



A micro computer controlled high speed high resolution cyclic voltammeter
by Russell Allen Bonsteel

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry
Montana State University
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Abstract:

In cyclic voltammetry, the technique of applying known voltages to an electrochemical cell and recordings the response waveform on an x-y recorder is a area of significant growth. In its infancy, the voltages applied to the cell were delivered by manual control through a network of vacuum tubes, resistors, and capacitors. The waveform response curves were both crude in accuracy and precision. The next generation of electronics brought about the operational amplifier. While this increased the accuracy of the waveforms, reproducibility was still lagging because of the manual timing application of the input voltages, especially for multiple run sequences.

It is proposed that by using state of the art integrated circuits and computer control that the manual application of the voltages can be eliminated and thereby increase both the precision and the reproducibility of the voltammetric waveform.

With the implementation of the integrated circuits and computer control new schematic designs had to be employed. Solid state analog switches were used to route precise currents or voltages to carefully matched operational amplifiers. Timing routines were generated to maximize the amount of data to be collected and stored in computer memory. A sophisticated language called FORTH was ascertained to be the best vehicle to communicate between the computer and the cyclic voltammetric interface.

The results were excellent on the implementation of the voltages to the electrodes in the chemical cell. With the computer control, precision up to ± 7 parts per one thousand was achieved using a ten volt reference. By being able to store the analog data as a digital number, computer enhancement of the cyclic waveforms i.e. background elimination of supporting electrolytes are now also obtainable.

With the newly constructed cyclic voltammeter an investigation of the reduction of Lindane, a chlorinated pesticide, at sweep rates up to fifty times faster then previously accomplished was carried out. This data allowed extrapolation back to soil redox potential levels and may allow estimating the life span of the pesticide in the reductive environment.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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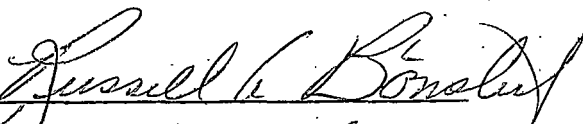
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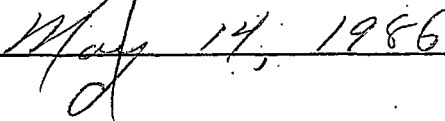


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ABSTRACT

In cyclic voltammetry, the technique of applying known voltages to an electrochemical cell and recording the response waveform on an x-y recorder is a area of significant growth. In its infancy, the voltages applied to the cell were delivered by manual control through a network of vacuum tubes, resistors, and capacitors. The waveform response curves were both crude in accuracy and precision. The next generation of electronics brought about the operational amplifier. While this increased the accuracy of the waveforms, reproducibility was still lagging because of the manual timing application of the input voltages, especially for multiple run sequences.

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With the implementation of the integrated circuits and computer control new schematic designs had to be employed. Solid state analog switches were used to route precise currents or voltages to carefully matched operational amplifiers. Timing routines were generated to maximize the amount of data to be collected and stored in computer memory. A sophisticated language called FORTH was ascertained to be the best vehicle to communicate between the computer and the cyclic voltammetric interface.

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With the newly constructed cyclic voltammeter an investigation of the reduction of Lindane, a chlorinated pesticide, at sweep rates up to fifty times faster than previously accomplished was carried out. This data allowed extrapolation back to soil redox potential levels and may allow estimating the life span of the pesticide in the reductive environment.

INTRODUCTION

The Electrode Processes

Two types of electrical processes occur at electrodes. One involves the transfer of electrons across the metal-solution interface. This process causes oxidation or reduction to occur. Since these reactions are governed by Faraday's law (i.e. the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called Faradaic processes. Electrodes at which Faradaic processes occur are sometimes called charge transfer electrodes. Under some conditions a given electrode-solution interface will show a range of potentials where no Faradaic reactions occur because such reactions are thermodynamically or kinetically unfavorable. However other processes, involving the electrode interface structures can occur such as adsorption and desorption with changing potential or solution composition. These processes are called nonfaradaic processes.¹

Nonfaradaic currents arise from the formation of an electrical double layer at the electrode-solution interface. When a potential is applied to a metallic electrode immersed in an electrolyte, a momentary surge of current creates an excess (or a deficiency) of negative

charge at the surface of the metal. Because of ionic mobility, the layer of solution immediately adjacent to the electrode acquires an opposing charge due to excess counter ions (see Figure 1a). According to the G-C-S theory (Gary-Chapman-Stern)² the charged layer consists of two parts: (1) a compact inner layer, in which the potential decreases linearly with distance from the electrode surface; and (2) a more diffuse layer, in which the decrease is approximately exponential (Figure 1b). This arrangement of negative and positive ions is termed the electrical double layer.

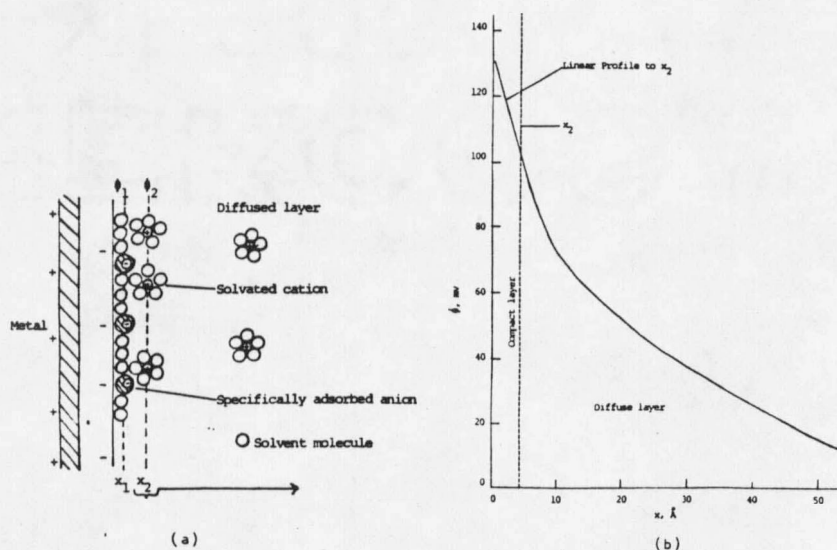


Figure 1. (a) Proposed model of the electrode-solution, double layer region. (b) Potential profile through the solution side of the double layer.

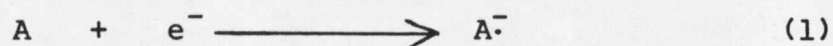
The double layer formed by an applied DC potential involves the development of a momentary current which then drops to zero as the electrode becomes polarized, no further current flows unless some faradaic process occurs. When an alternating potential is applied to the electrodes an alternating current flows in conjunction with the reversal of the charge relationship occurring with each half-cycle, as first negative and then positive ions are attracted to the electrode surface. A modest amount of electrical energy is consumed and converted to frictional heat from this ionic movement. Thus, each electrode surface behaves as a capacitor, the capacitance of which may be quite large (on the order of ten to a hundred microfarads per square centimeter).³ The capacitive current increases with both increasing frequency and increasing electrode size. By controlling these variables, it is possible to arrange conditions so that essentially all of the electricity flowing through the cell is carried across the electrode interface by this nonfaradaic process.

Voltammetry

Information concerning chemical reactions (i.e. Faradaic) can be gained from an electrochemical cell by sweeping thru a known potential region with time and recording the i-e curve directly. The potential is usually varied (ramped with sweep rates ranging from 0.04

volts/second to about 10 volts/second, but sweep rates slower than 2 mv/second and greater than 1000 volts/second have been used). The current is usually recorded as a function of time which is equivalent to recording current versus potential. The proper name for this method is Linear Potential Sweep Chronoamperometry, but is generally referred to as Linear Sweep Voltammetry (LSV).

The first part of Figure 2 (up to switching time t_s) shows a typical LSV applied potential and response curve where a species A picks up an electron and forms an anion radical A⁻ :



If this scan is begun at a potential well positive of E' (the formal potential of an electrode, see Figure 2a) for the reduction, only nonfaradaic currents flow for awhile. When the electrode potential approaches the vicinity of E' the reduction process becomes appreciable and measurable current flows. (The reduction actually proceeds at all potentials, but at potentials very positive of E' the reduction is very, very slow. These are reductions that can take place at "zero" voltage.) As the potential continues to go more negative, the surface concentration of A drops to near zero, mass transfer of A to the surface reaches a maximum rate, and then it declines as the depletion effect sets in due to lowering the bulk

concentration around the electrode. The observed current-potential curve is therefore peaked like that depicted in the first part of Figure 2b. The first one third of the curve is completely under Nernstian control (i.e. the concentrations of the oxidized and reduced species at the electrode surface can be assumed to be at their equilibrium values as governed by the Nernst equation), the second third (the hump) is under both Nernstian and diffusion controls, the last is under diffusion control (i.e. the movement of a species under the influence of a gradient of chemical potential) reducing only species A that diffuses onto the double layer surface.

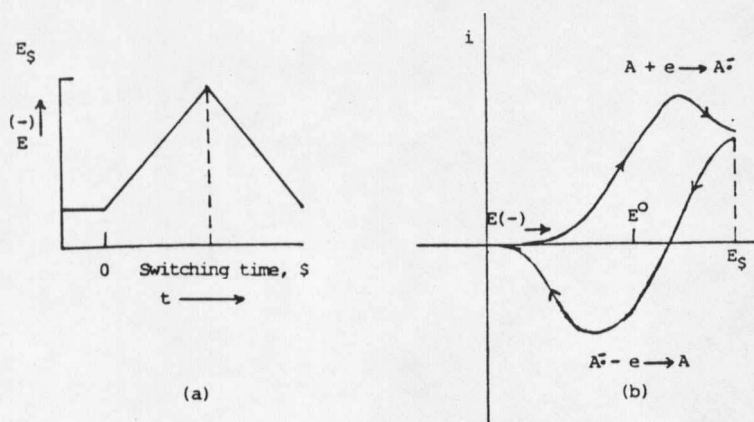


Figure 2. (a) Cyclic potential sweep.
(b) Resulting cyclic voltammogram.

