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ELECTROCHEMICAL TECHNIQUE FOR EVALUATING SURFACE AREA OF A TREATED COPPER FOIL

An OURE Research Project

Submitted by:

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INTRODUCTION

In order to increase the strength of copper foil bonded to a polymeric substrate material, a dendritic layer is electrodeposited onto the foil. Treating the foil in this manner causes its surface to be rough and porous, thus providing for better penetration of the adhesive and a greater surface area for bonding. The process is particularly helpful in the manufacturing of printed circuit cards, due to the added bond strength which greatly enhances the durability of the printed circuit cards.

Currently there is no method which will quantitatively measure the surface area produced by the electrodeposition procedure or the quality of the dendritic layer that is deposited. Therefore, it is desirable to develop a technique that can be used to properly characterize the quality of the dendritic layer. For this research, a unique method called the Small Amplitude Linear Voltammetry (SALV) method (see appendix A), was used in measuring the area of the dendritic layer. The SALV method can be used to accurately measure capacitance, which, as will be shown, directly relates to surface area.

Theory

It is well established that an electrical double layer exists at the interface between two immiscible media when one is an electrolytic solution. The electrical double layer consists of a layer of electrons (when dealing with metals or electronic conductors in contact with an electrolyte), a layer of adsorbed ions, and a diffuse double layer. The double layer consists of an ionic atmosphere in which ions of one sign are not in balance with ions of the opposite sign. The atmosphere of abnormal concentrations of ions decreases rapidly as the distance from the surface increases.

Due to the fact that a potential is developed across the double layer, but a net charge is not transferred through it, the double layer behaves electrically similar to a capacitor with a large specific capacity. The capacity of such a double layer may be very large when it is generated by an electrolytic solution in contact with a metal.[a]

When two metal electrodes are placed in an electrolytic solution, they combine to form an electrochemical cell, and an open circuit potential is developed. However, when connected to an electrical source, AC or DC, the cell electrically resembles a combination of electronic components. In fact, the cell can be roughly simulated with electronic components in an equivalent electrical circuit. As stated before, the metal/electrolyte interface acts like a capacitor. Ideally, no net charge will pass through the interface, but in real electrochemical cells, some charge will be transferred. The double layer, with its charge transfer characteristics taken into account, is electrically equivalent to a capacitor in parallel with a large resistor[b]. For a complete circuit, the electrolyte must be included. The electrolyte is highly conductive, yet it offers some resistance. In the equivalent circuit, the electrolyte can be represented by a small value resistor. The actual resistance of the electrolyte depends upon its type, concentration, and temperature, as well as the distance between the electrodes.

It has been shown[3] that the capacity of the double layer at an interface is directly proportional to the exposed surface area. If the surface of a sample has been treated in some manner and the surface area is increased, the total capacitance of that sample under the same conditions is also increased.

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[a] The specific capacity of the double layer may range from 10 to 50 μ-Farads per cm^3, depending on many factors such as temperature, potential, electrolytes, and materials used.[1,3]

[b] Approximately 1kΩ to 20kΩ.

Previous Experiments Concerning Double Layer Capacitance

Many experiments concerning double layer capacitance have been performed in the past using many different types of electrodes[1,2,3,4]. Many aspects of these experiments were used to develop a procedure using a copper electrode. The most important aspect of these experiments is that they proved that surface capacitance is directly, linearly proportional to surface area and surface potential.

In experiments referenced above the electrode metals (gold and mercury) were chosen for their properties. Neither of these metals are very reactive, and the experiments were for the most part not affected by adsorption of anions from the electrolyte onto the surface of the electrodes used.[4] Like gold, copper is a noble metal; however, anions are adsorbed onto the surface of copper from the electrolyte, and the capacitance measurements are affected.

Overview

The technique being examined in this study is based on the facts reviewed above. The primary objective of the experimentation is to show that the capacitance values determined in a standard electrochemical cell vary with surface area. The factor by which the capacitance values increase through treatment can then be used to indicate the quality of the treatment.

It has been quantitatively estimated by research personnel at Olin Corporation that bond characteristics are maximized when the surface area of a copper foil is increased by a factor of approximately five. This was a standard by which to compare untreated and treated samples.

Obviously for this type of measurement, it was not necessary for the values be exact. For the purpose of this test, a variance of values is acceptable. It was desired that values stay as close to the mean as possible, but since the purpose of this experiment is to explore the possibilities of this technique and not to perfect it, a maximum amount of error was not set. Because capacitance varies not only with surface area, but also with temperature, concentration of electrolyte, and applied voltage, consistent and stable parameters were used to ensure that the results were as accurate and precise as possible.

EXPERIMENTAL METHOD

The experiment consisted of two basic parts: 1) Finding an acceptable electrolyte or electrolytes to be used with copper in and electrochemical cell, and 2) measuring the surfaces of both treated and untreated copper foil with the proper electrolyte under different conditions.

Finding the acceptable electrolyte(s) was an extremely important part of the experiment. Any reaction between the electrolyte and the copper foil would defeat the purpose of the test because the surface area would constantly be changing, and disruption of the double layer would cause the capacitance values produced to be useless.

Many electrolytes were chosen initially with conductivity and reactivity in mind. Acids were an obvious choice because they would minimize oxidation at the surface of the copper. Chlorides were initially avoided, although one solution was eventually tried without success. To a degree the conductivity of the solution could be controlled by the concentration of the solution; however, at high electrolytic concentrations reactivity of the solution with the foil and excessive hydrogen evolution at the foil cathode became limiting factors. For this reason, concentrations of electrolytes were usually held between .05 and 1 molar.

Procedure

The electrochemical cell was made up of a copper foil cathode, designated the working electrode, and a platinum mesh anode, designated the counter electrode, submerged in the electrolyte. The platinum mesh allowed for the measured capacity of the cell to be equal to the capacity of the double layer of the copper foil due to the relatively large surface capacitance of the mesh in series with the copper foil. A mercury/mercurous sulfate electrode provided the reference for the voltage readings taken during the experiment. The copper foil sample was covered in electroplater's tape, a special tape that does not dissolve in acid or alkali solutions. The tape allowed for a standard area of exposure via a 1 cm^2 hole cut in it. A 250ml jacketed beaker contained the entire cell. The jacket allowed for temperature control of the electrolyte by allowing water whose temperature was controlled to pass through it.

Magnetic agitation was used before and between experiments, but not during the experiments in order to reduce effects on the surface of the electrode.

The capacitance values were taken by the method described in appendix A.

The process was repeated for all the different electrolytes under consideration. These were tested using polished copper foil samples to make the surface characteristics of each sample as standard as possible. Once the electrolytes were chosen, the polished samples, as well as treated and untreated copper foil samples, were tested at different temperatures, amplitudes, and cycle times.

EXPERIMENTAL RESULTS

The electrolytes initially tried were sulfuric acid (.5 M, .1 M, .05 M, and .01 M), .1 M hydrofluoric acid, sodium chloride (.5 M, .1 M, and .05 M), and .5 M potassium sulfate. These were used with polished samples of copper foil with 1 cm^2 of the surface exposed. Polished samples were used to try to standardize the samples as close to 1 cm^2 as possible, while not wasting samples of treated copper foil.

The first electrolyte considered, 0.1 M sulfuric acid, actually produced the most stable waveforms while not damaging the sample. None of the other electrolytes used gave stable or consistent waveforms without damaging the sample. This will be discussed in more detail later. However, a combination of equal parts of 0.1 M sulfuric acid and 0.5 M potassium sulfate also gave stable waveforms and consistent results. The 0.1 M sulfuric acid and the combination mixture were then used as primary electrolytes for further testing with treated and non-treated foil.

Once the electrolytes were selected, the samples were tested. For the test, three types of samples were used. Scanning Electron Microscope (SEM) photographs of these types of samples are shown in figures 1-3. A polished copper sample (fig. 1) was tested in order to give base-line data for copper. Treated copper foil samples were also tested. These have the copper dendrites electrodeposited onto them (fig. 2), and supposedly have a surface area approximately five times greater than the untreated foil. The untreated foil (fig. 3) tested for comparison was actually just the smooth, reverse side of the treated foil.

