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**THE DESIGN AND APPLICATION OF A  
PROGRAMMABLE COULOSTATIC POLARIZER**

**By**

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**A DISSERTATION**

**Submitted to**

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## ABSTRACT

### THE DESIGN AND APPLICATION OF A PROGRAMMABLE COULOSTATIC POLARIZER

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A microcomputer controlled coulstatic electrochemical instrument has been slightly modified. The design principles and applications of the instrument, the programmable coulstatic polarizer (PCP), will be discussed. The PCP consists of an electrochemical cell, a digitally controlled charge generator for adding charge to the electrode, a voltage measurement system to monitor the working electrode potential, a real time clock to control the timing of experiments, and a microcomputer system to control the operation of charge generator, voltage measurement system and real time clock.

When an electrochemical cell is controlled by a potentiostat which is generally employed in conventional instruments, an IR error which is the product of the portion

[illegible]

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1000 0.25

• •

of current and the portion of resistance sensed by the reference electrode always exists. This error can be significant if the solution resistance is high or if the current is large. The PCP is based on the coulometric polarization method which employs the addition of charge pulses to the electrode and measures the electrode potential between charge additions when there is no current in the solution. The potentials measured with coulometric method are thus free from IR error.

The PCP can be operated in ways analogous to many electrochemical polarization modes where the charge, current, or potential must be measured or controlled. These can be accomplished without modification of the instrument hardware.

Some applications of the PCP have been achieved as follows:

1. Fast measurement of electrode capacitance:

Capacitance measurements for mercury electrode in 1.0 M KCl solution can be obtained within 8 seconds with 2 % RSD.

2. Electrode capacitance measurements for low concentration of electrolyte solution:

The concentration of KCl solution for capacitance measurement on mercury electrode can be as low as 10  $\mu$ M.

3. Charging current compensation for constant chronopotentiometry:

Compensation of charging current using blank electrolyte (KCl) solution has been performed for the

solutions of  $\text{TlCl}$  in  $0.1 \text{ M KCl}$ . A dramatic correspondance of transition times with theory is obtained. In-situ compensation of charging current allows the detection limit for cadmium to be as low as  $0.25 \mu\text{M}$ .

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## CHAPTER 1

### INTRODUCTION

Electrochemical instruments are often based on the potentiostat which tries to maintain the potential of the working electrode equal to a control voltage provided by a signal generator. The control signal may have a constant value or vary with time. Figure 1-1 shows an equivalent circuit for an electrochemical cell which is controlled by a potentiostat(not shown). The solution resistance is represented by  $R_s$ . The resistance of an electrochemical reaction which depends on the kinetics and the availability of electroactive species is represented by  $R_o$ . The double layer capacitance of the working electrode appears in the equivalent circuit as  $C_{dl}$ . On the solution side of the electrode/solution interface, there are ionic species and solvent dipoles. A change in the electrode potential causes a change in the distribution of ions and the orientation of solvent dipoles. Thus, the electrode/solution interface responds like a capacitor. A detailed discussion of the double layer capacitance can be found in Chapter 3. In a potentiostat, the electrochemical cell is part of a feedback loop in which the cell current is continuously controlled in order to minimize the difference between the measured value of the electrode potential and the desired (control signal)

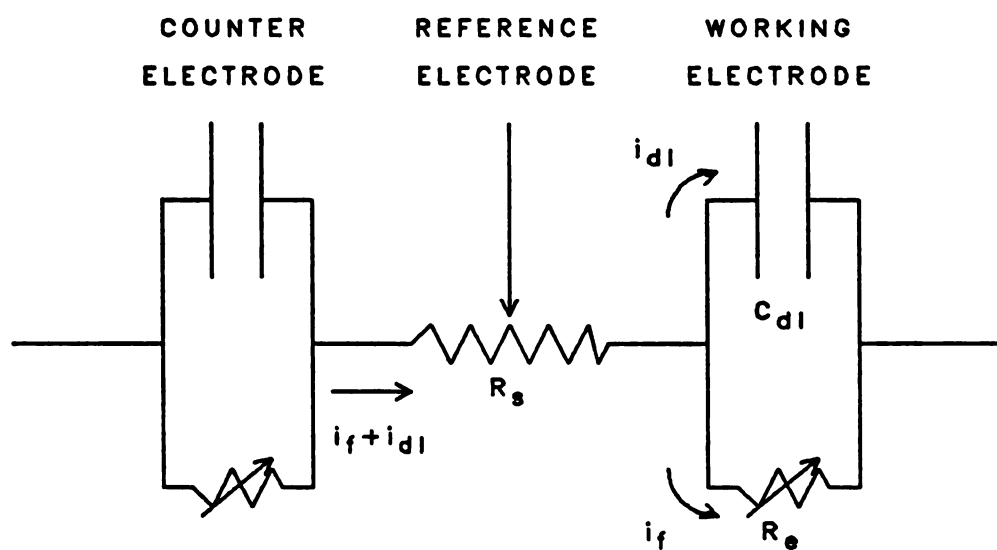


Figure 1-1. Equivalent circuit for an electrochemical cell controlled by a potentiostat

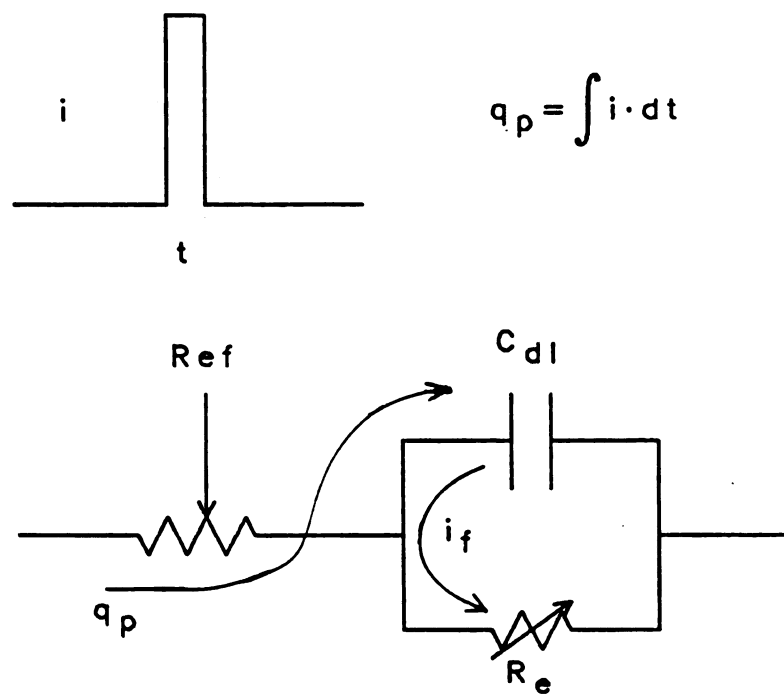
potential. However, the actual potential of the working electrode deviates from the measured value (and thus from the desired value) whenever there is a current in the cell. This deviation is caused by the IR drop which is the product of current  $I$  and the portion of the solution resistance  $R$  sensed by the reference electrode. In order to reduce the IR component of the measured voltage, solvents with high dielectric constant and high concentrations of supporting electrolyte are used. In some cases, a Luggin capillary reference electrode must be used to minimize the distance between the working and reference electrodes.

When the supporting electrolyte concentration is below 0.01 M (as is often the case when nonaqueous solvents are used), the IR drop can introduce a significant error in potential control.

Some electrochemists have tried to use potentiostats with positive IR compensating feedback (1-6) to reduce the error in potential control and enhance the system response. However, it has been found that the circuit tends to oscillate (3,5,6). A common method to compensate the solution resistance is to increase the level of compensation until the potentiostat/cell system is no longer stable. It was pointed out in a review paper (7) that this can be a rather inaccurate procedure, as many systems can be unstable at rather less than 100% compensation and, conversely, some systems are stable even beyond 100% compensation.

### A. Coulostatic Method

In the early 1960's P. Delahay and W. H. Reinmuth each published a series of papers in which they described the theory and applications of a new method, the coulостatic polarization method (8-12). Figure 1-2 shows an equivalent circuit of an electrochemical cell and an example of charge pulse for the coulostatic method. In the coulostatic method, a brief charge pulse (microsecond range) of  $q_p$  coulombs is injected into the cell and then the cell is kept in an open circuit condition. The quantity of charge may be controlled by applying a constant current  $i$  for a short period of time  $t$  or by injecting a known quantity of charge with a capacitor charged to a known voltage. After the charge pulse is injected, the Faradaic current  $i_f$ , or the charge consumed by the Faradaic process, is supplied by the charge on the double layer capacitor  $C_{dl}$ . The original coulostatic method usually involved the injection of a large charge pulse to alter the potential of an electrode from several to several hundred millivolts followed by the open-circuit monitoring of the potential. The potential/time curve can then be related to the electrode reaction processes of charge transfer, diffusion, and chemical kinetics (8,10,12). For example, for a simple redox system  $\text{Red} + ne^- \rightleftharpoons \text{Ox}$ , with both species soluble, with mass transport by semi-infinite diffusion, and with a constant double layer capacitance  $C_{dl}$ , the potential/time



**Figure 1-2.** An equivalent circuit and an example of charge pulse for coulometric method

relationships were derived for the following situations:

1. With a small potential perturbation  $\Delta E$  ( $nF\Delta E/RT \ll 1$ ) and with fast charge transfer reaction (12) (the rate of the reaction is completely limited by the diffusion of Red to the electrode surface),

$$\Delta E = \Delta E_i \cdot \exp(t/\tau_d) \cdot \operatorname{erfc}(t/\tau_d)^{1/2} \quad (1-1),$$

where  $\Delta E$  is the change of potential from its initial value,  $\Delta E_i$  is the initial potential perturbation,  $t$  is the time after charge injection, and

$$(\tau_d)^{1/2} = (RTC_{d1}/n^2F^2) \cdot ((C_{Red})^{-1}(D_{Red})^{-1/2} + (C_{Ox})^{-1}(D_{Ox})^{-1/2}) \quad (1-2),$$

where  $n$  is the number of electrons transferred,  $C_{Red}$  and  $C_{Ox}$  are the initial concentrations, other terms have their usual meaning.

2. With a small potential perturbation  $\Delta E$  and when the rate of charge transfer is limiting (12),

$$\Delta E = \Delta E_i \cdot \exp(-t/\tau_c) \quad (1-3),$$



where

$$\tau_0 = RTC_{d1}/nFi_0 \quad (1-4),$$

where  $i_0$  is the exchange current density for the charge transfer process.

3. With a large potential perturbation  $\Delta E$ , and with a fast charge transfer reaction,

$$\Delta E = (2nF(D_{Red})^{1/2}C_{Red}/(\pi)^{1/2}C_{d1})t^{1/2} \quad (1-5).$$

For  $C_{d1} = 20 \mu F/cm^2$ ,  $D_{Red} = 10^{-5} cm^2/sec$ , and  $n = 2$ ,  $\Delta E$  is equal to  $0.344 t^{1/2}$ ,  $0.0344 t^{1/2}$ ,  $0.00344 t^{1/2}$  volts/(sec) $^{1/2}$  for  $C_{Red} = 10^{-5}$ ,  $10^{-6}$ ,  $10^{-7}$  moles/liter, respectively (8,10).

The potential-time relaxation is a function of the double layer capacitance which is a function of potential. One of the major disadvantages of the original coulometric method is that the variation of double layer capacitance with potential complicates the analysis of the desired parameters.

The coulometric method reduces the effect of solution resistance because the current is zero when the electrode potential is measured. Therefore, the coulometric method can be applied to most non-aqueous solutions and lower concentrations of supporting electrolyte can be used to

reduce contaminations from the addition of the supporting electrolyte. In spite of the above advantages, which make the coulometric polarization an attractive technique for analytical applications, only a few applications of this method have been reported (some examples can be found in References 11,13-16). This may be due to the lack of rapid and intelligent control system with which to produce the traditional varieties of polarizing potential or current waveforms through charge pulse injection.

Charge pulse injection, which is used in traditional coulometric method to change the potential of a working electrode to a new value, can be used as well to maintain the electrode potential at a desired value as long as the size of the injected charge is small and the frequency of injection is sufficiently high.

The idea of controlling the electrode potential by charge injection has been used by Goldworth and Clem to develop the 'bipolar digipotentiogator' (17). The system uses the charge injection technique to maintain a desired potential and simultaneously serves as a current-to-digital converter. The system injects small charge pulses of constant size to the working electrode as often as needed to keep its potential at the desired value. The design of the bipolar digipotentiogator is based on dedicated hardware logic.

**B. A Microcomputer Controlled Instrument:**

**A Programmable Coulostatic Polarizer (PCP)**

In order to enhance the flexibility of the coulostatic method, a general purpose electroanalytical system based on a microcomputer-controlled coulostatic generator has been developed by Spyros Houdakis (18). This first microcomputer-controlled instrument has been improved substantially in this thesis work. The goals of the research work described here were to develop a flexible electrochemical instrument around the computer-controlled charge injection principle and to apply this instrument to some electrochemical experiments which standard electrochemical instruments cannot easily perform.

Computers have been used heavily during the last decade in the development of modern automated instruments. The dedicated computer can operate the instrument, calibrate the instrument, collect data, and make decisions during the course of the experiment. Microprocessors with greatly improved performance have been introduced into the market in recent years. Some microprocessors have an instruction cycle as low as 0.8  $\mu$ s. Microprocessors, with the aid of supporting chips such as memory, input-output registers, buffers, communication chips, interrupt controllers, timing controllers, etc., can be used as an intelligent controller for virtually any instrument. The microcomputer used in this instrument is a single microcomputer segment of a

multi-microcomputer system that has been developed in our research group (19). These microcomputers are based on the 8085 microprocessor chip first manufactured by Intel Corp.

The block diagram of the instrument is shown in Figure 1-3. It consists of:

1. an electrochemical cell with working, reference, and counter electrodes (W, R, and C),
2. a charge generator for the injection of charge to the electrode,
3. a voltage measurement system to monitor working electrode potential between charge injections,
4. a keyboard (KB) and a display (CRT) to allow operator communication,
5. a graphic controller to present the results of experiments in graphic form on the CRT,
6. a real time clock to control the timing of experiments, and
7. a floppy disk to store data.

The instrument is interfaced to a PDP 11/40 minicomputer to allow loading programs from its mass storage, and to use the minicomputer for faster data analysis and for hard copies of experimental results.

The instrument will be called the programmable coulstatic polarizer (PCP) since it is flexible through programming and can generate many types of coulstatic polarization waveforms. Several modes of operation of the

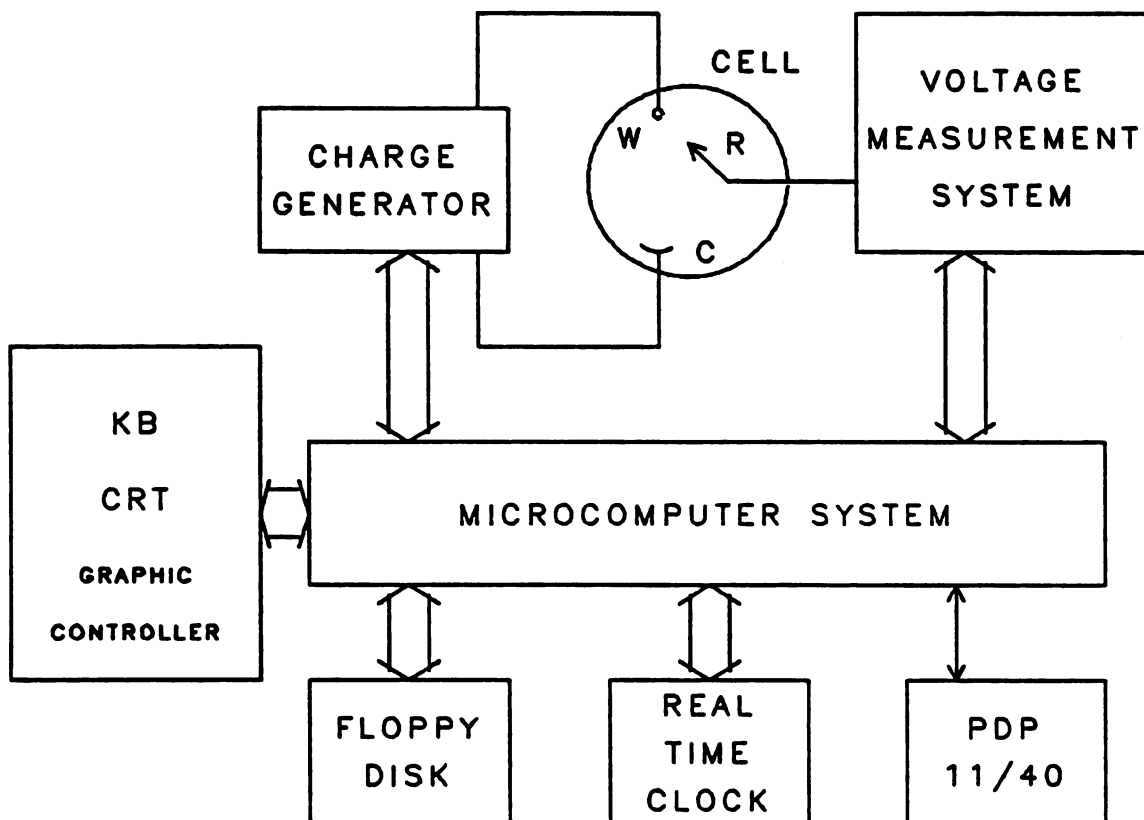


Figure 1-3.

Block diagram of the programmable coulostatic polarizer (PCP)

PCP will be described in Chapter 2, examples of applications will be presented in Chapters 3 and 4, and some possible applications will be discussed in Chapter 5.

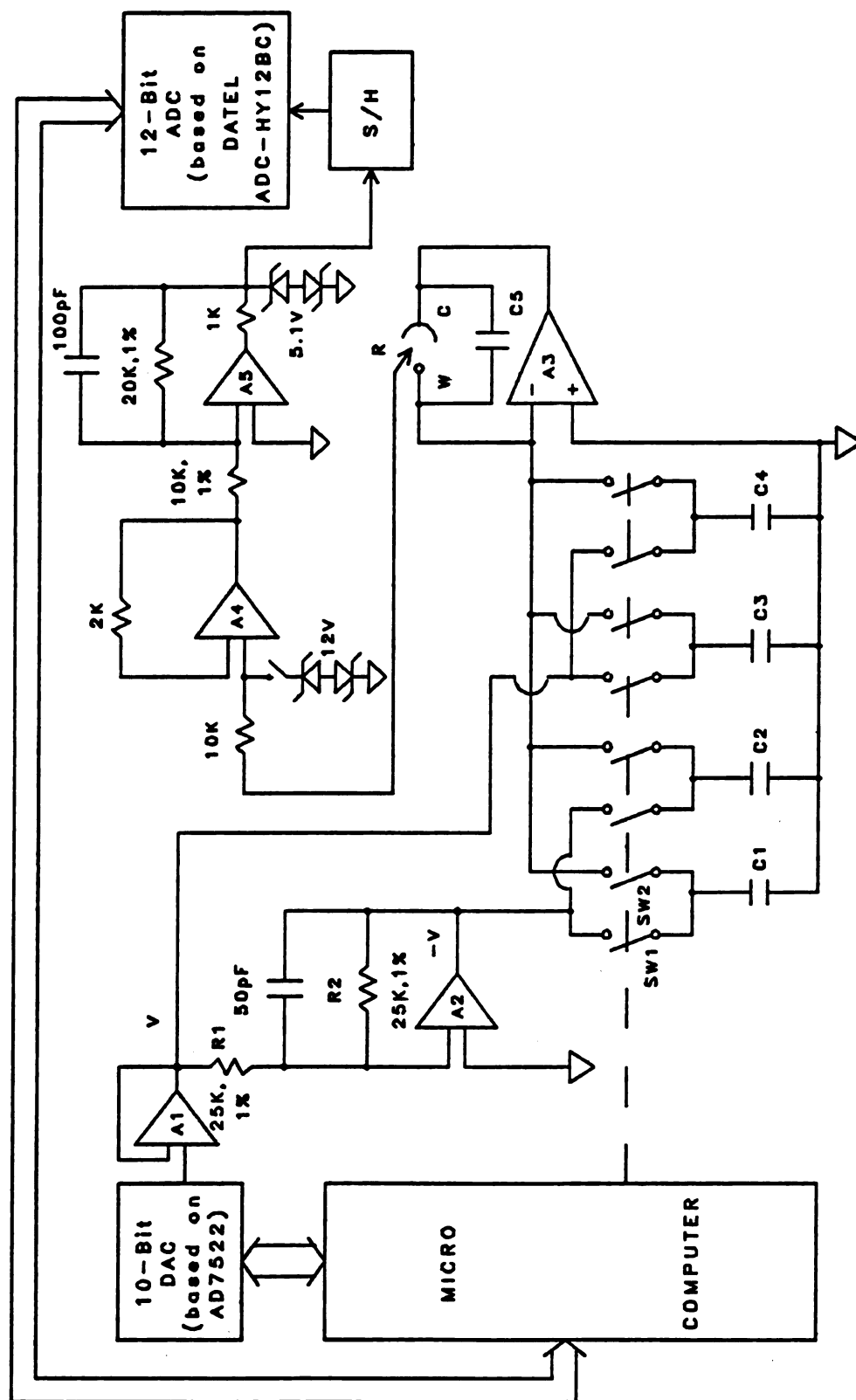
## CHAPTER 2

### THE DESIGN AND THE OPERATIONAL MODES OF THE PCP

#### A. Description of the Charge Generator and the Voltage Measurement System

Figure 2-1 shows a diagram of the charge generator and the voltage measurement system. The charge generator and the voltage measurement system are essentially the same as those designed by Spyros Hourdakis (18) except that a few components have been changed; a separate power supply is used, and grounding circuits have been redesigned and constructed in order to reduce noise. A detailed description of the circuits can be found in Hourdakis' thesis (18). Some modifications to these circuits will be discussed in Chapter 6. The design principles and important characteristics of the components and circuits will be discussed in this chapter.

The charge generator consists of a 10-bit digital-to-analog converter (DAC) and several capacitors, switches, and operational amplifiers. The microcomputer can control the DAC to produce a programmable voltage  $V$ . If the data for the DAC control is stored in the computer memory, the process of reading the data and controlling the DAC takes about 17  $\mu$ s. The DAC is of bipolar construction with a maximum output voltage of  $\pm 2.5$  V. It has a quantization





level of 4.88 mV. It is based on the AD7522 chip from Analog Devices which has maximum differential non-linearity of  $\pm 1/2$  LSB and an overall non-linearity of less than 0.05% full scale range.

The inverter, which consists of operational amplifier A2, and resistors R1 and R2, converts the programmed voltage V to the voltage -V of equal magnitude, but with opposite polarity. Both voltages V and -V are available simultaneously in order to save the time of reprogramming the DAC if the opposite polarity of voltage is needed.

The microcomputer can control the closing of switches by which the capacitors C1 or C2 can be charged to -V or the capacitors C3 or C4 charged to +V. A capacitor which has a capacitance below 0.01  $\mu$ F, takes less than 13  $\mu$ s to reach 1/2 LSB (2.44 mV) for a step change of 2.5 V or less.

The switches are SIGNETICS SD5000 FET analog switches with on resistance of 30  $\Omega$  and off resistance of  $10^{10}$   $\Omega$ . The leakage current is below 1 nA. The input capacitance is below 2.4 pF and the output capacitance is below 1.3 pF. Probably due to the coupling of the switch capacitance with the power sources ( $\pm 15$ V), a small amount of charge (about 20 pC) is always injected to the working electrode together with of the desired charge. This error is corrected by adjusting the baseline value of the DAC for a specific size of capacitor used. The adjustment can be performed automatically with the program BLVC.MAC which can be found

in Appendix B. The operational amplifier A3 is a Datel AM 405-2 FET input, high-speed amplifier with high input impedance of  $10^{12} \Omega$  and a fast slew rate of 120 V/ $\mu$ s. The amplifier can supply a continuous current of  $\pm 10$  mA and a peak current of  $\pm 50$  mA.

The microcomputer can connect the capacitor which has been charged to the inverting input of operational amplifier A3 by closing the proper switch (e.g., switch SW2 for the capacitor C1). The connection of the capacitor to the amplifier makes the voltages different at the two inputs of the amplifier. When the operational amplifier A3 detects a voltage difference between its two inputs, it amplifies this difference by a very large gain which is usually between  $10^4$  and  $10^5$ . The voltage of the capacitor (one of C1-C4) usually exceeds  $\pm 100$  mV and the result of this amplification exceeds the power supply voltage ( $\pm 15$ V). In this situation, the output voltage limits at 1 or 2 V less than the power supply voltages. The change of output voltage of A3 creates a potential drop across the solution and charge flows from the output of A3 through the counter electrode, through the solution, through the working electrode to the capacitor in order to reduce the voltage difference between the inputs of the amplifier A3. The current continues until the voltages at both inputs of A3 are equal. A consequence of this process is that the capacitor (one of C1-C4) is discharged and the charge is

transferred to the working electrode. If the working electrode is an ideal polarizable electrode (an electrode which does not leak any charge across the electrode solution interface), the charge is accumulated on the electrode. If it is not, the accumulated charge is equal to the charge injected minus the charge consumed by the Faradaic process. A capacitor C5 is placed in the feedback loop of amplifier A3 to prevent oscillation. The capacitor does not slow down the response of the circuit significantly if its value is small (such as below 1000 pF). The recommended value for this capacitor is between 100 and 1000 pF which is usually much less than the value of the electrode double layer capacitance. When a charge pulse is injected, a very small portion (between 0.01 and 0.1 %) of the charge goes to the capacitor C5 if the electrode capacitance has a value of 1  $\mu$ F. This error is so small that it can be neglected. Using this circuit, a charge can usually be injected to the working electrode within 50  $\mu$ s for solutions with an electrolyte concentration above 0.01 M.

The voltage measurement system consists of a voltage follower A4, an amplifier A5 with a gain of 2, a sample and hold circuit, and a 12-bit analog-to-digital converter (ADC). The ADC is a DATEL ADC-HY12BC 12-bit successive approximation analog-to-digital converter with a conversion time of 8  $\mu$ s and an input range of  $\pm 5$  V. The voltage of the reference electrode is amplified with a gain of 2 before

it is fed in the input of the ADC. The resolution of the ADC is 2.44 mV which corresponds to 1.22 mV resolution in the electrode potential measurement. The purpose of using the amplifier with a gain of 2 and the low pass active filter is to reduce noise. The operator can regard the quantization level of the voltage measurement system and of the electrode potential as 1.22 mV.

The microcomputer can command the ADC to convert the electrode potential to digital form. The microcomputer can then store the data, or compare the measured potential to the desired value and use this information to control the potential or make other types of decisions.

Several capacitors and associated switches can be used in the charge generator to enable the injection of both positive and negative polarities and different sizes of charge.

The charge generator and the voltage measurement system perform only two simple operations on the electrochemical cell: inject charge pulses to the working electrode and measure the potential of the working electrode. The use of a microcomputer as the control element of the operation of the PCP gives greater flexibility than it is found in conventional instruments. The operator has the ability, by programming, to determine how the operations of the charge generator and the voltage measurement system are to be used in order to perform an experiment, and he or she can program

the instrument to produce and apply any complex potential or current waveforms to the electrode. The flexibility of the PCP allows the operator to perform whichever electrochemical technique provides the best response for the investigated chemical system and also to perform some experiments which are difficult to perform with other instruments.

In addition to the flexibility of implementing a variety of polarization modes, the PCP maintains the characteristic advantages of coulometric method, i.e., IR drop errors can be eliminated so that higher solution resistance causes fewer problems and double layer capacitance information is available to aid in separating double layer charging and Faradaic current. Several operational modes are discussed in this chapter.

#### B. Controlled Charge Mode

The operator can program the DAC to obtain a voltage  $V$ , and select a switch to charge a capacitor  $C$ , in order to produce a charge of value  $C \cdot V$  coulombs which can then be transferred to the double layer of the working electrode. By choosing the capacitor value and the DAC voltage, the operator has the flexibility of generating a charge that can vary in size over several orders of magnitude. This allows the effect of the charge injection on the electrode potential to be varied from a fraction of a millivolt to several volts. The electrode potential is monitored both

before and after the charge injection.

The application of this operational mode to electrode capacitance measurement will be discussed in Chapter 3.

#### C. Controlled Current Mode

The equivalent of controlled current can be obtained either by controlling the quantity of charge per pulse to be injected to the working electrode and keeping charge injection rate constant, or by keeping the quantity of charge constant and controlling the charge injection rate. The current applied is equal to the charge per pulse times the frequency of pulse injection.

The application of this operational mode to constant current chronopotentiometry will be discussed in chapter 4.

#### D. Controlled Potential Mode

Controlled potential experiments can be achieved by comparing the measured potential to the desired potential at any specific time. If there is a difference, an appropriate amount of charge (e.g., the amount to make 1 mV potential perturbation) can be injected to the electrode in order to reduce the difference. This process can be repeated to within the resolution of the charge injection or potential measurement, whichever is larger. The desired potential can then be programmed to vary with time. Virtually all kinds of controlled potential experiments (e.g., cyclic voltammetry,

pulse polarography, chronocoulometry, rotating disk voltammetry, etc.) can be performed in this way by using the PCP.

#### E. Open Circuit Mode

If no charge is injected on the electrode, the cell is in an open circuit condition. The measured potential is then obtained when there is no current passing through the solution. In this mode, the PCP can be used for the potentiometric measurements of a PH electrode or other ion selective electrodes.

#### F. Combinations of Modes

The PCP can switch from one mode of operation to another by changing from the program for one mode to that of the other. There are several advantages associated with this: First, the switching of the PCP from one mode of operation to another is fast. In most cases, the switching time is between 10  $\mu$ s and 1 ms. Second, the switching is done by software and involves no undesired charge added to the cell. Third, due to this flexibility, the PCP at times can perform some types of multi-mode experiments which cannot be carried out with other instruments. Fourth, the need for several differential instruments to perform various kinds of experiments can be avoided.

## CHAPTER 3

### EXAMPLE OF CONTROLLED CHARGE EXPERIMENT:

#### ELECTRODE CAPACITANCE MEASUREMENTS

##### A. Introduction

A capacitance measurement technique developed in this thesis work is discussed in this chapter. The technique is based on the charge injection method. Because charge pulses can be applied to the electrode automatically and very rapidly, capacitance measurements can be made very quickly. The potential is measured when there is no current passing through the solution so solution resistance causes fewer problems than with continuous current methods. Electrode capacitances can thus be obtained in solutions of quite dilute electrolyte. For example, capacitance measurements were obtained from a hanging mercury drop electrode (HMDE) in various concentrations of KCl solution down to  $10^{-5}$  M. For concentrations of KCl above 0.01 M, 37 equally spaced data points with 2 % relative standard deviation over a 1.45 V potential range were obtained within 30 seconds. The capacitances of a HMDE in dilute potassium chloride solutions were obtained within 150 seconds for a  $10^{-4}$  M solution and within 30 minutes for a  $10^{-5}$  M solution.



## B. Background on Double Layer Capacitance Measurements

### 1. Qualitative Description of Electrical Double Layer

'Electrical double layer' is a term used to describe the array of charged particles and oriented dipoles which exist at any material interface. The modern qualitative picture of the electrical double layer at a metal-electrolyte solution interface is based on the model proposed by D. C. Grahame (20-22). The model is a modification of previous ones proposed by Gouy, Chapman, and Stern (23-26). The interface consists of several regions: (a) the metallic region, and, on the solution side, (b) an inner layer region of a few Å next to the metallic surface, and (c) an outer, or diffuse layer region which extends into the bulk solution a distance of several Å to a few hundred Å.

The metallic surface may bear positive or negative electric charge resulting from an excess or deficiency of electrons. The electric charge may be imposed on the metal by an external source of electric charge or current, or it may be generated by a Faradaic reaction at the interface. The inner layer, which is on the solution side of the interface next to the metallic surface, contains solvent molecules and sometimes other neutral molecules. When the electrode potential is near or more positive than the potential of zero charge, in most electrolyte solutions the inner layer also contains a fractional monolayer of ions

(usually anions) which are said to be specifically adsorbed. The plane which is formed by the electric centers of these adsorbed ions is called the inner Helmholtz plane (IHP).

When the interaction between an ion and the metal is not strong enough to desolvate the ion, the ion can not come as close to the metal as can those ions which are specifically adsorbed. The plane passing through the electrical centers of these solvated ions is called the outer Helmholtz plane (OHP). The principal interaction between the metal and the solvated ions is the ordinary long-range coulombic force and this is the basis of the Gouy-Chapman theory (23-25). The interaction of these ions with the metal is essentially independent of their chemical properties but dependent on their ionic charges and radius. The solvated ions near the electrode are said to be nonspecifically adsorbed. Due to the thermal motions of these ions, not all of them are located at the OHP, instead, they are contained in a three dimensional region, the diffuse layer, which extends from OHP into the bulk of the solution. The diffuse layer is very thin. For example, 99.99 % of excess charges in the diffuse layer for a uni-valent electrolyte at a concentration of  $10^{-1}$  M is within  $8.9 \cdot 10^{-7}$  cm, and at  $10^{-5}$  M is within  $8.9 \cdot 10^{-5}$  cm from the surface of the metallic electrode.

The metallic surface may bear a net electric charge and the solution side may have an excess of charged particles or

a net orientation of dipoles. The electrode interface looks like a capacitor and has the property of capacitance under equilibrium conditions. The differential capacitance of an electrode at constant chemical composition is defined as  $(\partial q^M / \partial E)_\mu$ , where  $q^M$  is the charge density on the metallic electrode, and  $E$  is the electrode potential. This term is very similar to  $(Q/V)$ , the capacitance for an ideal capacitor.

## 2. Usefulness of Double Layer Studies

The measured fundamental parameters of electrode kinetics may be strongly dependent on the structure of the double layer. The rate constant  $k$  for a given electrode reaction might be a function of supporting electrolyte or its concentration. When there is no apparent reaction involving the electroactive species of interest (e.g. complexation or ion-pairing), a non-linear plot of the logarithm of the rate constant  $k$  versus potential can be observed.

Most of these effects can be understood and interpreted in terms of the effect of electrolyte on the potential profile in the double layer region. In addition to the means of controlling electrode potential, double layer studies will provide chemists with a means to affect an electrochemical reaction through the variation in electrolyte composition.

In trace analysis, adsorption of electroactive species

sought may become a predominant factor for some electroanalytical techniques. For example, in chronopotentiometry, adsorption of an electroactive constituent can give rise to an increased transition time. Failure to take account of adsorption can lead to serious errors. If the adsorption is properly interpreted, the sensitivity of an electroanalytical technique may be enhanced.

The double layer charging current, which is a non-Faradaic current required by the electrode during a change of electrode potential or area, is involved in all controlled potential techniques. The measurement of the double layer capacitance can help one to be aware of the relative magnitudes of the charging and Faradaic currents in an experiment. Moreover, a knowledge of the double layer capacitance may be used for the compensation of the double layer charging as will be demonstrated in chapter 4.

### 3. Methods for the Measurement of Double Layer Capacitance

If the phenomena predicted by a theory do not agree with the experimental results, the theory is considered deficient. Double layer capacitance measurements are generally used in electrochemistry to test how good a theory on double layer structure is. A number of methods for the measurement of double layer capacitance have been developed and the more important ones will be discussed.

One type of capacitance measurement is performed by taking the second derivative of a curve of surface tension versus electrode potential. Let us consider the situation of a liquid mercury electrode in an electrolyte solution. The interfacial tension  $\gamma$  of a mercury-solution interface varies with the electrode potential  $E$ . If  $\gamma$  is plotted vs.  $E$ , the result is known as an electrocapillary curve. All electrocapillary curves may be described by the electrocapillary equation developed by Grahame and Whitney (27), which is a differential equation relating the interfacial tension to the temperature, pressure, electrode potential, and chemical potentials of the components. The starting point of the derivation of the electrocapillary equation is the Gibbs adsorption equation. Some important relationships have been derived from the electrocapillary equation, e.g.:

$$q^m = (\partial\gamma/\partial E)_\mu \quad (3-1)$$

$$C_{d1} = (\partial^2\gamma/\partial E^2)_\mu \quad \text{and} \quad (3-2)$$

$$\gamma = \gamma_{pzc} - \int \int_{pzc}^E C_{d1} \cdot dE^2 \quad (3-3)$$

where  $q^m$  is the charge density on the mercury electrode,  $C_{d1}$  is the double layer capacitance, and  $pzc$  represents the potential of zero charge on the electrode.

The capacitance of an electrode can be obtained by measuring the surface tension  $\gamma$  of the electrode, and then taking the second derivative of the electrocapillary curve,  $(\partial^2 \gamma / \partial E^2)_\mu$ . The limitation of this method is that it can usually be applied to liquid electrodes only.

Capacitance measurements are commonly performed with an AC bridge. Bridge measurements provide a direct way to compare unknown impedances with known standard impedances. The impedance may be supplied by a pure resistor, capacitor, or inductor, or may be supplied by a circuit represented by some series or parallel combination of resistors, capacitors, and inductors. The major advantage of this method is that it allows one to very accurately obtain electrode capacitance and kinetic parameters at high concentrations of electrolyte solution (e.g. above  $10^{-3}$  M). This method has several disadvantages: First, it is tedious to adjust the values of resistors and capacitors in order to match the unknown impedance of the cell. Second, it requires significant skill to perform the experiment. Third, it can require more than 30 minutes to take data for the entire potential range (usually between 1 V and 2 V) and the electrode (especially for a solid one) may be more subject to the adsorption of organic impurities if it is left in the solution so long. Fourth, it cannot generally be applied to the determination of double layer capacitance with media of low conductivity or dilute electrolyte

solutions (e.g. below  $10^{-3}$  M for strong electrolyte).

Most commercial instruments presently available use a lock-in amplifier technique to measure electrode capacitance. The capacitance measurement can usually be completed within a few minutes. But again, these instruments are not well suited for very dilute electrolyte solutions.

L. Ramaley and co-worker (28) developed two methods of capacitance measurement. One method involved the application of a rectangular current waveform to the electrode. The capacitance  $C_{dl}$  was obtained by measuring the slope of the electrode potential vs. time curve:

$$C_{dl} = i \cdot dt/dE \quad (3-4),$$

where  $i$  is the current density applied to the electrode, and  $dE/dt$  is the slope of the potential time curve. Because a constant current is applied to the electrode and the solution resistance does not change during the current pulse, the IR drop is constant and it does not affect the value of  $dE/dt$ . This can be very important in high resistant solutions. The other method involved the use of small sinusoidally varying potential of constant amplitude. With an oscilloscope as a fast detection system, they measured electrode capacitance with a sweep speed of a volt per second or more for solutions with high conductivity.

The speed and ease of measurement is important for the measurement of capacitance of silver in perchlorate solution (29).

P. Delahay and co-workers (30) used a coulometric charging method to change the electrode potential slightly (5-15 mV) and measure the potential change due to a known charge. The charge  $Q$  on a small capacitor (500 pF) which had been charged to at least 1 V was transferred to the working electrode by a differential electrometer-amplifier. Measurements were read out on an oscilloscope and compared with those obtained with a dummy cell. Because of the temporary overload of the amplifier, they took readings 50 to 100 ms after the pulse and extrapolated the results back to time zero when necessary. The capacitance  $C_{dl}$  of the electrode is  $Q/V_s$ , where  $Q$  is the charge transferred to the electrode and  $V_s$  is the potential change resulting from the charge addition. The major advantage of this method is that double layer capacitance can be measured in media of low conductivity.

#### C. Description and Test of the Technique:

The technique for capacitance measurement developed in this research work is based on the ideas of P. Delahay and his co-workers (30), except that we have used a microcomputer for automatic charge injection and data collection. These allow the capacitance to be measured very



quickly. Because a fast response amplifier (AM 405-2) was used, the overloading of the amplifier is not the limiting factor in the delay time required for potential measurement. The potential perturbation can be measured at a shorter time after the charge pulse using this technique than the method developed by P. Delahay and co-workers. For example, with a concentration of KCl of  $10^{-3}$  M, the delay time can be as short as 6.4 ms. (The shortness of delay time is limited by the resistance of the electrolyte, not by the amplifier overloading.) Multiple measurements also enhance the precision of the results.

Figures 3-1 to 3-3 show a flow chart of the program which was used for the capacitance measurement. The operator sets up the parameters such as initial potential  $E_{init}$ , final potential  $E_{final}$ , potential perturbation  $\Delta E$  for capacitance measurement, potential interval  $E_{inc}$  between two adjacent data points, desired minimum number of repetitive measurements  $N_d$  for each potential, delay time  $t_d$  between charge injection and voltage measurement, etc., before starting the data acquisition.

