THE ANODIC OXIDATION OF METHANOL ON PLATINUM IN ALKALINE SOLUTION

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ABSTRACT

The electrochemical oxidation of methanol on platinum was studied as a function of temperature, composition of electrolyte and pretreatment of the electrode. The majority of the data were obtained with the linearly varying potential technique. Results indicate that the oxidation of methanol in alkaline solution proceeds at a potential some 200-300 mV. less positive than in acid, (potentials versus the hydrogen electrode in the same solution). Peak currents for a bright platinum electrode are independent of stirring and increase with increasing voltage sweep rates. From the effect of temperature on the reaction rate, it is evident that the formation of platinum oxide is not the rate determining step. Current transients at low potentials indicate that the initial step involves the abstraction of a hydrogen atom; and that the oxidation of the remaining methanol fragment determines the reaction rate.

INTRODUCTION

In recent years, the anodic oxidation of methanol on platinum in both acidic and basic media, has been studied in considerable detail. The impetus for these investigations is derived from a search for suitable fuels to replace hydrogen in the fuel cell. Breiter et. al. (1,2) have studied the oxidation processes in acid solution; and found the current to be proportional to the amount of methanol adsorbed on the surface of the electrode. These authors propose that the initial step in the reaction is the direct oxidation of the methanol molecule (adsorbed) to a methanol radical and a hydrogen ion.

The anodic oxidation in alkaline solution has been studied by Vielstich (3) and Buck and Griffith (4). Vielstich (3) concludes that rather than the direct electrochemical oxidation of the methanol, the platinum reacts to form a platinum hydroxide which in turn oxidizes the methanol chemically. The formation of the platinum hydroxide must then be rate determining. Vielstich supports his hypothesis by the fact that the current peak in the current-voltage characteristic is normally independent of the oxidizable substance. The fact that methanol in 6-8 Molar alkali is oxidized spontaneously at temperatures exceeding 80°C is explained by assuming a base catalyzed dehydrogenation mechanism.

Buck and Griffith (4) studied the anodic oxidation processes in both acid and alkali media. For the basic system, these authors

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calculated a Tafel slope of 0.21 - 0.28V.; and they concluded that the rate determining step in alkaline solution involves the reaction of a methylate and two hydroxide ions with the transfer of two electrons.

Some further work was done recently by Liang and Franklin (5), who studied the anodic oxidation of formic acid and formaldehyde in addition to that of methanol. Oxley, et. al. (6) investigated the anodic processes in acid by studying the potential decay curves. The effect of the reductive adsorption of CO_2 was studied by Giner (7).

Although a good deal of work has been done in this field, the factors which govern the shape of the current - voltage curve obtained by the linearly varying potential technique (L.V.P.) are, in general, still unknown. In this paper, we describe some work carried out in order to ascertain which variables dictate the general shape of the i-V curve determined by the technique cited above. Furthermore, we will examine the theories outlined above concerning the oxidation of methanol in the light of some current transient measurements, and the effect of temperature.

EXPERIMENTAL

The electronic equipment used in these experiments is based on the use of operational amplifiers to control the potential of the working electrode. The basic circuitry is due to De Ford (8). A modification permitting compensation of the IR voltage drop between reference and working electrodes has been described elsewhere (9). A block diagram indicating the essential components of the instrument is shown in Fig. I. The integrator shown in Fig. I may be used to generate a single sweep or a triangular wave. In normal experimentation, a triangular wave was applied to the working electrode.

The electrolysis cell was of the conventional H-type with a sintered glass disc between anode and cathode compartments. A working electrode of bright platinum foil ($1cm^2$) was spot-welded to a platinum wire sealed in soft glass. The counter electrode consisted of a platinized platinum foil, of $1cm^2$ geometric area.

The electrode assembly and cell were washed initially with aqua regia followed by a dilute solution of hydrofluoric acid. Further washing with copious quantities of distilled water was carried out before the cell was assembled for use. The hydrofluoric acid solution did not appear to have any deleterious effects on the platinum-soft glass seal.

The electrochemical cell was thermostatted in a water bath to $\pm 0.2°C$. Nitrogen was normally bubbled through the cell at all times. The nitrogen was pre-conditioned by passing it through a solution identical to that in the cell.

A mercury-mercuric oxide reference electrode was used in all experiments. Since adequate IR (reference to working electrode) compensation was achieved electronically, no great care was taken to place the tip of the reference electrode very near the working electrode surface. All potentials in this paper will be cited with respect to the potential of the hydrogen electrode in the same

solution. Rather than calculate the potential of the Hg/HgO electrode versus that of this hydrogen electrode for each set of conditions, its value was determined experimentally. Before the potential of the Hg/HgO reference electrode was measured, it was established that the potential of the hydrogen electrode is not significantly affected by the presence of methanol at temperatures below 60°C.