The three types of samples were tested at three different temperatures, 5°C, 25°C, and 40°C. This was done to examine the affect temperature has on capacitance and on the experiment itself.

The resultant waveforms encountered in this experiment due to using the SALV method varied due to factors such as type of electrolyte and amplitude of signal applied to the circuit. Three samples of the waveforms are shown in figures 4-6. Figure 4 shows a waveform that is very sharp and has a long linear region and gave very consistent values of capacitance as shown to the right. However, consistency is not necessarily dependent upon waveform quality. This is apparent when examining figures 5 and 6. The waveforms are noisy and show oscillations, yet a representative line can be determined and relatively consistent values can be determined. The most important result from each test was consistency, not waveform quality.

The results of the three tests are summarized in table 1. Table 1 consists of the average of the capacitance values of each sample at each set of conditions. The overall values for each condition were averaged and a ratio of the treated side to the untreated side capacitance values was calculated. This ratio was then theoretically equal to the factor by which the surface area was increased.

DISCUSSION

Examination of table 1 reveals that the ratios for the standard capacitance values of the treated foil to those of the untreated foil were relatively high, which implies that the surface area of the rough foil was much higher than that of the untreated foil. Results from samples tested using the 0.1 M sulfuric acid shows consistency at 25°C and 40°C, as do those tested with the mixture of sulfuric acid and potassium sulfate. However, the values of capacitance and the subsequent ratios for treated to non-treated samples were lower at 5°C. The treated to non-treated surface capacitance ratios for both electroyltes at the two higher temperatures were approximately five, which corresponds to what Olin Research Laboratory suggested should occur. The lower capacitance values at the lowest temperature were expected, but it is possible that other factors not yet fully understood had an effect which caused a disproportionality in these values. These factors, as well as others not necessary to discuss in detail during these initial tests may need further consideration in the future.

Establishment of a baseline data set was attempted using polished copper foil samples.

The samples were polished with .5 micron alumina, to make the actual area as close to 1 cm^2 as possible. As the Scanning Electron Microscope photograph in fig. 1 shows, even fine polishing is not enough to insure that the sample is completely flat. The polished surface is actually not very different from the regular backside foil, as shown in figure 3. Without a standard base-line for data, accuracy was virtually impossible to determine. The best indication of accuracy of this method is in the equivalent circuit tests discussed in appendix A. Still, the determination of the accuracy does not affect the usefulness of the results of this experiment since the values determined for treated and untreated samples were relative to one another under standard conditions.

Amplitude of the applied signal appeared to have some effect on the quality of the waveforms. This was probably due to the fact that noise levels were not as much of a factor because they are constant, and the signal to noise ratio is larger. The larger signal to noise ratio allows for the waveforms to be more distinct and thereby reduce the error of the analyses.

Higher amplitude of voltage may not be desirable due to the potential effect on the sample. It is usually better to provide conditions which do not effect the cell. In the future, the adverse effects of higher amplitudes will have to be weighed against the benefits in order to determine whether risk of damaging the sample is worth the gain.

The period of the cycle of the applied signal theoretically should not have had an effect on the actual capacity of the double layer, but it did appear to have an effect on the ability to analyze the waveforms. The results of the experiment showed that the precision of the calculated values tended to be higher at longer cycle times. The higher precision is most likely due to the fact that the linear region is longer at the higher cycle times, thereby making the evaluation easier to perform.

Both electrolytes provided good results without damaging the sample, but the inherent characteristics of each electrolytic solution gave different results with varying temperatures. The 1:1 mixture of sulfuric acid and potassium sulfate had a higher resistance and had less effect on the surface than did the 0.1 M sulfuric acid. The lower resistance of the sulfuric acid combined with the higher temperature of the 40°C tests allowed for oscillations in the waveform and caused the precision of the analysis to be lower. The higher resistance of the 1:1 mixture tended to be too high at 5°C, causing the waveform to become curvy and the noise level to become excessive due to the smaller amplitude of current.

The accuracy and precision of this method are very difficult to determine, but this can be addressed when additional standards are provided by Olin. The results provided do indicate a potential for high precision and accuracy. For example, from data obtained so far, the precision could be increased by optimizing conditions and increasing the number of test runs. As study continues on this method, accuracy and precision will be increased until they meet the standards set forth by the industries that will use this method.

SUMMARY

Analysis of the primary results obtained during this research study have led to the following conclusions:

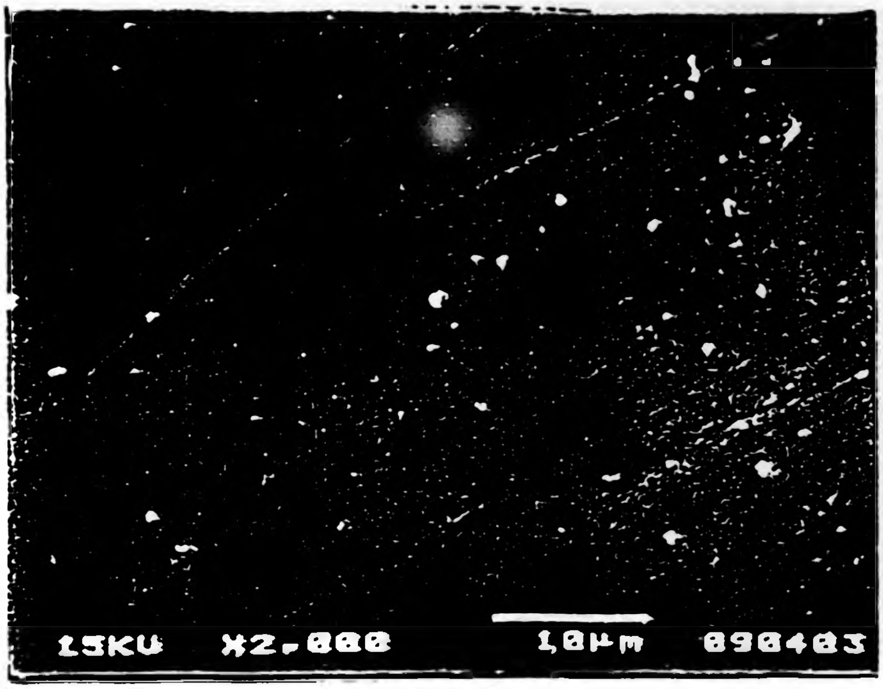
- A new, unique method was demonstrated capable of measuring the capacitance of not only electronic components, but its capacity of the double layer which exists at the interface between an electrolyte and a conducting metal, such as copper.

- The change in surface area of a treated copper foil can be indicated by changes in surface capacitance of that copper foil.

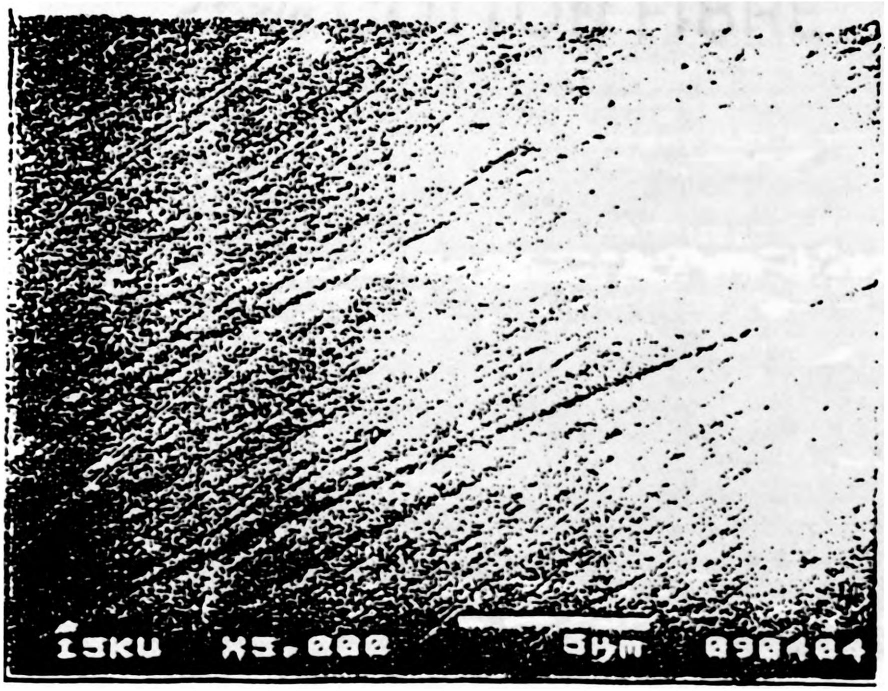
- The factor by which the area of the copper foil changes can be estimated by comparing the capacitances of the initial and final samples. The increase in capacitance was approximately 5, which compared very favorably to the quantitative estimate of area increase approximately 5 given by Olin Research Laboratories.

