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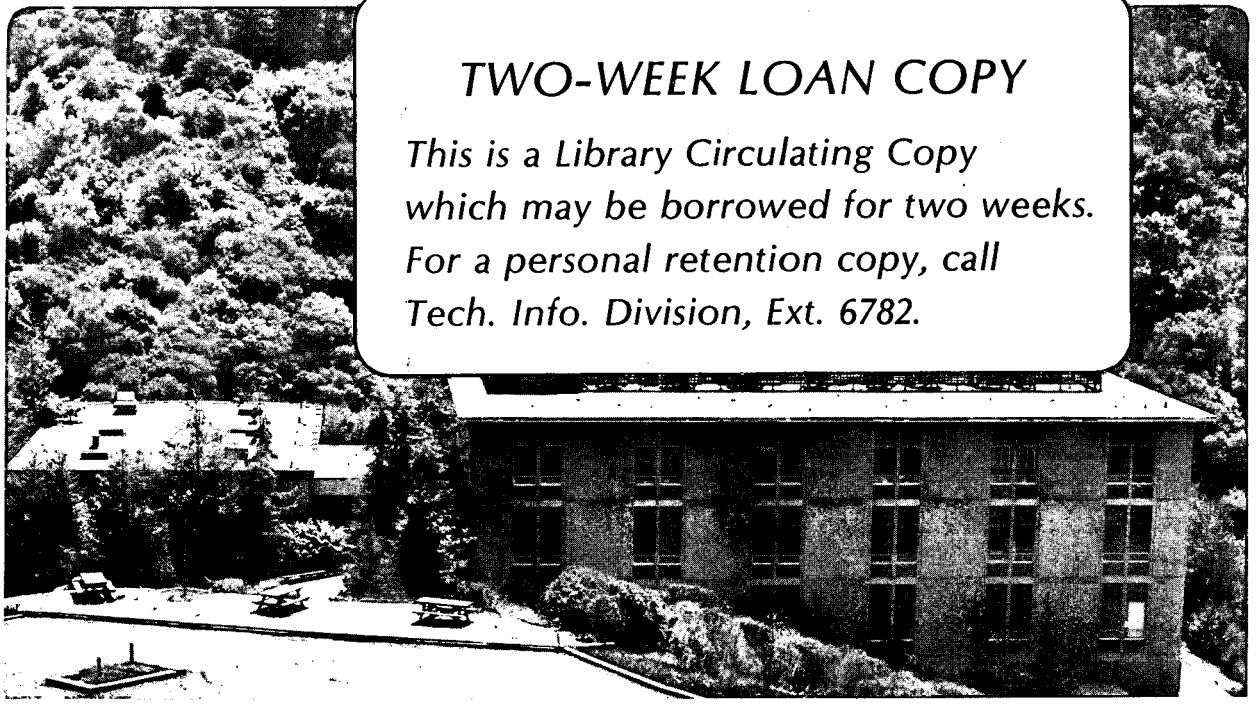
September 1983



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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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DIFFUSION CONTROLLED MULTISWEEP CYCLIC VOLTAMMETRY

III. DEPOSITION OF SILVER ON STATIONARY AND ROTATING DISK ELECTRODES

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ABSTRACT

An experimental study of diffusion controlled silver electrodeposition has been carried out in order to investigate the applicability of the model for reversible metal deposition during multisweep cyclic voltammetry. For a stationary planar electrode excellent agreement between theory and experiment has been obtained for the position of the cathodic current maxima on the potential axis as well as for the dependence of their magnitude on parameters such as sweep rate, cathodic reversal potential, and number of applied sweeps. Anodic currents measured at the foot of the wave deviated from theoretical predictions as a consequence of the small but uncompensated resistance of the electrolyte. In an effort to predict and therefore control the amount of deposit, integral charges associated with each sweep have been measured and successfully correlated with the parameters of the experiment. It has been found that at mM concentrations, deposit thicknesses of the order of up to 20 monolayers can be formed with quantitative control. Experiments with a rotating disk electrode have demonstrated that a periodic current response is obtained upon multiple sweeping as predicted by theory. First sweep and periodic currents normalized with respect to the limiting current could be correlated with the dimensionless sweep rate in accordance with the theoretical predictions. Contrary to previous investigations, the diffusion coefficient of the silver ion was determined

by limiting current measurements and the value thus obtained was subsequently used to successfully correlate stationary electrode cyclic voltammetry data. During limiting current measurements with very slow sweeps, the development of surface roughness was observed as a significant increase of the current from the constant value obtained at faster sweeps. Based on the dimensionless sweep rate, a semiempirical criterion was developed for the optimal conditions for the potentiodynamic determination of steady state limiting currents, the use of which may eliminate errors arising from both transient effects and surface area increase due to roughness.

Key words: electrode, deposition, mass transport, voltammetry, silver

1. INTRODUCTION

In previous communications (1,2) we presented calculations for diffusion-controlled cyclic voltammetry (CV) for both a stationary planar and a rotating disk electrode (RDE) for reversible depositions at unit deposit activity. These represented extensions to previous linear sweep voltammetry (LSV) analysis for the stationary electrode (3) and the RDE (4), and were carried out in order to predict the effects of multiple sweeping on the deposition current and charge. For an experimental investigation of the theoretical predictions, we chose the electrodeposition of Ag for several reasons. The kinetics of this reaction are very fast, so the reaction can be considered reversible and controlled by diffusion as required by the theory. The equilibrium potential is sufficiently anodic to allow for a wide selection of values for the potential at which the sweep is reversed (other reversible systems such as Sn^{+2}/Sn do not allow for this possibility due to the onset of H_2 evolution). Since Ag deposits are usually rough and the amount of deposit is quantitatively related to sweep rate, manipulation of sweep rate values can be used to induce electrochemically noticeable roughness, thereby contributing to a quantification and possibly an elucidation of this phenomenon. Previous investigations (5,6) of the Ag system by LSV have shown agreement between theory and experiment for stationary electrodes but the value of the diffusion coefficient of the Ag^+ ion used by Mamantov, et al. (5) originated from a non-electrochemical measurement by Stackelberg, et al. (7). On the other hand, Bachmann and Dohrmann (6) obtained their diffusivity value by essentially fitting the Delahay LSV model (3). In the present investigation, consistency is sought by measuring diffusivity from limiting currents and

using the value thus obtained to correlate stationary electrode and RDE single sweep and multisweep voltammetry data. Also in limiting current measurements by Kraichman and Hogge (8) as well as in a previous LSV-RDE study by Andricacos and Cheh (4), gelatin was used in the electrolyte as a leveling agent, but as we are interested in this study in the effects of roughness on multisweep voltammetry, no leveling agents were employed.

2. EXPERIMENTAL

Experiments were performed in a glass three-compartment cell. Silver wires were used for both reference and counter electrodes. The working electrode was a Pine Instruments Au RDE with a geometrical area of 0.46 cm^2 polished to a mirror finish. When rotating, it was driven by a Pine Instruments Analytical Rotator assembly. The electrolyte composition was $1.1(2) \times 10^{-3}$ $AgNO_3$ in 1 M $HC\ell O_4$; it was prepared from reagent grade $AgNO_3$ (Allied Chemical), electronic grade $HC\ell O_4$ (Apache Chemicals), and pure H_2O (Harleco). No further purification was attempted. The electrode potential was controlled with a PAR potentiostat (Model 173D) connected to a PAR Universal Programmer (Model 175). The potentiostat was equipped with a digital coulometer (PAR Model 379) and both current and integral charge were recorded either with a X-Y recorder or an oscilloscope depending on the sweep rate.

The Au RDE at zero rotation speed served as a stationary planar electrode. It was preferred relative to other possibilities since its configuration minimized possible natural convection complications, i.e. downward facing with the density increasing from top to bottom (9). An inert substrate was chosen instead of Ag to avoid repeated polishing and subsequent irreproducibilities in the initial condition of the surface.

The Au RDE was initially immersed in the O_2 free electrolyte at a potential of 0.200 V anodic to that of the reference Ag wire and was subsequently cycled in the UPD region. Figure 1 shows a typical voltammogram obtained at 0.050 Vs^{-1}. Peaks I,I' represent underpotential deposition and stripping, whereas peaks II,II' probably originate from an alloying state (10). These peaks were invariant with rotation speed whereas peaks III,III' were rotation dependent and were taken as bulk deposition. Bulk deposition occurred at potentials slightly anodic to zero vs. Ag wire since the Nernstian potential is apparently not established at monolayer coverages. If the cathodic sweep is extended well into the bulk deposition region, the resulting diffusion controlled peak is of lower magnitude compared to an electrode initially covered with Ag. A simple excursion into the UPD region is thus not sufficient to establish the Nernstian equilibrium potential of Ag corresponding to unit activity at the surface. Unit activity was achieved by preplating the RDE surface at -0.025 V and 1600 rpm until a deposit equivalent to a charge of ca. 10^{-2} C cm^{-2} had accumulated on the surface. The potential of the preplating was chosen sufficiently away from the limiting current to avoid powder formation (9). Upon opencircuiting, the RDE potential was within 0.001 V relative to the Ag wire and remained constant for at least 15 min. The potentiostat was reconnected and the electrode potential adjusted so that exactly zero current passed as judged by the digital coulometer registering less than 10^{-7} C for at least 1 min. This procedure guaranteed that the anodic reversal potential was exactly the equilibrium at unit surface activity. After this initial preparation, the cathodic reversal potential was chosen and multisweep measurements were taken. Upon completion of the measurements, the electrode potential was

swept into the anodic region again and the deposited Ag was stripped at +0.020 V. After some time the anodic current dropped to ca. 0, leaving residual Ag at a surface activity consistent with an equilibrium potential of 0.020 V. Slow sweeping at 0.001 Vs^{-1} in the anodic direction resulted in stripping of all deposited Ag both during preplating and CV measurement. For each sweep rate the procedure was repeated and yielded results reproducible to better than 1%. For the limiting current measurements, the preplating step was omitted.