If the potential sweep (Figure 2b) were reversed, at E' the electrode potential would be going more positive and also near the electrode surface there would still be a large concentration of the (just formed) oxidizable anion radical, A⁻. As the potential now approaches, then passes, E' the electrochemical balance at the surface grows more and more favorable toward the neutral species, A.



The anion radical becomes reoxidized and an anodic current flows. For basically the same reasons the reversal current has a shape similar to that of the forward peak current except that it starts at the residual cathodic current level.

The current at point E\$ on Figure 2b abruptly shifts due to a change from nonfaradaic charging to discharging reforming the double layer capacitance when the potential scan is reversed.⁴

DC and AC voltammetry are a valuable variation of the simple form of Linear Sweep Voltammetry (LSV). In DC LSV a initial step potential and/or a ramping potential is applied to the working electrode of the electrochemical cell. The procedure for AC LSV is identical to the DC LSV except that a small sinusoidal AC voltage of selected frequency is superimposed upon the DC waveform. The output is a plot of the magnitude of the AC component of the

current vs. the DC voltage, E_{dc} . By separating the long term diffusion caused by E_{dc} from the rapid diffusional fluctuations due to E_{ac} , treatment of AC voltammetry is greatly simplified. E_{dc} sets up mean surface concentrations of electroactive substances that look like bulk values to the AC perturbations because of the difference in time scales. Bard defines the faradaic impedance in terms of bulk concentrations; thus the current response in AC voltammetry as a function of E_{dc} is readily obtained by substituting the surface concentrations imposed by E_{dc} directly into the impedance relations. The mean surface concentration of A and A enforced by E_{dc} depends on several factors: (a) the way in which E_{dc} is varied; (b) whether or not there is periodic renewal of the diffusion layer (i.e dropping mercury electrode); (c) the applicable current-potential characteristics; and (d) homogeneous or heterogeneous chemical processes (or reactions) associated with the overall electrode reaction.

Cyclic AC voltammetry is a simple extension of the linear sweep technique by adding the reverse scan for E_{dc} . While conventional cyclic voltammetry is especially informative about the qualitative aspects of an electrode process, the response waveforms lend themselves poorly to quantitative evaluations of electrochemical parameters. However cyclic AC voltammetry retains the diagnostic utility of conventional cyclic measurements, but it does so

with an improved response function that permits quantitative evaluations as precise as those obtainable with the normal AC approaches.

Treatment of cyclic AC voltammetry follows the same pattern as normal DC voltammetry. The AC and DC time scales are independently variable, but are assumed to differ. Then a treatment of the DC aspect yields mean surface concentrations, which are used to calculate the faradaic impedances that define the AC response by amplitude and phase angle. The electrode is assumed to be stationary and the solution is regarded as inactive for the duration of the DC cycle.^{6,7}

In voltammetric experiments, a three electrode cell is preferred (see Figure 3). The three electrodes are the working or indicator electrode, the auxiliary or counter electrode, and the reference electrode. The current is passed between the working electrode and the auxiliary electrode. The auxiliary electrode is usually made of an inert material (platinum, pt.) that does not produce substances by electrolysis that will reach the working electrode and cause an interfering reaction.^{8,9}

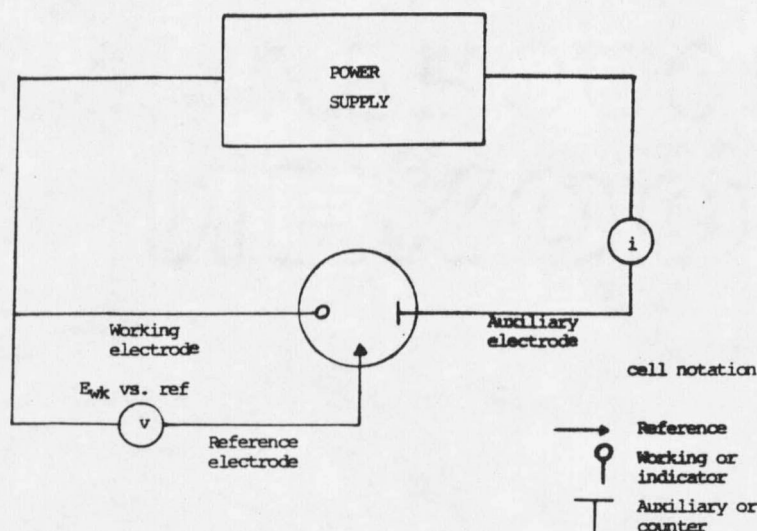


Figure 3. Three electrode cell and notation for the different electrodes.

A high input impedance is maintained between the working electrode and the reference electrode so that negligible current is drawn through the reference electrode. Since negligible current is drawn, its potential will remain constant and equal to its open-circuit value. This also significantly reduces the I.R. drop in the cell, which otherwise would introduce an apparent error in the cell voltage. However not all of the I.R. drop is removed from the voltage measuring by this technique. Because the reference electrode is not at the actual surface of the working electrode there is some small uncompensated solution resistance R_u .¹⁰ The resistance can be taken into account by the following formula, using a planar electrode with uniform current density across its surface:

$$R_u = x/kA \quad (3)$$

where x is the distance of the reference electrode from the working electrode, k is the solution conductivity and A is the working electrode area. Thus by knowing the R_u of the cell, for selected currents, a selected voltage correction can be given by the use of positive feedback to suppress the unwanted R_u .

Resistive Effects within the Electrochemical Cell

The R_u caused by the solution is only one of the resistive effects within the electrochemical cell (see Figure 4). Two more sources of uncompensative resistance within the cell are caused by the double layer capacitance and the ohmic resistance.

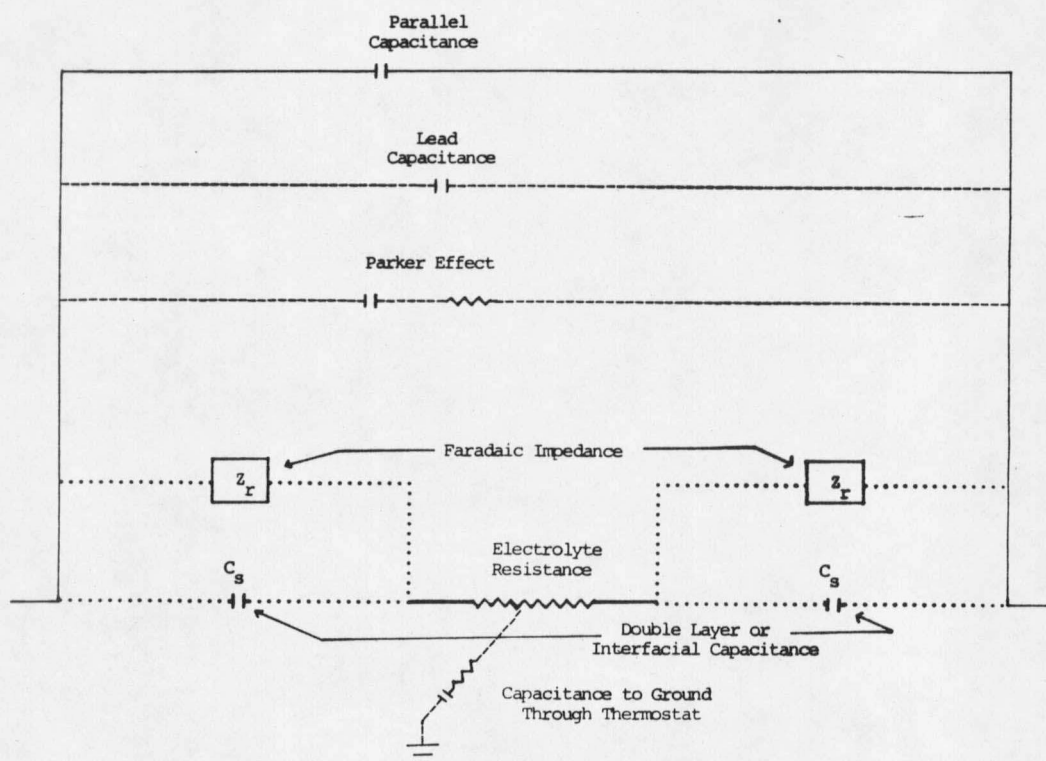


Figure 4. Electrical equivalent circuit for a conductance cell.

As previously stated at each electrode-solution interface there is a substantial capacitance. This ordering of ions due to the charge on the electrode surface and the trailing off of the mixture of positive and negative ions into the bulk solution constitutes the double layer.

If a small voltage is applied to the cell, a charging current flows until the double-layer capacitor is charged to its equilibrium value. If the voltage is increased, the charge accumulated in the double-layer capacitor increases

until a voltage is reached where an electron-transfer takes place across the electrode/solution interface, accompanied by oxidation at the positive electrode, and reduction at the negative electrode. This faradaic process can be represented by a voltage dependent resistance (nonlinear) which partially short circuits the double layer. In the equivalent circuit, the faradaic impedance is represented as a complex impedance in parallel with the double-layer capacitance, which in effect lowers the overall resistance of the cell.¹¹

In the electrolytic solution, the charge carriers are ions which constitute the flow of current instead of electrons as in a metal wire. Under the influence of the electric field the cations migrate towards the cathode and the anions toward the anode. Because of the varying sizes of ions there is a velocity dependent retarding force which opposes the accelerating force of the electric field. This results in a constant drift velocity per ion specie in a given electric field. From this a close approximation of the solution resistance can be calculated.¹²

By using an AC rather than a DC voltage the resistance effects can be reduced. Each process (double-layer capacitance, faradaic effects, and ohmic resistance) proceeds at a different rate so that its relative energy dissipations vary with frequency. Therefore as the frequency increases the concentration-polarization can be

reduced or eliminated. Then by reducing the applied voltage the faradaic resistances can be eliminated, particularly if there is a fast electron transfer in both directions.¹³

Even though increasing the frequency can eliminate some resistance problems, there are other problems that cause stray capacitance within the cell. Ways which are serious are the stray capacitance between the cells' connecting leads, the electrode lead resistance themselves, and through stray currents created by cell design geometry (sometimes called the Parker effect).¹⁴

STATEMENT OF PROBLEM

In 1982 a dc cyclic voltammeter was built in this lab using eight double pole switches, three rotary switches, five potentiometers, and an assortment of operational amplifiers with corresponding hardware (resistors, capacitors, and transistors). This instrument was used to investigate the electrochemical properties of surfactants, used to solubilize pesticides. These surfactants e.g. Tetradecyltrimethylammoniumbromide, both cationic and anionic, had long hydrocarbon tails varying from C-10 to C-16. They were used in solutions where micelles were present and the pH and oxygen content varied.¹⁵ The accuracy of each run singly had been good but the reproducibility on consecutive runs with the "same" parameters set in was not. The factors that contributed most to the repetitive cyclic voltammeter problems were:

- 1) the timing variation for switching various currents or potentials to the cell using manual switches and potentiometers, 2) the renewing of the electrode double layer to give a consistently reproducible collection of ions and molecules before each run. Also there was a need to allow "enhancement of data", e.g. to be able to cancel out the background current due to the electrochemical

reaction of solvent impurities and double layer charging of the electrode. Another requirement was a need to examine in detail selected portions of the curve under investigation.