- Waveform quality, which affects the accuracy of the calculations, can be maximized by controlling the concentration (and therefore the conductivity) of the electrolyte, the signal to noise ratio, and the period of the applied signal.

The study of the relationship between capacitance and area has led to the development of a potential technique that has direct applications in industry. Though the investigation was very preliminary in nature, the results of this study correspond well with the theoretical analysis. Additional work in this area seems warranted in order to complete the development of this procedure.

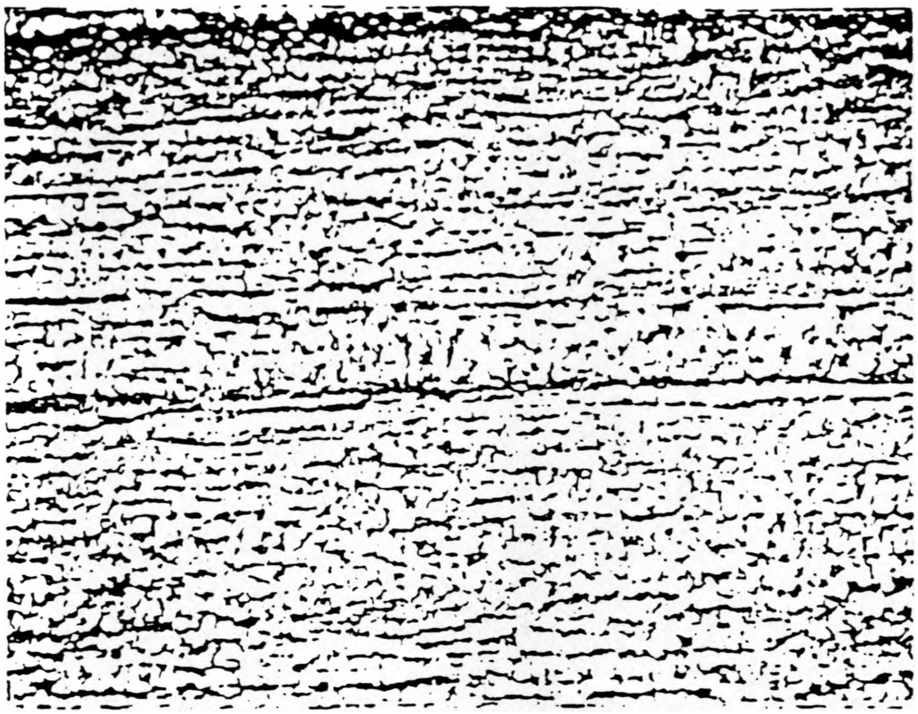


POLISHED COPPER FOIL (2000x)
(Smooth)

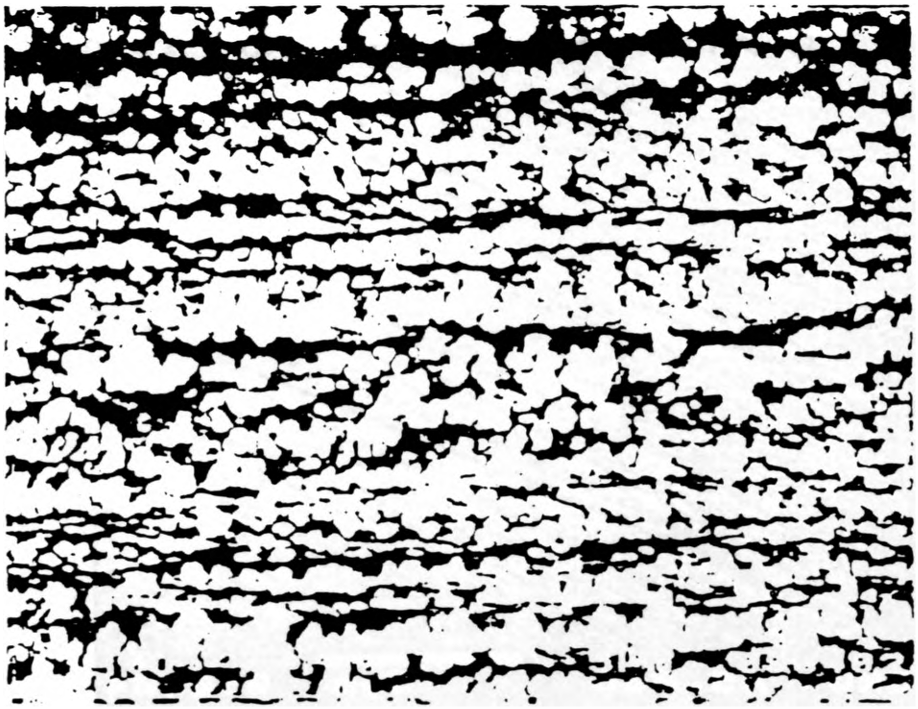


POLISHED COPPER FOIL (5000x)
(Smooth)

FIGURE 1

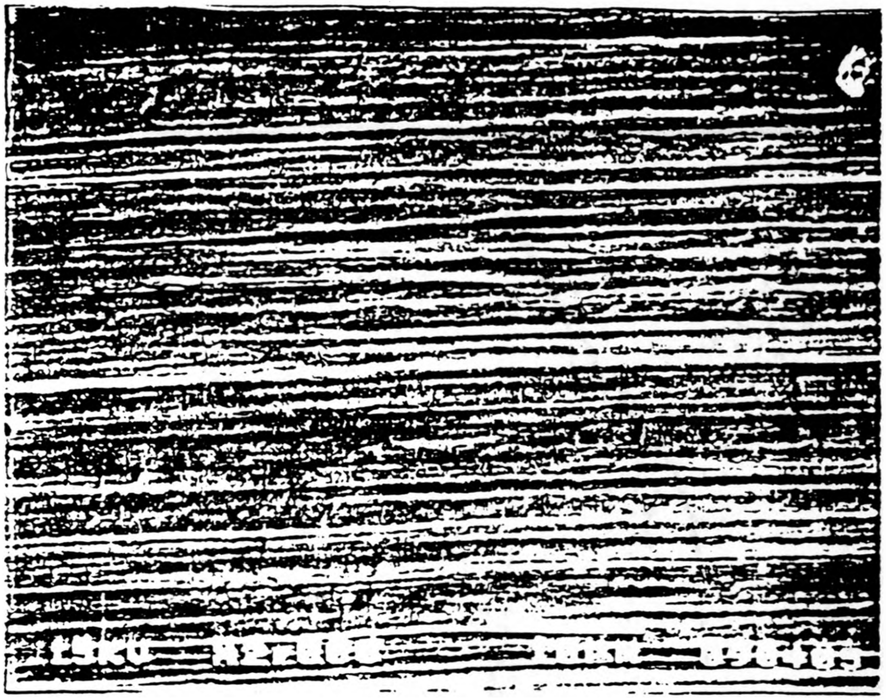


TREATED COPPER FOIL (2000x)
(Rough)