After the operator starts the program, the PCP measures the electrode potential and compares it to the desired initial value  $E_{init}$ . If there is any difference in the potential values, the PCP injects charge pulses of proper polarity in order to bring the electrode potential to the initial value. After the initial potential is reached, the

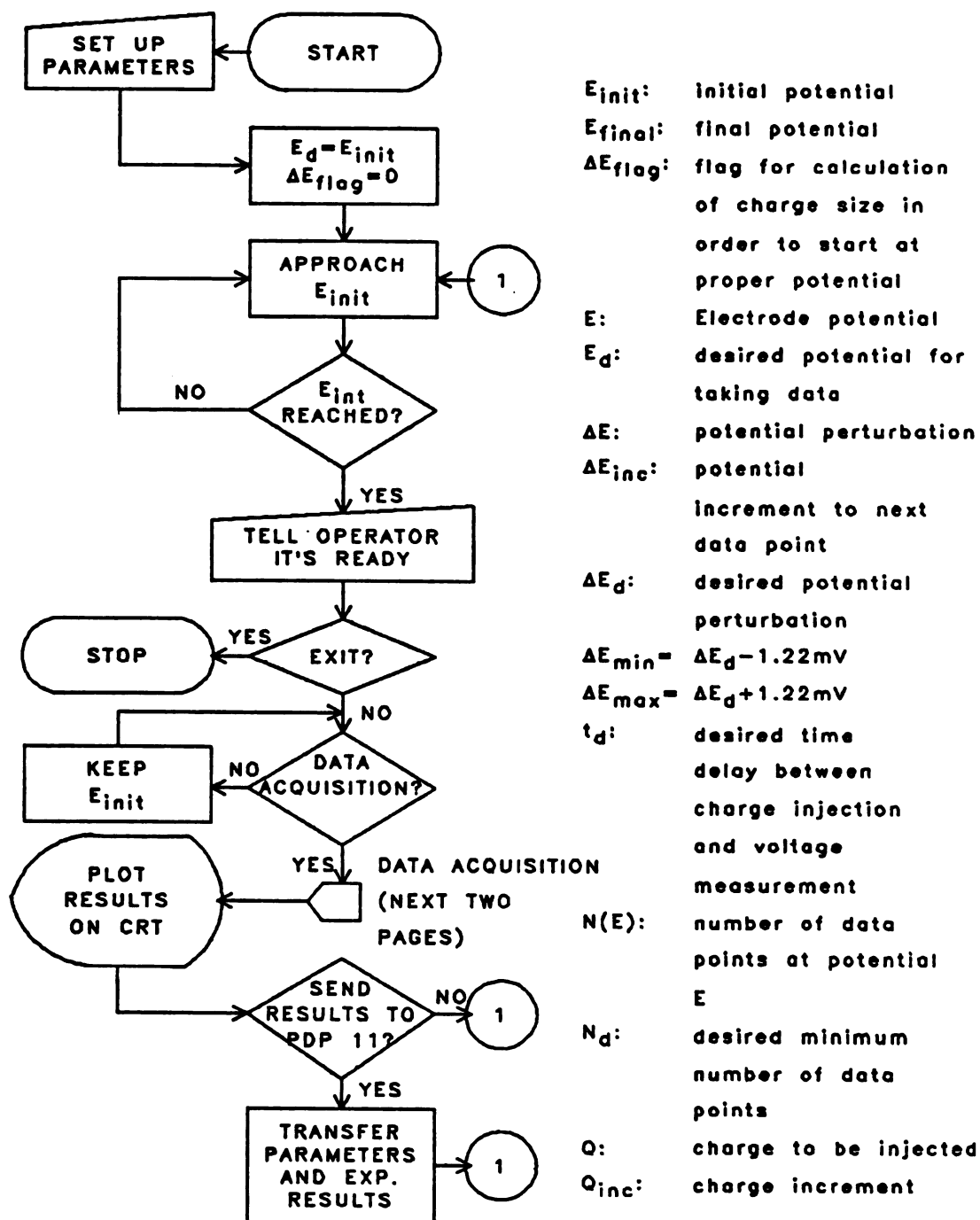


Figure 3-1. The first part of the flow chart of the program for the capacitance measurement

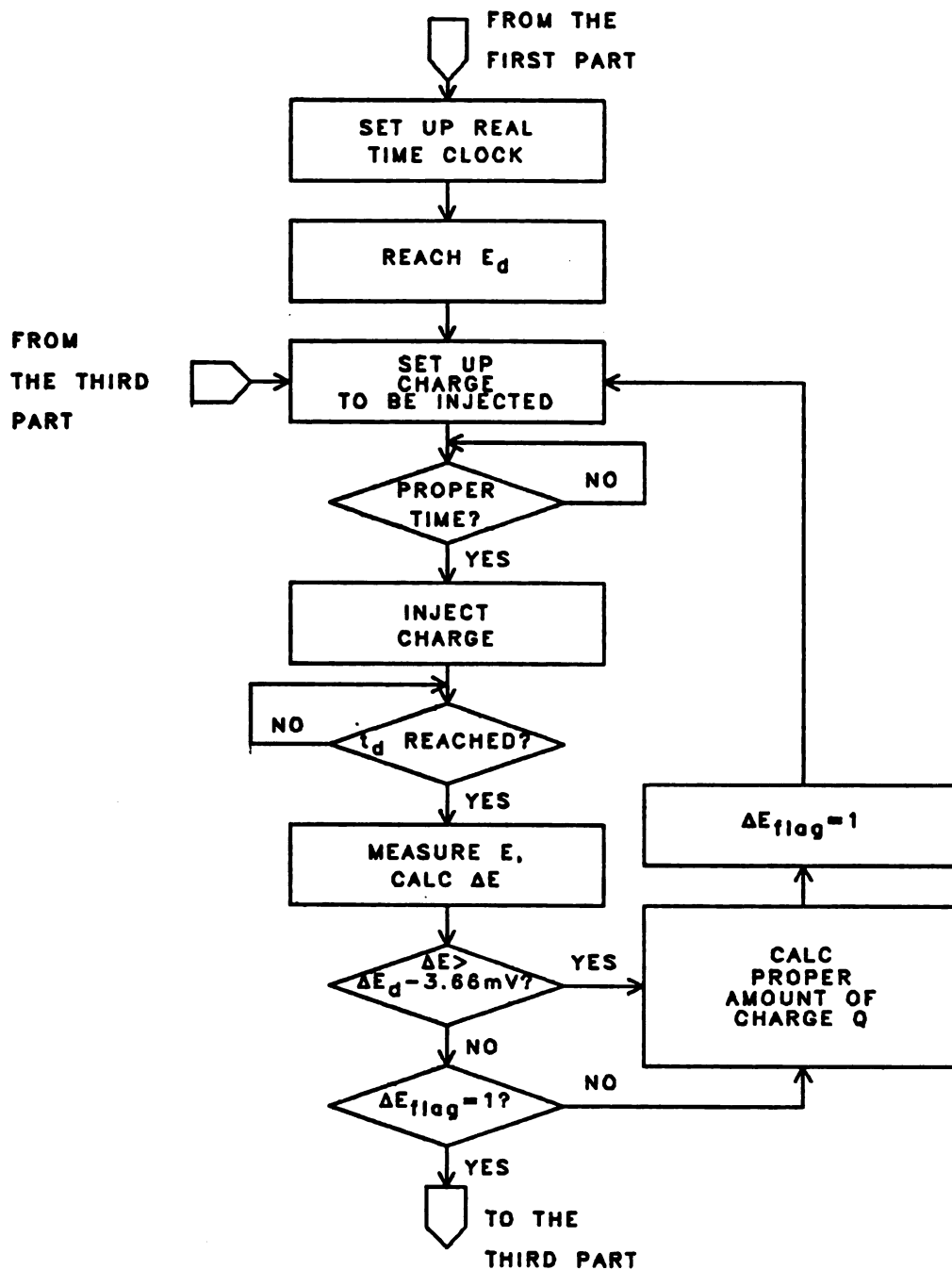


Figure 3-2. The second part of the flow chart of the program for the capacitance measurement

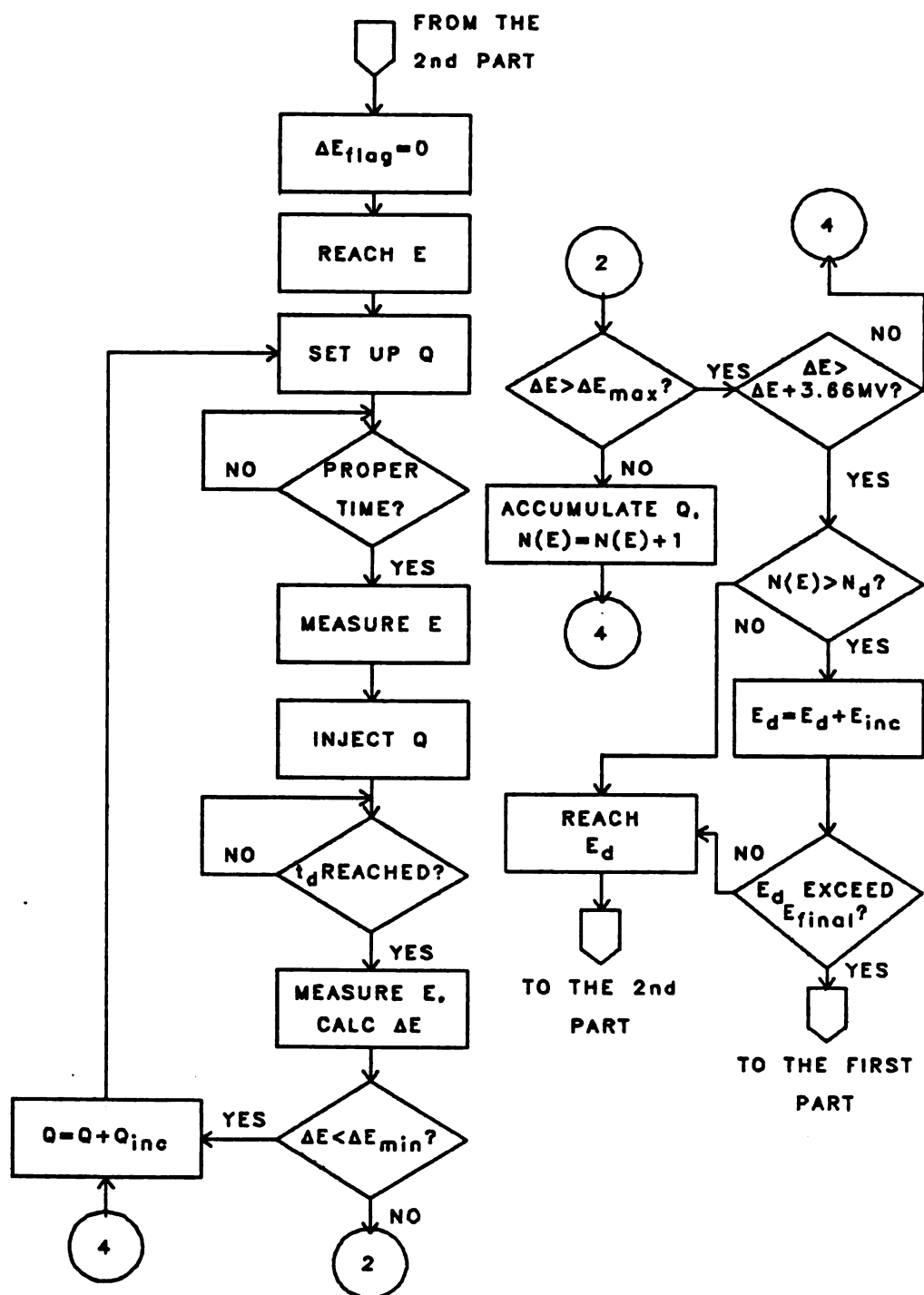


Figure 3-3. The third part of the flow chart of the program for the capacitance measurement

PCP keeps the electrode potential at this value by adding charge as needed until the operator commands the PCP to execute data acquisition. An amount of charge previously specified by the operator is injected to the electrode and the potential  $E$  is measured after some delay time  $t_d$ . The potential perturbation  $\Delta E$  due to the charge injection is calculated and compared to the desired value  $\Delta E_d$ . The computer automatically calculates the amount of charge  $Q$  to be injected on the electrode in order to make  $\Delta E = \Delta E_d - 3.66 \text{ mV}$ . For a typical measurement,  $\Delta E_d = 9.77 \text{ mV}$  which corresponds to 8 times the least significant bit (LSB). The quantization level of the voltage measurement system is  $1.22 \text{ mV}$ . A potential change of  $9.77 \text{ mV}$  is selected because it is not large and can be used for differential capacitance measurements. The value  $\Delta E_d - 3.66 \text{ mV}$  is chosen for two reasons: The first is because the quantity of charge  $Q$  to be injected will be incremented and the number of charge injections which will make  $\Delta E$  within  $\Delta E_d \pm 1.22 \text{ mV}$  will be counted. The value  $\Delta E_d - 3.66 \text{ mV}$  is not too far from the value  $\Delta E_d - 1.22 \text{ mV}$  and starting the charge incrementation from the amount of charge which will achieve this potential perturbation can save experimental time. The second reason is that the value  $\Delta E_d - 3.66 \text{ mV}$  differs from the value  $\Delta E_d - 1.22 \text{ mV}$  by  $2.44 \text{ mV}$ , which corresponds to 2 LSB. This difference can provide some noise rejection.

The size of charge  $Q$  is incremented automatically after

$\Delta E = \Delta E_d - 3.66 \text{ mV}$  is reached, the potentials are measured before and after charge injection, and the potential perturbation is calculated for each injected charge pulse. If  $\Delta E$  is within  $\Delta E_d \pm 1.22 \text{ mV}$ , the amount of injected charge is accumulated and the counter is incremented by 1. As soon as  $\Delta E \geq \Delta E_d + 3.66 \text{ mV}$ , the computer will read  $N(E)$ , the content of the counter for potential  $E$ . The computer compares  $N(E)$  to  $N_d$ , the desired minimum number of data points previously specified by the operator. If  $N(E) \geq N_d$ , the control will go to the next potential and perform charge injections and data collection until the final potential is reached. If  $N(E) < N_d$ , more data points will be taken before going to the next potential. The results are plotted on a CRT display immediately after the experiment is completed to allow the operator to observe the experimental results.

According to the manufacturer, the calibration of the analog-to-digital converter (ADC) is accurate to  $\pm 1/2$  least significant bit (LSB) which corresponds to  $\pm 0.61 \text{ mV}$  of electrode potential in this instrument design. Although it is possible to reduce this uncertainty by using an ADC with higher resolution, the cost will be higher. The voltage differences  $\Delta V_1$  and  $\Delta V_2$  shown on Figure 3-4 may not be equal even if they give the same results in the conversion to the digital domain. The consequence of this is that different amounts of charge  $Q_a$  and  $Q_b$  are required to make the voltage

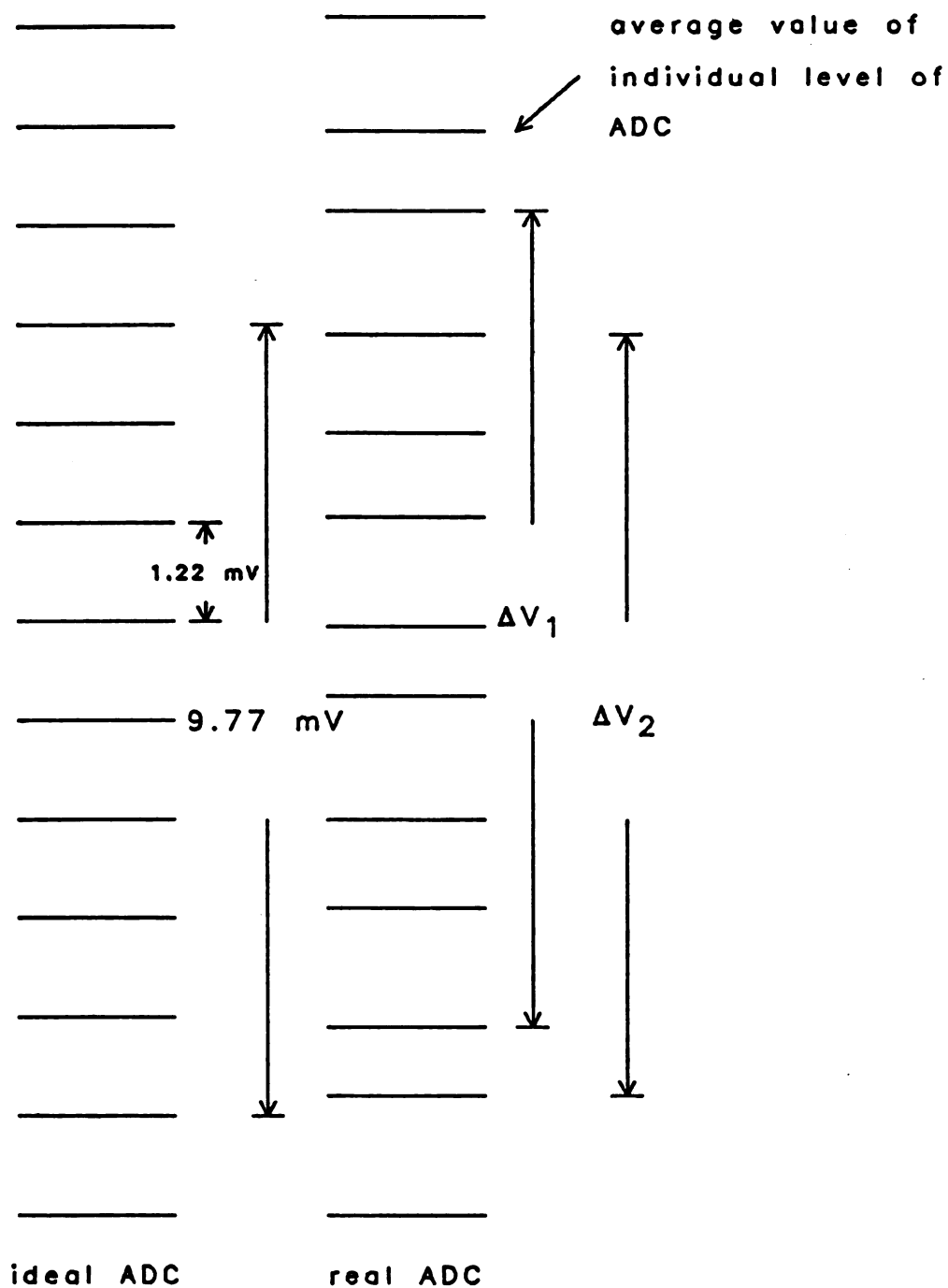


Figure 3-4. Calibration error in analog-to-digital converter (ADC)

perturbation  $\Delta V_1$  and  $\Delta V_2$  respectively although the ADC reports them as the same. This can introduce error in the calculation of capacitance if the results are interpreted as  $Q_a/(\Delta V_{ideal} \cdot A)$  and  $Q_b/(\Delta V_{ideal} \cdot A)$ , where  $A$  is the area of the electrode and  $\Delta V_{ideal}$  is the ideal voltage perturbation corresponding to the obtained digital result from ADC.

Figure 3-5 shows the capacitance curve obtained for a 0.995  $\mu F$  capacitor using the equation:

$$C = Q_1 / (N_1 \cdot \Delta V_{ideal}) \quad (3-5),$$

where  $C$  is the calculated capacitance,  $Q_1$  is the accumulated charge. The number of charge injections is  $N_1$ , and  $\Delta V_{ideal} = 9.77$  mV. A dummy cell shown in Figure 3-6 with the capacitor  $C_{dm}$  in the feedback loop was used and more than 1000 data points were taken for each voltage. The capacitor  $C_{dm}$  is mylar and the capacitance is constant throughout the voltage range used in all of the following experiments.

A method to reduce this calibration error was needed in order to improve the results. Equation 3-6 shows the double layer capacitance  $C_{dl}(E)$  at potential  $E$  in terms of the accumulated charge injected to the electrode  $Q_{e1}$ , the number of charge injections  $N_2$ , the potential perturbation  $\Delta E$ , and the electrode area  $A$ . A dummy cell with capacitance  $C_{dm}$  is used to perform a similar experiment. Equation 3-7 relates the accumulated charge  $Q_{dm}$ , the number of charge injections



DUMMY CELL,  $C_{dm} = 0.995 \text{ uF}$

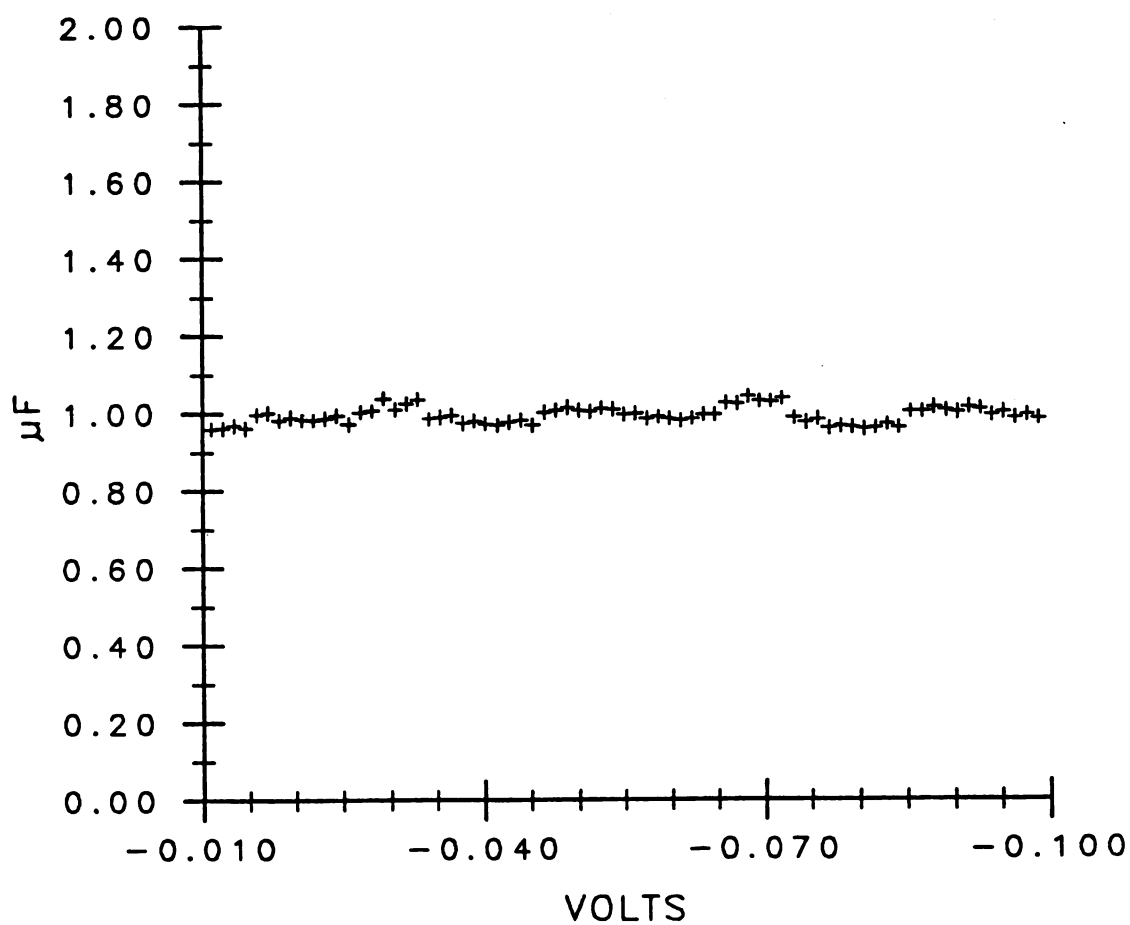
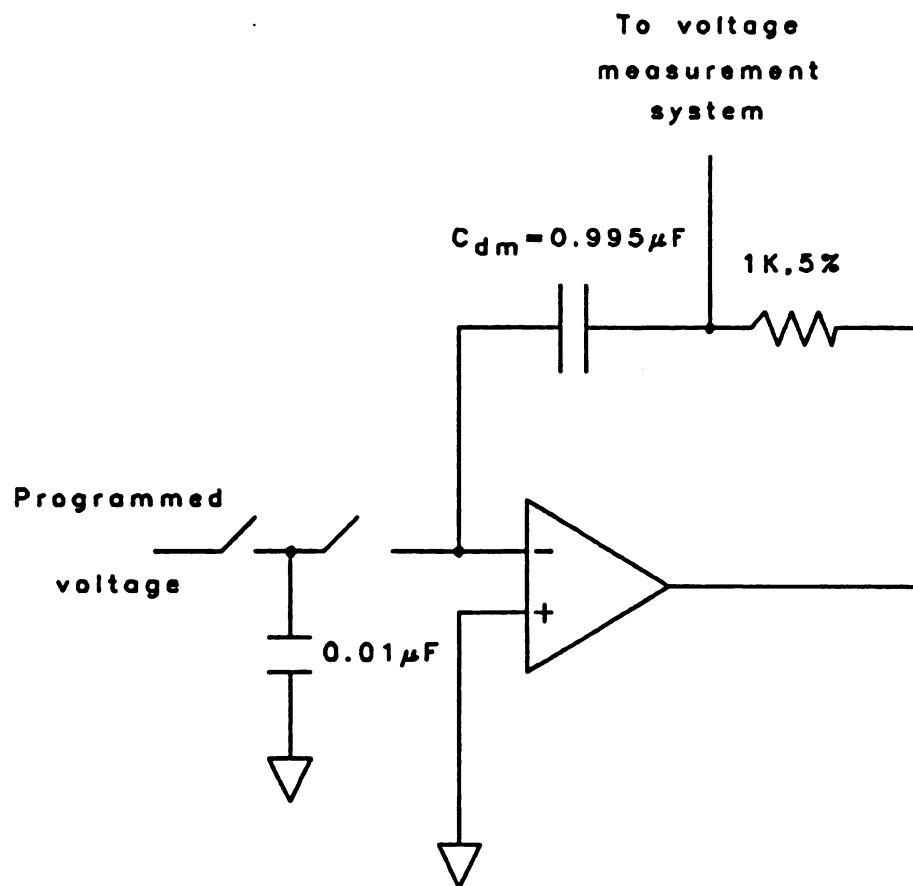


Figure 3-5.

Effect of Calibration error in  
analog-to-digital converter on  
the capacitance measurement



**Figure 3-6.** Dummy cell configuration for testing the capacitance measurement technique

$N_1$ , and the voltage perturbation  $\Delta V$ , which is equal to  $\Delta E$  at the same voltage or potential. If Equation 3-6 is divided by Equation 3-7, Equation 3-8 is obtained.

$$Q_{e1}/(N_2 \cdot \Delta E \cdot A) = C_{d1} \quad (3-6)$$

$$Q_{dm}/(N_1 \cdot \Delta V) = C_{dm} \quad (3-7)$$

$$Q_{e1} \cdot N_1 \cdot C_{dm} / (N_2 \cdot A \cdot Q_{dm}) = C_{d1} \quad (3-8)$$

By doing this, the error or uncertainty in  $\Delta E$  or  $\Delta V$ , in the calibration of ADC is cancelled out. If  $C_{dm}$  is known,  $C_{d1}$  can be calculated accurately without being affected by the calibration error.

Two identical experiments were performed with the same dummy capacitor. The capacitance of the capacitor  $C_{dm2}(V)$  at voltage  $V$  is calculated by assuming that the capacitance  $C_{dm1}$  of the capacitor is constant ( $0.995 \mu F$ ) and by using Equation 3-9 which is similar to Equation 3-8.

$$C_{dm2}(V) = Q_2 \cdot N_1 \cdot C_{dm1} / (N_2 \cdot Q_1) \quad (3-9),$$

where  $Q_1$  and  $Q_2$  are accumulated charges for individual experiments,  $N_1$  and  $N_2$  are the number of charge injections for individual experiments, and  $C_{dm1} = 0.995 \mu F$ .

Figure 3-7 shows the results obtained by this method.

DUMMY CELL,  $C_{dm} = 0.995 \text{ uF}$

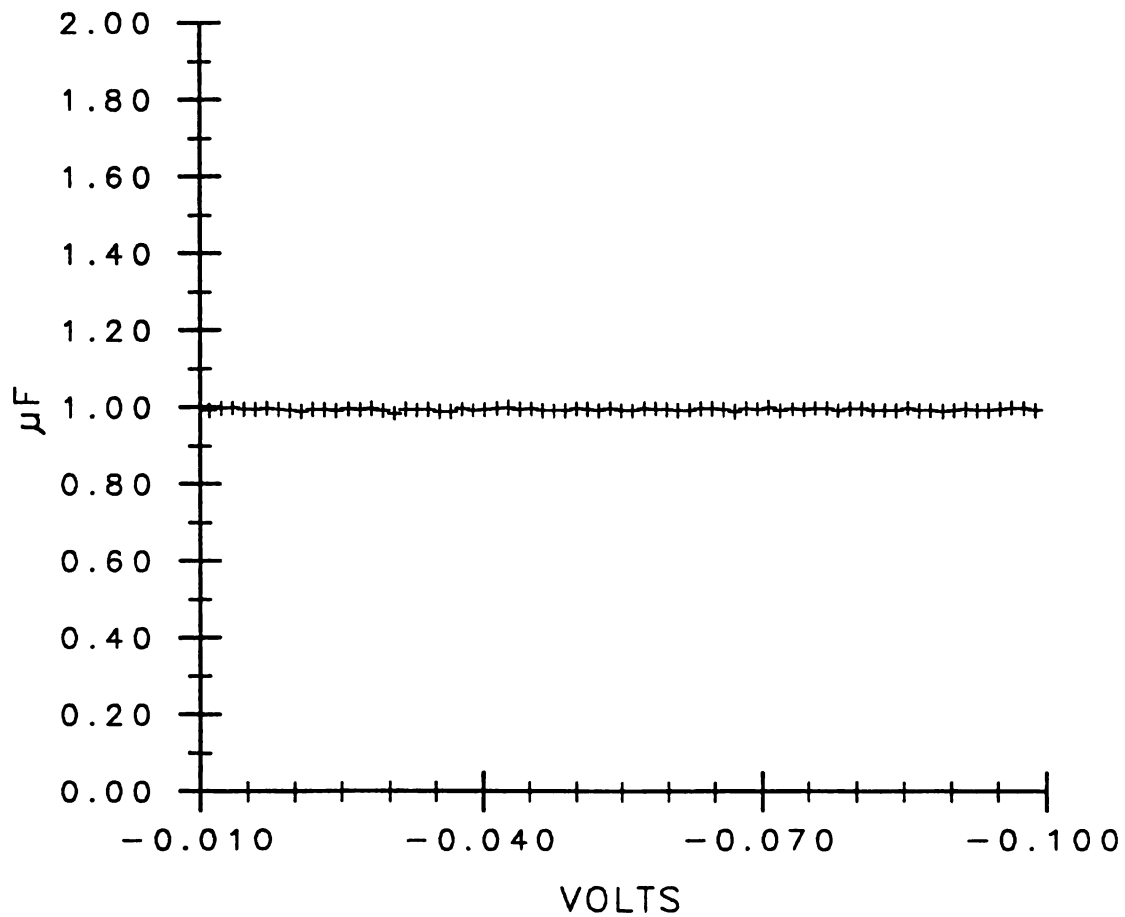


Figure 3-7. Results of removing calibration error of ADC

In each experiment, the desired minimum number of charge injections,  $N_d$ , is 1000. The method clearly removes the effect of calibration error in ADC.

Quantization error is encountered in all analog-to-digital conversions. A common method to reduce the quantization error is to add to the signal white random noise whose amplitude is comparable to the quantization level of the ADC and then average repetitive measurements. The standard deviation of the average from a number of measurements can be less than the quantization level of the ADC.

Although  $\Delta\Delta E$ , the difference in potential perturbations of two adjacent charge injections, is usually smaller than the quantization level of the voltage measurement system (in this instrument design, the quantization level is 1.22 mV), the quantization error is less for two reasons: First, the amount of charge injected to the electrode is incremented and averaged through the potential difference window  $\Delta E_d \pm 1.22$  mV several times until the number of data for each potential is greater than  $N_d$ . Second, the potential before charge injection to make the perturbation  $\Delta E$  has a small random variation.

According to Kelly and Horlick (31), the standard deviation of quantization noise is  $v_1/12^{0.5}$ , where  $v_1$  is the magnitude of the quantization level. In this case,  $v_1 = 1.22$  mV. Since voltage differences are taken, the standard

deviation should be  $1.22 \cdot 2^{0.5} / 12^{0.5}$  mV. If N is the number of data points to be averaged, the estimated standard deviation is

$$1.22 \cdot 2^{0.5} / ((N-1)^{0.5} \cdot 12^{0.5}) \text{ mV} \quad (3-10).$$

For a typical application where  $\Delta E = 9.77$  mV and  $N = 20$ , the estimated % relative standard deviation (% RSD) is

$$(1.22 \cdot (2)^{.5} / ((20-1)^{.5} \cdot 9.77 \cdot (12)^{.5}) \cdot 100\% = 1.17\% \quad (3-11).$$

For  $\Delta E = 9.77$  mV and  $N = 100$ , it is

$$(1.22 \cdot (2)^{.5} / ((100-1)^{.5} \cdot 9.77 \cdot (12)^{.5}) \cdot 100\% = .512\% \quad (3-12).$$

For  $\Delta E = 9.77$  mV and  $N = 1000$ , it is

$$(1.22 \cdot (2)^{.5} / ((1000-1)^{.5} \cdot 9.77 \cdot (12)^{.5}) \cdot 100\% = .161\% \quad (3-13).$$

By choosing the value of N, the desired precision of the measurement can be obtained. Figures 3-8 and 3-9 illustrate the precision of this technique. The experimental results were calculated using Equation 3-9. Figure 3-8 shows the results obtained with  $N_{d1} = 100$  and  $N_{d2} = 1000$ , where  $N_{d1}$  is the desired minimum number of charge injections for the first scan and  $N_{d2}$  is the desired minimum

## DUMMY CELL

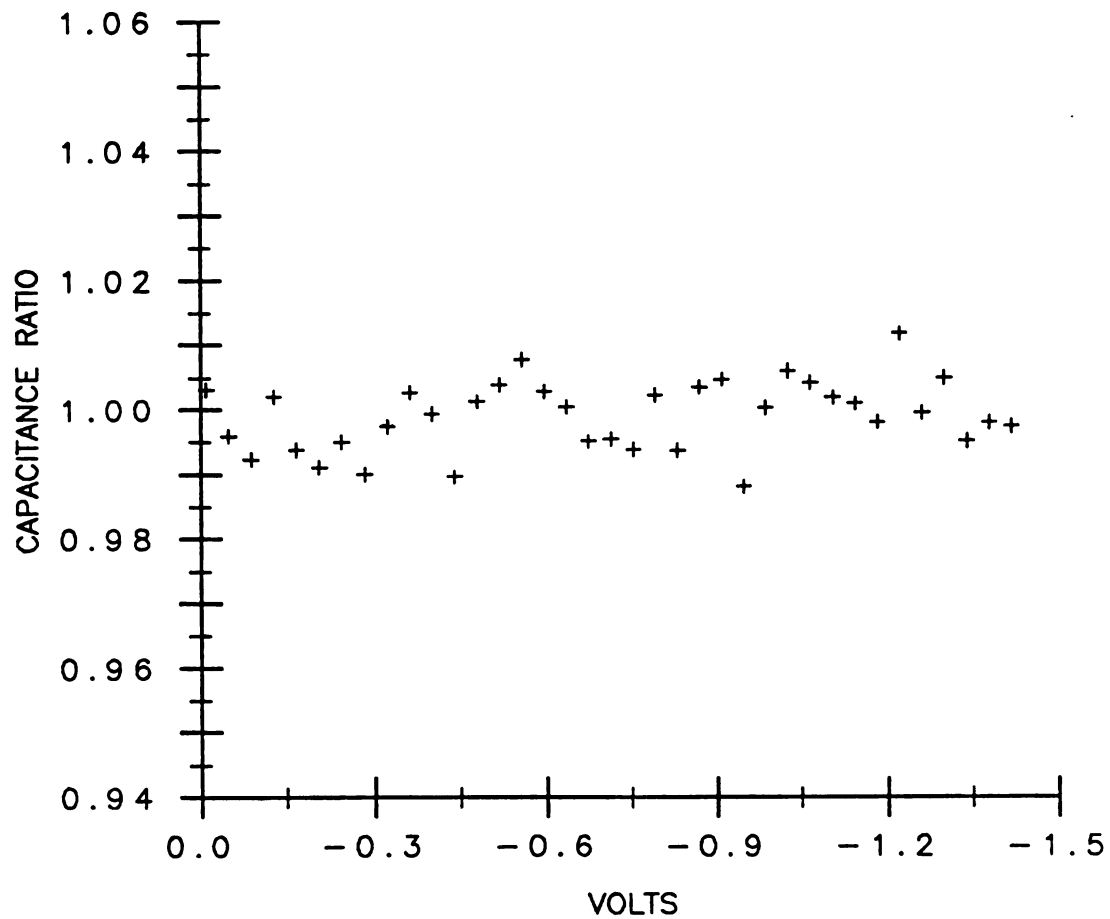


Figure 3-8.

Capacitance ratio obtained with  
 $N_{d1}=100$ ,  $N_{d2}=1000$ , and  $t_d=0.8$  ms

## DUMMY CELL

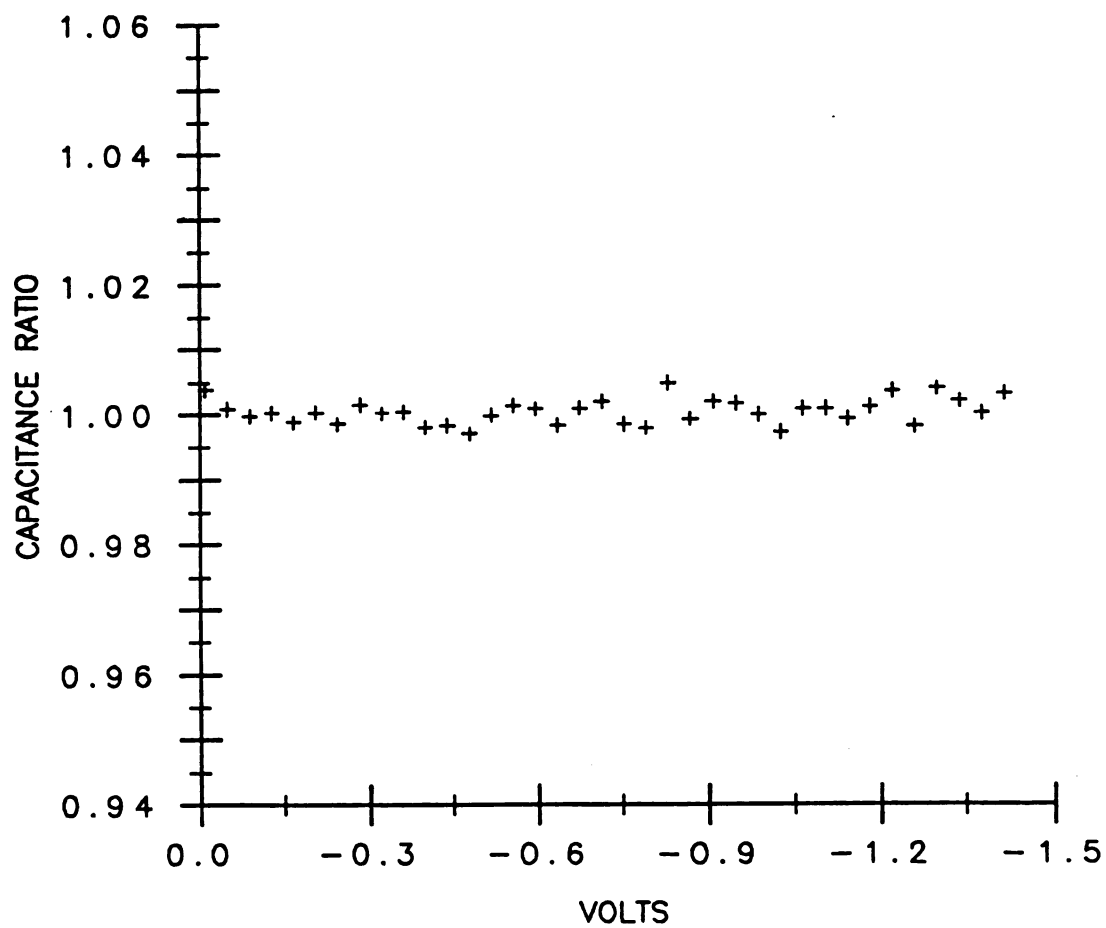


Figure 3-9.

Capacitance ratio obtained with  
 $N_{d1}=1000$ ,  $N_{d2}=1000$ , and  $t_d=0.8$  ms



number of charge injections for the second scan. The average relative standard deviation was found to be 0.54 %. Figure 3-9 shows the results obtained with  $N_{d1} = 1000$  and  $N_{d2} = 1000$ . The average relative standard deviation was found to be 0.19 %. The capacitance measurement results obtained in the next section are all performed using  $N_{d2} = 1000$  for the dummy cell measurements.

#### D. Double Layer Capacitance Measurements for Mercury Electrode in KCl Solutions

When the capacitance measurement technique was tested with a mercury electrode in KCl solutions, a hanging mercury drop electrode (HMDE) was used as a working electrode and the capillary of the HMDE was siliconized on a daily basis to prevent capillary action of the test solution. A micrometer drive HMDE was used. The weight of mercury with the turning of 200 divisions of the micrometer drive was measured (0.2112 grams). The weight (8.45 mg) of each mercury drop with the turning of 8 divisions was calculated by dividing the weight (0.2112 g) by 25 (assuming that the micrometer drive is uniform). The area ( $0.0352 \text{ cm}^2$ ) of the mercury drop was calculated by assuming that it has a spherical shape. The reproducibility of the area was determined by measuring the amount of charge required to make a potential perturbation of 400 mV (for details, see the integral capacitive charge measurement in Chapter 4) in

0.1 M KCl solution for 20 different mercury drops under the same experimental condition. The relative standard deviation of the area was found to be 1.1%.

A saturated calomel electrode (SCE) was used as the reference electrode. A 1.0 cm<sup>2</sup> platinum gauze was used as a counter electrode. Potassium chloride solutions were used because KCl is the most commonly used supporting electrolyte for analytical work. By using KCl solutions, the leakage of a trace amount of KCl from the SCE reference electrode causes fewer problems. Sodium fluoride solutions are generally used to test Gouy-Chapman double layer theory (23-25) because it is believed that sodium fluoride does not adsorb on the mercury surface. However, for experimental simplicity, KCl solutions were used to test the performance of the PCP for capacitance measurements. Reagent grade potassium chloride had been recrystallized before it was used. Solutions were prepared with de-ionized water which had been passed through an ion-exchange column manufactured by Millipore. The solution in the cell was de-aerated with nitrogen gas which had been passed through a vanadous chloride solution to remove trace oxygen. All experiments were performed at room temperature between 20.5 and 21.5 °C except when noted otherwise.

Figure 3-10 shows the capacitance curves obtained with 1.0 M KCl solution. These curves were obtained with  $N_{d1} = 100$ ,  $N_{d2} = 1000$ , and  $t_d = 0.4, 0.8, 1.6, 3.2$  ms. The

1.0 M KCl

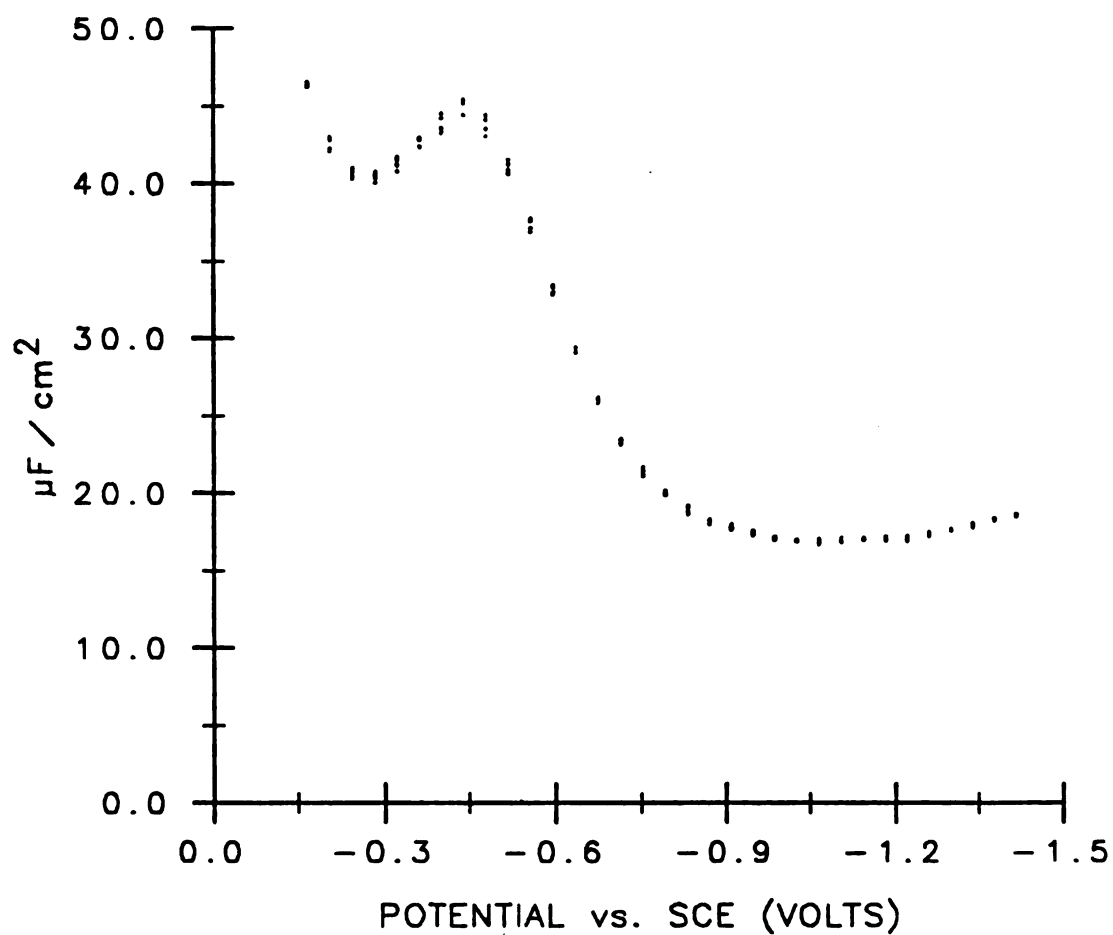


Figure 3-10.