3. RESULTS AND DISCUSSION

A. Cyclic Voltammetry on a Stationary Planar Electrode

Figure 2a shows a typical multisweep voltammogram for Ag deposition on the Ag-preplated Au horizontal disk electrode. The same voltammogram appears in Fig. 2b but unfolded in time. The second representation is better if the emphasis is on the measurement of current peak heights. Figure 2c is the corresponding charge/potential diagram. Since such diagrams have not appeared in the literature before, a brief qualitative description will be given here. The curve 0-a-b-c in Fig. 2c corresponds to the charge in the first complete sweep, including both cathodic and anodic portions. Point a is the value of the charge at the end of the first cathodic sweep, i.e. at the cathodic reversal potential. During the reverse sweep, the charge continues to increase in the cathodic direction until it reaches an extremum at point b; this corresponds to the potential at which the current changes from cathodic to anodic. Since the current remains anodic until the end of the reverse sweep, the cathodic charge decreases from point b to c. For a very short time after c, the decrease continues corresponding to that interval during the second sweep that the

current is anodic. At point d, the current becomes cathodic and the cathodic charge starts increasing again. The general features of the charge/potential diagram are retained as the number of applied sweeps, is increased. However, relative magnitudes change and the quantitative aspects of this change will be discussed below.

a. Peak Potentials

The overpotential at which the cathodic current maximum is observed is predicted (3) to be equal to 0.854 (RT/nF) = 0.022 V for ℓ=0 (T=25°C, n=1) and increases (2) to at most 1.3 (RT/nF) = 0.033 V upon multiple sweeping; it is independent of the sweep rate, diffusivity, and bulk concentration for reversible depositions at unit deposit activity. These predictions were verified to within 0.003 V.

b. Cathodic Current Maxima

The theoretical analysis predicts cathodic current maxima given by the relations (2):

$$i^{\ell}_{c,max}[(at_c)^{\ell}_{max};a\Theta] = A\ c^b\ v^{1/2}\ I^{\ell}_{c,max}[(at_c)^{\ell}_{max};\ a\Theta] \qquad [1]$$

$$\text{and } A = (nF)^{3/2}\ (RT)^{-1/2}\ D^{1/2}$$

where ℓ is the number of already applied complete sweeps, v the dimensional sweep rate, c^b the bulk concentration of Ag^+, a=(nF/RT)v, $(at_c)_{max}$ is the dimensionless peak overpotential in multiples of RT/nF, Θ the time duration of each anodic or cathodic part of the sweep, and $a\Theta$ is the dimensionless reversal overpotential in multiples of RT/nF. $I^{\ell}_{c,max}$ is the maximum value within a sweep of the cathodic current density function, the values of which can be computed from the equations given in Ref. 2.

Experiments were performed at three cathodic reversal overpotentials: 0.104, 0.155, and 0.411 V, corresponding to $a\Theta$ = 4, 6, and 16, respectively. The anodic reversal potential was always at the equilibrium. Values of the current function necessary for the calculations are given in Table 1. Plots of $i^{\ell}_{c,max}$ vs. $v^{1/2}$ are shown in Fig. 3. The solid lines in these figures correspond to the theoretical predictions of eq. [1] and agree very well with the experimental data. Since this is the case, a value for D_{Ag^+} can be extracted from the multisweep CV data and eq. [1] as was done by Bachmann and Dohrmann (6) using the Delahay model (3) predictions for LSV (ℓ=0). The value extracted from the CV data was 1.4 (2) x 10^{-5} cm^2s^{-1} which is also consistent with the value calculated from the RDE limiting current measurements to be described.

The value of the potential at which the sweep is reversed is immaterial for the current maximum during the first sweep (ℓ=0). However, it significantly affects its magnitude during subsequent sweeps. As $a\Theta$ increases, the height of the second (ℓ=1) maximum decreases. Furthermore, the differences between sweeps for ℓ>1 decrease with increasing $a\Theta$. This is in agreement with the computational observation (2) that in the limit $a\Theta\rightarrow\infty$, the current becomes periodic. It is interesting to note that even after 10 sweeps the cathodic current density maxima computed on the basis of the geometrical area of the electrode are still described by eq. [1].

c. Anodic Current Maxima

These are the anodic currents measured at the end of the ℓth anodic or the beginning of the ℓ+1 cathodic sweep, i.e. they are the currents measured at the equilibrium potential for ℓ>0. They are described by an equation identical to eq. [1], the only difference being in the values of

the current function:

$$i^{\ell}_{a,max} = A\ c^{b}\ v^{1/2}\ I^{\ell}_{a,max} \qquad [2]$$

$I^{\ell}_{a,max}$* values relevant to the experimental conditions of the present study are given in Table 1. Figure 4 shows a comparison between the predictions of eq. [2] (solid lines) and the experimental points.

It is observed that the measured currents are lower than those predicted by eq. [2]; the deviations are more pronounced at the higher sweep rates and the lower values of $a\Theta$. Such deviations would be expected from a small iR effect since the current variation near the equilibrium potential is very steep and it becomes steeper the faster the sweep rate and the smaller the $a\theta$ value. An alternative effect with a similar pattern of deviation with sweep rate and $a\Theta$ can be thought of as arising from finite kinetics of the dissolution reaction. However, no additional evidence for kinetic limitations was observed. It should be noted that anodic current deviations are not expected to propagate with ℓ since they occur over very short time intervals. Maximum anodic currents do not exhibit a strong dependence on either the number of cycles or the reversal potential. Generally, they increase with ℓ and $a\Theta$, and this behavior is not difficult to rationalize in terms of the computed concentration profiles (1).

c. Cathodic Charges

Integral cathodic charges as functions of ℓ and $a\Theta$ are shown in Figures 5 and 6. In Fig. 5 the quantity q_c is the amount of charge accumulated during the ℓ+1 cathodic sweep; its value can be read off easily from

*Equivalently, $I_c^{\ell+1}(0;a\Theta)$

a charge/potential diagram such as the one appearing in Fig. 2c. For instance, for $\ell=0$, q_c^0 is the value at point a; for $\ell=1$, q_c^1, i.e. the charge during the second cathodic sweep, is the difference between points e and c; for $\ell=2$, q_c^2 is the difference between points g and f, and so on.

Charge has a linear dependence on the inverse of the square root of the sweep rate (2) as shown by

$$q_c^\ell(a\Theta) = B\ c^b\ v^{-1/2}\ Q_c^\ell(a\Theta)$$

$$\text{and } B = (nFRTD)^{1/2} \qquad [3]$$

where Q_c^ℓ is the charge density function, values of which are given in Table 1, computed from the equations of Ref. 2. Good agreement between eq. [3] and experiment can be seen in Fig. 5, except in the case for $a\Theta=16$ and $\ell>0$ in the low sweep rate range. The charge deviations under these conditions are not accounted for by the anodic current deviations in Fig. 4. Although one would expect that lower measured anodic currents would yield higher cathodic charges, the time duration over which these lower anodic currents are measured is too small to account for the deviations appearing in Fig. 5. We attribute these deviations to a roughness effect. Although it may not affect the value of the current density at any given potential, its effect is enhanced when one integrates over the entire current curve. This explanation is consistent with deviations appearing at conditions that produce high total charge, e.g. low sweep rates, high reversal potentials, and values of ℓ greater than 0.

As can be seen from Fig. 5, the amount of deposit accumulated even after multiple potential sweeps is very small. Assuming that the formation of a Ag monolayer requires 2×10^{-4} C cm^{-2}, it is seen that the largest value

($a\Theta$=16), v=0.010 Vs^{-1}) measured on the first sweep corresponds to about 15 monolayers. During the reverse sweep the charge remains almost constant (e.g. points a and d on Fig. 2c) and increased by about 10 more monolayers during the second cathodic sweep (ℓ=1). Although the net amount is only of the order of 20 monolayers, a roughness effect is detectable from the deviations of the charge from that predicted by the theory. It should be noted that if the roughness originated from preplating it should manifest itself during the ℓ=0 sweep; however, the ℓ=0 results agree with eq. [3] in which the geometrical area of the electrode has been used.

A plot of the dimensionless net charge density function, Q_n^ℓ, is shown in Fig. 6. Theoretical predictions (2) are given in Table 1, whereas experimental values are obtained from

$$Q_n^\ell(a\Theta) = q_n^\ell(a\Theta)/B\ c^b v^{-1/2} \qquad [4]$$

where q_n^ℓ is the value of the charge at the equilibrium potential. For instance, with reference to Fig. 2c, q_n^0 corresponds to point c, q_n^1 to the difference between points f and c, and so on. Q_n^ℓ depends only on ℓ and $a\Theta$ but not on the sweep rate. Therefore, for fixed ℓ and $a\Theta$, Q_n^ℓ should be the same irrespective of which pair of q_n^ℓ and v values is used. Results in Fig. 6 have been computed for v=0.150 Vs^{-1} and the corresponding q_n^ℓ values; however, if data for 0.010 Vs^{-1} were used, the deviations observed for $a\Theta$=16 and ℓ=1,2 should appear in Q_n^ℓ as values higher than the ones obtained for v=0.150 Vs^{-1}.

