

THE UNIVERSITY OF CALGARY

**Minimization of Nonuniform Potential Distribution in Thin-layer  
Electrochemical Cells**

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

CALGARY, ALBERTA

CANADA

OCTOBER, 2000

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0-612-64941-5

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## **ABSTRACT**

In this work, a thin-layer cell with improved potential distribution on the surface of the working electrode was designed. Two general approaches were taken in order to minimize the uneven distribution of potential. The first approach was to divide a single rectangular Pt working electrode into five smaller electrodes. The individual segments were controlled electronically by an appropriate circuit to have identical currents, so that while the whole electrode area is available to the electrochemical reaction, the potential distribution on this large area is that associated with much smaller electrodes.

The second approach was to use two counter electrodes that were positioned on opposite sides of the rectangular thin-layer cavity. The flow of current from both sides of the working electrode network cuts the effective length of the current path in half, greatly improving the potential distribution across the electrode.

The performance of the cell was investigated for both aqueous and nonaqueous solutions by cyclic voltammetry and potential step experiments. Peak separation in cyclic voltammetry measurements and total electrolysis time in potential step measurements were taken as a diagnostic of how evenly the potential was distributed inside the cell. The results of both types of experiments indicated that using two counter electrodes instead of only one, improves the distribution of potential significantly. A further

improvement in potential distribution was observed when the electronic circuit was used to force identical currents through individual segments. This was evidenced by smaller peak separation in cyclic voltammetry experiments and shorter analysis time in potential step experiments.

The diffusion of the electroactive material from the bulk solution through the edges of the thin-layer cavity (edge effect) was also looked at. A getter electrode was made by grounding the outer segments, to electrolyze the material before diffusing into the inner segment, while current was collected from the inner segment. This effectively reduced the current due to the diffusion of the electroactive species from the bulk solution into the thin-layer cavity.

## ACKNOWLEDGEMENT

I would like to express my sincere gratitude and appreciation to my supervisor, Dr. A. Scott Hinman, for his endless guidance, support and encouragement throughout this work. I also extend my thanks to Dr. Viola I. Birss for her participation as a member of my supervisory committee as well as her contribution to my education and her helpful advice and encouragement.

I wish to thank Ms. Greta Prihodko, whose generous assistance and friendship has been invaluable.

Special thanks are due to Anne Co, Gabriella Pietraru, Anna Carnini, Peyman Khalafpour, Jennifer Wong, Erfan Abu Irhayem, Heather Andreas, Rudolf Potucek, Aislinn Sirk, Melanie Lee Paulson, Dr. Scott Paulson, and Dr. Shen-Jiang Xia, for their precious friendship and support during my stay in Calgary.

Many thanks go to Kim Wagstaff for his endless help with the computer related problems. Thanks are also due to Keith Collins, Michael Siewert, and David Malinsky for their assistance with the electronic problems.

Financial support from the Department of Chemistry (University of Calgary), and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Special thanks also go to my parents (Jamileh and Javanshir), and brother (Yasha), whose unfailing support has always allowed me to fulfill my dreams.

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# CHAPTER ONE

## INTRODUCTION

### 1.1 History and background

Anson at the California Institute of Technology first introduced thin-layer electrochemistry to electrochemists [1, 3]. He was investigating the behavior of iron (II)-iron (III) at a platinum wire electrode by first dipping the electrode in the active electrolyte, then removing it from this solution, washing it for a period of time and placing it in an inert electrolyte. The chronopotentiograms collected indicated that the electroactive species had been adsorbed to the surface of the electrode. Also, the amount of the adsorbed species was diminished with increasing washing time, which was an indication of a slow desorption process taking place. However, he made an interesting discovery. When the electrode area was diminished (by cutting the platinum wire), the electrochemical signal observed was not affected. He soon recognized that the seal of the platinum wire in the glass had been broken and a micro-fissure between the platinum and the glass had been formed. A small amount of solution would then diffuse into the micro-fissure during the dipping time and cause the electrochemical signal that was observed. The longer the dipping time, the more the amount of the diffused solution. This solution of course could not be removed completely during the washing period. This would then explain the behavior, which was earlier thought of as being a slow desorption process. The electrochemical signal, of course could not be affected by the length of the platinum wire. Christensen and Anson then prepared electrodes with a

controlled fissure volume, which can be considered as the first thin-layer electrochemical cells [2, 3].

In thin-layer electrochemistry a large area to volume ratio is achieved by trapping a few microliters of the solution containing the electroactive species in a thin cavity of 2-100  $\mu\text{m}$  thickness. In theory, diffusion limitations within the thin-layer cavity can be ignored, provided that the thin-layer thickness,  $l$ , is smaller than the diffusion layer thickness or  $l \ll (2Dt)^{1/2}$ , where  $D$  is the diffusion coefficient of the electroactive reactants, and  $t$  is the experiment time, i.e., the reaction is given sufficient time, and the thin-layer thickness is sufficiently small [4]. This leads to a flat concentration profile for the reactants all through the cell. The concentration of the reactants is constant at a given time, while it decreases with time. Very short analysis times are possible in thin-layer cells, since all the electroactive species have immediate access to the large electrode surface.

Thin-layer coulometry is considered to be a very good alternative to conventional coulometric measurements of the number of electrons involved in the electrochemical reaction, because of the very short times possible for exhaustive electrolysis. Conventional coulometry for determining the number of the electrons involved in an electrochemical reaction involves stepping the potential from a value well before the occurrence of electrolysis to a value at which the reaction goes to completion. A current starts to flow which decays gradually towards zero. The area under the current-time curve is then integrated to give the total charge passed during the electrolysis. Knowing the concentration of the reactants, and the Faraday number, this provides us with the number of electrons involved in the reaction of interest. It usually takes minutes to hours for the

electrolysis to complete. Furthermore, the accurate determination of the end point is seldom possible, because of the background current resulting from the continuous electrolysis of the solvent, electrolyte and impurities. In thin-layer electrolysis, however, very short analysis times are possible, and the uncertainty in determining the end point is reduced [5-7].

During voltammetric measurements in a diffusion controlled system, after the peak current is reached, diffusion of the electroactive species from the bulk solution to the electrode surface where the reaction happens, becomes the rate determining step. At this point, the current starts to decay in proportion to  $t^{-1/2}$ . In a thin-layer cell, however, provided that the perfect thin-layer conditions are met, i.e., the thin-layer cavity is sufficiently thin and at longer times, the system is assumed to be diffusion free. Current falls back to zero and a Gaussian shape current/potential curve results. This, together with the fact that peak potentials in thin-layer voltammetry occur at the standard formal potential of the electroactive system, results in highly resolved consecutive peaks in voltammetric work [5].

Furthermore, the equations that govern thin-layer electrochemistry are usually just a combination of Faraday's law and the Nernst equation, or Faraday's law and an equation defining the rate of the reaction for that system. These equations are very easy to work with and interpret [7]. Thin-layer cells have also been used for studies of adsorption and kinetics of electrochemical reactions [4, 25-34].

Short analysis times, and the simple equations that thin-layer systems obey, make this electrochemical technique one of the best and most powerful techniques for spectroelectrochemical studies [4, 7-24]. Light of an appropriate wavelength is shone on

the solution under study, while an electrochemical reaction occurs on top of a working electrode. In the *transmission* mode, light is directed through an *optically transparent thin-layer electrode* (OTTLE), which can be a thin film of semiconductor (e.g., SnO<sub>2</sub> or In<sub>2</sub>O<sub>3</sub>) or a metal (e.g., Au or Pt) deposited on a glass, quartz, or plastic substrate or a gold or platinum minigrid, and absorbance changes resulting from species produced or consumed in the electrochemical process are measured. In the *reflectance* mode, light passes through the solution onto a solid working electrode which reflects it back through the solution. The intensity of light prior and following electrolysis provides a means of comparison between the oxidized and the reduced forms of species in the thin-layer cavity. Spectroelectrochemistry provides useful information about the mechanism and the kinetics of an electrochemical reaction, as well as structural information about the species involved.

## 1.2 Theory of linear sweep thin-layer voltammetry

For the general reversible one electron reaction of the type  $\text{Red} \rightleftharpoons \text{Ox} + ne$ , and the perfect thin-layer conditions discussed above, where all the electroactive species are distributed in the thin-layer cavity uniformly, the current for an oxidation reaction in voltammetric work, where the potential is scanned from a value well before the electrochemical reaction of Red, to a value where the reaction can proceed to completion, is given by the differential form of Faraday's law [5, 35]:

$$i = nFV (d C_{\text{Red}} / d t) \quad (1-1)$$

where  $i$  is the oxidation current,  $n$  is the number of electrons involved in the oxidation,  $F$  is the Faraday number,  $V$  is the volume of the solution, and  $C_{\text{Red}}$  is the concentration of the reactant, the reduced form for an oxidation reaction.

The relative concentrations of the reactants and the products are also given by the Nernst equation at any time, as the reaction is reversible:

$$E = E^\circ + \frac{RT}{nF} \ln (C_{\text{Ox}} / C_{\text{Red}}) \quad (1-2)$$

$E$  represents the potential of the cell,  $E^\circ$  is the standard electrode potential which is the cell potential when the reactants and products are at unit activity.  $R$  is the gas constant,  $T$  is the absolute temperature,  $n$  and  $F$  again represent the number of electrons transferred in the reaction and Faraday number, respectively, and  $C_{\text{Red}}$  and  $C_{\text{Ox}}$  are the concentrations of the reduced and the oxidized forms in the reaction.

As long as the concentrations of the reactants and the products are uniform within the thin-layer cavity:

$$C^\circ_{\text{Red}} = C_{\text{Red}} + C_{\text{Ox}} \quad (1-3)$$

Here,  $C^\circ_{\text{Red}}$  is the initial concentration of the reduced form (the reactant). The current-potential curve obeys the following equation:

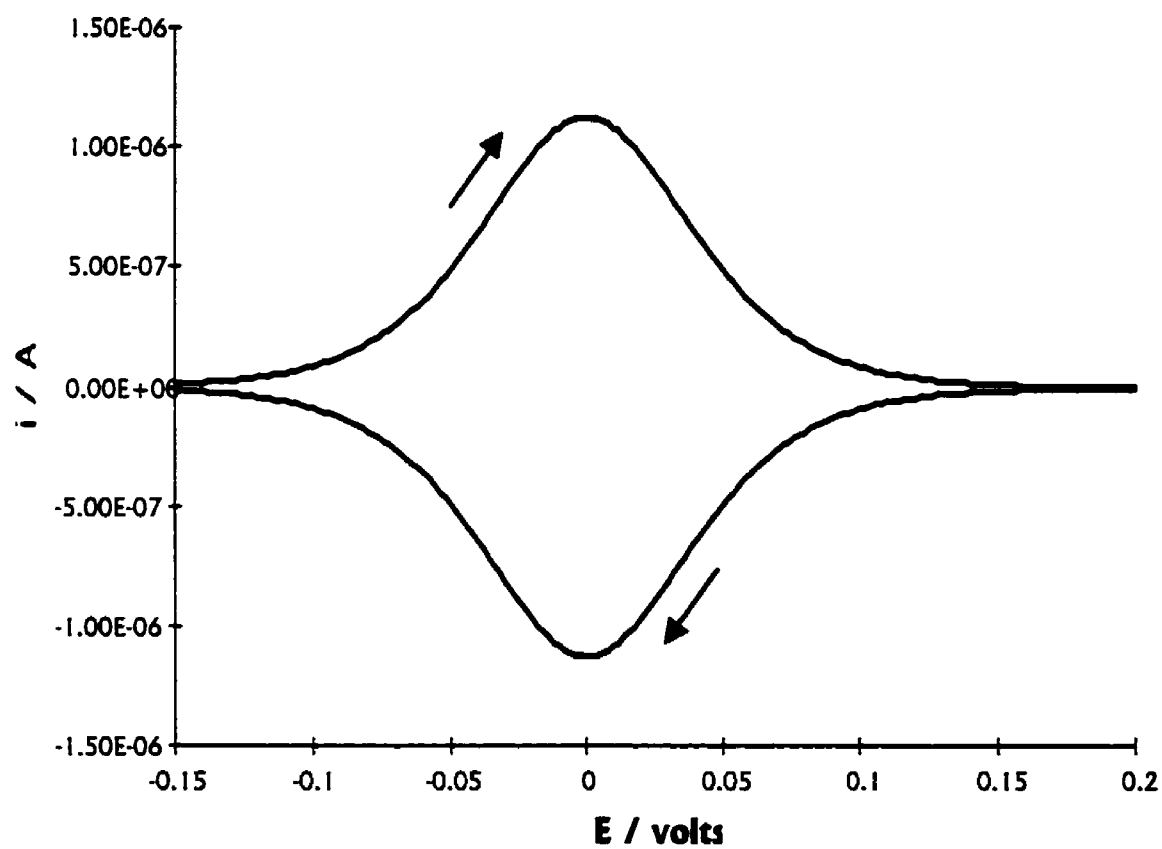
$$i = \frac{n^2 F^2 V C_{ox}^o v}{RT} \left\{ \frac{\exp [ nF (E - E^o) / RT ]}{(1 + \exp [ nF (E - E^o) / RT ])^2} \right\} \quad (1-4)$$

which was first derived by Hubbard and Anson. Here,  $v$  is the potential sweep rate. All the other symbols represent the same parameters as was stated before.

The peak current occurs at  $E^o$  and is given by:

$$i_p = \frac{n^2 F^2 V C_{ox}^o v}{4RT} \quad (1-5)$$

In the cyclic version of linear sweep voltammetry, the potential is swept linearly from a value before any electrode reaction occurs, known as the *initial potential*, to a predetermined value where the reaction is complete, known as the *switching potential*, where the direction of scan is reversed. Fig 1.1 shows the calculated cyclic voltammogram for a reversible one electron reaction of the type  $\text{Red} \rightleftharpoons \text{Ox} + ne$  [5]. Equation (1-4) indicates that in the absence of any resistance in the solution, the current/potential curve of a reversible electrochemical system has a Gaussian shape, in which the oxidation and reduction peaks are mirror images and the peak currents occur at exactly the formal potential of the electroactive system. However, in practice, some resistance always exists in the cell that causes an amount of peak separation and distortion in the peaks, so that this mirror image shape can never be seen for a real



**Fig 1.1** Theoretical thin-layer cyclic voltammogram of a reversible one electron reaction of type  $\text{Red} \rightleftharpoons \text{Ox} + ne^-$ .

thin-layer system. The above equations are calculated, ignoring the diffusion of the species within the thin-layer cavity. The concentrations are assumed to be uniform within the cell as was specified by equation (1-3) previously. These circumstances exist in the cell whenever  $v$  meets the requirements specified by equation (1-6) [4], [7]:

$$|v| \leq (RT / nF) (\pi^2 D / 3l^2) \log (1 + \epsilon) / (1 - \epsilon) \quad (1-6)$$

in which  $\epsilon$  is the maximum relative error in applying equation (1-4), and  $l$  is the cell thickness. For example, if  $l=10^{-3}$  cm,  $D=10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>, and  $T=300^\circ$  K, then  $i$  is given by equation (1-4) within a relative error  $\epsilon$  whenever the magnitude of  $v$  is less than 10 mV/ sec [6]. The resulting equations considering diffusion within the cavity are difficult to handle, and for most practical purposes, diffusion of the species within the cavity can be ignored, provided that the cavity is thin enough (smaller than 10  $\mu$ m) and very slow sweep rates (smaller than 10 mV/sec) are used [5].

### 1.3 Resistance effects in thin-layer cells

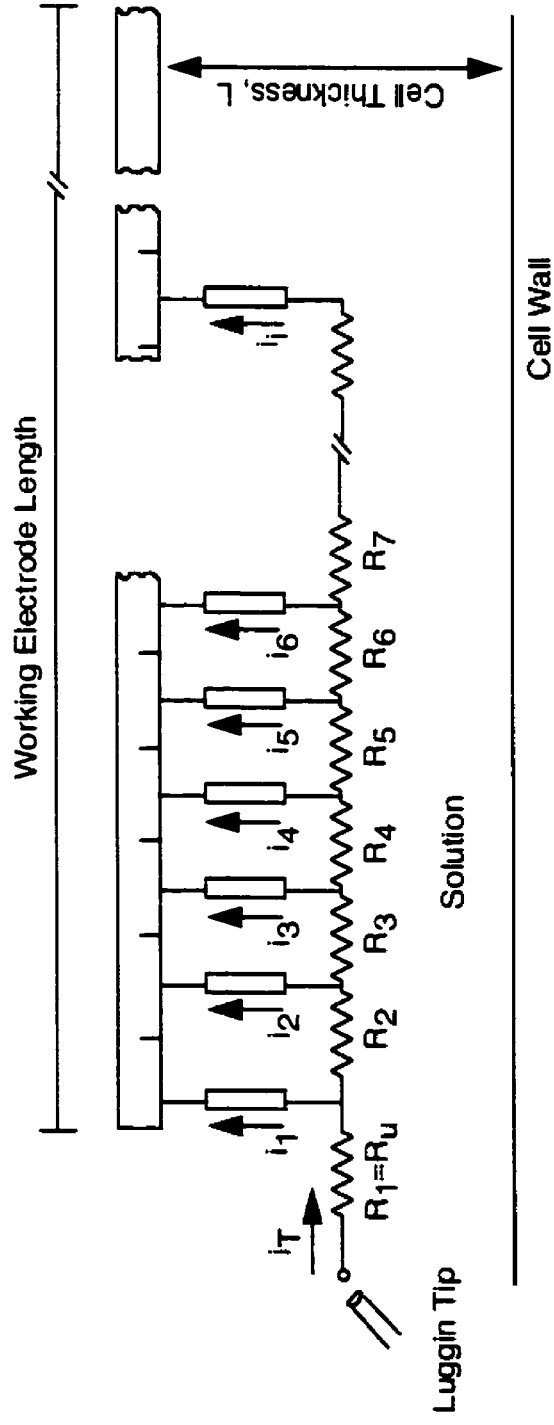
The solution inside the cell always presents some resistance to the flow of current. This is called "ohmic" resistance,  $R_\Omega$ . This resistance is defined by the following equation:

$$R_\Omega = \rho (L / A) \quad (1-7)$$

The proportionality factor,  $\rho$ , is called the specific resistivity and is the resistance of a cubic centimeter of the solution to the flow of electricity, with units of  $\Omega\text{-cm}$ .  $\rho$  is unique for a specific medium.  $L$  is the length of the current path in cm, and  $A$  is the cross sectional area of the solution in  $\text{cm}^2$ . Thus the higher  $L$  and the lower  $A$ , the more the ohmic resistance in the cell.

In general, thin-layers of solution, with very small cross-sectional areas, present a very high resistance to the flow of current inside the cell. This, together with the fact that optimum placement of the reference electrode inside the cell is often not possible, leads to a very large solution resistance between the working and the reference electrode, known as the uncompensated resistance. Furthermore, extending the working electrode dimension along the current path to achieve a large electrode area results in the existence of points on the surface of the working electrode that are farther from the counter electrode, with more ohmic drop and thus less current densities than points closer to the counter electrode. As a result the potential is distributed nonuniformly on the working electrode surface [36–42]. Nonuniform potential distribution results in ineffective use of the working electrode area, which in turn results in longer analysis times. In voltammetric work, this causes poor resolution between the consecutive peaks.

A.S. Hinman, S. Pons, and J. Cassidy, have done numerical calculations of thin-layer voltammograms [5]. The model used by them to discuss the resistive effects in the solution and thus the potential distribution across the working electrode considered that the thin-layer cavity can be divided into a number of volume increments, with each successive increment being displaced a distance  $dx$  from the so-called Luggin capillary (Fig 1.2). The Luggin capillary makes ionic contact between the reference electrode



**Fig 1.2** Model for the potential distribution at rectangular thin-layer electrodes.

and the working electrode. The potential between the tip of the Luggin capillary and the edge of the working electrode is being controlled and measured by the potentiostatic system. Greater solution resistances are presented to the volume increments that lie at successively larger distances from the Luggin tip. The volume and the individual resistances of each increment can be easily calculated.

The volume of each increment for a rectangular working electrode segment was calculated from

$$V = \text{width} \times \text{thickness} \times dx \quad (1-8)$$

The uncompensated resistance,  $R_u$ , between the Luggin tip and the first increment was calculated from

$$R_u = \rho \text{ dref} / (\text{width} \times \text{thickness}) \quad (1-9)$$

where dref is the distance away from the Luggin tip. Other resistances were calculated from

$$R = \rho dx / (\text{width} \times \text{thickness}) \quad (1-10)$$

The total current flowing inside the cell ( $i_t$ ) was initially estimated by the Hubbard and Anson equation (equation (1-4)) assuming uniform potential distribution and using the entire cell volume. The potential sensed at the first volume increment,  $E_1$ , was then calculated from

$$E_1 = E_{\text{appl}} - i_t R_u \quad (1-11)$$

The current flowing into the first volume element,  $i_1$  was then calculated by setting  $E=E_1$  and using the volume of the first increment,  $V_1$ , and equation (1-4).

The total current that now flows through the rest of the cell is

$$i_t - i_1 = \sum_{i=2}^n i_i \quad (1-12)$$

The potential at the second volume increment is

$$E_2 = E_1 - R_2 \sum_{i=2}^n i_i \quad (1-13)$$

Again the current  $i_2$ , flowing into the second volume element, was calculated knowing  $E_2$ . All the individual potentials and currents were calculated in this way.

Generally,

$$\sum_{j=i}^n i_j = i_t - \sum_{j=1}^{i-1} i_j \quad (1-14)$$

and

$$E_i = E_{i-1} - R_i \left( i_t - \sum_{j=1}^{i-1} i_j \right) \quad (1-15)$$

and equation (1-4) were used to calculate the individual potentials and currents. The individual currents were then summed and compared to the initial total current estimated by equation (1-4). If the initial estimate agreed within 0.1% of the sum of the individual currents, it was assumed to be correct. If it did not, a new estimate was calculated on the basis of

$$i_t' = i_t - C$$

where  $C$  was a small value calculated by the program on the basis of the difference between the initial estimate and the sum of the individual currents calculated. The above procedure was repeated until the desired degree of convergence was obtained.

These calculations were done for two geometries, a rectangular and a planar disk thin-layer working electrode. In comparing the radial and the rectangular geometries, it was found that the radial geometry is the superior geometry in terms of more even potential distribution. It was also shown that increasing the uncompensated resistance,  $R_u$ , has the effect of displacing the peak potentials to higher values, but has very little effect on the peak currents. If the length of the rectangular working electrode is increased along the current path, the distribution of potential on the surface of the working electrode becomes more uneven. As the electrode gets bigger, potential is distributed more nonuniformly and the peaks get more distorted, with both peak potential and peak currents being affected. Thus, potential is spread more uniformly in electrodes of smaller area. However, the diffusion of the electroactive species from the bulk of the solution into

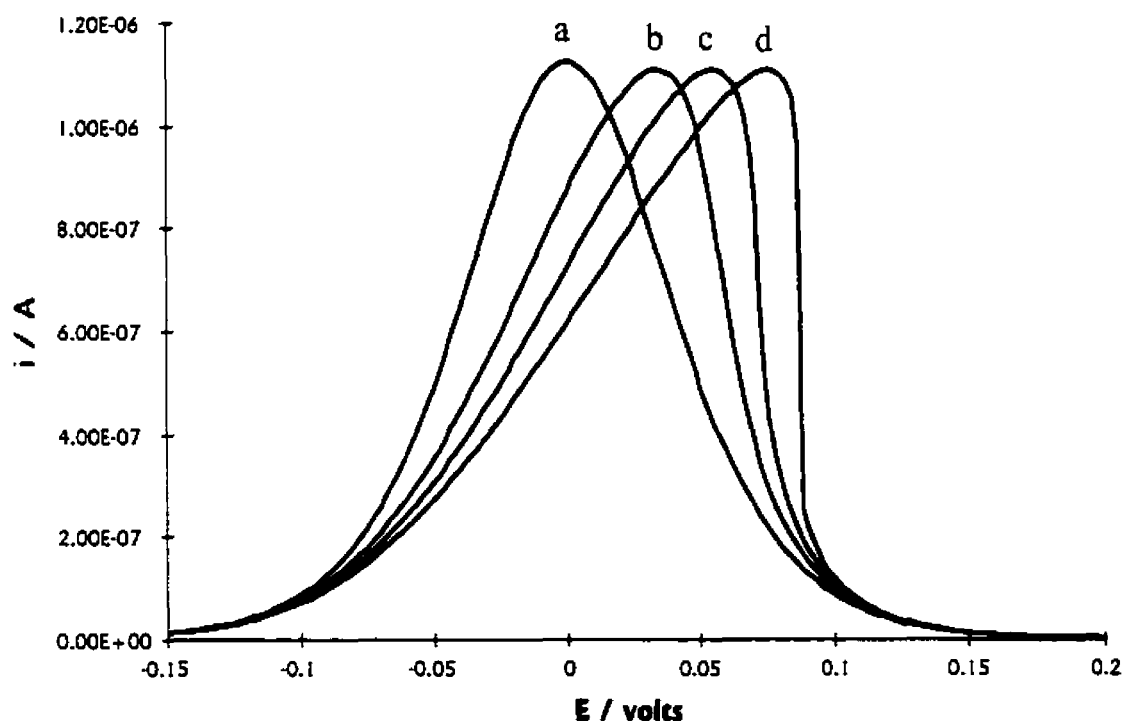
the cavity will be much more serious with smaller electrodes and so there is a limit to how much we can reduce the area of the electrodes. This will be discussed later on.

Fedkiw and coworkers got the same results from their calculations [39]. They formulated two parameters, a dimensionless reference electrode location, and a dimensionless resistance, and showed that the peak shape and potential distribution in thin-layer voltammetry depended only on these parameters. The voltammograms calculated using this model were identical to those calculated by Hinman et al [5].

A Pascal program was written in our lab to calculate the resistive effects on thin-layer voltammograms, using the same algorithm used by Hinman et al [5]. This program is included in the appendix of this thesis. Fig 1.3 shows the effect of increasing the uncompensated resistance by increasing the distance between the working electrode and the reference electrode. The Luggin capillary has been displaced farther away from the working electrode from (a) to (d). As can be seen, the peak potentials are being moved to higher values as the Luggin capillary is being displaced farther away from the working electrode.

Fig 1.4 shows the effect of increasing the length of the working electrode along the current path. More IR drop results at the points that are farther away from the counter electrode and thus the distribution of potential gets more uneven from (a) to (d), as the length of the electrode is increased along the current path. This not only causes a displacement in peak potentials, but also affects the peak currents. Peak currents get smaller as the distribution of potential gets more uneven in the cell.