Capacitance curves of HMDE in 1.0 M KCl solution obtained with  $N_{d1}=100$ ,  $N_{d2}=1000$ , and  $t_d = 0.4, 0.8, 1.6, 3.2$  ms with the higher capacitances corresponding to the longer times

capacitance values increased with increasing values of  $t_d$  (the delay time between charge injection and voltage measurement)  $N_{d1}$  is the minimum number of charge injections for the electrochemical cell, and  $N_{d2}$  is the minimum number of charge injections for the dummy cell.

Figure 3-11 shows the capacitance curves obtained with 0.1 M KCl solution. These curves were obtained with  $N_{d1} = 100$ ,  $N_{d2} = 1000$ , and  $t_d = 0.2, 0.4, 0.8, 1.6, 3.2, 6.4$  ms.

Figure 3-12 shows the capacitance curves obtained with 0.01 M KCl solution. These curves were obtained with  $N_{d1} = 100$ ,  $N_{d2} = 1000$ , and  $t_d = 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8$  ms.

The capacitance approaches a fairly constant value after some delay time. This is because it takes some time for the charge to be injected to the electrode and the charge needs to be distributed evenly on the electrode before an accurate reading can be taken. For lower concentrations of KCl solution, it takes longer to get a constant capacitance value (equal charge distribution) because the solution is less conductive.

Figure 3-13 shows the capacitance curves obtained with  $10^{-3}$  M KCl solution. These curves are obtained with  $N_{d1} = 100$ ,  $N_{d2} = 1000$ , and  $t_d = 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, 25.6$  ms.

In order to speed up the cell response, the first attempt was to decrease the solution resistance between the

0.1 M KCl

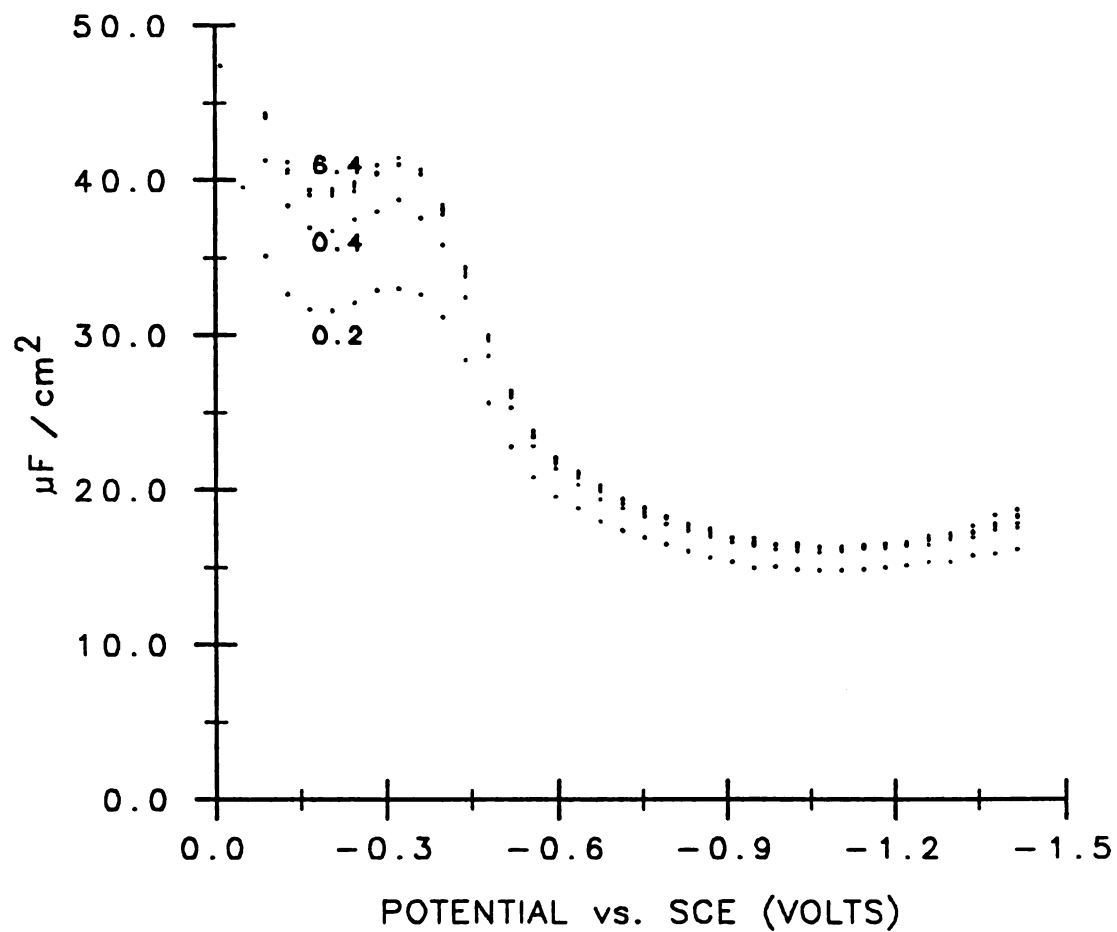


Figure 3-11.

Capacitance curves of HMDE in 0.1 M KCl solution obtained with  $N_{d1}=100$ ,  $N_{d2}=1000$ , and  $t_d = 0.2, 0.4, 0.8, 1.6, 3.2, 6.4$  ms with the higher capacitances corresponding to the longer times

0.01 M KCl

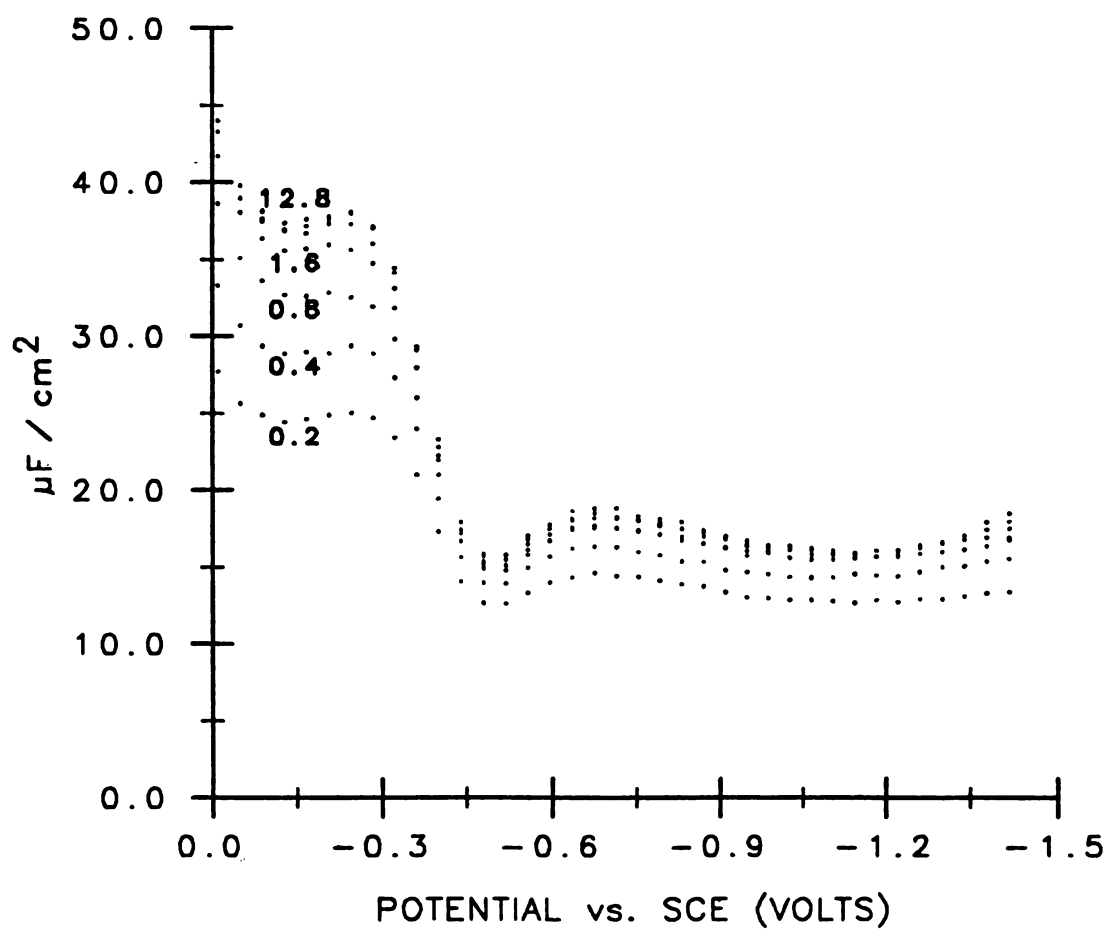


Figure 3-12.

Capacitance curves of HMDE in 0.01 M KCl solution obtained with  $N_{d1}=100$ ,  $N_{d2}=1000$ , and  $t_d = 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8$  ms with the higher capacitances corresponding to the longer times

0.001 M KCl

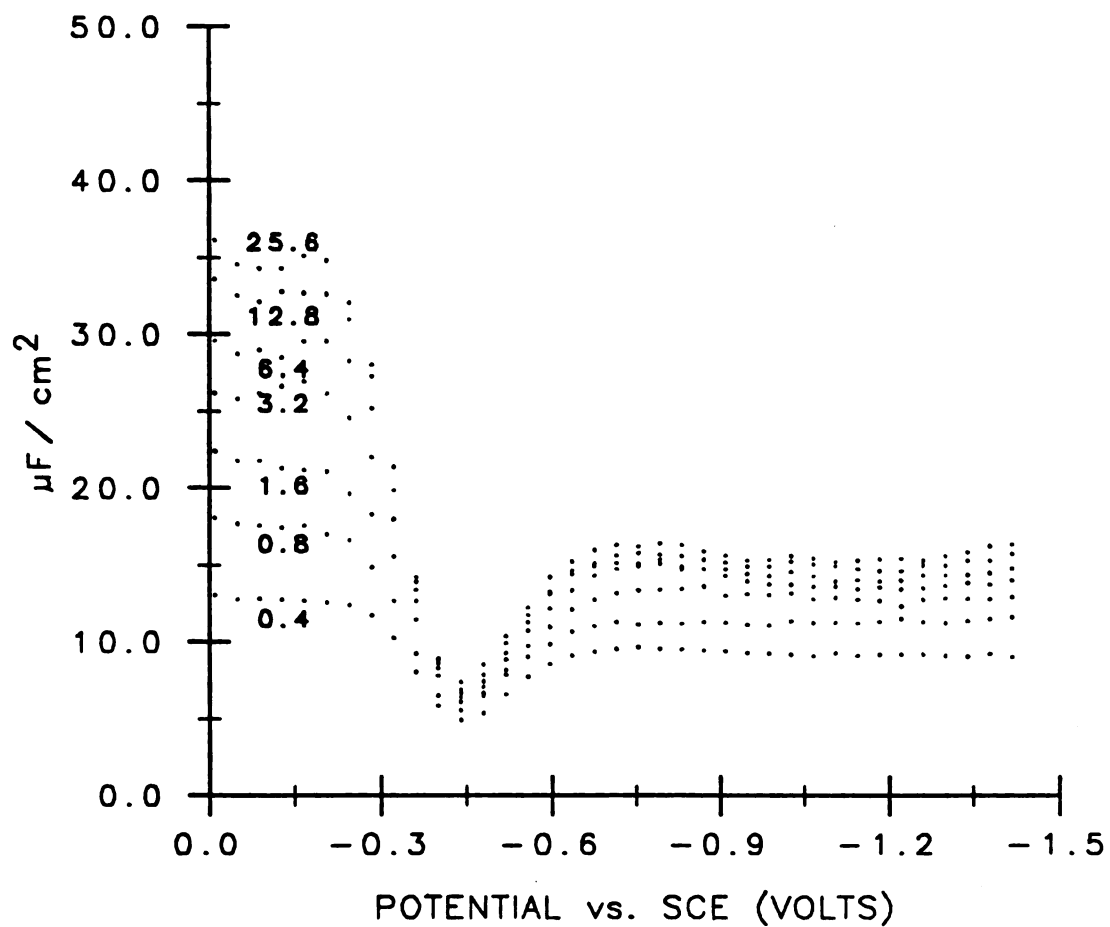


Figure 3-13.

Capacitance curves of HMDE in  $10^{-3}$  M KCl solution obtained with  $N_{d1}=100$ ,  $N_{d2}=1000$ , and  $t_d = 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, 25.6$  ms with the higher capacitances corresponding to the longer times

working electrode and the counter electrode by putting the counter electrode as close to the HMDE working electrode as possible. The shortest distance between the counter electrode and the HMDE was approximately 0.15 cm and the capacitance curves for KCl solutions mentioned previously in this section were all obtained by this cell geometry. However, this cell geometry was actually found to slow down the cell response because of the lack of uniformity of the current density.

In order to obtain a more uniform current density, a cell with the counter electrode about 1.0 cm away from the HMDE and with the SCE reference electrode on the other side of the HMDE was used for the following experiments of capacitance measurement. A salt bridge filled with the same concentration of test solution was placed between the SCE and the test solution in order to reduce the leakage of KCl from the SCE to the test solution. This salt bridge was used for all KCl concentrations below  $10^{-3}$  M.

Figure 3-14 shows the capacitance curves obtained with  $10^{-3}$  M KCl solution and with the improved cell geometry. These curves were obtained with  $N_{d1} = 100$ ,  $N_{d2} = 1000$ , and  $t_d = 0.2, 0.3, 0.4, 0.8, 1.6, 3.2$  ms. The capacitance curve obtained with  $t_d = 6.4$  ms almost coincides with that obtained with  $t_d = 3.2$  ms. For clarity, it has been omitted from the figure. If we compare these results to those shown on Figure 3-13, clearly, we find that the new cell geometry



0.001 M KCl

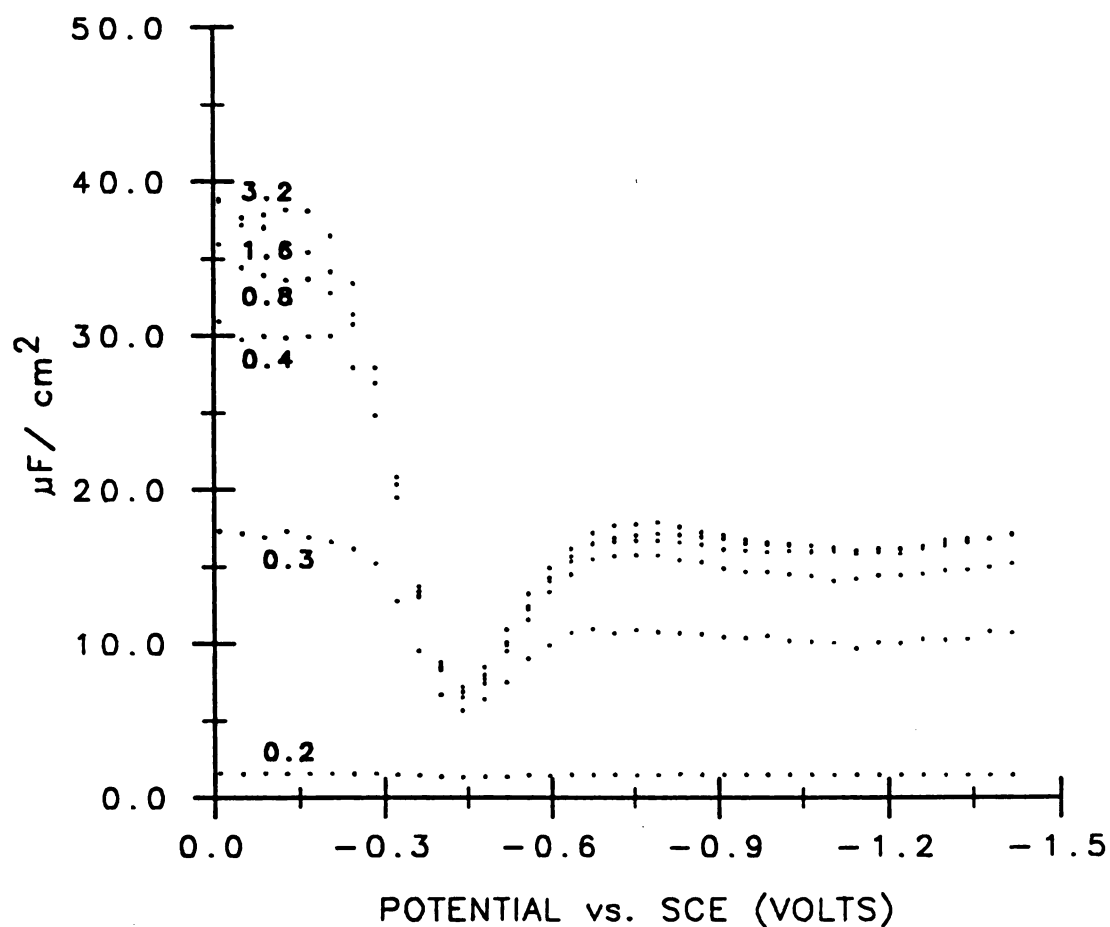


Figure 3-14.

Capacitance curves of  $10^{-3}$  M KCl solution obtained with improved cell geometry. These curves are obtained with  $N_{d1}=100$ ,  $N_{d2}=1000$ , and  $t_d = 0.2, 0.3, 0.4, 0.8, 1.6, 3.2$  ms with higher capacitances corresponding to the longer times.

improves the cell response significantly.

Figure 3-15 shows the capacitance curves obtained with  $10^{-4}$  M KCl solution. These curves were obtained with  $N_{d1} = 20$ ,  $N_{d2} = 1000$ , and  $t_d = 0.8, 1.6, 3.2, 6.4, 12.8, 25.6$  ms. The number 20 instead of 100 was used for  $N_{d1}$  to reduce experimental time although this resulted in some sacrifice in precision. A typical time spent for data collection at  $10^{-4}$  M with  $t_d = 12.8$  ms is 150 sec. The estimated precision due to quantization error for  $N_{d1} = 20$  is 1.17 % RSD according to Equation 3-11.

Figure 3-16 shows the capacitance curves obtained with  $10^{-5}$  M KCl solution. These curves were obtained with  $N_{d1} = 20$ ,  $N_{d2} = 1000$ , and  $t_d = 12.8, 25.6, 51.2, 102.4$  ms.

Figure 3-17 shows the capacitance curves for a range of KCl solution concentrations. Each curve was obtained from the capacitance values which approached a relatively constant value at the longer delay times. The delay times  $t_d$  were 0.4, 1.6, 6.4 ms for 1.0, 0.1, 0.01 M KCl solutions respectively, and the  $t_d$ 's were 6.4, 12.8, 102.4, ms for  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  M KCl solutions with improved cell geometry. For a  $10^{-5}$  M KCl solution, the capacitance did not quite reach a constant value, especially at the more positive potentials. This makes the determination of the capacitance value somewhat difficult.

The major sources of error will be discussed. The % RSD of the area of HMDE is 1.1 %. The estimated

$10^{-4}$  M KCl

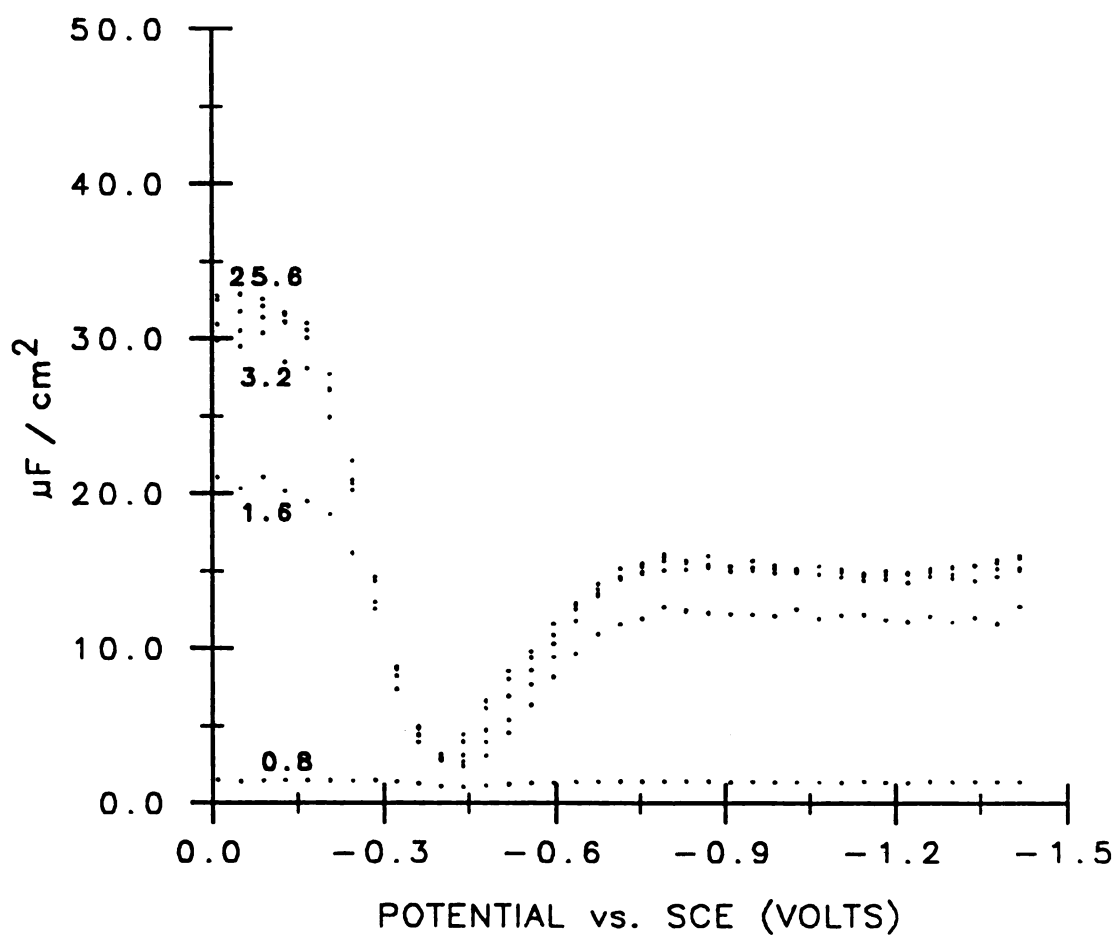


Figure 3-15.

Capacitance curves of HMDE in  $10^{-4}$  M KCl solution obtained with  $N_{d1}=20$ ,  $N_{d2}=1000$ , and  $t_d = 0.8, 1.6, 3.2, 6.4, 12.8, 25.6$  ms with the higher capacitances corresponding to the longer times

$10^{-5}$  M KCl

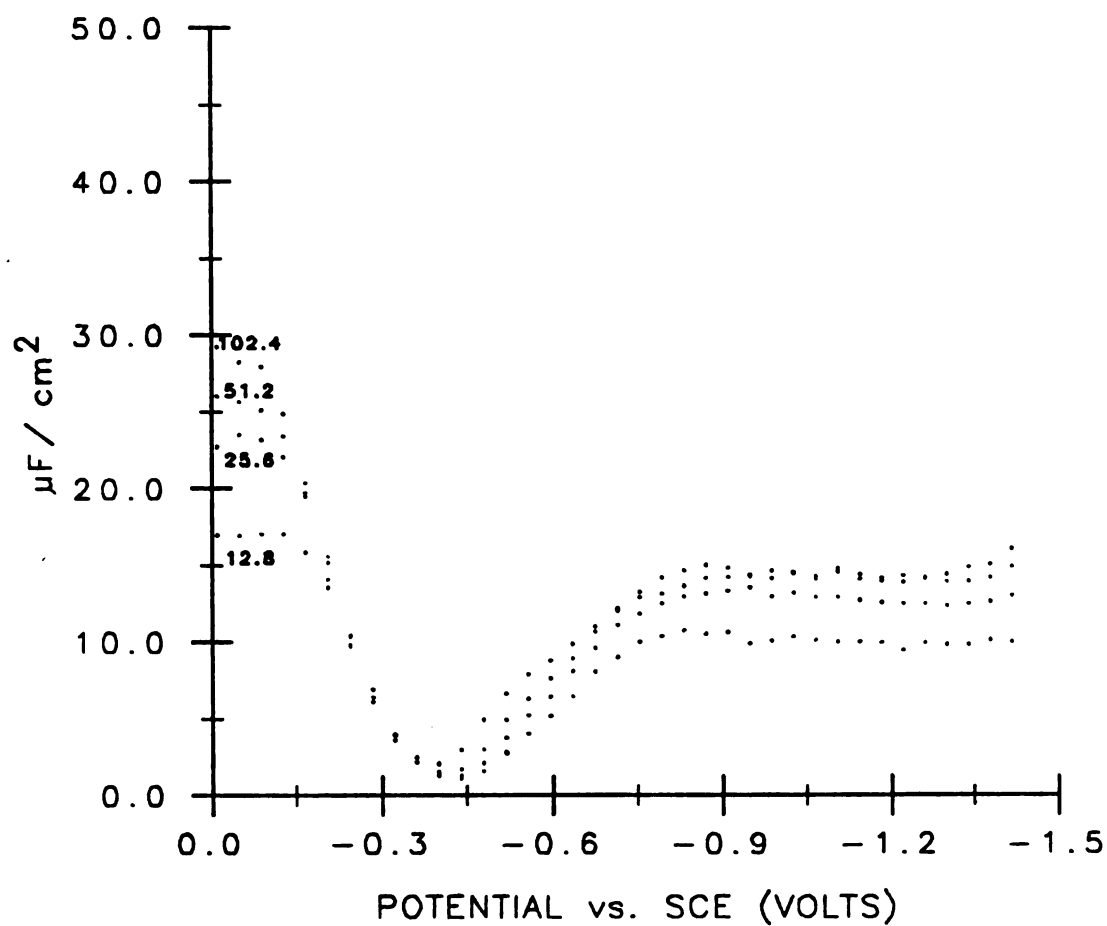


Figure 3-16.

Capacitance curves of HMDE in  $10^{-5}$  M KCl solution obtained with  $N_{d1}=20$ ,  $N_{d2}=1000$ , and  $t_d = 12.8, 25.6, 51.2, 102.4$  ms with the higher capacitances corresponding to the longer times

## KCl SOLUTIONS

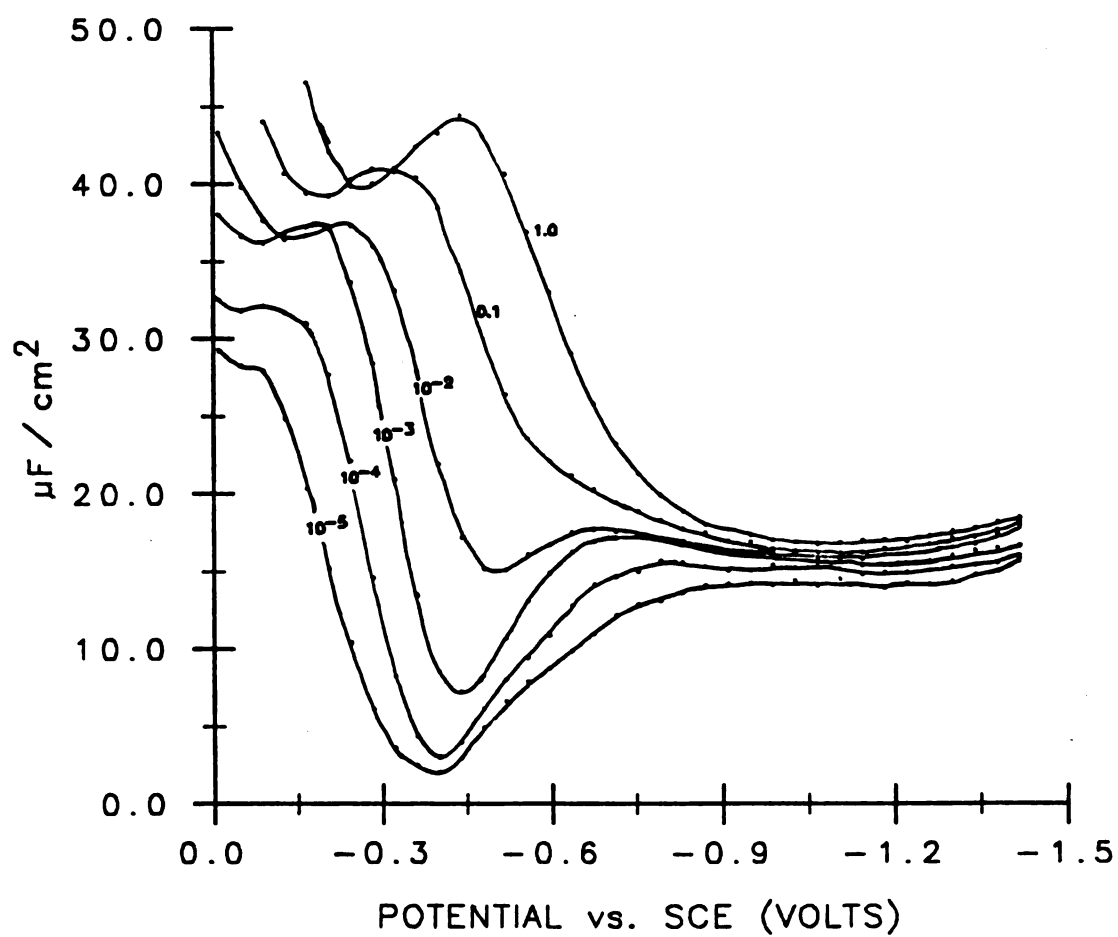


Figure 3-17.

Capacitance curves of KCl solutions with concentrations of 1, 0.1, 0.01,  $10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$  M

quantization error for  $N_{d1} = 20$  is 1.17 % RSD and for  $N_{d1} = 100$  is 0.51 % RSD according to Equations 3-11 and 3-12. The impurities in the KCl solutions may be an important consideration when KCl concentration is high, e.g. above  $10^{-3}$  M; however, no significant drift of capacitance curves were observed after the capacitance reached a constant value. The leakage current (1.9 nA) from the analog switches is the main source of error when the concentration of KCl is low (below  $10^{-3}$  M) and  $t_d$  is large. The reduction of oxygen or reduction of other electroactive species is the second; fortunately, it tends to cancel out the error of current leakage. The measurement error of the double layer capacitance,  $\Delta C_{d1}$ , due to the current leakage can be estimated by the equation

$$\Delta C_{d1} = (1.9 \text{ nA}) \cdot t_d / (A \cdot (0.00977 \text{ V})) \quad (3-14),$$

where  $A$  is the electrode area  $0.0352 \text{ cm}^2$ . Table 3-1 lists the expected error due to the leakage of current of the switch.

Table 3-1      Estimated error due to the switch current  
leakage for the capacitance measurement

$t_d$ (ms)	Error ( $\mu F/cm^2$ )
1.6	0.0088
3.2	0.018
6.4	0.035
12.8	0.071
25.6	0.14
51.2	0.28
102.4	0.57

This error estimation suggests that the capacitance can be obtained accurately for concentrations of KCl solutions above  $10^{-4}$  M if the leakage of current is the only concern. The largest relative error for  $10^{-4}$  M KCl solution due to the current leakage is

$$(0.071 \mu F/cm^2)/(2.95 \mu F/cm^2) \cdot 100\% = 2.4\% \quad (3-15),$$

where  $2.95 \mu F/cm^2$  is the minimum capacitance of  $10^{-4}$  M KCl solution within the potential window tested. The estimated % RSD for individual potential due to the quantization error of ADC is 0.51 % for  $N_{d1} = 100$ , and 1.17 % for  $N_{d2} = 20$ .

For  $10^{-5}$  M KCl solution, the error in the capacitance measurement due to the switch leakage current can be as high

as  $0.57 \mu\text{F}/\text{cm}^2$ . Some uncertainty in the capacitance value is also observed at potentials more positive than  $-0.15 \text{ V}$  vs. SCE.

#### E. Discussion

Figure 3-18 shows the results obtained with this technique and the results obtained by D. C. Grahame (32) for  $0.1 \text{ M KCl}$  solution at  $25^\circ\text{C}$ . These results agree with each other within experimental error.

The advantages of the technique are: First, the tedious manual work in adjusting resistors and capacitors to match up the cell impedance can be avoided. Second, the computer can take data automatically and human error can be avoided. Third, no special skill is required to take data. Fourth, fast data collection allows better results to be obtained. It is known that the capacitance of an electrode usually changes with time due to the adsorption of impurities. For a solid electrode, it is more difficult to renew the electrode surface than for a mercury electrode. Faster data collection will be subject to less error because the electrode has less time to adsorb impurities. For concentrations of  $\text{KCl}$  solutions above  $10^{-3} \text{ M}$ , data can be obtained within 30 seconds for  $N_{d1} = 100$ , and within 8 seconds for  $N_{d1} = 20$ . For  $10^{-4} \text{ M}$ , a typical experiment time is 150 seconds for  $N_{d1} = 20$ . Although measurements at a stationary mercury electrode are probably subject to some



0.1 M KCl

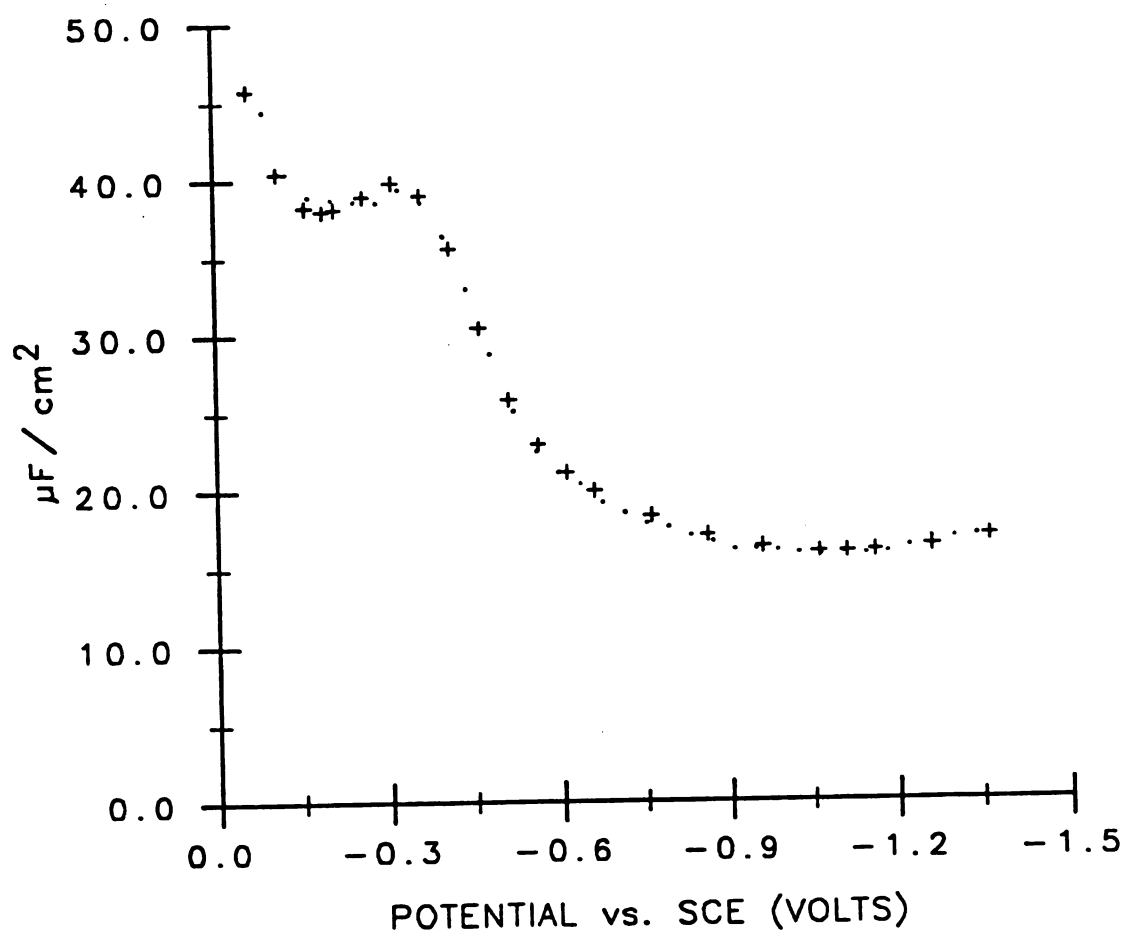


Figure 3-18.

Capacitances of mercury electrode in  
0.1 M KCl solution

.... this work;

+++. Grahame's data

poisoning, in this research work no significant time dependence effects on capacitance measurements were observed.

For some solid electrodes, measurement speed may be more important than accuracy or precision of measurement. (Errors of several percent of error may be tolerable.) With some sacrifice in precision (using  $N_{d1} = 20$ , the expected precision due to the quantization of ADC is 1.17 % RSD), a capacitance profile (37 data points) can be obtained within 8 seconds for 1 M KCl solution.

Based on the charge injection principle, further enhancement of the speed of capacitance measurement can be achieved by using a higher resolution ADC which would require less data averaging.

The major disadvantage of this technique is that it is not suitable for capacitance measurements with electroactive species in the solution.

The cell geometry can probably be improved further to provide more uniform current density and faster response by using a fine-tipped capillary (33) with a cylindrical counter electrode surrounding the capillary.

## CHAPTER 4

### EXAMPLE OF CONTROLLED CURRENT EXPERIMENT: CONSTANT CURRENT CHRONOPOTENTIOMETRY WITH CHARGING CURRENT COMPENSATION

#### A. Introduction

When a constant current is applied to an electrode, part of the current goes to charge the double layer capacitance. The desired constant Faradaic current is no longer constant because of the charging current. The chronopotentiogram (potential vs. time curve) obtained is distorted by the charging current. As will be noted later in this chapter, the transition time (the time interval between two sharp potential changes) is longer than that predicted by the theory.

A method has been developed in this thesis work to compensate the charging current in order to make the Faradaic current constant using the charge injection method. Charge pulses are injected at a constant rate. The portion of the charge which has been consumed by Faradaic process from the beginning of the experiment to any specific injection time has been calculated by subtracting the charge which has gone to charge the double layer capacitor from the total charge injected. If there is any deviation between the desired Faradaic charge and actually consumed Faradaic

charge, a mechanism to minimize this deviation has been developed and used to make the Faradaic current constant. The mechanism of charging current compensation will be discussed in section C.

A great improvement of the correspondance between the measured transition times with the transition times predicted by the theory for a series of concentrations of  $TlCl$  in  $0.1\text{ M } KCl$  solution is demonstrated in Section D. In-situ compensation of charging current allows the detection limit for cadmium to be as low as  $2.5 \cdot 10^{-7}\text{ M}$ .

## B. Historical Background

If we apply a controlled current to an electrochemical cell and plot the potential as a function of time, we obtain a so called chronopotentiogram. As the name of chronopotentiometry infers, the potential is monitored as a function of time.

The most commonly used chronopotentiometric technique is to apply a constant current to an electrochemical cell. Let us suppose that we have a solution which contains sufficient supporting electrolyte and an electroactive species in the oxidized form  $Ox$ . The species  $Ox$  can undergo the reaction,  $Ox + ne^- \rightarrow Red$ , by supplying electrons to the electrode. When a constant current  $i$  is applied to the electrode, the species  $Ox$  is reduced at a constant rate. The potential of the electrode moves rapidly to some value

which is a characteristic of the redox couple. The potential varies with time as the Ox/Red concentration ratio changes at the electrode surface as a result of the conversion of Ox to Red. After the concentration of Ox at the electrode surface drops to zero, the flux of Ox to the electrode is no longer sufficient to bear the impressed current and the electrode potential changes very rapidly until the reduction of another electroactive species (when there is such a species which is reducible at more negative potential) or the decomposition of the solvent occurs. The time interval between these two sharp changes of the potential is called the transition time,  $\tau$ . The transition time  $\tau$  is related to a number of variables including the Ox concentration by the Sand equation (34):

$$i\tau^{1/2} = \pi^{1/2} n F A D_{Ox}^{1/2} C_{Ox} / 2 \quad (4-1)$$

where  $i$  is the applied constant current,  $n$  is the number of electrons involved in the electrochemical reaction,  $F$  is the Faraday,  $A$  is the area of the working electrode,  $D_{Ox}$  is the diffusion coefficient of Ox, and  $C_{Ox}$  is the bulk concentration of Ox.

The measured  $\tau$  can be used to determine the number of electrons involved in the reaction, or the diffusion coefficient  $D_{Ox}$ , or the concentration  $C_{Ox}$ . The transition time does not depend on the reversibility of the



electrochemical reaction since a constant current is forced through the cell to cause a constant rate of reaction. The independence of the transition time on reversibility is an advantage in analytical applications, especially for reactions which are not very reversible. The potential of the electrode during the transition, on the other hand, depends on the reversibility of the reaction. Therefore, chronopotentiometry can be used for studying the kinetics of electrochemical reactions. For a reversible reaction, the relationship between the electrode potential  $E$  and the time  $t$  (35) is:

$$E = E_{\tau/4} + (RT/nF) \cdot \ln((\tau^{1/2} - t^{1/2})/t^{1/2}) \quad (4-2),$$

where  $E_{\tau/4}$ , the potential at the time  $\tau/4$ , is:

$$E_{\tau/4} = E_f^\circ - (RT/2nF)(D_{\text{Ox}}/D_{\text{Red}}) \quad (4-3),$$

where  $E_f^\circ$  is the formal potential of the redox couple, and  $D_{\text{Red}}$  is the diffusion coefficient of Red.

For a totally irreversible reaction, the relationship between the potential  $E$  and the time  $t$  (36) is:

$$E = E_f^{\circ} + (RT/\alpha n_a F) \ln(nFA C_{Ox} k^{\circ}/i) \\ + (RT/\alpha n_a F) \ln(1-(t/\tau)^{1/2}) \quad (4-4),$$

where  $\alpha$  is the transfer coefficient,  $n_a$  is the number of electrons involved in the rate determining step,  $k^{\circ}$  is the standard heterogeneous rate constant. The electrode potential shifts negatively with increasing current.

Chronopotentiometry can be used for the measurement of adsorption and surface film formation (37). By impressing high current to the electrode, the electrons consumed by the diffusion of  $Ox$  to the electrode surface can be minimized. Thus,

$$\lim_{i \rightarrow \infty} it = nF\Gamma A \quad (4-5),$$

where  $\Gamma$  is the surface excess, in moles/cm<sup>2</sup>, of the adsorbed material.

If a reverse current is applied to the electrode after some experimental time  $t_1$ , some of the Red formed during the forward period is oxidized to  $Ox$ . The potential changes rapidly when the concentration of Red at the electrode surface drops to zero. The separation of the forward and reverse waves on the potential axis can be related to the reversibility of the electrochemical reaction.