Figure 6 indicates that potential sweeping from the equilibrium to some reversal value and back, always results in the formation of a net deposit on the surface. The amount is maximum for the first sweep but

decreases considerably upon multiple sweeping. In the limit $\ell \to \infty$ the hypothetical charge density during the complete sweep is predicted (2) to be 0, and this trend appears in Fig. 6.

B. Cyclic Voltammetry on a Rotating Disk Electrode

Experiments were performed at two rotation speeds, 80 and 400 rpm, and at sweep rates varying from 0.050 to 10 Vs^{-1}, corresponding to a variation in the dimensionless sweep rate, σ, between 5 and 215. Double layer currents were corrected for with a constant value of 50 $\mu f\ cm^{-2}$ measured by the method of Bachmann and Dohrmann (6). Since the double layer capacitance is a potential dependent quantity errors are introduced especially at sweep rates higher than 2 Vs^{-1} at which double layer currents are a significant portion of the measured total.

A representative RDE voltammogram appears in Fig. 7a, obtained at 0.1 Vs^{-1} and a rotation speed of 80 rpm. The value of the dimensionless sweep rate

$$\sigma = \frac{nF}{RT} v \frac{\delta^2}{D} \qquad [5]$$

where δ is the thickness of the Levich diffusion layer, is ca. 11 at this sweep rate and rotation speed. Since $\sigma>3$, a peak of magnitude $i^o_{c,max}$ should appear on the first sweep (1,4), as was observed. For $\sigma>4$, this peak is the same as if the electrode were stationary. If ω is increased to 400 rpm, the $\sigma>3$ condition is not satisfied and no current peak should appear; such a peak was not observed when ω was increased to 400 rpm. The sweep in Fig. 7a was reversed at an overpotential of 0.300 V where a limiting current was observed. Since the characteristic time of the RDE, δ^2/D, was approximately 2.8 s and the duration, Θ, of each sweep 3s, the periodicity

criterion (1) requiring $\Theta > \delta^2/D$ was strictly satisfied. It is then expected (1) that the current response during the second cathodic sweep be periodic, i.e. not change during multiple sweeping. This behavior is confirmed in Fig. 7a; the height of the periodic cathodic current maximum, $i_{c,max}$, is lower than $i^o_{c,max}$ and does not change upon multiple sweeping.* Similarly, the magnitude of the anodic current, i_a, at the foot of the wave is always constant, provided that the periodicity criterion is satisfied. It should be noted here that it is not always possible to meet the periodicity requirement exactly. For instance, with a characteristic time of 2.8 s (80 rpm) and a sweep rate of 1 Vs^{-1}, 2.8 V of potential range are required. However, even for $\Theta > 0.1(\delta^2/D)$ the deviation of the current from that for the exact periodic state is not experimentally significant as was confirmed by the observed voltammetry.

Figure 7b is the charge/potential diagram corresponding to the RDE voltammogram of Fig. 7a. Due to the electrode rotation more deposit is accumulated on the RDE than on the sationary electrode at the same conditions. The amount of deposit, and the equivalent charge, is mostly defined by Θ and the limiting current, i_L. Since the electrode current is near i_L for most of the time, and since the excess cathodic charge in the cathodic current peak is partially counterbalanced by the anodic charge near the equilibrium potential, the charge/potential diagrams have a much simpler (nearly linear) appearance than the stationary electrode diagrams (Fig. 2c).

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*Errors arising from double layer capacitance corrections are more significant in the value of the periodic current maximum since $i_{c,max} < i^o_{c,max}$ and their difference increases with increasing σ.

LSV current functions are related to σ by (1,4)

$$J^{o}_{c,max} = \frac{i^{o}_{c,max}}{i_L} = 0.61\ \sigma^{1/2},\ \sigma>4 \qquad [6]$$

It should be noted that an experimental investigation of eq. [6] does not require knowledge of the bulk concentration of the reactant or the electrode area as long as it remains constant during the performance of the experiment. Due to the dimensionless nature of eq. [5], it is possible that different combinations of rotation speed and sweep rate yield the same value of σ. On the other hand, the measured peak currents when normalized with respect to the appropriate i_L, should yield the same J. This was in fact observed as shown by the results of Fig. 8.

The periodic current maxima correlation (1)

$$J_{c,max} = \frac{i_{c,max}}{i_L} = 0.88\ \sigma^{0.251},\ \sigma>9 \qquad [7]$$

is seen (Fig. 9) to agree well with the experimental data. Again $J_{c,max}$ is independent of electrode area and reactant bulk concentration. In addition, its value for a particular σ does not depend on the particular combination of ω and v that gives rise to this value of σ. The dependence of $J_{c,max}$ on σ is weak and requires a large range of sweep rates for its experimental determination. However, if low rotation speeds are used this is not a significant disadvantage. At low rotation speeds the periodic state is established, unlike the ℓ-dependence of a stationary electrode response, and can be retained for longer times since deposit accumulation is also lower.

Figure 10 shows the dependence of the periodic dimensionless anodic current function maximum on σ, which is predicted (1) to be

$$J_a = \frac{i_a}{i_L} = 1 - \sigma^{1/2},\ \sigma>9 \qquad [8]$$

The experimental observations deviate from the predictions of eq. [8] in a manner analogous to the i_a for the stationary electrode. The deviation is higher at the higher rotation speed and this is consistent with an iR effect since at higher rotation speeds anodic current variations are steeper near the equilibrium potential.

C. Limiting Current Measurements

Limiting currents were measured potentiodynamically in the rotation speed range 100-6400 rpm and were found to depend linearly on $\omega^{1/2}$ with zero intercept. Based on the geometrical area of the electrode, the extracted value for D_{Ag^+} was $1.4(2)\times10^{-5}$ cm^2s^{-1} in excellent agreement with the one reported by Bachmann and Dohrmann (6), and consistent with the value obtained from the CV data analysis above.

The possible errors associated with the determination of limiting currents by potential sweeping have been the subject of some discussion in the literature (11). It is believed that if the sweep rate is very high the resulting mass transfer situation is transient and does not yield an accurate measurement of mass transfer coefficients in the steady state. On the other hand, if the sweep rate is very low, and the reaction under study is electrodeposition, the onset of surface roughness with characteristic size similar to the diffusion layer thickness may also yield an erroneous limiting current measurement.

The fact that the potentiodynamically measured limiting currents yielded a value of D_{Ag^+} that is consistent with other literature indicates these objections to the potentiodynamic method require qualification. The more serious limitation is related to the control of the total amount of deposit during the time period required for limiting current measurements.

Potentiodynamically, the amount of deposit is not controlled directly, but indirectly by choice of rotation rate and sweep rate. The choice of these two parameters must be made judiciously to obtain true limiting current measurements that are relatively unaffected by surface roughness. For the combination of rotation rate and sweep rate such that $\sigma>3$, as in Fig. 7, the limiting current can be measured with the deposition of less than 1 $mC \cdot cm^{-2}$. There may be circumstances where i_L measurement using $\sigma>3$ is not possible, due to very high sweep rates or to insufficient potential range (competing reactions). However, when $\sigma<3$, the current increases more sharply to i_L (1) so that the measurement can be made in a narrower potential region, but the quantity of deposit will be much larger, and the possibility of roughness effects much greater. Roughness effects were clearly evident for some combinations of rotation rate and sweep rate, as shown in Fig. 11.

For very low values of the sweep rate (0.002 and 0.005 Vs^{-1}, Fig. 11) there appear to be well defined conditions at which the current increases beyond the I_L value. Since the electrode potential is such that no other reactions besides Ag deposition can occur, this increase must be attributed to an increase of the effective surface area of the electrode through the formation of irregularities of characteristic dimension comparable to the thickness of the diffusion layer. It is also possible that these irregularities once formed may further enhance mass transfer through their effect on the hydrodynamics of the system. Table 2 shows results obtained at different sweep rates and rotation speeds for the potential and the integral charge at which the measured current becomes greater than the limiting current. Several features of these results should be noted: at the same rotation speed, less deposit and more overpotential is required

at increasing sweep rates; at the same sweep rate, the critical overpotential increases with increasing rotation speed; assuming uniform deposition the height of the deposit at the onset is at least 100 times smaller than the boundary layer thickness.

It should be noted also that the characteristis amounts of Ag deposited in Table 2 are approximately 10-100 times greater than in the other CV curves which were used to test the RDE theory. Collectively, these observations indicate that the irregularities are confined to a very small (e.g. 1%) fraction of the total surface, possibly at the very edge of the disk. We do not, however, offer a definitive physical interpretation of the surface roughness.

4. CONCLUSIONS

An experimental investigation of Ag deposition by multisweep cyclic voltammetry has shown excellent agreement between experiment and a model assuming reversible kinetics at unit activity of the deposit. The anodic reversal potential was set to equal the equilibrium potential of the electrode while sweep rate, number of applied sweeps, and cathodic reversal potential were treated as parameters.