Figure 5. Typical cyclic voltammograms run on "old" instrument. Two consecutive runs of Technizene in TEABr.

Figure 5 shows a voltammogram for Technizene (2,3,5,6-Tetrachloronitrobenzene) with two runs without

stirring and a minimal wait period. It is obvious to see that the two waveforms are different and that the peak currents are different. This presents serious problems for determining the intrinsic heterogeneous rate constant for the irreversible reduction of compounds. Accurate determination of these constants depends on obtaining peak electrode current and potentials at a large series of sweep rates under identical conditions.

Pesticide residues in the environment are a great concern because of the detrimental effects they may have on numerous organisms. One of the ways that pesticides are decomposed is by natural reduction (electron transfer) in anaerobic soil. However, because the soil has a low redox potential i.e. depending upon moisture content and amount of substrate, the rate for this processes is hard to determine for many chemicals. An estimate of the time frame for the reductive degradation of a pesticide may be ascertained in the laboratory by measuring the intrinsic rate constant from data obtained by cyclic voltammetry, only at much higher potentials, and then extrapolating back to the soil's redox potential.

An instrumental solution to the waveform variability problem, computer enhancement, and its application to reductive degradation of pesticides at the soils redox potential is the goal of this research.

EXPERIMENTAL

ACCV Hardware

Ac cyclic voltammetry (ACCV) has been known and has been in use for the past twenty years. Since the development of the operational amplifier both precision and accuracy have greatly improved.¹⁶ However until the last several years computer interfacing with the electrochemical cells has been uncommon. With the new microprocessors and minicomputers, the data collection has been greatly enhanced and most of the human error (e.g. setting of potentiometers, voltages, sweep speeds, and recording data) has been eliminated.

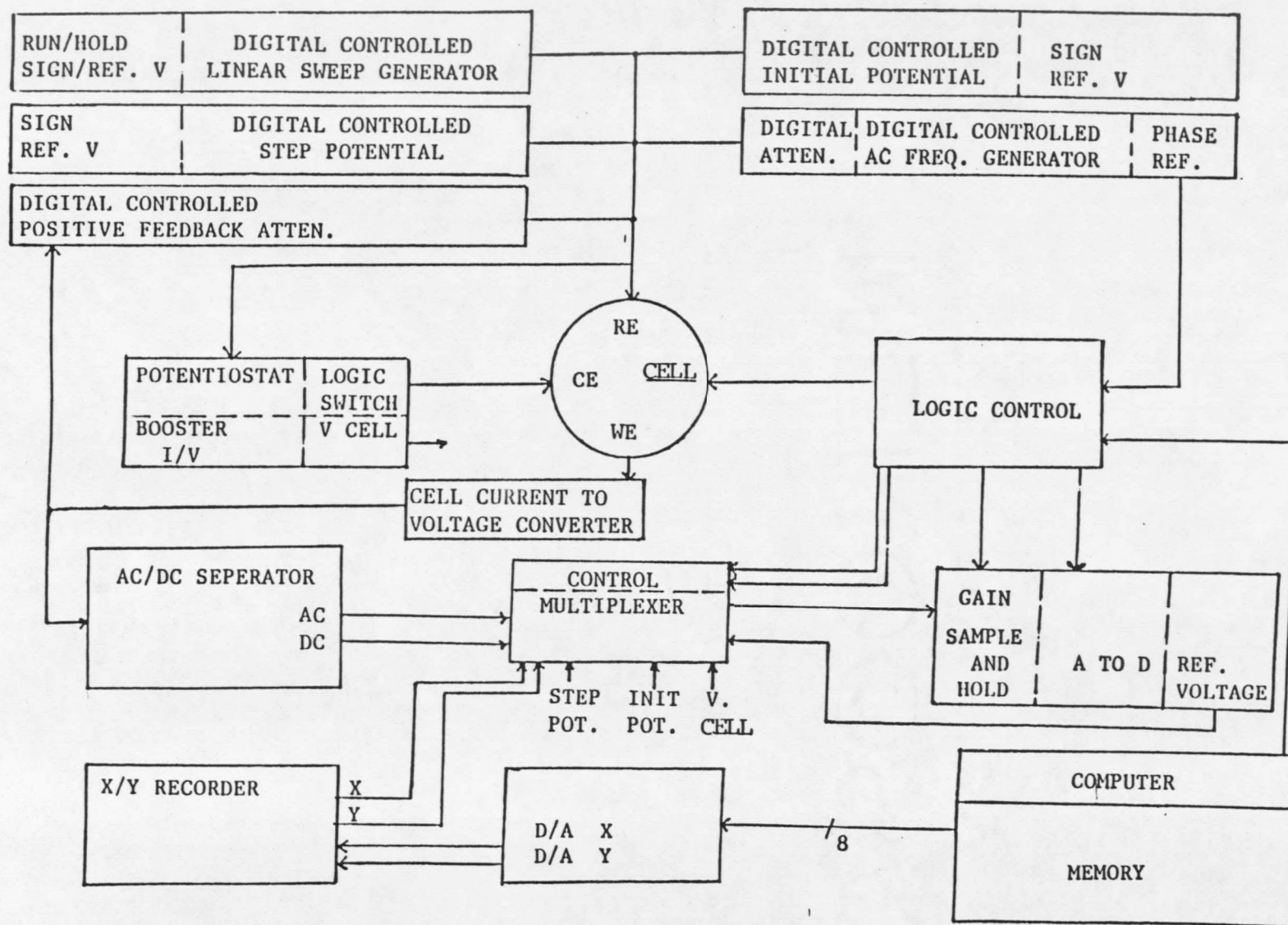
The extent of interfacing depends on what is to be accomplished with the ACCV; what potentials are to be applied and retrieved and the various control sections of the voltammeter that need to be digitally controlled. For the ACCV that was constructed, the following modules were built to have a direct linkage to the computer (see Figure 6):

1. Interface
2. Initial DC potential
3. Dc step potential
4. Dc sweep generator

5. Ac sine wave generator
6. The potentiostat
7. Ac and DC response separator
8. Gain control and positive feedback
9. Sample and hold with d/a converter
10. X and y recorder output

Interface

An Apple II e was used as the base computer.¹⁷ Slot #5 of the Apple was made available via a 50 pin connector ribbon cable to bring the timing signals, address lines, and data lines to the ACCV interface board (see Figure 7). Address lines were used to decode and select for one of sixteen ports using two 74LS138 (one of eight decoder/demodulator chips) in parallel.¹⁸ For all the output ports except the DC sweep generator, nine AD 7542 cmos digital to analog converters with 12 bit resolution¹⁹ were used with accompanying operational amplifiers to complete the interfacing.



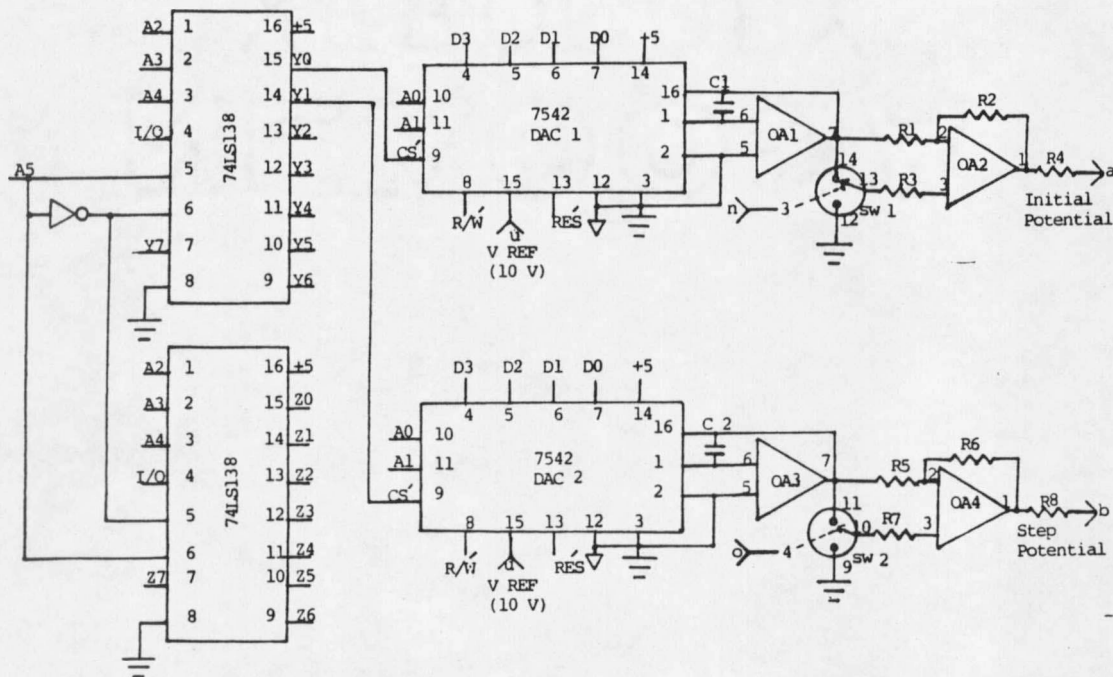


Figure 7. Computer interfacing; A/D Converters Initial Potential and Step Potential.