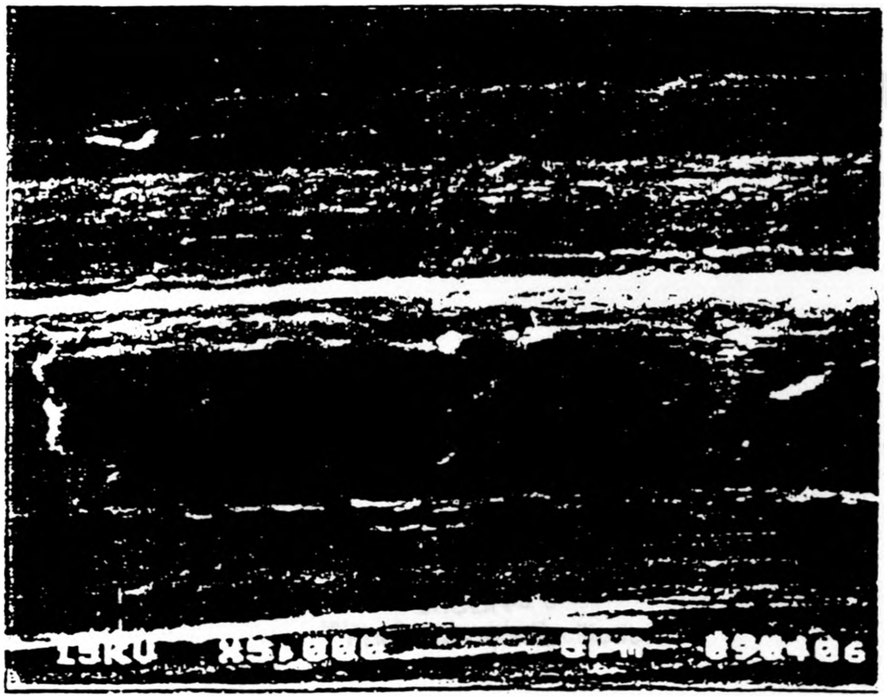


TREATED COPPER FOIL (5000x)
(Rough)

FIGURE 2

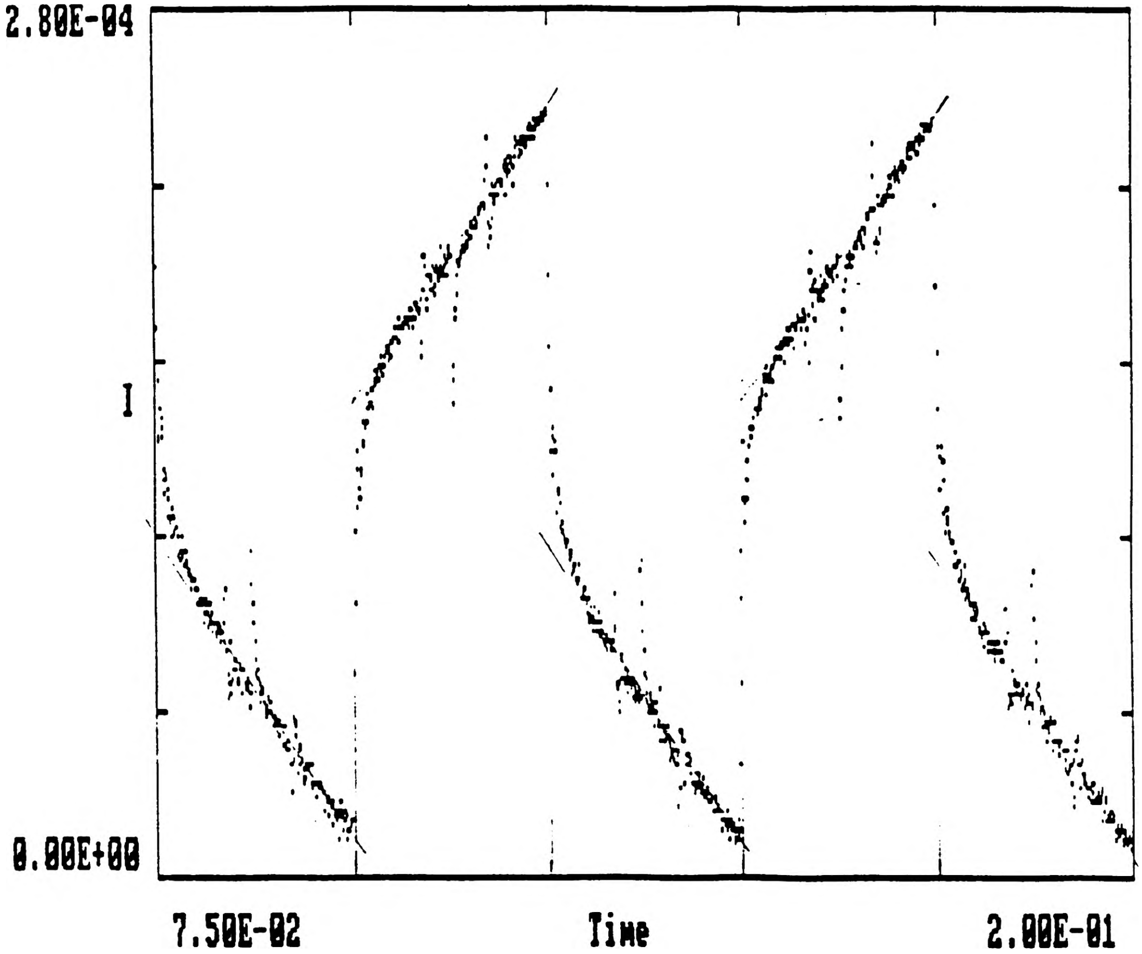


REGULAR COPPER FOIL (2000x)
(Backside)



REGULAR COPPER FOIL (5000x)
(Backside)