For the stationary electrode, cathodic current maxima (peaks) were observed that continuously decreased in magnitude with increasing number of applied sweeps and the peak potential in the cathodic direction. Peak heights were a linear function of the square root of the sweep rate with slopes which depend on the value of the current function at a given cathodic reversal potential as well as on the diffusion coefficient of the ion, its bulk concentration, and the area of the electrode. Although each complete sweep results in the formation of a net deposit, the electrode geometrical or projected area could be used to compute current densities at mM concen-

trations even after the application of 10 complete sweeps at 0.010 Vs^{-1} extending for 0.411 V in the cathodic potential region. The current measured at the equilibrium potential is zero initially but becomes anodic upon multiple potential sweeping. Its measured value was considerably lower than that predicted by the theory and this deviation was attributed to the uncompensated resistance of the electrolyte. Although this resistance is small, its effect in the measured current near the equilibrium potential is significant due to the very steep variation of the current function at this point. However, the deviation did not propagate with further cycling probably because it occurs over a very short time interval, i.e. the integrated charge deviation is a negligible fraction of the total net charge. The integral charges associated with each potential sweep on the stationary electrode followed a linear dependence on the inverse of the square root of the sweep rate. As the number of applied sweeps increases less deposit is formed during a cathodic sweep. However, even at deposit thicknesses of the order of 20 monolayers, a surface roughness effect was observed as a deviation of the measured charge density from the value computed on the basis of the geometrical area of the electrode.

Cyclic voltammetry experiments performed on the RDE verified the prediction that a periodic current response is obtained during the second and subsequent potential sweeps, provided that the periodicity criterion is satisfied. Although this criterion requires that the duration of each sweep be greater than the RDE characteristic time, it was found that for sweep durations of up to 10 times less the resulting periodic current response was not different than the one obtained when the periodicity requirement was strictly satisfied. The reversible deposition theory predicts that cathodic

current maxima are obtained provided that the dimensionless sweep rate σ exceeds 3, and this prediction was experimentally verified.

When the magnitudes of the cathodic current maxima were normalized with respect to the limiting current at a particular rotation speed, the resulting dimensionless quantity was correlated to the dimensionless sweep rate. For $\sigma>9$, the periodic dimensionless current was shown to vary linearly with $\sigma^{1/4}$. It was concluded that cyclic voltammetry on the RDE should be performed at low rotation speeds to avoid excessive deposit accumulation and the need for high sweep rates. At these rotation speeds, the limiting current as well as the first and periodic current maxima are well defined and the RDE correlations can be subsequently used for diagnostic purposes without accurate knowledge of the value of the electrode surface area or the bulk concentration of the reacting species.

In correlating cyclic voltammetry data for both stationary and rotating disk electrodes knowledge of the diffusion coefficient of the reacting ion is required. In this investigation a diffusivity value for D_{Ag^+} was obtained by RDE potentiodynamic limiting current measurements. At moderate sweep rates, a limiting current plateau was obtained which was accurately described by the Levich equation. However, at much lower sweep rates non-uniform deposit accumulation caused the limiting current to increase above its previously determined value. In order to avoid surface roughness and transient effects and also in order to maximize the potential range over which the limiting current is observed, it is concluded that the optimal value of the sweep rate is the one just before the appearance of the cyclic voltammetry current peak. For reversible deposition reactions this value can be found from the requirement that the dimensionless sweep rate be equal to 3.

ACKNOWLEDGMENT

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Table 1. Computed Vales of the Dimensionless Current and Charge Density Functions for Multi-sweep Cyclic Voltammetry (Reversible Deposition at Unit Deposit Activity on a Stationary Planar Electrode)

	$a\Theta$	$I^{\ell}_{c,max}$	$I^{\ell}_{a,max}$	$Q^{\ell}_{c}(a\Theta)$	$Q^{\ell}_{n}(a\Theta)$
	4	0.610†	0.785	1.917	1.982
0	6	0.610	0.829	2.505	2.738
	16	0.610	0.899	4.368	5.282
	4	0.390	0.829	1.163	0.993
1	6	0.355	0.868	1.439	1.345
	16	0.294	0.926	2.171	2.475
	4	0.353	0.848	1.026	1.764
2	6	0.320	0.886	1.253	1.035
	16	0.268	0.938	1.827	1.901
	4	0.299	0.890	0.873	0.372
10	6	0.270	0.923	0.964	0.503
	16	0.232	0.964	1.296	0.924

†Independent of $a\Theta$; computed in Ref. 3.

Table 2. Characteristic Values for the Potential and Integral Charge at which Deviation from the Limiting Current Occurs.

ω/ rpm	v/ $V \cdot s^{-1}$	$-\eta$/[a] V	$q \times 10^2$/[b] $C \cdot cm^{-2}$	$\delta \times 10^3$/[c] cm	$\ell \times 10^6$/[d] cm	δ/ℓ
3600	0.005	0.250	7.0	0.9	7.4	125
	0.010	0.350	5.2		5.5	169
	0.020	0.400	3.0		3.2	286
2500	0.002	0.175	10.1	1.1	11	104
	0.005	0.300	7.3		7.8	142
	0.010	0.425	5.3		5.6	198
1600	0.002	0.200	9.4	1.4	10	139
	0.005	0.350	6.9		7.4	189

[a]Cathodic overpotential at which deviation occurs.

[b]Integral charge at η.

[c]Thickness of the Levich diffusion layer.

[d]Deposit thickness equivalent to q; deposit assumed uniform with a density of 10.5 $g \cdot cm^{-3}$.

FIGURE CAPTIONS

Fig. 1. Cyclic voltammogram of a stationary Au disk electrode immersed in 1.1×10^{-3}M $AgNO_3$ + 1M $HC\ell O_4$; sweep rate: 0.050 $v \cdot s^{-1}$; the potential region is anodic to a Ag wire reference electrode in the same electrolyte.

Fig. 2. Cyclic voltammetry of Ag deposition on a stationary electrode; a) multisweep current/potential diagram obtained at 0.050 $v \cdot s^{-1}$ for a cathodic reversal overpotential of 6 (RT/F) or a $\theta = 6$. b) identical to a) but recorded on a time axis. c) charge potential diagram recorded simultaneously with a) and b).

Fig. 3. Dependence of the cathodic peak current density on the square root of the sweep rate, the number of applied sweeps, and reversal potential; solid lines are predictions of eq. [1] (stationary electrode cyclic voltammetry).

Fig. 4. Dependence of the maximum anodic current on the square root of sweep rate, the number of applied sweeps, and reversal overpotential; solid lines are predictions of eq. [2] (stationary electrode cyclic voltammetry).

Fig. 5. Dependence of integral cathodic charges on the inverse square root of the sweep rate, the number of applied sweeps, and reversal overpotential; solid lines are predictions of eq. [3] (stationary electrode cyclic voltammetry.

Fig. 6. Dependence of the net charge density function on reversal overpotential; solid lines are theoretical predictions and points are experimental results correlated by eq. [4] (stationary electrode cyclic voltammetry).

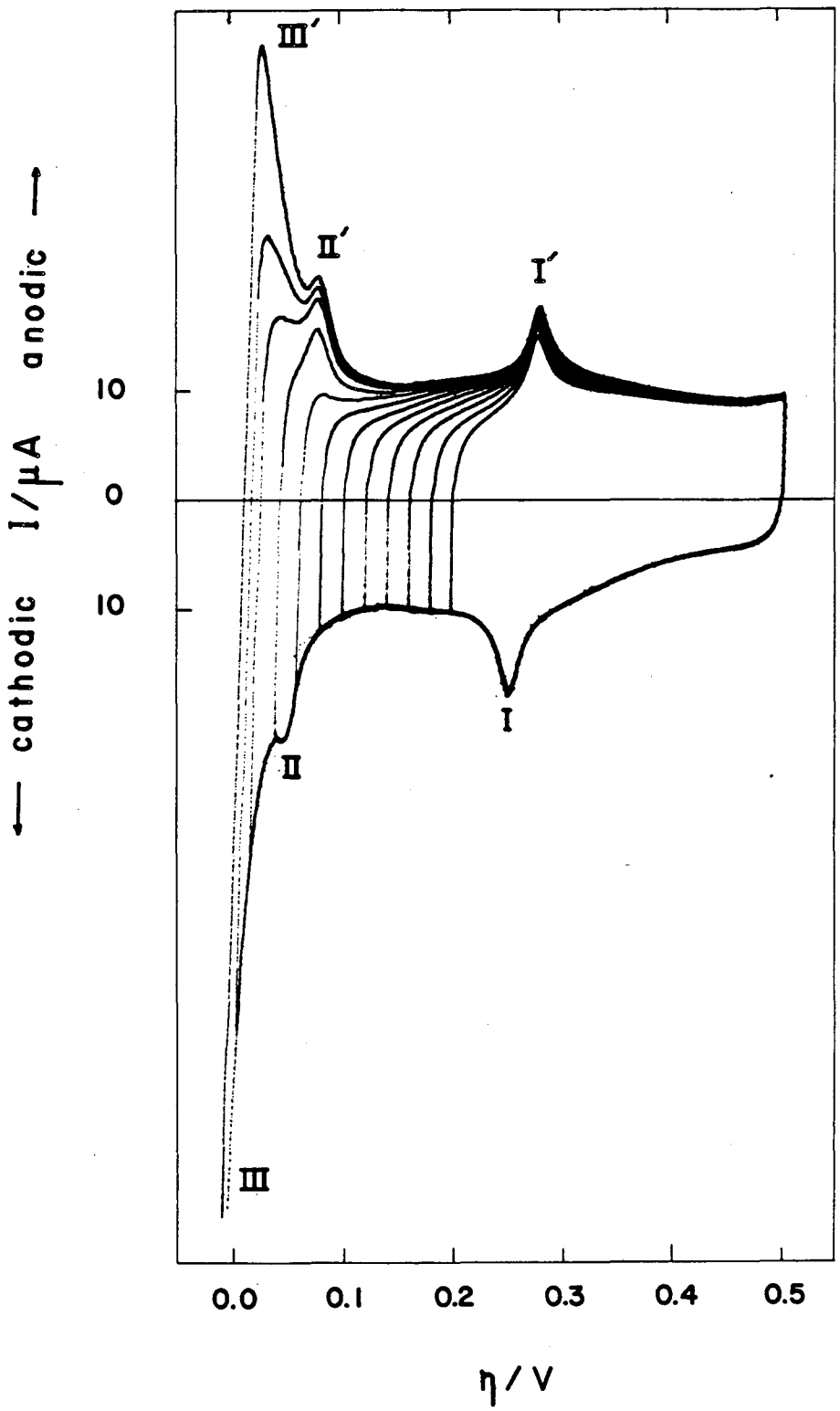
Fig. 7. Cyclic voltammetry of Ag deposition on a rotating disk electrode a) multisweep current/potential diagram obtained at 0.100 $v \cdot s^{-1}$ and ω = 80 rpm showing the first sweep and periodic current responses. b) charge/potential diagram recorded simultaneously with a).