Initial DC Potential

The DAC 7542 acts as a digitally controlled precision variable resistor to convert the reference voltage into a current. When selected, a digital number between 0 and 4096 which corresponds to voltages from 0 volts to the reference voltage (i.e. 10 volts) is entered at the computer terminal. Since the DAC 7542's have only four data input lines and the micro processor is a twelve bit processor, computer software is used to bring the data into the DAC's in three clock cycles four bits at a time. Operational amplifier OA #1 is used to develop the DC voltage from the current output (pin 1) of the DAC. If a

negative DC voltage is desired, a sign conversion switch (AD 7512) is used, controlled by the computer software, and fed into a unity gain operational amplifier OA #2. The output of OA #2 is converted from a voltage to a current by a 10K ohm resistor and the resulting current is fed into the common bus line to the input of the potentiostat.

DC Step Potential

The DC step potential allows the cell voltage to be stepped a specific amount and then returned, or to increment the voltammeter voltage in steps (called stair step voltammetry). The amount to be incremented is determined by the operator and the computer software. The electronics of the DC step potential circuit is identical to the initial potential circuit and the output is also converted to a current and applied to the common bus line going to the potentiostat.

DC Sweep Generator

The heart of the interface board that controls all the logic and switching, is the R6522 control chip,²⁰ that has a variety of functions including two output ports A and B with 8 control lines each. Several of the control lines are made available to select the switches used within the ACCV circuits. Port A control lines, PA2 to PA6, are used to regulate the output of the logarithmic digital to analog

converter, DAC 76²¹ (see Figure 8). PA0 and PA1 of the R6522 chip output control signals to turn on two switches; a run/hold switch to feed a DC voltage to the integrator, OA #17, and a run/stop switch to zero (clear) the integrator. PA7 is the sign change bit for the DAC 76. The output voltage from the operational amplifier OA #15 is 0 to -12 volts when pin 16 is made the output (logic 1 at PA7 6522 chip) and 0 to +12 volts when pin 17 is the output (logic 0 at PA7 6522 chip).

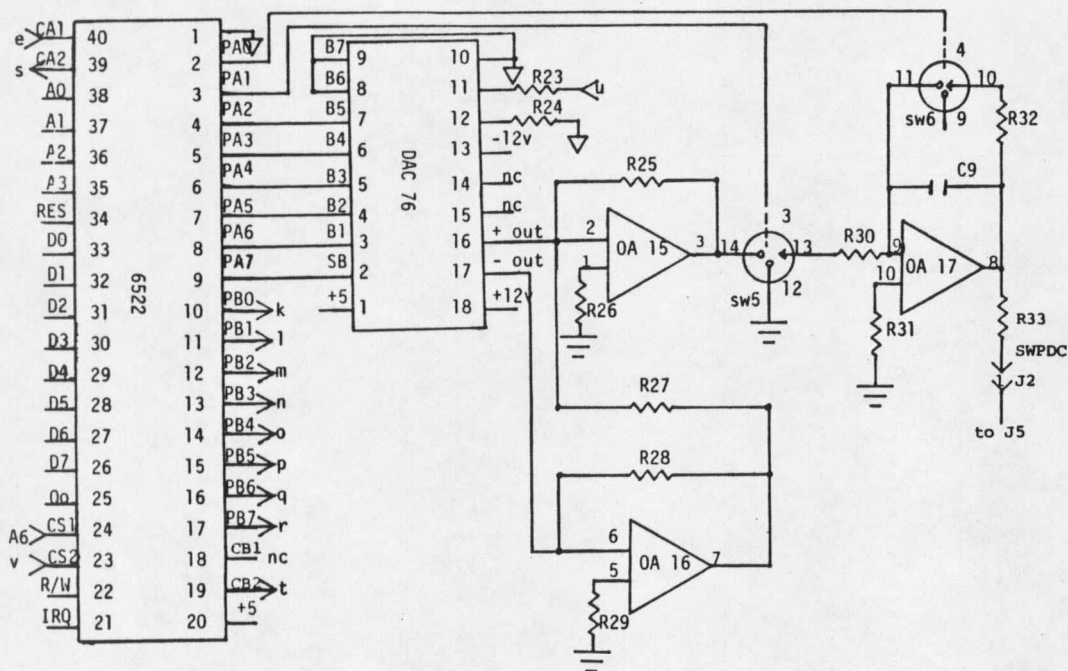


Figure 8. Logic Control and Sweep Generator.

When the voltage from OA #15 (positive or negative) is applied to the inverting input of the integrating operational amplifier OA #17, an RC time constant is

developed by the integrating circuit R30 and C9, causing a (positive or negative) ramping DC voltage which is applied to the bus line feeding the potentiostat.

AC Sine Wave Generator

The sine wave generator circuit is shown in Figure 9. The frequency of this sine wave oscillator is a linear function of a digitally controlled input. The digital controller is made up of two digital to analog converters, DAC 7542 acting as digitally variable resistors in place of two passive resistors normally present in a standard sine wave generator of this type.

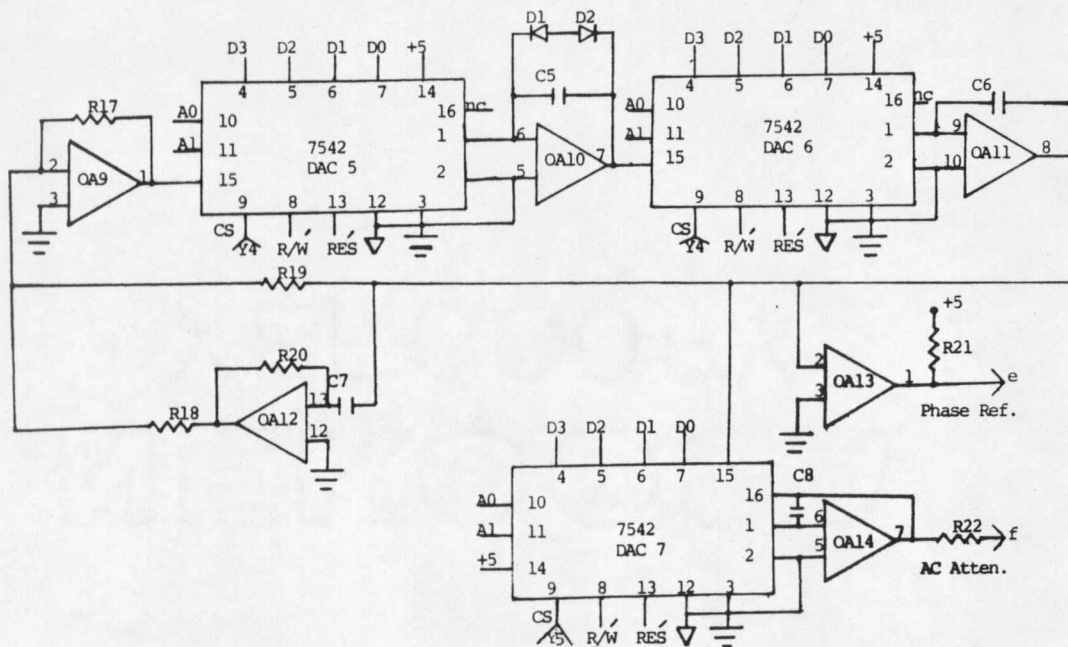


Figure 9. AC Generator, Attenuator, and Phase Reference.

It can be shown from basic circuit analysis that the frequency of oscillation is given by:

$$F_o = 0.159(R_{19}/C_5 C_6 VR_1 VR_2 R_{17})^{0.5} \quad (4)$$

with the conditions for oscillations being given by:

$$C_7 R_{20} R_{17}/R_{19} \geq G \quad (5)$$

where G is a gain constant. The frequency of oscillation is a function of the virtually grounded variable resistors VR1(DAC 5) and VR2(DAC 6). Because the two variable resistors are digitally controlled modules their output values are given by:

$$VR_1 = VR_2 = R_0 (2^n - 1)/N \quad (6)$$

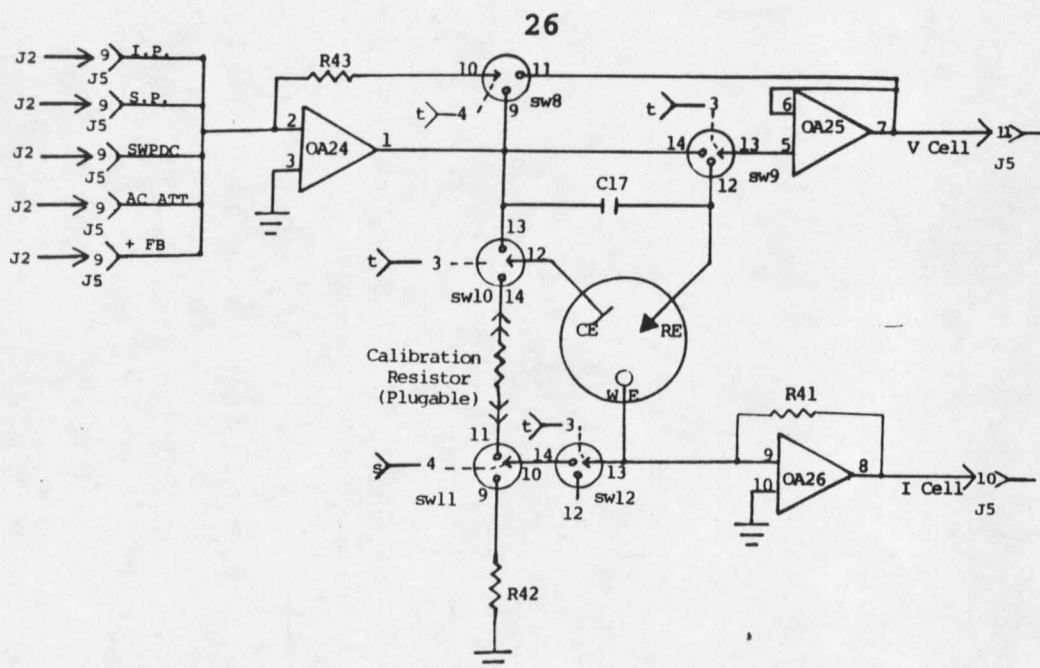
where n is the number of digital bits available, N the digital number programmed (set), and R_0 is a constant. The relationship between the output frequency and N is perfectly linear.²²

The output of the frequency generator OA #11 pin 8 is fed into both OA #13 which converts the sine wave to a square wave as a phase reference and to the voltage reference pin 15 of another DAC 7542, used this time as a digitally controlled attenuator. (Which can attenuate the sine wave from the reference voltage level to 0 volts.)