Harleco carbon dioxide free sodium hydroxide and ACS analytical reagent grade methanol were used in all experiments. The appropriate concentrations of reactant and electrolyte were prepared by dilution of the concentrated material with doubly distilled water.

Since it is normally difficult to obtain reproducible results when the history of the electrode is not clearly defined, a pre-treatment was devised to promote reproducibility. Initially, oxygen was evolved from the electrode at 5mA/cm^2 for 5 seconds. The electrode potential was then reduced to the initial value for the subsequent linearly varying potential sweep. After maintaining the potential at this value for 2 minutes, a repetitive triangular wave was applied to the working electrode. Nitrogen was bubbled through the electrolyte to remove oxygen produced during the pre-treatment as effectively as possible. This type of pre-treatment normally gave results reproducible to $\pm 5\%$.

RESULTS AND DISCUSSION

The major portion of this work consisted of an investigation of the system, bright platinum/2M methanol, 4.5 M sodium hydroxide. Unless stated otherwise in the text, it will be assumed understood that this is the experimental system. The advantage of the high concentration of methanol is that normally the background current caused by charging of the double layer and adsorption of oxide or hydroxide species is negligibly small over an appreciable potential range, as compared to the oxidation current of the methanol. The last statement is not necessarily true at temperatures near 0°C.

The system cited above was chosen to study the effects of voltage sweep rate, temperature, and voltage sweep range on the current-voltage characteristic. In addition, a study was made of the effects of electrolyte and methanol concentration on the general features of the current-voltage curve, and on the current at constant potential.

The normal voltage sweep range was within the limits of +300 to +1400 mV. It is felt that the adsorption and possible evolution of hydrogen at lower potentials and the evolution of oxygen at higher potentials only complicates the interpretation of the data. Of course, in basic solution even at +300 mV. a small amount of hydrogen is adsorbed.

LINEARLY VARYING POTENTIAL EXPERIMENTS

General Current-Voltage Curve and the Effect of Temperature

In Fig. 2 we show the least complex of the i-V curves obtained in this study. The curve is for the 2M CH_3OH/4.5M NaOH system at 60°C and a voltage sweep rate of 100 mV./sec. Both the

i-V curves for the initial sweep and a "steady state" curve are shown. By steady state, we refer to the condition when subsequent voltage scans do not alter the curve significantly.

From Fig. 2, we note that the current at low potentials for the initial sweep lies below that for the steady state curve. At higher potentials, the i-V curves cross and the current for the initial sweep exceeds that of the steady state scan. This sequence of events is a function of the experimental conditions. The i-V curve for increasing potentials in Fig. 2 (later referred to as the forward sweep) has a single maximum and no plateaus or inflections. This feature is rather different from the curve obtained by Breiter (2) for the oxidation of a molar methanol in molar perchloric acid solution. Fig. 2 also shows the i-V curve for the decreasing potential sweep (later referred to as the reverse sweep). The current maximum for the reverse sweep does not lie outside the forward i-V curve as has been observed for some methanol-acid systems (1). The actual potential of the current peak for the reverse sweep depends markedly on the experimental conditions; and will be considered in some detail later on in this paper.

As shown in Fig. 2 the currents in the low potential region, i.e. at potentials below that of the current maximum are greater for the reverse than the forward sweep. This "hysteresis loop" is less pronounced in the alkaline than in the acid system (c.f. Breiter (4)). Although the effect decreases with increasing temperature, it is still present at 60°C.

Fig. 3 depicts the i-V characteristic for the same system at 0°C. The actual currents at the same potentials are obviously much lower than at 60°C. Decreasing the temperature has altered the general shape of the i-V curve quite considerably. The current for the initial forward sweep lies below that of the steady state curve at all potentials; and the loop formed as a result of the difference between currents for forward and reverse sweeps is appreciably larger than at 60°C. Furthermore, at the lower temperatures the i-V curve for the reverse sweep is much less symmetrical about the potential of the current maximum, and the curve shows an inflection. The "back" side (negative resistance portion) of the forward curve, i.e. at potentials exceeding that of the current maximum, shows a shoulder at 0°C which is absent at 60°C.

Having discussed the general properties of the i-V curves in some detail, we shall now consider possible explanations for the "hysteresis loop" for forward and reverse sweep currents, and the effect of temperature on the shoulder and inflection on the i-V characteristic shown in Fig. 3.

A number of suggestions have been made to account for the hysteresis loop referred to above. Giner (7) has suggested that a reduced form of CO_2 is adsorbed on the electrode surface while the electrode is maintained at its initial potential; say below 250 mV. in molar acid. The reduced CO_2 may be formed from either CO_2 or carbonate in solution or from methanol. This reduced CO_2 then acts as a poison to the oxidation reaction. It has also been suggested that the effects might result from a lower concentration of adsorbed methanol during the reverse sweep, and that oxidation proceeds more readily on a bare surface.