Fig 1.5 shows the results of varying the solution resistance. Increasing the solution resistance causes more IR drop across the working electrode, thus causing a poorer



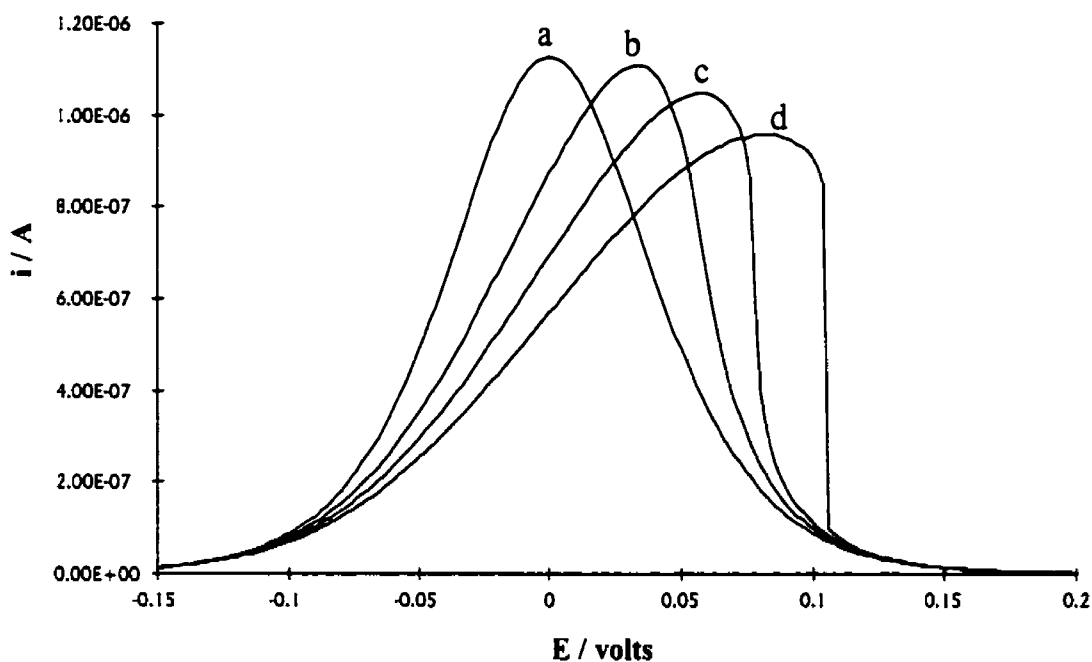
**Fig 1.3** Effect of the distance between the Luggin tip and the leading edge of the working electrode,  $d_{ref}$ , on the calculated thin-layer voltammograms for a reversible one electron reaction: sweep rate = 0.002 V/sec; cell thickness =  $2.5 \times 10^{-3}$  cm; working electrode width = 0.7 cm; working electrode length = 0.3 cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>

(a) theoretical response with  $\rho = 0$

(b)  $d_{ref} = 0.15$  cm,  $\rho = 250 \Omega\text{-cm}$

(c)  $d_{ref} = 0.3$  cm,  $\rho = 250 \Omega\text{-cm}$

(d)  $d_{ref} = 0.45$  cm,  $\rho = 250 \Omega\text{-cm}$



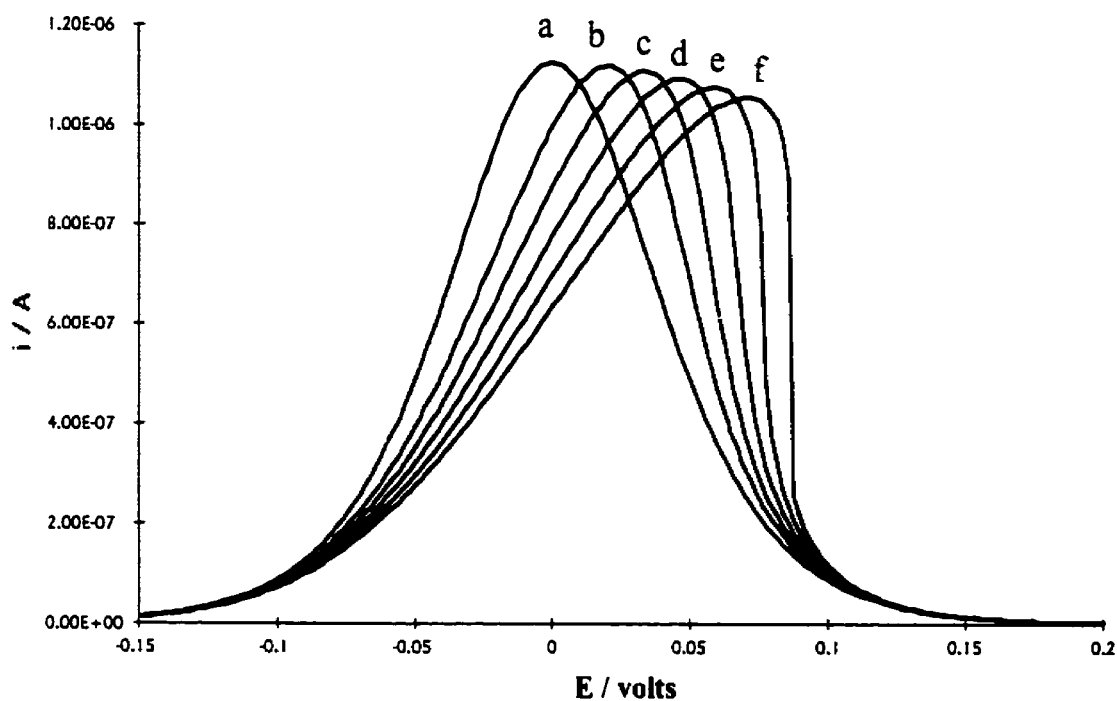
**Fig 1.4** Effect of increasing the working electrode length,  $L$ , along the current path in the rectangular geometry: sweep rate = 0.002 V/sec; cell thickness =  $2.5 \times 10^{-3}$  cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>;  $d_{ref} = 0.15$  cm; The area is the same in all cases. A reversible one electron reaction was assumed.

(a) theoretical response with  $\rho = 0$

(b)  $L = 0.3$  cm,  $\rho = 250 \Omega\text{-cm}$

(c)  $L = 0.045$  cm,  $\rho = 250 \Omega\text{-cm}$

(d)  $L = 0.6$  cm,  $\rho = 250 \Omega\text{-cm}$



**Fig 1.5** Effect of solution resistance,  $\rho$ , on the calculated thin-layer voltammograms for a reversible one electron reaction: sweep rate = 0.002 V/sec; cell thickness =  $2.5 \times 10^{-3}$  cm; working electrode width = 0.7 cm; working electrode length = 0.3 cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>

(a) theoretical response with  $\rho = 0 \text{ } \Omega\text{-cm}$

(b)  $\rho = 150 \text{ } \Omega\text{-cm}$

(c)  $\rho = 250 \text{ } \Omega\text{-cm}$

(d)  $\rho = 350 \text{ } \Omega\text{-cm}$

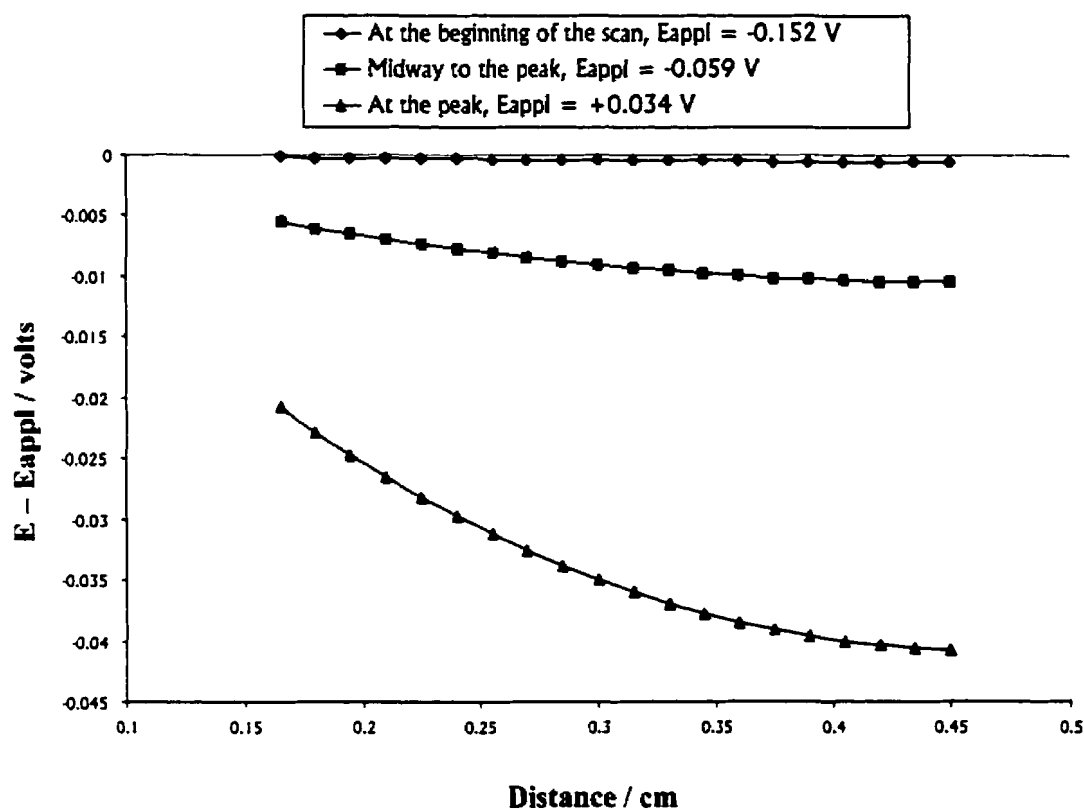
(e)  $\rho = 450 \text{ } \Omega\text{-cm}$

(f)  $\rho = 550 \text{ } \Omega\text{-cm}$

potential distribution. This effect is similar to increasing the length of the working electrode along the current path. Potentials are being displaced to higher positive values for the oxidation reaction as the distribution of potential gets more uneven. Peak currents drop down at the same time.

We calculated the potential distribution across the working electrode for different values of applied potential, using the same program. A potential range of  $-0.15$  V to  $+0.248$  V was chosen for the calculation. The standard formal potential was assumed to be  $0.0$  V. A total of 20 volume increments was assumed with each successive increment being displaced  $0.015$  cm from the Luggin tip. The total working electrode length was  $0.3$  cm. Working electrode width was assumed to be  $0.7$  cm. Solution concentration was  $10^{-9}$  mol/cm<sup>3</sup>. Solution resistivity was  $250$   $\Omega$ -cm.

As is indicated by Fig 1.6, at potentials well before the peak potential, where the magnitude of current flowing in the cell is negligible, the IR drop inside the cell is also negligible and thus potential is distributed evenly through the cell. As the applied potential gets closer to the peak potential, current becomes more significant and, accordingly, the IR drop inside the cell becomes more significant. Potential is no longer the same as the applied potential at the increments farther from the Luggin tip, and drops exponentially. After the peak, where the current inside the cell starts to drop down, IR drop starts to become less significant in the cell and the potential distribution inside the cell becomes more even. Therefore the potential/distance plot flattens out again.

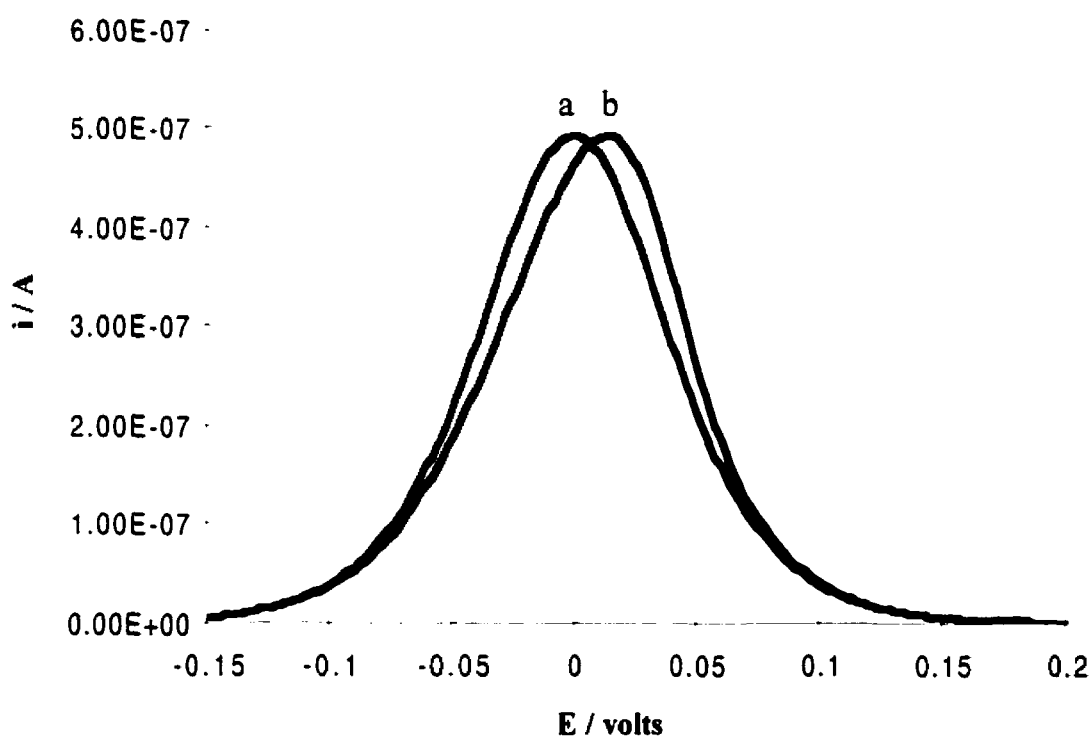


**Fig 1.6** Plot of potential variations with the distance from the Luggin tip: solution resistivity ( $\rho$ ) =  $250 \Omega\text{-cm}$ ; sweep rate =  $0.002 \text{ V/sec}$ ; cell thickness =  $2.5 \times 10^{-3} \text{ cm}$ ; working electrode width =  $0.7 \text{ cm}$ ; working electrode length =  $0.3 \text{ cm}$ ; concentration =  $1.0 \times 10^{-9} \text{ mol/cm}^3$

## 1.4 Objectives of this work

Potential is distributed more evenly on the surface of smaller area thin-layer electrodes. Therefore, using smaller electrodes can reduce the problems associated with uneven potential distributions. A large electrode area can be segmented into several smaller electrodes separated by thin insulating spacers. It is possible to control the potential at the first electrode segment, and to then electronically control the currents at each subsequent segment to be identical to the current at the first segment. This should result in identical current/potential characteristics at each segment. As the electrode area gets smaller, smaller total solution resistance is presented towards the flow of the current and thus smaller IR drop would result. Therefore, the distribution of potential would improve significantly inside the cell. However, all the current in the cell has to pass through the first segment, so if identical currents are forced through the individual electrode segments electronically, the total current through the first segment is  $n \times i$ ,  $n$  being the number of the electrode segment in the multiple electrode network and  $i$  being the current associated with a single segment. If this is true, then cutting the resistance in the cell by a factor of  $n$  would result in multiplication of the current by a factor of  $n$ . The question arises as to whether potential distribution improvement is effective.

We investigated the above problem by the same computer program we used to calculate the potential distribution inside the cell. Fig 1.7 shows the effect of solution resistance on the calculated current/potential characteristic of a single thin-layer electrode. As was seen before, solution resistance has the effect of distorting the voltammogram. If the length of the thin-layer electrode is tripled, then the solution resistance for this electrode triples.



**Fig 1.7** Effect of solution resistance on the calculated voltammograms for a single thin-layer electrode: sweep rate = 0.002 V/sec; cell thickness =  $2.5 \times 10^{-3}$  cm; working electrode width = 0.7 cm; working electrode length = 0.3 cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>. A reversible one electron reaction was assumed.

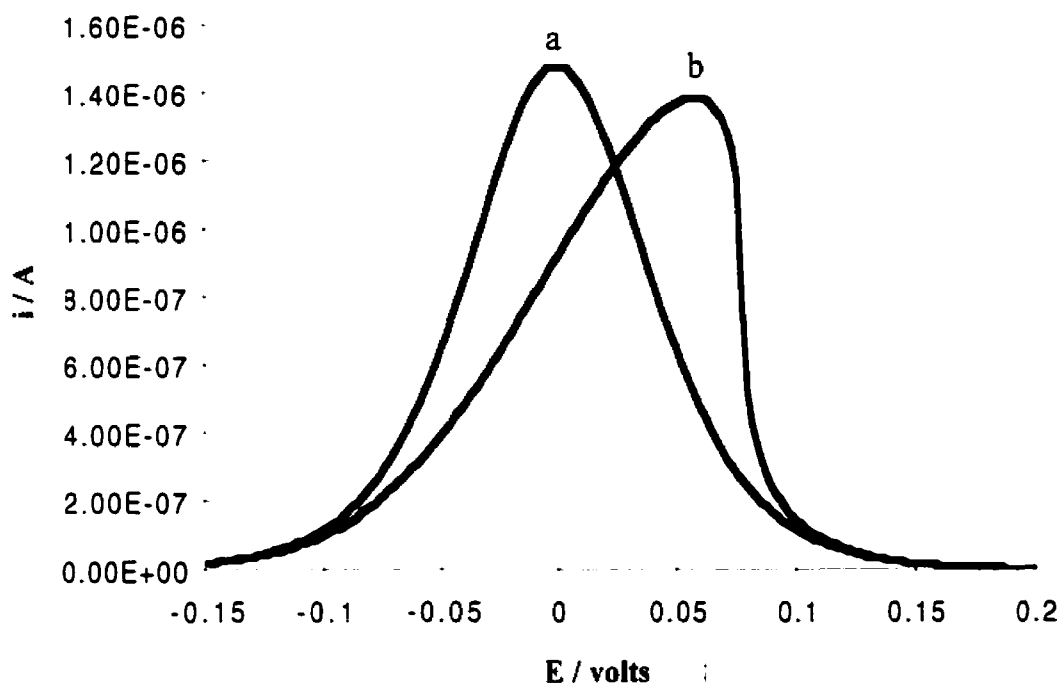
(a) Theoretical response with  $\rho=0$

(b)  $\rho=250 \Omega\text{-cm}$

Fig 1.8 shows the current/potential characteristic of this electrode. As is indicated in Fig 1.8, the voltammogram is significantly more distorted when the resistance inside the cell is tripled by tripling the length. Fig 1.9, on the other hand, is an indication of the effect of tripling the total current inside the cell without altering the length. As the current is increased, the IR drop increases, and thus the distribution of potential gets worse. However, in comparing figures 1.8 and 1.9, it is apparent that the effect of increasing the current on the distribution of potential is less than the effect of increasing the resistance inside the cell by the same amount. Therefore, we are justified to say that even if the total current inside the cell is increased by using the electronic circuit to control the currents across the individual segments, the potential distribution is still improved.

However, as the electrodes get smaller, the electrode edge area to electrode surface area ratio gets larger. As a result, the problem of diffusion of the electroactive species from the bulk solution and through the edges of the thin-layer cavity into the cavity (edge effect), is more serious for such small electrodes. These diffused electroactive materials get electrolyzed and add to the electrolysis current observed, as soon as they are inside the cavity. This is specially problematic in coulometric measurements, where the determination of the end point based on the complete decay of current, is a critical factor in accurate measurements. Small electrodes are also not suitable in spectroelectrochemical measurements because of the small optical target they provide.

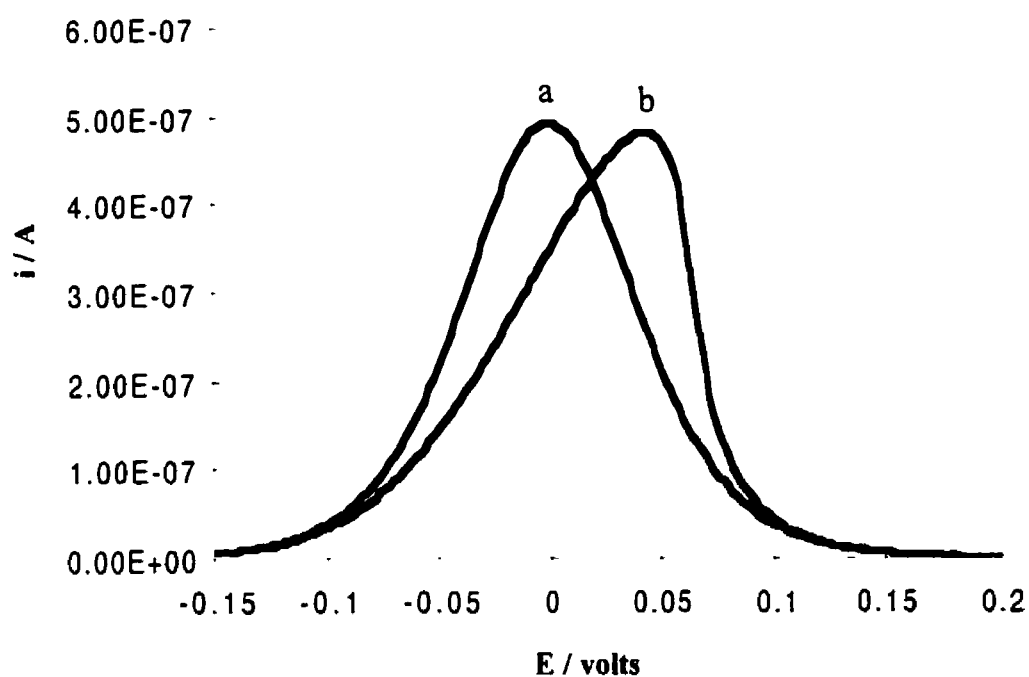
Edge effects can be reduced in a thin-layer cell by a “getter” electrode [3]. This is again possible by segmenting a larger electrode to smaller electrode segments. In a getter electrode, an electrode segment is used as a working electrode and the two segments on its sides are grounded. The potential at the working electrode lead of the potentiostat is



**Fig 1.8** Effect of solution resistance on the calculated voltammograms for a single thin-layer electrode: sweep rate = 0.002 V/sec; cell thickness =  $2.5 \times 10^{-3}$  cm; working electrode width = 0.7 cm; working electrode length = 0.9 cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>. A reversible one electron reaction was assumed.

(a) Theoretical response with  $\rho=0$

(b)  $\rho=250 \Omega\text{-cm}$



**Fig 1.9** Effect of increasing the total current across the working electrode by the electronic circuit, on the calculated voltammograms for a reversible one electron reaction: sweep rate = 0.002 V/sec; cell thickness =  $2.5 \times 10^{-3}$  cm; working electrode width = 0.7 cm; working electrode length = 0.3 cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>.

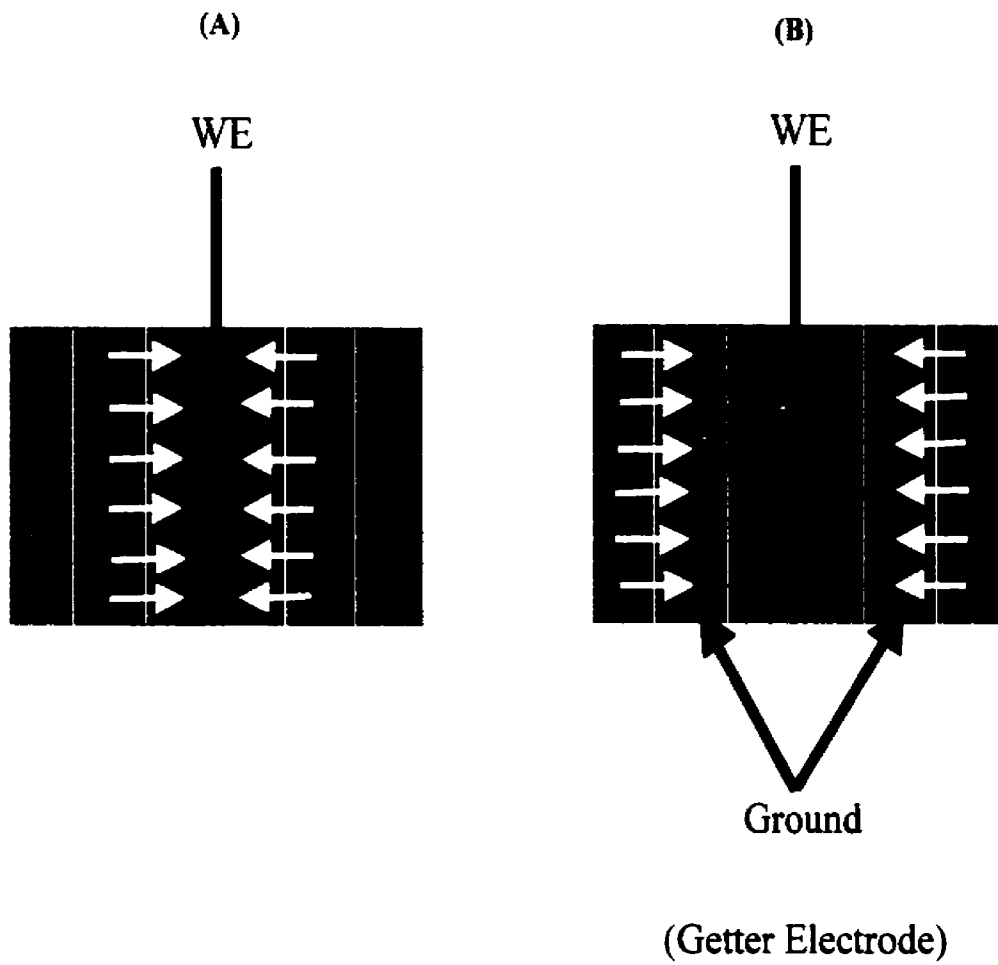
(a) Theoretical response with  $\rho=0$

(b)  $\rho=250 \Omega\text{-cm}$

is connected to the input of a current follower and is at virtual ground. Therefore, in a getter electrode, the electrochemical reaction is happening on the surface of all three electrodes, whereas the current is only being collected from the middle electrode which is directly connected to the working electrode lead of the potentiostat. Thus, the edges of the thin-layer cavity have moved away from the working electrode and less current due to the diffusion from the edges can be seen by the working electrode. Fig 1.10 shows a schematic of a getter electrode.

The objectives of this work are:

1. To design and construct a thin-layer cell with a segmented working electrode.
2. To design and construct an electronic circuit to control the potential on the first electrode segment and to force identical currents to the subsequent segments.
3. To study the distribution of potential inside the cell for both aqueous and nonaqueous solutions using voltammetric and potential step techniques.
4. To reduce the edge effect in the thin-layer cell using a getter electrode.