The attenuated AC signal is used in conjunction with either the initial potential, step potential, or sweeping DC voltage as a superimposed signal to cause an AC perturbation on the counter electrode of the electrochemical cell.

The Potentiostat

The potentiostat is the heart of any voltammeter system. This is the point where all the entered control currents are summed and sent to the electrochemical cell through the summing amplifier OA #24 (see Figure 10). Operational amplifier OA #25 is the voltage reference amplifier to the electrochemical cell. OA #26, a current amplifier, takes the cell reaction current, both AC and DC, to the response separator to be separated and 'read' by the computer.



AC and DC RESPONSE Separator

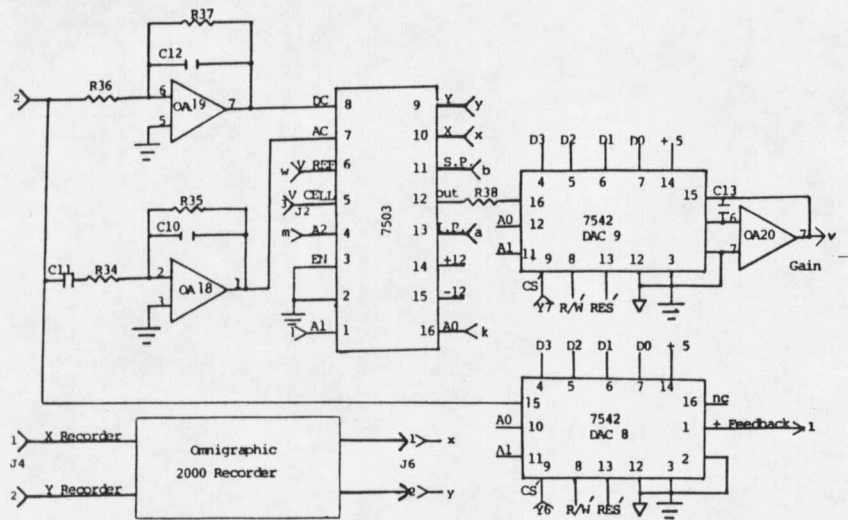


Figure 11. AC/DC Separator, + Feedback, and Omnigraphic Recorder.

The DC separator, which looks at the pure resistive effects of the cell (0 degree phase shift), is comprised of OA #19 a voltage amplifier with an integrator C12 capacitor selected to limit the high frequency AC signal to a low level.

Positive Feedback and Gain

In the positive feedback circuit, the cell current (as a voltage) is taken directly from the current amplifier OA #26 and inserted into a digitally controlled resistor DAC 7542. This DAC controlled by software enables a portion of the cell current to be feedback in a "positive" sense to the potentiostat bus line to appear as an offset voltage on the counter electrode that matches the IR drop due to the uncompensated cell resistances. The program for the

positive feedback circuit is used to compensate for uncompensated IR drop within the cell and must also prevent oscillation in the cell. The digital signal to this converter (DAC 8) which acts as an attenuator, is increased stepwise until oscillations occur in the potentiostat then the digital signal is backed off to below the threshold level.^{24,25}

The gain control circuit (DAC 7542, a computer controlled resistor module) sets the relative size of all the voltages sent to the A to D converter (ADC 574A) which is read by the computer. Eight different potentials are relayed to the gain control DAC via an one in eight multiplexer, 7503.²⁵ The voltages selected for the multiplexer are: (1) initial potential, (2) step potential, (3) voltage reference (from OA #23), (4) the cell voltage, (5) separated AC, (6) separated DC, (7) X recorder (cell voltage), and (8) Y recorder (cell current).

Sample and Hold with Analog to Digital Converter

The sample and hold circuit, which consists of a voltage follower (current amplifier) with a holding capacitor, works in conjunction with the analog to digital converter (AD574A),²⁶ Figure 12. The AD 574A is a complete 12 bit successive-approximation unit with 3-state output buffer circuitry and a 12 bit accurate 10 volt

reference voltage. This voltage reference is used as the reference source for the DAC 7542's and the DAC 76.

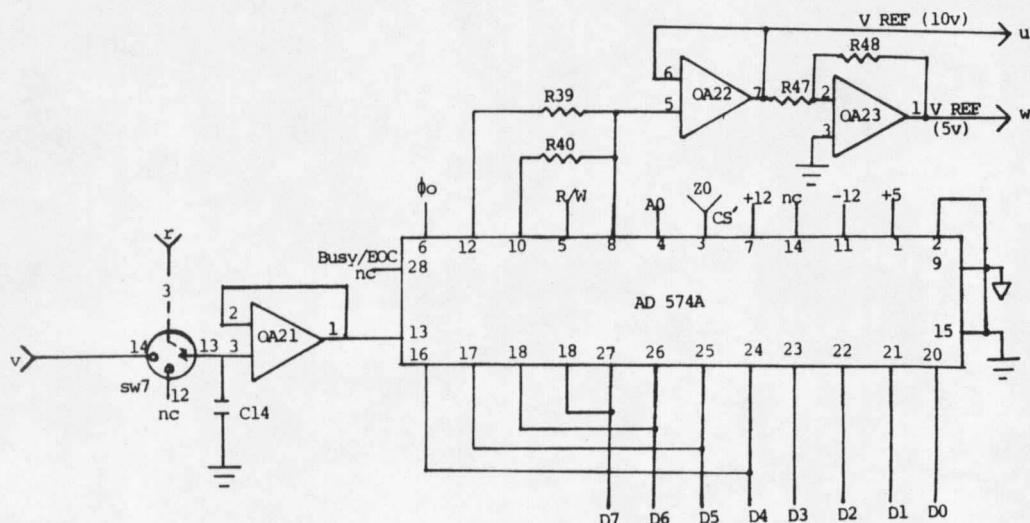


Figure 12. Sample and Hold, A/D Converter, and Voltage Reference Generators.

From the electrochemical cell all of the derived voltages are analog and to be processed by the computer these signals must be converted into digital numbers. During the read operation the sampling capacitor, C14, holds the changing analog voltage at a fixed level long enough for the A to D to convert it to digital data and with software to transfer this information back to the computer. The data is then stored and processed to the screen and/or printer as an analog number.

X and Y Recorders

Since a cyclic voltammogram is a plot of voltage (X axis) vs. current (Y axis), two DAC 7542's are used. The circuitry for both the x and y channels of the recorder are identical to the circuitry for the initial potential and step potential except the output voltage, not a current, is fed to the recorder, thus they do not have output resistors. The analog signals from the electrochemical cell, the voltage and the current, are digitized by the AD 574A and transferred to the computers memory where it is stored in an array. Since the response time of the computer is faster than that for the omnigraphic 2000 recorder, the data is held by software and the speed of data transfer is then matched to that of the recorder.

The Electrochemical Cell

The physical dimensions of the electrochemical cell (a cylinder) is 4.5 cm high by 2.5 cm in diameter giving an overall volume of 22cm^3 . The cell was filled with a 10 ml sample of electrolyte and two to five microliters of solute dissolved in a solvent. The three electrode array (working, counter, and reference) have dimensions of 0.5 cm by 0.5 cm for the working and counter electrodes and a four millimeter glass tube with a frit made up of porus vycor with a silver wire coated with a silver chloride for the reference electrode. Within the cell is also an argon

inlet line and a stirring bar.

The platinum working electrode is mercury coated by first cleaning the platinum with hot concentrated nitric acid and rinsing in distilled water. The electrode is then held in a 1 N solution of perchloric acid over a mercury pool for several minutes at a potential of three volts or enough to evolve hydrogen gas at the electrode surface. After several minutes of evolving hydrogen gas the electrode is dipped into the mercury pool maintaining the three volt potential for an additional minute allowing the mercury to adhere to the platinum surface.²⁷

Argon, when it is discharged from its bottle is dry, and to prevent electrolyte evaporation the argon is presaturated with distilled water by allowing it to flow through a column of distilled water in a thermostated unit to maintain the same temperature as the cell.

When chemical reactions approach thermodynamic equilibrium they become very sensitive to their environment. Three conditions within a cell that can cause a thermodynamic change in a reaction are: (1) aerobic vs. anaerobic conditions; (2) temperature changes; and (3) changes in the electrode surface.

Aerobic vs. Anaerobic

Because oxygen is chemically reactive with many substances and electrochemically reducible, the electrochemical process requires the exclusion of oxygen. This is generally done by purging the system with a flow of an inert gas (e.g. nitrogen, argon, helium, etc).

The choice of inert gas used is argon which is bubbled into the solution at 15 psi. The reason for argon is two fold; the solute that is being used is a surfactant and nitrogen which, when it is used, causes the surfactant to bubble whereas the argon does not. Secondly, the argon which is heavier than the oxygen floods the cell and displaces the oxygen, but helium and nitrogen which are lighter than oxygen may leave an oxygen residue at the solutions surface.²⁸

Temperature

Diffusion coefficients in aqueous solutions have a temperature coefficient of about + 2%/degree.²⁹ Which means that the voltammetric peak current increases about 1 to 2%/degree. The rate of follow-up chemical reactions of reactive species produced at the electrode surface depends even more strongly on temperature. For these reasons, temperature control to +/- 0.1 degree celsius or better is required for reproducible and careful quantitative work.

This is accomplished by circulating water in a jacketed cell.³⁰

The Electrode Surface

To be able to determine reaction rate or an oxidation/reduction sequence, a reference point for the reaction is necessary. To accomplish this the electrodes must be 'clean' (no double-layer capacitance) to start with. Cleaning the electrode surface can be done by stirring the solution fast enough and long enough to get a randomized mixing of anions and cations in the sample solution. For good reproducibility between runs each mixing should be consistent (i.e. the same speed and time). This can be accomplished very precisely by using computer control and a zero crossing triac driver (solid state digital to high voltage relay, see Figure 13).³¹ The zero crossing switch is used to prevent noise pulses which can interfere with the voltammeter or the computer.