FIGURE 3



36
36
36
36

FIGURE 4
Sharp waveform

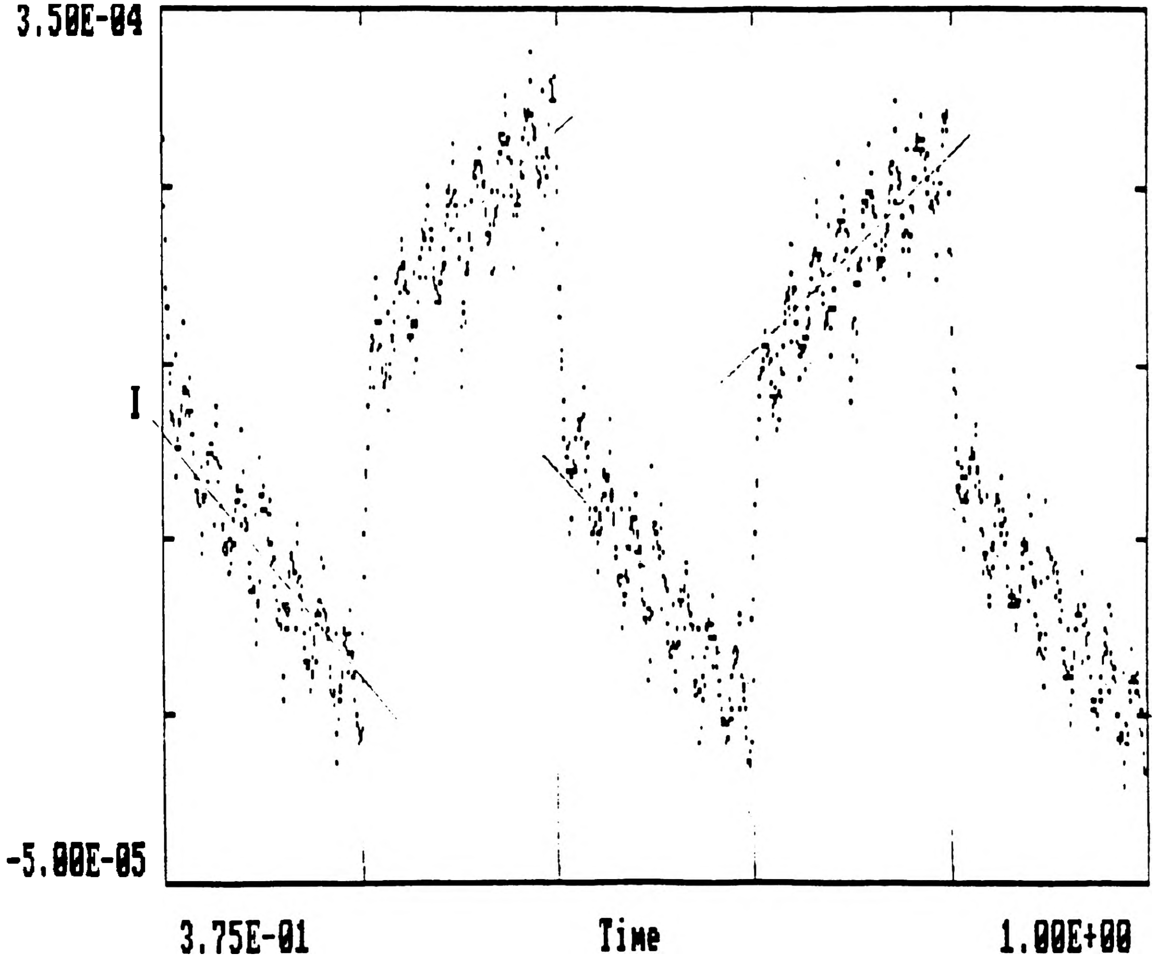


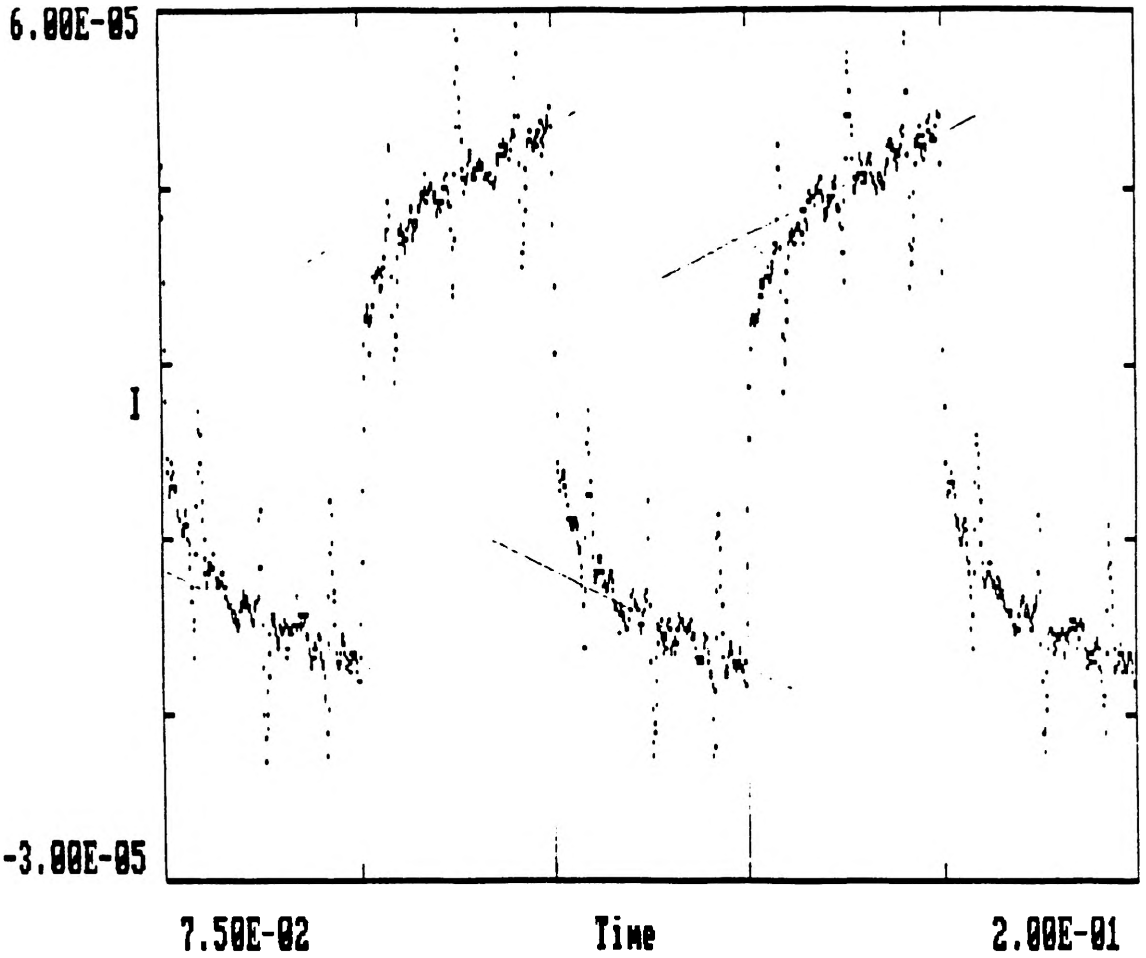
FIGURE 5
Waveform with Oscillations

209

198

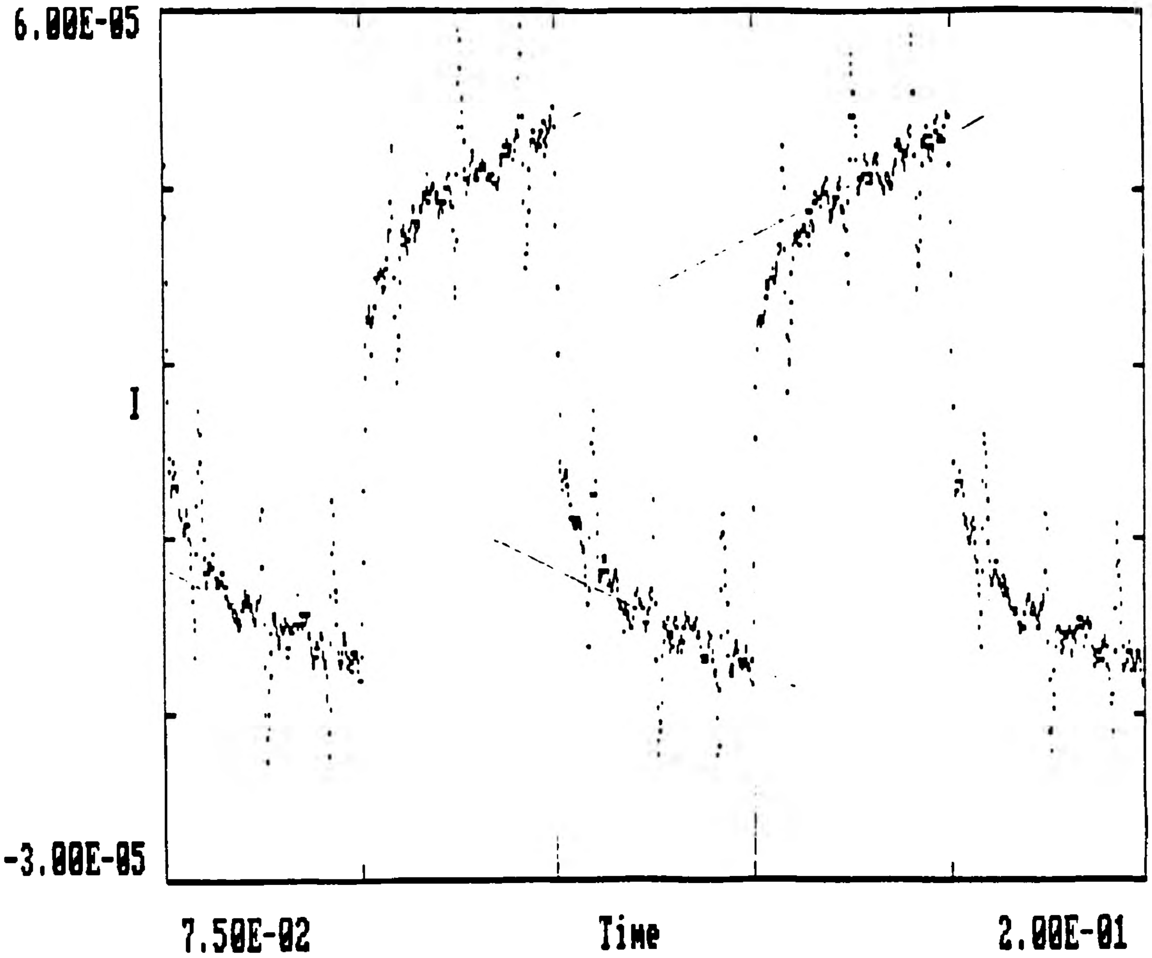
205

205



28
29
28
29

FIGURE 6
Noisy Waveform



28

29

28

29

FIGURE 6
Noisy Waveform

Table 1

SURFACE AREA DETERMINATION RESEARCH PROJECT

DATA SUMMARY

	SAMPLE AVG (micro-farads)		AVERAGE (micro-farads)	RATIO TREATED/BACKSIDE
@25C 1:1 .1M H_2SO_4 : .5M K_2SO_4				
BACKSIDE	38.7	37.8	38.25	
TREATED SIDE	157.8	154.8	156.3	
POLISHED SAMPLE	38.8	39	38.9	4.09
@25C .1M H_2SO_4				
BACKSIDE	35.7	38.7	37.2	
TREATED SIDE	200.2	204.9	202.6	
POLISHED SAMPLE	33.8	32.9	33.35	5.44
@40C 1:1 .1M H_2SO_4 / .5M K_2SO_4				
BACKSIDE	47.2	39.4	43.3	
TREATED SIDE	205.6	197.5	201.6	
POLISHED SAMPLE	61.6	48.4	55	4.65
@40 C .1M H_2SO_4				
BACKSIDE	33.1	39	36.05	
TREATED SIDE	193.6	196.3	195	
POLISHED SAMPLE	35.9	38.9	37.4	5.41
@5C 1:1 .1M H_2SO_4 / .5M K_2SO_4				
BACKSIDE	34.3	28.6	31.45	
TREATED SIDE	118.3	110.4	114.4	
POLISHED SAMPLE	37.8	39.4	38.6	3.64
@5 C .1M H_2SO_4				
BACKSIDE	35.4	34.2	34.8	
TREATED SIDE	171.1	164.4	167.8	
POLISHED SAMPLE	27.6	28.4	28	4.82

APPENDIX A

Small Amplitude Linear Voltammetry (SALV)

It is well understood that a capacitive circuit will have an effect on an AC waveform when applied to the circuit. When the affected waveform is analyzed, the characteristics of the circuit can be determined. There are different methods of doing this; However, the SALV method uses a completely different approach than conventional methods.

THEORY

When a small amplitude, low frequency, triangular wave (as in figure A1) is applied to a capacitive circuit, the waveform is obviously effected. When the triangular wave is applied to a simple capacitor, as shown in figure A2-a, the affected waveform would resemble fig. A2-b. If the triangular waveform were applied to a parallel resistive-capacitive circuit such as shown in figure A3-a, the affected waveform would resemble fig. A3-b. If the same waveform were applied to the previous circuit in series with a small value resistor, as represented by figure A4-a, the affected waveform would ideally resemble fig. A4-b. The circuit represented by figure A4-a is an equivalent circuit for the capacitive electrochemical cell for which the SALV method was designed to measure the capacitance of. The capacitance of the circuit is equivalent to the capacitance of the double layer.

To calculate the capacitance (C) of the double layer from the waveforms, the relationship:

$$i = C(dV/dt)$$

must be noted; where i is current, and (Dv/dt) signifies the time rate of change of the voltage

(V). Now,

$$\triangle i = i_{a'} - i_a = i_b - i_{b'}$$

and

$$\triangle V = V_b - V_a = V_b - V_c$$

So now,

$$\triangle i = C[(Dv/dt)_{a\to b} - (Dv/dt)_{b\to c}]$$

$$\triangle i = C\left[\frac{(V_b - V_a)}{t_{1/2}} - \frac{(V_c - V_b)}{t_{1/2}}\right]$$

$$\triangle i = C\frac{(2^* \triangle V)}{t_{1/2}} = C\frac{(4^* \triangle V)}{t_t}$$

$$C = \frac{t_t{}^* \triangle i}{4^* \triangle V}$$

It can be seen that the capacitance, C, of the double layer can be calculated by multiplying the period of one cycle of the triangular wave by the current change in the resulting waveform, and then dividing by four times the amplitude of the applied waveform.

EXPERIMENTAL METHOD

The equipment used by this method is a system of components collectively referred to as the EG&G Model 378 Electrochemical Impedance System. The block diagram is shown below in figure A5. For this method, the Model 5208 Two Phase Lock-in Analyzer is not actually used, but connections to the cell are made through the electrometer that is connected to the analyzer. The electrometer uses three leads for connection to the electrodes; the working electrode, counter electrode, and reference electrode. A computer (in this case an IBM XT) provides all the commands to run the Model 273 Potentiostat/Galvanostat via the Headstart software package. The computer tells the potentiostat what signal to apply and at what bias.

The galvanostat measures the resulting current waveform and the open circuit potential, and feeds the data to the computer to be stored, plotted, or printed. The printed current waveforms can then be analyzed as described above.