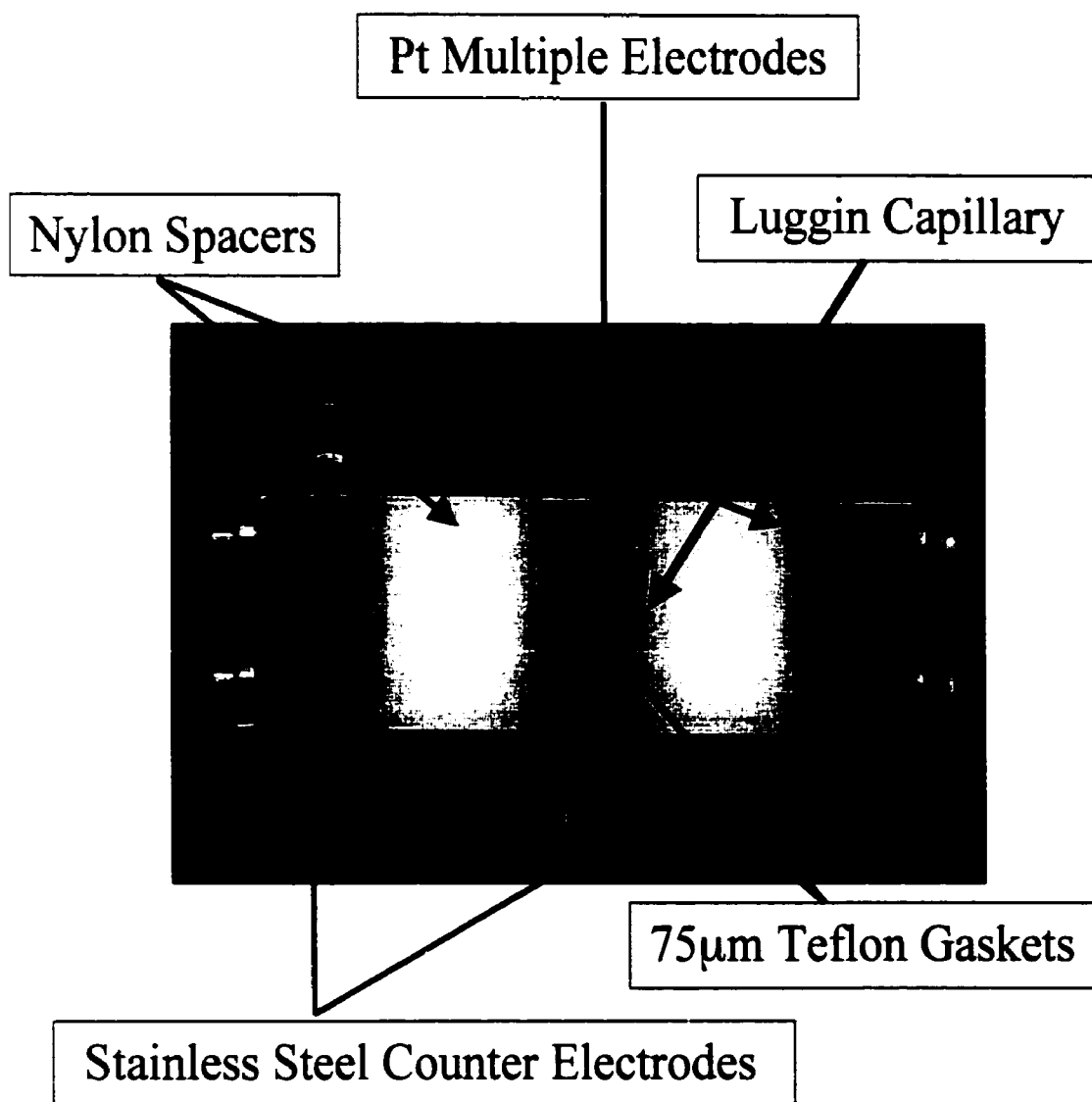
**Fig 1.10** Schematic of (A) Edge effect for the middle segment (B) Edge effect in getter electrode.

## CHAPTER TWO

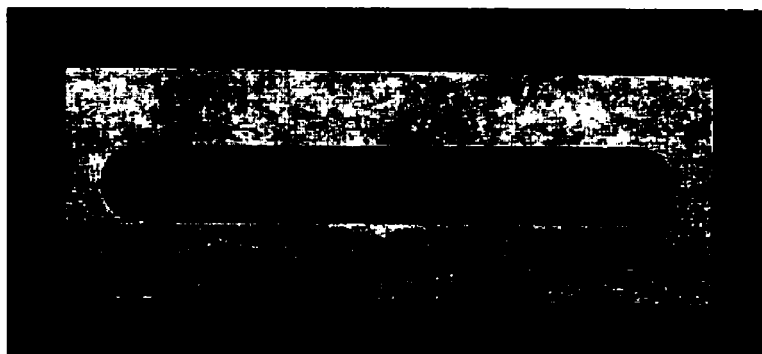
### EXPERIMENTAL

#### 2.1 Cell design

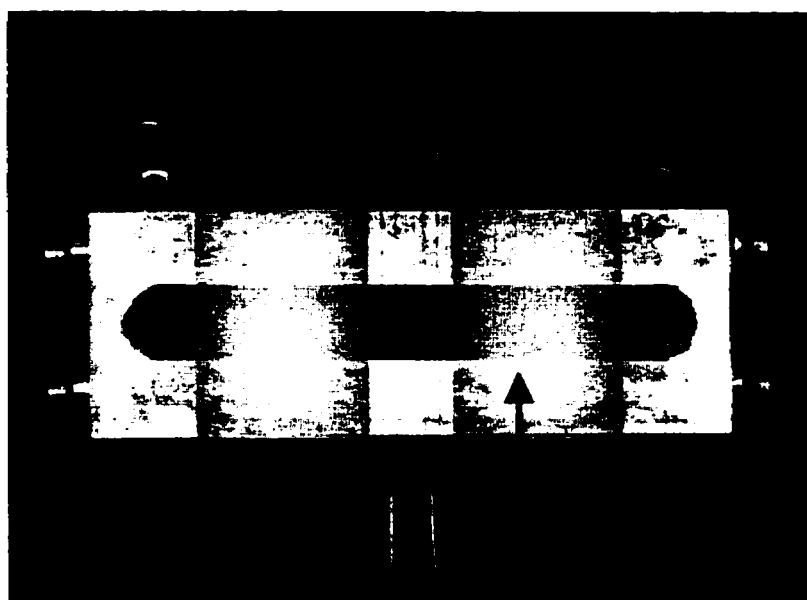
Figure 2.1 illustrates the thin-layer cell designed in our lab. The working electrode is a segmented Platinum thin-layer electrode, which consists of five individual smaller segments separated by thin insulating Teflon spacers of  $75\text{ }\mu\text{m}$  ( $0.003''$ ) thickness. The Platinum segments were cut from Platinum foil,  $0.5\text{ mm}$  thick. Four of these segments are  $1.5\text{ mm}$  wide and the one in the middle is  $3\text{ mm}$  wide. All the electrodes are  $25\text{ mm}$  long. The Platinum segments are soldered to Brass plates,  $25\text{ mm}$  tall. Two stainless steel counter electrodes are placed on both sides of the multiple electrode network. The counter electrodes are  $11.5\text{ mm} \times 25\text{ mm}$  and  $25\text{ mm}$  tall and contain compartments to be filled with the solution. Two Nylon spacers of  $20\text{ mm} \times 25\text{ mm}$  and  $25\text{ mm}$  tall separate the two counter electrodes from the segmented working electrode. A Luggin capillary is built into one of the Nylon spacers,  $1.5\text{ mm}$  away from the segmented working electrode. All parts are aligned together by means of four insulating Nylon screws. The whole assembly facing down, is put on a gasket cut from weighing paper of  $25\text{ }\mu\text{m}$  ( $0.001''$ ) thickness, and then on a microscope slide to create the thin-layer cavity (Fig 2.2). Silicone grease is applied onto both sides of the gasket to help it stick better to both the assembly and the microscope slide. The reference electrode goes into a hole built into one of the Nylon spacers, that narrows down to form the Luggin capillary as indicated in Fig 2.3. Working electrode connections are possible by means of wires soldered to the Brass plates. Connections to the counter electrodes can be made by the screws attached to them.



**Fig 2.1** Platinum multiple electrode thin-layer cell



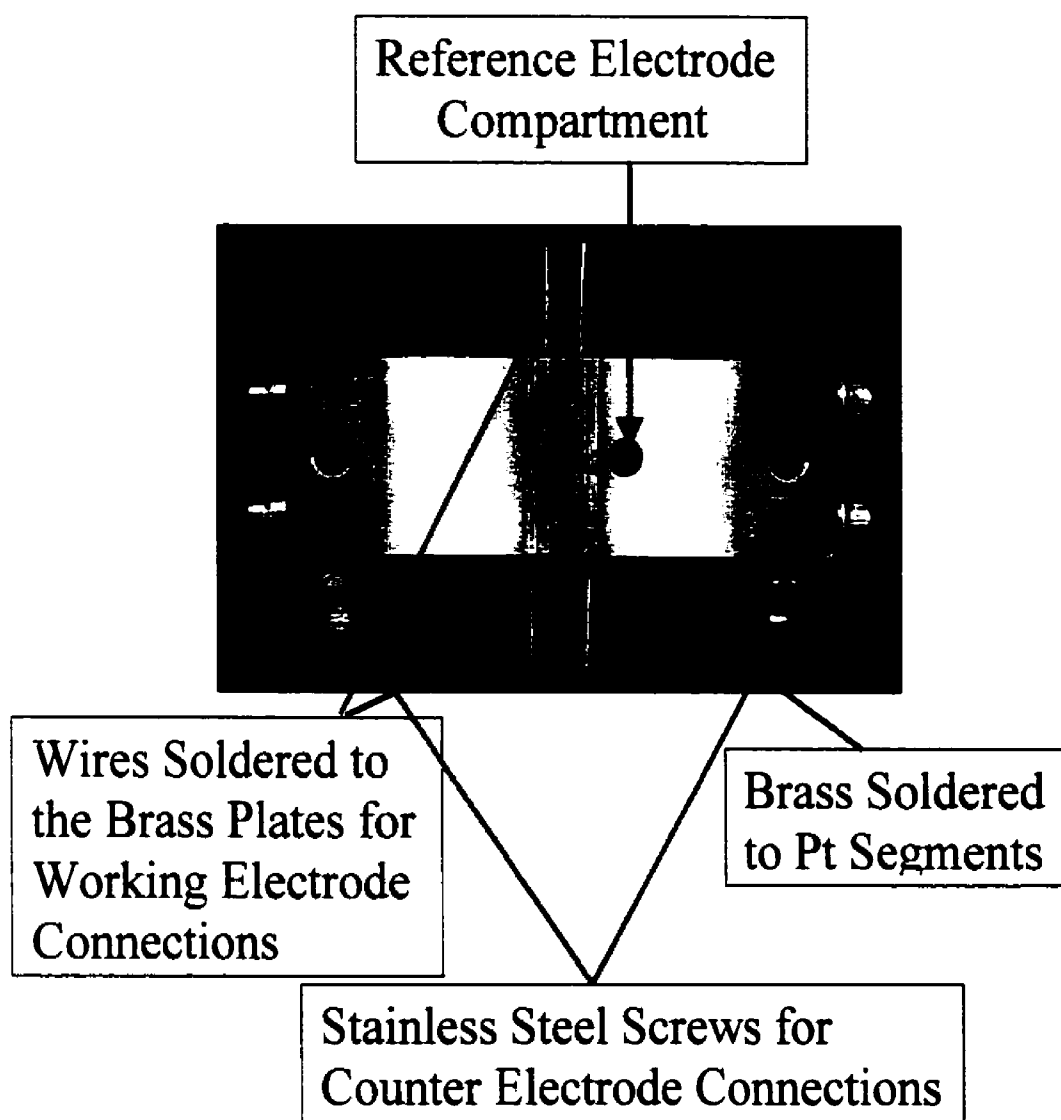
(A)



(B)

25  $\mu$ m Gasket &  
Microscope  
Slide

**Fig 2.2** (A) The 25  $\mu$ m gasket (B) Platinum multiple electrode thin-layer cell. The 25  $\mu$ m gasket and the microscope slide create the thin-layer cavity.



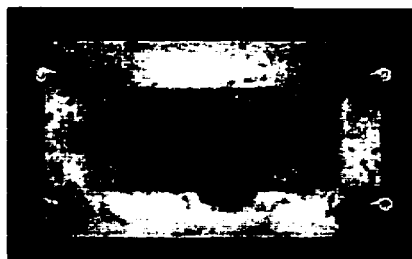
**Fig 2.3** Platinum multiple electrode thin-layer cell. Top view

The cell is then mounted inside an appropriate clamp, shown in figures 2.4 and 2.5, to ensure a fixed cavity thickness. The solution is introduced into the cell by a Pasteur pipette through the holes built into the counter electrodes, and the reference electrode compartment. A window is provided at the bottom for possible spectroelectrochemical applications (Fig 2.6B). RTV silicone sealant is applied around the edges of the thin-layer cavity to prevent leakage.

Prior to assembly, the surface of the multiple electrode assembly was sanded on 1200 and 1500 grit sandpapers placed on a heavy plate glass. It was then polished with 1.0  $\mu\text{m}$  Alumina particles on a soft polishing felt mounted on a flat plate glass surface to ensure a very flat surface.



(A)



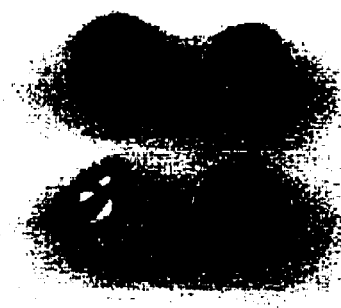
(B)



(C)

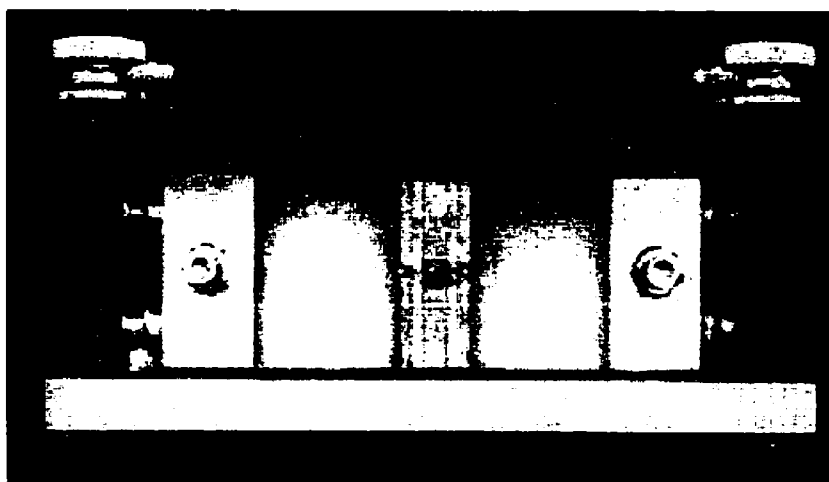


(D)



(E)

**Fig 2.4** Cell and clamp components.



**Fig 2.5** Platinum multiple electrode cell mounted in a clamp. Side view.



(A)



(B)

**Fig 2.6** Platinum multiple electrode thin-layer cell. (A) Top view, (B) Bottom view

## 2.2 Electronic circuit

Fig 2.7 shows the schematic of the electronic circuit designed to control the current through individual segments to identical values.  $Z_1$ ,  $Z_2$ , and  $Z_3$  are the working electrode impedances. Operational Amplifier 1, (OA1), is a current follower that generates a voltage,  $V_{out}$ , proportional to the current,  $i_{in}$ , through the first electrode segment,  $Z_1$ . For OA1, the output voltage is

$$V_{out} = -i_{in} \times 10k$$

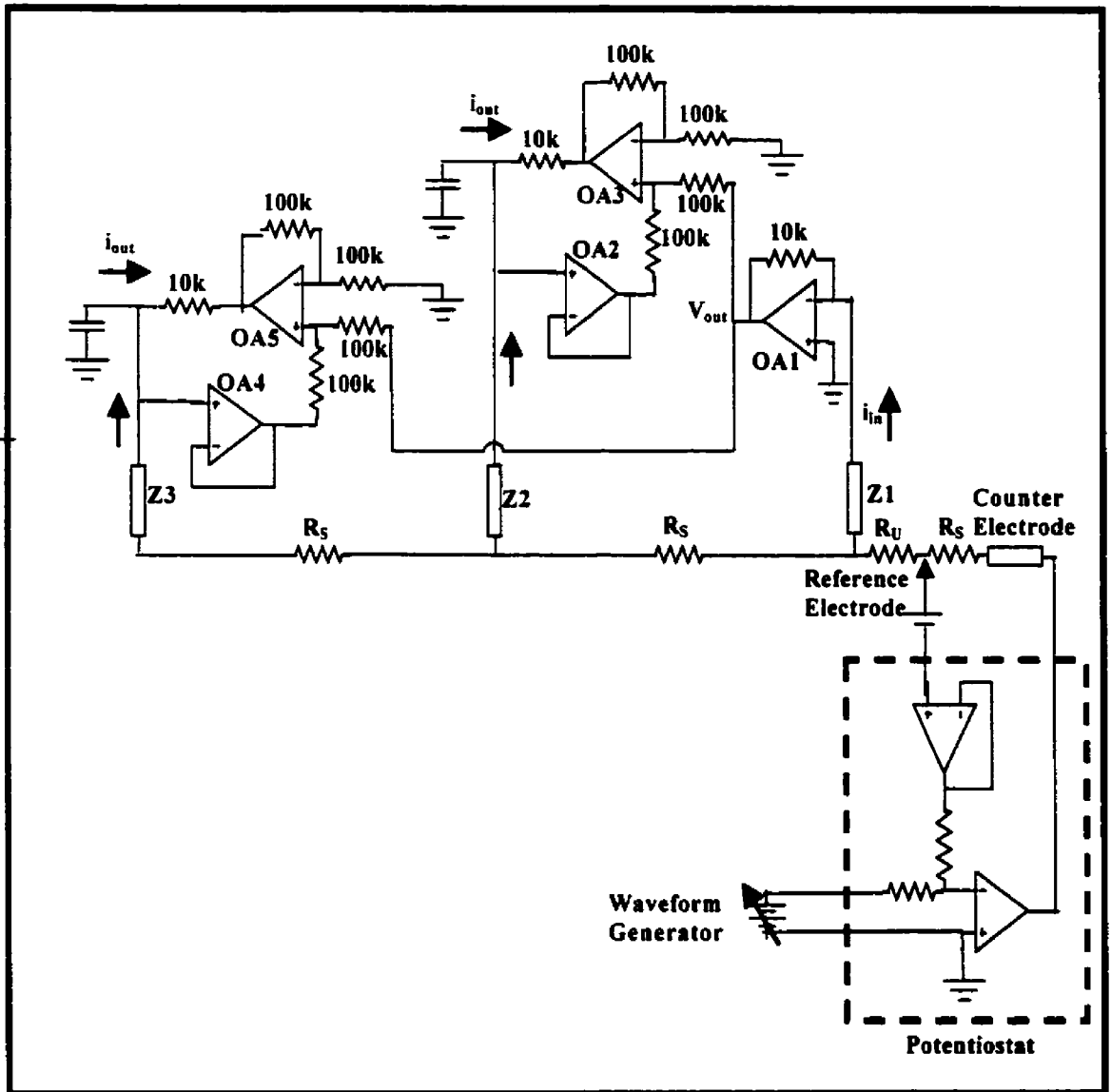
$i_{out}$ , the current on the second segment,  $Z_2$ , is determined by  $V_{out}$ , the voltage supplied by OA1 to the bipolar current source [43] comprised of the OA2, OA3 combination, such that,

$$i_{out} = -V_{out} / 10k$$

Therefore,

$$i_{out} = i_{in}$$

The current on the third segment is also controlled by the voltage  $V_{out}$ , supplied to the OA4, OA5 combination and is identical to  $i_{in}$ . Therefore, the currents through all three segments controlled by this circuit are identical.



**Fig 2.7** Schematic of the electronic circuit for the control of currents through the electrode segments. All the Op-Amps were TL 081.

## 2.3 Instrumentation

A TYPE DT 2101 potentiostat from HI-TEK Instruments was used for all linear sweep voltammetry and potential step measurements. The waveform generator used to apply potential to the potentiostat was a model PP R1 from HI-TEK instruments. A model BD 90 X-Y recorder was used to collect the current/potential responses in linear sweep voltammetry experiments. The current/time responses of solutions in potential step measurements were collected by a Macintosh II computer fitted with a G. W. Instruments MacAdios II analog-digital interface. All the Op-Amps used were TL081 from ACTIVE Components. An Ag/AgCl (0.1 M KCl) reference electrode was used for the aqueous solutions. For the nonaqueous solutions the reference electrode was an Ag wire quasi-reference electrode.

## 2.4 Chemical reagents

Deionized water was used as the solvent for all the aqueous solutions.  $K_4Fe(CN)_6^{-4}$  and KCl were used as received from BDH. All aqueous solutions contained 1mM potassium ferrocyanide as the electroactive reagent, and 0.1M potassium chloride as the supporting electrolyte. The solvent used for the nonaqueous solutions was acetonitrile (BDH). Ferrocene was used as received from Aldrich. Anhydrous tetraethylammonium perchlorate (GFS) was also used as received. All nonaqueous solutions contained 5 mM ferrocene as the electroactive material, and 0.2 M tetraethylammonium perchlorate as the supporting electrolyte.

## CHAPTER THREE

### Linear sweep voltammetry

#### 3.1 Aqueous solutions

##### 3.11 Effect of uncompensated resistance

A series of cyclic voltammograms were obtained during linear sweep voltammetry, using the cell discussed previously and a 1mM aqueous solution of potassium ferrocyanide,  $K_4Fe(CN)_6$ , with 0.1M KCl as the supporting electrolyte. The  $Fe(CN)_6^{3-} / Fe(CN)_6^{4-}$  pair undergoes a reversible one electron reaction. The potential was scanned linearly from 0.0 to + 0.4 volts during the forward scan, and from + 0.4 to 0.0 volts during the backward scan at a rate of 2 mV/sec.  $Fe(CN)_6^{4-}$  loses one electron and oxidizes to  $Fe(CN)_6^{3-}$  during the forward or anodic scan and the opposite happens during the reverse or the cathodic scan. The formal standard potential of the system was found to be +0.219 volts vs Ag/AgCl (0.1M KCl) reference electrode. This potential resulted from averaging the potential values of the forward and the reverse peaks.

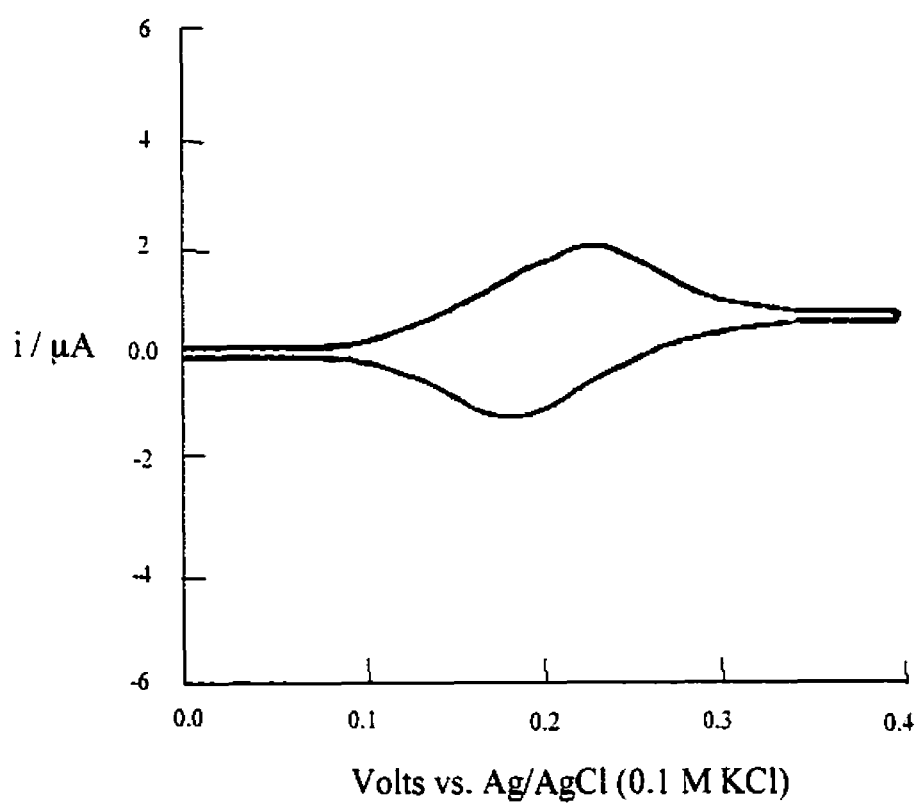
We ran cyclic voltammetry for each individual electrode segment of the multiple electrode network. Only the stainless steel counter electrode closer to the reference electrode was used for all the measurements. All the other conditions were as stated above. The results are listed in Table 3.1. For clarification, the electrode segment lying closest to the reference electrode will be called segment 1, and the ones lying farther from the reference electrode will be segments 2, 3, 4, and 5, respectively.

**Table 3.1** Peak separations and peak currents for the individual working electrodes.

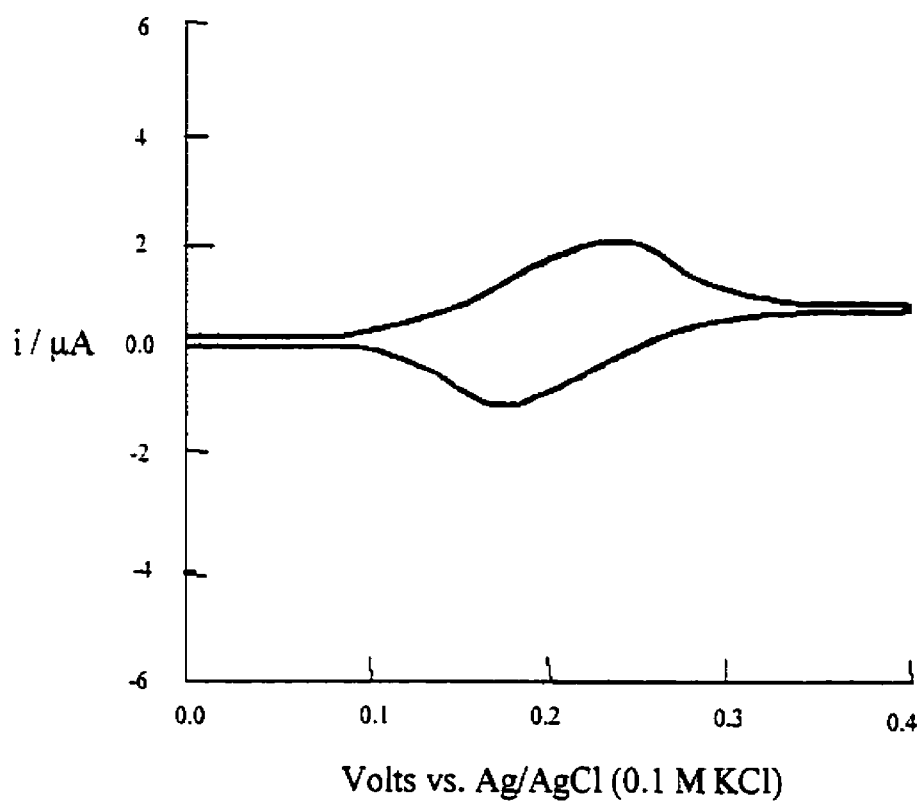
| Working electrode | Peak separation (mV) | Peak current ( $\mu\text{A}$ ) |
|-------------------|----------------------|--------------------------------|
| 1                 | 42                   | 1.7                            |
| 2                 | 57                   | 1.5                            |
| 3                 | 110                  | 3.0                            |
| 4                 | 97                   | 1.4                            |
| 5                 | 112                  | 1.3                            |

The voltammograms obtained were distorted due to two effects: the uncompensated resistance and the solution resistance in the cavity. Segments 1, 2, 4, and 5 have the same dimensions, and thus the same resistance through the solution above them. The only difference is that they are placed at different distances from the reference electrode and thus have different uncompensated resistances associated with them. According to Hinman et al. [5] and Fedkiw et al. [39], we expected to see the peak separation increase from 1 to 5, as the result of increasing uncompensated resistance. Segment 3, lies farther away from the Luggin capillary than 1 and 2, therefore, it has higher uncompensated resistance than 1 and 2. At the same time it has twice the dimensions of all the other segments along the current path, and should feel more IR drop across its surface. Thus there is more uneven potential distribution on its surface than the other four smaller segments.