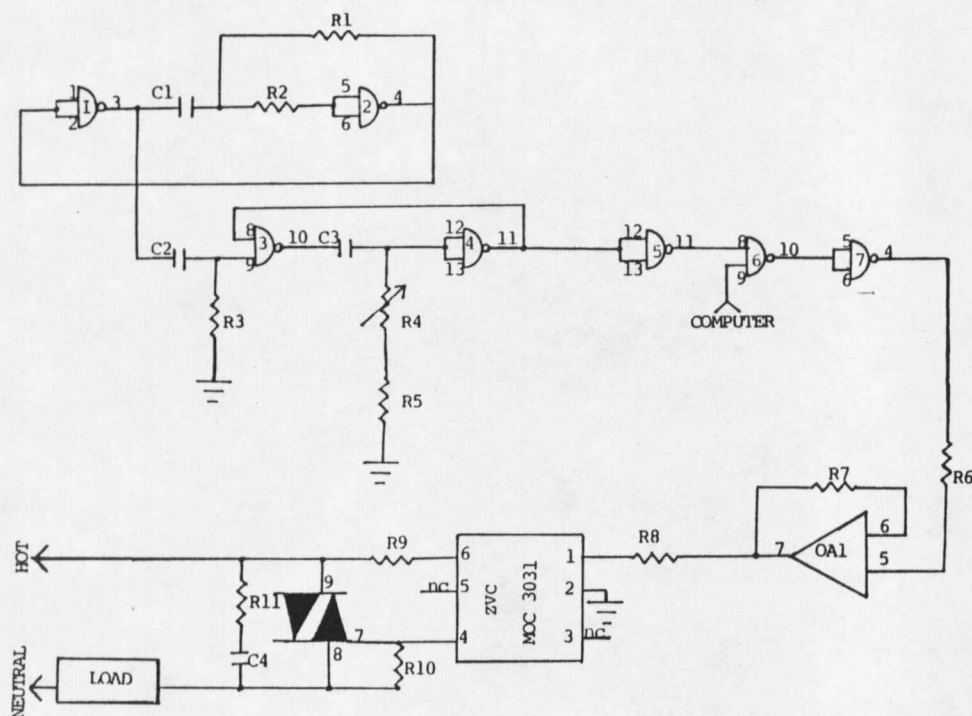


Figure 13. Magnetic Stirrer Controller.

The digital logic that is used to perform this task uses an astable multivibrator to gate a monostable multivibrator which sets up a variable 'time on' positive waveform for the stirring motor. When this positive waveform is 'ANDed' with the positive five volt signal (logic 1) from the computer, the stirring motor is energized through the zero crossing triac. The length of motor on time is therefore controlled by the computer's software.

ACCV SoftwareForth

The software package developed for the ACCV is extensive. The language called FORTH has many uses but was developed primarily for instrumentation. There are numerous reasons why FORTH is good but one reason makes it an outstanding tool for research, its indirect threaded format structure.

Threaded format structure is a bottom up configuration which requires that all 'words' (sub programs) are to be defined before using them. Each word has a definition which may be anything from a mathematical formula to an error message. A complete program does not have to be written to test a portion of an instrument, just the area that deals with the section under investigation.^{32,33}

The ACCV Program

The ACCV program is based on a menu driven system. The main menu is the main branching point in the program. The full auto test, the selected tests, calibrate instrument, single run, multiple runs, and quit program are the six sub-programs that make up its itinerary (Figure 14).

A C CYCLIC VOLTAMMETRY

MAIN MENU

1. Initialize Program
2. Calibrate Program
3. Full Auto Test
4. Selected Tests
5. Run Menu
6. Quit Program

Please type number of item selected

Figure 14. Main Menu for the ACCV.

Test Programs

The full auto test and selected test are identical except that the full auto is a threaded test going from one section of the instrument to another without manual instruction or intervention. The tests are to measure each of the digital to analog converters, the analog to digital converter, and the AC generator by loading a voltage value at the computer terminal and reading the correct voltage response at the computer screen/printer and/or at the test points on the ACCV multilplexer, AD 7503, using a voltmeter. If any of the integrated circuit outputs are outside of specifications then the calibrate program is called and ran. This allows a positive or negative offset and span correction to be applied to the offending DAC or ADC to bring in the correct voltage.

Calibrate Program

In the calibrate instrument menu (see Figure 15) there are five sub-routines for the complete calibration of the ACCV. Although the AC frequency generator and attenuator hardware is physically in place in the interface the software for it has not yet been completed as is the programming for the positive feedback. The other four: the A to D, the D to A's, the sweep rate generator, and the cell current constant have been completed. These will briefly discussed.

CALIBRATE INSTRUMENT

MENU

1. A to D Converter Tables
2. D to A Voltage Converters
3. Sweep Rate Generator
4. AC Frequency Generator
and Attenuator
5. Cell Current Constants
6. Quit Program
7. Return to Main Menu

lease type number of item selected

Figure 15. The Calibrate Menu.

A to D Converter

In the case of the gain control circuit a maximum output to the A to D converter should be within sixty to one hundred percent of full scale for best sensitivity. A test run for the maximum current peak on the cyclic voltammogram is made and peak current is compared against the current saturation level. A software program was generated to take the calibrated gain at all gain levels (between 0 and 21) and fill the proper table for saving in the running file for the run sub-program.

D to A ConverterS

The D to A converter subcalibrate program gives the user a message on the full scale (± 10000 millivolts) and the zero offset (0 millivolts) for both the positive and negative outputs. The digital to analog converters measured in this sub-program are the Initial Potential DAC, the Step Potential DAC, the X Recorder DAC, and the Y Recorder DAC.

Sweep Rate Generator

The sweep rate program initiates a sweep rate table (both positive and negative), also for the running file, with a printed message giving the sweep rate number (0 to 31), the number of millivolts per second initial voltage, the value of the voltage at the end of the run, and the number of 40 millisecond repetitions it take to achieve the

final voltage.

Cell Current Constant

When the current is finally 'read' by the A to D converter it is stored as a digital number. To do any quantitative work that number must be converted to the actual current value from the cell. This conversion number is done during calibration. A known voltage is applied to a 'dummy' cell with a 10,000 ohm resistor acting as the cell resistance. A cell current now can be calculated and then used to convert the digital number to their respected current values.

The Run Programs

Figure 16 shows the run menu is basically divided into three sections, the single run, the multiple runs, and data enhancement.

RUN MENU

1. Single Run
2. Multiple Runs
3. Data Enhancement
4. Return to Run Program
5. Quit Program
6. Return to Main Menu

Please type number of item selected

Figure 16. The Run Menu.

The Single Run

In the case of the single run the operator has the option of using the last run parameters which have become the default values or of changing any of the parameters individually. Timing is very critical in the run area of the ACCV program. When the respective voltages: initial potential, step potential, and limit potentials (voltage points where the voltammogram sweep is to reverse) are entered along with the desired resolution, the total number of data points to be collected are calculated (maximum 4095). From this value and the sweep rate, the number of clock cycles (clock cycle is 0.9777777 usec) per data point are found.

A limiting factor is the conversion rate speed at which the analog to digital converter (ADC) can convert the analog current or voltage to a digital number and store it in a designated place in the computer memory. The 'fast' limit for the ACCV is approximately 100 microseconds per data point, equivalent to about 10 volts per second at 1 mV resolution. Down to 6 milliseconds per data point the pen of the Omnigraphic 2000 x-y recorder cannot follow accurately the data transferred to it. At slower sweep rates the recorder can follow the data in real time. In all cases, the data is stored into computer memory and at the end of the run all parameters and run identification

are saved to mass storage (floppy disc). The data which can be brought back into computer memory from the disc is transferred to the recorder DAC by a delay loop that matches the response time of the x-y recorder.

The Multiple Runs

In the multiple runs sub-program, the sequence and timing requirements are the same except that a program loop is generated to implement successive runs, manually at different sweep rates, until the requested cycles are completed. There are four different scenarios for the multiple runs. Two in delayed time (data to mass storage first) and two in real time (data to x-y recorder and mass storage) both have the option of stirring or not stirring between runs and all have a table for variable sweep rates to be set as desired.

Data Enhancement

The results of being able to store the response current or voltage as a high resolution (12 bit) digital number has enabled voltammetry to benefit from precision data enhancement. With the cyclic voltammeter built in 1982, background currents due to solvent and/or contaminant reaction and double layer charging could only be removed manually from the reactive species voltammograms obtained on the X-Y recorder. With the current software program, now both the background and the reactive species plus

background can be stored into memory and then unwanted background eliminated by subtracting data point by data point.

Another section of the enhancement program allows the user to select only specific areas of the response curve for analysis. Since the currents are stored in memory under sequential addresses, by selecting a beginning and an ending address all the current numbers between the two limits will be processed to find the potential at the maximum current point or to be transferred to the x-y recorder to produce an expanded segment of the voltammogram. This program will also allow data averaging or curve fitting to reduce noise in the future.

The main menu is the main branching point for selection of the calibration, testing or running sub-programs. But after any run sub-program is finished the computer automatically returns the user to the run program menu where another run or return to main menu can be selected.

RESULTS AND DISCUSSION

Spikes and Noise

Of all the problems associated with constructing and programming of the ACCV, one stood out as the most significant. Due to the stringent timing requirements of data collection an assembly language routine was employed in this program section. However during the test after this routine was employed, when the voltammeter was selecting the dc current mode on the multiplexer (7503), many spikes of two to three volts in magnitude were noted (Figure 17).