Fig. 8. Dependence of the first sweep cathodic current maximum on the dimensionless sweep rate; solid line is the prediction of eq [6] (RDE cyclic voltammetry).

Fig. 9. Dependence of the periodic cathodic current maximum on the dimensionless sweep rate; solid line is the prediction of eq. [7] (RDE cyclic voltammetry).

Fig. 10. Dependence of the periodic anodic current maximum on the dimensionless sweep rate; solid line is the prediction of eq. [8] (RDE cyclic voltammetry).

Fig. 11. Potentiodynamic limiting current determination at 1600 rpm and 1: 0.025 Vs^{-1}; 2: 0.005 Vs^{-1}; 3: 0.002 Vs^{-1}.



XBL 836-10355

Fig. 1

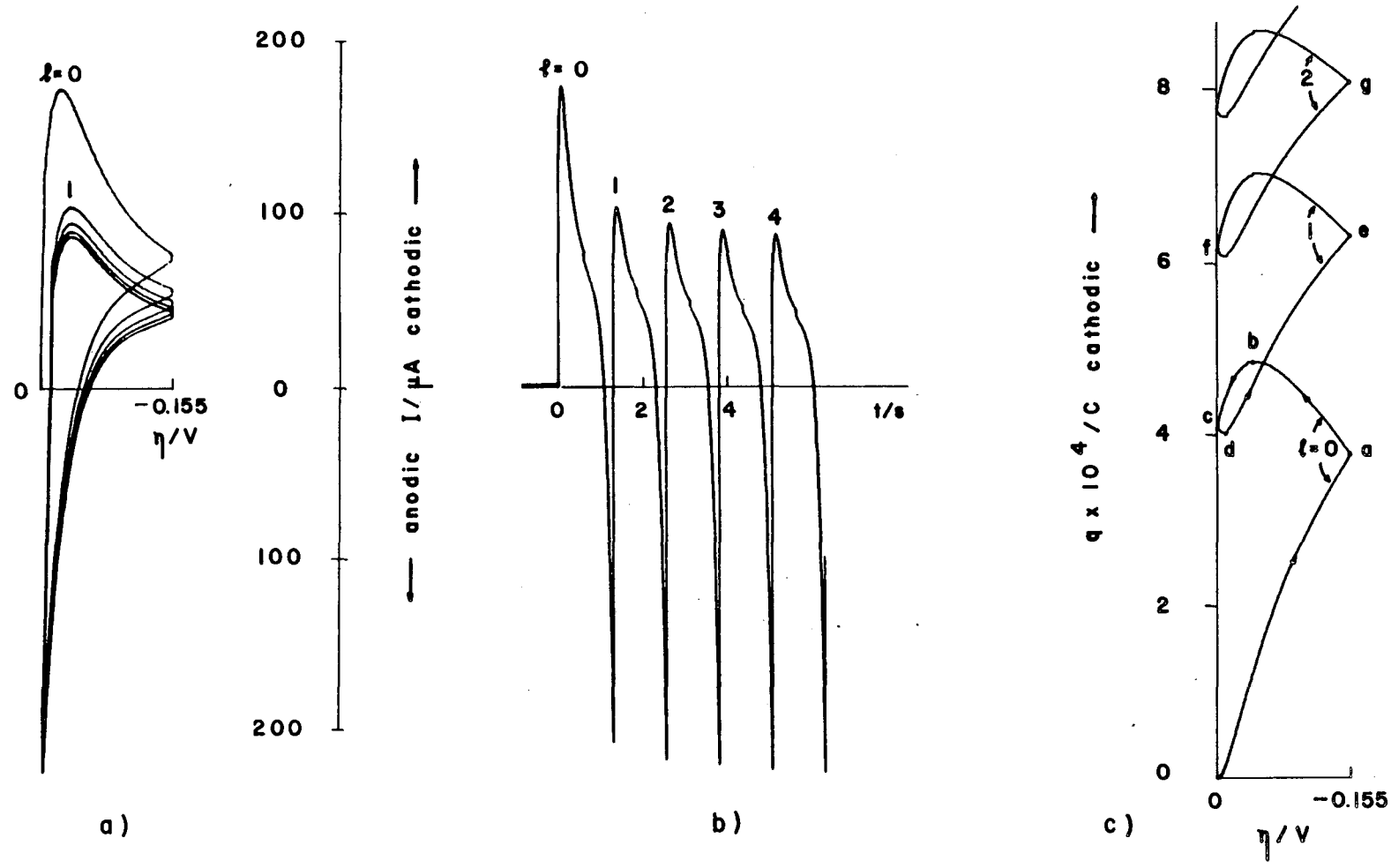


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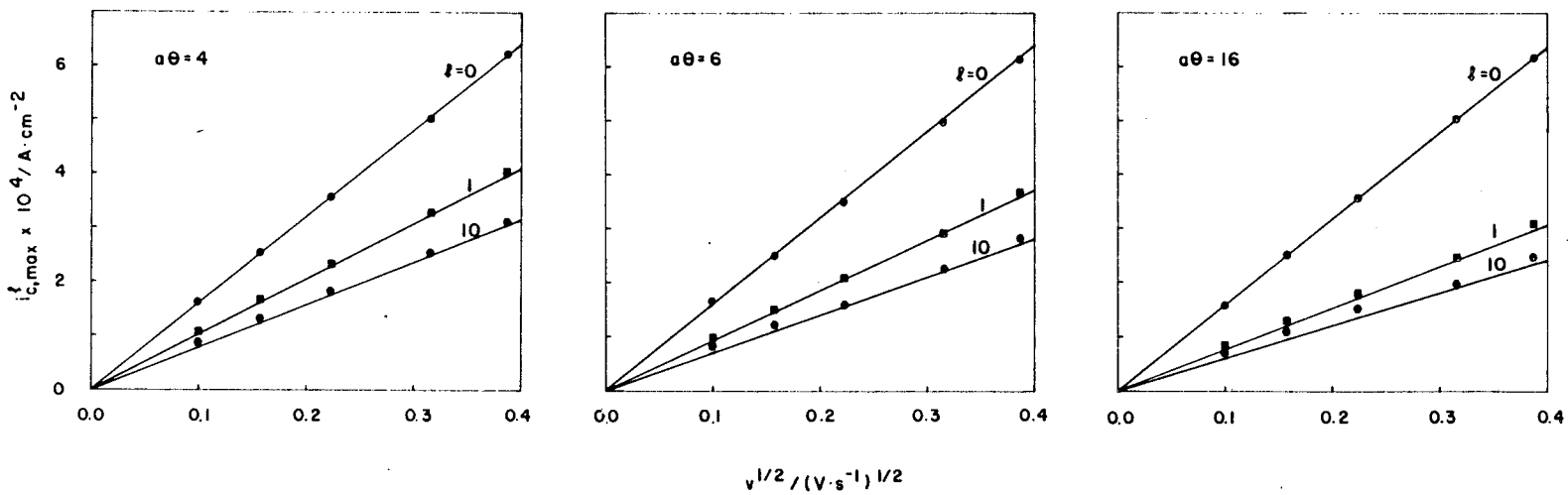
Fig. 2