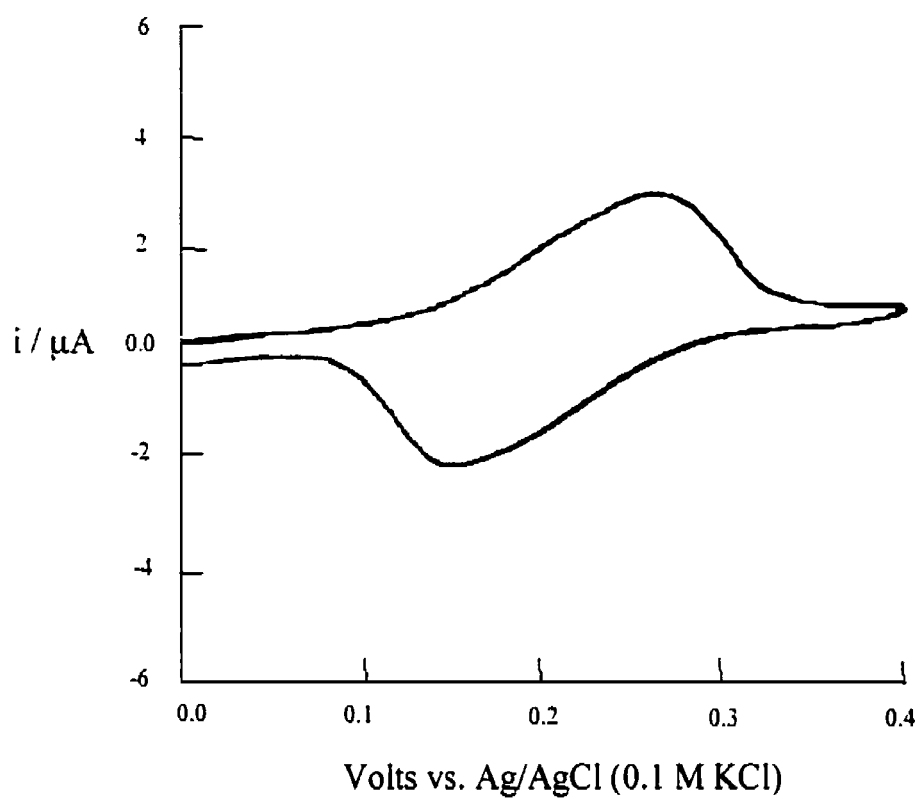
As was indicated in Table 3.1, a peak separation of 42 mV was observed for segment 1, whereas, this value was increased to 57 mV for segment 2 because of higher uncompensated resistance for this segment. Peak separation for 3 was 110 mV. This was expected before, as both higher uncompensated and solution resistances are associated with it. Peak separation was found to be 97 mV for 4, and 112 for 5. Figures 3.1-3.5 show these thin-layer voltammograms obtained for the individual working electrode segments.



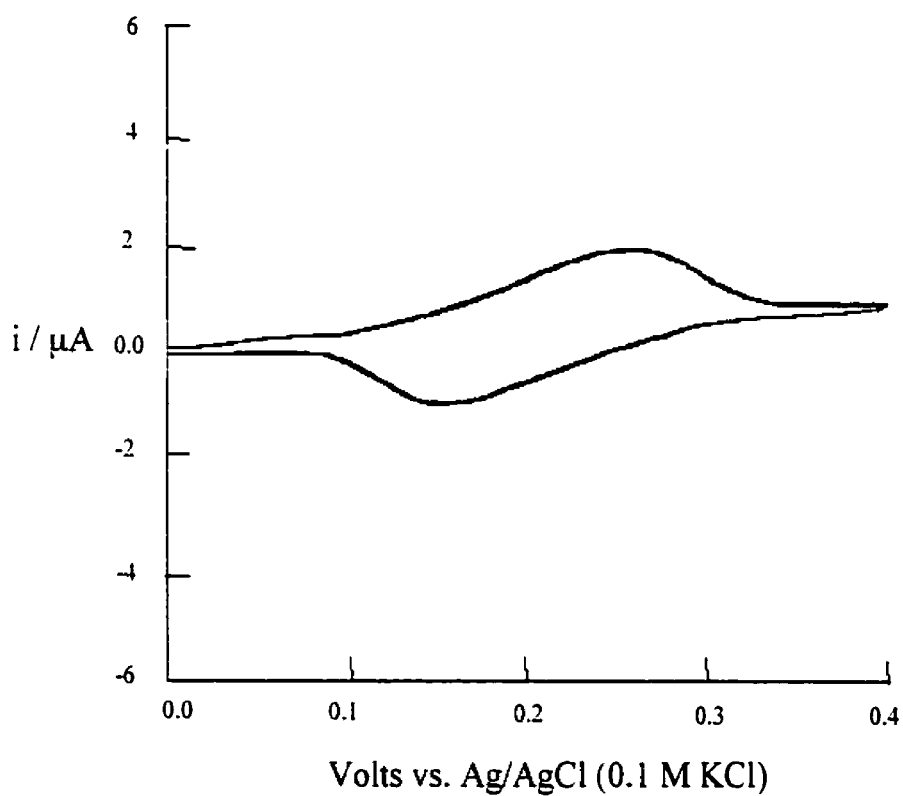
**Fig 3.1** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at working electrode 1. The scan rate was 2 mV/sec.



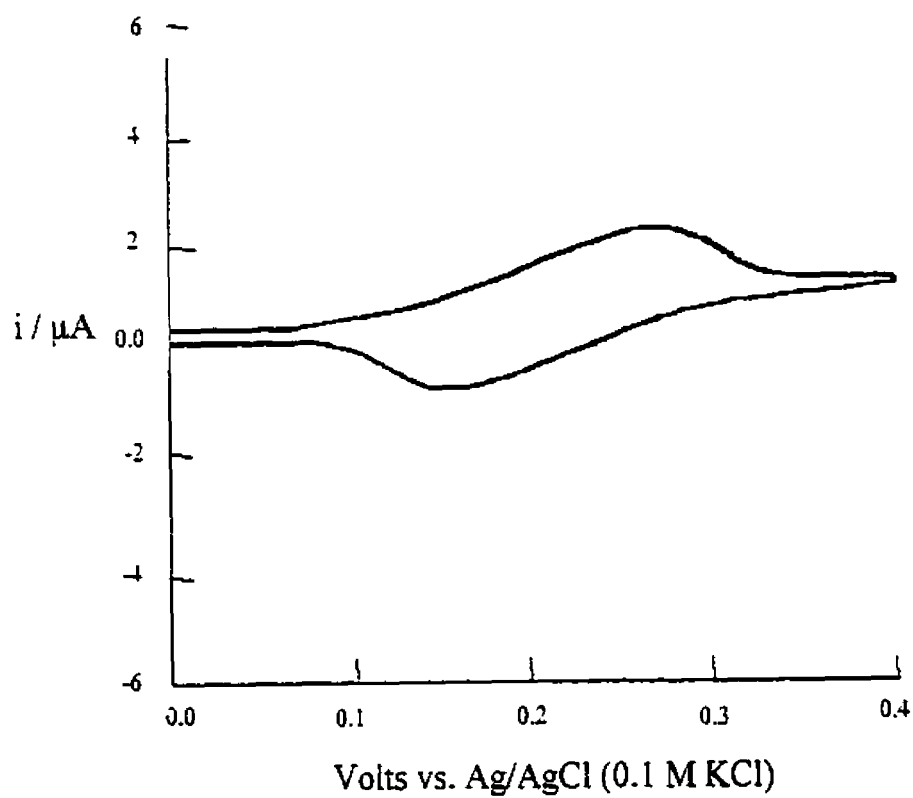
**Fig 3.2** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at working electrode 2. The scan rate was 2 mV/sec.



**Fig 3.3** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at working electrode 3. The scan rate was 2 mV/sec.



**Fig 3.4** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at working electrode 4. The scan rate was 2 mV/sec.



**Fig 3.5** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at working electrode 5. The scan rate was 2 mV/sec.

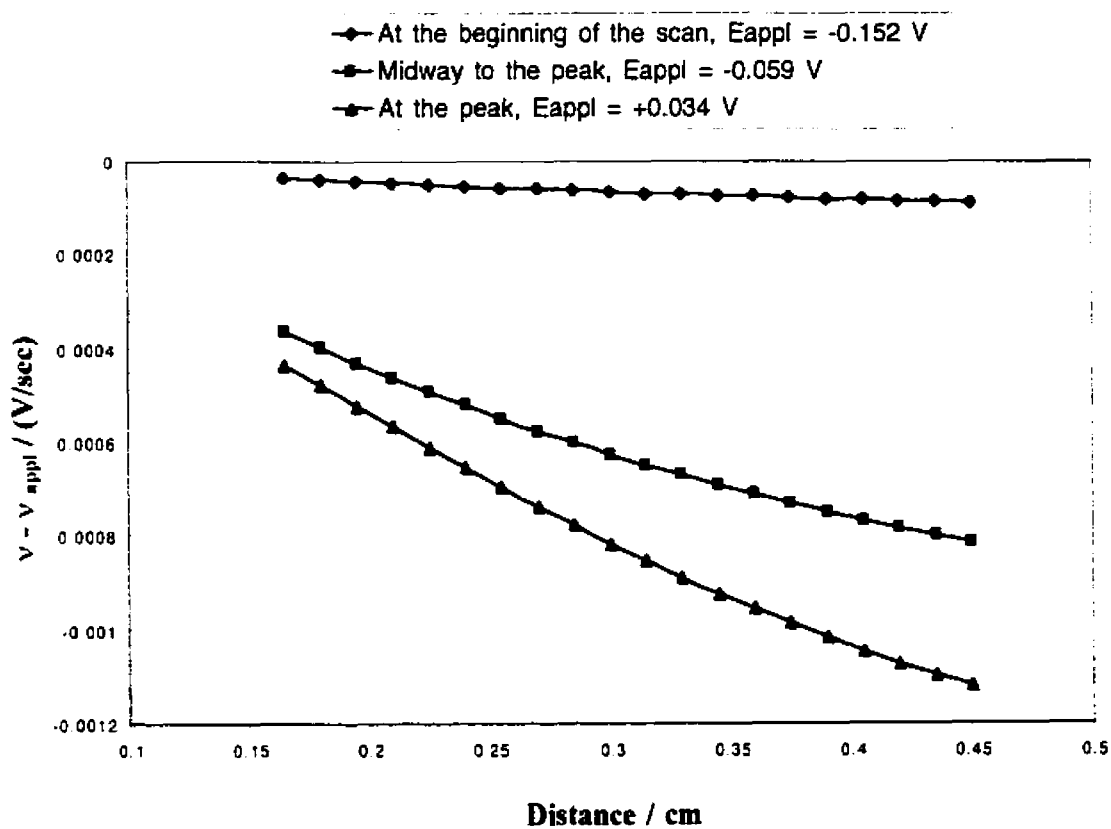
The trend in peak separation in all experiments was as expected from the model suggested by Hinman et al. According to that model and Fig 1.3, moving the Luggin capillary would only result in the displacement of the peak potentials. This should in theory, have no or very little effect on the magnitude of peak currents, whereas, according to Table 3.1, peak currents also decrease as the reference electrode moves farther away from the working electrode. As is indicated in equation (1-5), peak current in a thin-layer voltammogram depends on the number of the electrons involved in the reaction, the volume of the solution in the thin-layer cavity, the concentration of the electroactive material, and the sweep rate. In all the cyclic voltammograms obtained above, all these experimental conditions were the same. The only consideration is that, sweep rate was considered to be a constant in the calculations done by Hinman et al. We already know that more solution resistance and thus more potential drop exists for the points that are farther away from the counter electrode, and the distribution of potential gets poorer as the working electrode gets longer along the current path. Therefore, it is reasonable to say that as the potential drops more seriously for the subsequent points on the working electrode, sweep rate, being the rate of potential change, also varies for the subsequent points. Sweep rate variations certainly affect the observed peak currents. Failure to account for this variation of sweep rate in Hinman's model may explain why the model does not predict the effect of displacement of the reference electrode on the peak current.

We had already calculated the potential distribution across the electrode surface using the Pascal program. Knowing the potentials at each point and the time, we were able to calculate the sweep rates at each point along the current path. The same conditions

used for potential distribution calculations were used here. The potential range was from  $-0.15$  V to  $+0.248$  V. The standard formal potential was assumed to be  $0.0$  V. A total of 20 volume increments was assumed with each successive increment being displaced  $0.015$  cm from the Luggin tip. The total working electrode length was  $0.3$  cm. The working electrode width was assumed to be  $0.7$  cm. Solution concentration was  $10^{-9}$  mol/cm<sup>3</sup>, and a value of  $250 \Omega\text{-cm}$  was chosen for the solution resistivity.

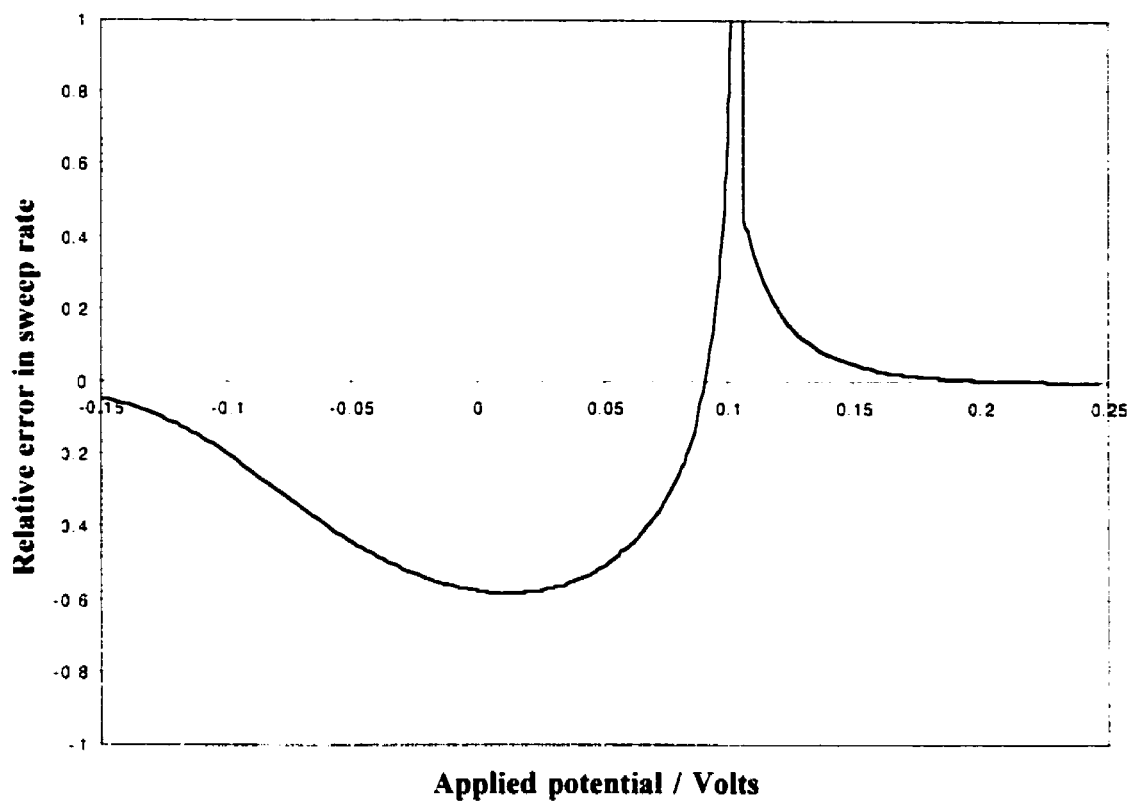
Fig 3.6 is a plot of sweep rate distribution across the working electrode at different applied potentials. The applied potentials chosen were the same as the ones chosen for the potential distribution plots (Fig 1.6). At the applied potential of  $-0.152$  volts, where there is no significant change in the potential at different points on the working electrode, sweep rates are almost constant. As the current peaks, e.g., at an applied potential of  $-0.059$  V, the magnitude of potential drop on the subsequent points on the working electrode becomes more and the rate of change in the potential at different points on the working electrode becomes less than the applied rate. Therefore, a drop in the magnitude of sweep rates along the current path is observed. At the applied potential of  $+0.034$  volts, where the peak occurs, the sweep rate changes along the current path become very significant. After this point however, IR drop becomes less with a decrease in the magnitude of the current flowing in the cell. Therefore, the sweep rate starts to get closer to the applied value until there is no significant electrochemical reaction going on. The sweep rate then becomes a constant.

It is also interesting to observe the variations of sweep rate with the applied potential at a certain point on the working electrode. Fig 3.7 is an illustration of the



**Fig 3.6** Plot of sweep rate variations with the distance from the Luggin tip. The applied sweep rate is 0.002 V/sec.

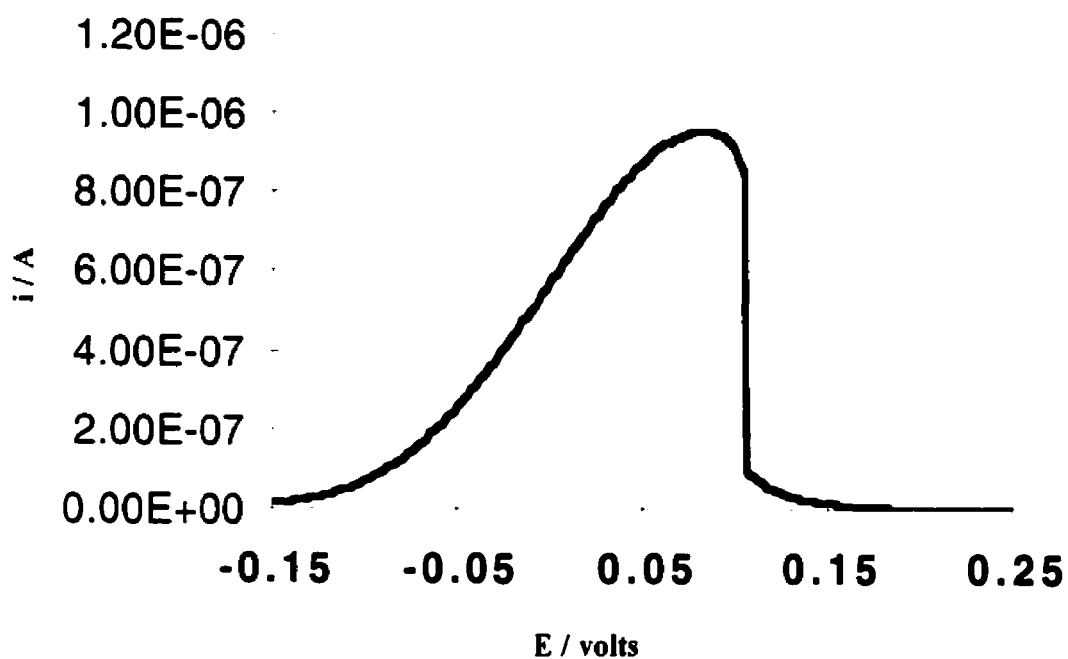
solution resistivity ( $\rho$ ) = 250  $\Omega$ -cm; cell thickness =  $2.5 \times 10^{-3}$  cm; working electrode width = 0.7 cm; working electrode length = 0.3 cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>.



**Fig 3.7** Plot of the relative error in sweep rate with the applied potential at 0.3 cm on the working electrode. The applied sweep rate is 0.002 V/sec. All conditions are as in Fig 3.6. Relative error in sweep rate goes off the scale at around 0.1 volts.

relative error in sweep rate with the applied potential at the 20<sup>th</sup> increment or 0.3 cm on the working electrode. This was plotted using the same results from the sweep rate distribution calculations. As the applied potential becomes higher, so does the current inside the cell, and sweep rate drops become more apparent. According to Fig 3.7, the relative error in sweep rate at around the peak ( $E_{\text{appl}} = + 0.034 \text{ V}$ ) is more than 50%. The magnitude of sweep rate continues to decrease until the peak, after which the current starts to drop quite rapidly. Fig 3.8 shows the calculated voltammogram for the same conditions. As can be seen in this figure, current first starts to decrease gradually after the peak and suddenly a very sharp drop in the current occurs. Sweep rates also start to increase gradually after the peak with the slow decrease in current until the sudden decrease in the magnitude of current inside the cell causes a sharp and rapid increase in the magnitude of sweep rate. At this point, suddenly the IR drop inside the cell falls to near zero. Therefore, there is a huge difference in the sweep rate at this potential and the potential before it. After the current falls sharply back to around zero, it stays there and becomes constant and so does the sweep rate.

We tried to incorporate the sweep rate variations into the program and calculate the current/potential curves using the same algorithm. The real sweep rate values were calculated using the calculated potential values. These were included in the iteration for the calculation of the current/potential curves. However, the program was not able to converge when these sweep rates were incorporated into it. A different algorithm might be able to solve this problem.



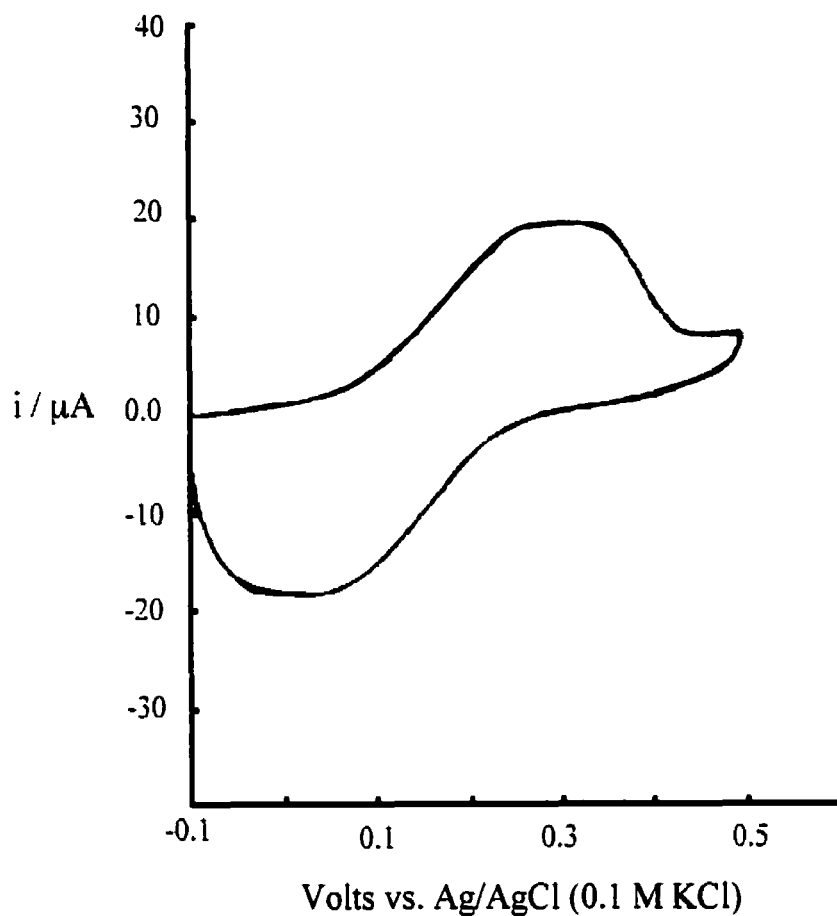
**Fig 3.8** Calculated thin-layer voltammogram for a 0.3 cm long working electrode at an applied sweep rate of 0.002 V/sec.

solution resistivity ( $\rho$ ) = 250  $\Omega$ -cm; cell thickness =  $2.5 \times 10^{-3}$  cm; working electrode width = 0.7 cm; concentration =  $1.0 \times 10^{-9}$  mol/cm<sup>3</sup>.