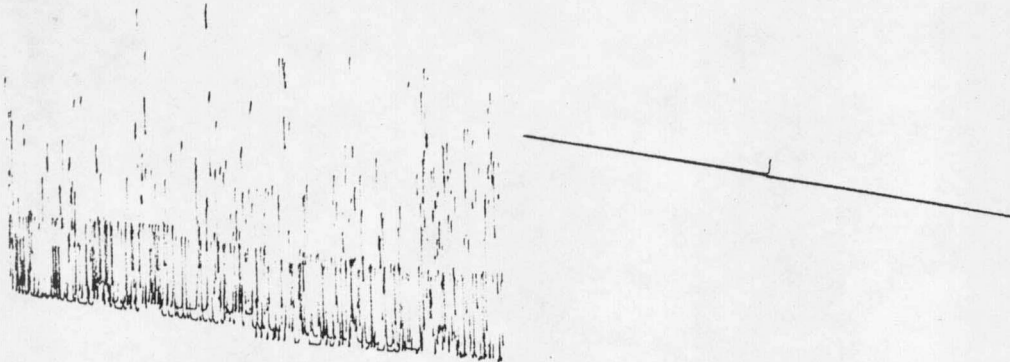


Figure 17. Example of spike problem of the ACCV.

The multiplex channel is selected by the I/O logic chip 6522A (VIA) with a number between 0 to seven (binary 000 to 111). Fortunately, during initial testing, when a binary seven (which multiplexed the cell voltage) was selected the subsequent waveform was clear of spikes. But when any of the other channels were selected, spikes appeared. It was further noted that when the multiplex address number had more than one zero that the spikes increased in number, with the address for DC current (000) having the most spikes of all. Removing the multiplexer chip and hard wiring the dc current line from OA #19 pin seven (see Figure 10) to R38 did not change the situation. Spikes in the the same ratio and magnitude were still there when any of the offending channels where selected although the multiplexer was removed. The circuit showed upon close inspection that only the ORB bits of the 6522A I/O chip where being used under these conditions and the problem might involve the ORB register.

SCR # 8

10 5 L: BM7 1- # LDA ORB AND ORB STA ATOD LDA N 1- STA

Figure 18. The ORB section of the ACCV assembly language code.

The only place in the assembly language routine in CV-R where ORB is involved is screen eight, line ten, (see Figure 18). Here the accumulator is loaded with the

channel #, 'ANDed' with whatever bit pattern there is from the ORB register and the result stored back in the ORB Register to clear the hold switch. Immediately following this the A to D byte was read into the accumulator and its value showed occasional random hi bytes.

The spikes were removed from all channels of the multiplexer when the assembly language routine was rearrange to separate the loading and storing of the ORB register from the sample taking routine of the A to D and the sample and hold switch was left on until after the A to D was complete.

When a dummy cell was installed in the potentiostat there was no observable noise on the system, but when a real cell with a solution of ten ml of 0.1 M sodium sulfate was used with the three electrode system, high frequency noise signal was seen in the x-y recorder and in the data file. Sawyer,³⁴ in his book "Experimental Electrochemistry for Chemists", recommends putting a damping capacitor between the counter electrode and the reference electrode to stabilize this common type of oscillations. The filter capacitor (C12) in the AC/DC separator circuit was also increased to give a time constant of C12 R36 of 5 milliseconds. A combination of 0.33 uf for the C17 (potentiostat capacitor) and 0.1 for the C12 gave the best noise suppression at all sweep rates for this cell, using the large Platinum flag electrodes

(0.25cm² area).

Input Voltages

Both accuracy and precision (reproducibility) have been increased because of the implementation of integrated circuits. Through the calibrate program it is now possible to know exactly the voltages (as current values) that are being applied to the cell and that the response current from the cell is also correct. In Table 1 the initial potential (DAC #1), as loaded from the keyboard is compared to the multimeter reading at the input to the electrochemical cell on the potentiostat (OA #24 pin 1) and at the input to the sample and hold circuit (SW #7 pin 14). A gain value of two (4095/4010) is typed in to compensate for the signal attenuation, caused by resistor precision (or lack of it) between the cell and the sample and hold.

Table 1. Voltage comparisons in mV and % error after calibration on Initial Potential DAC.

Component name	Keyboard	OA #24	% Error	SW #7	% Error
I.P. DAC					
RUN# 1	180	-187	4.0	166	7.6
RUN# 2	4000	-3980	.5	3940	1.5
RUN# 3	8000	-8050	.625	8000	0.0
I.P. DAC					
RUN# 1	-180	177	1.6	-194	7.8
RUN# 2	-4000	4030	.75	-4000	0.0
RUN# 3	-8000	8050	.625	-8000	0.0

The largest error occurs at the lowest input voltages because the DAC's are digitally controlled and subject to a ± 1 difference in the least significant bit, thus the lower voltage values and are subject to more error.

Under these conditions of gain the DC sweep generator had been operated at its maximum of ± 12000 mV/second sweep rates with a two mV/data point resolution (to avoid over running timing) with good results. Higher sweep rates could be achieved with this system e.g. 100,000 mV/second by modifying the RC values of the sweep rate generator, but the resolution would have to be cut to 10 mV/data point to allow the A to D conversions to keep up. In Table 2 the actual sweep rate voltage, entered on the computer in mV/second are compared to the signal (from the DAC 76) at the input of the integration circuit, SW #5 (start/stop run, see Figure 7).

Table 2. Sweep rate voltage comparisons in mV and % error after calibration on DAC 76.

	Keyboard	SW #5	% Error	Keyboard	SW #5	% Error
1.	63	90	42.8	-44	-50	13.6
2.	157	179	14.0	-141	-137	2.8
3.	359	326	9.2	-249	-236	5.2
4.	1072	1000	6.7	-1076	-1015	5.7
5.	2315	2200	5.0	-1917	-1837	4.2
6.	3206	3050	4.9	-3212	-3080	4.1
7.	5718	5440	4.9	-5607	-5440	3.0
8.	7507	7940	5.8	-7261	-7940	9.3
9.	11763	11110	5.7	-10159	-9520	6.3

The keyboard input voltage is in millivolts and the % error is a relative error. On the runs, 1-3 is in the low range 0 - 500 millivolts, 4-6 is in the middle range 500 - 5000 millivolts, and 7-9 is in the upper range 5000 - 12000 millivolts. The primary operating range and area of greatest consistency is the medium to low upper ranges 500 - 8000 millivolts. The % error in this range has a mean of 5.4 %, a standard deviation of 1.25 %, and a standard deviation from the mean of 0.27 %. The lower sweep rate values show the most error because again the lower bits are subjected to the +/- 1 difference in the least significant bit.

Waveform Reproducibility

Because of the complete computer control over the stirring time and intensity of the solution, the variability of mixing of the double layer at the electrode surface is now removed. With the use of timing loops (software), an exact time length can be generated for each stirring sequence along with a ten second wait period to allow the solution to come to rest. More important to waveform reproducibility than the stirring sequence, is the time allowed for the electrode to approach a point of equilibrium with regard to adsorption and redox. The longer the wait period between runs, the higher the initial

current values. A complete run including computer program compiling time is approximately five minutes. All this waiting time has to be taken into consideration for good quantitative results. Figure 19 a and b, depicts two runs each of an air saturated 0.1 molar solution of sodium sulfate. The first run of Figure 19a had a five minute wait period (upper trace) and a forty second wait period (lower trace). Figure 19b is the same sample, with identical parameters, but with two runs each having a forty second delay from the previous run.

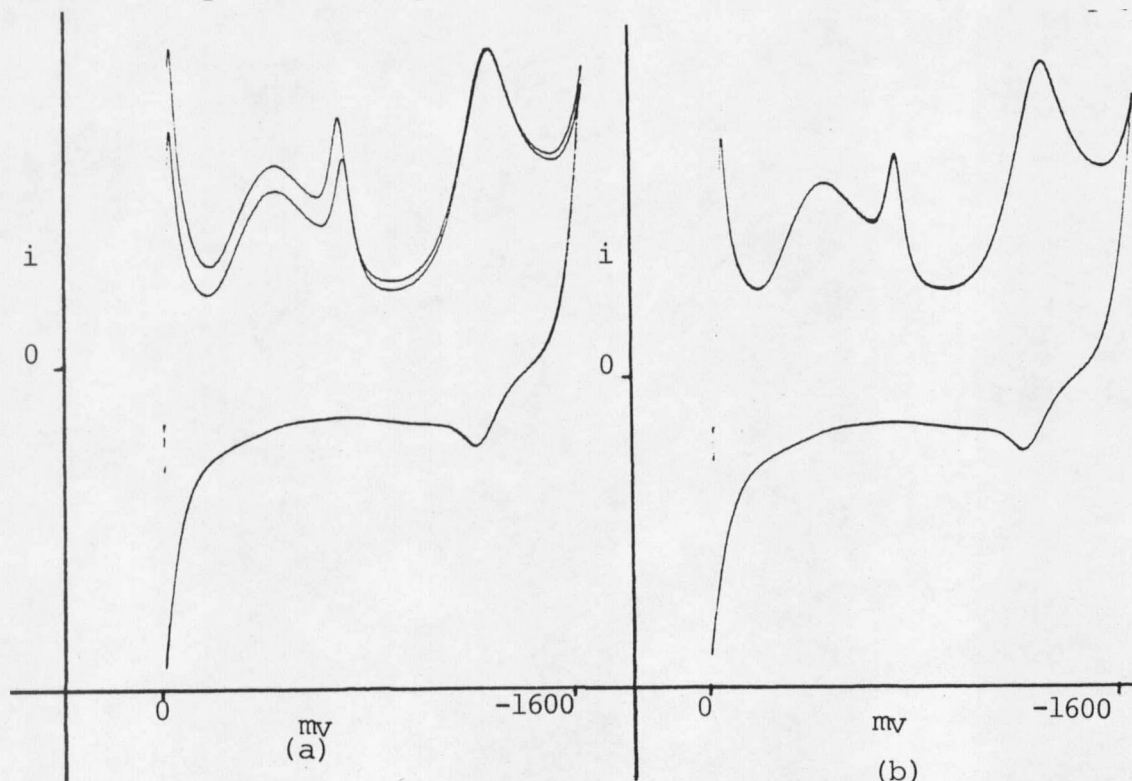


Figure 19. (a) 0.1 M Sodium Sulfate saturated with air, 4023 mV/sec, init. potential -400 mV, neg limit -1600 mV, two runs, five minute and forty second wait periods. (b) 0.1 M Sodium Sulfate, two runs, identical conditions, forty seconds wait period each.