Although it cannot be denied that both explanations, in view of experimental results for the acid system, appear reasonable; the results for the basic system do not support this explanation. Let us consider the reduced CO_2 hypothesis. We have found that the hysteresis loop is not significantly dependent on the initial potential and on the time that the potential was maintained at its initial value. In our work, the initial potential was always maintained above the potential of the hydrogen electrode in the same solution. Giner (7) reports that in the acid system the reduced CO_2 species is produced below 250 mV.; but in the basic system the corresponding potential should be several hundred millivolts less positive. According to this author, the reduced species is oxidized at potentials exceeding 400 mV. Hence, it does not seem likely that the reduced CO_2 hypothesis is applicable to the basic system. Furthermore, one should observe an effect of the holding time (time that the potential is maintained at its initial value) at the initial potential. This is not observed. A possible explanation is that the adsorption of the reduced species is so rapid that when the holding time exceeds one second, no further effect will be observed.

To account for the hysteresis loop by assuming that the reaction occurs more rapidly on a bare surface would seem contradictory to the fact that the current at relatively high surface coverages, 0.3 - 0.8, appears to be proportional to the surface coverage.

A possibility that the hysteresis loop is due to removal of a poisonous intermediate at potentials when the surface oxide is present does not seem applicable since the loop is present even when the most positive potential is less than that where oxide adsorption is possible. It could be thought that the increased currents on the reverse sweep are due to activation of the electrode by adsorption. and reduction of the surface oxide resulting in a different reaction product. Although this possibility cannot be discounted for the alkali system, it does not seem valid in the acid system where the difference in current for reverse and forward sweeps is much too large. The reason for postulating a different reaction product for a more active electrode is that the reaction product is known to depend on the electrode catalyst material (11).

A possible explanation for this phenomenon, which to the best of our knowledge has not been explored previously, is that a reaction consisting of an adsorbed methanol species and a methanol molecule involving a bare surface site is responsible. It is proposed that this reaction occurs in conjunction with the normal reaction of the adsorbed methanol. In this manner, the lower surface coverage in the reverse sweep should yield a somewhat higher reaction rate and at coverages between 0.3 and 0.8 the reaction rate could be proportional to the adsorbed material. It must be emphasized, however, that this explanation is speculative and more data regarding the various steps in the reaction mechanism are necessary.

The fact that the hysteresis loop in alkali is somewhat smaller than that in acid may be due to a closer concurrence of the adsorption isotherm for the forward and reverse sweeps. To our knowledge, no data regarding these isotherms are available for the basic system.

The inflection on the i-V curve for the reverse sweep may be due to an appreciable oxide reduction current. Such an explanation is not satisfactory, however, since the inflection changes to a minumum when this cathodic current is made negligibly small. It is possible that this inflection results from the same process as that which causes the shoulder on the forward curve at 0°C. The shoulder is presumeably caused by interaction of the surface oxide, a methanol species and a bare site. It seems improbable that the current can be ascribed to removal of adsorbed methanol, or a different reaction occurring on the oxide surface. At these potentials the surface concentration of methanol must be very small, and if a different reaction on the surface oxide causes the shoulder, then one would not expect the current to decrease with increasing potential. The oxide concentration (surface coverage) at the potential of the inflection in the i-V curve for the reverse sweep should be very similar to that at the potential of the shoulder on the forward curve. It is, therefore, not inconceivable that a relation exists.

The lack of an inflection at higher temperatures (60°C) is probably due to the fact that the surface oxide is reduced at a higher potential and hence the peak current for the main reaction for the reverse sweep is much higher, thereby making the "surface phenomena" less significant.

The shift of the potential of the current maximum on the reverse sweep to lower values as the temperature is lowered is also thought to be a result of a shift in the potential at which the surface oxides are reduced. It is known that the reduction of the surface oxides occurs at less positive potentials as the temperature is lowered (12). Hence, the current peak should also be shifted to less positive potentials.

The Dependence of the Tafel Slope on Temperature

A few log i-potential curves for the anodic oxidation of methanol at 60°C are depicted in Fig. 4. The Tafel slopes for the initial, and steady state forward and reverse sweeps are 125± 15 mV. and 170± 20 mV., respectively. These values were found to be essentially independent of temperature for the initial and steady state reverse sweeps.