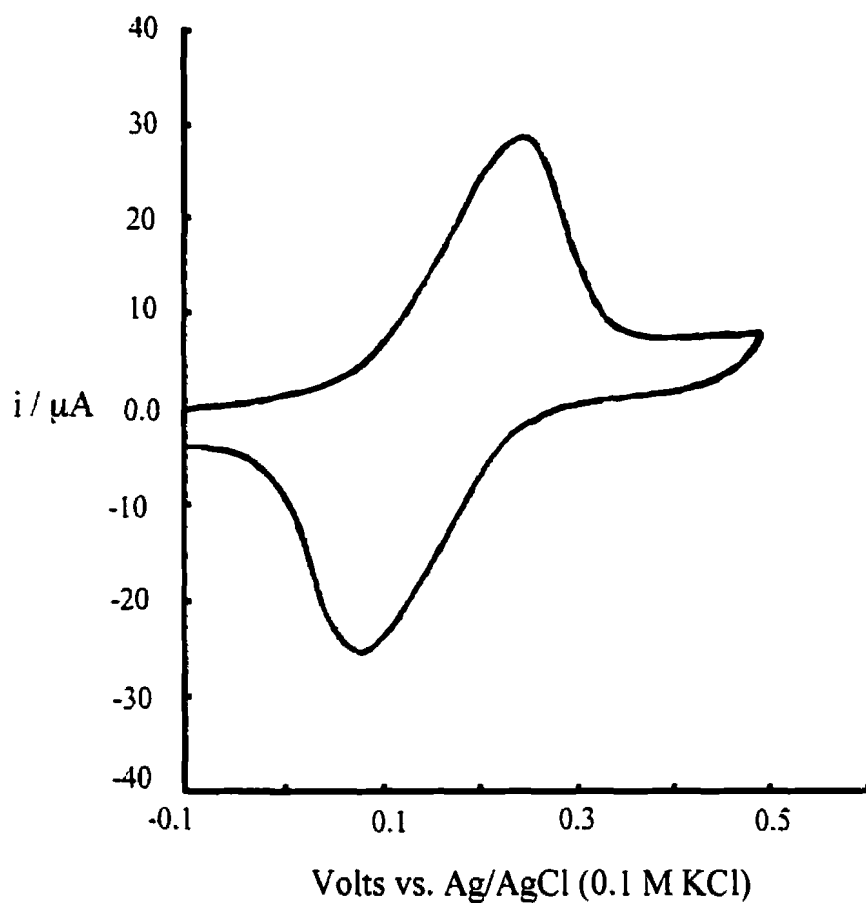
### 3.1.2 Effect of using two counter electrodes

Fig 3.9 shows the voltammogram of the potassium ferrocyanide solution obtained with all five electrode segments shorted together and used as the working electrode. Only the counter electrode closest to the Luggin capillary was used. Potential was swept from  $-0.1$  V to  $+0.5$  V and from  $+0.5$  V back to  $-0.1$  V at a rate of 5 mV/sec. As can be seen in this figure, the voltammogram was significantly distorted. The voltammogram shows a peak separation of 300 mV and a peak current of 18  $\mu$ A. Here, large currents that flow through the electrode of large surface area lead to a potential drop of very high magnitude which in turn leads to a very poor potential distribution inside the cell. The uneven potential distribution is again a combination of the effects of the uncompensated resistance and the solution resistance inside the cell. The uncompensated resistance here is the same as when only segment I was used. On the other hand, the solution resistance is now much higher as the length of the electrode has become much larger. Therefore, the contribution of the uncompensated resistance to the total resistance is now less than when only segment I was used and the solution resistance is now mostly responsible for the poorer potential distribution.

Fig 3.10 shows the voltammogram obtained from the same solution and in the same experimental conditions. Here again all five electrode segments were shorted together and used, but this time both counter electrodes were connected to the counter electrode lead of the potentiostat. The voltammogram obtained showed a peak separation of 175 mV and a peak current of 23  $\mu$ A. Peak separation is almost cut in half in this case.



**Fig 3.9** Thin-layer cyclic voltammogram of 1 mM  $K_4Fe(CN)_6$  in 0.1 M KCl at all five electrodes. The counter electrode closer to the Luggin capillary was used. The scan rate was 5 mV/sec.



**Fig 3.10** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes. Two counter electrodes were used. The scan rate was 5 mV/sec.

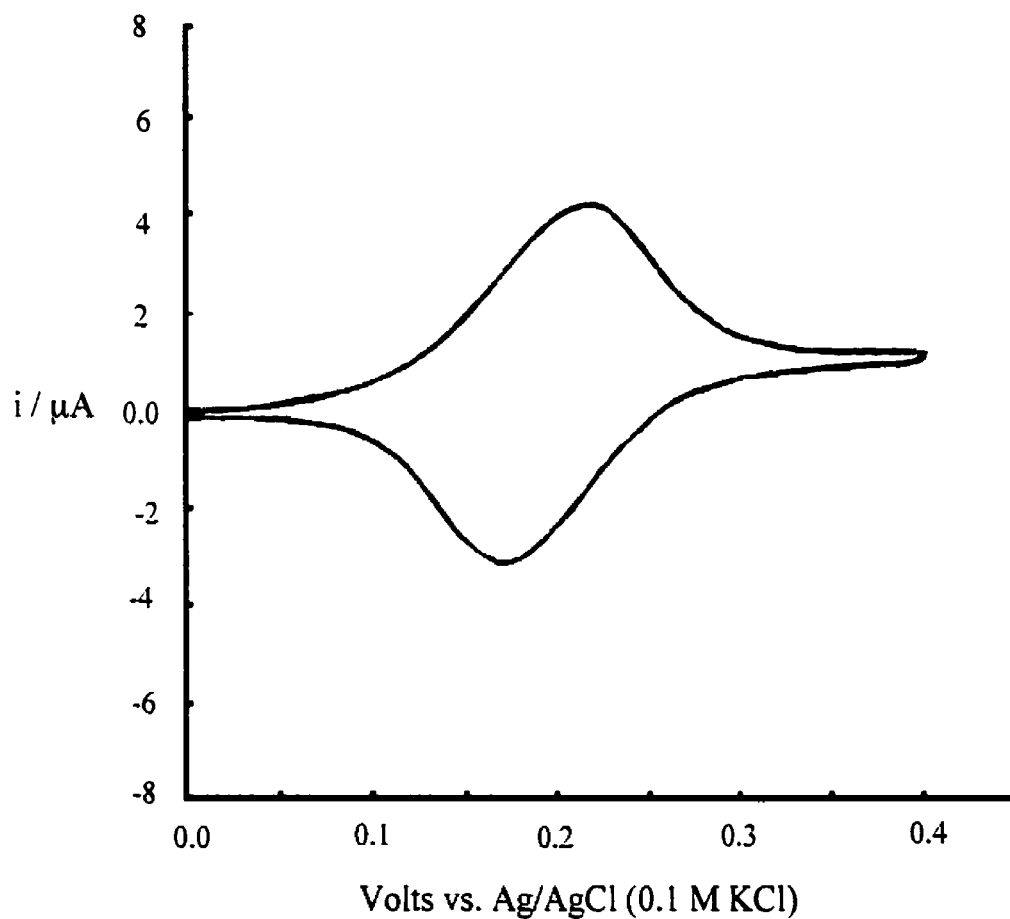
The two counter electrodes that are located on the opposite sides of the working electrode network provide two current paths that flow from the opposite sides towards the network. This causes the potential gradient to flatten out significantly. Clearly, use of two counter electrodes on both sides of the working electrode network improves the distribution of the potential to a large extent. When the potential distribution is improved, peaks get less distorted and the peak current increases.

We ran three separate cyclic voltammetry experiments with the same potassium ferrocyanide solution at a scan rate of 2 mV/sec. The first used segments 1 and 5 shorted together as the working electrode, the second used 2 and 4 shorted together as the working electrode, and the third used segment 3 as the working electrode. Both counter electrodes were used in these experiments. The results are shown in Table 3.2.

Here again, 1&5, 2&4, and 3 all have the same length along the current path, and thus the same resistance through the solution above them. However, the uncompensated resistance increases from 1&5 to 3, as 1&5 is the closest to the Luggin capillary. Therefore, as is already shown in Table 3.1 and figures 3.1-3.5 for the single electrode segments, the distribution of potential was expected to get worse from 1&5 to 3. Figures 3.11-3.13 show the thin-layer voltammograms at 1&5, 2&4, and 3, respectively. As is indicated in Table 3.1, a peak separation of 47 mV was obtained when 1&5 was used as the working electrode. Peak separation was found to be 65 mV with 2&4 as the working electrode, which was 17 mV more than when 1&5 was used. The amount of peak separation was increased to 72 mV with segment 3 as the working electrode. Therefore, potential is distributed most uniformly on 1&5.

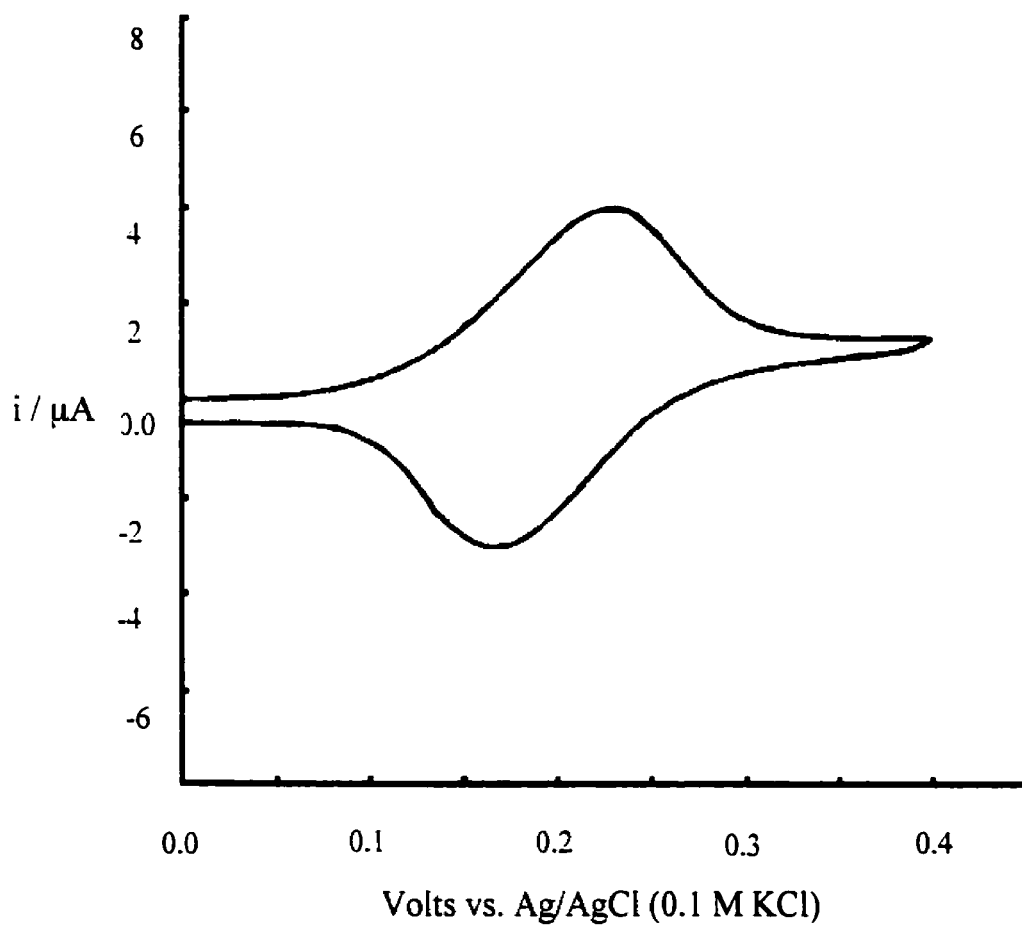
**Table 3.2** Peak separations and peak currents for segments, 1&5, 2&4, and 3.

| <b>Workingelectrode</b> | <b>Peak separation (mV)</b> | <b>Peak current (<math>\mu</math>A)</b> |
|-------------------------|-----------------------------|-----------------------------------------|
| 1&5                     | 47                          | 3.4                                     |
| 2&4                     | 65                          | 3.1                                     |
| 3                       | 72                          | 2.8                                     |



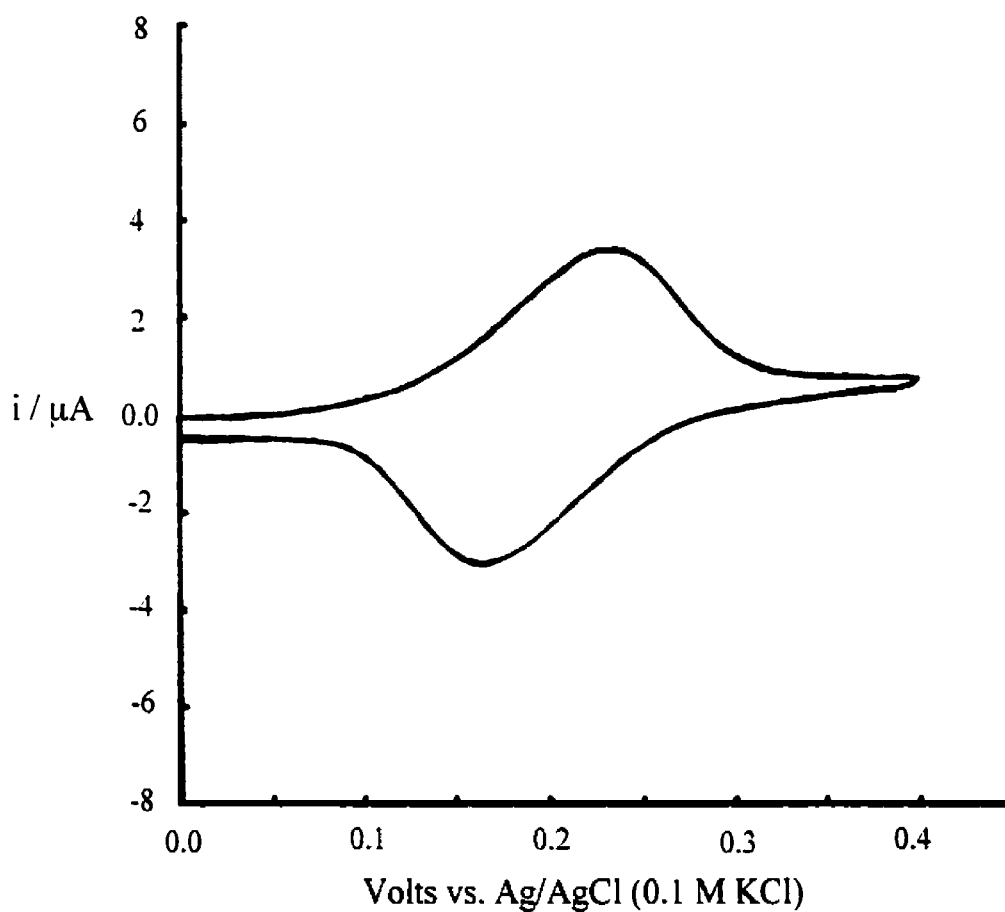
**Fig 3.11** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 1&5.

Two counter electrodes were used. The scan rate was 2 mV/sec.



**Fig 3.12** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 2&4.

Two counter electrodes were used. The scan rate was 2 mV/sec.



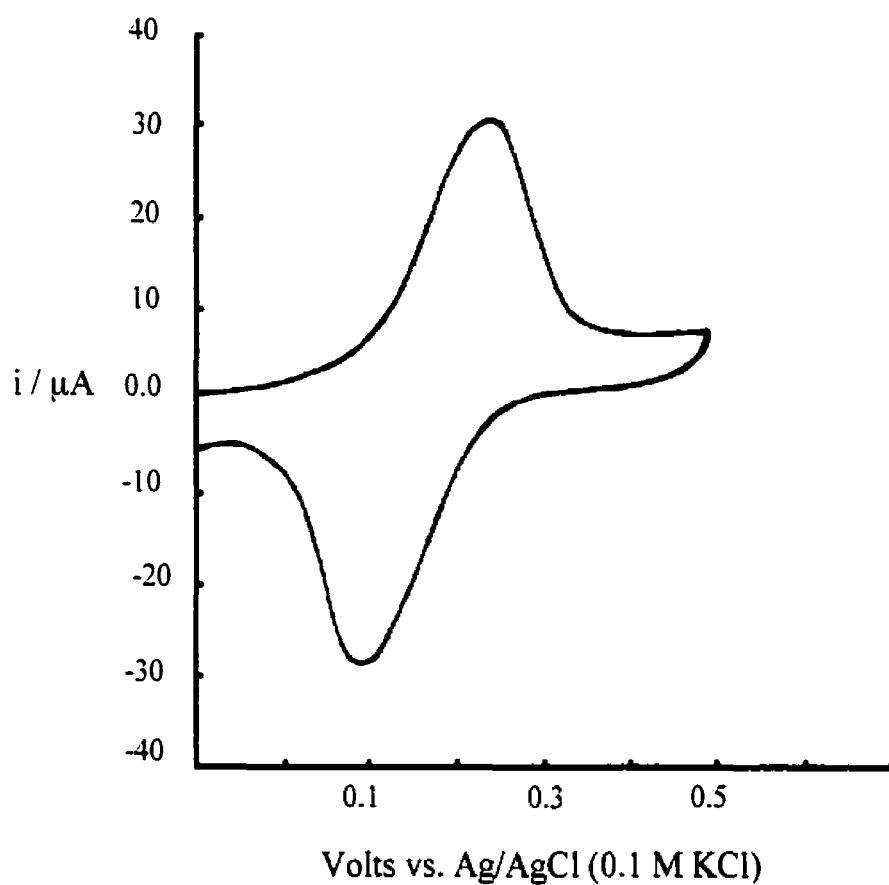
**Fig 3.13** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 3. Two counter electrodes were used. The scan rate was 2 mV/sec.

For 1 and 5 shorted together, the potential gradient is symmetrical as 1 and 5 each lie the same distance away from the counter electrodes. The same holds for 2 and 4 shorted together. For 3, the gradient is also symmetrical as this electrode is equidistant from both counter electrodes.

### **3.1.3 Effect of utilizing the electronic circuit for control of currents at the individual segments.**

As was said before, potential is more evenly distributed on the surface of electrodes with smaller area. In this work, a single Pt electrode was segmented into five smaller electrodes with the intention of controlling the potential on the first segment and forcing identical currents that are proportional to the potential at first segment, to the remaining segments by the designed electronic circuit.

Fig 3.14 shows the cyclic voltammogram obtained using the circuit for control of the currents on the surface of the individual electrode segments. The scan rate was 5 mV/sec. Again both counter electrodes were used. The total current was monitored as the potential difference across a 10k resistor in series with the counter electrode. Segments 1 and 5 were shorted together and connected to OA1 in the electronic circuit shown in Fig 2.7. Segments 2 and 4 were shorted together and connected to the OA2, OA3 combination, and 3 was connected to the OA4, OA5 combination. Therefore, the currents through 2&4 and 3 were identical to each other and to the current through 1&5. Peak separation in the voltammogram (Fig 3.14) obtained was found to be 155 mV, which is another 20 mV reduction in peak separation relative to the voltammogram in Fig 3.10,



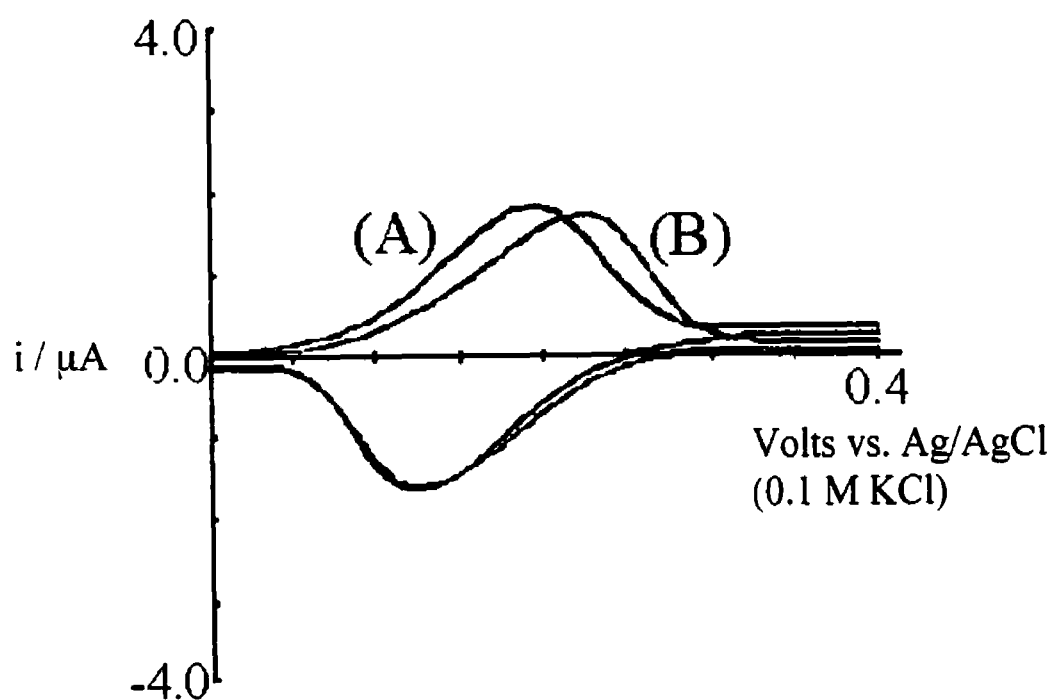
**Fig 3.14** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl using the electronic circuit to force identical currents through all the segments with 1&5 as the control electrode. Two counter electrodes were used. The scan rate was 5 mV/sec.

where no current control was utilized. As was seen before, 1&5 has the most even potential distribution associated with it. Therefore, this segment was chosen to be connected to OA1 as the control electrode. The potential at 1&5 is controlled by OA1, and the currents through 2 & 4 and 3 are then made identical to that through 1&5.

All the electrode segments are now being used, but the distribution of potential is that associated with 1&5 with a better potential distribution. This led to less peak separation. Peak current was found to be 26  $\mu\text{A}$ , which is slightly more than when no electronic control of current is involved as the result of potential distribution improvement.

### **3.1.4 Reduction of edge effects in thin-layer cells**

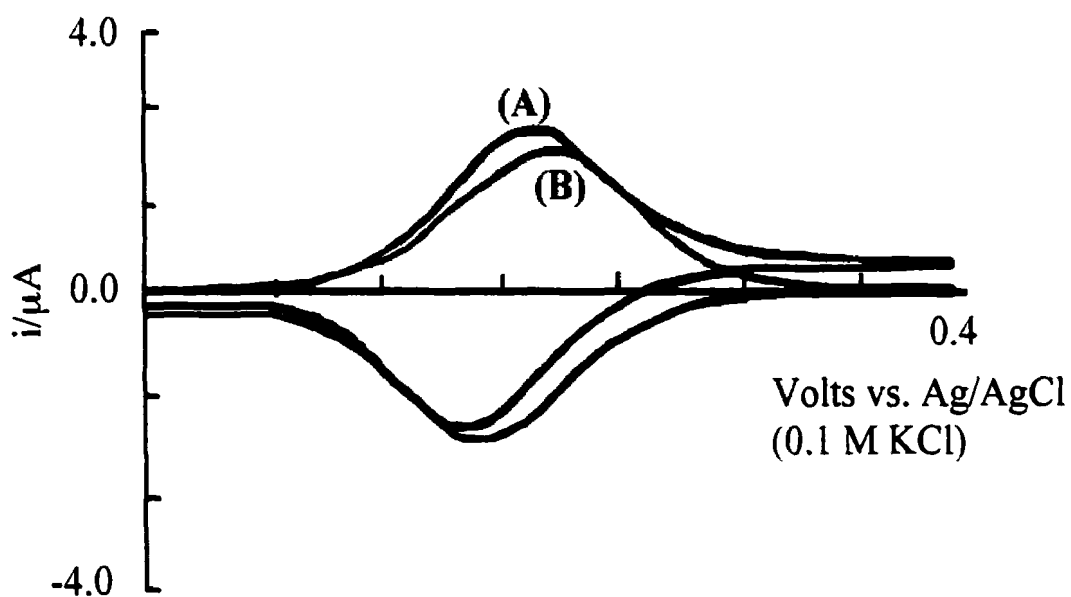
Fig 3.15(A) is the thin-layer cyclic voltammogram at segment 3 alone. The same solution and experimental conditions as before were used. The scan rate was 2 mV/sec and two counter electrodes were used. A peak separation of 67.5 mV was found for this voltammogram. Fig 3.15 (B) shows the thin-layer cyclic voltammogram of the same solution again at segment 3, when the two segments, 2 and 4, on the sides of 3, are connected to the ground of the potentiostat. This structure is called a “getter electrode”. In Fig 3.15, the current at potentials past 0.35 volts is primarily due to diffusion into the thin-layer from the edges of the electrode. As can be seen, the current due to this edge effect has been reduced noticeably when the getter electrode is used. However, there is a trade off with peak separation. Peak separation has been increased to 97.5 mV when 2 and 4 are grounded.



**Fig 3.15** Reduction of edge effect by a getter electrode. Two counter electrodes are used. (A) Cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 3; (B) Cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 3, with 2 and 4 grounded. The scan rate was 2 mV/sec.

A schematic of a getter electrode is shown in Fig 1.10. In (A), the cyclic voltammogram was collected by the working electrode lead of the potentiostat connected to segment 3. As can be seen, the current collected is due to the electrolysis of both the electroactive species that were inside the thin-layer cavity from the beginning and the electroactive species diffused inside the cavity from the bulk of solution, during the scan. This adds to the current seen at any time during the voltammetry. Since the working electrode lead of the potentiostat always sits at virtual ground, in (B), 2, 3, and 4, are all sitting at the same potential. As a result, the thin-layer cavity in which the electrochemical reaction is happening is now a larger area. However, the current collected by the working electrode lead of the potentiostat is that of segment 3. Therefore, the edges of the cavity through which the diffusion of the electroactive material is taking place, have moved away from where the current is being collected and thus that part of the current due to the electrolysis of the diffused material through the edges is at least partly eliminated. At the same time, as the dimension of the working electrode along the current path in a getter electrode is larger, the total current inside the cell is greater. This leads to higher IR drops inside the thin-layer cavity, and thus a more uniform distribution of potential results, which in turn causes more peak separation.

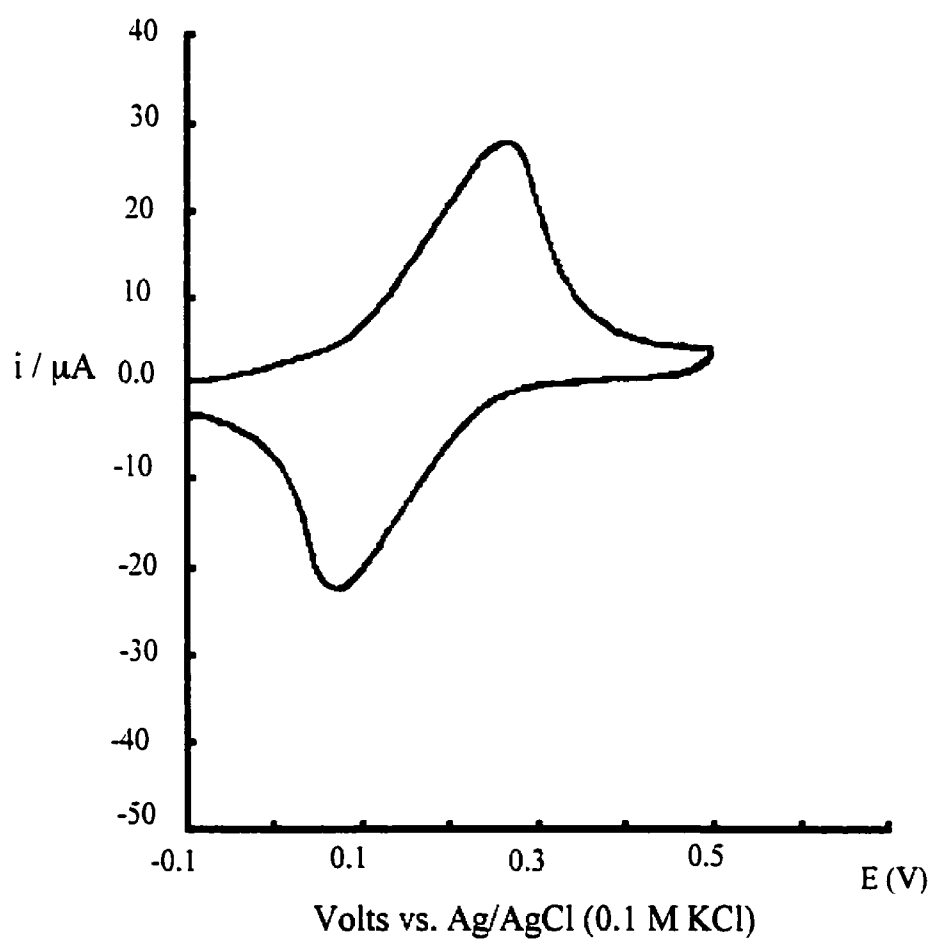
Fig 3.16 shows the edge effect reduction for segment 2. In (A), segment 2 was the working electrode. Peak separation was found to be 57 mV. In (B), current is collected by the working electrode lead of the potentiostat, while 1 and 3 are grounded. Peak separation in (B) was increased to 77 mV. Here the effect of making a getter electrode is a little bit more pronounced.