The initial tests on the SALV method of testing capacitance values were conducted on equivalent circuits (see figure A4-a) which represent components of the electrochemical cell. The components used were capacitors and resistors with varying values, but all within expected values of the electrochemical cell. Different cycle periods were tried, as were different combinations of capacitors and resistors. The circuits consisted of a fixed capacitor in parallel with a fixed resistor, while the series resistor was varied from zero to 100 ohms. This was done to determine the accuracy of the method while finding which combinations worked to give the most accurate results and the sharpest waveforms.

EXPERIMENTAL RESULTS

The sharpness of the waveform is important when trying to maximize the precision of the test. Examples of different types of resultant waveforms are shown in figures A6-A8. Noisy and oscillating waveforms (see fig. A6) tend to leave more room for interpretation for the most representative line, as do curvy waveforms (see fig. A7). Sharp waveforms (see fig. A8) make the interpretation easy, but do not necessarily give the most accurate results.

The results of these tests are shown below in table A1. The values for the capacitor given are from the capacitor itself and not from a calibrated measuring device. Most of the combinations tested gave results that easily fall within the ±10% tolerance given by the manufacturer of the capacitor. Some of the results were hampered by noise and oscillations. The sharp waveforms tended to give results that were very close to the manufacturers rating on the capacitors.

DISCUSSION

Upon examining the test results of the equivalent circuits, a definite pattern became apparent. The resultant waveforms that contained oscillations and noise tended to come from the circuits where the series resistance was very low or zero. The waveforms that were curvy and had a smaller linear region resulted from circuits that had high series impedances relative to the corresponding parallel impedances. The sharp resultant waveforms tended to result from circuits that had a series resistance that was approximately a tenth to a hundredth that of the parallel resistance.

The initial concerns when dealing with the accuracy of this method in determining capacitance values for a real electrochemical cell were two-fold. First, an electrochemical cell is not at equilibrium when a voltage is passed through it. It was thought that there may be considerable noise developed when applying the voltage, or at least the resulting waveform would probably not be as steady as the ones for the fixed capacitors. This could be dealt with by averaging the waveform as much as possible, but it may still affect the precision. Secondly, the capacitance of the double layer is affected by voltage. In other words, the actual capacitance of the double layer will change as the applied signal changes from peak to peak. This was not considered too much of a problem because the amplitude of the applied waveform is small and the resulting analyses is averaged.

SUMMARY

The SALV method of determining capacitance is not widely used, but shows much potential in electrochemical applications. The advantages for using this method are substantial, while the disadvantages are few and relatively easy to overcome. The advantages are:

- The SALV method is time efficient, taking only a few minutes to perform each test.
- It is a fairly accurate method, under the proper conditions, especially when considering the accuracy of alternate methods.
- Because it uses a low amplitude of voltage, it can be used in electrochemical applications while minimizing effects on the material being tested.

The disadvantages to this method were discussed above, but briefly they are:

- When using this method to measure the capacitance of the double layer, the actual capacitance changes with the voltage as the waveform is applied. This can be dealt with by averaging the results from the analysis of the waveform.
- The electrochemical cell is disturbed by voltage, and is therefore not at equilibrium when the test is run. This can be minimized by use of small amplitude voltages and through aver-aging the results from the analysis of the waveform.