If both the forward and reverse processes are diffusion



controlled, if both currents have the same magnitude, and if the reaction has no chemical complications, the transition time for the reverse process,  $\tau_2$ , is related to the time  $t_1$ , the time of applying the reverse current, by (38)

$$\tau_2 = t_1/3 \quad (t_1 \leq \tau) \quad (4-6).$$

If the Red undergoes some chemical reaction to form products  $P_{Red}$  which do not react in the same manner as Red does, the effect will be evident in the resulting chronopotentiogram. For example, if  $P_{Red}$  does not oxidize within the range of potentials in the experiment, the transition time  $\tau_2$  will be shorter than  $t_1/3$ . The chronopotentiometric potential/time relationships for a number of common electrochemical reaction mechanisms have been derived by several chemists (38-42). Current reversal chronopotentiometry and cyclic chronopotentiometry can be used for studying the kinetics of electrochemical reactions (43,44).

Chronopotentiometric techniques have not been widely used for the past 10 to 15 years. A major reason that they have not is that the electrode potential changes during a chronopotentiometric experiment and a fraction of the impressed current is always consumed by the charging of double layer capacitor and not by the Faradaic process. Theoretically, a chronopotentiogram rises very rapidly at

the beginning and at the end. However, due to the charging current which decreases the rate of the Faradaic process, the chronopotentiogram rises slower especially at the beginning and at the end where the rapid voltage change requires more charging current. The chronopotentiogram distortion makes the determination of transition time more difficult and less accurate when the concentration is below  $10^{-3}$  M. Chronopotentiometric techniques can be useful if the effect of double layer charging can be removed.

The effect of double layer capacitance on the distortion of chronopotentiograms has been considered by several chemists (45-50). All authors have assumed that the double layer capacitance is independent of electrode potential. If one takes 10 seconds as the transition time, the lower limit for practical analytical applications is at about  $10^{-4}$  M concentration level (51).

Several graphical methods (36,45,48,52-55) have been proposed to determine the transition time from a chronopotentiogram. However, none of these methods yield a constant value for  $i\tau^{1/2}/C$  which should be constant according to the Sand's equation (Equation 4-1).

Several chemists have tried to generate a constant Faradaic current by adding the required charging current. L. Gierst (56) and P. Mechelynck (57) developed a device with a capacitor parallel to the electrochemical cell in the circuit. A capacitor with capacitance approximately equal

to the double layer capacitance of the working electrode was chosen for the device. The current needed for charging the capacitor was added to the constant current and the resulting current was impressed on the electrochemical cell. The major disadvantages of this technique are: 1. The correction of charging current is not exact because the double layer capacitance changes as a function of potential. 2. The device can not handle chronopotentiometric experiments with short transition time (below a few seconds).

W. D. Shults and co-workers (58) developed an apparatus with a function similar to the ones developed by L. Gierst (56) and P. Mechelynck (57). Instead of a capacitor, they used a blank cell with the same electrode area and with a solution containing only the supporting electrolyte. The change of double layer capacitance with potential can be taken into account by this method.

The apparatus developed by Gierst and Mechelynck and by Shults tend to cause the problem of overshooting due to the positive feedback. When there is some small time delay in the addition of charging current, the reduction of Ox will be subject to a suddenly increased current which causes a smaller transition time than there should be. Shults and co-workers used their apparatus only for long transition time such as 6 - 40 seconds. According to W. H. Reinmuth (59), these apparatus can only be applied to long transition

time because of the inherent instability.

P. Bos and E. Van Dalen (60) developed an apparatus based on the same principles as the one of W. D. Shults and co-workers. The apparatus was protected against overloading by the charging current. The shortest transition time can be as short as 0.1 second. With the transition time at about 11 seconds, the former obtained fairly constant  $i\tau^{1/2}/C$  values (1.9 % RSD) for a mercury electrode in  $Tl^+$  and  $KNO_3$  solution with  $Tl^+$  in the concentration range between  $3.25 \cdot 10^{-5}$  M and  $6.5 \cdot 10^{-4}$  M. There are still some disadvantages in using this method: 1. Two cells must be used. 2. The areas and the capacitances of both electrodes can be difficult to match, especially for solid electrodes. 3. The shortest transition time (0.1 second) which can be applied is not very short.

#### C. Description and Test of the Method

In this section a method for obtaining a constant Faradaic current based on a charge injection method will be discussed.

The capacitive charge has been given this name because it is directed to the double layer capacitance. The charge required to change the potential of an electrode from one fixed potential to any other potential will be designated as an integral capacitive charge. Before the charging current compensation is accomplished, the integral capacitive

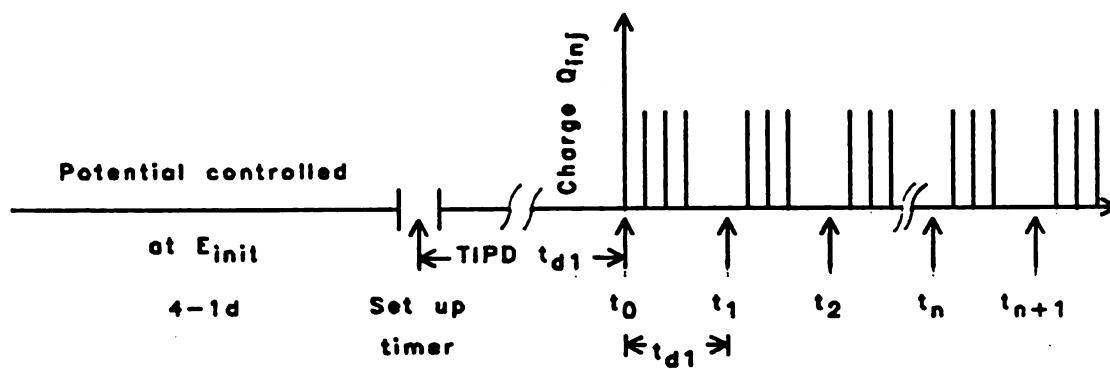
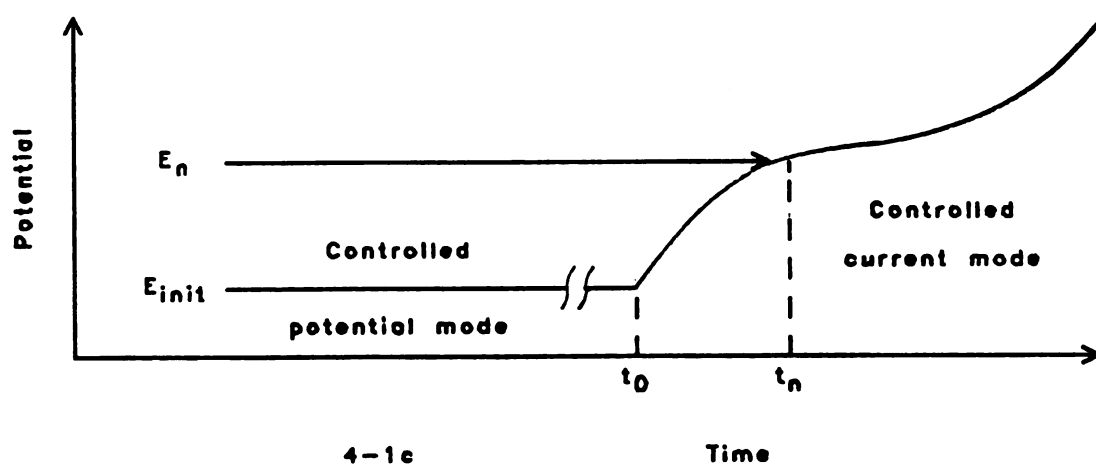
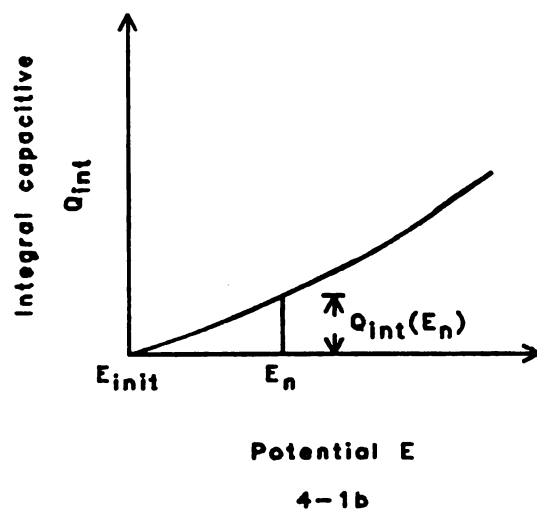
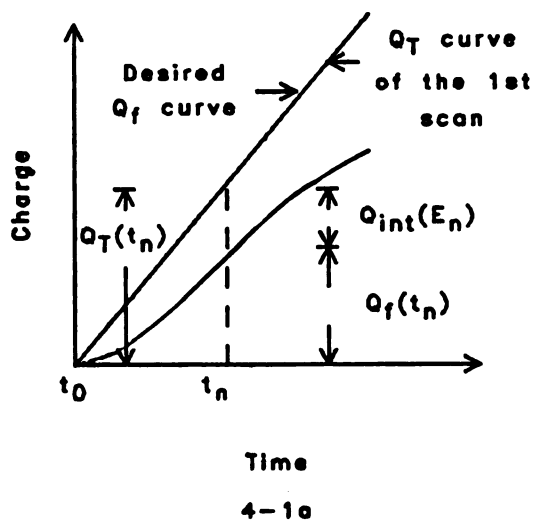
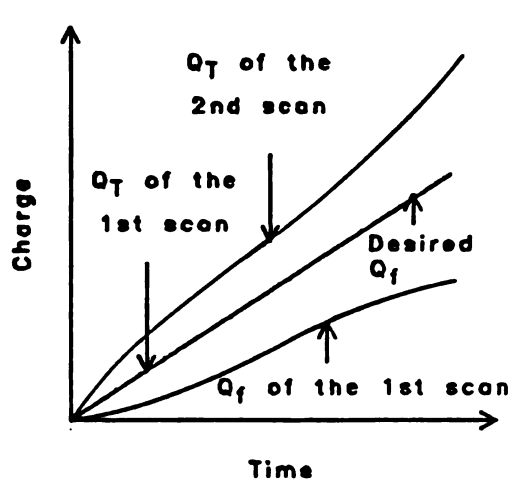
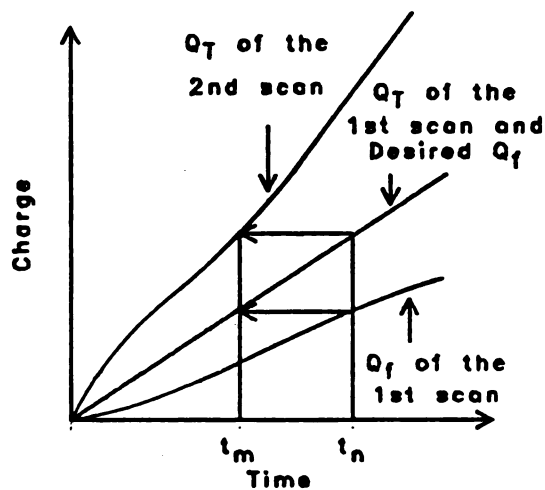


Figure 4-1.

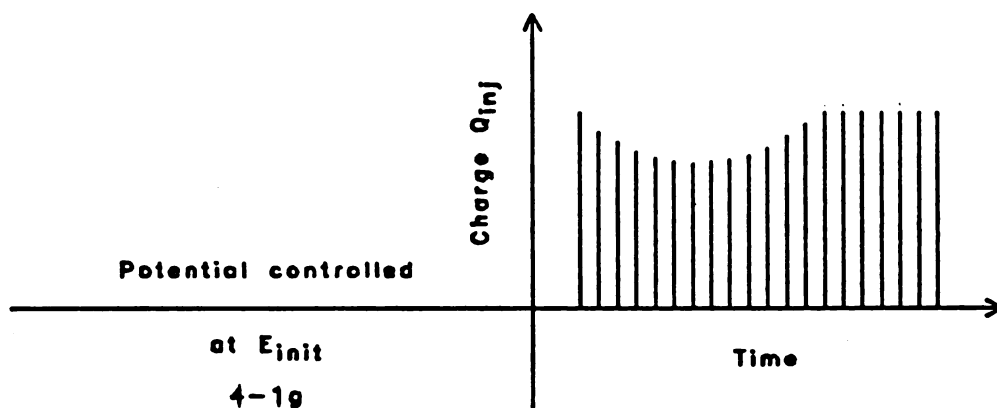
Illustration of the compensation of charging current, the first part.



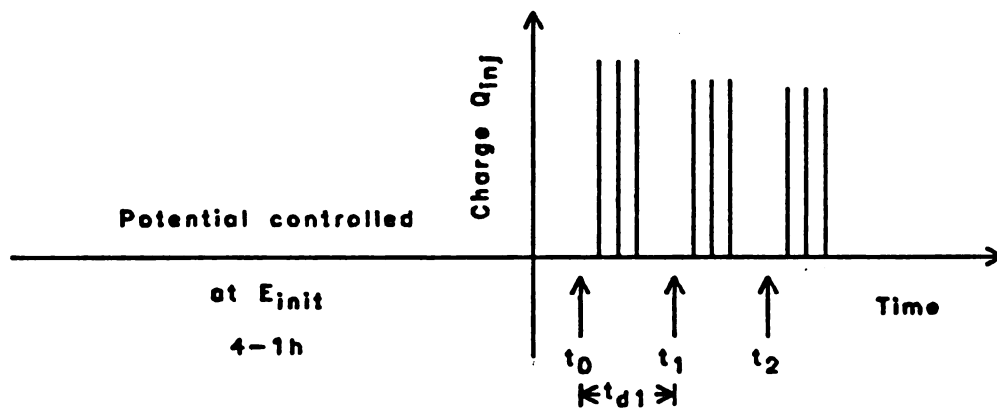
4-1e Graph for the simple method of compensation



4-1f Graph for the method actually used



4-1g



4-1h

Figure 4-1.

Illustration of the compensation of charging current, the second part.

charges of the working electrode must be measured over the potential range of interest. The results are stored in the memory of the computer. Figure 4-1b illustrates the integral capacitive charge  $Q_{int}$  required to make the potential perturbation from the potential  $E_{init}$  to the potential  $E$  for a working electrode in a solution. The solution may be a blank solution containing only the supporting electrolyte and the solvent, or it may be the solution to be tested. Although the integral capacitive charge measurement may be subject to some error when the test solution contains electroactive materials, the error is small for low concentrations of electroactive species as will be shown in Figures 4-14 and 4-15 (less than 11 % error for  $2 \cdot 10^{-5}$  M  $Cd^{+2}$  and less than 4 % error for  $5 \cdot 10^{-6}$  M  $Cd^{+2}$  in 0.01 M KCl solution).

Figure 4-2 shows the process of measuring the integral capacitive charge. The operator sets up the parameters such as initial potential  $E_{init}$ , final potential  $E_{final}$ , charge to be injected  $Q_1$ , delay time for charge injection  $t_d$ , etc. For the reaction  $Ox + ne^- \rightarrow Red$ ,  $E_{final}$  is more negative than  $E_{init}$  and  $Q_1$  is negative. After the operator starts the program, the PCP measures the electrode potential and compares it to the desired initial value  $E_{init}$ . If there is any difference in these two potential values, the PCP injects enough charge pulses of proper polarity to bring the electrode potential to the initial value. After the initial





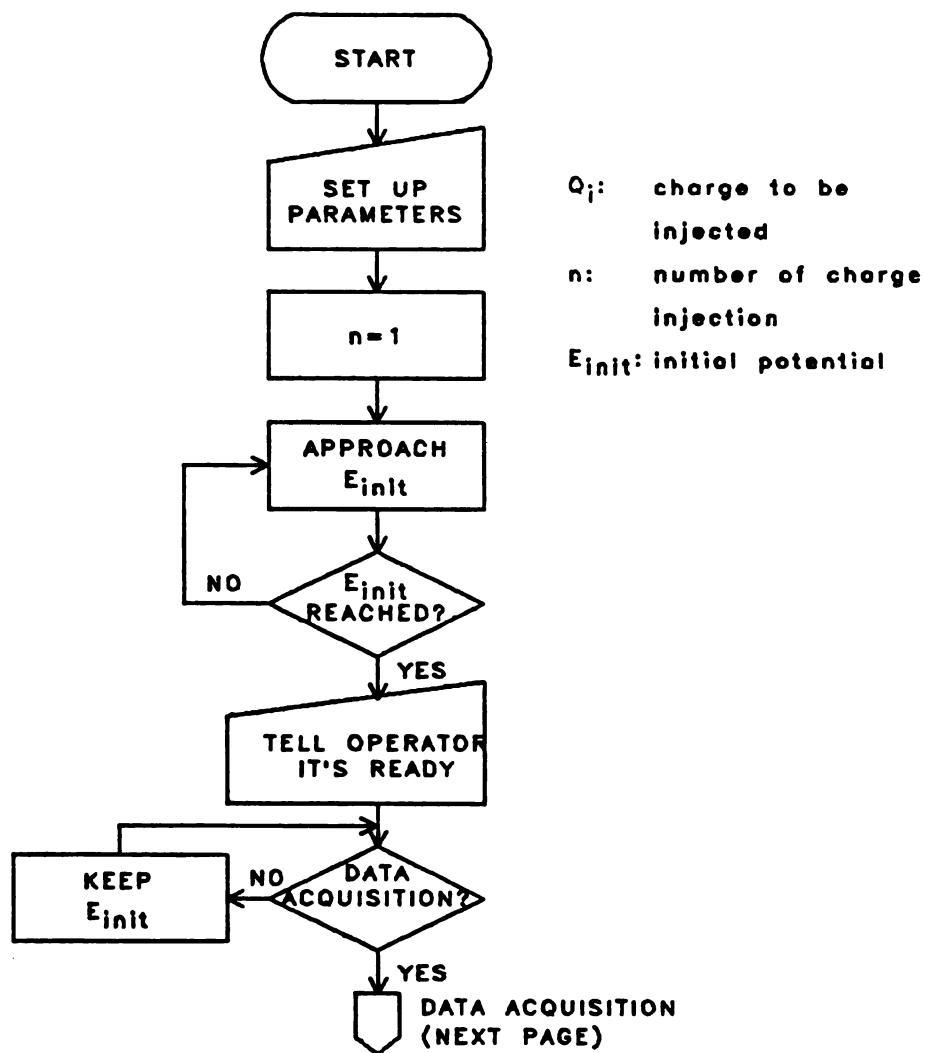


Figure 4-2. Flow chart of the program for the measurement of integral capacitive charge; the first part

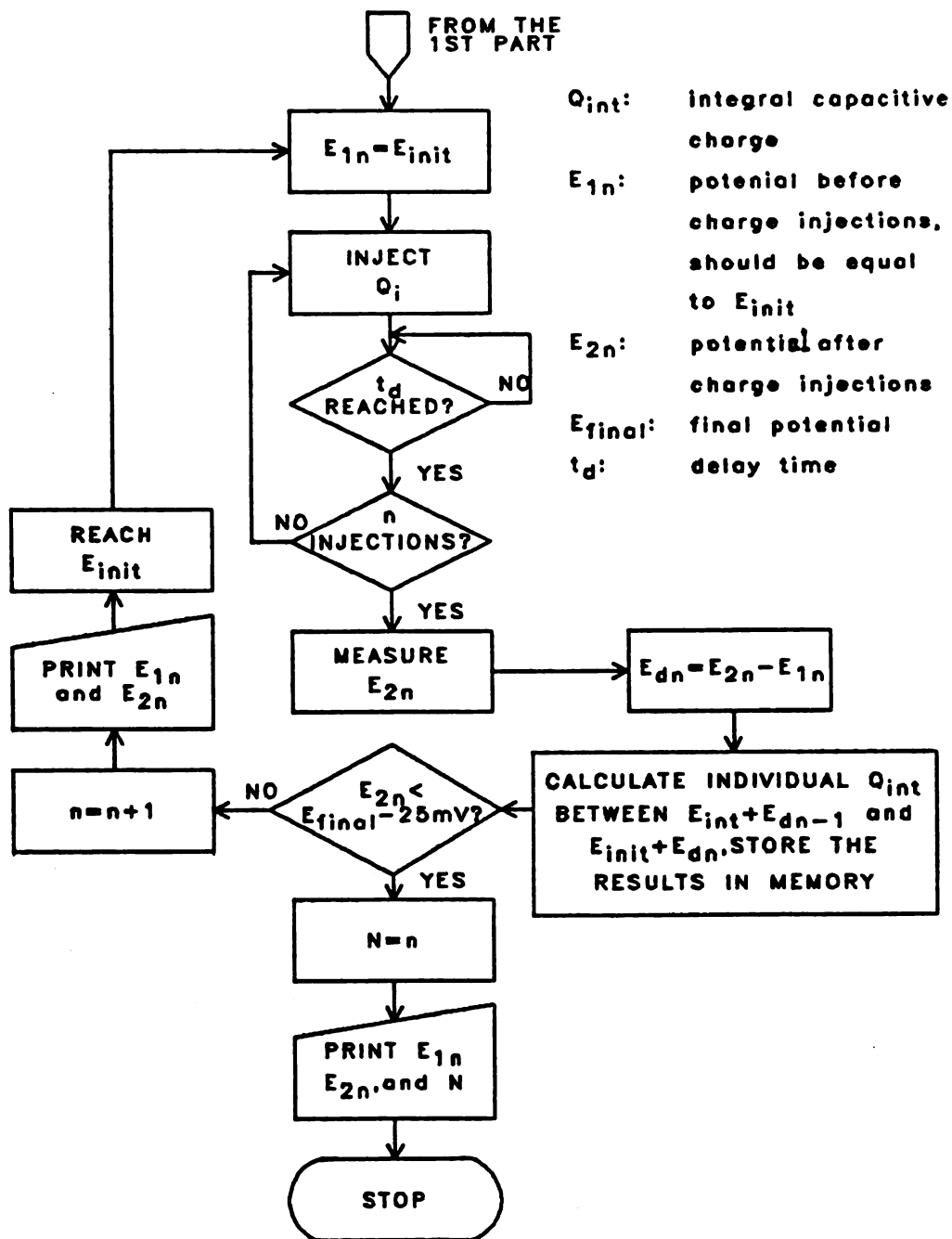


Figure 4-2.

Flow chart of the program for the measurement of integral capacitive charge, the second part

potential is reached, the PCP reports to the operator that it is ready to execute data acquisition. The PCP keeps the electrode potential at  $E_{init}$  by adding charge pulses as needed until the operator commands the PCP to execute the data acquisition. After the data acquisition starts, the PCP makes sure that the potential  $E_{11}$  before charge injection is equal to  $E_{init}$ , then injects the charge  $Q_1$  to the electrode and measures the potential  $E_{21}$  after some slight delay time  $t_d$ . The minimum time required by the computer programming is about 50  $\mu s$  for each charge injection. The PCP calculates the potential difference  $E_{d1}$  resulting from one injection of charge  $Q_1$  by the equation:  $E_{d1} = E_{21} - E_{11}$  ( $E_{d1}$  should have a negative value). The integral capacitive charge  $Q_{int}$  for the individual value of potentials between  $E_{init}$  and  $E_{init} + E_{d1}$  such as  $E_{init}$ ,  $E_{init} - 1.22$  mV,  $E_{init} - 2.44$  mV, ...,  $E_{init} + E_{d1}$ , is calculated by assuming that  $Q_{int}$  is linear within the potential range. The results are stored in the memory of the computer. On the screen, the PCP reports the values  $E_{11}$  and  $E_{21}$ , the potentials before and after charge injection. A similar  $n$ th process is performed to bring the electrode potential to  $E_{init}$ , to inject charge  $Q_1$   $n$  times, to measure the electrode potential after charge injections  $E_{2n}$ , to calculate the potential difference  $E_{dn} = E_{2n} - E_{1n}$  ( $E_{1n} = E_{init}$ ), to calculate the individual capacitive charge for the potentials within the range  $E_{init} + E_{dn-1} - 1.22$  mV and  $E_{init} + E_{dn}$ , and to report

the values  $E_{1n}$  and  $E_{2n}$ , the potentials before and after charge injections. When the process has been completed for a potential which is more negative than  $E_{final} - 24.4$  mV, the PCP reports the value  $N$ , the number of charge injections that have been performed during the most recent series of charge injections. When this occurs, the measurement of the integral capacitive charge has been completed. The capacitive charge for the individual potential between  $E_{init}$  and  $E_{final} - 24.4$  mV such as  $E_{init}$ ,  $E_{init} - 1.22$  mV, ...,  $E_{final}$ , ...,  $E_{final} - 24.4$  mV, is stored in the memory of the microcomputer during the execution of this program. In order to provide a wider range of capacitive charge memory file, the value  $E_{final} - 24.4$  mV is selected to be more negative than  $E_{final}$ . To obtain fairly accurate capacitive charge for the individual potential, a value of 10 mV to 20 mV for the potential range between  $E_{dn-1}$  and  $E_{dn}$  is suggested for any electrode which have fairly constant value of double layer capacitance within the potential range (such as mercury electrode in 0.1 M or 0.01 M KCl solutions).

For the compensation of charging current using a blank cell, the integral capacitive charge should be measured before testing the solution of interest. For the compensation of charging current in-situ, the integral capacitive charge may be measured after each chronopotentiometric scan.

To perform charging current compensation, the

operator prepares the solution to be tested and sets up the parameters such as the initial potential  $E_{init}$ , the final potential  $E_{final}$ , the time interval between two potential measurements  $t_{d1}$ , maximum number of charge injections within the period  $t_{d1}$ , a number TIPD for the amount of delay time  $TIPD \cdot t_{d1}$  to keep the electrode potential at  $E_{init}$  after setting up the timer and before executing data collection, etc. The operator then initiates the program to perform charging current compensation. The process of performing the first chronopotentiometric scan is shown in Figures 4-1c, 4-1d, and 4-4. The PCP brings the electrode potential to the initial value  $E_{init}$  and informs the operator that it is ready to begin the data acquisition. The operator can start the data acquisition after this point has been reached; however, it will be found advantageous to wait for a while (e.g., 10 seconds) for the electrode to reduce any impurities which are present in its vicinity and are reducible at  $E_{init}$ . After the operator commands the PCP to start the data acquisition, the PCP sets up the timer, keeps the potential at  $E_{init}$  for a period  $TIPD \cdot t_{d1}$ . The PCP measures the electrode potential at the times  $t_0$  and stores it in the computer memory, injects a charge pulse or a number of charge pulses to the electrode, waits until  $t_1$  is reached, then measures the electrode potential and injects another charge pulse or more charge pulses. The PCP continues to measure the electrode potential and to inject a

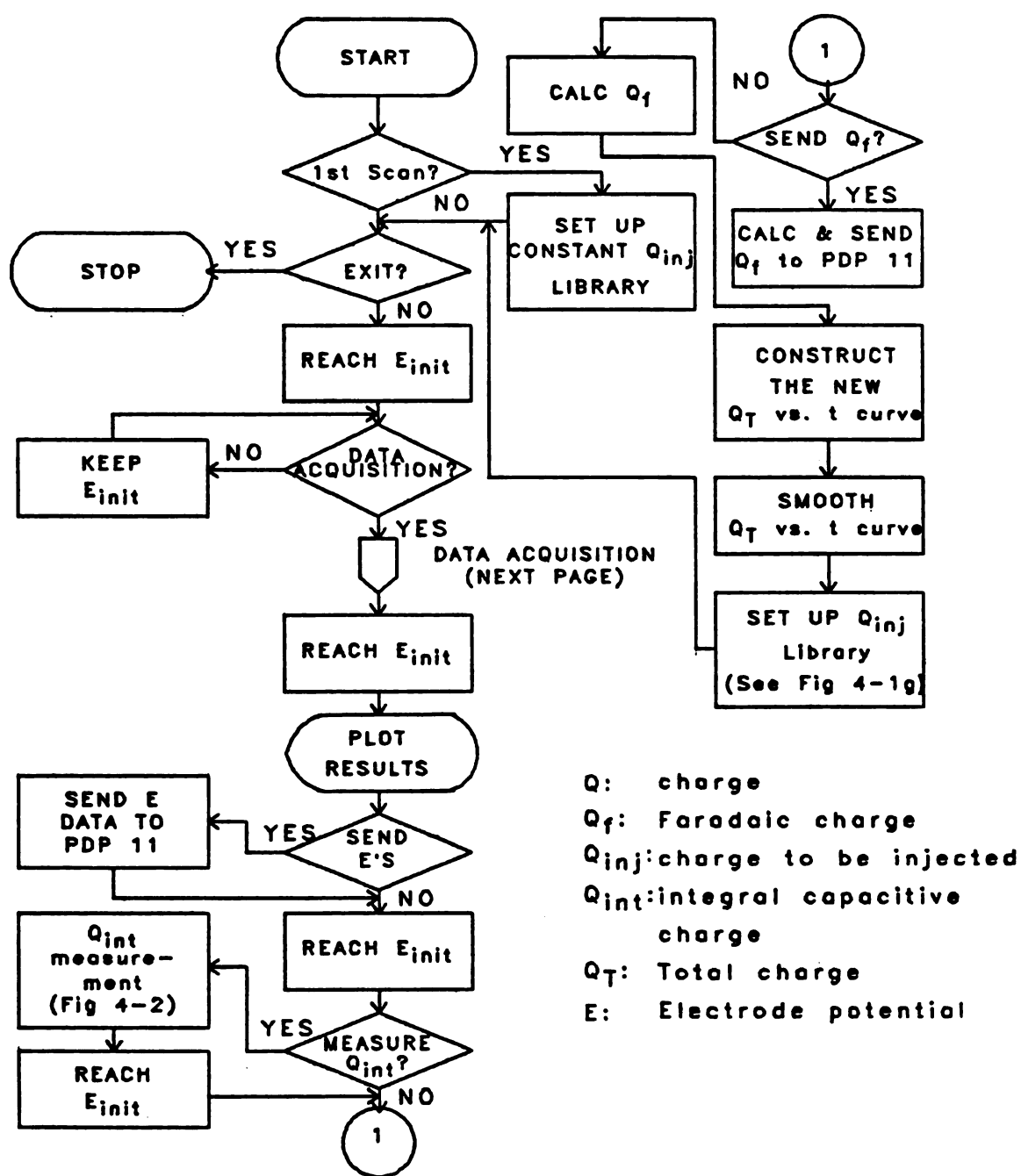


Figure 4-3. Flow chart of the program for chronopotentiometry with charge-compensating current compensation.

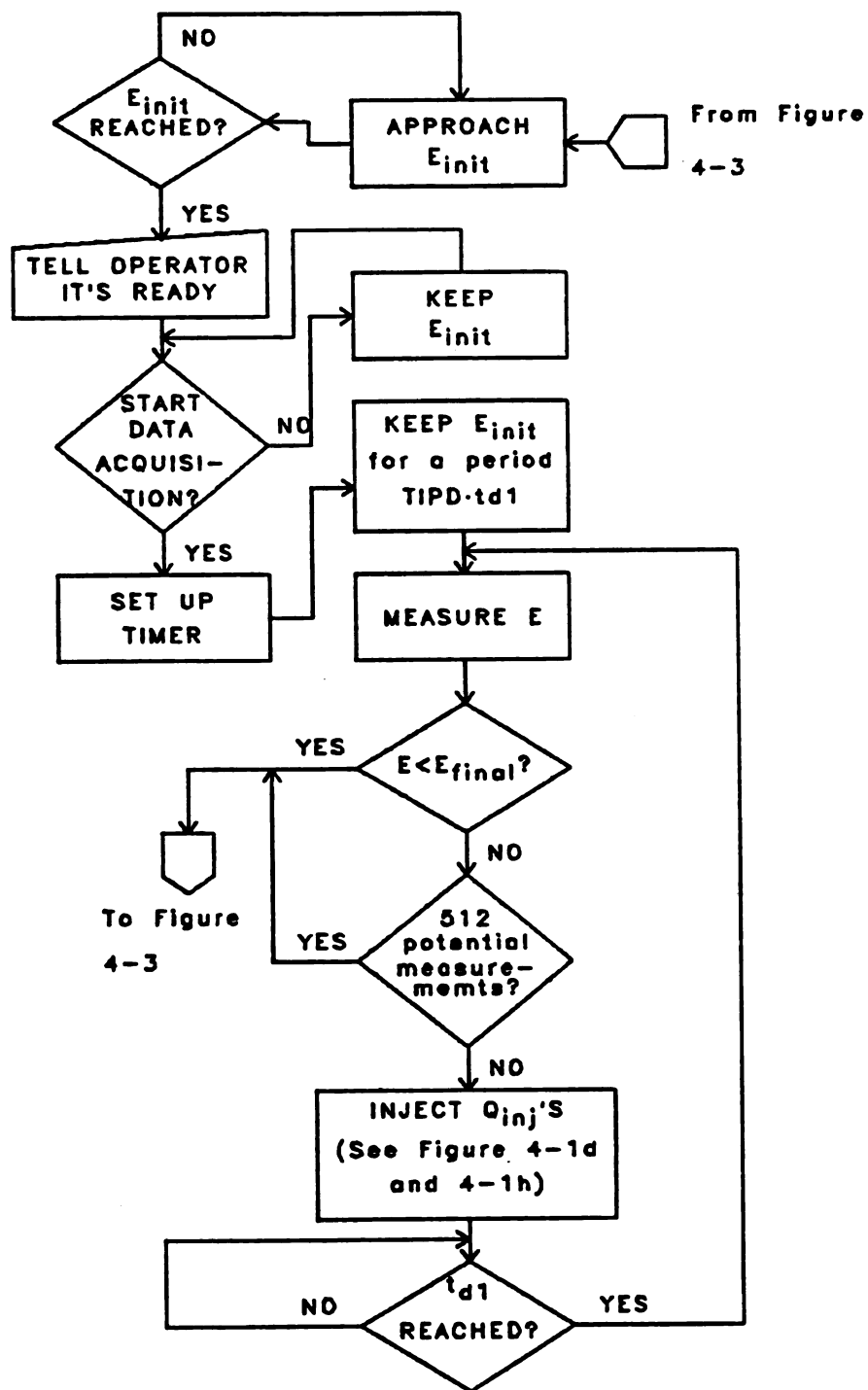


Figure 4-4. Flow chart of the program for data acquisition of a chronopotentiogram

constant quantity of charges within  $t_{d1}$  time interval until the electrode potential is equal to or more negative than  $E_{final}$ , or until 512 potentials are measured, whichever occurs first. The electrode potentials at the time  $t_0$ ,  $t_1$ ,  $t_2$ , ..., etc. are stored in the memory during the data acquisition.

For the injection of a charge pulse between two adjacent potential measurements, the minimum value of  $t_{d1}$  is 156  $\mu$ S. For the injection of two charge pulses, it is 205  $\mu$ S. For the injection of 10 charge pulses, it is 601  $\mu$ S. A detailed calculation of the minimum value of  $t_{d1}$  can be found in Appendix A.

After the first scan, in order to restore the desired initial concentration of Ox in the vicinity of the electrode surface, the electrode potential is brought to the value  $E_{init}$  to oxidize Red back to Ox for a reversible reaction, or not to reduce Ox any more for an irreversible reaction. This is necessary in the situation in which an HMDE is used and the same mercury drop will be used, or in the situation in which a solid electrode is used, because the solution near the electrode is not well stirred. After the potential reaches  $E_{init}$ , the chronopotentiogram, the E vs. time curve, will be plotted on the screen. The operator may save the results. The PCP holds the electrode potential at  $E_{init}$ . The operator may perform the capacitive charge measurement with the same solution when the in-situ compensation is



desired. It is advantageous to do so for in-situ compensation of charging current since the problem of drift of electrode capacitance can be reduced.

As shown on Figures 4-1 and 4-3 the PCP identifies the electrode potential  $E_n$  at the time  $t_n$  (Figure 4-1c) and locates the integral capacitive charge  $Q_{int}(E_n)$  for the potential  $E_n$  (Figure 4-1b). The Faradaic charge  $Q_f(t_n)$  (Figure 4-1a), which has been consumed at the time  $t_n$ , is calculated by the equation:

$$Q_f(t_n) = Q_T(t_n) - Q_{int}(E_n) \quad (4-7),$$

where  $Q_T(t_n)$  is the total charge injected at the time  $t_n$  of the most recent scan (In the first scan, the  $Q_T$  vs. time curve is the desired  $Q_f$  curve).

There are many possible methods of adjusting the total charge curve in order to make the Faradaic charge curve approach the desired straight line. As shown on Figure 4-1e, a simple method is to add the charge difference between  $Q_f(t_n)$  and the desired  $Q_f$  value to  $Q_T(t_n)$  of the most recent scan. Instead of this simple method, I used a method which provides faster compensation. This method is illustrated in Figure 4-1f. The PCP locates the time  $t_m$  at which  $Q_f(t_n)$  should have been consumed. For the next scan, the total charge at  $t_m$  will be the total charge which has been injected at  $t_n$  of the previous scan. The  $Q_T$  vs.  $t$

curve is extended to a higher quantity of charge by extrapolating the end portion of the curve.

If the potential  $E_{n1}$  (not shown) at the time  $t_{n1}$  is more negative than the potentials before  $t_{n1}$ , and if  $E_{n2}$  is the first potential which is more negative than  $E_{n1}$ , the capacitive charge corresponding to the potential change is divided evenly in the time period between  $t_{m1}$  and  $t_{m2}$ . ( $t_{m1}$  and  $t_{m2}$  are determined in the same manner as  $t_m$  is determined.) The total charge curve is smoothed and then divided into small charge segments to be injected in the next scan as shown in Figures 4-1g and 4-1h. The smoothing is performed by using a small time window to average the data within it. If the capacitive charge is not distributed evenly within  $t_{m1}$  and  $t_{m2}$ , or if the smoothing is not performed, the injection of a large charge pulse or large charge pulses resulting from the compensation of charging current may generate a potential spike of a few millivolts in the next chronopotentiogram. A time window of less than 5 % of the transition time is suggested for smoothing. This kind of charging current compensation can be repeated a number of times until the Faradaic charge curve is close to the desired straight line or until the chronopotentiogram rises rapidly at the beginning and at the end.

This method of charging current compensation was tested with a dummy cell whose configuration is shown in Figure 4-5. The charge injected into the capacitor  $C_{dm1}$  was

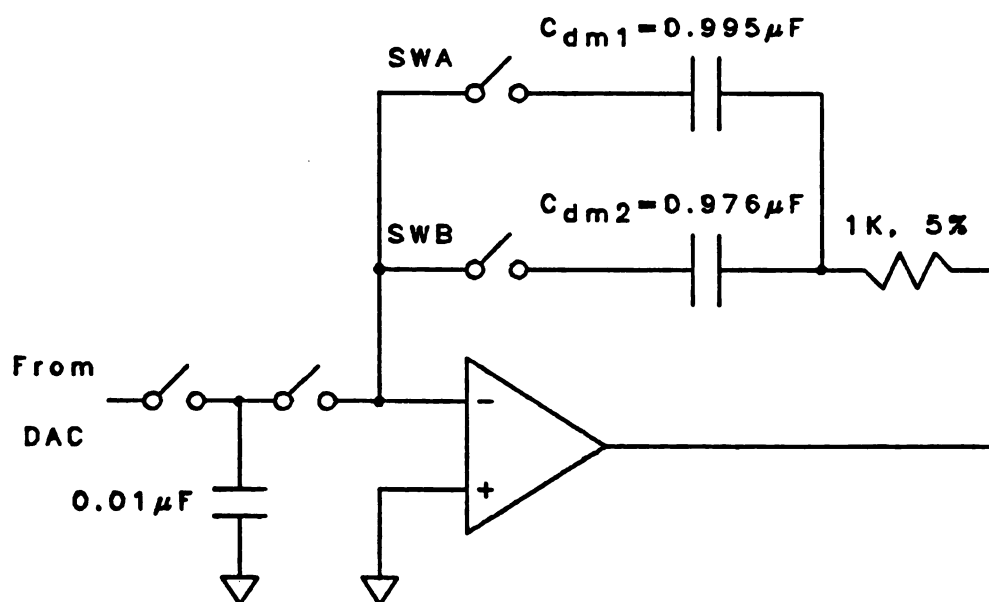


Figure 4-5. Circuits of dummy cell for the test of charging current compensation for chronopotentiometry  
 $C_{dm1}$ : the charging capacitor  
 $C_{dm2}$ : the Faradaic capacitor

considered as the capacitive charge which would be compensated. The charge injected into the capacitor  $C_{dm2}$  was considered as the Faradaic charge. With both capacitors in the feedback loop and after compensating for the charging current, the results should look as if only the capacitor  $C_{dm2}$  were present.

Figure 4-6 shows the voltage vs. time curve obtained by applying a constant current to the dummy cell with only the capacitor  $C_{dm2}$  in the feedback loop (only the switch B was closed).

The integral capacitive charge was obtained with only the capacitor  $C_{dm1}$  in the feedback loop. Both capacitors  $C_{dm1}$  and  $C_{dm2}$  were then put in the feedback loop and the compensation of the capacitive charge of  $C_{dm1}$  was performed. Curve 0 of Figure 4-7 shows the voltage vs. time curve obtained by applying the constant current to both capacitors and without any charging current compensation. The capacitive charge of the capacitor  $C_{dm1}$  was compensated in the subsequent scans according to the method described above. In Figure 4-7, the curve 1 corresponds to the results obtained in the first compensation the charging current, curve 2 corresponds to the second compensation, and so on. The fact that curves 1, 2, and 3 almost coincide suggests that the effect of the presence of the capacitor  $C_{dm1}$  in this cell configuration can be eliminated with just one compensation. The fact that one compensation is

## DUMMY CELL

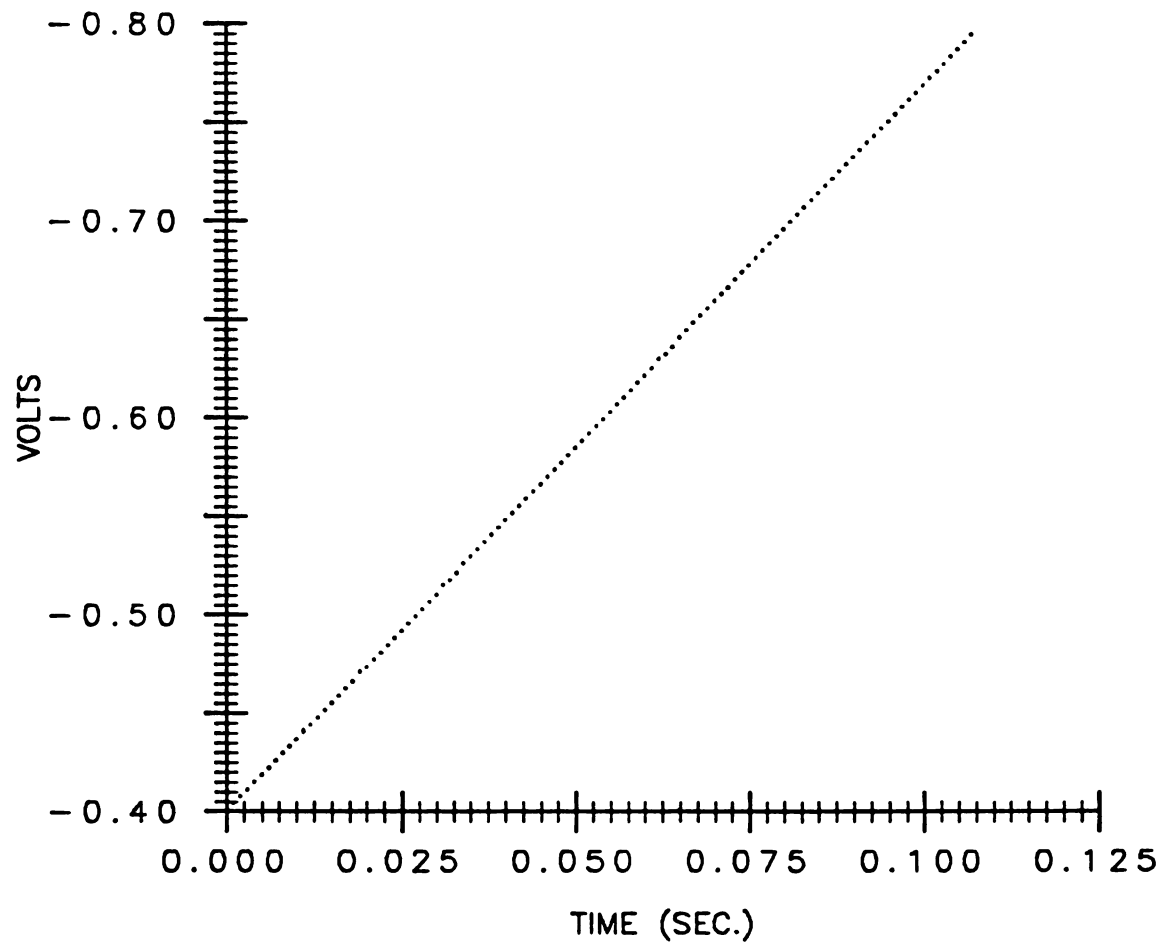


Figure 4-6.