There are times when renewing the double layer of the electrode surface is not desired, especially when looking at just a diffusion process within the cell. But how much is the stirring going to effect the output waveform of the samples? Figure 20 shows three waveforms superimposed on each other, with one second, ten second, and fifteen second actual stirring time and identical wait periods of five minutes.

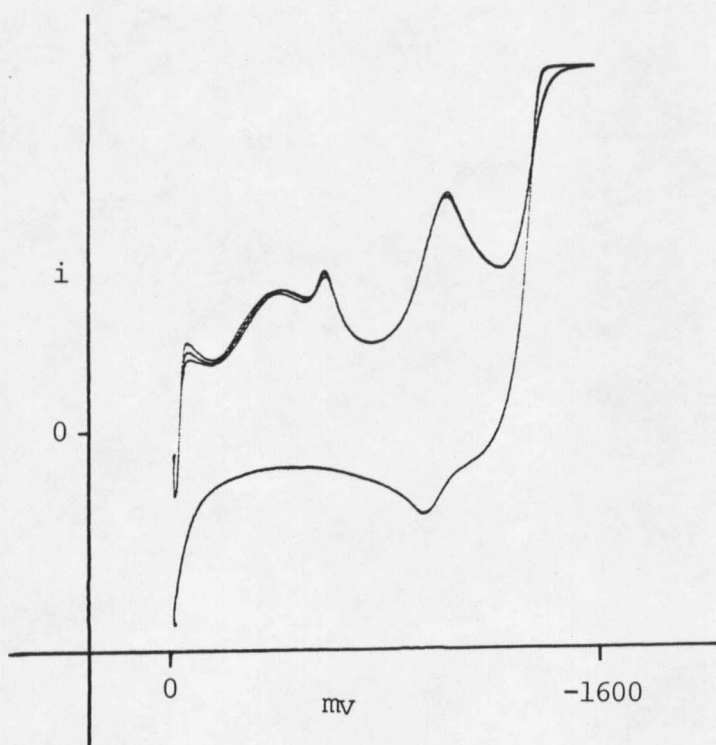


Figure 20. Effects of stirring at three time intervals: one second, ten seconds, fifteen seconds.

With the increased stirring time the peak currents only grew slightly larger. By comparing the waveforms in Figures 19 and 20, it seems that the stirring had only a slight effect and it is mainly the precision in starting each run at the same time or the same equilibrium point that gives good quantitative results.

Real Time Versus Delay Time

In all cases, whether the ACCV is running in real time (slow speed) with the x-y recorder operating concurrently or delay time (fast speed), the data first goes to computer memory, at the end of the run all current samples as digital numbers will be sent into mass storage for later evaluation. The question arises is there an error when the current sample is converted into a digital number then back again to a current to the x-y recorder. Figure 21 shows again the comparison for the sodium sulfate solution. The first run is in real time and superimposed the same results only in a delayed plot after the raw data was brought back from mass storage.

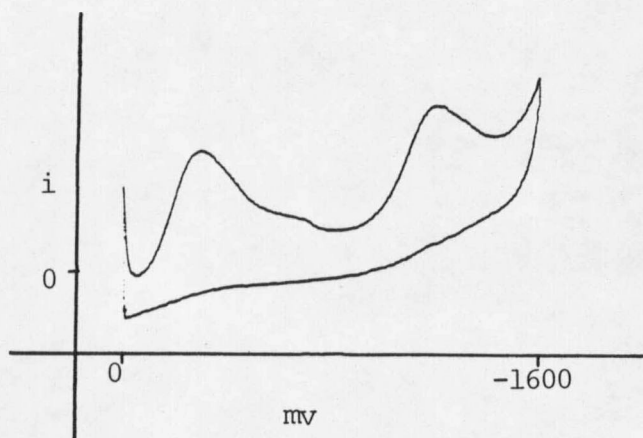


Figure 21. 0.1 M Sodium Sulfate saturated with air, 65 mV/second sweep rate, two runs, one in real time superimposed with a delay plot from mass storage.

Again the currents on each of the cyclic waveforms show that the waveforms are identical, which substantiates the precision of the digital integrated circuits of the ACCV. By careful and frequent calibration of the digital I/O circuits their errors can be kept to a minimum.

Background Elimination

When the cell potential for a Mercury electrode goes far enough negative then current rises exponentially due to electrolyte or solvent reduction, which limits the effective potential range of the system. If the background current is allowed to rise to more than ten to twenty percent of full scale then a portion of the response from the reactive species may be lost. This situation can only come about at fast sweep rates, where the double layer charging current is large. By using the data enhancement

program, background elimination for selected areas of the response curve can be obtained. Figure 22a shows a cyclic voltammogram with Lindane (5×10^{-4}) as the reactive species and Tetraethylammoniumbromide and Tetradecyltrimethylammoniumbromide (a surfactant) as the supporting electrolytes. In Figure 22b the voltammogram is of the electrolytes alone while 22c is the resultant waveform with the electrolyte background having been subtracted.

The area at the extreme negative limit (-1600 MV), has little informational value because of the high solvent current peak. By adjusting the negative limit inward (more positive) to remove the high current peak and then doing a background elimination of the whole waveform a smooth resulting curve (Figure 22c) is obtained with clearly defined current peaks.

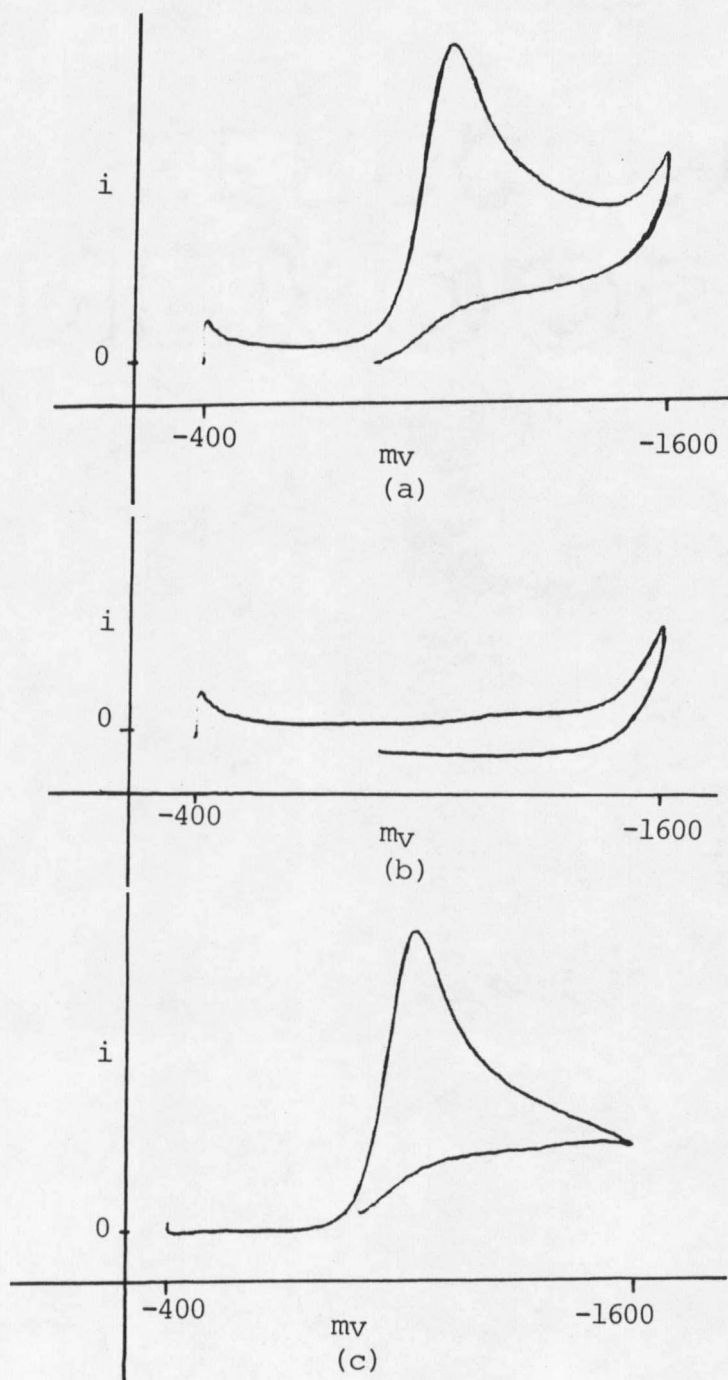


Figure 22. Background elimination of Tetraethylammoniumbromide and Tetradecyltrimethylammoniumbromide from Lindane. reduction. (a) Reactive species and background. (b) Background only. (c) Background eliminated.

SUMMARY

As electronic devices e.g. integrated circuit chips, operational amplifiers, and analog switches improve so does voltammetry. Three areas that have showed marked improvement in ac cyclic voltammetry because of the electronics are: 1) computer control of summing point currents, 2) precision (reproducibility) of successive waveforms, and 3) data enhancement.

With previous voltammeters the waveforms were the exact cell response of the currents supplied to the working electrode to the x-y recorder (magnified by the mechanical response time of the recorder). But because of the manual switching of voltages and the inability of being able to superimpose correct voltage offsets to the operational amplifiers, precise application of currents to the cell was difficult. With the DAC 7542's and the calibrate software program now exact offset voltages, if needed, could be implemented on to the operational amplifiers to output precision currents to the summing point in the potentiostat.

Reproducibility is only partially guaranteed by the precision of the digital resistors (DAC 7542's) supplying the currents to the cell. The cell itself, at the electrode-solution interface, is responsible for the

waveform consistency. Previously the cell solutions were stirred using a Corning magnetic stirrer to renew the electrode surface. With computer software and the enhancement of the Corning stirrer, using a digital stirring motor switch with a digital to high voltage triac driver, concise stirring routines were generated thus allowing the electrode-solution interface to have the same random mixing of ions for each run. But more important than that is the ability with complete computer control to have exact times between each run to guarantee that the solution is at the same point in equilibrium every time, thus giving very precise waveforms and digital data stored in mass storage.

Data enhancement has had the greatest impact on the development of the new cyclic voltammeter. By being able to digitalize the current from the electrochemical cell as a digital number it allows the user to reproduce any section of the waveform at will, to eliminate background interference, or to pick out the potential of the reactive species at its maximum current points.

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