XBL 836-10362

Fig. 3

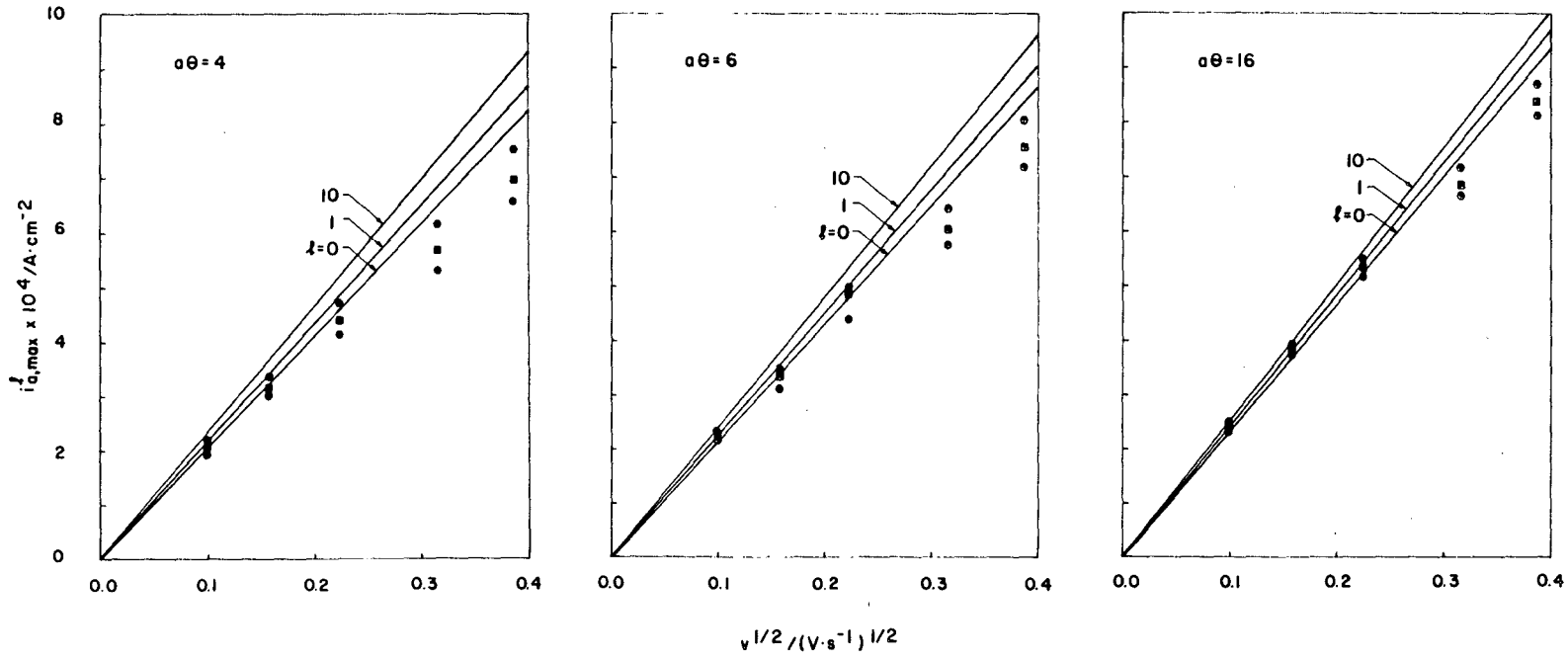


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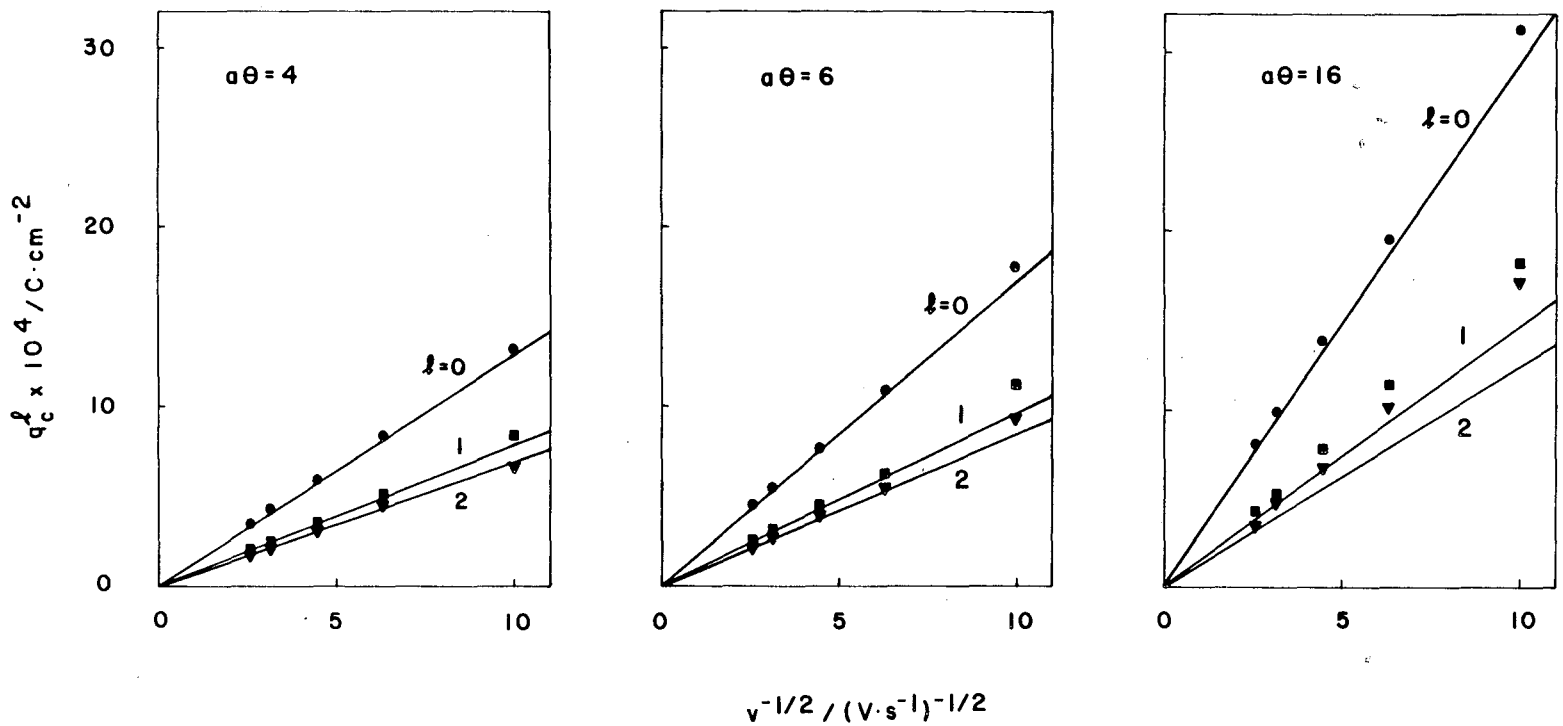
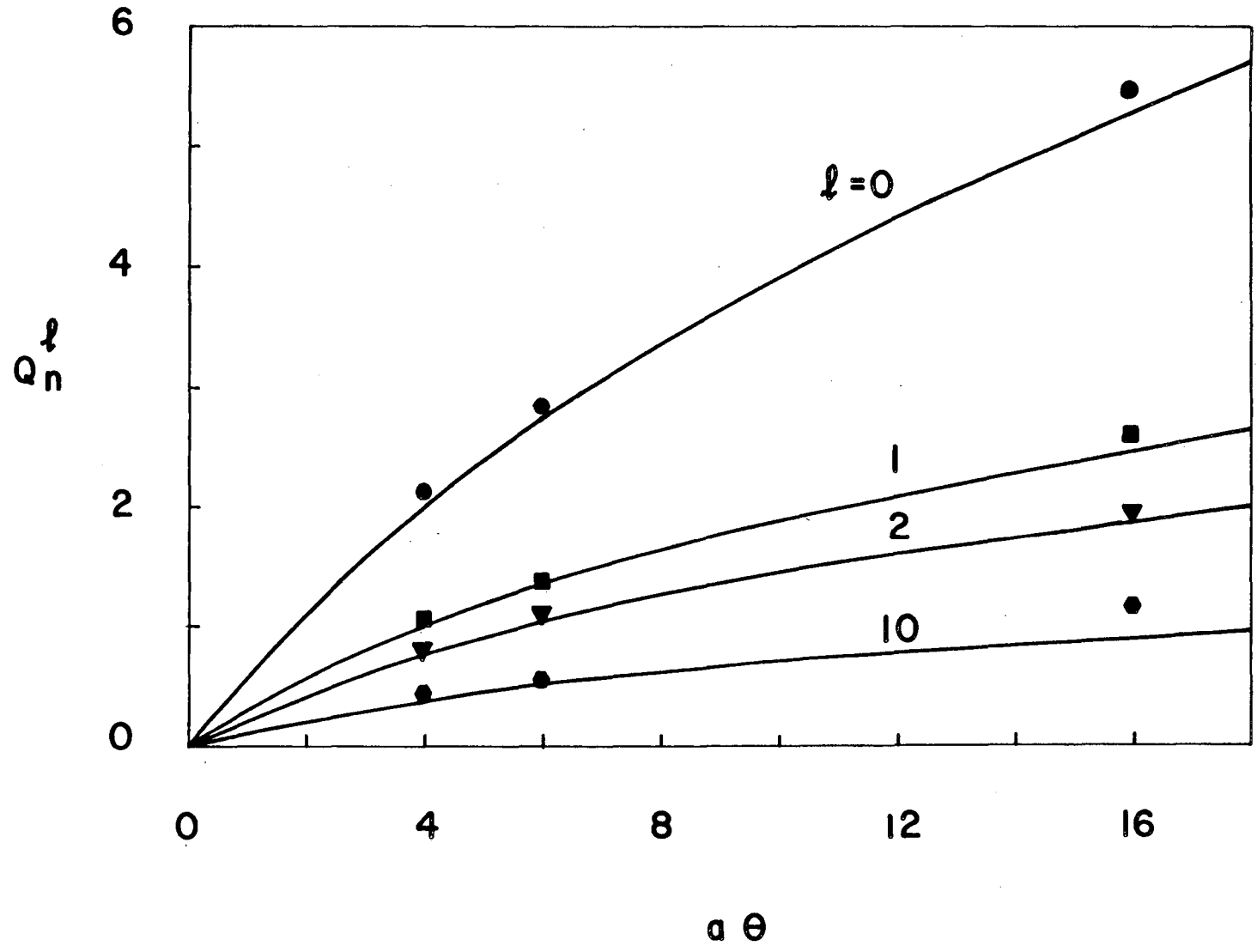
Fig. 4