Voltage-time curve obtained with  
one dummy capacitor,  $C_{dm2}$ .

## DUMMY CELL

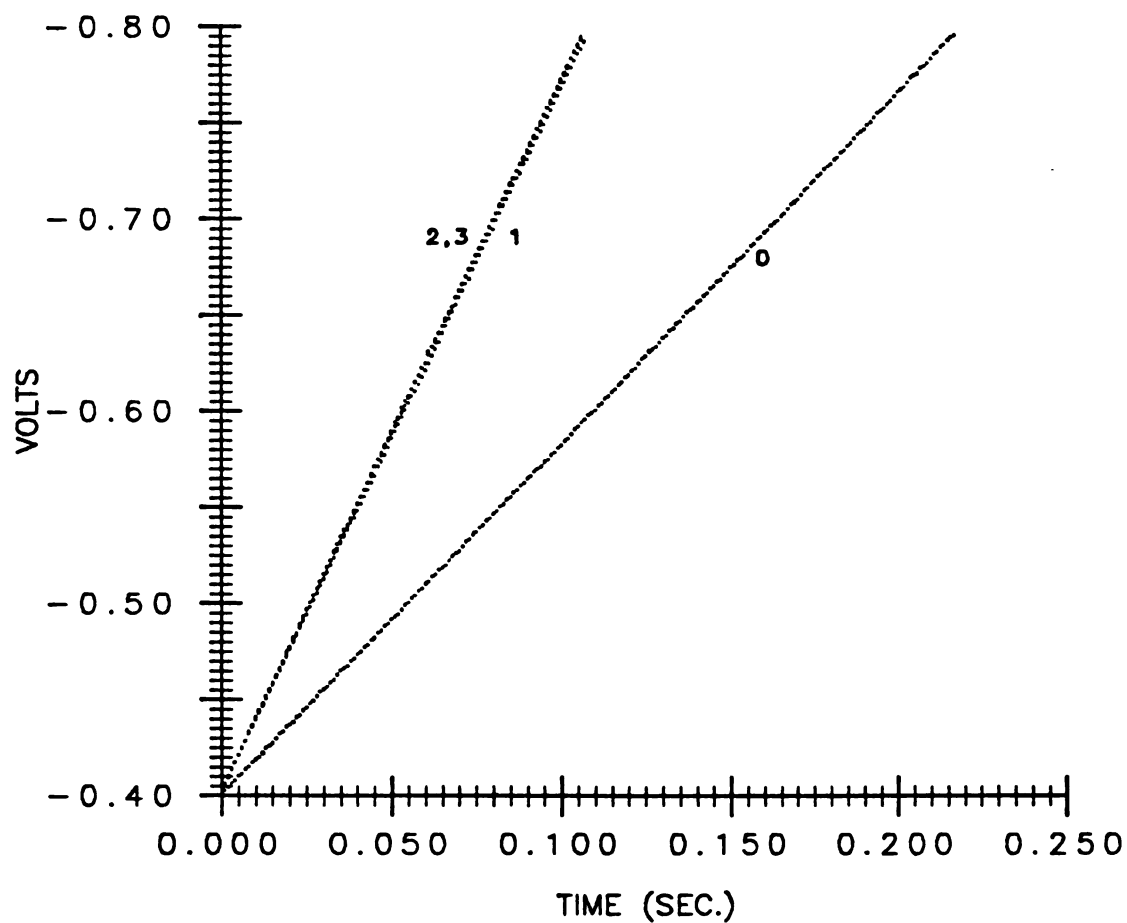


Figure 4-7.

Voltage-time curves obtained with  
two dummy capacitors

Curve 0: no charging current compensation

Curve 1: the first compensation

Curve 2: the second compensation

Curve 3: the third compensation

sufficient for this cell configuration can also be predicted through simple geometry.

Curve 1 of Figure 4-8 (the same as the curve of Figure 4-6) shows the results obtained with only  $C_{dm1}$  in the feedback loop. Curve 2 of Figure 4-8 is equivalent to the curve 3 of Figure 4-7 and shows the results obtained with both capacitors in the feedback loop and with the compensation of the capacitive charge of  $C_{dm1}$ . Clearly, this method of charging current compensation removes the capacitance effect.

The application of this method to two chemical systems will be discussed in Sections D and E. Reagent grade cadmium chloride and thallium chloride were used. Reagent grade potassium chloride had been recrystallized once before its use as a supporting electrolyte. Solutions were prepared with de-ionized water which had been passed through an ion-exchange column manufactured by Millipore. The time windows for smoothing the total charge curve was less than 5 % of the transition time for Thallium solutions and for cadmium solutions with concentration above  $10^{-6}$  M. For lower concentrations of cadmium solution, time windows were less than 15 % of the transition time. Each solution was de-aerated with nitrogen gas which had been passed through a vanadous chloride solution to remove oxygen. All experiments were performed at room temperature between 20.5 and 21.5 °C.

## DUMMY CELL

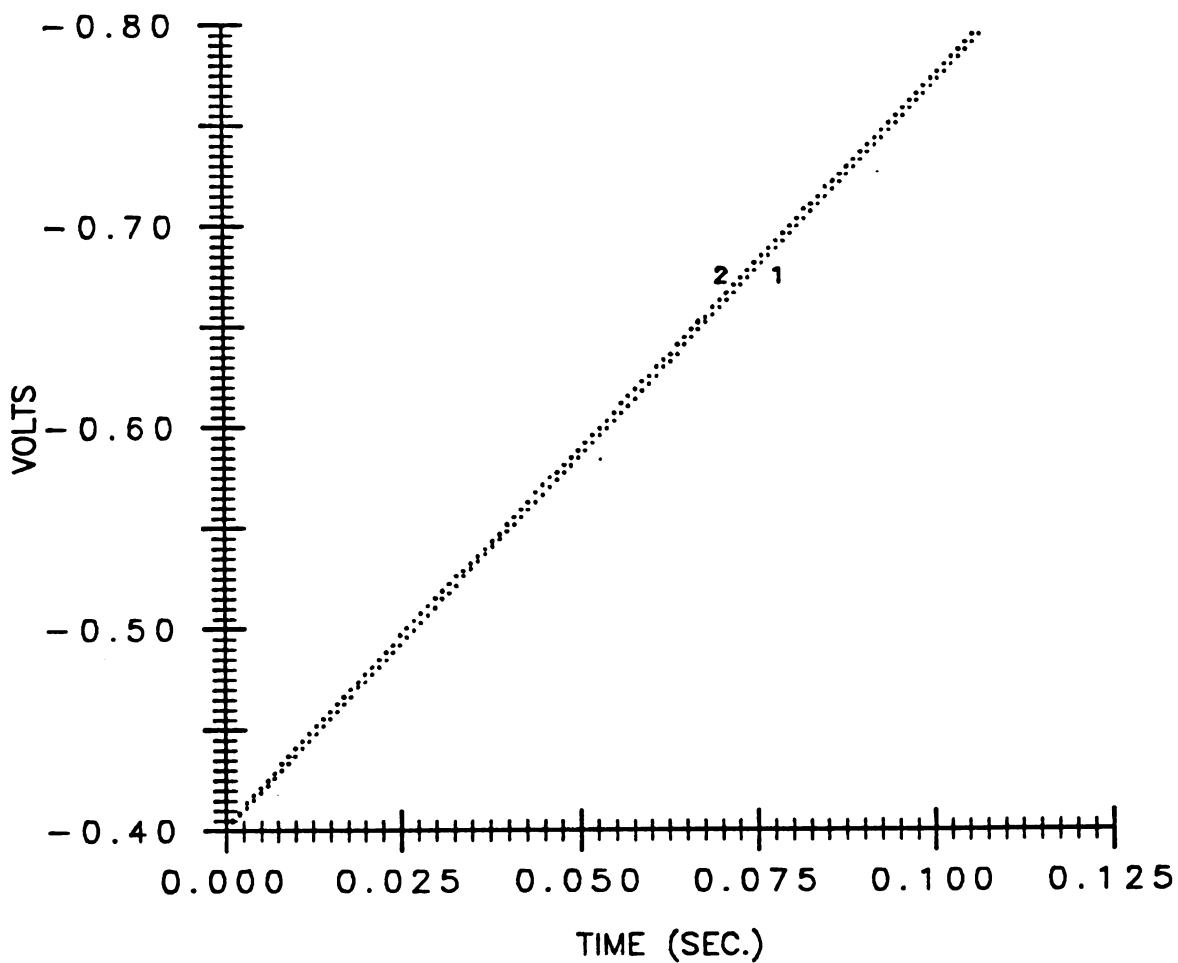


Figure 4-8.

Voltage-time curves

Curve 1: only  $C_{dm2}$  in the feedback loop

Curve 2: both capacitors in the feedback loop and with the compensation for  $C_{dm1}$



#### D. Compensation of Charging Current for the System

TlCl in 0.1 M KCl solution.

The method of compensation of charging current was tested with TlCl in 0.1 M KCl solution and with a sitting mercury drop electrode. The charging current was compensated with a blank solution (0.1 M KCl). If the effect of charging current is removed, the value  $i\tau^{1/2}/C_{Ox}$  should be constant according to the Sand's equation (Equation 4-1). As long as there is no adsorption of Ox ( $Tl^+$ ), the presence of Ox ( $Tl^+$ ) does not change the capacitance of the electrode, and proper experimental precautions have been observed (e.g., use a short transition time to avoid possible convection). Many chemical systems could be selected to test the method of charging current compensation for chronopotentiometry since the reversibility of the reaction  $Ox + ne^- \rightleftharpoons Red$  is not an important issue. The charging current has a more profound effect on the chronopotentiogram of one electron transfer reaction than on than of a multi-electron transfer reaction.  $Tl^+$  is selected because its reduction involves only one electron transfer. The tested concentration range of  $Tl^+$  was between  $10^{-3}$  M and  $10^{-5}$  M. Since KCl and TlCl are both uni-valent electrolyte and the concentration of KCl (0.1 M) is at least 100 times higher than that of  $Tl^+$ , the selection of KCl concentration should effectively remove the migration of  $Tl^+$  as a result of changing the electrical field in the vicinity of the

electrode surface during a chronopotentiometric experiment.

To avoid the tedium of coating the contact for a hanging mercury drop electrode (HMDE), a sitting mercury drop electrode (SMDE) was used. A platinum wire of 0.01 inch in diameter sealed in soft glass was used to construct the sitting mercury drop electrode. One end of the soft glass and the sealed platinum was ground with 3 micron aluminum oxide then bent to a U-shape. The platinum wire of the other end was soldered with a copper wire which facilitated an electrical connection to the PCP. The ground platinum tip was coated with mercury according to Wang's method (61). This background current of the SMDE is not significant compared to the desired Faradaic current (the background current was 1.4 % of the desired Faradaic current at  $10^{-5}$  M  $Tl^{+}$  concentration level). A fresh mercury drop was obtained by transferring a fixed volume of mercury from an HMDE to the SMDE. The potential of the SMDE was kept at  $E_{init}$  for 10 seconds to reduce impurities before starting the acquisition of data. The background current was corrected by adding it to the desired Faradaic current.

Figure 4-9 shows the capacitive charge obtained with the SMDE in 0.1 M KCl solution with  $t_d = 1.24$  ms (see Figure 4-2). Forty charge increments were used to measure the integral capacitive charge for the potential perturbation from -0.325 V to -0.725 V vs. SCE. The times required for this potential perturbation are 4.6 ms and 49.6 ms for  $t_d$

0.1 M KCl

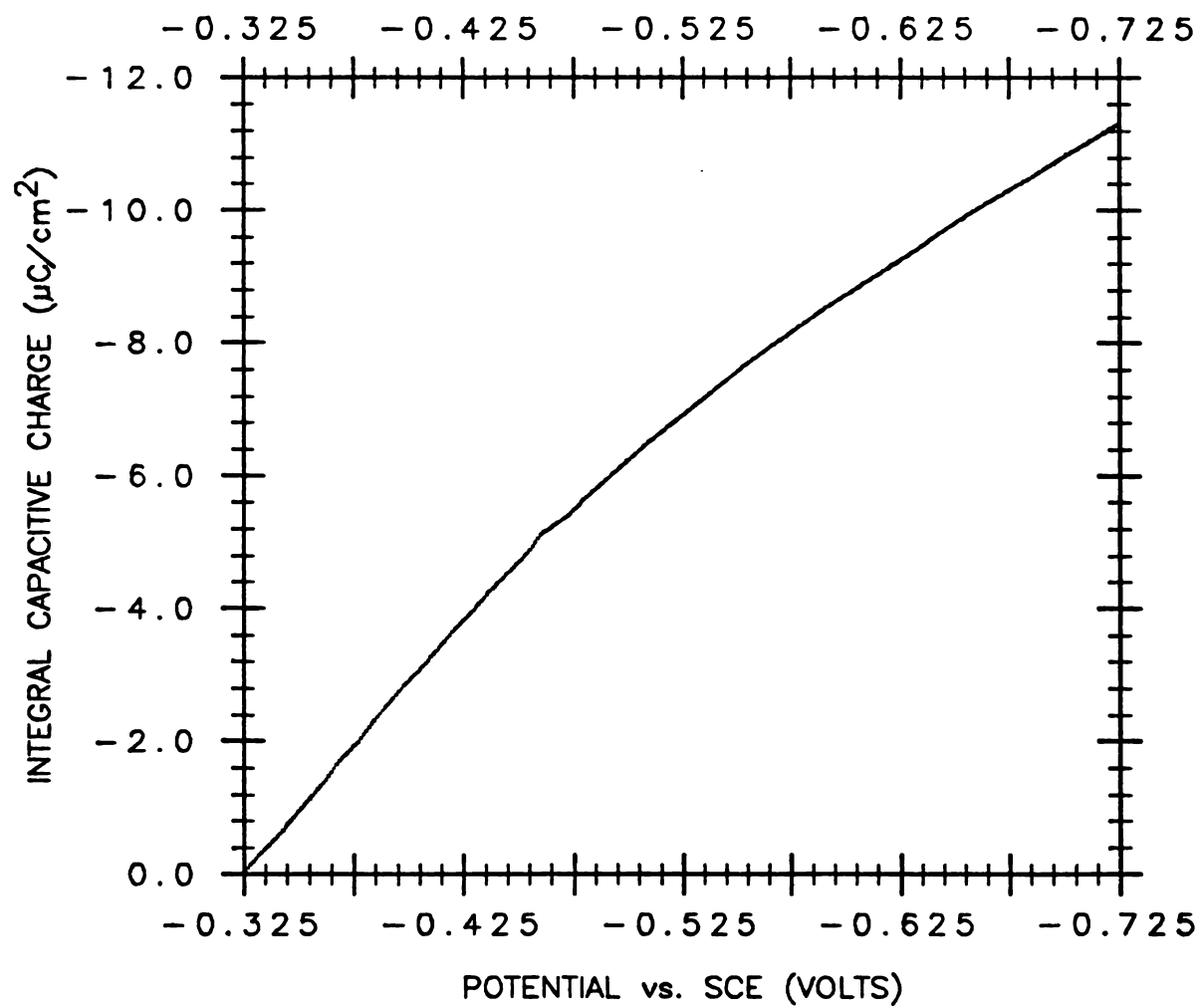


Figure 4-9.

Integral capacitive charge of SMDE in  
0.1 M KCl solution

0.115 ms and 1.24 ms respectively. The curve of integral capacitive charge was not changed significantly by changing  $t_d$  (within 2.2 % for  $t_d$  between 0.115 ms and 1.24 ms).

Figures 4-10 and 4-11 show an example of the compensation of charging current for  $10^{-4}$  M TlCl in 0.1 M KCl solution. Curve 0 of Figure 4-10 shows the chronopotentiogram obtained without any compensation of charging current. Curve 0 of Figure 4-11 is the Faradaic charge vs. time curve of the first scan (without any charging current compensation). Curve 1 of Figure 4-10 shows the chronopotentiogram obtained with the first compensation of charging current. Curve 1 of Figure 4-11 is the Faradaic charge curve corresponding to the first compensation. Curve 2 of Figure 4-10 shows the chronopotentiogram obtained with the second compensation, etc. After a few compensations, the transition time approached a constant value.

Table 4-1 lists the transition times corresponding to the number of charging current compensations for a number of concentrations. In each case, the same  $i/C$  value of  $1.02 \text{ A}\cdot\text{cm}^{-2}\cdot\text{mole}^{-1}\cdot\text{liter}$  was used. The transition times were obtained by the graphical method of Delahay and Mattax (36,54). The method is demonstrated by the graphing and finding of the time interval corresponding to the line segment AB for curve 0 of Figure 4-10. After a few compensations, the transition time approached a constant

1

POTENTIAL  $V^s$ , SCE (VOLTS)

1

Pi

$10^{-4}$  M TICI in 0.1 M KCl

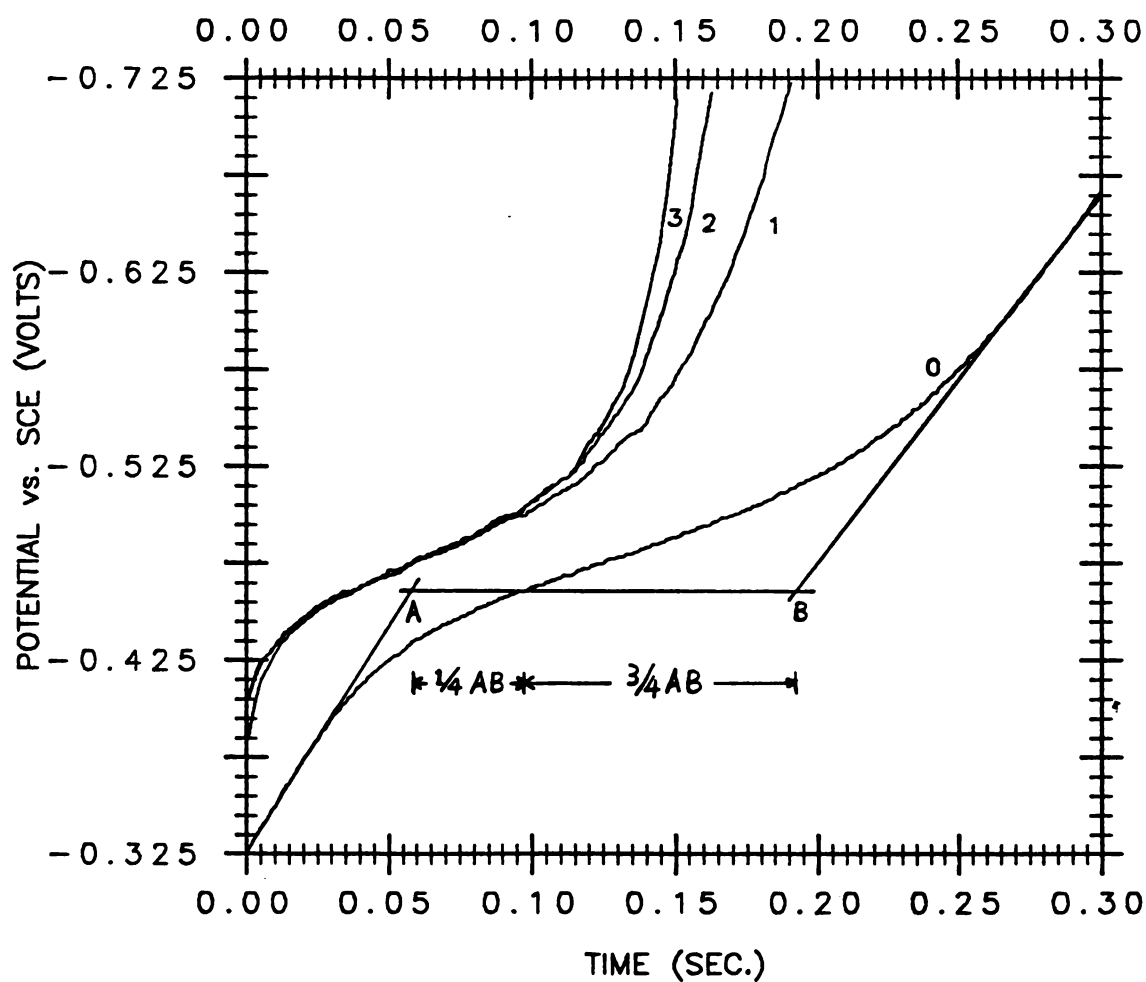


Figure 4-10. Chronopotentiograms of  $10^{-4}$  M TICI solution  
 Curve 0: No charging current compensation  
 Curve 1: the first compensation  
 Curve 2: the second compensation  
 Curve 3: the third compensation

$10^{-4}$  M TICI in 0.1 M KCl

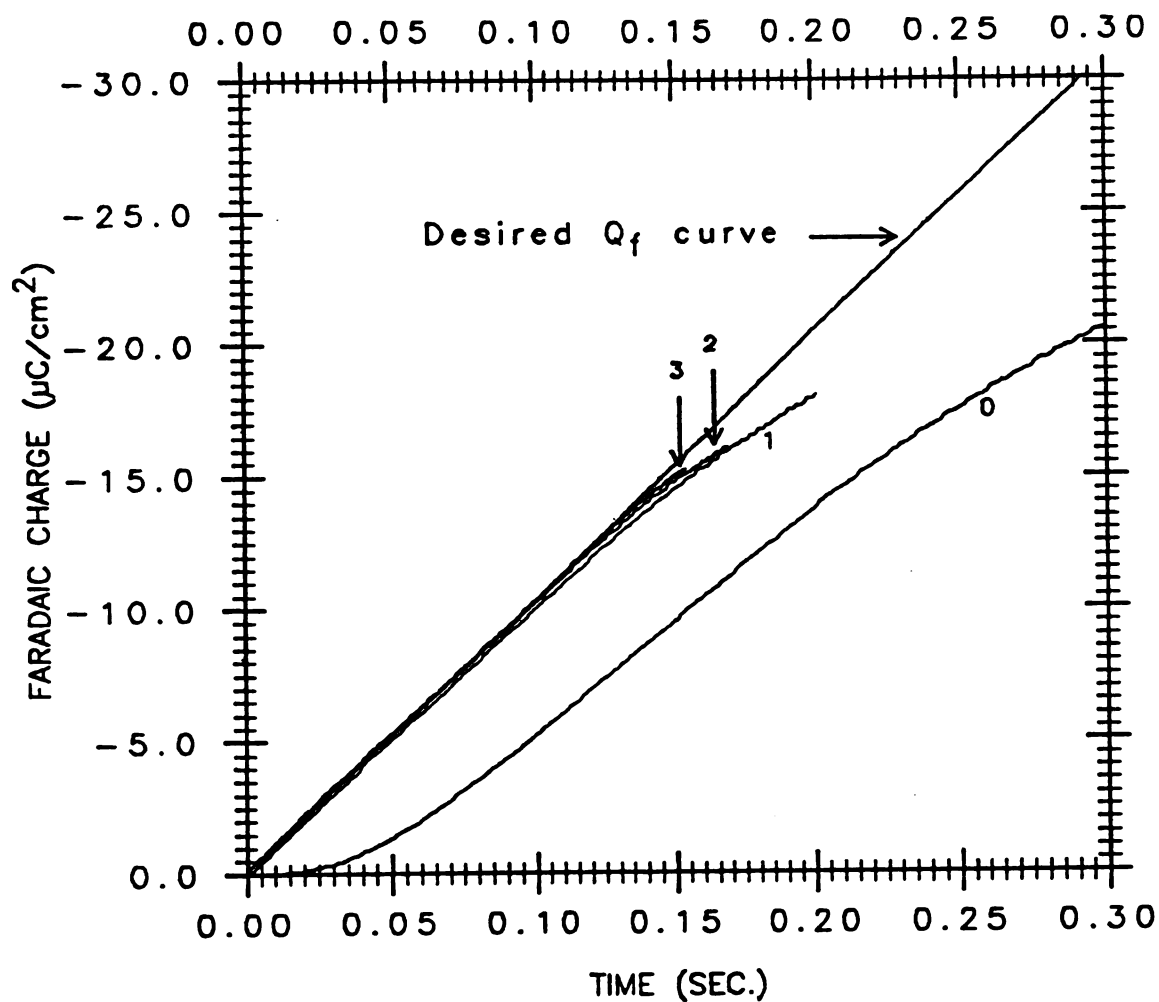


Figure 4-11. Faradaic charge curves for SMDE in  $10^{-4}$  M TICI and 0.1 M KCl solution  
 Curve 0: no charging current compensation  
 Curve 1: the first compensation  
 Curve 2: the second compensation  
 Curve 3: the third compensation

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Table 4-1. Transition times (seconds) of various concentrations of  $\text{TlCl}$  as a function of number of charging current compensations

Number of compensations \ $M \text{ Tl}^+$	$10^{-3}$	$5 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$10^{-4}$	$5 \cdot 10^{-5}$
0	0.121	0.126	0.128	0.133	0.145
1	0.111	0.110	0.109	0.113	0.112
2	0.112	0.108	0.108	0.112	0.106
3	0.112	0.108	0.108	0.112	0.106

Figure 4-12 shows a plot of  $i\tau^{1/2}/C$  vs. log concentration of  $\text{Tl}^+$  with and without charging current compensation. The transition times with charging current compensation were the constant values achieved after scans. The averaged transition time for each concentration was obtained by taking the average of 9 transition times. These 9 transition times were obtained from 3 solutions with 3 transition time from each solution. It is clear that the plot of  $i\tau^{1/2}/C$  vs.  $C$  is more dramatically constant with charging current compensation.

# TiCl in 0.1 M KCl

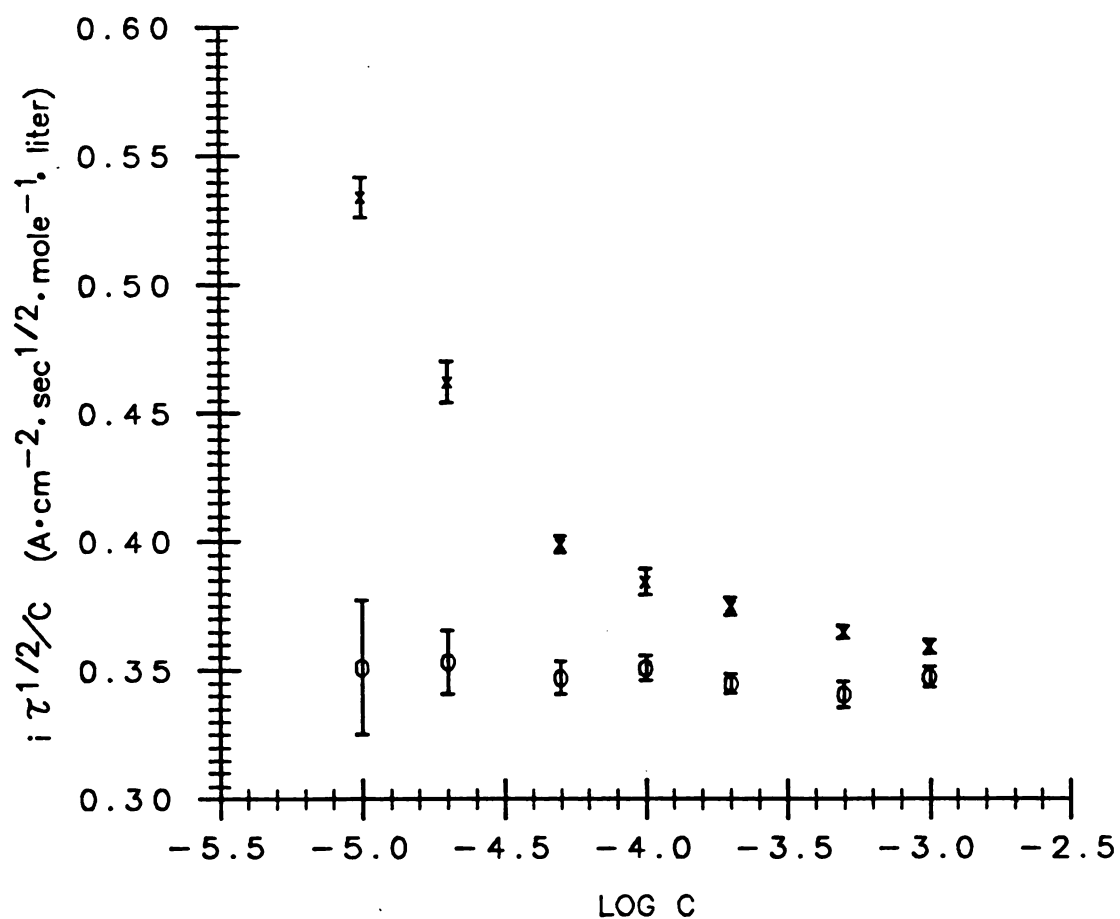


Figure 4-12.

$i\tau^{1/2}/C$  vs. log concentration (M) of  $Ti^{+}$   
 o, with charging current compensation  
 x, without charging current compensation

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E. In-Situ Compensation of Charging Current as a Sensitive Technique for the Detection of  $\text{Cd}^{+2}$

In order to test the sensitivity of the method, longer transition times were used to enhance the ratio of the Faradaic to the capacitive charges. Transition times between 1.6 sec and 7.5 sec were used. These transition times were kept short in order to avoid the effect of natural convection. Concentrations of cadmium solutions between  $2 \cdot 10^{-6}$  M and  $2.5 \cdot 10^{-7}$  M in 0.01 M KCl solution were tested with an HMDE. A low concentration of supporting electrolyte solution of 0.01 M KCl was used in order to decrease the introduction of impurities with the supporting electrolyte. In order to avoid the uncertainty of integral capacitive charge due to the variation of electrode area, a single mercury drop was used for each solution in both capacitive charge measurements and chronopotentiometric scans (This could be done because the concentration of cadmium is low). The electrode potential was brought to  $E_{\text{init}}$  (-475 mV vs. SCE) after each chronopotentiometric scan. The electrode potential was then kept at  $E_{\text{init}}$  for 10 to 20 seconds before measuring the integral capacitive charge of the electrode in the same solution. It was found that if the electrode was kept at  $E_{\text{init}}$  for a time as short as 2 seconds, the measured capacitive charge is essentially the same. After the capacitive charge was measured, the electrode potential was held at  $E_{\text{init}}$  for 3 minutes before

starting the next chronopotentiometric scan for those scans whose transition time almost approached a constant value. For the first few scans, only one minute time interval was used in order to save time. The purpose of doing this is to strip out most of the cadmium which had been deposited on the mercury drop.

Figure 4-13 shows the chronopotentiograms obtained with  $2 \cdot 10^{-5}$  M  $\text{CdCl}_2$  in 0.01 M KCl solution. A desired Faradaic current density of  $3.5 \mu\text{A}/\text{cm}^2$  was used. Curve 0 shows the results obtained without any compensation of charging current. Curve 1 shows the results obtained with the first compensation of charging current, curve 2 shows the results obtained with the second compensation of charging current, etc.

The integral capacitive charge of the HMDE in the solution containing  $2 \cdot 10^{-5}$  M  $\text{CdCl}_2$  and 0.01 M KCl decreases about 2 % during the time interval between two adjacent chronopotentiometric scans. The rate of decrease is so small that it does not introduce significant error in the charging current compensation.

For the capacitive charge measurement, between 20 and 25 charge increments (see Figure 4-2) were used to change the electrode potential from -475 mV and -775 mV vs. SCE. The time required to make the potential perturbation is between 1.3 ms and 1.6 ms which is considerably less than the transition time used (between 1.7 and 7.4 seconds);

$2 \cdot 10^{-5}$  M  $\text{CdCl}_2$  in 0.01 M KCl

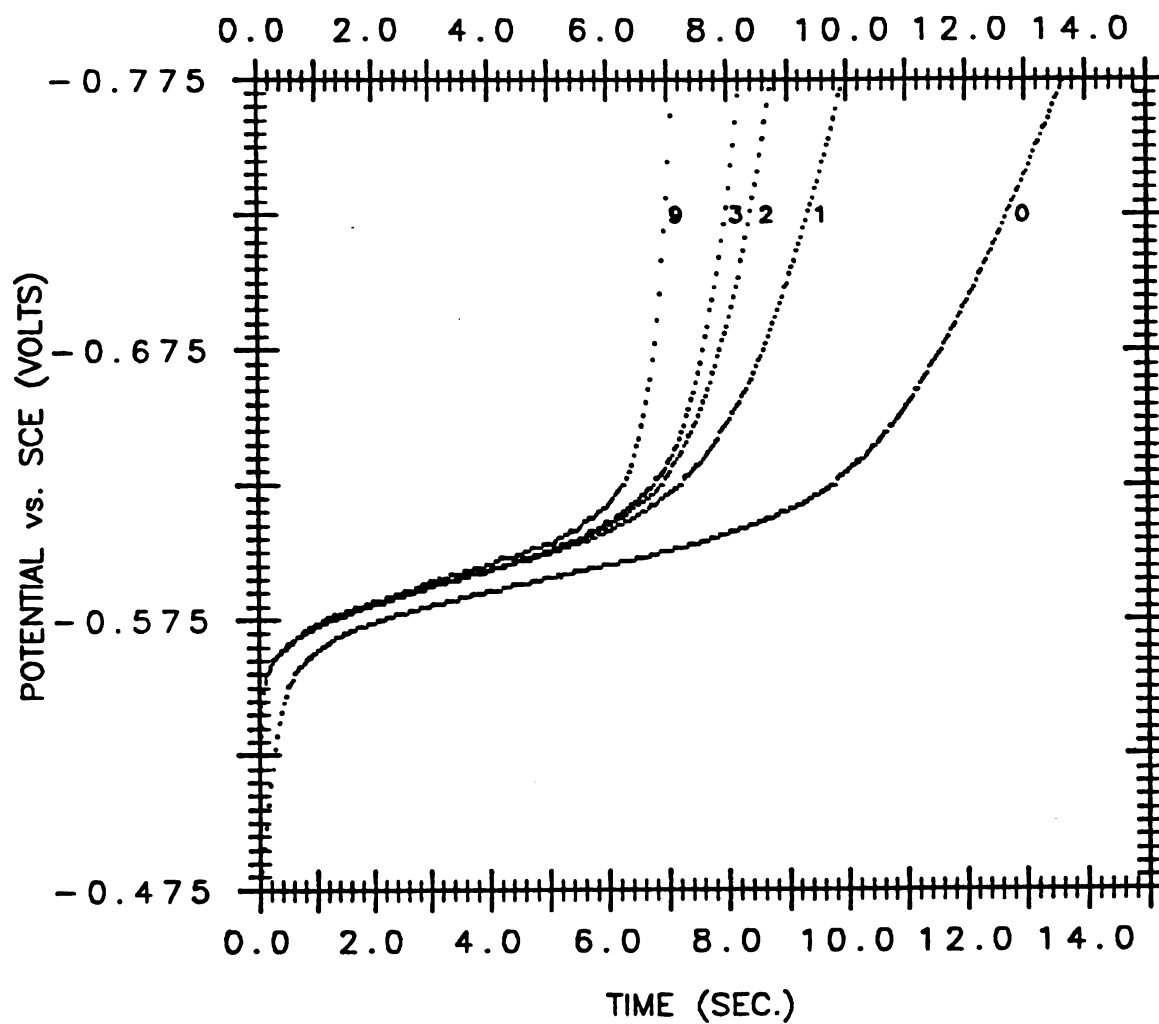


Figure 4-13. Chronopotentiograms of  $2 \cdot 10^{-5}$  M  $\text{CdCl}_2$   
The number besides the curve corresponding  
to the number of charging current  
compensation

therefore, the Faradaic charge consumed in the time interval for capacitive charge measurement is much less than the Faradaic charge consumed in the chronopotentiometric experiment.

Figure 4-14 shows the comparison of the measured integral capacitive charge obtained with a fresh mercury drop in 0.01 M KCl solution (curve 1) and in  $2 \cdot 10^{-5}$  M  $\text{CdCl}_2$  and 0.01 M KCl solution (curve 2). The fact that the measured integral capacitive charge is higher for cadmium solution than for plain supporting electrolyte solution is principally due to the reduction of some cadmium ions during the period of capacitive charge measurement.

For lower concentration of cadmium solutions, the error involved in the capacitive charge measurement due to Faradaic reaction is less. For example, the integral capacitive charge measured with  $5 \cdot 10^{-6}$  M  $\text{CdCl}_2$  has a lower error as shown in Figure 4-15. Even with the solution of  $2 \cdot 10^{-5}$  M  $\text{CdCl}_2$  in 0.01 M KCl, it is still advantageous to compensate for the charging current because the charging current is still the major error.

Figure 4-16 shows another example of in-situ charging current compensation. The test solution contained  $10^{-6}$  M  $\text{CdCl}_2$  and 0.01 M KCl. A steady state background current of  $0.017 \mu\text{A}/\text{cm}^2$  (10 % of the desired Faradaic current) was determined at  $E_{\text{init}}$  (-475 mV vs. SCE). The background was corrected by adding it to the Faradaic current of 0.17

0.01 M KCl w/o  $2 \cdot 10^{-5}$  M  $\text{CdCl}_2$

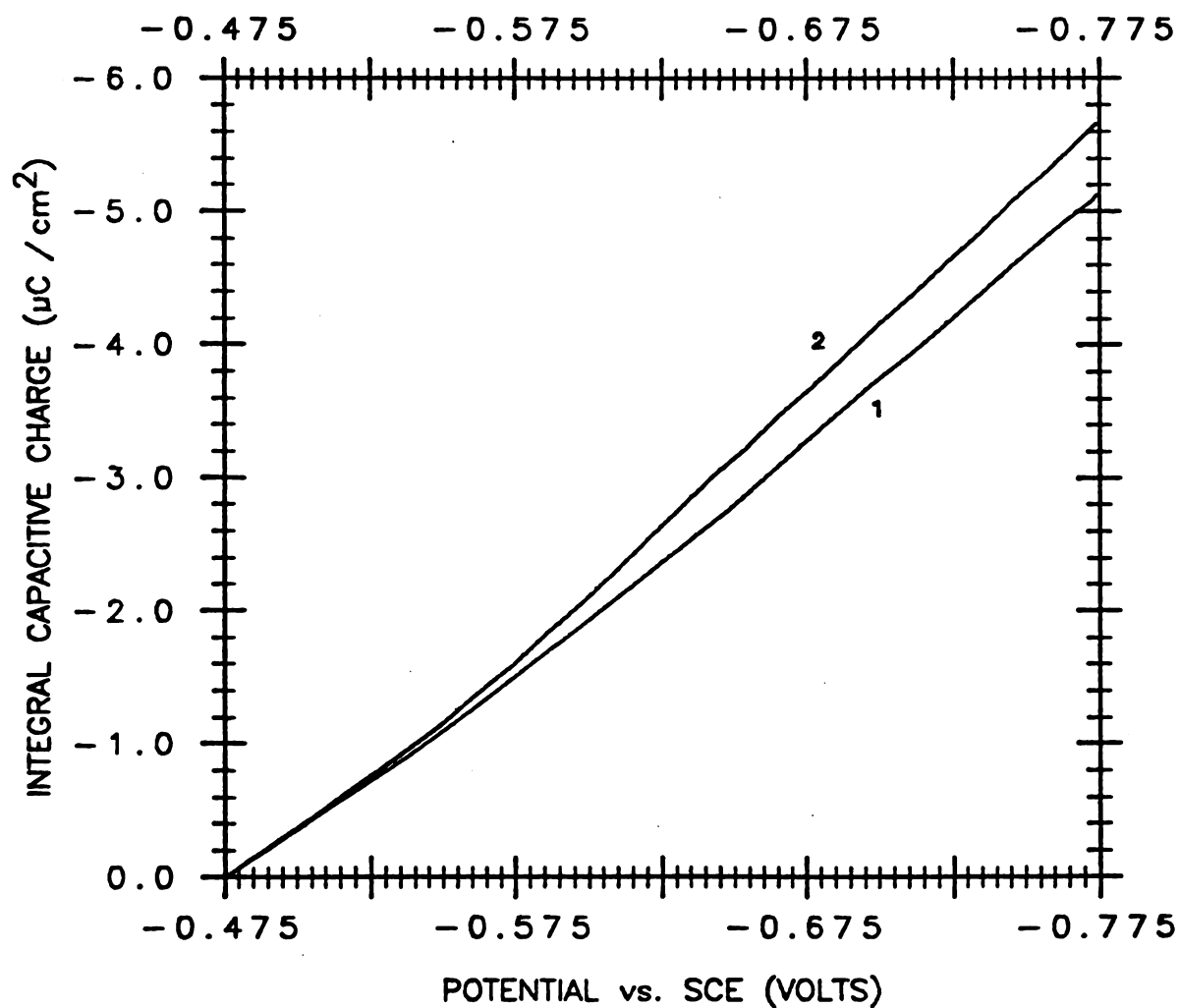


Figure 4-14.