**Fig 3.16** Reduction of edge effect by a getter electrode. Two counter electrodes are used. (A) Cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 2; (B) Cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 2, with 1 and 3 grounded. The scan rate was 2 mV/sec.

Generally, edge effects are more severe for smaller electrodes. As the dimensions of the electrode get smaller, the edge area over the surface area ratio gets larger. The current due to edge effects is therefore a larger proportion of the total current. This is even worse for working electrodes with circular geometry, as there is even greater edge area / surface area ratio for smaller circular electrodes than the rectangular ones.

Edge effects can be reduced using the electronic circuit in Fig 2.7. If segment 3 is connected to OA1; 2&4 are connected to the OA2, OA3 combination; and 1&5 are connected to the OA4, OA5 combination, then the currents on the surfaces of 2&4, and 1&5, are going to be made identical to the magnitude of the currents on the surface of 3 by the circuit. Figure 3.17 shows the cyclic voltammogram when electrode 3 is thus used as the control electrode. In comparing this to the voltammogram of Fig 3.13 at electrode 3 where other segments were unused, a significant reduction in edge effect is apparent. since the reactant is now oxidized at segments 2 and 4 before it can diffuse into segment 3. It is also apparent that the peak separation in Fig 3.17 is greater than that in Fig 3.13. This is because the total current is in fact three times greater, leading to larger IR drops.



**Fig 3.17** Thin-layer cyclic voltammogram of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl using the electronic circuit to force identical currents through all the segments, with 3 as the control electrode. Two counter electrodes were used. The scan rate was 5 mV/sec.

### 3.2 Nonaqueous solutions

Nonaqueous solution are inherently more resistive towards the flow of current. Resistivity values of between 200 to 400  $\Omega$ -cm are often seen for these solutions [44]. While higher resistivity values than the above can also be found for some nonaqueous solutions, there is hardly any electrochemistry done in such resistive media. Thin-layer measurements are extremely difficult in many non-aqueous solutions because of the high solution resistance. Potential distribution corrections are thus more important for these solutions.

A series of voltammograms was obtained using 5 mM ferrocene in acetonitrile with 0.2 M tetraethylammonium perchlorate as the supporting electrolyte. In all the voltammograms, the potential was scanned from -0.1 to +1.00 volts during the anodic scan and from +1.00 to -0.1 volts during the cathodic scan. Sweep rate was 5 mV/sec. The peak potential occurred at 0.557 V vs. Ag wire. Peak potential was calculated as the average between the anodic and the cathodic peaks. Results of the cyclic voltammetry measurement with the nonaqueous solution are summarized in Table 3.3. Table 3.4 also summarizes the results of cyclic voltammetry measurements with the aqueous solution, for comparison.

As is indicated in Table 3.3, if all five Pt segments were shorted together and used as the working electrode and the counter electrode closer to the reference electrode was used, a serious peak separation of 450 mV and a peak current of 43  $\mu$ A was observed for the voltammogram. The high resistance of the solution caused more IR drop compared to the case of the aqueous solution (Table 3.4), and a very poor distribution of potential

**Table 3.3** Peak separations and peak currents for the nonaqueous solution in cyclic voltammetry experiments.

| <b>Working electrode</b>                                                 | <b>Peak separation/ mV</b> | <b>Peak current / <math>\mu\text{A}</math></b> |
|--------------------------------------------------------------------------|----------------------------|------------------------------------------------|
| Five Pt segments and one counter electrode                               | 450                        | 43                                             |
| Five Pt segments and two counter electrodes                              | 240                        | 69                                             |
| Five Pt segment, two counter electrodes and 1&5 as the control electrode | 220                        | 71                                             |
| Five Pt segment, two counter electrodes and 3 as the control electrode   | 265                        | 60                                             |

**Table 3.4** Peak separations and peak currents for the aqueous solution in cyclic voltammetry experiments.

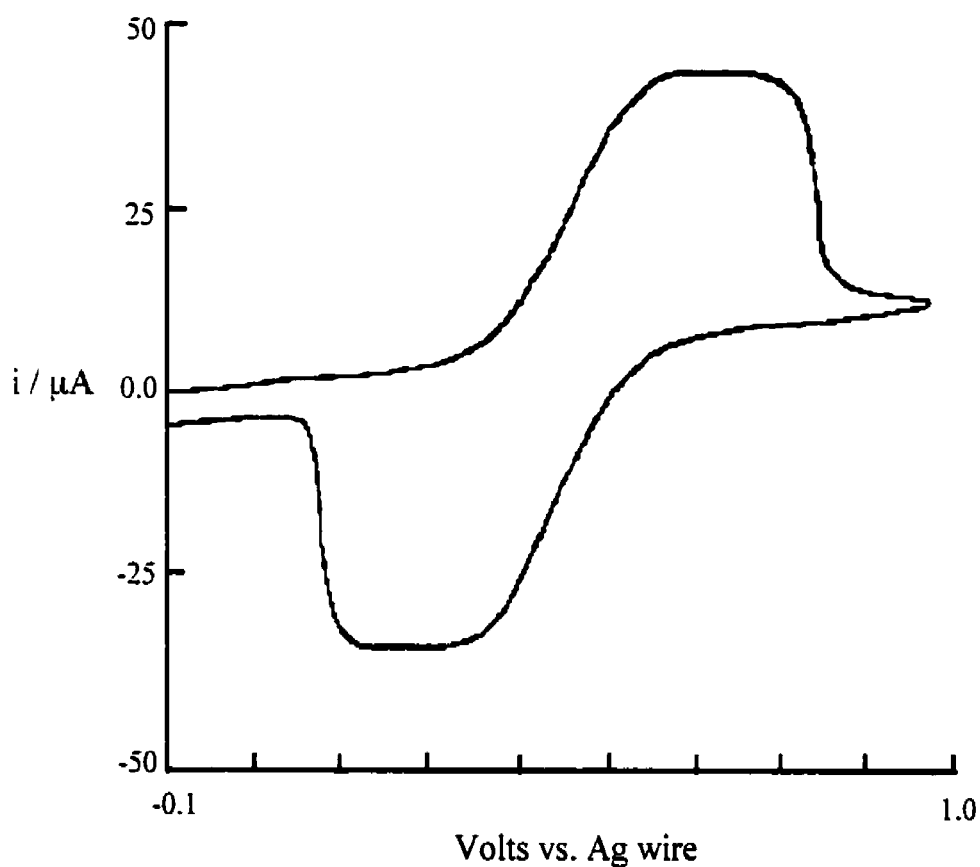
| Working electrode                                                        | Peak separation / mV | Peak current / $\mu\text{A}$ |
|--------------------------------------------------------------------------|----------------------|------------------------------|
| Five Pt segments and one counter electrode                               | 300                  | 18                           |
| Five Pt segments and two counter electrodes                              | 175                  | 23                           |
| Five Pt segment, two counter electrodes and 1&5 as the control electrode | 155                  | 26                           |
| Five Pt segment, two counter electrodes and 3 as the control electrode   | 190                  | 21                           |

results. The peaks were severely distorted (Fig 3.18) indicating that a large resistance and thus a very nonuniform potential distribution existed in the cell. If all five Pt segments were shorted together and used with both stainless steel counter electrodes, peak separation was almost cut into half (Table 3.3). The thin-layer voltammogram was less distorted (Fig 3.19) compared to when only one counter electrode was used.

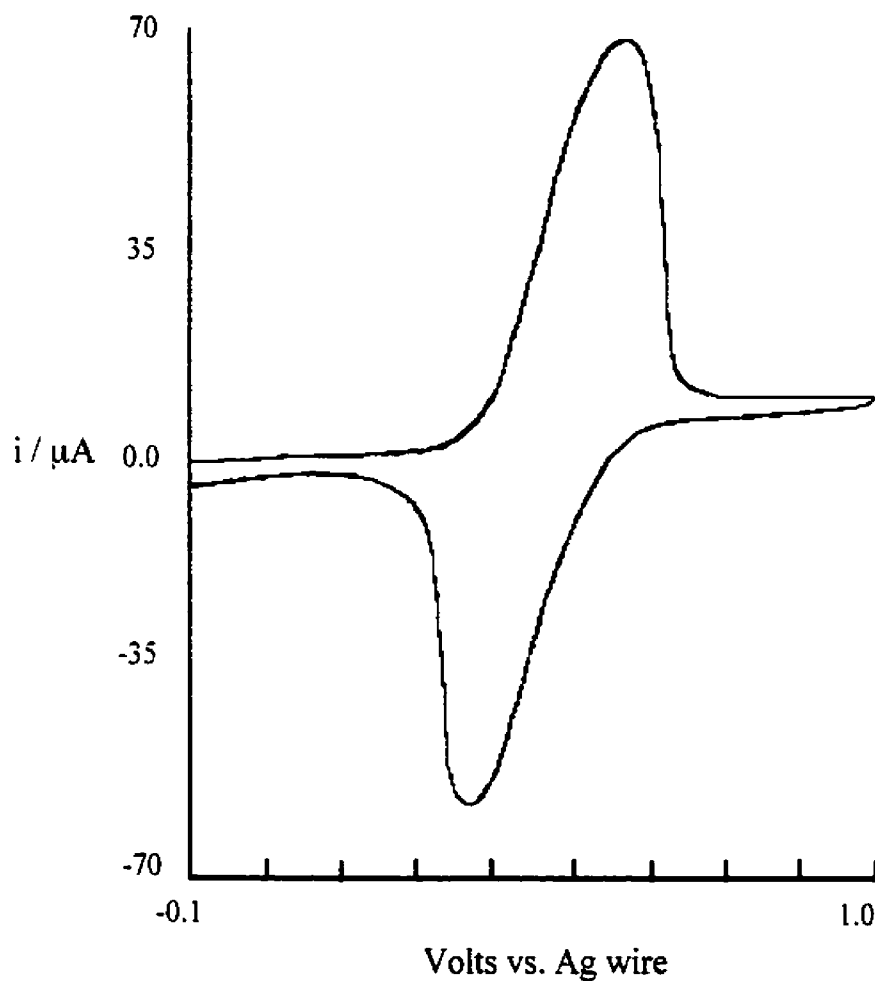
Fig 3.20 shows the voltammogram obtained from the same solution when the electronic circuit was used. Both stainless steel counter electrodes were used. 1&5 was connected to OA1 as the control electrode in the electronic circuit of Fig 1.10. 2&4 was connected to the OA2, OA3 combination, and 3 was connected to the OA4, OA5 combination. According to Table 3.3 and Fig 3.20, the voltammogram was again less distorted than when the current was not controlled by the circuit.

Fig 3.21 shows the voltammogram obtained when 3 was connected to OA1 as the control electrode. 2&4 was also connected to the OA2, OA3 combination, and 1&5 was connected to OA4, OA5 combination. so that currents on all three segments would be identical to that on 3. While peak separation was more than when 1&5 was used as the control electrode, due to the higher uncompensated resistance associated with segment 3, less current due to the edge effect was observed in the voltammogram.

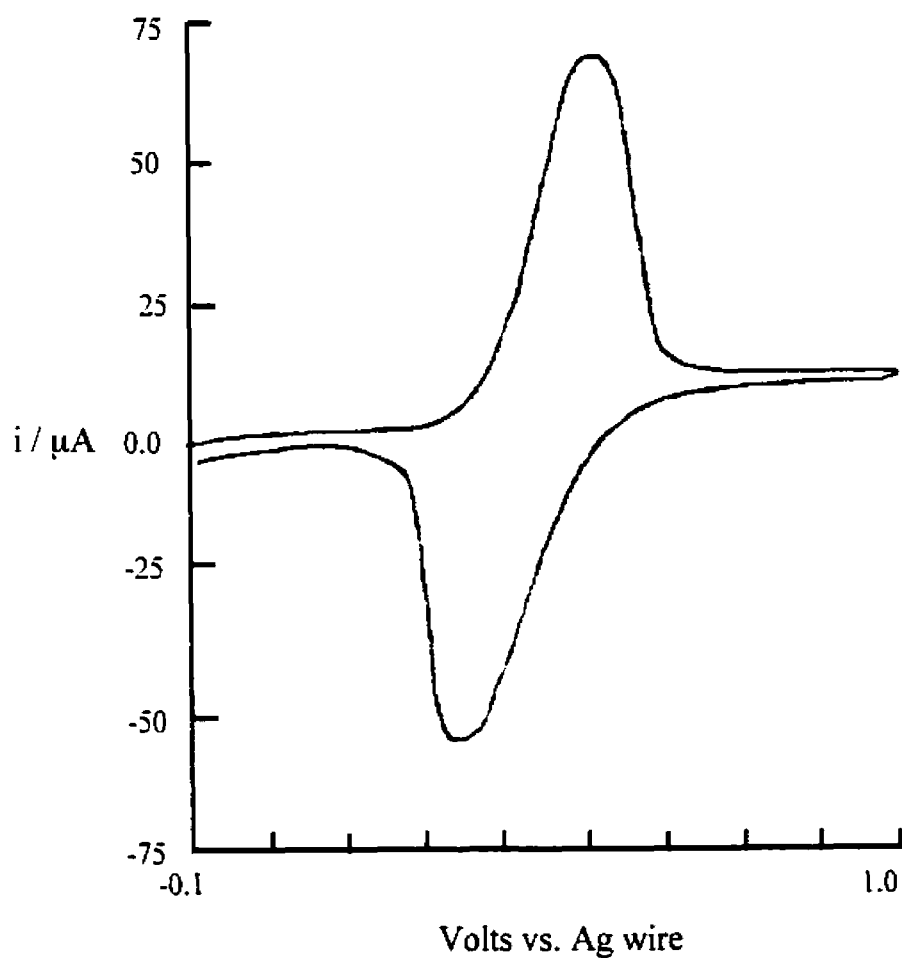
In comparison between tables 3.3 and 3.4, it is clear that the trend in peak separation is the same as for the aqueous and nonaqueous solutions. The only difference is that the magnitude of peak separations in the nonaqueous solutions are much higher than the aqueous solutions because of the higher inherent solution resistance associated with the nonaqueous solutions. Therefore, the improvement in the potential distribution is more pronounced in nonaqueous media.



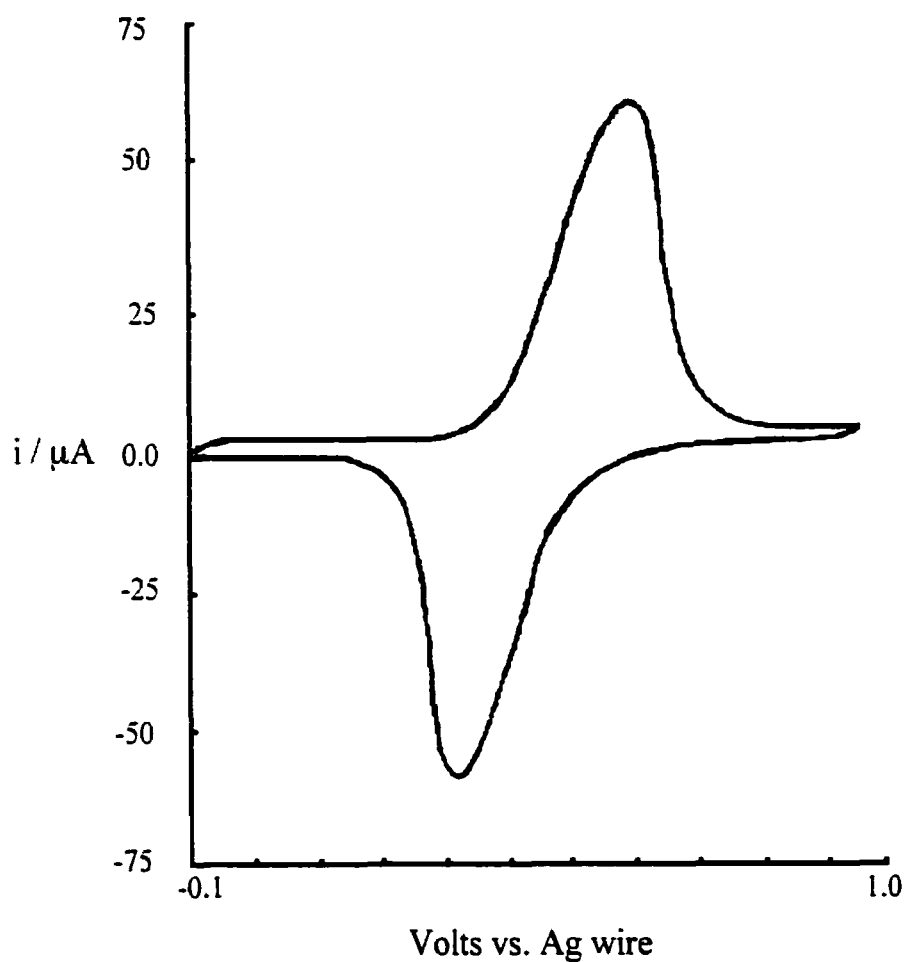
**Fig 3.18** Thin-layer cyclic voltammogram of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five Pt segments. The counter electrode closer to the Luggin capillary was used. The scan rate was 5 mV/sec.



**Fig 3.19** Thin-layer cyclic voltammogram of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five Pt segments. Two counter electrodes were used. The scan rate was 5 mV/sec.



**Fig 3.20** Thin-layer cyclic voltammogram of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate using the electronic circuit to force identical currents through all the segments, with 1&5 as the control electrode. Two counter electrodes were used. The scan rate was 5 mV/sec.



**Fig 3.21** Thin-layer cyclic voltammogram of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate using the electronic circuit to force identical currents through all the segments, with 3 as the control electrode. Two counter electrodes were used. The scan rate was 5 mV/sec.

## CHAPTER FOUR

### POTENTIAL STEP MEASUREMENTS

#### 4.1 Aqueous solutions

##### 4.1.1 Amperometric measurements

As was mentioned before, thin-layer cells offer very short electrolysis times to the electrochemist. In potential step experiments, the potential is stepped from a value well before the electrochemical reaction of interest can happen to a value well after the reaction, and is held at that value for a period of time during which the current is allowed to decay. The current/time characteristic of the system under investigation is collected meanwhile. The area under the current/time plot represents the total charge that is passed during the electrolysis. Thin-layer electrolysis measurements take place in considerably shorter times than the conventional bulk electrolysis experiments. Furthermore, determination of the endpoint is much easier when thin-layer cells are used because the current falls rapidly to background levels. In bulk electrolysis, the current decays very slowly, making it difficult to judge when background levels have been reached. However, the high resistance inside the thin-layer cells and the resulting non-uniform potential distribution often prevents the cell from functioning in its best way and complete electrolysis would take longer than expected by the theory. Improvement of potential distribution in thin-layer cells is important in potential step measurements for the reason of achieving even shorter electrolysis times.

The same aqueous solution as before was used for potential step experiments. The potential was first held for 4 seconds at 0.0 mV, after which it was stepped to 400 mV

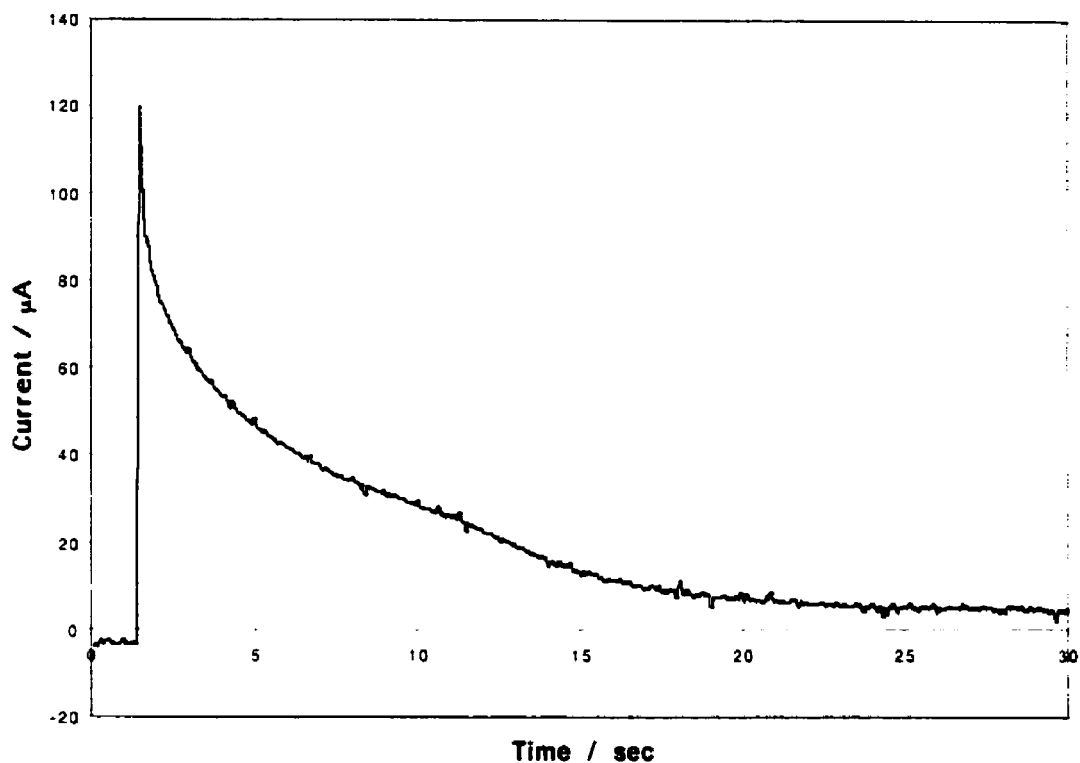
and was held there to let the current decay back to background levels. The total experiment time was 30 seconds.

As is shown in Table 4.1, it took ~18 seconds for the current to decay to a nearly constant value, when all five electrode segments were shorted together and used as the working electrode, and the counter electrode closer to the reference electrode was used. This time was reduced to ~12 seconds when both stainless steel counter electrodes were used with of all five working electrode segments used. The smaller analysis time achieved when two counter electrodes were used is an indication of an improvement in potential distribution and confirms the results of the cyclic voltammetry measurements.

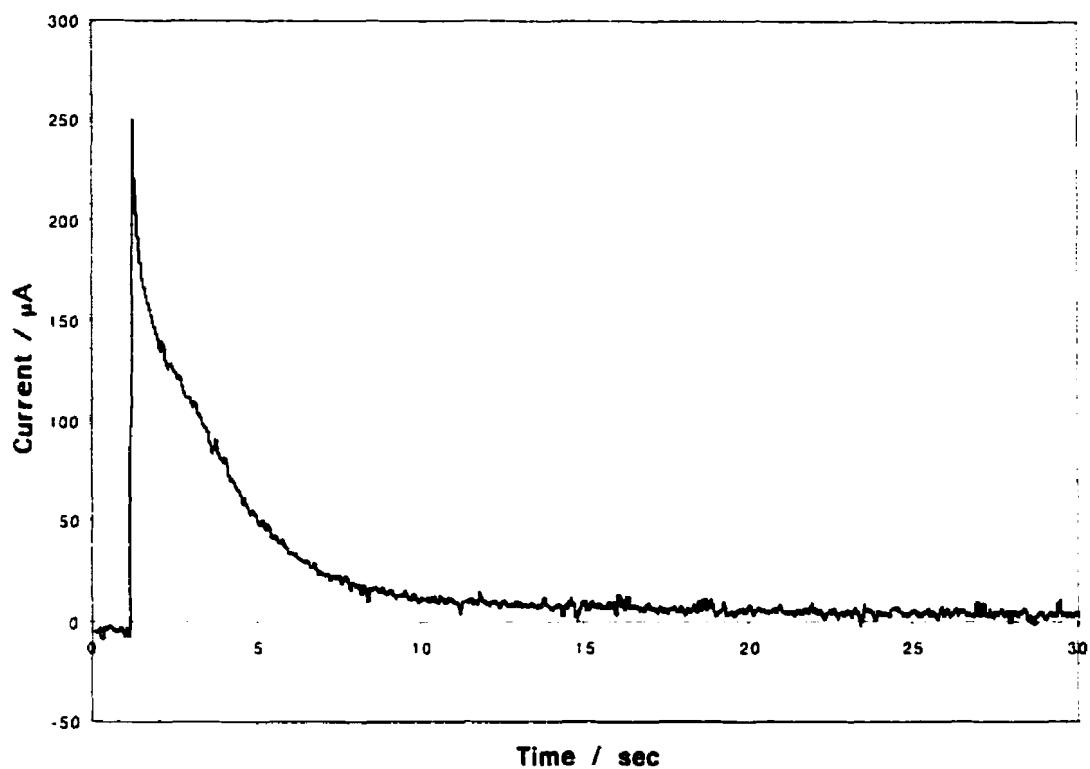
If segments 1 and 5 were shorted together and connected to OA1; 2 and 4 were shorted together and connected to the OA2. OA3 combination; and 3 was connected to the OA4. OA5 combination the electrolysis time was found to be 7 seconds. Therefore, the potential distribution was further improved by forcing identical currents through all electrodes. On the other hand, if 3 was connected to OA1; 2&4 was connected to the OA2. OA3 combination, and 1&5 was connected to the OA4. OA5 combination; the electrolysis time was increased to 9 seconds. Thus the potential distribution got worse as the control electrode was segment 3 with more uncompensated resistance. Figures 4.1-4.4 show these current/time curves obtained during the amperometric measurements.