Figure A1
Applied Signal

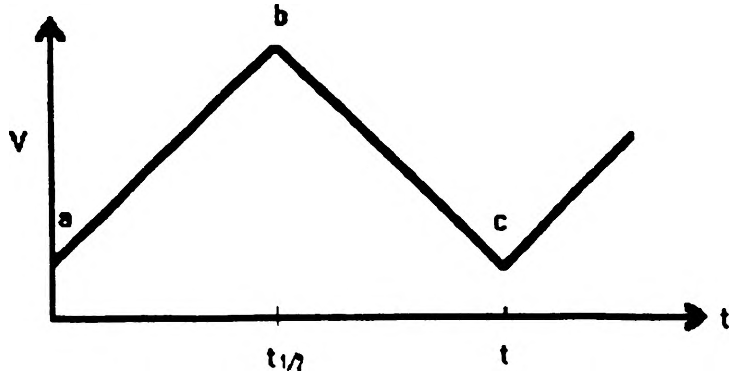


Figure A2-a

Equivalent Circuit

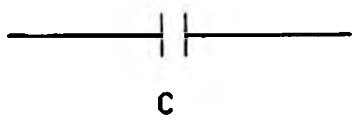


Figure A2-b
Resultant waveform

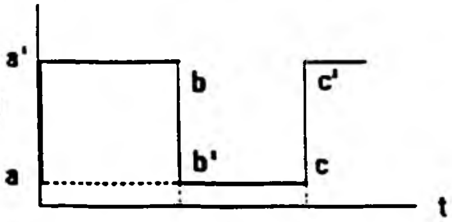
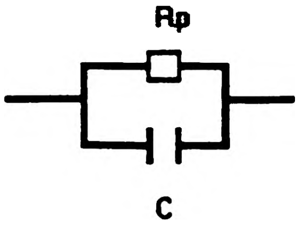
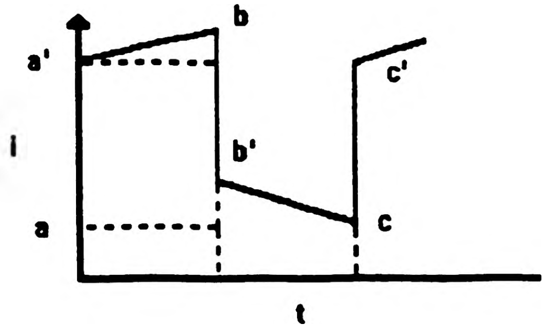


Figure A3-a



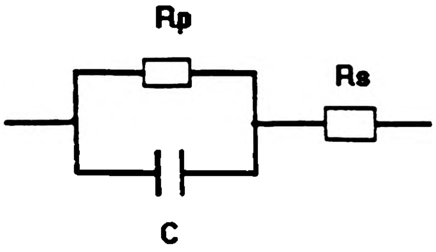
Equivalent Circuit

Figure A3-b



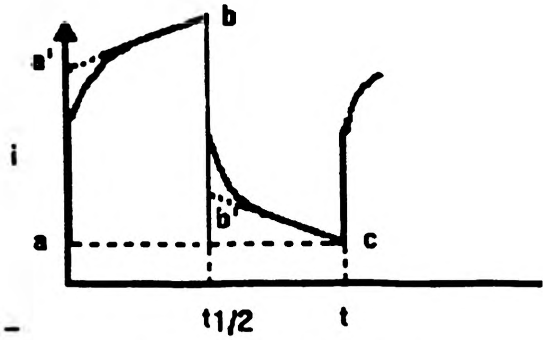
Resultant Waveform

Figure A4-a



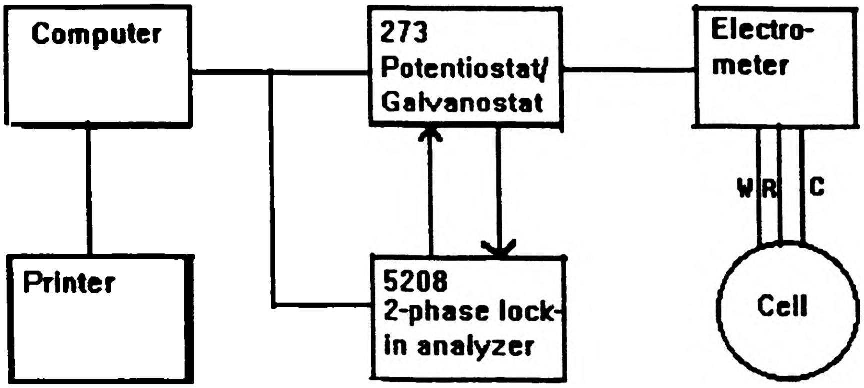
Equivalent Circuit

Figure A4-b



Resultant Waveform

Figure A5
Model 378 Electrochemical Impedance System



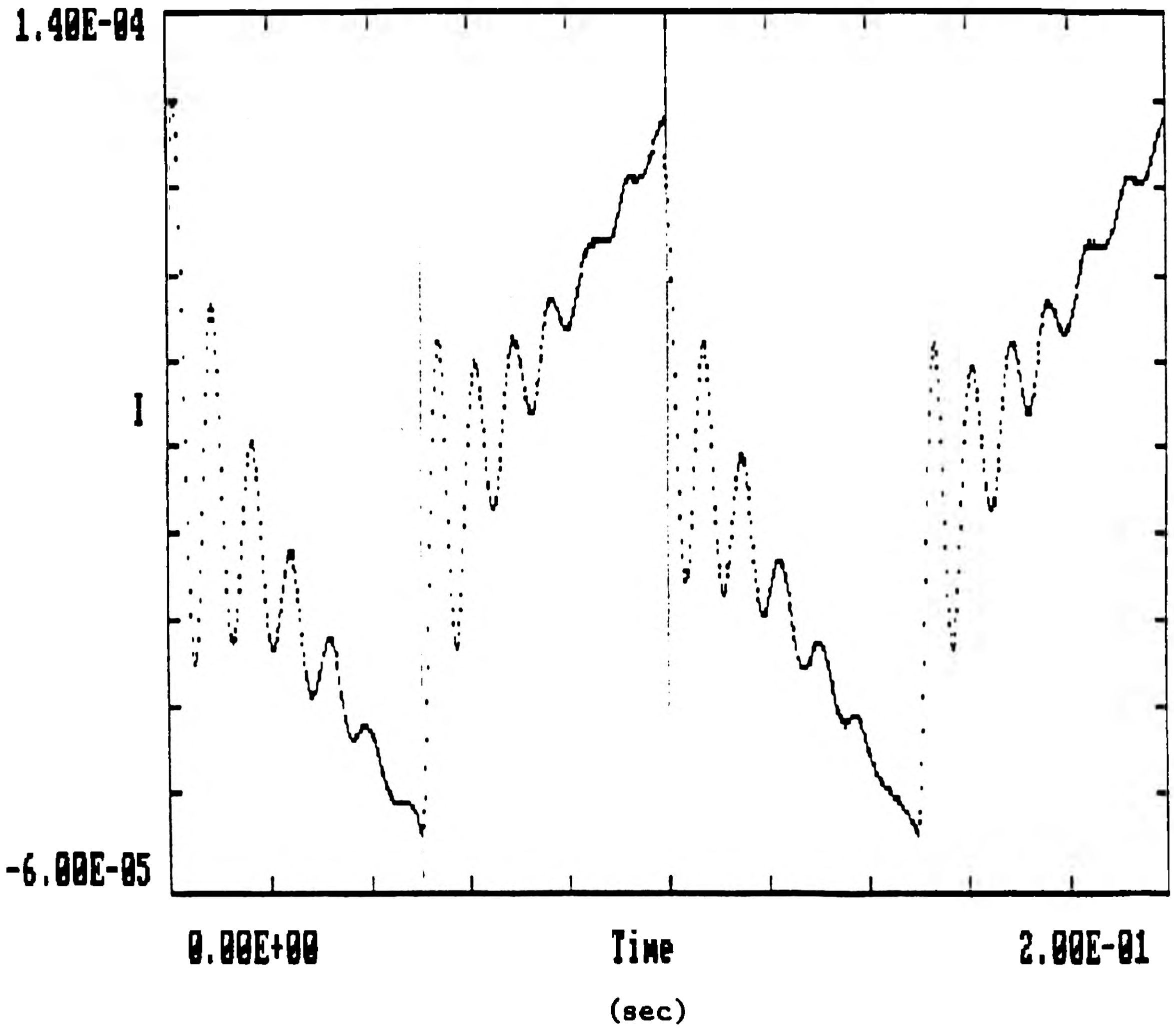


FIGURE A6
Noisy Waveform (oscillations)