Measured integral capacitive charge for  
0.01 M KCl solution  
Curve 1: without  $\text{CdCl}_2$   
Curve 2: with  $2 \cdot 10^{-5}$  M  $\text{CdCl}_2$



0.01 M KCl W O  $5 \times 10^{-6}$  M  $\text{CdCl}_2$

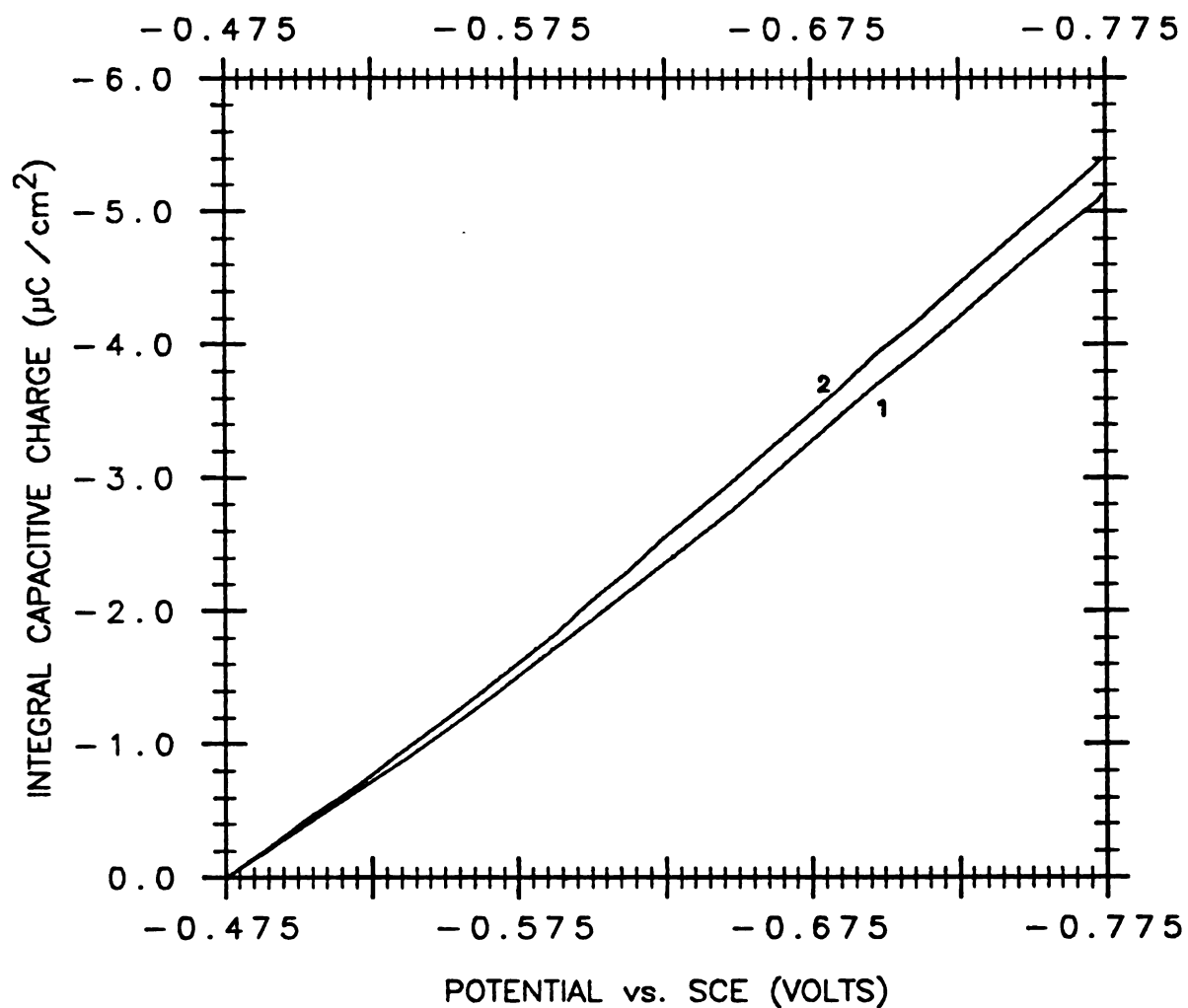


Figure 4-15.

Measured integral capacitive charge for  
0.01 M KCl solution  
Curve 1: without  $\text{CdCl}_2$   
Curve 2: with  $5 \times 10^{-6}$  M  $\text{CdCl}_2$

$10^{-6}$  M  $\text{CdCl}_2$  in 0.01 M KCl

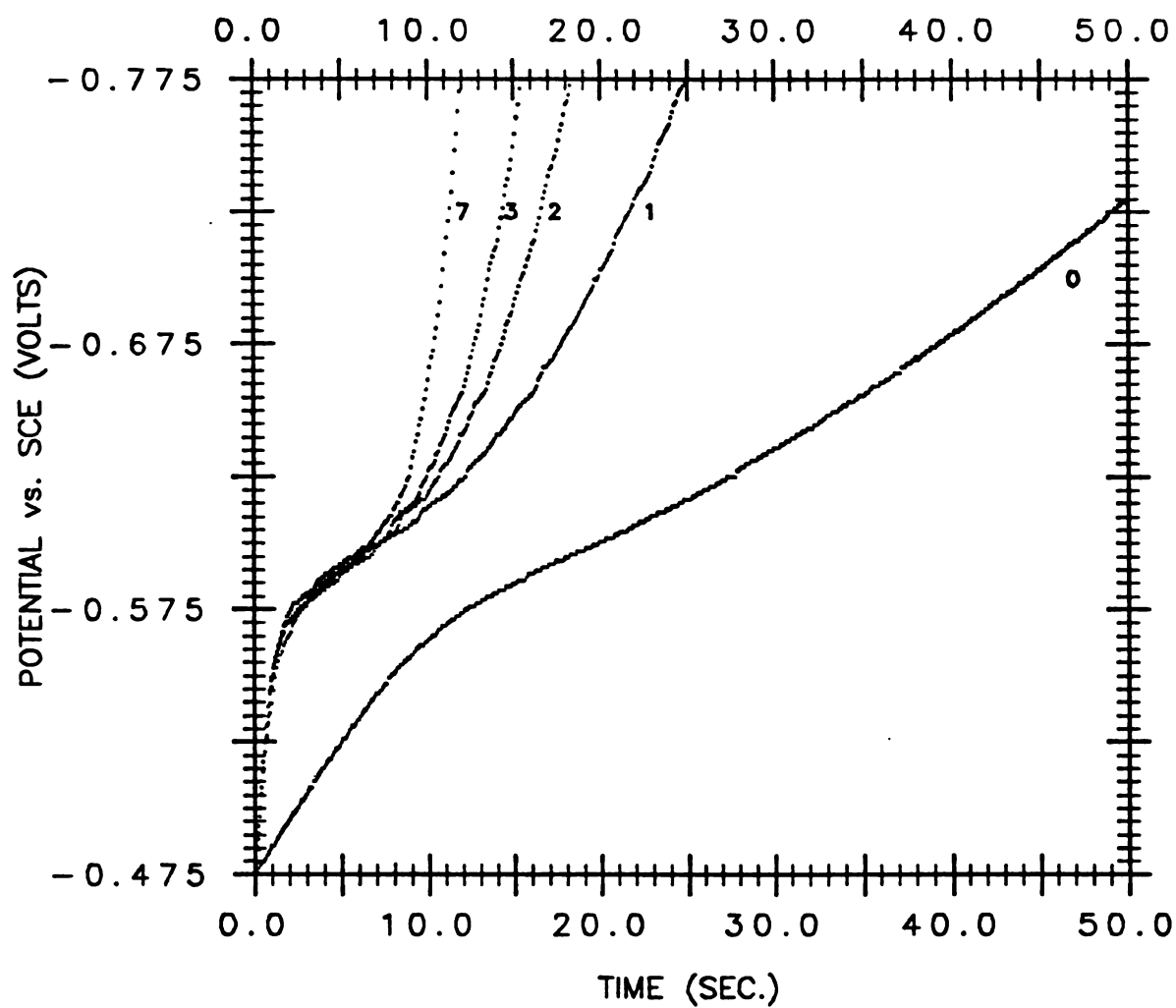


Figure 4-16. Chronopotentiograms of  $10^{-6}$  M  $\text{CdCl}_2$   
The number besides the curve corresponding  
to the number of charging current  
compensation

$\mu\text{A}/\text{cm}^2$ . Curve 0 shows the chronopotentiogram obtained without any charging current compensation. Curve 1 is obtained with the first compensation of charging current, curve 2 is obtained with the second compensation, etc.

Figure 4-17 shows a chronopotentiogram of  $5 \cdot 10^{-7} \text{ M Cd}^{+2}$  obtained after the transition time approached a constant value.

Table 4-2 lists the desired Faradaic current  $i_f$  applied to the electrode, the transition time  $\tau$ ,  $i\tau^{1/2}$ , and the ratio of background current  $i_b$  to  $i_f$  for a number of concentrations.

$5 \cdot 10^{-7}$  M  $\text{CdCl}_2$  in 0.01 M KCl

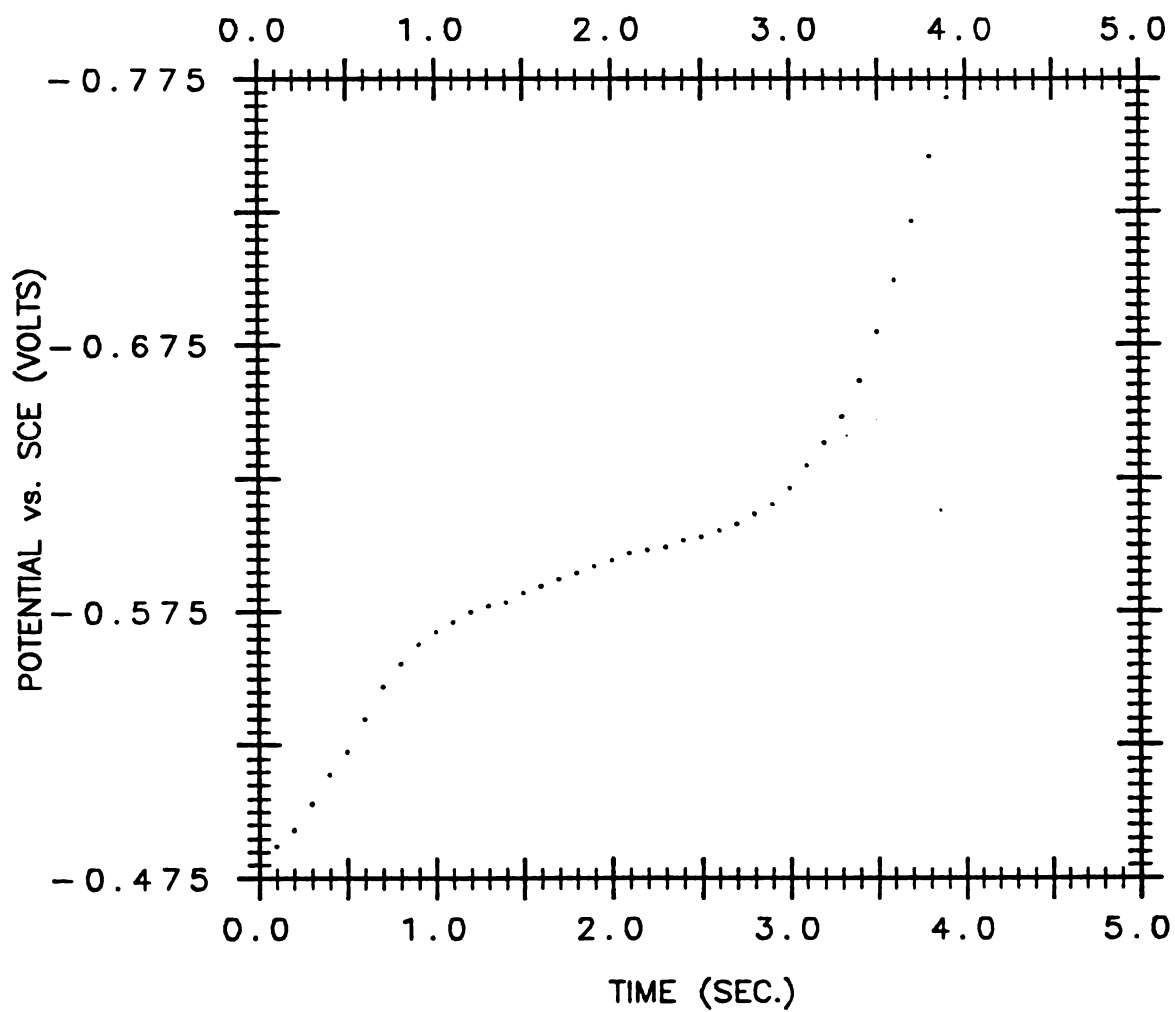


Figure 4-17.

Chronopotentiograms of  $5 \cdot 10^{-7}$  M  $\text{CdCl}_2$   
with charging current compensation

Table 4-2. List of  $i_f$ ,  $i_b/i_f$ ,  $\tau$ ,  $i\tau^{1/2}$  for  $\text{CdCl}_2$  solutions.

$M \text{ Cd}^{+2}$	$2 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$10^{-5}$	$5 \cdot 10^{-6}$
$i \text{ (}\mu\text{A/cm}^2\text{)}$	$3.5 \pm 4\%$	$2.6 \pm 4\%$	$1.7 \pm 4\%$	$0.87 \pm 4\%$
$i_b/i_f \cdot 100\%$	0%	0%	0%	0%
$\tau \text{ (sec)}$	6.2	6.5	6.6	7.4
$i\tau^{1/2} \text{ (}\mu\text{A} \cdot \text{sec}^{1/2}/\text{cm}^2\text{)}$	8.6	6.6	4.5	2.4

$M \text{ Cd}^{+2}$	$2 \cdot 10^{-6}$	$10^{-6}$	$5 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$
$i \text{ (}\mu\text{A/cm}^2\text{)}$	$0.35 \pm 4\%$	$0.17 \pm 4\%$	$0.17 \pm 4\%$	$0.087 \pm 7\%$
$i_b/i_f \cdot 100\%$	5%	10%	10%	30%
$\tau \text{ (sec)}$	7.2	6.1	1.7	2.2
$i\tau^{1/2} \text{ (}\mu\text{A} \cdot \text{sec}^{1/2}/\text{cm}^2\text{)}$	0.93	0.43	0.22	0.13

Figure 4-18 shows a plot of  $i\tau^{1/2}$  vs. concentration of cadmium. Theoretically,  $i\tau^{1/2}$  should be proportional to the concentration according to Equation 4-1. A fairly linear  $i\tau^{1/2}$  vs.  $C$  relationship was obtained.

#### F. Discussion

The method of charging current compensation can effectively remove the effect of double layer charging as it was shown in the previous two sections. The potentials are monitored while there is no current passing through the solution. As a result of this, potential measurements can be made more accurately, and the solution resistance causes



$\text{CdCl}_2$  in 0.01 M KCl

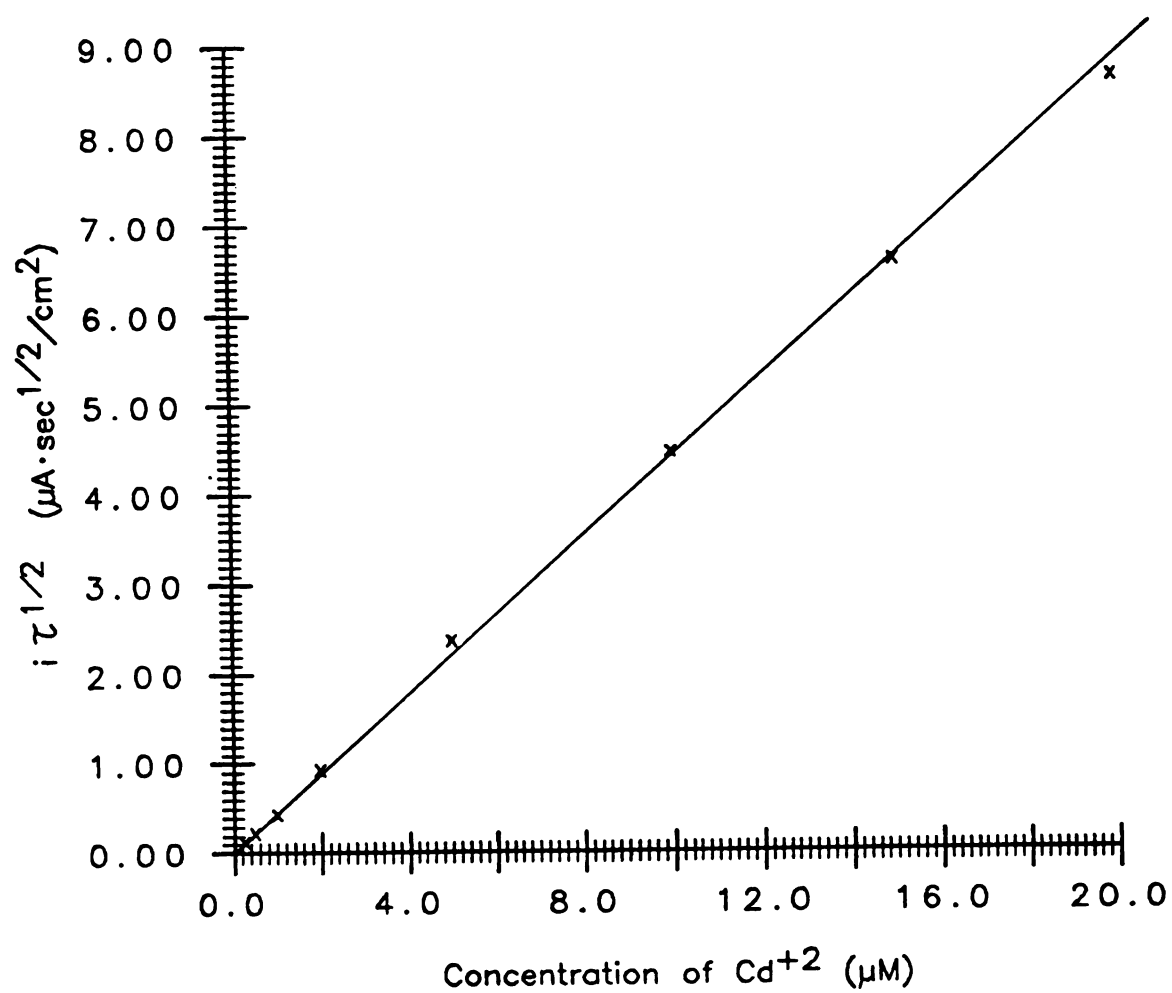


Figure 4-18.  $i\tau^{1/2}$  vs. concentration of  $\text{Cd}^{2+}$

fewer problems. Therefore, this method can be applied to solutions of non-aqueous solvents, which may not be able to dissolve much electrolyte (the concentration of electrolyte may be as low as 0.1 mM).

According to Bos and Van Dalen (60), for the reaction  $\text{Ox} + ne^- \rightarrow \text{Red}$ , it is advantageous to keep the electrode potential at a value which is somewhat (e.g., 100 mV to 200 mV) more positive than the  $E^\circ$  of the redox couple to reduce impurities which react rapidly at this potential. They used a potentiostat to control the potential before the cell was switched to an amperostat. The PCP serves both as a potentiostat and an galvanostat. Switching from the controlled potential mode to the controlled current mode by the PCP is practically instantaneous and does not cause any problems such as a current spike.

Bos and Van Dalen's apparatus (60) can perform charging current compensated chronopotentiometric experiments whose transition times are as short as 0.1 second. The method developed in this thesis work can handle chronopotentiometric experiments at least 10 times faster. For example, if 30 potential measurements are desired, the minimum time required for taking these data is

$$0.156 \text{ ms} \cdot 30 = 4.7 \text{ ms} \quad (4-8),$$

where 0.156 ms is the minimum time required between two



adjacent potential measurements.

If the Bos and Van Dalen's device is used for charging current compensation, two cells must be used. One of them contains the solution of interest. Another is the blank cell which contains solution of supporting electrolyte only. The blank cell is used for generating charging current. The areas and the surface conditions of the working electrodes in these two cells must be identical; otherwise, the compensation will be subject to error. When solid electrodes are used, it is difficult to match electrodes because of the surface roughness, the adsorption, and the oxide film formation.

With the technique of in-situ compensation of charging current developed in this thesis work, the capacitive charge was measured with the same electrode in the same solution. The effort of preparing a blank cell can be saved. When the solution does not contain high concentrations of electroactive species (upper limit about  $2 \cdot 10^{-3}$  M), the charging current can be compensated more accurately with this method since the capacitive charge of the same electrode is used. The drift of the quantity of measured capacitive charge was not a serious problem for mercury electrode since the time interval between two adjacent chronopotentiometric scans was four minutes or less. A drift of less than 2 % was observed in that time interval. The time interval can be shortened to enhance the speed of

analysis or to reduce the drift of capacitance value in the following situations: 1. A shorter transition time is used. (smaller diffusion layer thickness makes it quicker to restore the initial  $Ox$  concentration.) 2. A solid electrode is used and with knocking the electrode after each scan (to restore the initial  $Ox$  concentration at the electrode surface).

With the technique of in-situ compensation of charging current, the effect of adsorption of non-electroactive materials on the capacitance measurement can be taken into account since the capacitive charge is measured with the same electrode between two chronopotentiometric scans. In the situation in which the electroactive species is adsorbed on the electrode and it reacts rapidly, the charge consumed by this Faradaic reaction is included in the measured capacitive charge. The measured capacitive charge will be compensated in the next scan. Thus, the effect of the adsorption of this type of electroactive species is removed. In this situation, the method only takes the diffusion of electroactive species into account. As a result of this, it gives a better analytical working curve. These reasons, discussed above, probably explain why this technique improves the sensitivity of chronopotentiometry by more than one order of magnitude. The sensitivity of this technique is similar to that of pulse polarography.

The major limitation of the PCP is that high current

densities cannot be employed. For example, in the case of a chronopotentiometric experiment, current densities above  $\text{mA/cm}^2$  range cannot be applied. The program for performing a chronopotentiometric experiment involves reading the DAC values from the computer memory, calling a program to inject charge pulses, calling a program to measure the potential, etc. All of these processes require time. When high concentrations of supporting electrolytes are used (e.g., above 0.01 M), the speed of operation of the PCP is mainly limited by the speed of the microcomputer. The maximum current which can be applied to an electrode is limited by the speed of the PCP. A large potential perturbation, due to each charge injection, is certainly not desirable in any chronopotentiometric experiments. If 3 mV is set as the tolerable potential perturbation resulting from a charge injection, and if the electrode capacitance is  $20 \mu\text{F/cm}^2$ , the maximum current that can be applied to the electrode is

$$(3 \text{ mV}) \cdot (20 \mu\text{F/cm}^2) / (156 \mu\text{s}) = 0.38 \text{ mA/cm}^2 \quad (4-9),$$

where  $156 \mu\text{s}$  is the minimum time required between two adjacent voltage measurements. If higher current densities are desired, a faster computer or a hardware charge injection and measurement system should be used.

## CHAPTER 5

### SOME POSSIBLE APPLICATIONS OF THE PCP

Several operational modes of the PCP have been discussed in Chapter 2. In this chapter, some possible applications of these operational modes will be discussed. Most of them have not been investigated. However, the expected performance will be discussed at the best of my knowledge.

#### A. The applications of the controlled charge mode

##### 1. Traditional Coulostatic Method

A large charge pulse can be applied to the working electrode in order to bring the electrode potential to a value where the species of interest will react. The potential can then be monitored as a function of time. The decay of potential can be related to the kinetics of the reaction (12,62) or the concentration of the electroactive species (8,11,14,63). The time required for the voltage measurement system (VMS) is 8  $\mu$ s. The minimum sampling time required for each data point is between 20 and 25  $\mu$ s if the time required for commanding the VMS to convert data, for reading the converted data, and for storing the data are included. The voltage sampling speed is moderate. For very fast reactions, the PCP is not suitable. The resolution of

VMS is 1.22 mV which should be adequate for most experiments. The DAC has 10-bit resolution and is bipolar. The uncertainty in output voltage for each digital data is  $\pm 1/2$  LSB which corresponds to  $\pm 2.5$  mV. The relative error of charge can easily be less than 1% if proper voltage of DAC is selected (e.g., more than 0.5V out of the full range 2.5V).

## 2. Electrode Capacitance Measurement

For the measurement of differential capacitance, as discussed in Chapter 3, the PCP can inject an amount of charge appropriate for the desired potential perturbation (e.g., 10mV). The entire capacitance-voltage profile of an electrode can be obtained in as little as 8 seconds. The capacitance measurement is very accurate since the calibration error of the ADC is reduced (see Chapter 3) and the operator can select the number of iterations of measurement in order to attain the desired precision. Usually, the experimental technique is the main source of error.

For the measurement of integral capacitance, a method has been discussed in Chapter 4 which requires a few milliseconds for a potential perturbation of 0.4V. A faster program could be developed which would reduce the time to about 50  $\mu$ s. If only one measurement is performed for each potential and if the potential perturbation is large (e.g., more than 100mV), the relative error in capacitance

measurement is not large since the potential uncertainty is only 1.22 mV.

### 3. Coulometric Titrations

Precise amounts of charge can be used to generate titrant electrochemically. The electrode potential can be monitored as a function of time or as a function of charge added.

A four electrode system can be employed with a very small change to the basic electronic circuitry. The current applied between the working and counter electrodes generates the desired titrant at the working electrode. In order to prevent the reaction products at the counter electrode from getting into the sample solution, the counter electrode can be separated from the sample solution by a fritted glass. A simple differential amplifier is needed. The reference electrode and the indicator electrode can be connected to the inputs of this differential amplifier and the output of the differential amplifier can be connected to the VMS. Using a computer controlled system such as the PCP, a high current can be applied to generate titrant very quickly at first and then the current or the rate of charge injection can be decreased around the end point to allow the solution well mixed. By doing this, the analysis time can be shortened. A computer based instrument such as the PCP also provides advantages in the continuous monitoring of analyte, some of these advantages are automatic current range

selection, recording and warning. In the monitoring of olefins and sulfur compounds in petroleum using coulometric titration, electrochemically generated bromine can be added to petroleum streams (64). The bromine in the solution reacts with the sample components and causes a decrease in the concentration of bromine. The PCP can adjust the rate of generating of bromine in order to maintain its concentration at a specific level. One problem in using a conventional coulometric titrator is that the current applied between the working and counter electrodes generates an IR drop between them. The reference and indicator electrode should be positioned on an equal potential contour. This consideration caused by simultaneous electrochemical generation and detection has prompted the use of spectrophotometric end point detection in some applications of coulometric titration. Using the PCP, the current between working and counter electrode is zero at the moment when potential is sampled so the problem of IR drop would be eliminated.

## B. The Application of the Controlled Current Mode

### 1. Constant Current Chronopotentiometry

The application of PCP to constant current chronopotentiometry has been discussed in Chapter 4. A major advantage is that it is free from IR drop.

## 2. Programmed Current Chronopotentiometry

An instrument has been constructed by a group of electrochemists (65) for chronopotentiometry with current that varies along with any selected power of time,  $t^q$ . The transition time  $\tau$ , which is the time interval between two sharp potential changes, is related to the concentration  $C$  by

$$\tau^{(q+1/2)} = kC \quad (5-1),$$

where  $k$  is a constant.

The advantage of this method is that a wide range of concentrations can be measured on a convenient time scale.

With PCP, a simple method to obtain a programmed current is to vary the quantity of charge to be injected to the electrode and keep the time interval between two adjacent charge injections constant. The main disadvantage using PCP is that a high current density (above about 1 mA/cm<sup>2</sup>) cannot generally be employed partially due to the inherent complication of the programming.

## 3. Electrode Pretreatment

Sometimes a clean and a reproducible electrode surface can be obtained by heavily anodizing (e.g., 1 sec at 10 to 100 mA/cm<sup>2</sup>) the electrode surface to remove adsorbed material. This current density for this application is not anticipated to be a problem since the programming is not as



complicated and the potential variation of the electrode is not as vital as that of controlled current experiments. The electrode's oxide layer is then reduced at a potential sufficient to remove it, but neither the hydrogen ions or the solvent are reduced. The pretreatment cycle is repeated before every experiment, usually in the test solution.

Through the use of the PCP, complex current or potential waveforms with precise timing control can be applied to the electrode for pretreatment. The experiment following the pretreatment can be carried out with the same instrument and can be completed automatically. This special capability results from the PCP's ability to switch polarization modes without disconnecting the cell or causing any undesirable electrical stress at the working electrode.

#### C. The Application of the Controlled Potential Mode

Virtually all kinds of controlled potential experiment (e.g., cyclic voltammetry, pulse polarography, chronocoulometry, rotating disk voltammetry, etc.) can be performed using the PCP.

For pulse polarography, the PCP can usually attain a potential step within the resolution of VMS (1.22 mV) in a few milliseconds. This is not extremely fast compare to most commercial instruments although most of them sample the current between 30-50 ms after the pulse. For solution of lower conductivity, the PCP has advantages over most

commercial instruments since it is applicable to these solutions. One disadvantage of the PCP is that the resolution of the VMS is not high. A certain amount of electroactive species must be reacted before the PCP can detect it. The lower limit of detectable concentration depends on the technique applied. Generally, The PCP could be well suited for concentration of electroactive species above  $10^{-7}$  M for direct analysis (For anodic stripping voltammetry, much lower concentration can be achieved.). If a lower detection limit is desirable, a higher resolution ADC could be used. However, there may not be much advantage to do so. In most cases, the background current is about the same level as the Faradaic current generated by this low concentration of electroactive species.

The PCP may have great advantages in the electrochemical detection for liquid chromatography. Because the coulometric method does not require high solution conductance, the PCP can be well suited for a wide range of solutions. The differential pulse detection for liquid chromatography can eliminate some electrode fouling problems (66). The PCP can be well suited for this application since it can step potential faster than most commercial instruments under the condition of high solution resistance.

One favorable aspect of the PCP for controlled potential experiments is that the charging current can be

integrated over a short period of time (e.g., 2 ms) after a potential step. The resulting information may be used to study either electrode capacitance or surface adsorption. However, because some Faradaic reaction will occur during this period, the PCP can not be applied to this method of studying surface phenomena accurately if the concentration of electroactive species is roughly above  $10^{-5}$  M. For small potential steps, the measured capacitive charge is subject to significant error because the resolution of VMS is 1.22 mV which may be a large fraction of size of the potential step.

#### D. The Applications of the Open Circuit Mode

Under the open circuit condition, the PCP can be used for the potentiometric measurements of PH electrode or other ion selective electrodes.

In normal pulse polarography, a potential waveform with potential pulses superimposed on a constant potential is applied to a working electrode. An operator with little experience may sometimes select an initial potential at which the electrode will dissolve, or the solvent will decompose, or the electroactive species of interest will start to react. If the potential in the open circuit condition is used as the initial potential, these problems can be avoided.

#### E. The Applications of the Combination of Modes

The PCP can switch from one mode of operation to another without any difficulty. The switching is achieved by software. Also, it is fast and produces no electrical stress on the working electrode.

Examples of possible application can be as follows:

The PCP can keep the working electrode potential at a desired value (controlled potential mode) then automatically switch to controlled current mode. During the controlled potential period, impurities easier to react than the species of interest can be consumed at the electrode surface. Thus, the interference of impurities can be reduced.

In controlled potential experiments, the information about the current can be the basis for some control decisions. For example, in cyclic voltammetry, if the current drops to a certain fraction of the peak current, the potential can start scanning in the reverse direction. Another example is for the preparations of desired concentrations of electrochemical species at the electrode. For example, the potential of the electrode can be kept at a value to achieve the desired initial concentration before switching to an experiment which could be a controlled charge experiment such as traditional coulometric experiment. The amount of current at the potential for preparing the desired concentration can be used for the

decision of switching to the experiment. With the PCP, a series of experiments of this kind with different initial condition can be performed automatically.

The PCP can keep the potential of the working electrode at a desired value (controlled potential mode), then inject a charge pulse to the electrode either for capacitance measurement or for traditional coulometric method (controlled charge mode).

In the compensation of charging current for chronopotentiometry which has been discussed in chapter 4, controlled charge mode is used to measure the capacitance of the working electrode. The measured capacitance is used in the controlled current mode to perform constant current chronopotentiometry with charging current compensation.

For normal pulse polarography, the open circuit mode can be used to obtain the potential at zero current. The potential may be used as the potential before voltage pulses are applied (controlled potential mode).

For charge step polarography (14), the potential of the electrode can be held at a value (controlled potential mode) where the electroactive species do not react before injection of increasing quantities of charge pulses (controlled charge mode). The slope of the potential decay after each charge pulse is injected can be monitored and plotted as a function of potential.

M. A. Schreiber and T. A. Last developed a computer

controlled coulostat (67). The basic design of their instrument is patterned after the one used by S. E. Hourdakis and C. G. Enke (18). They performed linear sweep anodic stripping voltammetry with a thin film mercury/wax-impregnated graphite electrode. The linear potential scan was achieved by injection of calculated quantity of charge at constant rate to keep the linear potential scan. The potential decay after each charge pulse injected was used to calculate the Faradaic component of the injected charge. The detection limit was 100 parts per trillion for cadmium.

The PCP can be used as a drop fall detector for dropping mercury electrodes as it was performed by Spyros Hourdakis (18). The idea is to inject a proper fixed quantity of charge to the electrode and measure the electrode potential difference before the charge injection and after the charge injection. The area of a drop of mercury is very small immediately after the previous drop falls. The potential change due to the injection of the charge pulse is more when the drop size is small than it is when the drop size is large. A sudden change of potential difference can be used for the detection of the time at which a drop falls.

The applications mentioned above are only a few of the many possible applications. Any complex potential or current waveform or any combination of the operational modes

which will give the best response to the chemical system can be used either for electroanalytical work or for fundamental electrochemical research.

## CHAPTER 6

### DESCRIPTION OF THE SYSTEM HARDWARE

#### A. Modification of the Charge Generator and the Voltage Measurement System

Figure 6-1 shows the circuits of the Digital-to-Analog Converter (DAC) of the charge generator. The AD 7522 chip is a 10-bit converter manufactured by Analog Devices. The DAC is bipolar with maximum output voltage of  $\pm 2.5$  V. The output voltage  $V$  is converted to  $-V$  by the inverter A4 so that both polarities of the voltage are available simultaneously. The circuits have been modified from S. Hourdakís' original design to provide faster responses for the application of this thesis work. The capacitor C1 has been changed from 560 pF to 150 pF and the capacitor C2 has been changed from 56 pF to 150 pF. These changes give the amplifier A1 a faster response. The output of A1 can come within 1/2 LSB (2.44 mV) of any output voltage in 9  $\mu$ s compared with 35  $\mu$ s in the original design. Resistors R6 and R7 have been changed from 10K $\Omega$ , 5% to 25K $\Omega$ , 1% to provide better accuracy for the inverted voltage  $-V$ . A capacitor C3 of 50 pF has been added in the feedback loop of A4 to improve the signal.

Figure 6-2 shows the modified circuit of the Analog-to-Digital Converter (ADC). A resistor R5 of 1K $\Omega$  is



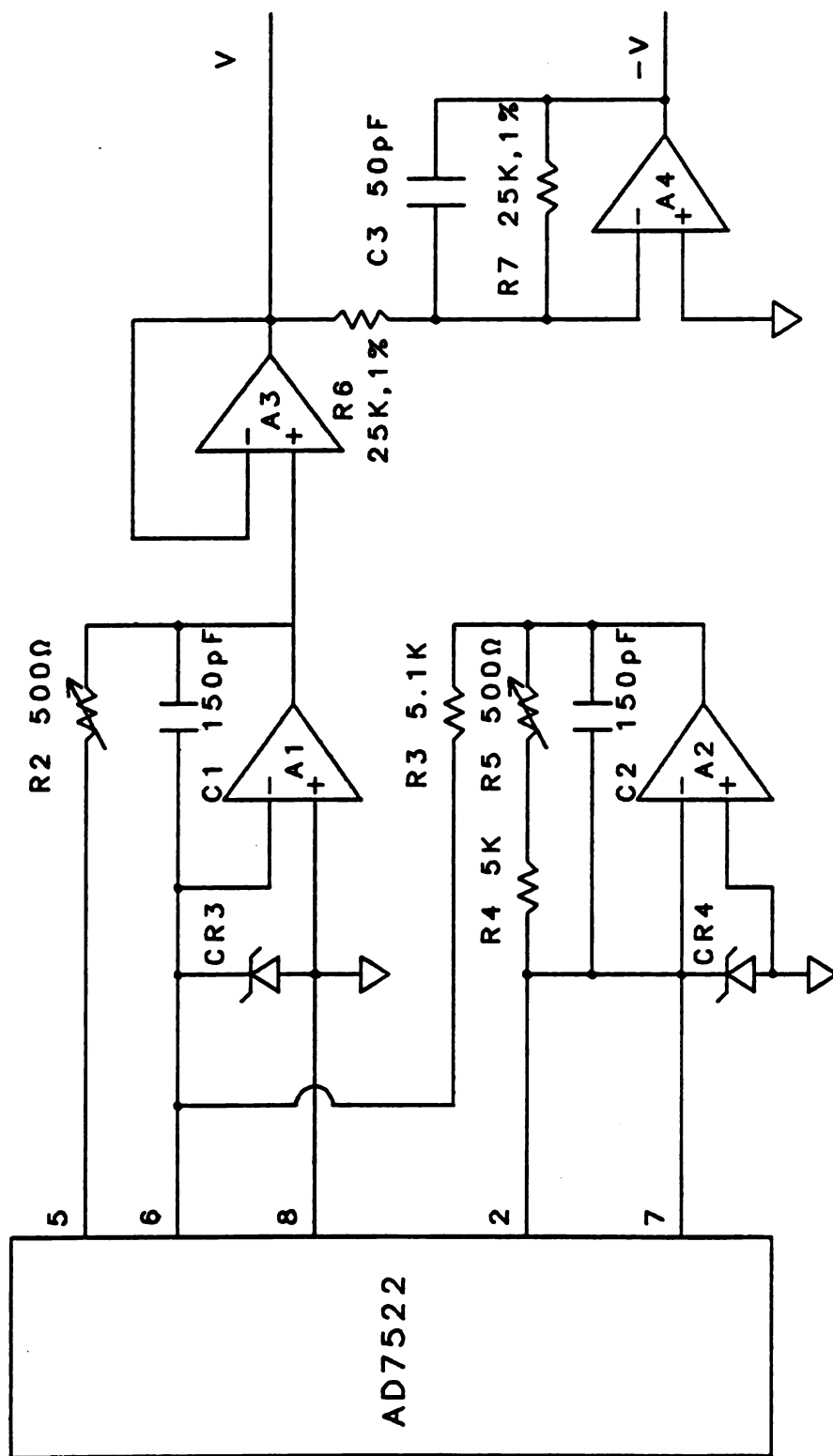


Figure 6-1. The bipolar Digital-to-Analog Converter

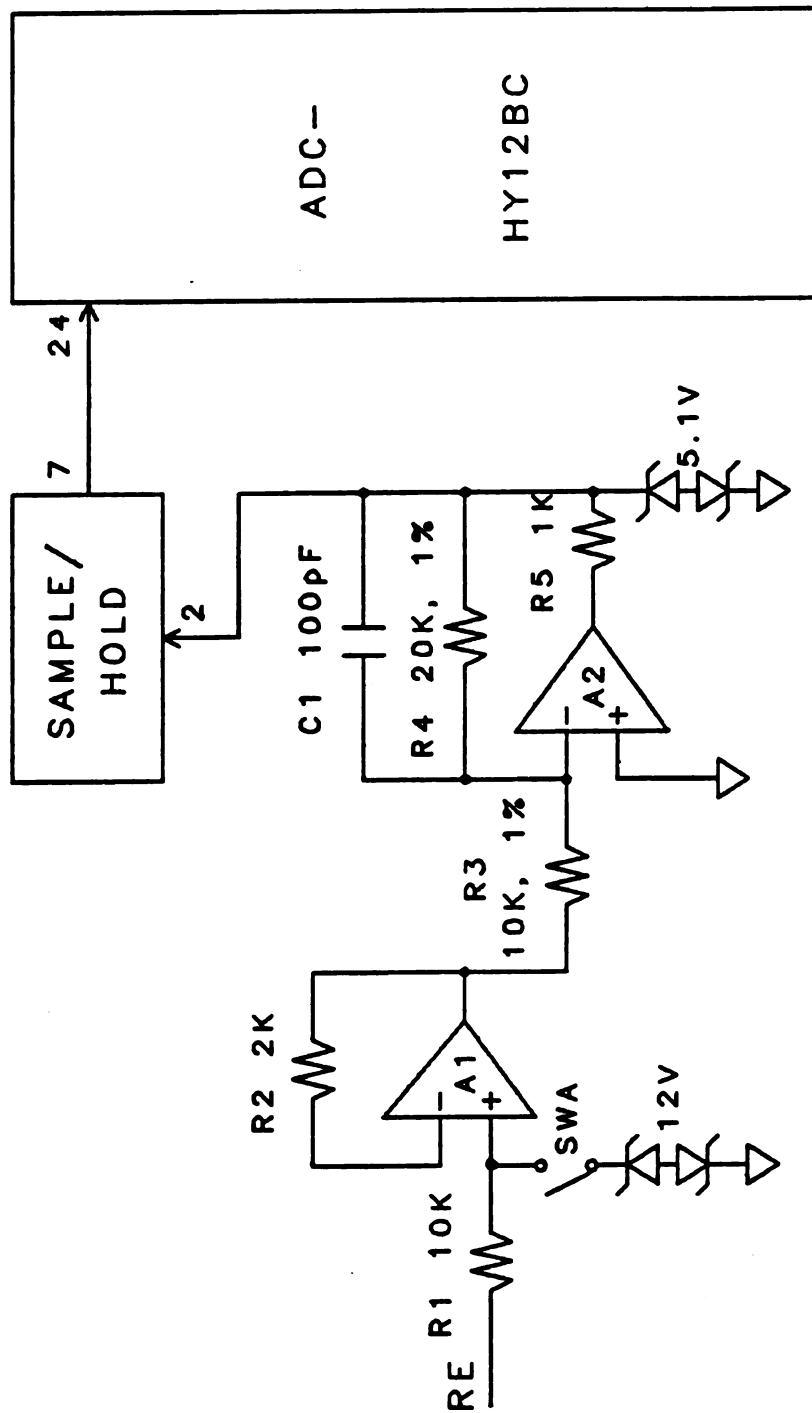
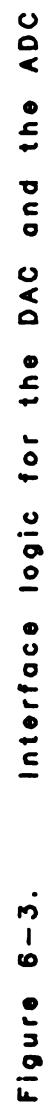


Figure 6-2. The voltage measurement system

added between the output of amplifier A2 and the 5.1 V Zener diodes to limit the output current for A1. A capacitor C1 of 100 pF is added in the feedback loop of A2 to reduce noise. These changes make the noise level very low without excessive reducing in the response speed. When the concentrations of KCl solution are above 0.01 M and the electrochemical cell has not been shielded, the noise level of the electrode potential is below 0.1 mV which is much less than the resolution of the VMS (1.22 mV). For very low concentration of supporting electrolyte such as  $10^{-5}$  M KCl solution, a shield on the electrochemical cell is required to reduce noise level below 1.22 mV. The switch SWA is added between the non-inverting input of the amplifier A2 and the 12 V Zener diodes. When a very dilute electrolyte solution (such as below  $10^{-5}$  M) is used, SWA can be kept open to prevent leakage current through the Zener diodes.

#### B. Interface Circuits

The circuits that interface the microcomputer to the DAC and the ADC provide the necessary digital signals to control them. Figure 6-3 shows the interface logic. Connections A6-A9 are address lines. Signal  $\overline{BS}$  is the board select signal for the charge generator and the voltage measurement system. When A9 is high and  $\overline{BS}$  is low, the 74LS138 decoder chip is selected. Under this condition, one of the outputs of 74LS138 can be selected (active low)



through proper signal levels on lines of A6-A8. Each output (Y0-Y5) of the 74LS138 chip is gated with  $\overline{WR}$  or  $\overline{RD}$  signal to make sure that the address lines are stable in order to provide a proper control signal. DAC LBS is for the loading the low byte (8-bit) data to the input buffer of the DAC. DAC HBS is for the loading of the high byte (2-bit) data to the input buffer of the DAC. The low byte should be loaded first. The DAC HBS also triggers a monostable (74LS221) to generate a 5  $\mu$ s duration pulse for loading the DAC register from DAC input buffer. The falling edge of ADC START triggers the ADC to begin the conversion. The rising edge of the ADC START triggers a D flip-flop (74LS74) to hold the voltage which the ADC is converting. The ADC LBEN enables the reading of low byte (8-bit) data of the ADC. It also clears the Q output of the 74LS74 to change the S/H chip to the sample state. The ADC HBEN enables the reading of the high byte (4-bit) data of the ADC. The ADC EOCEN enables the user to check the status of the end of conversion signal of the ADC. These control signals are connected to the DAC and ADC boards. Letter w indicates a connection to the wire wrap side of the board, and letter c indicates a connection to the component side of the board. The number which follows the letter c or w gives the pin number.