**Table 4.1** Results of the amperometric measurements for the aqueous solution.

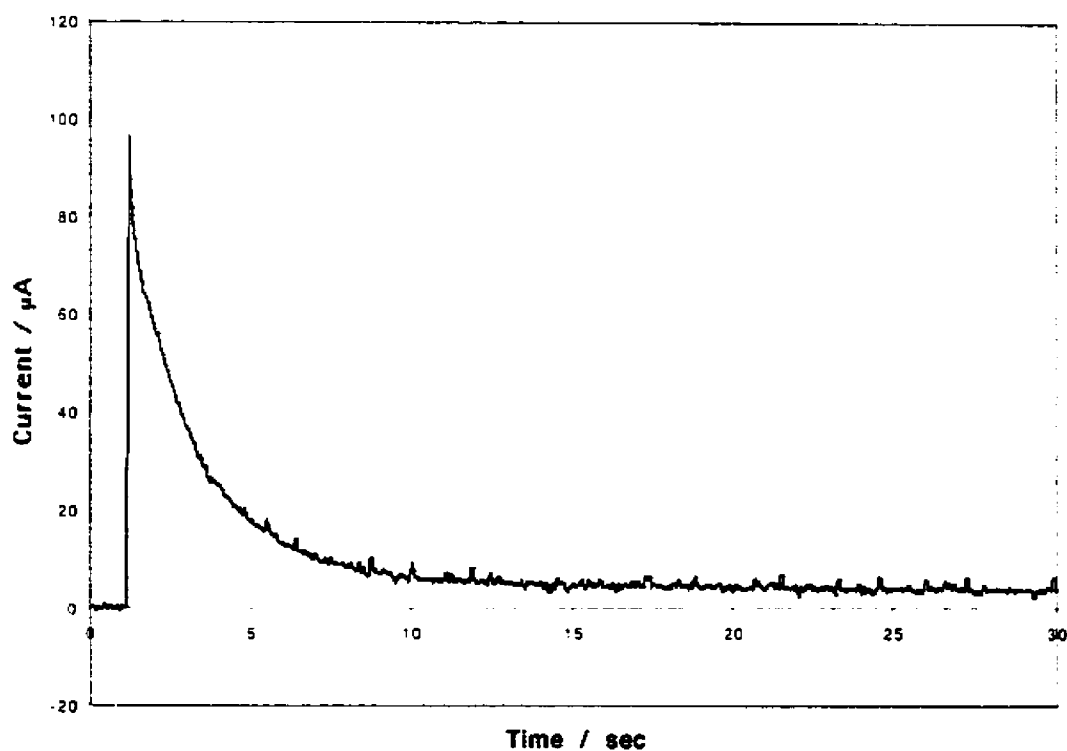
| Experiment condition                                                       | Electrolysis time / sec |
|----------------------------------------------------------------------------|-------------------------|
| Five Pt segments and one counter electrode                                 | ~18                     |
| Five Pt segments and two counter electrodes                                | ~12                     |
| Five Pt segments, two counter electrodes, and 1&5 as the control electrode | ~7                      |
| Five Pt segments, two counter electrodes, and 3 as the control electrode   | ~9                      |



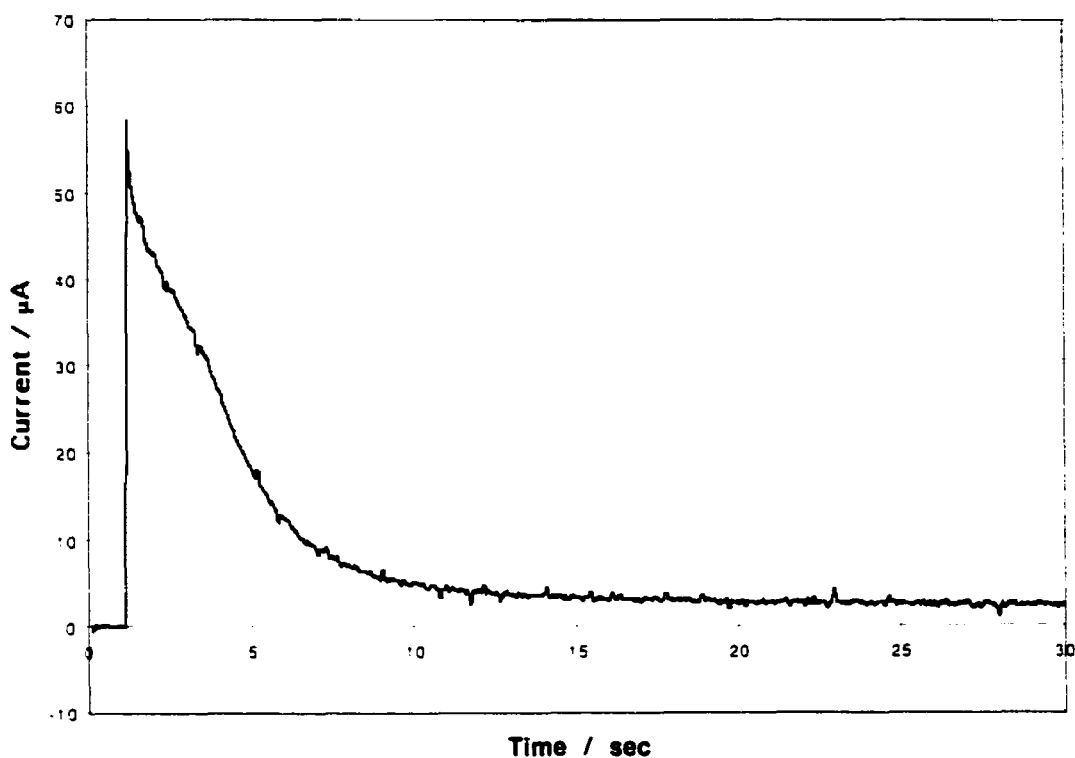
**Fig 4.1** Current/time characteristic of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes. The counter electrode closer to the Luggin capillary was used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds.



**Fig 4.2** Current/time characteristic of 1 mM  $K_4Fe(CN)_6$  in 0.1 M KCl at all five electrodes. Two stainless steel counter electrodes were used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds.



**Fig 4.3** Current/time characteristic of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes, using the electronic circuit to force identical currents through all the segments with 1&5 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds.



**Fig 4.4** Current/time characteristic of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes, using the electronic circuit to force identical currents through all the segments with 3 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds.

### 4.1.2 Coulometric measurements

In coulometric measurements, the current is integrated, so that the charge passed as a function of time is obtained. Integration smoothes random noises on the current/time plots. Therefore, coulometric records are generally less noisy than the amperometric plots. In addition, the contribution of the double-layer charging and the electrochemical reactions of adsorbed species are more distinguishable from those due to the diffusion of the electroactive materials and to the electrochemical reaction.

Equation (4-1) describes the charge/time relationship for an oxidation reaction in a diffusion-limited system [4].

$$Q = \frac{2nFAD_R^{1/2}C^\circ t^{1/2}}{\pi^{1/2}} + Q_{dl} \quad (4-1)$$

where  $Q$  is the total charge passed,  $n$  is the number of electrons involved in the electrochemical reaction,  $F$  is the Faraday number,  $A$  is the electrode area,  $D_R$  is the diffusion coefficient of the reactant, here being the reduced form,  $C^\circ$  is the initial concentration of the reactant, and  $t$  is the time.  $Q_{dl}$  represents the capacitive charge or the charge due to the charging of the double-layer. According to equation (4-1), the plot of  $Q$  vs.  $t^{1/2}$  is linear with an intercept of  $Q_{dl}$ , the charge required to charge up the double-layer.

In the case when a reactant adsorbs to the electrode surface, the  $Q$  vs.  $t^{1/2}$  relation becomes,

$$Q = \frac{2nFAD_R^{1/2}C^\circ t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA\Gamma_R \quad (4-2)$$

Here,  $nFA\Gamma_R$  is the faradaic component for the electrochemical reaction of adsorbed species.  $\Gamma_R$  is the *surface excess* of the reactant (here, the reduced form) in mole/cm<sup>2</sup>. Thus the plot of  $Q$  vs.  $t^{1/2}$  at later times, is displaced along the charge axis by a certain amount. The slope of equation (4-2) is often used for the determination of diffusion coefficient, and the intercept is used to determine the surface excess.

In a thin-layer system, similar to the case of an adsorbed reactant, rapid electrolysis of the thin-layer solution confined next to the electrode is expected. This is followed by electrolysis of species diffusing into the cavity from the bulk of solution. By analogy to the case of adsorbed reactant, the coulometric response may be anticipated to follow equation (4-3).

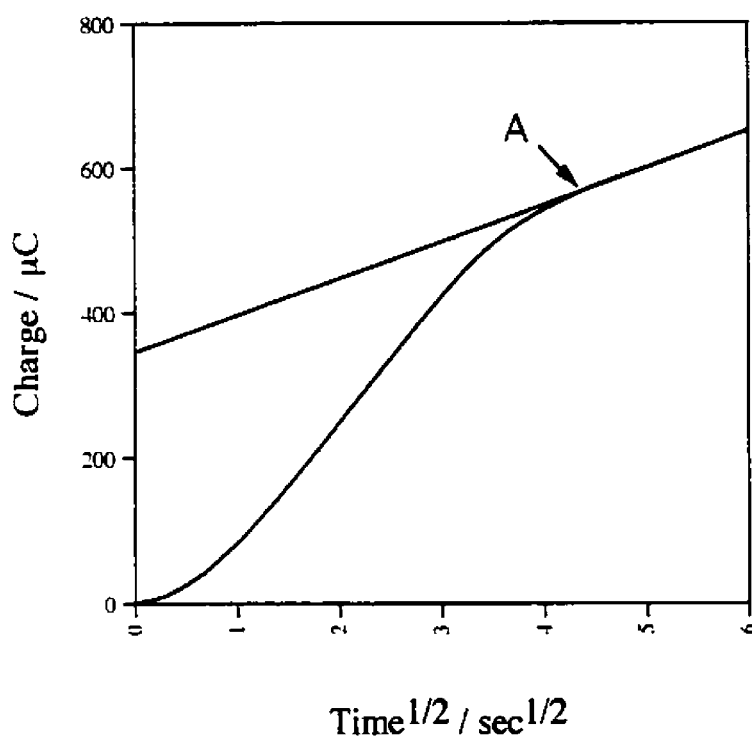
$$Q = \frac{2nFAD_R^{1/2}C^\circ t^{1/2}}{\pi^{1/2}} + Q_{tl} + Q_{dl} \quad (4-3)$$

where,  $Q_{tl}$  is the charge due to the electrolysis in the thin-layer cavity. At later times, a plot of  $Q$  vs.  $t^{1/2}$  is expected to give a straight line displaced upward by an amount  $Q_{tl}$ .

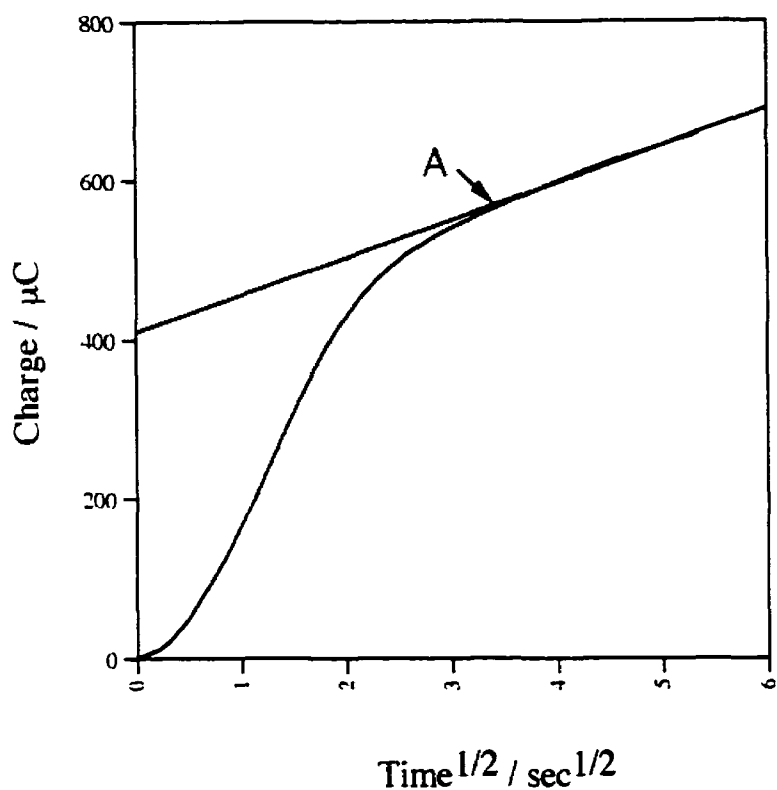
The area under the current/time plots of figures 4.1-4.4 were integrated and plotted against time. The results of these integrations are summarized in Table 4.2. Figures 4.5-4.8 show the actual charge/ $t^{1/2}$  plots. At later times, linear behavior is observed, indicating completion of electrolysis and diffusion control. In comparing the two cases where all five Pt segments were shorted together as one working electrode, it was found that when

**Table 4.2** Results of the coulometric measurements for the aqueous solution.

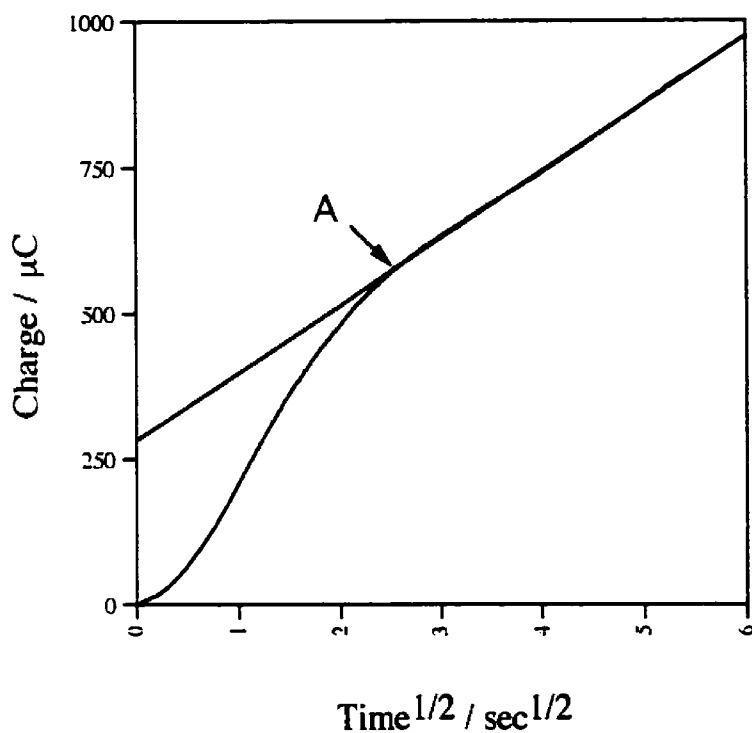
| <b>Experiment conditions</b>                                               | <b>Electrolysis time / sec</b> | <b>Total charge / <math>\mu</math> C</b> | <b>Slope / <math>\mu</math>C. sec<sup>-1/2</sup></b> | <b>Intercept / <math>\mu</math>C</b> |
|----------------------------------------------------------------------------|--------------------------------|------------------------------------------|------------------------------------------------------|--------------------------------------|
| Five Pt segments and one counter electrode                                 | 18.5                           | 570                                      | 51.0                                                 | 345.6                                |
| Five Pt segments and two counter electrodes                                | 12.6                           | 570                                      | 46.8                                                 | 409.6                                |
| Five Pt segments, two counter electrodes, and 1&5 as the control electrode | 6.8                            | 560                                      | 115.3                                                | 282.3                                |
| Five Pt segments, two counter electrodes, and 3 as the control electrode   | 9                              | 540                                      | 75.3                                                 | 311.7                                |



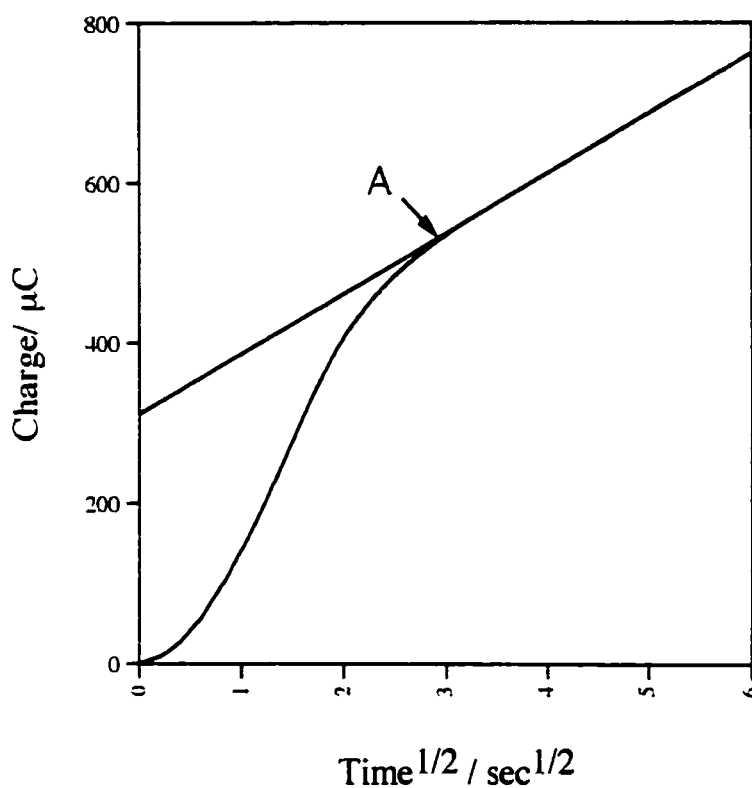
**Fig 4.5** Charge/time characteristic of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes. The counter electrode closer to the Luggin capillary was used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds. Point A is the onset of the diffusion-controlled behavior.



**Fig 4.6** Charge/time characteristic of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes. Two counter electrodes were used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds. Point A is the onset of the diffusion-controlled behavior.



**Fig 4.7** Charge/time characteristic of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes, using the electronic circuit to force identical currents through all the segments with 1&5 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds. Point A is the onset of the diffusion-controlled behavior.



**Fig 4.8** Charge/time characteristic of 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl at all five electrodes, using the electronic circuit to force identical currents through all the segments with 3 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag/AgCl (0.1M). The potential was pulsed to 400 mV from an initial value of 0.0 mV. The total experiment time was 30 seconds. Point A is the onset of the diffusion-controlled behavior.

one counter electrode was used (Table 4.2), the time corresponding to the endpoint (point A in Fig 4.5) was 18.5 seconds. At this point, the total charge passed was  $\sim 570 \mu\text{C}$ . The intercept of this plot, resulting from the extrapolation of the straight part due to the diffusion charge, has a value of  $345.6 \mu\text{C}$ . When two counter electrodes were used, the electrochemical reaction endpoint was reached in 12.6 seconds, which confirms the results from the amperometric measurements. The total charge corresponding to the endpoint (point A in Fig 4.6) was found to be  $\sim 570 \mu\text{C}$  which is the same charge as the case of using only one counter electrode.

When the circuit was used to force identical currents to the electrode segments, with 1&5 as the control electrode, then most of the charge was passed at 6.8 seconds (point A in Fig 4.7). This is considerably less than when the circuit was not used. The total charge associated with this point was  $\sim 560 \mu\text{C}$ , which is in very close agreement with the charges found in the previous experiments. On the other hand, when segment 3 was the control electrode, the endpoint (point A in Fig 4.8) was reached at 9 seconds. The longer time reflects the fact that there is more uneven potential distribution in the cell when 3 is the control electrode. The charge corresponding to the endpoint was found to be  $\sim 540 \mu\text{C}$  which is still within reasonable agreement. When using the circuit, current was collected from the output of OA1, which is the current through only 1&5. Therefore, currents were multiplied by 3 before integration, to get the total current inside the cell.

Equation (4-3) assumes that at  $t = 0$ , the double-layer is charged instantly and the system is diffusion –controlled. This may not be true in reality for two main reasons:

1. The high uncompensated resistance inside the cell and the resulting IR drop, would cause a delay in double-layer charging. The RC time constant associated with charging the double-layer increases along the current path.
2. Since the thin-layer cavity has a finite thickness, a finite time is required for complete electrolysis to occur and to establish pure diffusion control.

Therefore, we are justified to say that the intercept of this plot is not really a good indication of where the reaction gets into the pure diffusion-controlled situation. On the other hand, the charges at the onset of diffusion-controlled behavior (point A) were in very close agreement. Therefore, we believe that taking the charge corresponding to point (A) as the total charge passed during the electrolysis is a reasonable choice.

The slope of the diffusion-controlled part of the plot is an indication of the amount of charge due to the diffusion. There may be some contribution to the charge from oxidation of impurities, oxidation of solvent, and formation of Pt oxide on the surface as well. The slopes of the two plots obtained without the use of the circuit were very close, as indicated in Table 4.2. The slopes of the plots obtained using the circuit, however, are significantly larger than the slopes of the plots obtained when the circuit was not used. When 1&5 is the control electrode, the potential at 1&5 is controlled, and identical currents are forced to the other segments. Therefore, the total current in the cell is now three times the current on just 1&5. The current at 1&5 is a contribution of two currents: a) the current due to the electrochemical reaction, and b) the current due to the electrolysis of the diffused species (edge effect) and the impurities. Segment 1&5 is the only segment that suffers from the diffusion through the edges of the cavity when the circuit is being used. The circuit imposes this additional current on the other segments, so

that diffusion current is three times that when no current is used. When the slope increases, the intercept resulting from the extrapolation of the diffusion-limited part becomes smaller. Of course, this slope is less in the case of 3 as the control electrode than 1&5 as the control electrode, because the current due to the diffusion through the edges is negligible for 3. However, the slope is still larger for 3 as the control electrode, than when the circuit is not used. This might be due to the fact that when the circuit is not used, the potential drops along the current path and there is a large potential drop at 3, whereas, when 3 is used as the control electrode, the potential at this segment is being controlled and thus, is higher. The higher potential may result in larger current due to impurity oxidation, solvent oxidation, or oxide formation. The circuit imposes the additional current on the other electrodes as well.

## **4.2 Nonaqueous solutions**

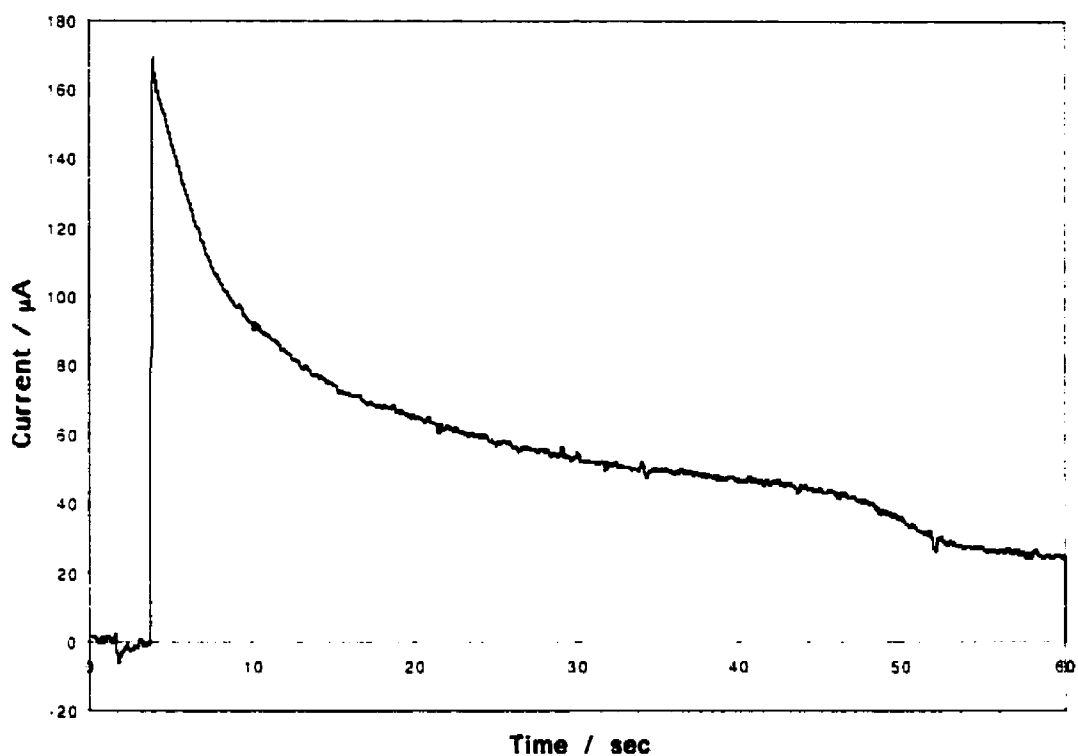
### **4.2.1 Amperometric measurements**

Potential improvement in thin-layer cells is more critical for more resistive nonaqueous solutions. Results from the amperometric experiments for 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate (Figures 4.9-4.12) are summarized in Table 4.3. The potential was pulsed from -0.1 volts to +1.00 volts and was held there for a total of 60 seconds. Fig 4.9 shows the current/time behavior of the above solution when all five Pt segments are shorted together and the counter electrode closer to the reference electrode was used. It took ~50 seconds for the current to decay to background levels. When two counter electrodes were used with the five Pt segments shorted together (Fig 4.10), the electrolysis time was reduced to ~ 20 seconds. The difference between the electrolysis times when one and two counter electrodes are used, is much more drastic than in the case of the aqueous solution. This indicates how serious the uneven potential distribution is and how important it is to improve this distribution in nonaqueous solutions.

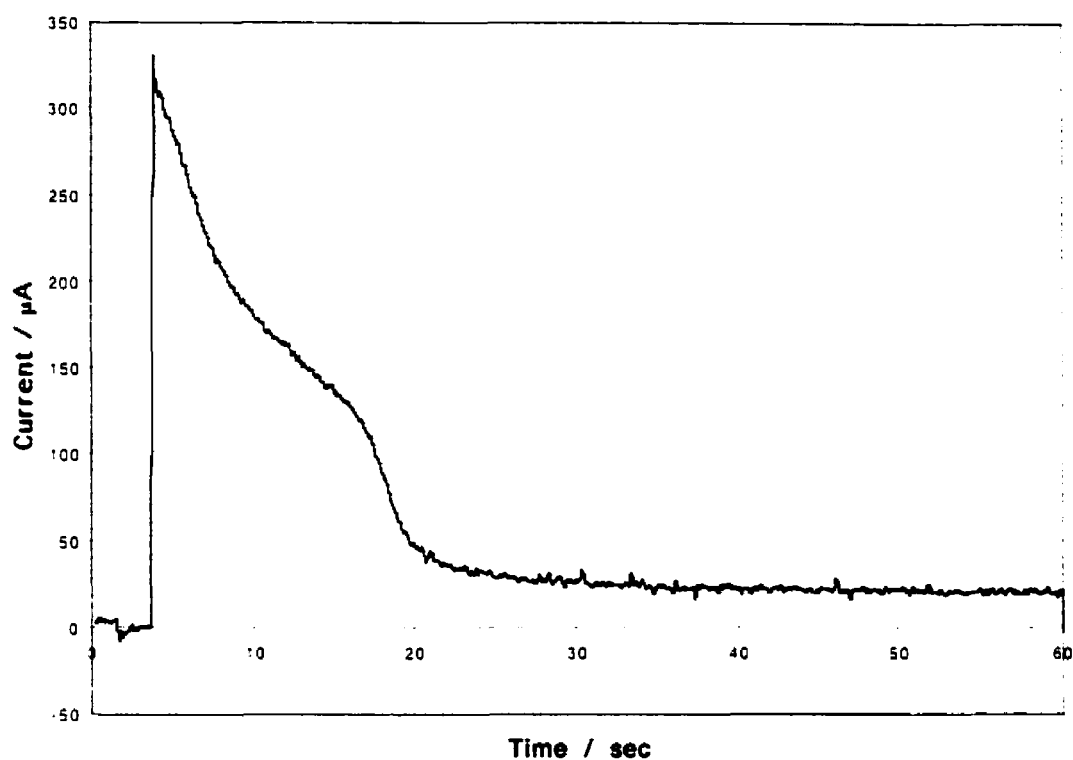
When 1&5 was connected to OA1 of the electronic circuit, the electrolysis time was further reduced to ~12 seconds. Current fell sharply to background levels. However, when segment 3 was connected to OA1 as the control electrode, electrolysis took more time than when 1&5 was the control electrode. The more uncompensated resistance associated with 3, and the resulting potential drop across the working electrode, caused the electrolysis time to increase to about 20 seconds. Fig 4.12 shows the current/time plot of this system when 3 is the control electrode.