The Tafel slope for the steady state forward sweep for this range of potentials is markedly dependent on the temperature. Decreasing the temperature from 60° to 0°C caused its value to rise from 170±20 mV. to 240±25 mV. The latter value is in reasonable accord with that reported by Buck and Griffith (4) for the oxidation of methanol on a platinized platinum ball at 25°C, at a voltage sweep rate of 8 mV./sec. and methanol concentration below 0.025M. Hence, as the temperature is raised, the Tafel slopes for steady state reverse and forward sweep converge.

A value of 125±15 mV. is readily, although possibly naively, interpreted in terms of a one electron transfer mechanism having a symmetrical energy barrier. However, since the surface concentration of methanol changes with potential during the scan it cannot be assumed that this slope is characteristic of the electron transfer reaction. Breiter (1), assuming Langmuir kinetics, and correcting the observed currents for the effect of the surface coverage, calculated a value of 0.67 for αn. If we consider that the effect of

decreased surface coverage results in an apparently increased Tafel slope, it would appear that our value of 125mV. is similar to that observed by Breiter (1), indicating that the rate determining steps are the same in acid and base.

The Effect of Voltage Sweep Range

In general, the Tafel slopes are not significantly affected by the voltage sweep range provided the maximum and minimum potentials are not within the range of oxygen or hydrogen evolution.

The current maxima normally decrease with decreasing most positive potentials attained during the sweep and the number of cycles required to attain a steady state i-V curve increases. Fig. 5 depicts the effect of decreasing the maximum potential attained during a potential scan. Reference has already been made to the inflection on the i-V curve for the reverse sweep (see Fig. 3). This inflection changes to a marked minimum as the most positive potential during the sweep is decreased from 1400 to 900mV. The nature of the hysteresis loop is not significantly affected by the maximum potential provided it exceeds the potential of the current maximum during the forward sweep.

The Effect of Voltage Sweep Rate

As found by other investigators, the current maximum rises with increasing voltage sweep rate. The fact that stirring does not effect the current-voltage characteristic shows that increased currents at higher sweep rates cannot be accounted for by a diffusion process in the bulk of the solution. In addition, the increased currents can neither be accounted for by higher double layer charging currents, since these are negligible at the higher methanol concentrations. It would appear that this phenomenon is a result of a higher concentration of adsorbed materials at the peak potential as the sweep rate is increased. It has been shown indirectly that the concentration of methanol on the surface at constant potential increases with increasing sweep rates (1). Furthermore, the inhibiting effect of the surface oxide should decrease as the sweep rate is raised since the oxide adsorption reaction is rather irreversible.

Earlier reference has been made to the shoulder on the i-V curve at potentials exceeding that for the current maximum (see Fig. 3). The data on Fig. 2 would seem to indicate that this feature disappears as the temperature is raised. However, even at 60°C, the shoulder may be made to reappear when the voltage sweep rate is increased to 500 mV/sec. Such behavior is characteristic of a surface reaction; and it was interpreted in this manner earlier. The greater prominence of the shoulder at the lower temperatures may be ascribed to the fact that the current for the main reaction is relatively more temperature dependent.

Raising the voltage sweep rate causes the potential of the current maximum for the reverse sweep to decrease. This is not too surprising since it was assumed that the decrease in current beyond the maximum on the forward sweep is caused by surface oxides; and the peak current for the oxide reduction shifts to lower potentials

as the sweep rate is increased. At increased sweep rate, the inflection on the i-V curve for the reverse sweep becomes more prominent. This feature appears only at the lower temperature.

The Effect of Solution Composition

As the methanol concentration is raised, the current at constant potential increases. However, at concentrations exceeding 10 Molar, the current begins to decrease. For the concentration range 0.1 -2M, the slope of the log i vs. log c plot at constant potential is unity, indicating that the reaction is directly proportional to the methanol concentration. The shape of the current voltage curves over the range of concentrations where the log i vs. log c plot is linear is not significantly affected unless the surface reaction i.e. oxide adsorption, becomes appreciable. This occurs at the higher sweep rates.

Fig. 6 depicts the curve obtained for a solution 0.1M in methanol. During the reverse sweep, cathodic currents are observed and the normal reverse sweep peak current is absent. Furthermore, a current minimum and a plateau are observed on the forward sweep. Similar features have been observed for the anodic oxidation of methanol in acid. The phenomena are different in nature, however, in that for the basic system the minimum and plateau are due to the oxide adsorption currents which cannot be the explanation for the acid system since the observed currents are too high.

The effect of the concentration of sodium hydroxide between 0.01 and 4.5M is small. The general shape of the current-voltage curve does not seem to be affected significantly as the concentration is varied between the limits cited.