The switch decoding circuits are shown in Figure 6-4. The microprocessor can turn on the desired switch by writing proper digital data to the latch (74174). Only one switch

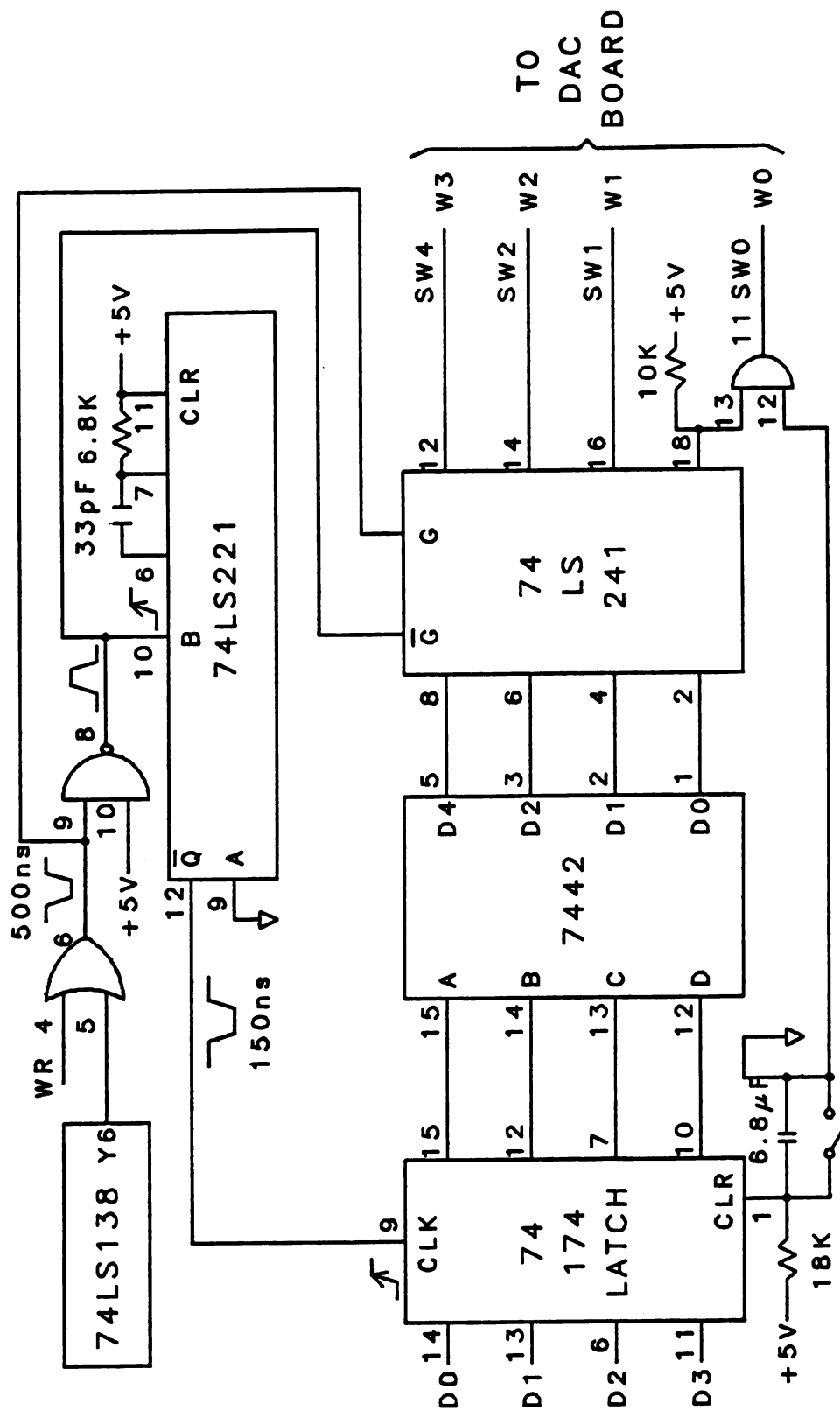


Figure 6-4. Switch decoding circuits

can be turned on at any time.

When the proper address is sent to the decoder chip (74LS138) for programming the switches, the output (Y6) of 74LS138 goes low. The output is gated by the  $\overline{WR}$  signal to make sure that the address lines are stable and the computer is sending data. The duration of the low pulse of the output of the OR gate is about 500 ns. This signal is inverted by the NAND gate. The 74174 chip is used to latch data when the microprocessor programs the switches. The 7442 decoder chip selects one of the outputs through the input data. Only one switch is active (active low) at any time. The tri-state driver (74LS241) is used to drive the switch controlling signals and to turn its own output off when the data is being loaded into the the latch (74174). When the inputs of 7442 change, its outputs also change. The transitions of the outputs of 7442 is gated off by the tri-state driver in order to avoid the situation that a switch is being turned on while another switch is being turned off. The 74LS221 monostable multivibrator chip is used to generate a delayed (about 150 ns) low-to-high transition of the output (pin 8) of the NAND gate. This delayed transition makes sure that the data (D0-D3) are correct at the time of loading the latch. The delay (150 ns) is much shorter than the gating off time of the 74LS241 chip. The outputs of 7442 will be stable before the gates of 74LS241 are turned on again.

A power-up clear and a switch for hardware clear are connected to the latch. The switch 0 is selected when the latch is cleared. The switch 0 is used to connect a  $1K\Omega$  feedback resistor between the output and the inverting input of the charging amplifier (the amplifier for adding charge to the electrode) to protect the amplifier (see Figure 35 of S. Hourdakís's dissertation (18)).

### C. The Real Time Clock

The real time clock is based on the AM 9513 system timing controller chip manufactured by the Advanced Micro Devices, Inc. The chip includes five general-purpose 16 bit counters. A variety of internal frequency sources and external pins may be selected as inputs for individual counters. Both hardware and software gating of each counter is available. The counters may be programmed to count up and down in either binary or BCD. The usage of this chip allows complex timing control to be feasible.

In order to make the programming easy, a crystal of 1.000000 MHz is selected to generate an accurate counting source. The data bus lines (DB0-DB7) and  $\overline{RD}$ ,  $\overline{WR}$  inputs of AM 9513 are connected to the microcomputer bus. The  $\overline{CS}$  of AM 9513 comes from one of the UNQUAL (not gated with  $\overline{WR}$  or  $\overline{RD}$ ) outputs of the  $\overline{CS}$  board designed by Bruce Newcome (19). Each pin of the outputs (OUT1-OUT5), of the source inputs (SRC1-SRC5) and of the gate inputs (GATE1-GATE5) is



connected to 4 patch wire sockets to enable interconnection between them or to other sources. A 50 pin connector is soldered on the real time clock board to make any connection to any device which needs accurate timing control or provides pulses to be counted.

The usage of AM9513 and the design of the real time clock board allow a flexible timing control for most electrochemical experiments. Detail programming of the timing controller and the connections between the outputs, sources and gates can be found in the programs TICP.MAC and TIM12.MAC in Appendix B.

## APPENDIX A

### Equation and Some Examples for the calculation of minimum values of $t_{d1}$ for Chronopotentiometric Experiments

M is the number of charge injections between two adjacent potential measurements. N is the number of extra software loop for charging the capacitor and injection of charge to the electrode ( $N = \text{SWDLY1} + \text{SWDLY2} - 2$ ). See programs CHGADM.MAC and SWDLYB.MAC in Appendix B.

$$\text{Minimum } t_{d1} = 155.5 + 49.5(M-1) + M \cdot N \cdot 4.55 \mu s$$

	Minimum $t_{d1}$ ( $\mu s$ )	
M=1	155.53	+1·N·4.55
M=2	205.03	+2·N·4.55
M=3	254.53	+3·N·4.55
M=4	304.03	+4·N·4.55
M=5	353.53	+5·N·4.55
M=6	403.03	+6·N·4.55
M=7	452.53	+7·N·4.55
M=8	502.03	+8·N·4.55
M=9	551.53	+9·N·4.55
M=10	601.03	+10·N·4.55

Minimum  $t_{d1}$  ( $\mu s$ ) for 0.01 M KCl solution ( $\text{SWDLY1} = 2$ ,  
 $\text{SWDLY2} = 3$ ).

M=1:	169.18	M=2:	232.33	M=3:	295.48
M=4:	358.63	M=5:	421.78	M=6:	484.93
M=7:	548.48	M=8:	611.23	M=9:	674.38
M=10:	737.53	M=11:	800.68	M=12:	863.83
M=13:	926.98	M=14:	990.13		

## APPENDIX B

### Programs for Data Acquisition and Data Analysis

The names and the functions of the programs for data acquisition and data analysis are listed below.

Table B-1. The names and functions of the data acquisition programs

Name	Function
CAPSEQ	Controls the sequential operations for capacitance measurements
TIM12	Sets up timer for capacitance measurements
BLVC	Calibrates DAC baseline values
CAP	Measures capacitances
TICP	Sets up timer for chronopotentiometric experiment
ICAPN	Measures integral capacitive charges
CPSEQB	Controls the sequential operations for chronopotentiometric experiment
CPADCN	Measures electrode potential and stores it in memory
CHGADM	Injects a charge pulse or charge pulses to the electrode
VBACK	Bring the potential back to the initial value

Table B-2.            The names and functions of the data analysis programs

Name	Functions
CAP.FTN	<ol style="list-style-type: none"><li>1. Divides one binary file by another for capacitance measurements; one data set is from the results of an electrochemical experiment, the other is from the results of a dummy cell</li><li>2. generates a C. G. Enke <math>\beta</math> Co. standard data file and a parameter file</li></ol>
CONCPAD.FTN	<ol style="list-style-type: none"><li>1. Converts ADC values obtained in a chronopotentiometric experiment to a C. G. Enke <math>\beta</math> Co. standard data file and a parameter file</li></ol>

```

SUBR CAPSEQ
CAPSEQ: PUSH    H           ; SAVE REGS
        PUSH    PSW         ;
CAPSQ0: LXI     H, VINIT    ;
        CALL    VAPR        ; APPROACH THE INITIAL
                                ; VOLTAGE
        LDA     VAPFLG      ; GET THE FLAG
        CPI     0           ; GET THE VOLTAGE?
        JNZ     CAPSQ0      ; NO, DO IT AGAIN
        CALL    READY       ;
CAPSQ1: LXI     H, VINIT    ;
        CALL    VAPR        ;
        LDA     EFLAGS      ;
        RRC             ;
        JNC     CAPSQ1      ; KEY BOARD IS NOT TYPED
        LDA     BUFO        ; GET THE CHARACTER
        CPI     CTRZ        ; CONTROL Z
        JZ      CAPSQ7      ; EXIT
        CPI     'g          ; GO
        JNZ     CAPSQ1      ; NO
        CALL    CAP         ;
        LXI     H, CAPSMO    ;
        CALL    PRINT       ; CLEAR GRAPHICS?
        MVI     A, 30.       ; DELAY FOR 3 SEC.
CAPSQ2: LXI     H, 10000.    ;
        CALL    DELAY       ;
        DCR     A           ;
        JNZ     CAPSQ2      ;
        LDA     EFLAGS      ;
        RRC             ;
        JNC     CAPSQ3      ; KEYBOARD IS NOT TYPED
        LDA     BUFO        ; GET THE CHARACTER
        CPI     'b          ;
        CZ      BLANK       ; CLEAR SCREEN
        CPI     'y          ;
        CZ      CLEAR       ; CLEAR SCREEN
        CZ      BLANK       ; CLEAR THE SCREEN
        MVI     A, EFUO     ;
        CALL    EFCLR       ; CLEAR KB
        LXI     H, 10000.    ; DELAY
        CALL    DELAY       ; FOR .1 SEC.
CAPSQ3: CALL    CAPQR       ; DRAW THE RESULTS
        CALL    CAPUL       ; SEND DATA TO 11
        JMP     CAPSQ0      ; LOOP AROUND
CAPSQ7: MVI     A, EFUO     ; CLEAR KB EVENT FLAG
        CALL    EFCLR       ;
        POP     PSW         ; RESTORE REGS
        POP     H           ;
        RET                ;
CAPSMO: .ASCIZ  /CLEAR?/
;
;
; TIMING PROGRAM FOR THE CAPACITANCE MEASUREMENT

```

; CONNECT GATES 1 AND 2 TO +5 V

```

SUBR      TIM12
TIM12:    PUSH      H          ; SAVE REGS
          PUSH      D          ;
          PUSH      PSW        ;
          CALL      TIRSET     ; RESET TIMER
          MVI       A, 1       ; COUNTER #1 MODE REG
          STA       TICMD      ;
          LXI       H, TIDATA  ; GET ADDR OF TIMER DATA
          ; PORT
          MVI       M, 242     ; ENABLE SPECIAL GATE
          ; FROM LOAD REG, REPETITIVELY
          ; BIN, DOWN, ACTIVE HIGH
          ; TOGGLE, DELAYED
          MVI       M, 233     ; ACTIVE HIGH LEVEL GATE N, F1
          XCHG
          LHLD      TIPD       ; GET TIMER DELAY
          XCHG
          MOV       M, E       ; TO LOAD REG
          MOV       M, D       ;
          MOV       M, E       ; TO HOLD REG
          MOV       M, D       ;
          MVI       M, 202     ; COUNTER #2 MODE REG
          ; ENABLE SPECIAL GATE
          ; FROM LOAD REG, ONCE
          ; BIN, DOWN, ACTIVE HIGH
          ; TOGGLE, DELAYED
          MVI       M, 220     ; ACTIVE HIGH LEVEL GATE N
          ; TCN-1
          XCHG
          LHLD      TIDD       ; GET TIMER DELAY
          DCX       H          ; DECREMENT TO MATCH
          ; DELAY = TIPD * TIDD
          XCHG
          MOV       M, E       ; TO LOAD REG
          MOV       M, D       ;
          MOV       M, E       ;
          MOV       M, D       ;
          POP       PSW        ; RESTORE REGS
          POP       D          ;
          POP       H          ;
          RET                ; AND GO HOME

```

```

;
; THIS ROUTINE DETERMINES THE DAC VALUE
; FOR ADDING ZERO CHARGE

```

```

SUBR      BLVC
BLVC:     PUSH      H          ; SAVE REGISTERS
          PUSH      D          ;
          PUSH      B          ;
          PUSH      PSW        ;
          CALL      LPTI       ; OUTPUTS TO TERMINAL ONLY
          CALL      BLVC1      ; COMPARE VINIT & VFINAL

```

```

                JM      BLVC5          ; VFINAL IS MORE POSITIVE
                JNZ     BLVC11         ; VFINAL IS MORE NEGATIVE
BLVC4:          MVI     A, 1          ; STORE THE RATIO
                STA     BLDAR1        ;
                MVI     A, 0          ;
                STA     BLDAR2        ;
                JMP     BLVC47         ;
; GET TO THE DESIRED VOLTAGE, ADD CHARGE AND CHECK
; THE DIRECTION OF VOLTAGE
BLVC1:          LXI     H, BLAD1      ; ADD FOR VOLTAGE TO BE
                ; APPROACHED
                MVI     A, 100        ; 100 TIMES
BLVC2:          CALL    VAPR          ; APPROACH THE DESIRED
                ; VOLTAGE
                CALL    ADC6DE        ; GET ADC VALUE IN DE
                CALL    ADCBDP        ; PRINT THE VALUE
                CALL    CRLF          ; CARRIAGE RETURN, LINE FEED
                DCR     A              ;
                JNZ     BLVC2         ; LOOP AROUND TILL DONE
                MVI     A, 377        ; 255 TIMES AGAIN
BLVC3:          CALL    VAPR          ;
                DCR     A              ;
                JNZ     BLVC3         ;
                CALL    ADC6DE        ; GET ADC VALUE INTO DE
                XCHG                ; GET INTO HL
                SHLD    BLVCV1        ; STORE IT
                LHLD    BLDA1        ; DAC VALUE FOR ADDING
                ; CHARGE
                XCHG                ; INTO DE
                LDA     BLSW          ; SW #
                MOV     B, A          ;
                LDA     BLNUM1        ; NUMBER OF CHARGE ADDITIONS
                MOV     C, A          ;
                CALL    CGADD        ; ADD CHARGE HL=DAC VALUE
                ; C=# OF LOOP
                CALL    ADC6DE        ; GET ADC VALUE IN DE
                LHLD    BLVCV1        ; GET VINIT
                XCHG                ; (DE)=VINIT (HL)=VFINAL
                PUSH    H              ; SAVE V FINAL
                LXI     H, VINITM      ;
                CALL    PRINT         ; PRINT VINIT
                CALL    ADCBDP        ;
                CALL    CRLF          ;
                LXI     H, VFINLM      ;
                CALL    PRINT         ;
                POP     H              ;
                XCHG                ; (DE)=VFINAL (HL)=VINIT
                CALL    ADCBDP        ;
                CALL    CRLF          ;
                CALL    DCMPL        ; (DE)-(HL) FLAGS BASED ON
                ; RESULTS
                RET                  ; AND GO HOME
; VFINAL IS MORE POSITIVE

```

```

BLVC5:  CALL    DSUB          ; (HL)=(HL)-(DE)
        MOV     A,L          ;
        STA     BLDAR1       ; STORE THE RATIO FOR MORE
                                ; POSITIVE V
        LXI     H,BLDA1      ; GET ADDRESS OF DAC VALUE
        CALL    DCXM         ; INCREASE MEMORY WORD,
                                ; DECREASE DAC VALUE
        CALL    BLVC1        ; DO IT AGAIN
        JM      BLVC5        ; STILL MORE POSITIVE
        JZ      BLVC4        ; VFINAL=VINIT
        CALL    DSUB         ; HL=HL-DE
        CALL    HLTCMP       ; TWO'S COMPLEMENT OF HL
        MOV     A,L          ;
        STA     BLDAR2       ; STORE THE RATIO FOR
                                ; MORE NEGATIVE V
        JMP     BLVC47       ; FINISH
; VFINAL IS MORE NEGATIVE
BLVC11: CALL    DSUB          ; HL=HL-DE
        CALL    HLTCMP       ; TWO'S COMPLEMENT OF HL
        MOV     A,L          ;
        STA     BLDAR2       ; STORE THE RATIO FOR
                                ; MORE NEGATIVE V
        LXI     H,BLDA1      ; GET ADDRESS OF DAC VALUE
        CALL    INXM         ; DECREASE MEMORY WORD,
                                ; INCREASE DAC VOLTAGE
        CALL    BLVC1        ; DO IT AGAIN
        JZ      BLVC4        ; VFINAL=VINIT
        JP      BLVC11       ; STILL MORE NEGATIVE
        CALL    DSUB         ; HL=HL-DE
        MOV     A,L          ;
        STA     BLDAR1       ; STORE THE RATIO FOR
                                ; MORE POSITIVE V
        LXI     H,BLDA1      ; ADJUST DAC TO BE
                                ; MORE POSITIVE
        CALL    DCXM         ;
BLVC47: POP     PSW          ; RESTORE REGISTERS
        POP     B            ;
        POP     D            ;
        POP     H            ;
        RET                 ; AND GO HOME
BLFLO:  .BLKB 1             ; 1: VFINAL+, 0: VFINAL-
BLVCV1: .BLKB 2             ; TEMP VOLTAGE STORAGE
;
;
; BLDA1: BASELINE VOLTAGE FOR DAC
; MO:    MINIMUM DATA POINTS FOR EACH POTENTIAL STEP
; NO:    SHORTER # OF LOOPS FOR KEEPING POTENTIAL
; N1:    LONGER # OF LOOPS FOR LEEPING POTENTIAL
; N2:    DAC INCREMENT FOR CAPACITANCE MEASUREMENT
; SWA:   SWITCH # FOR ADDING CHARGE, USE #4
; SWDLY1: DELAY FOR CHARGING CAPACITOR,
;         USE 10 IS ENOUGH FOR .1 uF CAP
; VSTPO: VOLTAGE STEP FOR CAPACITANCE MEASUREMENT

```



```

;VSTP1: VOLTAGE STEP FOR POTENTIAL SCANNING
;
;
;
; MTMP: VOLTAGE APPROXIMATION FLAG 1=>ADJUSTED
; OTHERS => NOT ADJUSTED
; MTMP1: TEMPORARY CHG QUANTITY
; MXTMP: POTENTIAL BEFORE CHG ADD
; MXTMP1: DAC VALUE FOR CHARGE ADDITION
; MXTMP2: ADDR FOR STORING SUMMATION OF CHARGE
; MXTMP3: ADDR FOR STORING # OF DATA POINTS FOR THE POTENTIAL
; DELAY = TIPD * TIDD
; TIPD >= 32, TIDD >= 4
CAP: SUBR CAP
      PUSH H ; SAVE REGS
      PUSH D ;
      PUSH B ;
      PUSH PSW ;
      LHLD VINIT ; INITIAL VOLTAGE
      SHLD MXTMP ;
      LXI H, ADCLIB ; STARTING ADDR FOR STORING
                        ; SUMMATION OF CHG
      SHLD MXTMP2 ;
      LXI D, CAPEND ; ENDING ADDR
CAP1: MVI M, 0 ; CLEAR MEM
      INX H ; INCREASE MEM ADDR
      CALL DCMP ; DE-HL
      JNZ CAP1 ;
      LXI H, 1 ;
      SHLD DATAN ; CLEAR # OF DATA POINTS
      LXI H, 0 ;
      SHLD MX2TM5+2 ; CLEAR HIGH WORD FOR ADD
      MVI A, 0 ;
      STA MTMP ; CLEAR VOLTAGE
                        ; APPROXIMATION FLAG
                        ; 1=> ADJUSTED
                        ; 0=> NOT ADJUSTED
      CALL TIM12 ; SET UP COUNTER #1 & #2
      MVI A, 141 ;
      STA TICMD ; LOAD AND ARM COUNTER #1
      LXI H, TCLIB ; STARTING ADDR FOR STORING
                        ; # OF DATA POINTS FOR
                        ; EACH VOLTAGE
      SHLD MXTMP3 ;
      LXI D, TCLIB+4000 ;
CAP2: MVI M, 0 ; CLEAR MEM
      INX H ; INCREASE MEM ADDR
      CALL DCMP ; DE-HL
      JNZ CAP2 ;
CAP3: LXI H, MXTMP ;
      CALL VAPN1 ; KEEP AT THE POTENTIAL
                        ; FOR A WHILE (LONGER)
      LHLD DAO ; GET DAC VALUE

```

```

XCHQ          ; INTO DE
CALL          ; SET UP DAC AND CHQ CAP
LDA           ; GET TIMER STATUS
ANI           ; OUT1
JNZ           ; 1, CHECK FOR 1 -> 0
CAP3A: LDA     ;
ANI          ;
JZ           ;
JMP          ;
CAP3B: LDA     ; 0 -> 1
TICMD        ; CHECK FOR 1 -> 0
ANI          ;
JNZ          ;
CAP3C: MVI     ;
A, 352       ;
STA          ; SET OUT2
TICMD        ; LOAD AND ARM COUNTER #2
MVI          ;
A, 142       ;
STA          ;
TICMD        ;
LDA          ;
SWA          ;
STA          ; SEND THE CHQ TO ELECTRODE
SW           ;
CAP4: LDA     ;
TICMD        ;
ANI          ; COUNTER #2 STATUS BIT
4            ; NOT YET, WAIT
JNZ          ; MEASURE THE POTENTIAL
CALL         ; GET POTENTIAL BEFORE
ADC6DE       ; CHARGE ADDITION
LHLD         ;
MXTMP        ;
XCHQ         ;
CALL         ; GET VOLTAGE DIFFERENCE
DSUB         ;
LXI          ;
D, 0         ;
CALL         ;
DCMP         ;
JM           ;
CAP6         ; O. K.
; CHQ NOT ENOUGH, ADD MORE
LHLD         ; GET DAC VALUE FOR CAP
DAO          ; INTO DE
XCHQ         ; GET BASELINE DAC VALUE
LHLD         ; HL-DE
BLDA1        ;
CALL         ;
DSUB         ;
XCHQ         ;
MVI          ;
A, 2         ;
CALL         ; DE=DE*A
DMULT        ; GET BASELINE DAC VALUE
LHLD         ; CALC NEW DAC FOR CAP
BLDA1        ; STORE IT
CALL         ; ADD CHQ AGAIN
DSUB         ;
SHLD         ;
DAO          ;
JMP          ;
CAP6: SHLD    ; STORE POTENTIAL DIFFERENCE
MXTMP4       ; VOLTAGE STEP FOR CAP
LDA          ; START FROM 3LSB LESS
VSTPO       ;
DCR          ;
A           ;
DCR          ;
A           ;
DCR          ;
A           ;
CMP          ;
L           ;
JZ           ; PROPER VOLTAGE TO START
CAP20        ; VOLTAGE TOO LITTLE
JP           ; CHECK APPROXIMATION FLAG
CAP10: MVI    ;
A, 1         ;
; VOLTAGE TOO MUCH, CALC PROPER CHARGE

```

```

        STA      MTMP          ; SET APPROXIMATION FLAG
        LHLD     DAO           ; GET DAC VALUE FOR CAP
        XCHG     ; INTO DE
        LHLD     BLDA1         ; GET BASE LINE DAC VALUE
        CALL     DSUB          ; HL=HL-DE
        XCHG     ;
        LDA      VSTPO         ; DESIRED VOLTAGE STEP
                                ; FOR CAP
        DCR      A             ; DECREMENT BY 3
        DCR      A             ;
        DCR      A             ;
        CALL     DMULT          ; DE=DE*A
        LDA      MXTMP4        ; GET ACTUAL VOLTAGE STEP
        CALL     DIV           ; DE=DE/A
        LHLD     BLDA1         ; GET BASELINE DAC VALUE
        CALL     DSUB          ; CALC THE DAC VALUE FOR CAP
        SHLD     DAO           ;
        JMP      CAP3          ; TRY TO APPROXIMATE THE CHG
                                ; ADD AGAIN
; VOLTAGE TOO LITTLE, CHECK APPROXIMATION FLAG.
; IF APPROXIMATED, GO AHEAD AND DO IT
CAP15:  LDA      MTMP          ; GET APPROXIMATION FLAG
        CPI      1             ; APPROXIMATED?
        JNZ      CAP10        ; NOT YET, APPROXIMATE IT
                                ; ONCE
CAP20:  MVI      A, 0           ;
        STA      MTMP          ; CLEAR APPROXIMATION FLAG
; STARTING ADDING INCREMENTING CHG IN ORDER TO MEASURE CAP
CAP21:  LHLD     DAO           ; GET DAC VALUE
        SHLD     MXTMP1        ;
CAP22:  LHLD     MXTMP1        ; GET DAC VALUE FOR CHG ADD
        XCHG     ; INTO DE
        LHLD     BLDA1         ; GET DAC BASELINE VOLTAGE
        CALL     DSUB          ; HL-DE
        XCHG     ; RESULTS INTO DE
        LHLD     BLDA1         ; GET BASELINE DAC VALUE
        DAD      D             ; CALC DAC VALUE FOR
                                ; REVERSE CHARGE
        CALL     CGADD         ; ADD THE CHG TO ELECTRODE
        LDA      SWDLY3        ; GET SWITCH DELAY
        CPI      0             ; NO DELAY?
        JZ       CAP22D        ; YES
        CALL     VAPDEL        ; DELAY FOR A WHILE
CAP22D: LXI      H, MXTMP      ; GET POTENTIAL BEFORE
                                ; CHARGE ADDITION
        CALL     VAPNO         ; APPROACH THE POTENTIAL
                                ; (SHORTER)
        LHLD     MXTMP1        ; GET DAC VALUE
        XCHG     ; INTO DE
        CALL     DACSUP        ; SET UP DAC, CHG CAP
        LDA      TICMD         ; GET TIMER STATUS
        ANI      2             ; OUT1
        JNZ      CAP22B        ; 1, CHECK FOR 1-> 0

```

```

CAP22A: LDA    TICMD    ;
        ANI    2        ;
        JZ     CAP22A   ;
        JMP    CAP22C   ; 0 -> 1
CAP22B: LDA    TICMD    ; CHECK FOR 1 -> 0
        ANI    2        ;
        JNZ    CAP22B   ;
CAP22C: MVI    A, 352    ;
        STA    TICMD    ; SET OUT2
        MVI    A, 142    ;
        STA    TICMD    ; LOAD AND ARM COUNTER #2
        LDA    SWA       ;
        STA    SW        ; ADD CHQ TO ELECTRODE
CAP24:  LDA    TICMD    ; CHECK COUNTER #2
        ANI    4        ; COUNTER #2 STATUS BIT
        JNZ    CAP24     ; NOT YET, WAIT
        CALL   ADC6DE    ; GET THE POTENTIAL
        LHL    MXTMP     ; GET POTENTIAL BEFORE
                        ; CHARGE ADDITION
        XCHG          ;
        CALL   DSUB      ; POTENTIAL AFTER CHQ ADD -
                        ; POTENTIAL BEFORE CHQ ADD
        LDA    VSTPO     ; VOLTAGE STEP FOR CAP
        SUB    L         ;
        JNZ    CAP30     ; VOLTAGE NOT EQUAL DESIRED
                        ; VALUE
; VOLTAGE WITHIN DESIRED VALUE +- 1LSB
CAP24A: LHL    MXTMP1    ; GET DAC VALUE FOR CAP
        XCHG          ; INTO DE
        LHL    BLDA1     ; GET BASELINE DAC VALUE
        CALL   DSUB      ; HL-DE
        SHLD   MX2TM5    ;
        LHL    MXTMP2    ; GET ADDR FOR CHQ SUMMATION
        LXI    D, MX2TM4 ;
        MVI    A, 4      ;
        CALL   MTRF      ; TRANSFER PREVIOUSLY
                        ; SUMMED CHQ
                        ; INTO MX2TM4
        CALL   DDADD      ; (6) = (4) + (5)
        LHL    MXTMP2    ; GET ADDR OF SUM OF CHQ
        XCHG          ; FOR DESTINATION
        LXI    H, MX2TM6 ; GET ADDR OF SOURCE
        CALL   MTRF      ; TRANSFER 4 BYTES OF MEM
        LHL    MXTMP3    ; GET ADDR OF COUNTER OF
                        ; # OF CHQ ADD
        CALL   INXM      ; INCREMENT THE COUNT
        LHL    MXTMP1    ; GET DAC VALUE
        LDA    N2        ;
        MOV    E, A      ;
        MVI    D, 0      ;
        CALL   DSUB      ; HL-DE
        LXI    D, 0      ;
        CALL   DCMPL     ; DE-HL

```

```

                JZ      CAP25      ; MOST NEGATIVE VOLTAGE
                                ; ALLOWED
CAP25:          JP      CAP26      ; OUT OF BOUNDARY
                SHLD    MXTMP1     ; STORE DAC VALUE FOR NEXT
                                ; CHQ ADD
                JMP     CAP22      ; ADD MORE CHQ TO GET CAP
CAP26:          CALL    ERROR      ; SEND ERROR MESSAGE
                JMP     CAP41      ; GO TO NEXT VLOTAGE STEP
; VOLTAGE NOT WITHIN TO THE DESIRED VALUE +- 1LSB
CAP30:          CPI     1          ;
                JZ      CAP24A     ;
                CPI     -1         ;
                JZ      CAP24A     ;
                CPI     -2         ;
                JM      CAP40      ; VOLTAGE HIGH ENOUGH
                LHLD    MXTMP1     ; GET DAC VALUE
                LDA     N2         ; GET DAC STEP
                MOV     E, A       ;
                MVI     D, 0       ;
                CALL    DSUB       ; CALC NEXT DAC VALUE
                LXI     D, 0       ; MOST NEGATIVE DAC VALUE
                CALL    DCMP       ; DE-HL
                JZ      CAP31      ; HIGHEST VOLTAGE ALLOWED
                JP      CAP26      ; ERROR, GO TO NEXT STEP
CAP31:          SHLD    MXTMP1     ; STORE DAC VALUE FOR NEXT
                                ; CHQ ADD
                JMP     CAP22      ; ADD MORE CHQ TO GET CAP
; VOLTAGE HIGH ENOUGH, CHECK # OF DATA, IF ENOUGH,
; GO TO NEXT VOLTAGE STEP
CAP40:          LHLD    MXTMP3     ; GET ADDR FOR STORING
                                ; # OF DATA POINTS
                MOV     E, M       ; # OF DATA POINTS INTO DE
                INX     H          ;
                MOV     D, M       ;
                LHLD    MO         ; GET MINIMUM DATA POINTS
                                ; DESIRED
                CALL    DCMP       ; DE-HL
                JM      CAP21      ; NOT ENOUGH DATA POINTS,
                                ; GET THE STARTING POTENTIAL
                                ; QUICKLY AND DO IT MORE
; # OF DATA POINTS IS ENOUGH FOR THE VOLTAGE OF INTEREST,
; GO TO NEXT VOLTAGE
CAP41:          LHLD    MXTMP     ; GET THE VOLTAGE BEFORE
                                ; CHQ ADD
                LDA     VSTP1      ; VOLTAGE STEP FOR SCANNING
                CALL    HLPA      ; CALC VOLTAGE FOR NEXT STEP
                XCHG             ; RESULTS INTO DE
                LHLD    VFINAL     ; GET FINAL VOLTAGE
                CALL    DCMP       ; DE-HL
                JP      CAP30      ; VOLTAGE HIGH ENOUGH
                XCHG             ; NEXT VOLTAGE INTO HL
                SHLD    MXTMP      ; STORE IT
                LHLD    DATAN      ; GET # OF VOLTAGE STEP

```

```

      INX      H      ; INCREMENT ONE
      SHLD     DATAN   ; STORE IT
      LHLD     MXTMP3  ; GET ADDR FOR STORING # OF
                        ; DATA POINTS IN EACH STEP
      INX      H      ; INCREMENT BY 2
      INX      H
      SHLD     MXTMP3  ; STORE IT
      LHLD     MXTMP2  ; GET ADDR FOR STORING SUM
                        ; OF CHQ FOR THE VOLTAGE
                        ; STEP
      INX      H      ; INCREMENT BY 4
      INX      H
      INX      H
      INX      H
      SHLD     MXTMP2  ; STORE IT
      MVI      A, 0    ; CLEAR VOLTAGE
      STA      MTMP    ; APPROXIMATION FLAG
                        ; GO TO NEXT VOLTAGE STEP
CAP50: POP      CAP3   ; RESTORE REGS
      POP      PSW
      POP      B
      POP      D
      POP      H
      RET            ; AND GO HOME
;
;
; TIMER FOR CHRONOPOTENTIOMETRY, CONNECT OUT2 TO SRC2,
; GATES 1, 2, AND 4 TO +5V
; OUT4 TO GATE 3, -OUT4 TO IR3, OUT3 TO IR4
; IR3 AND IR4 ARE INPUTS OF THE INTERRUPT CONTROLLER OF 8259
      SUBR      TICP
TICP: PUSH     H      ; SAVE REGS
      PUSH     D
      PUSH     PSW
      CALL     TIRSET ; RESET TIMER
      MVI      A, 2   ; COUNTER 2 MODE REG
      STA      TICMD
      LXI      H, TIDATA ; GET ADDR OF TIMER DATA
                        ; PORT
      MVI      M, 242  ; ENABLE SPECIAL GATE,
                        ; FROM LOAD, REPETITIVELY,
                        ; BIN, DOWN, ACTIVE HIGH
                        ; TOGGLE, DELAYED
                        ; ACTIVE HIGH LEVE GATE N, F1
      MVI      M, 233  ; SAVE ADDR OF TIDATA
      XCHG     TIDD    ; DATA DELAY
      LHLD     TIDD
      XCHG
      MOV      M, E    ; TO LOAD REG
      MOV      M, D
      MOV      M, E    ; TO HOLD REG
      MOV      M, D
      MVI      M, 242  ; COUNTER 3 MODE REG
                        ; SAME AS COUNTER 2

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; GATE IS CONTROLLED BY OUT4
MVI      M, 233
MOV      M, E
MOV      M, D
MOV      M, E
MOV      M, D
MVI      M, 302
; COUNTER 4 MODE REQ
; ENABLE SPECIAL GATE
; RELOAD FROM LOAD OR HOLD
; COUNT ONCE, BIN, DOWN, ACTIVE
; HIGH TOGGLE, DELAYED
MVI      M, 202
; SRC2(CONNECT OUT2 TO SRC2)
; RISING EDGE,
; ACTIVE HIGH GATE N
XCHG
LHLD     TIPD
XCHG
MOV      M, E
MOV      M, D
MVI      M, 0
MVI      M, 2
MVI      A, 156
STA      TICMD
POP      PSW
POP      D
POP      H
RET
; AND GO HOME

;
; THIS ROUTINE ADDS CHARGE TO THE ELECTRODE AND CALCULATE
; THE INTEGRAL CAPACITIVE CHARGE FOR EACH VOLTAGE
; MXTMP1: COUNTER FOR THE VOLTAGE
; MXTMP2: THE SECOND VOLTAGE DIFFERENCE
; MXTMP3: CHARGE QUANTITY OF ONE ADDITION
; MXTMP4: ADDRESS FOR INTEGRAL CAPACITIVE CHARGE
; MXTMP5: ADDRESS FOR THE DIFFERENCE OF ADJACENT VOLTAGE
ICAPN:   SUBR      ICAPN
PUSH     H
PUSH     D
PUSH     B
PUSH     PSW
LXI      H, 0
SHLD     BICAP
SHLD     BICAP+2
LXI      H, 1
SHLD     MXTMP1
LDA      ICAPC1
LXI      H, ICAPDA
CALL     SMDAC
MVI      A, 1
STA      ICAPC2
ICPNOA: LXI      H, VINIT

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CALL VAPNO ;
CALL READY ; TELL US IT'S READY
ICPN0: LXI H,VINIT ; APPROACH THE VOLTAGE
CALL VAPR ;
CALL CHARIN ; IS KEYBOARD TYPED?
JNC ICPNO ; NO, WAIT
CPI 'g' ; GO?
JNZ ICPNO ; NO, WAIT
ICPN1: LXI H,VINIT ;
CALL VAPNO ; APPROACH THE VOLTAGE
LHLD ADCTMP ; GET THE VOLTAGE
XCHG ; (DE)=TEMP VOLTAGE
ICPN2: LXI H,VINIT ; APPROACH THE VOLTAGE
CALL VAPN1 ;
CALL ADC6DE ; GET THE DAC VALUE
LHLD VINIT ; GET INIT VOLTAGE
XCHG ; (HL)=DAC VALUE
CALL DCMP ; (VINIT)-ADC VALUE
JNZ ICPN2 ; ADC VALUE IS NOT EQUAL
; TO VINIT, DO IT AGAIN
SHLD ADCTMP ; STORE BEGINING POTENTIAL
LDA ICAPC2 ; GET NUMBER OF CHARGE LOOP
ICPN3: PUSH PSW ; SAVE # OF CHARGE LOOP
LDA ICAPSW ; GET SW #
MOV B,A ; INTO B
LDA ICAPDA ; GET DAC LOW BYTE
STA DACLB ;
LDA ICAPDA+1 ; GET DAC HIGH BYTE
STA DACHB ;
POP PSW ; GET # OF CHARGE LOOP
ICPN3A: PUSH PSW ; SAVE # OF CHQ LOOP LEFT
LDA ICAPC1 ; GET # OF SMALL CHQ LOOP
MOV C,A ; SAVE IT
ICPN3B: MVI A,1 ;
STA SW ; CHARGE UP CAPACITOR
LDA SWDLY1 ; GET SWITCH DELAY
ICPN3C: DCR A ;
JNZ ICPN3C ;
MOV A,B ; GET SWITCH NUMBER
STA SW ;
CALL SWDLYB ;
DCR C ; DECREASE SMALL CHQ LOOP
JNZ ICPN3B ; NO FINISH YET, DO IT AGAIN
POP PSW ; GET # OF CHQ LOOP
DCR A ; ALL DONE?
JNZ ICPN3A ; NO DO IT SOME MORE
CALL ADC6DE ; GET DAC VALUE
LHLD VFINAL ; GET FINAL VOLTAGE
MVI A,20. ; ADD ABOUT 20 mV MORE
CALL HLP A ;
CALL DCMP ; DE-HL, FLAGS BASED ON
; RESULTS
JP ICPN11 ; VOLTAGE IS MORE NEGATIVE

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CALL      ICPN4      ; OR EQUAL TO VFINAL
; CALCULATE THE CAP CHARGE &
; STORE THEM
JMP       ICPN1      ; DO IT SOME MORE
; CALCULATE CAPACITIVE CHARGE, STORE THEM AND
; INCREMENT NUMBER OF CHARGE LOOP
ICPN4:    LHL        ADCTMP      ;
XCHG      ; HL=POTENTIAL AFTER CHQ ADD
; DE=BEGINING POTENTIAL
PUSH      PSW        ; SAVE REG
LDA       DAADBF     ; GET BIN/DEC FLAG
CPI       2          ;
JZ        ICPN5      ; NO PRINTING
CALL      ADCBDP     ; PRINT BEGINNING POT
XCHG      ;
CALL      ADCBDP     ; PRINT POT AFTER CHQ ADD
XCHG      ;
CALL      LPCRLF     ; CARRIAGE RETURN, LINE FEED
ICPN5:    POP        PSW        ; RESTORE REG
CALL      DSUB       ; HL=HL-DE
JM        ICPN10     ; NOT ENOUGH CHARGE
SHLD      MXTMP2     ; STORE 2nd VOLTAGE
ICPN6:    LHL        ICAPDA     ; GET THE DAC VALUE &
; # OF CHARGE ADD
CALL      CQCALN     ; CALCULATE THE NUMBER
; OF CHARGE, HL=NEG CHARGE
SHLD      MXTMP3     ; CHQ QUANTITY OF ONE ADD
LDA       ICAPC2     ; GET # OF CHARGE LOOP
DCR       A          ; DECREMENT ONE CHQ # FOR
; THE FIRST COLTAGE
MOV       C, A       ;
MVI       B, 0       ;
CALL      DDMULT     ; (HLBC)=(HL)*(BC)
SHLD      MX2TM4+2   ;
MOV       L, C       ;
MOV       H, B       ;
SHLD      MX2TM4     ;
LHL       MXTMP1     ; GET THE 1ST VOLTAGE
DCX       H          ; DECREMENT ONE IN ORDER
; TO MAKE PROPER VOLTAGE
; DIFFERENCE
XCHG      ; INTO DE
LHL       MXTMP2     ; GET THE 2ND VOLTAGE
CALL      DSUB       ; CALC THE DIFFERENCE
SHLD      MXTMP3     ; STORE THE DIFFERENCE
LHL       MXTMP1     ; GET 1st VOLTAGE DIFFERENCE
XCHG      ; INTO DE
MVI       A, 4       ; 4 BITS FOR EACH DATA POINT
CALL      DMULT      ; DE=DE*A
LXI       H, BICAP   ; GET BASE MEMORY ADDR FOR
; ICAP
DAD       D          ; (HL)<-(HL)+(DE)
SHLD      MXTMP4     ; STORE ADDR FOR INT CAP CHQ

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                MVI      C, 1          ; COUNTER
                MVI      B, 0          ;
ICPN61:  LHLD      MXTMP3      ; GET CHQ OF ONE ADD
                PUSH     B          ; STORE COUNTER COUNTER
                CALL     DDMULT      ; (HLBC)=(HL)*(BC)
                PUSH     H          ;
                LHLD      MXTMP5      ; GET VOLTAGE DIFFERENCE
                XCHG          ; INTO DE
                POP      H          ;
                CALL     DDIVHB      ; (HLBC)=(HLBC)/(DE)
                SHLD     MX2TM5+2    ;
                CALL     HLXBC      ; (HL)<=>(BC)
                SHLD     MX2TM5      ;
                POP      B          ;
                INR      C          ; INCREMENT COUNTER
                CALL     DDADD      ; (4) + (5) => (6)
                LHLD      MXTMP4      ; GET ADDR FOR INT CAP CHQ
                MOV      E, L        ; INTO DE
                MOV      D, H        ;
                MVI      A, 4        ; 4 BYTES EACH DATA POINT
                CALL     HLP4        ; CALC NEXT ADDR
                SHLD     MXTMP4      ; STORE NEW CAP CHQ ADDR
                LXI      H, MX2TM6    ;
                CALL     MTRF        ; TRANSFER RESULTS TO MEM
                LXI      D, MXTMP1    ;
                LXI      H, MXTMP2    ;
                CALL     DCMPLM      ; ((DE))-((HL))
                JP       ICPN7       ; 1st VLOTAGE EQUAL TO OR
                                   ; GREATER THAN 2nd VOLTAGE
ICPN62:  XCHG          ; GET ADDR OF VOLTAGE
                                   ; COUNTER
                CALL     INXM        ; INCREMENT ONE
                JMP      ICPN61      ; CALCULATE TILL ITS DONE
ICPN7:   XCHG          ; GET ADDR OF VOLTAGE
                                   ; COUNTER
                CALL     INXM        ; INCREMENT ONE
                LXI      H, ICAPC2    ;
                INR      M          ; INCREMENT CHARGE LOOP
                RET              ; AND GO HOME
; NOT ENOUGH CHARGE
ICPN10:  POP      PSW          ; REMOVE JUNK
                LXI      H, ICAPC2    ; GET ADDR OF # OF CHARGE
                                   ; LOOP
                INR      M          ; INCREASE IT
                JMP      ICPN11      ; PROCEED THE EXP
ICPN11:  LDA      DAADBF        ; GET BIN/DEC FLAG
                PUSH     PSW        ; SAVE IT
                MVI      A, 0        ;
                STA      DAADBF      ; MAKE IT PRINT ADC VALUES
                CALL     ICPN4        ; PRINT VOLTAGES
                POP      PSW        ; RESTORE ORIGINAL BIN/DEC
                STA      DAADBF      ; FLAG
                                   ; AND STORE THEM

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      LXI      H,PICAP2      ; PRINT # OF LOOP
      CALL    SPRMPR        ;
      POP     PSW           ; RESTORE REGISTERS
      POP     B             ;
      POP     D             ;
      POP     H             ;
      RET                ; AND GO HOME
;
;
;
      SUBR      CPSEQB
CPSEQB:  PUSH    H           ; SAVE REGS
      PUSH    PSW          ;
      LXI      H, CPSEBM    ; INITIALIZE?
      CALL    PRINT        ;
CPSEB1:  CALL    CHARIN     ;
      JNC     CPSEB1       ;
      CPI     'y           ; YES
      JNZ     CPSEB2       ; NO
      CALL    CPSDLB       ; SET CP INITIAL LIB
CPSEB2:  LXI      H, CPSEM2  ;
      CALL    PRINT        ; EXIT?
      CALL    DELAY2       ; DELAY FOR 2 SEC
      LDA     EFLAG8       ; GET EVENT FLAG
      RRC      ; CARRY KEY BOARD IS TYPED
      JNC     CPSEB4       ; NO
      LDA     BUFO         ; GET THE CHARACTER
      CPI     'y           ; EXIT?
      JZ      CPSEB7       ; YES
CPSEB4:  CALL    CPB        ; CP & VOLTAGE BACK
      LXI      H, CPSEM1   ;
      CALL    PRINT        ; CLEAR GRAPHICS?
      CALL    DELAY2       ; DELAY FOR 2 SEC.
      LDA     EFLAG8       ; GET EVENT FLAG
      RRC      ;
      JNC     CPSB4A       ; KEYBOARD IS NOT TYPED
      LDA     BUFO         ; GET THE CHARACTER
      CPI     'b           ;
      CZ      BLANK        ; CLEAR VRAM
      CPI     'y           ;
      CZ      CLEAR        ; CLEAR GRAPHICS
      CZ      BLANK        ; CLEAR VRAM
      MVI     A, EFUO      ;
      CALL    EFCLR        ; CLEAR KB
      CALL    DELYP1       ; DELAY FOR .1 SEC
CPSB4A:  CALL    ADGR       ; DRAW THE VOLTAGE GRAPH
      CALL    CPADUL       ; SEND ADC VALUES
      CALL    CRLF        ; CARRIAGE RETURN, LINE FEED
      LXI      H, PCPCO2   ; CORRECTION RATIO
      SHLD    APARAM       ; ADDR FOR THE PARM
      CALL    PARMPR       ; PRINT THE PARAMETER
      CALL    TTYINB       ; INPUT A LINE, BREAK DOWN
      CALL    PARMCH       ; CHANGE THE PARAMETER

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CALL      VBACK      ; KEEP VINIT FOR A WHILE
LXI       H, PAVW     ; AVERAGE WIDTH
SHLD      APARAM      ; ADDR OF THE PARM
CALL      PARMPR      ; PRINT THE PARAMETER
CALL      TTYINB      ; INPUT A LINE, BREAK DOWN
CALL      PARMCH      ; CHANGE THE PARAMETER
CALL      VBACK      ; KEEP VINIT FOR A WHILE
LXI       H, CPSBM1   ; PRINT ICAPN?
CALL      PRINT       ;
CPSEB5:   CALL      CHARIN ;
JNC       CPSEB5      ;
CPI       'y          ; YES
CZ        ICAPN       ; GET NEW CAPACITIVE CHG
CALL      CPFCUL      ; SEND FC VALUES
CALL      CPTCNX      ; EXTRAPLOATE TC
CALL      CPTCSM      ; SMOOTH CHARGE JUMP
CALL      VBACK      ; KEEP VINIT FOR A WHILE
CALL      CPTCCF      ; CLEAR FLAGS
CALL      CPTCAV      ; AVERAGE TC
CALL      CPDTC       ; CHOP OFF TCLIB AND
                        ; FILL DAC LIB
                        ; LOOP AROUND
CPSEB7:   JMP       CPSEB2 ; RESTORE REGS
POP       PSW
POP       H
RET
CPSEBM:   .ASCIZ    /CPSDLB?/
CPSBM1:   .ASCIZ    /ICAPN?/
;
; THIS ROUTINE TAKES THE ADC VALUES FOR CHRONOPOT AND STORE
; IT IN MEMORY REFERED BY DE
SUBR      CPADCN
CPADCN:   STA      ADCST      ; STARTS ADC
LDA       VFINAL+1      ; GET FINAL VOLT HIGH BYTE
MOV       C, A          ; STORE IT
NOP       ; WAIT FOR ADC TO CONVERT
NOP
NOP
NOP
NOP
LDA       ADCHB          ; GET ADC HIGH BYTE
ANI       17             ; MASK OUT ALL BUT ADC BITS
STAX      D              ; STORE ADC HIGH BYTE
INX       D              ; INC MEM ADDR
CMP       C              ; COMPARE WITH VFINAL
                        ; HIGH BYTE
JZ        CPADN2         ; HIGH BYTE EQUAL,
                        ; COMPARE LOW BYTE
JP        CPADN3         ; ALL DONE
LDA       ADCLB          ; GET ADC LOW BYTE
STAX      D              ; STORE ADC LOW BYTE
INX       D              ; INC MEM ADDR
RET
CPADN2:   LDA       VFINAL      ; GET FINAL VOLTAGE LOW BYTE

