C:	CA	568		DEX	
944D:	DO CC	569		BNE	NEXMBT
944F:	60	570		RTS	
		571			

;

--End assembly, 1024 bytes, Errors: 0