Current Transients

In these experiments, the potential was raised to a value between 1200 and 1400 mV., and maintained at this point for about 10 minutes. The potential was then decreased instantaneously to a value between 200 and 400 mV.; and the current recorded. Fig. 7 depicts the current transient for the conditions cited. The initial portion when the current is negative has been omitted and the current to the left of the graph is a combination of the reduction of surface oxide and the oxidation of methanol. The peak current at 400 mV. is about 2.5mA/cm^2, some 20-50 times greater than that observed after one second. The area under the curve corresponds to the charge required to oxidize a monolayer of hydrogen. The reason for the experiment was to gain some insight into the relative rates of adsorption and oxidation at lower potentials. It must not be concluded that the peak current represents the maximum rate of methanol adsorption at this potential. Obviously the rate of adsorption is considerably faster, since the peak value includes a cathodic oxide reduction current.

Furthermore, it would appear that the initial reaction involves the abstraction of one or more hydrogen atoms which are oxidized instantaneously at a potential of 400 mV. The sluggish reaction is then ascribed to the oxidation of the remaining methanol radical.

CONCLUSIONS

We have already cited the reaction mechanism proposed by Vielstich (3), who assumes that the anodic oxidation of platinum to a platinum hydroxide is the rate determining step. The methanol subsequently reacts chemically with the metal hydroxide. The author supports his hypothesis by the fact that normally the potential of the peak current is independent of the oxidizable substance. This phenomenon is equally well explained by the assumption that a surface oxide or hydroxide inhibits the oxidation reaction. For, the formation of this inhibitor is essentially independent of fuel. Furthermore, it has been shown by Vielstich that at higher temperatures the potential required to oxidize methanol decreases. Although the author explains this phenomenon by assuming a base catalyzed dehydrogenation mechanism, we have found no evidence for his hypothesis since the i-V curves and Tafel slopes for the initial sweeps are not significantly dependent upon temperature between 0° and 60°C.

Furthermore, examination of the i-V curves for acid and base systems shows that the potentials at which appreciable currents are obtained shift about the same amount for both systems (about 300 mV.) as the temperature is raised from 25° to 85°C. It should also be stated that the equilibrium potential for the basic system is some 250 mV. more negative than that for the acid system; and if the reaction mechanism, Tafel slope and exchange current are the same for both systems, the oxidation of methanol in the basic system at 80°C should be quite appreciable near the potential of the hydrogen electrode in the same solution. It would then be reasonable to assume that if the dehydrogenation is base catalyzed it is also acid catalyzed.

In the basic system complete dehydrogenation of methanol would result in the formation of a carbon monoxide species on the electrode surface. It has been shown that the final product of the oxidation of methanol is either formate or carbonate (3). This implies that carbon monoxide fragments on the surface are further oxidized. Since the carbon monoxide normally inhibits anodic processes (7) it may be assumed that the substance is strongly adsorbed; and should, therefore, decrease the rate of dehydrogenation since the electrode surface is no longer available for catalysis. It appears to us, therefore, that a base catalyzed dehydrogenation mechanism is not responsible for the increased currents in the base system.

It is our hypothesis, in view of the current transient measurements, that even at the lower temperature the radicals are most difficult to oxidize and enhanced dehydrogenation should not influence the rate appreciably, at least not at the lower potentials. It seems to us that the initial reaction sequence can best be described by the following mechanism

$$CH_3OH \xrightarrow{fast} CH_3O_{ads} + H_{ads}$$

$$H_{ads} \xrightarrow{fast} H^+ + 1e$$

The CH_3O_{ads} is then further oxidized, and at potentials below 600 mV. this oxidation process is the rate determining step in the reaction. The actual intermediate formed from the adsorbed CH_3O will probably depend on the final product, whether this be

the carbonate or the formate ion. In general, it would be reasonable to assume that the intermediate lies between CH_3O and formaldehyde (or adsorbed formaldehyde) since the latter is much more readily oxidized than methanol (3).

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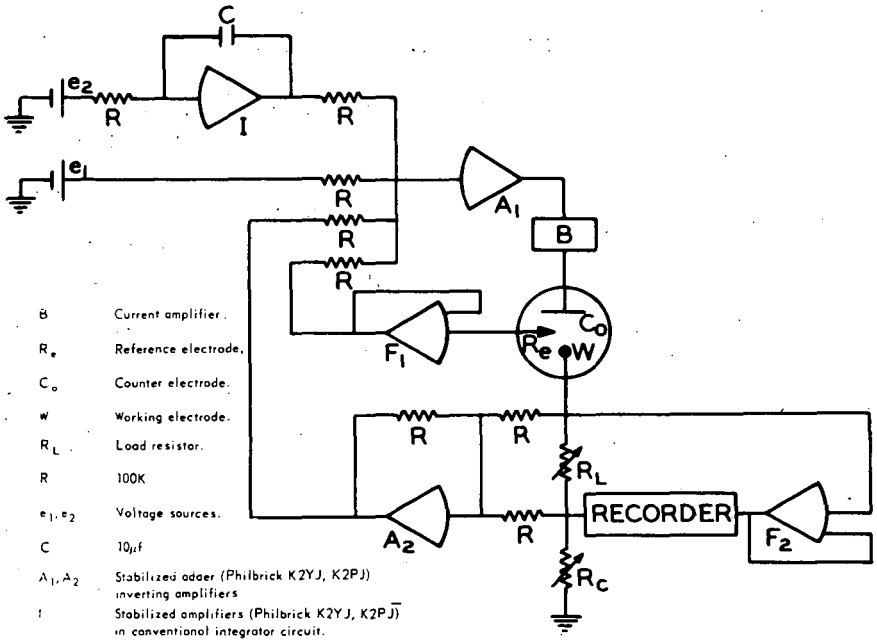