```

```

      MOV      C, A          ; STORE IT
      LDA      ADCLB        ; GET ADC LOW BYTE
      STAX     D            ; STORE ADC LOW BYTE
      INX      D            ; INC MEM ADDR
      CMP      C            ; VOLTAGE MORE NEG
                          ; THAN FINAL?
      RC          ; RETURN IF LESS NEG
      JMP      CP40         ; EXP IS DONE, LEAVE
CPADN3: LDA      ADCLB        ; GET ADC LOW BYTE
      STAX     D            ; STORE IT
      INX      D            ; INC MEM ADDR
      JMP      CP40         ; EXP IS DONE, LEAVE
;
; ADD CHARGE TO ELECTRODE, DAC VALUE & # OF CHG ADD FORM MEM
; HL = HL+2
      SUBR      CHGADM
CHGADM: MOV      A, M          ;
      STA      DACLB        ; SET DAC LOW BYTE
      INX      H            ;
      MOV      A, M          ; SET DAC HIGH BYTE
      STA      DACHB        ;
      INX      H            ; INC MEM ADDR
      ANI      374          ; MASK DAC HIGH BYTE TO GET
                          ; # OF CHARGE ADDITIONS
      RRC          ; ROTATE TO THE RIGHT
      RRC          ; POSITION
      MOV      C, A          ; SAVE NUMBER OF CHARGE
                          ; ADDITIONS
CGADM1: MVI      A, 1          ;
      STA      SW            ;
      LDA      SWDLY1        ; GET DELAY VALUE
CGADM2: DCR      A            ;
      JNZ      CGADM2        ; LOOP AROUND TILL IT IS
                          ; DONE
      MOV      A, B          ; SW # FOR CHARGING AMPLIFIER
      STA      SW            ; DUMP CHARGE TO
                          ; WORKING ELECTRODE
      CALL     SWDLYB        ; DELAY
      DCR      C            ; CHECK IF NUMBER OF CHARGE
                          ; ADDITIONS ARE DONE
      JNZ      CGADM1        ; NO DO IT AGAIN
      RET              ; AND GO HOME
;
;
; THIS ROUTINE COLLECTS DATA FOR CHROPOTENTIOMETRY EXP
      SUBR      CP
CP:    PUSH     H            ; SAVE REGS
      PUSH     D            ;
      PUSH     B            ;
      PUSH     PSW          ;
      LXI      H, 0          ; CLEAR REG
      DAD      SP            ; AND GET STACK POINTER
      SHLD     SSAV          ; AND SAVE IT

```

CP0:	LXI	H, VINIT	; GET ADDR FOR INIT VOLTAGE
	CALL	VAPR	; APPROACH THE VOLTAGE
	LDA	VAPFLG	; GET THE VOLT FLAG
	CPI	0	; EQUAL?
	JNZ	CP0	; NO, WAIT
	CALL	READY	; TELL US IT'S READY
CP1:	LXI	H, VINIT	; GET ADDR FOR INIT VOLTAGE
	CALL	VAPR	; APPROACH THE VOLTAGE
	CALL	CHARIN	; KEY BOARD TYPED?
	JNC	CP1	; NO, KEEP AT DESIRED
			; POTENTIAL
	CPI	'0	; 00?
	JZ	CP2	; YES
	CPI	'9	; 00?
	JZ	CP2	; YES
	CPI	'b	; BLANK?
	CZ	BLANK	; CLEAR VRAM
	JMP	CP1	; NO, WAIT
CP2:	CALL	OFF11	; IGNORE INTERRUPT FROM 11
	DI		; DISABLE INT
CP3:	CALL	TICP	; SET UP TIMER FOR CHRONOPOT
	LDA	TICMD	; GET TIMER OUTPUT STATUS
	ANI	10	; OUT 3
	JNZ	CP3	; NOT CORRECT, DO IT AGAIN
	CALL	CLRIN3	; CLEAR IN3
	CALL	CLRIN4	; CLEAR IN4
	MVI	A, 363	; GET A DI COMMAND
	STA	INTTLB+14	; DI AT LEVEL 3
	STA	INTTLB+20	; & 4
	MVI	A, 303	; GET A JUMP COMMAND
	STA	INTTLB+15	;
	STA	INTTLB+21	;
	LXI	H, CP40	; JMP TO SETTING UP
			; PARM ADDR FOR
	SHLD	INTTLB+16	; CHARGE ADD & VOLTAGE
			; MEASUREMENT
	LXI	H, CP30	;
	SHLD	INTTLB+22	; LAST DATUM HAS BEEN TAKEN,
			; FINISH UP EXP
	LXI	H, INTCMD	;
	MVI	M, 143	; RESET IS FF 3 & 4
	MVI	M, 144	;
	INX	H	;
	MOV	A, M	; INT MASK
	ANI	347	; ENABLE LEVEL 3 & 4
	MOV	M, A	;
	EI		; ENABLE INTERRUPT
CP4:	LXI	H, VINIT	;
	CALL	VAPR	; KEEP AT INIT VOLTAGE
	JMP	CP4	;
CP30:	POP	H	; REMOVE CALL
	LXI	H, CP32	;
	SHLD	INTTLB+22	; JMP TO CP32 ON NEXT INT

```

LXI      H, DACLIB      ;
LXI      D, ADCLIB      ;
LDA      SWA             ; GET SWITCH #
MOV      B, A            ; STORE IT IN B
MVI      A, EOI          ;
STA      INTCMD          ;
EI                     ;
CP31:    NOP             ;
NOP             ;
; 48 MORE NOP'S ARE OMITTED
;
JMP      CP31            ;
CP32:    DI              ;
CALL     CPADCN           ; GET POTENTIAL
CALL     CHOADM           ; ADD CHARGE
LDA      SWC              ; IF = 7,
STA      SW               ; TURN OFF SWITCH TO AVOID
; LEAKAGE
MVI      A, EOI          ; GET AN END OF INTERRUPT
; FLAG
STA      INTCMD          ; AND TELL THE INTERRUPT
; CONTROLLER
;
EI                     ;
RET      ; RETURN TO DUMMY ROUTINE
DI                     ;
CP40:    MVI      A, EOI   ; GET AN END OF INT FLAG
STA      INTCMD          ; AND TELL INT CONTROLLER
DCX      H               ; -1 DATA POINT
DCX      H               ;
CP41:    LXI      D, DACLIB ;
CALL     DSUB            ; HL-DE
CALL     RHLR            ; ROTATE HL RIGHT, D15=0
SHLD     DATAN           ; NUMBER OF DATA
CALL     TIRSET          ; RESET TIMER
MVI      A, EOI          ; GET AN END OF INT FLAG
STA      INTCMD          ; AND TELL INT CONTROLLER
CALL     CLRIN3          ; CLEAR IN3
CALL     CLRIN4          ; CLEAR IN4
MVI      A, 377          ; SET A RESTART 7
STA      INTTLB+14       ; FOR LEVEL 3
STA      INTTLB+20       ; & 4
LXI      H, INTCMD       ;
MVI      M, 143          ; RESET IS FF 3
MVI      M, 144          ; & 4
INX      H               ; INT MASK
MOV      A, M            ;
ORI      30              ; DISABLE LEVEL 3 & 4
MOV      M, A            ;
LHLD     SSAV            ; GET ORIGINAL STACK POINTER
SPHL     ; MOV HL TO SP
CALL     ON11            ;
CALL     CPADFX          ; FIX ADC LIB
LXI      H, PDATAN       ; GET ADDR OF PARM DATAN
CALL     SPRMPR          ; STORE IT,

```



```

; AND PRINT THE PARM
; RESTORE REGS
;
;
;
; ENABLE INT
; AND GO HOME
;
;
; ROUTINE TO BRING VOLTAGE BACK
SUBR      VBACK
VBACK:    PUSH      H          ; SAVE REGS
          PUSH      D          ;
          PUSH      PSW        ;
          MVI       D, 5       ; COUNTER
          MVI       E, 377     ;
VBACK1:   LXI       H, VINIT   ; APPROACH THE INITIAL
          ; VOLTAGE
          CALL      VAPR       ;
          LDA       VAPFLG     ; GET VOLTAGE FLAG
          CPI       0          ; EQUAL?
          JNZ       VBACK1     ; NOT YET
          DCR       E          ;
          JNZ       VBACK1     ;
          LXI       H, TIDD     ; TIMER DELAY
          CALL      DELAY      ; WAIT FOR A WHILE
          DCR       D          ; DECREMENT COUNTER
          JNZ       VBACK1     ;
          POP       PSW        ; RESTORE REGS
          POP       D          ;
          POP       H          ;
          RET                ;
;
;
;
SUBR      CPB
CPB:      CALL      CP        ; CHRONOPOTIOMETRY EXP
          CALL      VBACK     ; BRING VOLTAGE BACK
          RET                ; AND GO HOME
;
C*****
C
C      CAP. FTN
C      THIS ROUTINE DIVIDE ONE SET OF AVERAGED DATA
C      BY ANOTHER
C
C      C. C. LII 7/31/81
C      REVISED 10/24/81
C
C*****
C      DECLARE VARIABLES
C      BYTE      INFIL(32), INFIL(32), OTFILE(32), OTFIL1(32)
C      BYTE      IDAT(6144), DATE(10), CONC(40), TEMP(10)
C      REAL*8     D1, D2, DPN, DPM, DPO, DPP, DPQ, MF

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```

      INTEGER IDATA(3072), IDATA1(3072), IERR, ITABLE(96)
      INTEGER IERR1, ITABL1(96), ND, I1, I2, ND2
      INTEGER VINIT, VFINAL, VSTP0, VSTP1, MO, BLDA1
      INTEGER TIPD, TIDD, NO, N1, SWDLY1, SWDLY2, VAPDA, VAPDA1
      INTEGER VAPN, VAPN1, N2, SWDLY3, SWDLY4
      EQUIVALENCE(INFILE(1), TEST)
      DATA      EX/'EX'/
      LUN1=1
      LUN2=2
      LUN3=3
      LUN4=4
      LUN5=5
      LUN6=6
C      ASK FOR INPUT FILE NAME
5      WRITE(LUN5,900)
900    FORMAT('$FILE/FILE1, INPUT FILE: ')
C      READ THE INPUT FILE NAME
      READ(LUN5,905)INFILE
905    FORMAT(32A1)
C      CHECK IF USER HAS TYPED EXIT TO LEAVE ROUTINE
      IF(TEST.EQ.EX)GOTO 50
C      CALL UNFORM TO OPEN FILE TO READ ENABLE
      CALL      UNFORM(0, IERR, ITABLE, INFILE, 0, 1, LUN3)
C      CHECK FOR ERRORS
      IF(IERR.NE.0)GOTO 10
C      READ IN THE DATA USING UNFORM
      NUM=6144
      CALL      UNFORM(1, IERR, ITABLE, IDATA, NUM)
C      CHECK FOR ERRORS
      IF(IERR.NE.0)GOTO 20
C      ASK FOR 2nd INPUT FILE NAME
7      WRITE(LUN5,906)
906    FORMAT('$INPUT FILE1: ')
C      READ THE INPUT FILE NAME
      READ(LUN5,907)INFIL
907    FORMAT(32A1)
C      CALL UNFORM TO OPEN FILE TO READ ENABLE
      CALL      UNFORM(0, IERR1, ITABL1, INFIL, 0, 1, LUN2)
C      CHECK FOR ERRORS
      IF(IERR1.NE.0)GOTO 11
C      READ IN THE DATA USING UNFORM
      NUM=6144
      CALL      UNFORM(1, IERR, ITABL1, IDATA1, NUM)
C      CHECK FOR ERRORS
      IF(IERR.NE.0)GOTO 20
C      CLOSE INPUT FILE
      CALL UNFORM(2, IERR, ITABLE)
C      OPEN INPUT FILE AGAIN
      CALL UNFORM(0, IERR, ITABLE, INFILE, 0, 1, LUN3)
C      READ IN DATA USING UNFORM
      NUM=6144
      CALL UNFORM(1, IERR, ITABLE, IDAT, NUM)
      IF(IERR.NE.0) GO TO 20

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```

C      ASK FOR MULTIPLYING FACTOR
      WRITE(LUN5,908)
908    FORMAT(' $MULTIPLYING FACTOR(CAP/CM**2): ')
C      READ THE FACTOR
      READ(LUN5,909)MF
909    FORMAT(F15.7)
C      ASK FOR OUTPUT FILE
6      WRITE(LUN5,910)
910    FORMAT(' $OUTPUT FILE: ')
C      READ THE OUTPUT FILE NAME
      READ(LUN5,905)OTFILE
C      OPEN OUTPUT FILE USING ASSIGN
      CALL ASSIGN(4,OTFILE,32)
C      SEND HEADER TO OUTPUT FILE
      WRITE(LUN4,915)INFILE
915    FORMAT('HD ',32A1)
      WRITE(LUN4,915)INFIL
      ND=IDATA(1)
      NDO=ND-30
C      GET PARAMETERS
      J=3
      DO 110 I=1,10
      DATE(I)=IDAT(J)
      J=J+1
110    CONTINUE
      DO 115 I=1,40
      CONC(I)=IDAT(J)
      J=J+1
115    CONTINUE
      DO 120 I=1,10
      TEMP(I)=IDAT(J)
      J=J+1
120    CONTINUE
      VINIT = IDATA(32)
      VFINAL = IDATA(33)
      VSTPO = IDATA(34)
      VSTP1 = IDATA(35)
      MO = IDATA(36)
      BLDA1 = IDATA(37)
      TIPD = IDATA(38)
      TIDD = IDATA(39)
      NO = IDATA(40)
      N1 = IDATA(41)
      N2 = IDATA(42)
      SWDLY1 = IDATA(43)
      SWDLY2 = IDATA(44)
      SWDLY3 = IDATA(45)
      SWDLY4 = IDATA(46)
      VAPDA = IDATA(47)
      VAPN = IDATA(48)
      VAPDA1 = IDATA(49)
      VAPN1 = IDATA(50)
C      SEND NUMBER OF DATA POINTS TO OUTPUT FILE

```

```

WRITE(LUN4,920)NDO
920  FORMAT('NU ',I15)
      IF(VFINAL.GT. VINIT)GO TO 205
C    D5: AVERAGE VOLTAGE FOR CAPACITANCE MEASUREMENT
C    SCAN POSITIVELY
      D5=VINIT*1.0-VSTP0*.5
      D6=-VSTP1*1.0
      GO TO 207
205  D5=VINIT*1.0+VSTP0*.5
      D6=VSTP1*1.0
207  VOLT=2.4988-D5*.0012207031
C    READ IN THE DATA POINTS CONVERT THEM INTO VOLTAGE
C    AND SEND THEM TO THE OUTPUT FILE
      ND2=ND*3+1
      DO 100 I=92,ND2,3
      I2=IDATA(I)
      IF(I2.GE.0)GO TO 55
      D2=65536.+1.*I2
      GO TO 56
55   D2=I2
56   I1=IDATA(I+1)
      IF(I1.GE.0)GO TO 60
      D1=(65536.+1.*I1)*65536.
      GO TO 61
60   D1=I1*65536.
61   DPN=D1+D2
      DPM=IDATA(I+2)*1.0
      DPO=DPN/DPM
      I2=IDATA1(I)
      IF(I2.GE.0)GOTO 65
      D2=65536.+1.*I2
      GOTO 66
65   D2=I2
66   I1=IDATA1(I+1)
      IF(I1.GE.0)GOTO 70
      D1=(65536.+1.*I1)*65536.
      GOTO 71
70   D1=I1*65536.
71   DPN=D1+D2
      DPM=IDATA1(I+2)*1.0
      DPP=DPN/DPM
      DPG=DPO*MF/DPP
      WRITE(LUN4,925)VOLT,DPG
925  FORMAT('RD',2E15.7)
C    CALCULATES NEXT VOLTAGE
      D5=D5+D6
      VOLT=2.4988-D5*.0012207031
100  CONTINUE
      WRITE(LUN5,800)
800  FORMAT(1X,'PARAMETERS TO 1. TI 2. LP 3. NO OUTPUT ')
      READ(LUN5,805)I5
805  FORMAT(I5)
      IF(I5.EQ. 3)GO TO 190

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      IF(I5 .EQ. 2)GO TO 125
      LU=LUN5
      GO TO 130
125    LU=LUN6
130    WRITE(LUN5,810)
810    FORMAT(1X,'OUTPUT FILE1: ')
      READ(LUN5,905)OTFIL1
      CALL    ASSIGN(LUN1,OTFIL1,32)
      WRITE(LUN1,915)INFILE
      WRITE(LUN1,920)NDO
      WRITE(LU,811)INFILE
811    FORMAT(1X,'FILE',12X,32A1)
      WRITE(LU,812)(DATE(I),I=1,10)
812    FORMAT(1X,'DATE',12X,10A1)
      WRITE(LUN1,812)(DATE(I),I=1,10)
      WRITE(LU,815)(CONC(I),I=1,40)
815    FORMAT(1X,'CONC',12X,40A1)
      WRITE(LUN1,815)(CONC(I),I=1,40)
      WRITE(LU,816)(TEMP(I),I=1,10)
816    FORMAT(1X,'TEMP',12X,10A1)
      WRITE(LUN1,816)(TEMP(I),I=1,10)
      VIN=2.4988-VINIT*.0012207031
      WRITE(LU,820)VIN
820    FORMAT(1X,'VINIT',11X,F15.7,7X,'V')
      WRITE(LUN1,820)VIN
      VFI=2.4988-VFINAL*.0012207031
      WRITE(LU,821)VFI
821    FORMAT(1X,'VFINAL',10X,F15.7,7X,'V')
      WRITE(LUN1,821)VFI
      WRITE(LU,822)VSTPO
822    FORMAT(1X,'VSTPO',11X,I15)
      WRITE(LUN1,822)VSTPO
      WRITE(LU,823)VSTP1
823    FORMAT(1X,'VSTP1',11X,I15)
      WRITE(LUN1,823)VSTP1
      WRITE(LU,824)MO
824    FORMAT(1X,'MO',14X,I15)
      WRITE(LUN1,824)MO
      DA3=-(BLDA1-512)*4.8828125
      WRITE(LU,830)DA3
830    FORMAT(1X,'BLDA1',11X,F15.7,6X,'mV')
      WRITE(LUN1,830)DA3
      TI=1.*TIPD*TIDD
      WRITE(LU,835)TI
835    FORMAT(1X,'TIME DELAY',6X,F15.0,5X,'us. ')
      WRITE(LUN1,835)TI
      WRITE(LU,836)TIPD
836    FORMAT(1X,'TIPD',12X,I15)
      WRITE(LUN1,836)TIPD
      WRITE(LU,837)TIDD
837    FORMAT(1X,'TIDD',12X,I15)
      WRITE(LUN1,837)TIDD
      WRITE(LU,845)NO

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845      FORMAT(1X, 'NO', 14X, I15)
        WRITE(LUN1, 845)NO
        WRITE(LU, 846)N1
846      FORMAT(1X, 'N1', 14X, I15)
        WRITE(LUN1, 846)N1
        WRITE(LU, 853)N2
853      FORMAT(1X, 'N2', 14X, I15)
        WRITE(LUN1, 853)N2
        WRITE(LU, 847)SWDLY1
847      FORMAT(1X, 'SWDLY1', 10X, I15)
        WRITE(LUN1, 847)SWDLY1
        WRITE(LU, 848)SWDLY2
848      FORMAT(1X, 'SWDLY2', 10X, I15)
        WRITE(LUN1, 848)SWDLY2
        WRITE(LU, 854)SWDLY3
854      FORMAT(1X, 'SWDLY3', 10X, I15)
        WRITE(LUN1, 854)SWDLY3
        WRITE(LU, 855)SWDLY4
855      FORMAT(1X, 'SWDLY4', 10X, I15)
        WRITE(LUN1, 855)SWDLY4
        DA3=-(VAPDA-512)*4. 8828125
        WRITE(LU, 850)VAPN, DA3
850      FORMAT(1X, 'VAPDA', 6X, I3, ' *', F15.7, 6X, 'mV')
        WRITE(LUN1, 850)VAPN, DA3
        DA3=-(VAPDA1-512)*4. 8828125
        WRITE(LU, 851)VAPN1, DA3
851      FORMAT(1X, 'VAPDA1', 5X, I3, ' *', F15.7, 6X, 'mV')
        WRITE(LUN1, 851)VAPN1, DA3
        WRITE(LU, 849)MF
849      FORMAT(1X, 'MF(CAP/CM**2)', 3X, F15.7)
        WRITE(LUN1, 849)MF
        CALL CLOSE(LUN1)
        GO TO 190
C      NOW CLOSE THE STILL OPEN INPUT FILE USING UNIFORM
190      CALL UNIFORM(2, IERR, ITABLE)
C      CHECK FOR ERRORS
        IF(IERR.NE.0)GOTO 30
        CALL UNIFORM(2, IERR1, ITABL1)
C      CHECK FOR ERRORS
        IF(IERR1.NE.0)GOTO 30
C      SEND END OF DATA MAKER TO OUTPUT FILE
        WRITE(LUN4, 930)
930      FORMAT('ED ')
        WRITE(LUN5, 935)
935      FORMAT(' DATA CONVERSION COMPLETE ')
        GOTO 40
10      WRITE(LUN5, 940)
940      FORMAT(' INPUT FILE NOT FOUND ')
        GOTO 5
11      WRITE(LUN5, 940)
        GOTO 7
20      WRITE(LUN5, 945)
945      FORMAT('DATA CAN NOT BE READ OUT OF INPUT FILE ')

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      GOTO 50
30      WRITE(LUN5,950)
950     FORMAT(' INPUT FILE CAN NOT BE CLOSED ')
C      ADN CLOSE THE OUTPUT FILE
40      CALL      CLOSE(4)
C      RETURN TO BEGINNING TO CONVERT ANOTHER FILE
      GOTO 5
50      CALL      EXIT
      END
C*****
C
C      CONCPAD.FTN
C      THIS ROUTINE CONVERTS BINARY FILE OF
C      ADC VALUES TO C. G. ENKE & CO. STANDARD DATA FILE
C      AND A PARAMETER FILE
C
C      C. C. LII 4/22/81
C      REVISED 10/27/81
C
C*****
C      DECLARE VARIABLES
      BYTE      INFILE(32), OTFILE(32), OTFIL1(32)
      BYTE      IDAT(1204), DATE(10), CONC(40), TEMP(10)
      BYTE      NCAP(20)
      INTEGER   IDATA(602), IERR, ITABLE(96), ND
      INTEGER   VINIT, VFINAL, AVEW, BLDA1, CADDMN, COMAX
      INTEGER   CHON, CHQG, CPCOR1, CPCOR2, ICAPC1, ICAPC2
      INTEGER   ICAPDA, ICDN, ICAPSW, SWA
      INTEGER   SWDLY1, SWDLY2, TCENW, TIDDA, TIPD
      INTEGER   VAPDA, VAPDN, VAPDA1, VAPD1N
      EQUIVALENCE(INFILE(1), TEST)
      DATA      EX/'EX'/
      LUN1       = 1
      LUN3       = 3
      LUN4       = 4
      LUN5       = 5
      LUN6       = 6
C      ASK FOR INPUT FILE NAME
5      WRITE(LUN5,900)
900     FORMAT('$INPUT FILE: ')
C      READ THE INPUT FILE NAME
      READ(LUN5,905)INFILE
905     FORMAT(32A1)
C      CHECK IF USER HAS TYPED EXIT TO LEAVE ROUTINE
      IF(TEST.EQ.EX)GOTO 50
C      CALL UNFORM TO OPEN FILE TO READ ENABLE
      CALL      UNFORM(0, IERR, ITABLE, INFILE, 0, 1, LUN3)
C      CHECK FOR ERRORS
      IF(IERR.NE.0)GOTO 10
C      ASK FOR OUTPUT FILE
6      WRITE(LUN5,910)
910     FORMAT('$OUTPUT FILE: ')
C      READ THE OUTPUT FILE NAME

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```

      READ(LUN5,905)OTFILE
C      READ IN THE DATA USING UNIFORM
      NUM=1204
      CALL      UNIFORM(1,IERR,ITABLE,IDATA,NUM)
C      CHECK FOR ERRORS
      IF(IERR.NE.0)GOTO 20
C      CLOSE INPUT FILE
      CALL      UNIFORM(2,IERR,ITABLE)
C      OPEN FILE AGAIN
      CALL      UNIFORM(0,IERR,ITABLE,INFILE,0,1,LUN3)
C      READ IN DATA USING UNIFORM
      NUM=1204
      CALL      UNIFORM(1,IERR,ITABLE,IDAT,NUM)
      IF(IERR.NE.0)GO TO 20
C      GET PARAMETERS
      J=3
      DO 110 I=1,10
      DATE(I)=IDAT(J)
      J=J+1
110    CONTINUE
      DO 120 I=1,40
      CONC(I)=IDAT(J)
      J=J+1
120    CONTINUE
      DO 125 I=1,10
      TEMP(I)=IDAT(J)
      J=J+1
125    CONTINUE
      DO 130 I=1,20
      NCAP(I)=IDAT(J)
      J=J+1
130    CONTINUE
      VINIT   = IDATA(42)
      VFINAL  = IDATA(43)
      AVEW    = IDATA(44)
      BLDA1   = IDATA(45)
      CADDMN  = IDATA(46)
      COMAX   = IDATA(47)
      CHGN    = IDATA(48)
      CHGG    = IDATA(49)
      CPCOR1  = IDATA(50)
      CPCOR2  = IDATA(51)
      ICAPC1  = IDATA(52)
      ICAPC2  = IDATA(53)
      ICAPDA  = IDATA(54)
      ICDN    = IDATA(55)
      ICAPSW  = IDATA(56)
      SWA     = IDATA(57)
      SWDLY1  = IDATA(58)
      SWDLY2  = IDATA(59)
      TCENW   = IDATA(60)
      TIDDA   = IDATA(61)
      TIPD    = IDATA(62)

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VAPDA  = IDATA(63)
VAPDN  = IDATA(64)
VAPDA1 = IDATA(65)
VAPD1N = IDATA(66)
BLDA3  = IDATA(67)
IF(TIDDA .GE. 0)GO TO 126
TIDD=65536. +1. *TIDDA
GO TO 127
126    TIDD=TIDDA
C      OPEN OUTPUT FILE USING ASSIGN
127    CALL    ASSIGN(LUN4,OTFILE,32)
C      SEND HEADER TO OUTPUT FILE
      WRITE(LUN4,915)INFILE
915    FORMAT('HD ',32A1)
      ND=IDATA(1)
      NDO=ND-90
C      SEND NUMBER OF DATA POINTS TO OUTPUT FILE
      WRITE(LUN4,920)NDO
920    FORMAT('NU ',I15)
C      READ IN THE DATA POINTS CONVERT THEM INTO VOLTAGE
C      AND SEND THEM TO THE OUTPUT FILE
      ND=ND+1
      TI1=0.0
      DO 100 I=92,ND
      A=IDATA(I)
      B=2.4988-A*.0012207031
      WRITE(LUN4,925)TI1,B
925    FORMAT('RD',2E15.7)
      TI1=TI1+TIDD*2.0*10.**(-6)
100    CONTINUE
      WRITE(LUN5,800)
800    FORMAT(1X,'PARAMETERS TO 1.TI 2.LP 3.NO OUTPUT ')
      READ(LUN5,805)I5
805    FORMAT(I5)
      IF(I5 .EQ. 3)GO TO 190
      WRITE(LUN5,806)
806    FORMAT(1X,'CAPACITANCE FOR CHG ADD/ELECTRODE',)
      WRITE(LUN5,807)
807    FORMAT(1X,'AREA(uF/CM**2): ')
      READ(LUN5,808)C1
808    FORMAT(F15.7)
      IF(I5 .EQ. 2)GO TO 135
      LU=LUN5
      GO TO 140
135    LU=LUN6
140    WRITE(LUN5,810)
810    FORMAT(1X,'OUTPUT FILE1: ')
      READ(LUN5,905)OTFIL1
      CALL    ASSIGN(LUN1,OTFIL1,32)
      WRITE(LUN1,915)INFILE
      WRITE(LUN1,920)NDO
      WRITE(LU,811)INFILE
811    FORMAT(1X,'FILE',12X,32A1)

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      WRITE(LU, 812) (DATE(I), I=1, 10)
812    FORMAT(1X, 'DATE', 12X, 10A1)
      WRITE(LUN1, 812) (DATE(I), I=1, 10)
      WRITE(LU, 815) (CONC(I), I=1, 40)
815    FORMAT(1X, 'CONC', 12X, 40A1)
      WRITE(LUN1, 815) (CONC(I), I=1, 40)
      WRITE(LU, 816) (TEMP(I), I=1, 10)
816    FORMAT(1X, 'TEMP', 12X, 10A1)
      WRITE(LUN1, 816) (TEMP(I), I=1, 10)
      WRITE(LU, 817) (NCAP(I), I=1, 20)
817    FORMAT(1X, 'NCAP', 12X, 20A1)
      WRITE(LUN1, 817) (NCAP(I), I=1, 20)
      WRITE(LU, 818) C1
818    FORMAT(1X, 'CAP/AREA', 8X, F15.7, 8X, 'uF/CM**2')
      WRITE(LUN1, 818) C1
      TIENT=2. *TIDD*10. **(-6)
      CURNT=C1*(CHGN*CHQG*1.0)*.0048828125/TIENT
      WRITE(LU, 819) CURNT
819    FORMAT(1X, 'CURRENT', 9X, F15.7, 8X, 'uA/CM**2')
      WRITE(LUN1, 819) CURNT
      VIN=2.4988-VINIT*.0012207031
      WRITE(LU, 820) VIN
820    FORMAT(1X, 'VINIT', 11X, F15.7, 15X, 'V')
      WRITE(LUN1, 820) VIN
      VFI=2.4988-VFINAL*.0012207031
      WRITE(LU, 821) VFI
821    FORMAT(1X, 'VFINAL', 10X, F15.7, 15X, 'V')
      WRITE(LUN1, 821) VFI
      WRITE(LU, 822) AVEW
822    FORMAT(1X, 'AVEW', 12X, I15)
      WRITE(LUN1, 822) AVEW
      DA3=-(BLDA1-512)*4.8828125
      WRITE(LU, 823) DA3
823    FORMAT(1X, 'BLDA1', 11X, F15.7, 14X, 'mV')
      WRITE(LUN1, 823) DA3
      DA3=-(BLDA3-512)*4.8828125
      WRITE(LU, 828) DA3
828    FORMAT(1X, 'BLDA3', 11X, F15.7, 14X, 'mV')
      WRITE(LUN1, 828) DA3
      WRITE(LU, 824) CADDMN
824    FORMAT(1X, 'CADDMN', 10X, I15)
      WRITE(LUN1, 824) CADDMN
      DA3=-(CGMAX-512)*4.8828125
      WRITE(LU, 825) DA3
825    FORMAT(1X, 'CGMAX', 11X, F15.7, 14X, 'mV')
      WRITE(LUN1, 825) DA3
      WRITE(LU, 826) CHGN
826    FORMAT(1X, 'CHGN', 12X, I15)
      WRITE(LUN1, 826) CHGN
      WRITE(LU, 827) CHQG
827    FORMAT(1X, 'CHQG', 12X, I15)
      WRITE(LUN1, 827) CHQG
      WRITE(LU, 830) CPCOR1

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```

830      FORMAT(1X, 'CPCOR1', 10X, I15)
        WRITE(LUN1, 830)CPCOR1
        WRITE(LU, 831)CPCOR2
831      FORMAT(1X, 'CPCOR2', 10X, I15)
        WRITE(LUN1, 831)CPCOR2
        WRITE(LU, 832)ICAPC1
832      FORMAT(1X, 'ICAPC1', 10X, I15)
        WRITE(LUN1, 832)ICAPC1
        WRITE(LU, 833)ICAPC2
833      FORMAT(1X, 'ICAPC2', 10X, I15)
        WRITE(LUN1, 833)ICAPC2
        DA3=-(ICAPDA-512)*4. 8828125
        WRITE(LU, 840)ICDN, DA3
840      FORMAT(1X, 'ICAPDA', 5X, I3, ' ', F15. 7, 14X, 'mV')
        WRITE(LUN1, 840)ICDN, DA3
        WRITE(LU, 841)ICAPSW
841      FORMAT(1X, 'ICAPSW', 10X, I15)
        WRITE(LUN1, 841)ICAPSW
        WRITE(LU, 842)SWA
842      FORMAT(1X, 'SWA', 13X, I15)
        WRITE(LUN1, 842)SWA
        WRITE(LU, 847)SWDLY1
847      FORMAT(1X, 'SWDLY1', 10X, I15)
        WRITE(LUN1, 847)SWDLY1
        WRITE(LU, 848)SWDLY2
848      FORMAT(1X, 'SWDLY2', 10X, I15)
        WRITE(LUN1, 848)SWDLY2
        WRITE(LU, 849)TCENW
849      FORMAT(1X, 'TCENW', 11X, I15)
        WRITE(LUN1, 849)TCENW
        WRITE(LU, 850)TIDD
850      FORMAT(1X, 'TIDD', 12X, F15. 1, 14X, 'us')
        WRITE(LUN1, 850)TIDD
        WRITE(LU, 851)TIPD
851      FORMAT(1X, 'TIPD', 12X, I15)
        WRITE(LUN1, 851)TIPD
        TI=2*TIDD
        WRITE(LU, 852)TI
852      FORMAT(1X, 'TIME DELAY', 6X, F15. 1, 14X, 'us')
        WRITE(LUN1, 852)TI
        DA3=-(VAPDA-512)*4. 8828125
        WRITE(LU, 853)VAPDN, DA3
853      FORMAT(1X, 'VAPDA', 6X, I3, ' ', F15. 7, 14X, 'mV')
        WRITE(LUN1, 853)VAPDN, DA3
        DA3=-(VAPDA1-512)*4. 8828125
        WRITE(LU, 854)VAPD1N, DA3
854      FORMAT(1X, 'VAPDA1', 5X, I3, ' ', F15. 7, 14X, 'mV')
        WRITE(LUN1, 854)VAPD1N, DA3
        CALL      CLOSE(LUN1)
        GO TO 190
C      NOW CLOSE THE STILL OPEN INPUT FILE USING UNIFORM
190     CALL      UNIFORM(2, IERR, ITABLE)
C      CHECK FOR ERRORS

```

```
      IF(IERR.NE.0)GOTO 30
C      SEND END OF DATA MAKER TO OUTPUT FILE
      WRITE(LUN4,930)
930     FORMAT('ED ')
      WRITE(LUN5,935)
935     FORMAT(' DATA CONVERSION COMPLETE ')
      GOTO 40
10      WRITE(LUN5,940)
940     FORMAT(' INPUT FILE NOT FOUND ')
      GOTO 5
20      WRITE(LUN5,945)
945     FORMAT('DATA CAN NOT BE READ OUT OF INPUT FILE ')
      GOTO 50
30      WRITE(LUN5,950)
950     FORMAT(' INPUT FILE CAN NOT BE CLOSED ')
C      ADN CLOSE THE OUTPUT FILE
40      CALL      CLOSE(4)
C      RETURN TO BEGINNING TO CONVERT ANOTHER FILE
      GOTO 5
50      CALL      EXIT
      END
```

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