**Table 4.3** Results of the amperometric measurements for the nonaqueous solution.

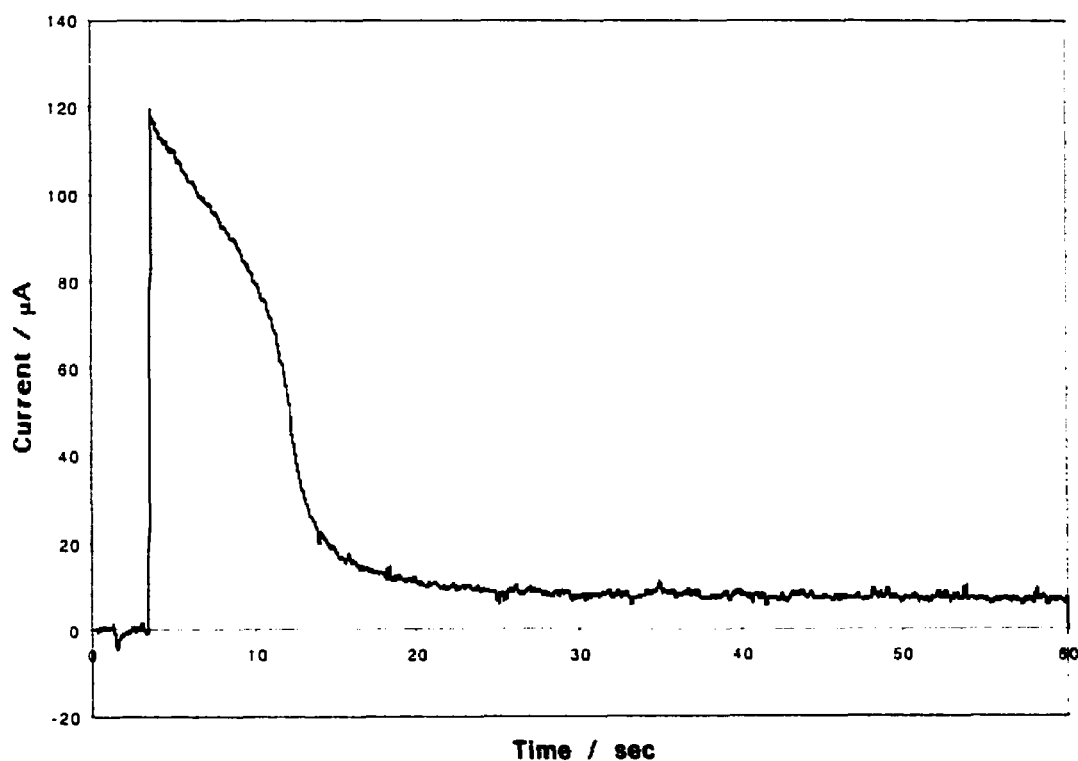
| Experiment condition                                                       | Electrolysis time / sec |
|----------------------------------------------------------------------------|-------------------------|
| Five Pt segments and one counter electrode                                 | ~50                     |
| Five Pt segments and two counter electrodes                                | ~20                     |
| Five Pt segments, two counter electrodes, and 1&5 as the control electrode | ~12                     |
| Five Pt segments, two counter electrodes, and 3 as the control electrode   | ~20                     |



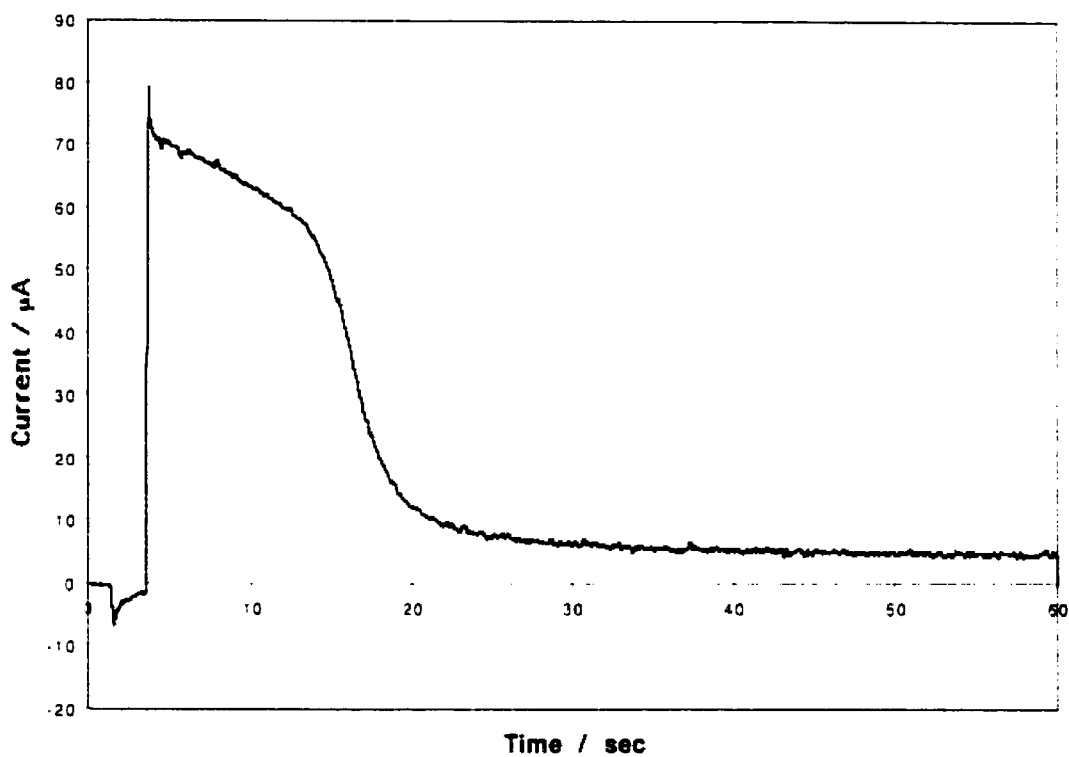
**Fig 4.9** Current/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes. The counter electrode closer to the Luggin capillary was used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds.



**Fig 4.10** Current/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes. Two counter electrodes were used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds.



**Fig 4.11** Current/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes, using the electronic circuit to force identical currents through all the segments with 1&5 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds.



**Fig 4.12** Current/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes, using the electronic circuit to force identical currents through all the segments with 3 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds.

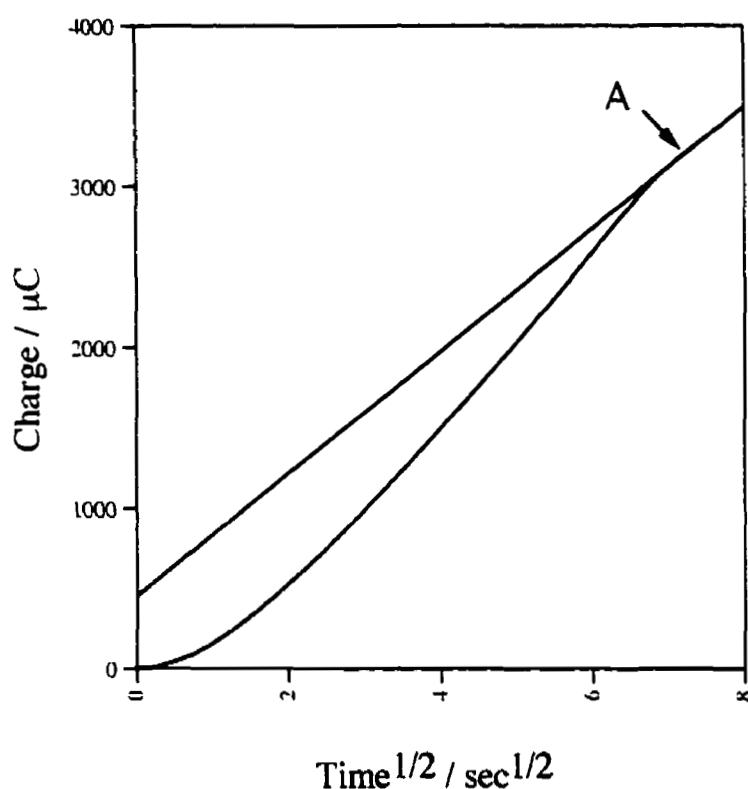
The charge vs. time curves for the nonaqueous system have a much more bumped appearance than in the aqueous systems. The current/time profile initially shows a relatively constant slope, after which it falls rapidly. This may be due to the higher solution resistance limiting the total current at the beginning of the potential step where the current is expected to be higher. Also, the theoretical chronoamperometric response has not, to our knowledge, been calculated. It seems possible that the sharp drop in current at later times might be associated with the concentration gradient within the thin-layer cavity extending all the way across the thin-layer thickness. At this point, it can extend no further, and the current drops rapidly.

#### **4.2.2 Coulometric measurements**

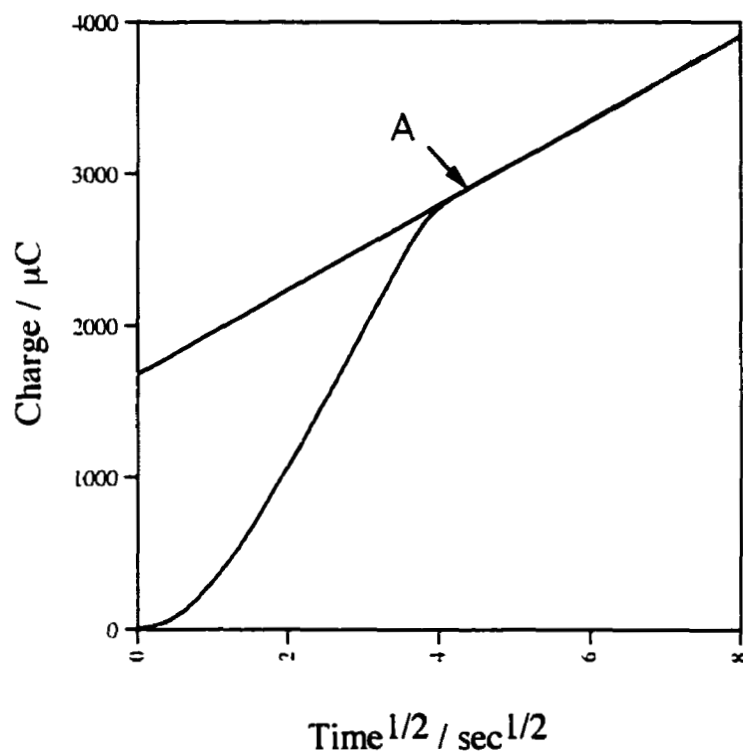
The area under each of the current/time plots discussed was integrated and again plotted against  $t^{1/2}$ . The total electrolysis time and the total charge passed during the electrolysis was obtained from these plots. The results are shown in Table 4.4. According to this table, the trend in the electrolysis times was as expected. There is, in fact, a very drastic improvement in the analysis time and therefore, potential distribution, by going to two counter electrodes instead of only one. Using 1&5 as the control electrode when utilizing the circuit, improves the distribution of potential as indicated by even smaller electrolysis time. Of course, when 3 was the control electrode, the time was increased compared to the case of 1&5 as the control electrode, and even when the electronic circuit was not used. Figures. 4.13-4.16 show the coulometric plots for the nonaqueous solution.

**Table 4.4** Results of the coulometric measurements for the nonaqueous solution.

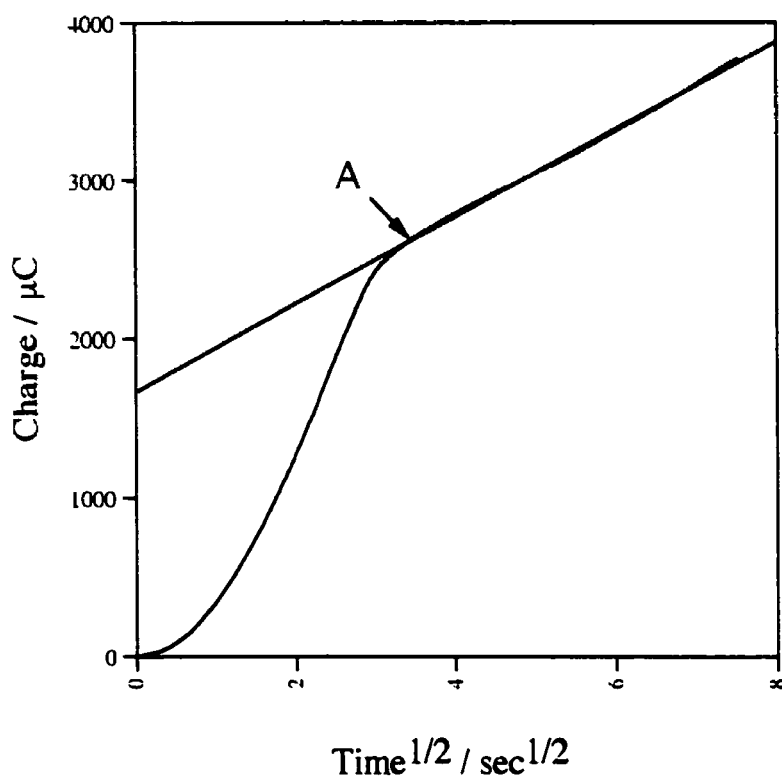
| <b>Experiment conditions</b>                                               | <b>Electrolysis time / sec</b> | <b>Total charge / <math>\mu\text{C}</math></b> | <b>Slope / <math>\mu\text{C} \cdot \text{sec}^{-1/2}</math></b> | <b>Intercept / <math>\mu\text{C}</math></b> |
|----------------------------------------------------------------------------|--------------------------------|------------------------------------------------|-----------------------------------------------------------------|---------------------------------------------|
| Five Pt segments and one counter electrode                                 | 51.8                           | 3160                                           | 380.1                                                           | 460.1                                       |
| Five Pt segments and two counter electrodes                                | 18.5                           | 2850                                           | 277.9                                                           | 1684.3                                      |
| Five Pt segments, two counter electrodes, and 1&5 as the control electrode | 11.9                           | 2560                                           | 275.9                                                           | 1671.9                                      |
| Five Pt segments, two counter electrodes, and 3 as the control electrode   | 19.36                          | 2560                                           | 197.9                                                           | 1783.6                                      |



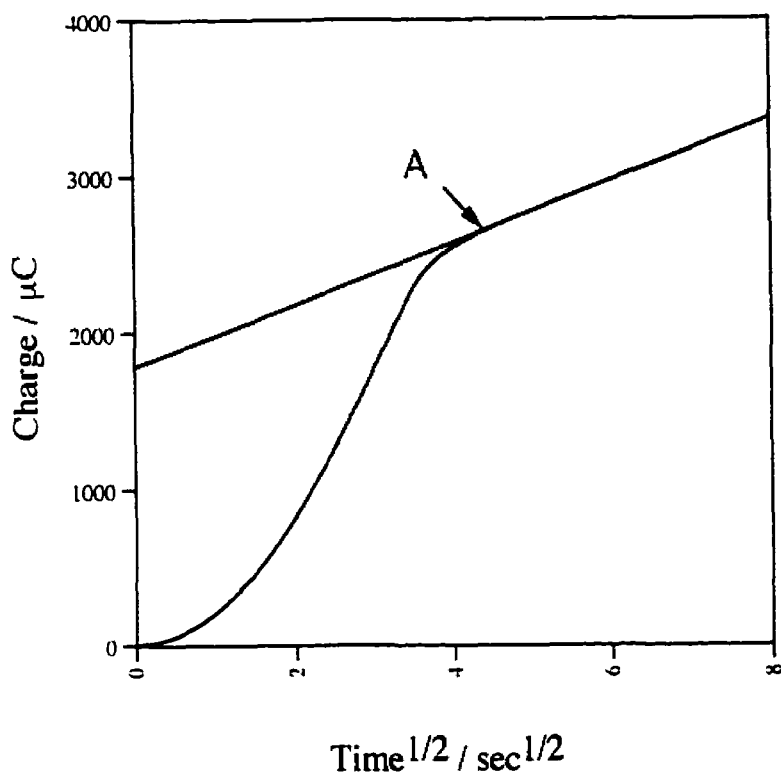
**Fig 4.13** Charge/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes. The counter electrode closer to the Luggin capillary was used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds. Point A is the onset of the diffusion-controlled behavior.



**Fig 4.14** Charge/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes. Two counter electrodes were used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds. Point A is the onset of the diffusion-controlled behavior.



**Fig 4.15** Charge/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes, using the electronic circuit to force identical currents through all the segments with 1&5 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds. Point A is the onset of the diffusion-controlled behavior.



**Fig 4.16** Charge/time characteristic of 5 mM ferrocene in 0.2 M tetraethylammonium perchlorate at all five electrodes, using the electronic circuit to force identical currents through all the segments with 3 as the control electrode. Two stainless steel counter electrodes were used. Reference electrode was Ag wire. The potential was pulsed to 1000 mV from an initial value of -100 mV. The total experiment time was 60 seconds. Point A is the onset of the diffusion-controlled behavior.

The total charges at the endpoint, observed at the onset of pure diffusion behavior, were within very close agreement. The total charge seen when only one counter electrode was used (Fig 4.13) was significantly higher than all the other plots. This can be attributed to more diffusion taking place because of the fact that longer time is needed for complete electrolysis in this system with very poor potential distribution. The experiment time here was 60 seconds. It looks like complete electrolysis needed more time than the experiment time. It is possible that the onset of the diffusion-controlled behavior be more distinguishable if the reaction was given more time. Therefore, the slope is not reliable for interpretation of the behavior of the system.

The slope of the plot when 3 was the control electrode was considerably smaller than all the other cases, indicating that less diffusion is taking place in this case.

The results of the amperometric and coulometric experiments agreed with the ones obtained from the voltammetric measurements. These experiments showed that the effect of improving the potential distribution is even more dramatic in the case of more resistive nonaqueous solutions.

## CHAPTER FIVE

### CONCLUSION

Potential distribution across the thin-layer working electrode was studied in a thin-layer electrochemical cell that was designed in our lab. Theoretically, all points on the surface of the working electrode should be equidistant from the counter electrode for a uniform distribution of potential on the working electrode surface. This criterion can hardly be met in a thin-layer cell in which current flowing between the thin-layer working electrode and the counter electrode travels the length of a very thin and comparatively long solution layer, introducing large potential drops and thus nonuniform potential distribution. The cell designed in this work, however, has the advantage of having two counter electrodes, providing two current paths on both sides of the thin-layer working electrode. Thus current traverses the length of the thin-layer solution from opposite sides of the working electrode and compensates to a great extent the loss of ohmic potential across the length of the working electrode.

In our work, the working electrode has been segmented into five smaller electrode segments. All these segments are used for the electrochemical reaction at the same time and thus a large surface area is available, while the current and thus the potential distribution on individual segments is controlled by a suitable electronic circuit. The reference electrode is also put in a luggin capillary built into the system at the closest distance possible to the working electrode segments, so that the uncompensated resistance is kept at its minimum.

A suitable electronic circuit that controls the currents on the surface of the individual segments has also been designed in our lab. The circuit is easy to make and to use. A previous circuit used to control currents at three working electrodes to identical values in a bulk electrolysis experiment employed 11 operational amplifiers, as compared to this circuit that only employs 5.

The function of the cell was investigated mostly by thin-layer cyclic voltammetry. Peak separation in a cyclic voltammogram is an indication of potential distribution inside the cell. Peak separations in the thin-layer voltammograms obtained showed that use of two counter electrodes greatly improves the distribution of potential on the working electrode surface. The electronic circuit also minimizes the nonuniform potential distribution. The effect of the circuit in potential distribution improvement is not as dramatic as using two counter electrodes instead of one. This is because when using the circuit the total current that flows inside the cell becomes larger, as we are forcing current across the individual electrodes. However, the circuit still proves itself to be useful. Potential improvement is more obvious and of course more useful when working in nonaqueous media with inherently larger solution resistances.

These results were further supported by chronoamperometric experiments. The total electrolysis time was greatly reduced using two counter electrodes as opposed to one. The experiment time was even less, utilizing the electronic circuit. Peak separations and experiment times obtained in the above experiments, showed a significant improvement in the distribution of potential in this cell.

The edge effect problem inside the thin-layer cavity was also investigated. Edge effects are mostly problematic in chronoamperometric measurements where the

background current can cause confusions over the determination of the electrolysis endpoint. This effect was reduced significantly by utilizing a getter electrode configuration.

Furthermore, we tried to investigate the effect of sweep rate on the peak current. This is a factor that needs to be included in the model discussed by Hinman et al. Unfortunately, the computer program was not able to solve the system produced by incorporating the sweep rate factor in it. However, we know that the variations in sweep rate also affect the currents inside the cell. A more rigorous theory should still be developed for thin-layer electrochemistry.

We have considered the thin-layer working electrodes with linear rectangular geometry. The model discussed by Hinman et al. shows that there is a more uniform distribution of potential across thin-layer electrodes with circular geometry. For future work, circular thin-layer electrodes should be considered. Segmenting the circular thin-layer electrodes and controlling the currents on them, using an appropriate electronic circuit, should have the same effect as for the rectangular thin-layer electrodes. However, the edge area over the surface area ratio is larger for the smaller circular electrodes than the rectangular electrodes of the same area. Therefore, the problem of diffusion of the electroactive species through the edges of the electrode, should become more serious when dividing the circular electrodes into smaller electrode segments.

We believe that by taking a working electrode and segmenting it into a greater number of even smaller electrodes than used in this work, the potential distribution can be even more improved in the cell. The smaller these electrode segments, the better the

distribution of potential on their surfaces. However, edge effects get much worse for smaller electrodes. Again a better electrode configuration should be useful in this case.

The shape of the current vs. time transients in the potential step experiments is not completely understood. Development of a theoretical model accounting for both the effects of solution resistance and diffusion within the thin-layer cavity would be useful as a guide to developing cell designs with faster response times.

While the present cell design has the potential for use in spectroelectrochemical studies, we have not used it in such studies. Further work utilizing this cell for *in situ* UV-visible and FTIR spectroelectrochemical studies would be of interest.

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## APPENDIX

**The Pascal program used for the numerical calculations of the resistive effects on thin-layer voltamograms.**

```
program exp;
```

```
const
```

```

FoverRT = 38.942; {just that}
Fday = 9.6487e4; { Faraday constant }
Estart = -0.152; {initial potential}
Einc = 0.002; {potential increment}
nuapp = 0.002; {applied potential scanrate }
conc = 1e-9; {concentration, moles per cubic cm}
dx = 0.015; {incremental dist. along current path, cm}
thick = 2.5e-3; {thin layer thickness in cm}
width = 0.7; {width of cavity in cm}
length = 10; {total # of dx increments, tot current path is length times dx}
rho = 250.0; {resistivity, ohm-cm}
dref = 0.15; {ref. elec. distance / cm}

```

```
var
```

```

x, y, mult, dmult, tvol, dvol, Ru, Rinc, dTime, SumCur, RemCur: real;
HACUR, Eapp, CUREst: array[1..200] of real;
dCUREst: array[1..length] of real;
Eest: array[1..length] of real;
i, j, k: integer;
filename, NewFileName, AnotherFileName: string;
F: text;

```

```
begin
```

```
{the following bit calculates theoretical Hubbard/Anson currents}
```

```
ShowText;
```

```
tvol := length * dx * thick * width;
```

```
mult := Fday * conc * tvol * FoverRT;
```

```
for i := 1 to 200 do
```

```
begin
```

```
  Eapp[i] := Estart + Einc * i;
```

```

x := exp(FoverRT * Eapp[i]);
y := (1 + x) * (1 + x);
HACUR[i] := nuapp * mult * x / y;
end;
Ru := rho * dref / (thick * width);
Rinc := rho * dx / (thick * width);
dvol := dx * thick * width;
dmult := Fday * conc * dvol * FoverRT;
dTime := Einc / nuapp;

writeln('Enter New File Name');
readln(NewFileName);
filename := NewFileName;
open(F, filename);

for i := 1 to 200 do
begin
  if i = 1 then

    CURest[i] := HACUR[i]
  else
    CURest[i] := CURest[i - 1];

  k := 0;
  repeat
  begin
    k := k + 1;
    writeln(k);
    if k > 1 then
      CURest[i] := CURest[i] - RemCUR / 2;
      Eest[1] := Eapp[i] - (CURest[i] * Ru);
      x := exp(FoverRT * Eest[1]);
      y := (1 + x) * (1 + x);
      dCURest[1] := nuapp * dmult * x / y;
      SumCur := dCURest[1];
      RemCUR := CURest[i] - SumCur;
      for j := 2 to length do
      begin

        Eest[j] := Eest[j - 1] - (RemCUR * Rinc);

```

```

    x := exp(FoverRT * Eest[j]);
    y := (1 + x) * (1 + x);
    dCUREst[j] := nuapp * dmult * x / y;
    SumCur := SumCur + dCUREst[j];
    RemCUR := CUREst[i] - SumCur;
  end;
end;
until (abs(RemCur) / CUREst[i] < 0.0001) or (k > 1000);

write(F, Eapp[i] : 7 : 7);
for j := 1 to length do
  begin
    write(F, ',', Eest[j] : 7 : 7);
  end;
write(F, chr(10));
end;
close(F);

writeln('Enter Another File Name');
readln(AnotherFileName);
filename := AnotherFileName;
open(F, filename);
for i := 1 to 200 do
  writeln(F, Eapp[i] : 6 : 3, ',', HACUR[i] : 12, ',', CUREst[i] : 12);
close(F);

end.

```