B	Current amplifier.
R_e	Reference electrode.
C_o	Counter electrode.
W	Working electrode.
R_L	Load resistor.
R	100K
e_1, e_2	Voltage sources.
C	10μf
A_1, A_2	Stabilized adder (Philbrick K2YJ, K2PJ) inverting amplifiers
I	Stabilized amplifiers (Philbrick K2YJ, K2PJ) in conventional integrator circuit.
F_1, F_2	Stabilized follower (Philbrick K2YJ, K2PJ).
R_c	Compensating resistor, continuously variable to 10 ohms.

FIGURE 1

Voltammetric Circuit for Continuous Ohmic Voltage Compensation

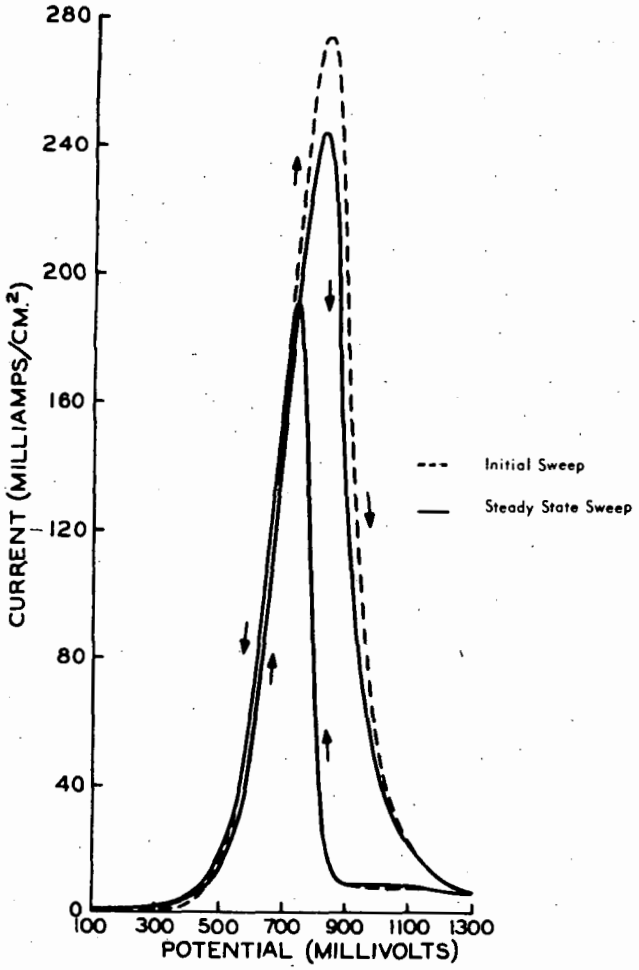

FIGURE 2

Current – Potential Curve for the System, Bright Pt/2M CH_3OH/4.5M NaOH at 60°C and a Voltage Sweep Rate of 100 mv/sec.