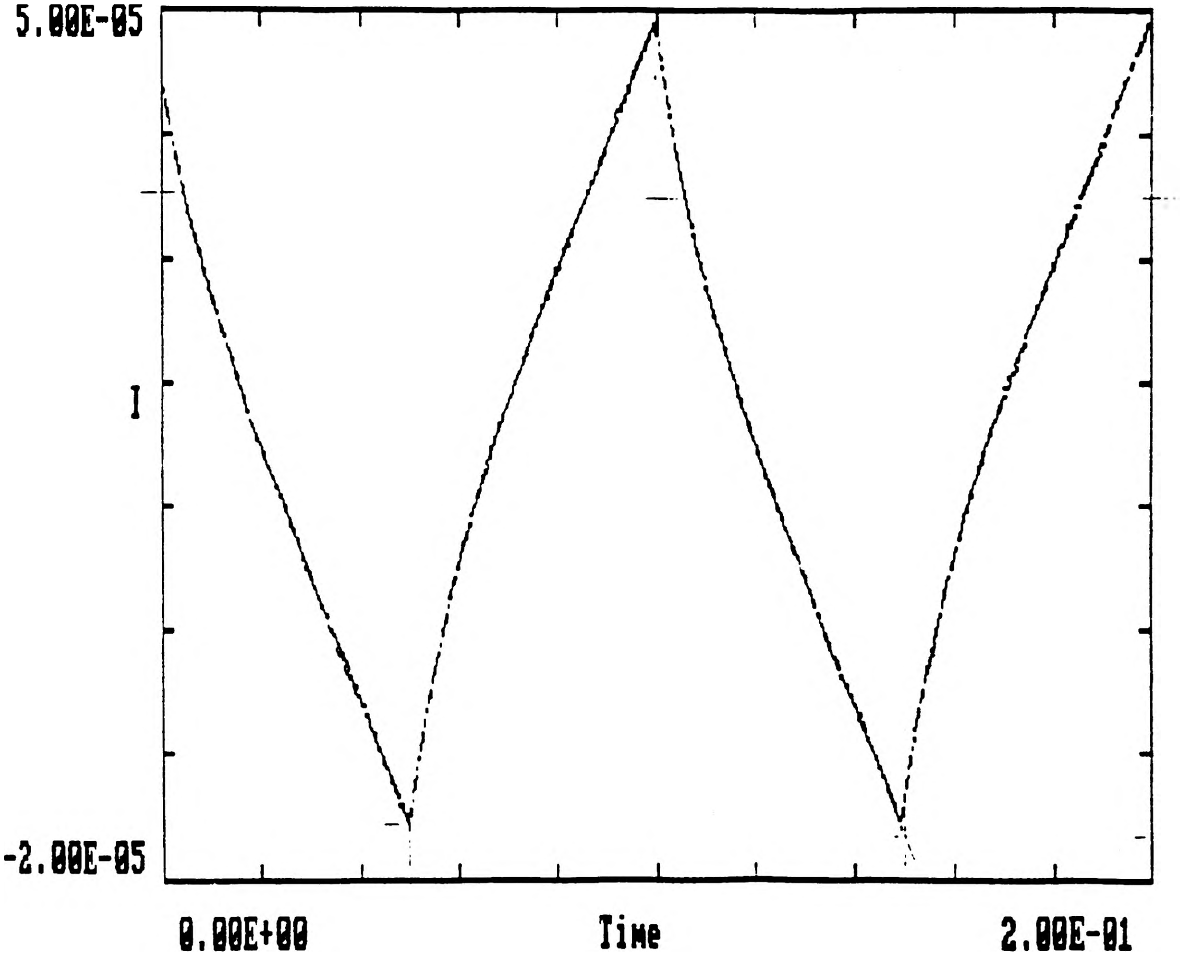


FIGURE A7
Curvy Waveform

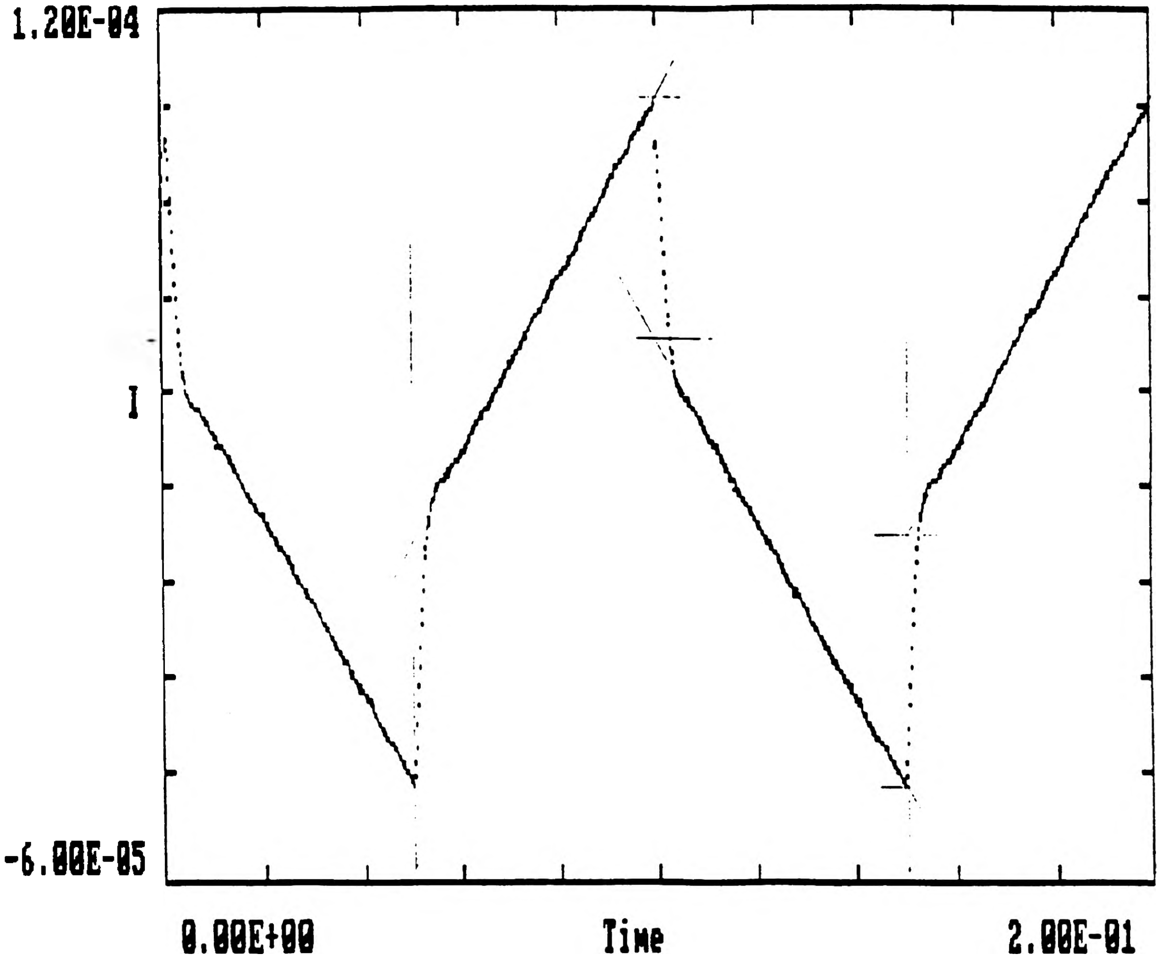


FIGURE A8
Sharp Waveform

TABLE A1
Small Amplitude Linear Voltametry Experimental Results on Equivalent Circuits

Circuit	R_s (ohms)	Period(sec)	Signal Amplitude		
			10 mv	100 mv	1 v
			Capacitance (µF)		
1.0KΩ//135µF	0	.25	Oscill	noisy	noisy
	10	.50	148	131	134
	100	1.00	133	131	129
1.0KΩ//24µF	0	.10	29	27.4	17.7
	10	.10	28.8	26.9	23.1
	100	.10	23.0	22.9	23.1
100Ω//135µF	0	.10	Oscill	156 (noisy)	156 (noisy)
	10	.10	133	131	126
	100	.10	Curvy	Curvy	Curvy
100Ω//24µF	0	.01	Oscill	26	24.1
	10	.01	21.1	21.5	21.4
	100	.01	Curvy	Curvy	Curvy

CIRCUIT	AVERAGE	%ERROR
1.0KΩ//135µF	134.3	.52%
1.0KΩ//24µF	24.7	2.91%
100Ω//135µF	140.4	4.00%
100Ω//24µF	22.8	5.91%

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