XBL 836-10360

Fig. 5



XBL 836-10359

Fig. 6

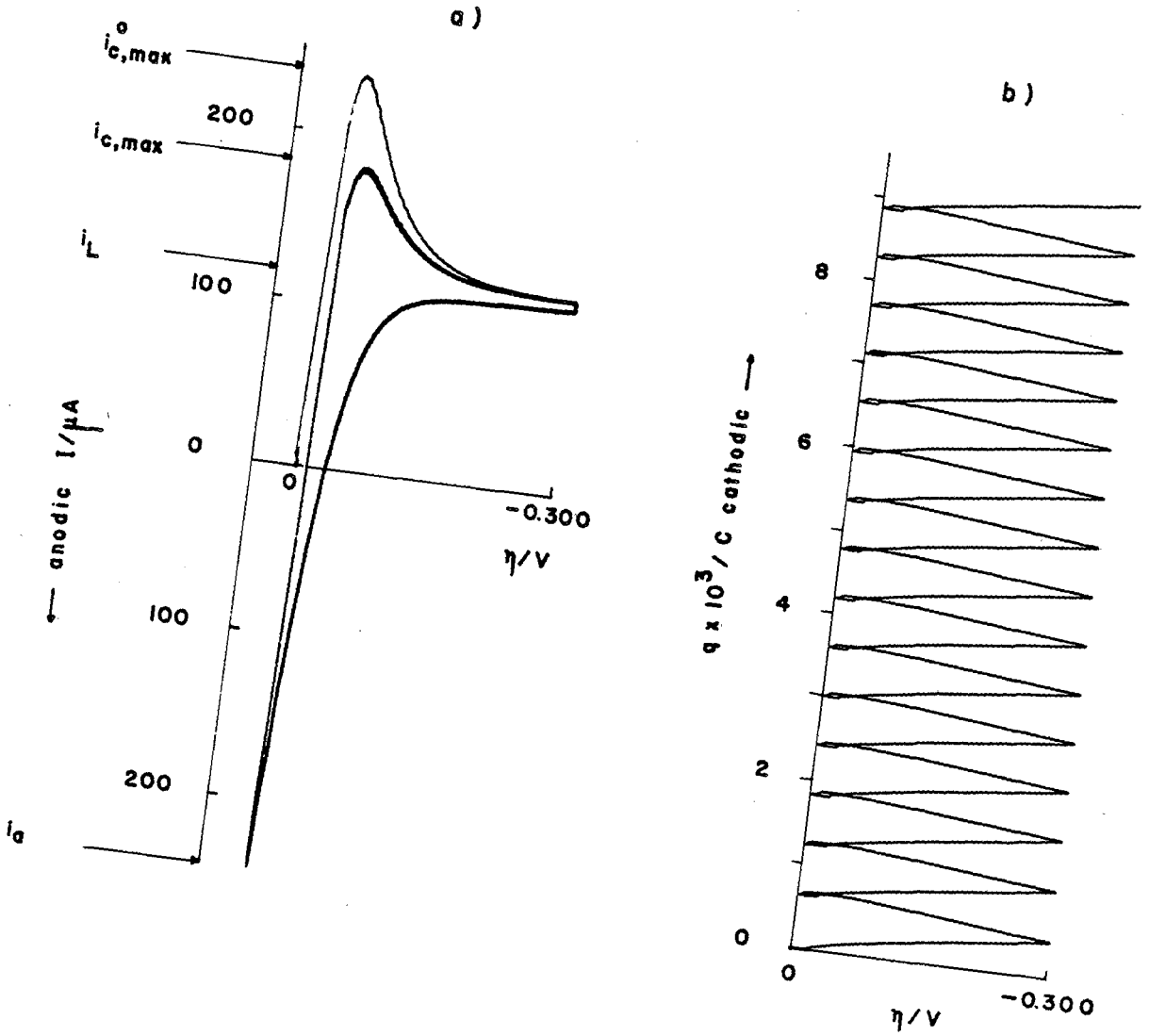


Fig. 7

XBL 836-10356

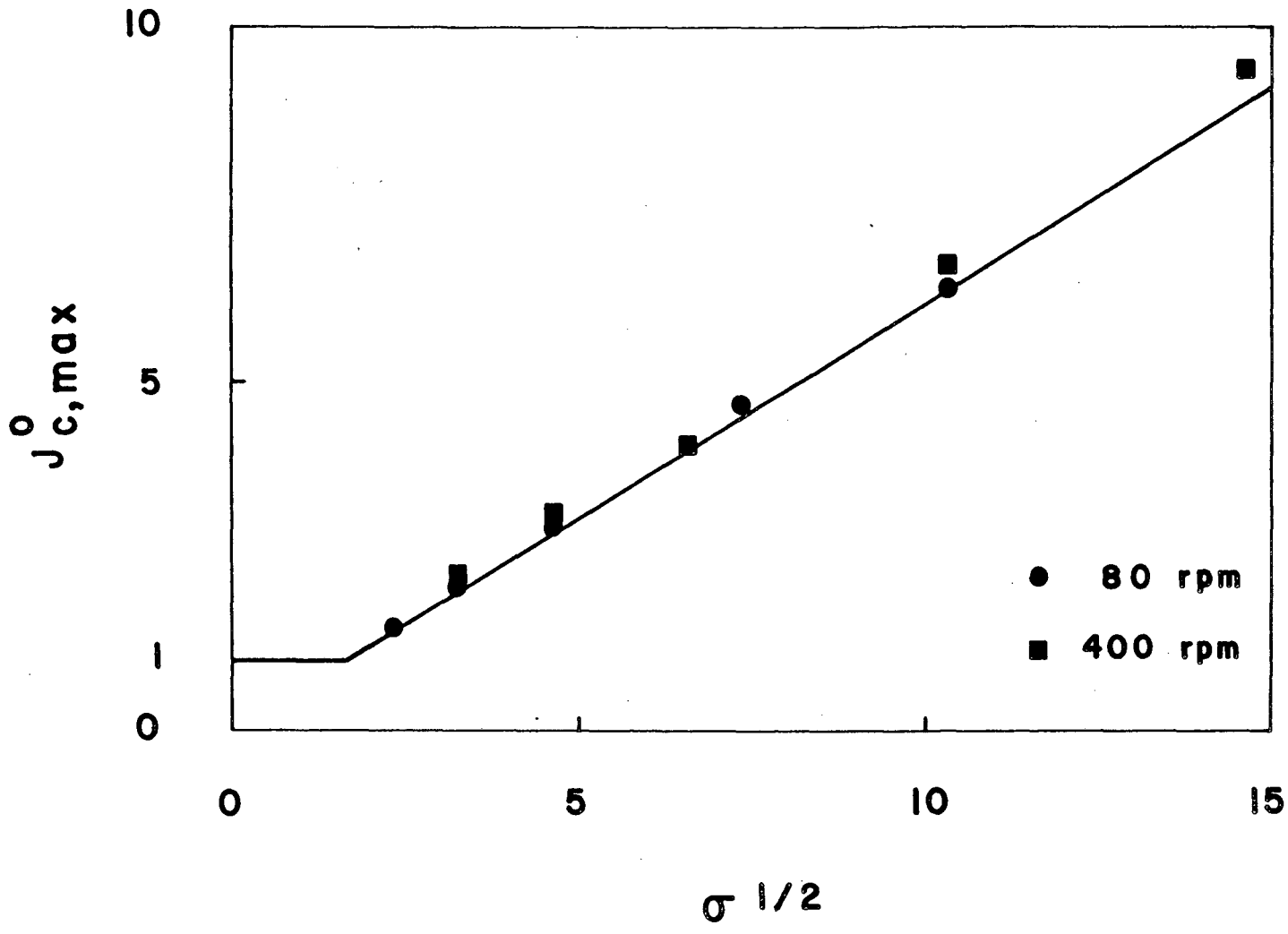


Fig. 8

XBL 836-10357

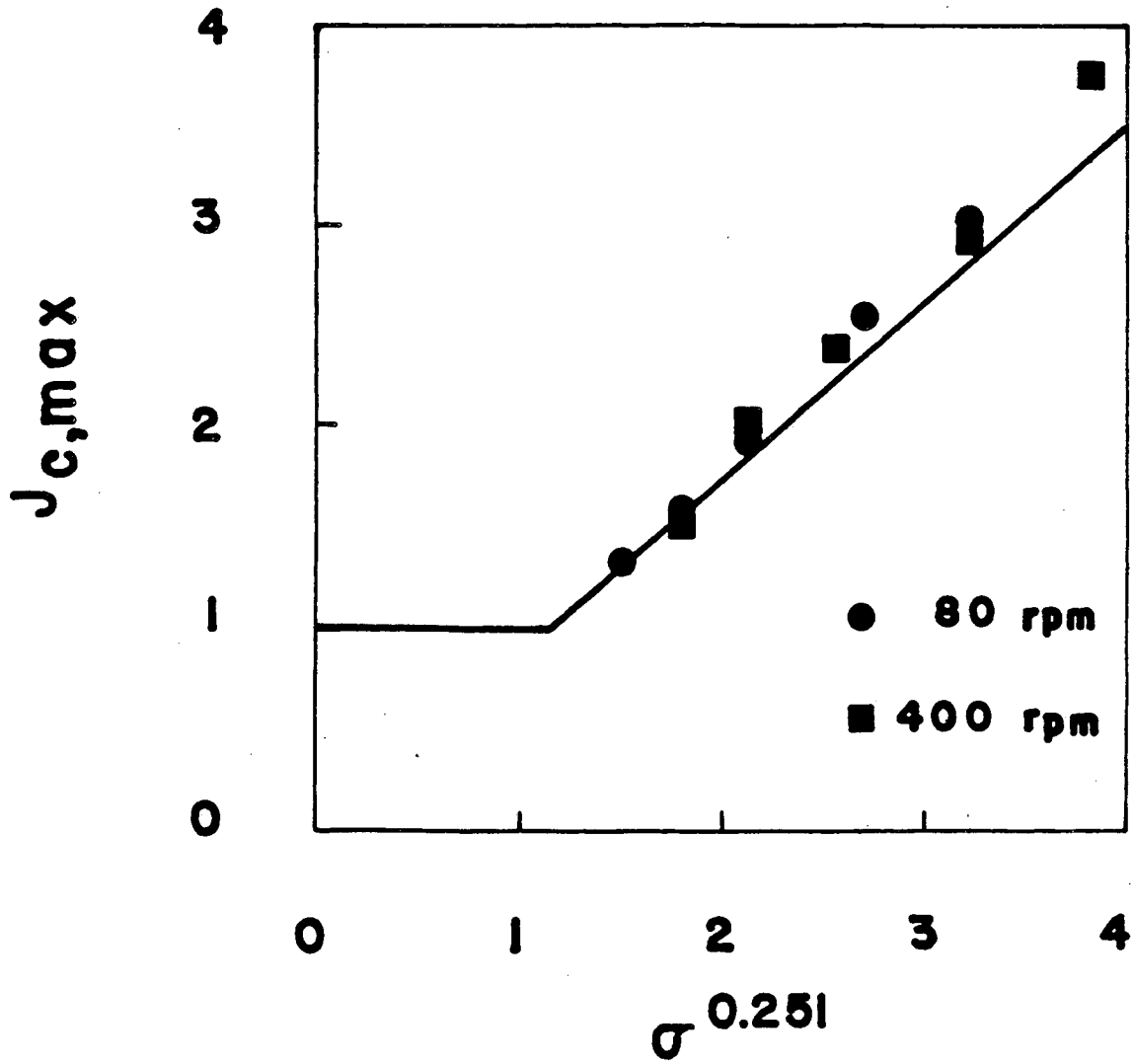


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Fig. 9