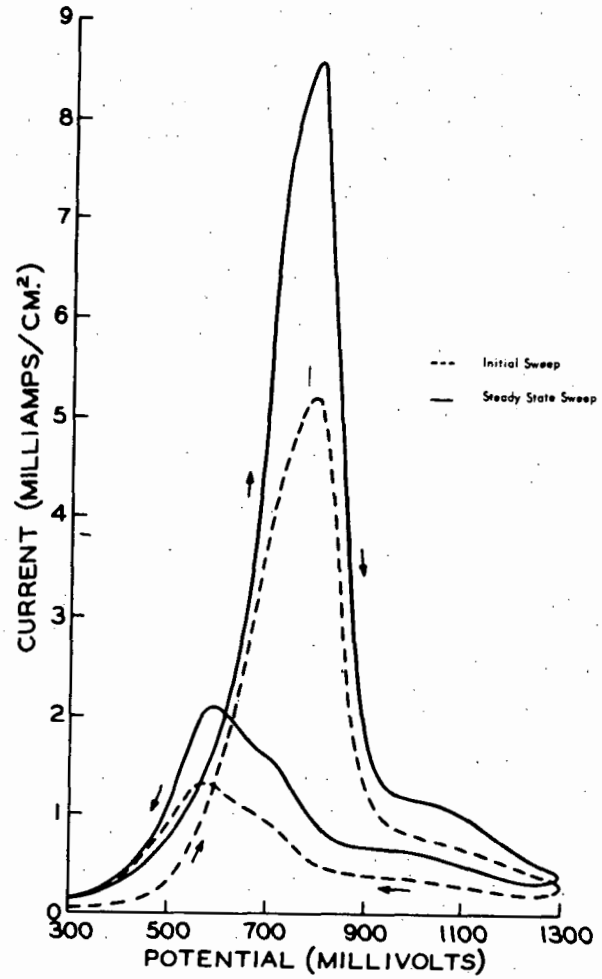

FIGURE 3

Current – Potential Curve for the System, Bright Pt/2M CH_3OH/4.5M NaOH at 0°C and a Voltage Sweep Rate of 100 mv/sec.

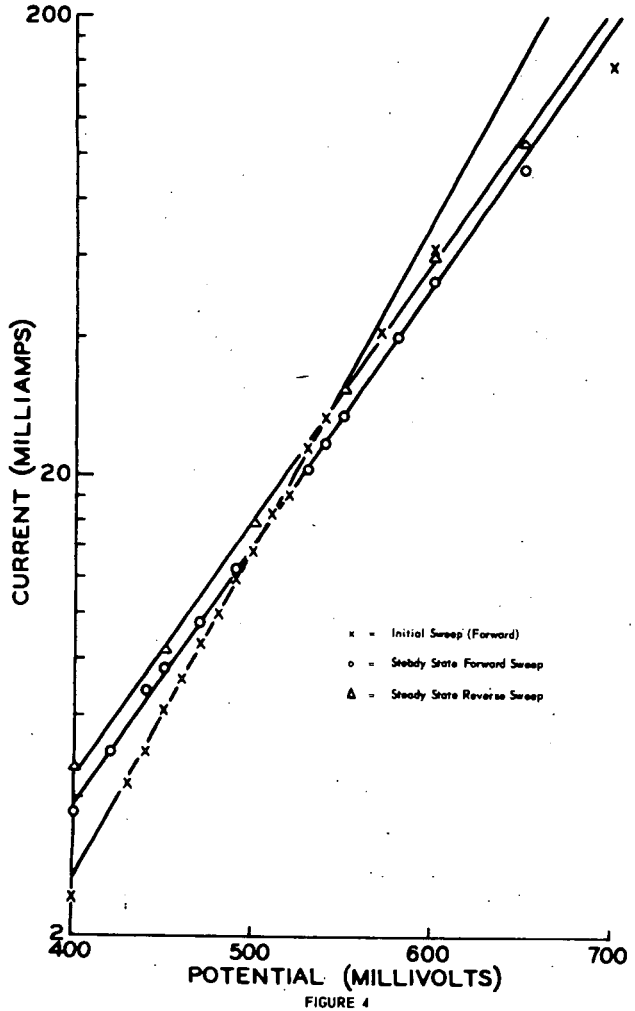

FIGURE 4

Log i Vs Potential for the System, Bright Pt/2M CH_3OH/4.5M NaOH at 60°C and a Voltage Sweep Rate of 100 mv/sec.

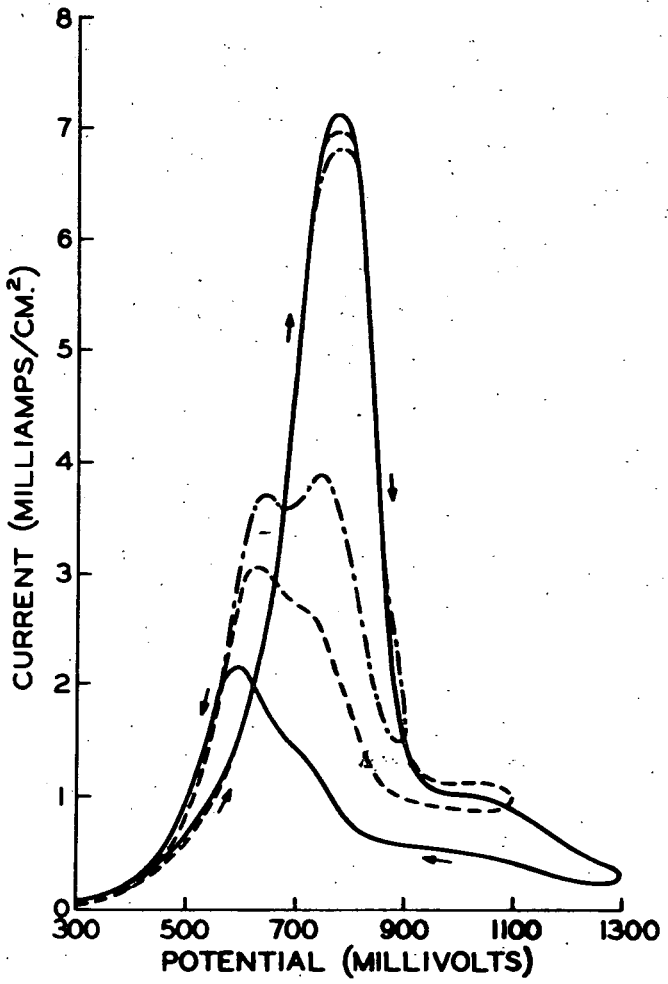

FIGURE 5

The Effect of the Final Potential on the Shape of the Current – Potential Curve at 0°C, Sweep Rate 100 mv/sec.

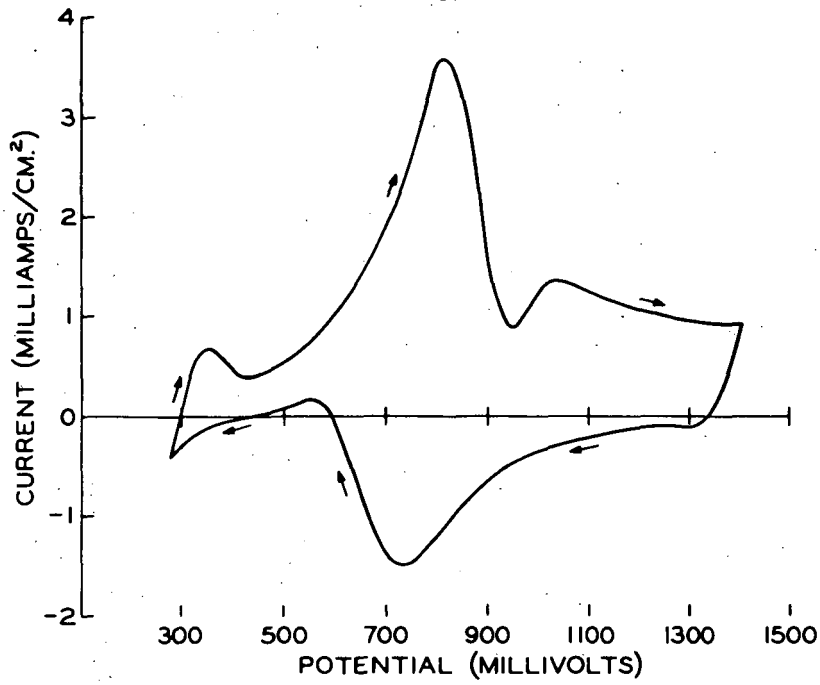

FIGURE 6

Current – Potential Curve of the System, Bright Pt/0.1M CH_3OH / 4.5M NaOH at 30°C and 500 mv/sec.

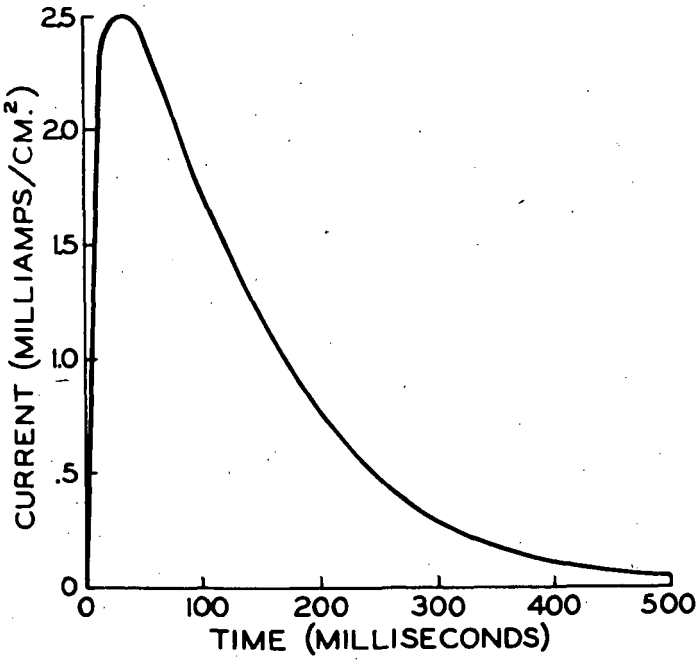

FIGURE 7

Current Transient at 400 mv for the System Bright Pt/ 1M CH_3OH/ 1M NaOH at 30°C.