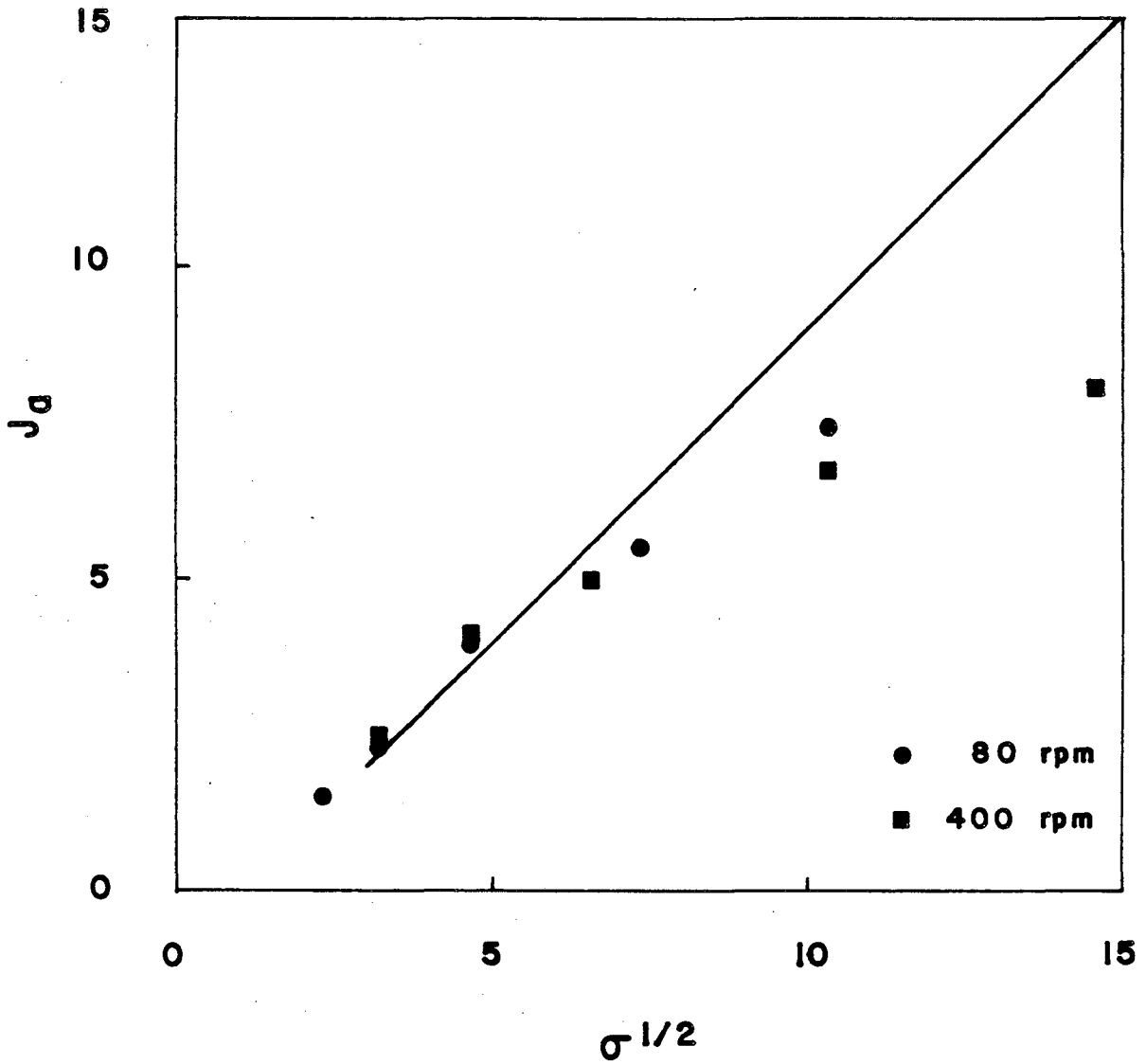

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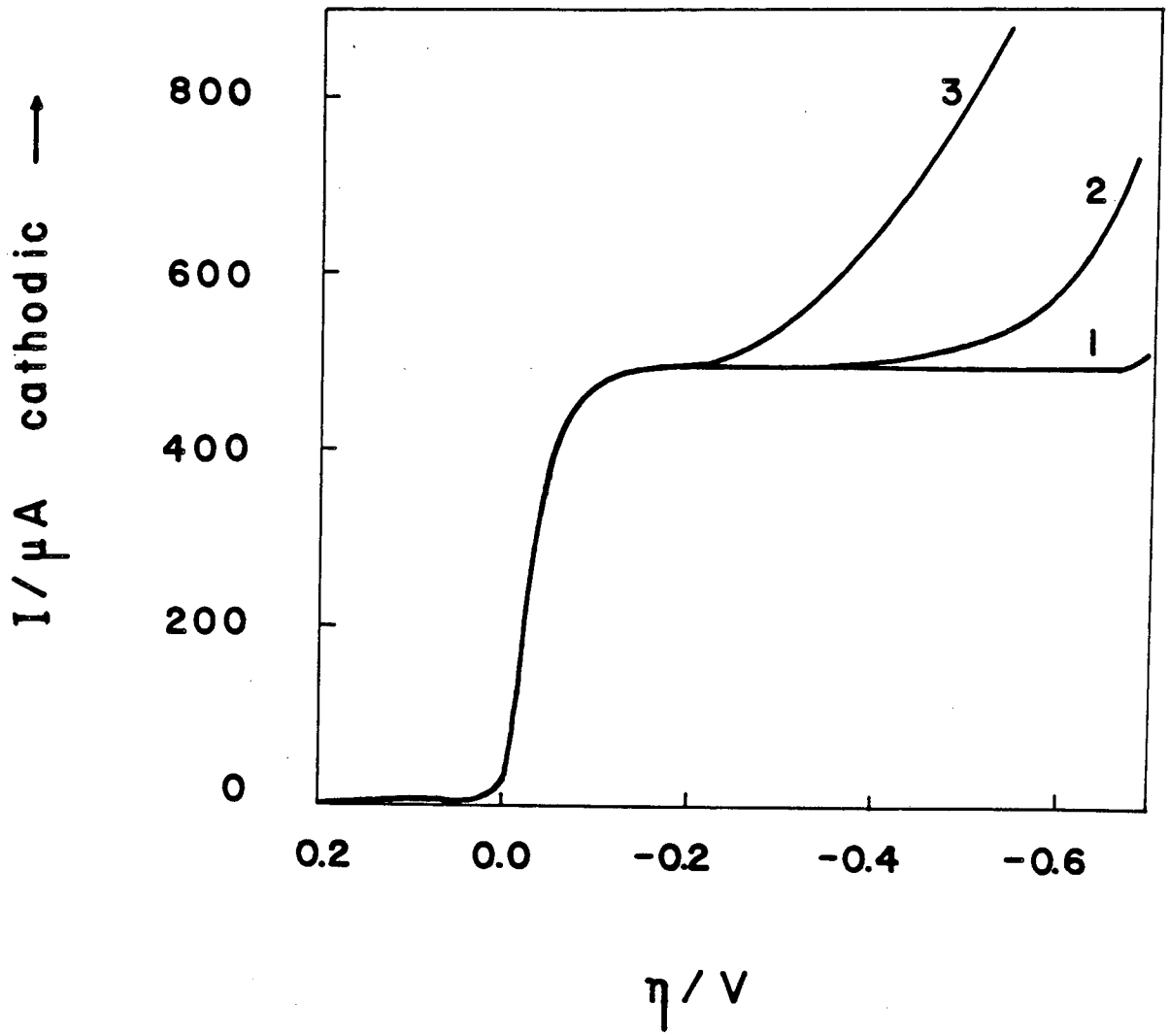
Fig. 10



XBL 836-10354

Fig. 11

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