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Detection of Nonuniform Current Distribution on a Disk Electrode

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Abstract

The relative merits of different methods of detecting a nonuniform current distribution on a disk electrode are discussed. Some implications of such a distribution are presented. Experimental results are reported for collection efficiency measurements on the system of Albery and Ulstrup.

Key words: ohmic potential drop, collection efficiency

Introduction

We consider here several aspects of the current and potential distribution on a rotating disk electrode, a problem for which a theoretical analysis has been presented earlier.[1-4] Since this electrode is popularly regarded to have a uniform current distribution, it is appropriate to give examples illustrating under what conditions a nonuniform distribution can be expected. We should also like to discuss possible methods of detecting that a nonuniform current distribution prevails. In this connection, new experimental data are given for one of these methods, that involving the rotating ring-disk electrode system as used by Albery and Ulstrup.[5]

Current Distribution on a Disk Electrode

The current distribution on a rotating disk electrode is described in detail in reference 2. On the basis of mass-transfer considerations alone, Levich[6] has shown that the current distribution should be uniform, and the disk surface is said to be uniformly accessible from a mass-transfer standpoint. This conclusion is valid at the limiting current, where the concentration of the reactant is zero over the entire surface of the disk electrode. (See, however, the paper[7] on the effect of radial diffusion.)

At currents below the limiting current, the ohmic potential drop tends to produce a nonuniform current distribution. The extreme case is the primary current distribution[1]

$$\frac{i}{i_{avg}} = \frac{0.5}{(1-r^2/r_o^2)^{1/2}} \quad , \qquad (1)$$

which corresponds to the solution of Laplace's equation for the potential when the potential in the solution adjacent to the electrode is uniform. Here, the disk electrode is taken to be embedded in a large, insulating plane with the counter electrode at infinity. The primary current distribution prevails when the surface overpotential for the electrode reaction is negligible and there are no mass-transfer limitations.

For intermediate cases, the current distribution can be described in terms of seven parameters,[2] of which we consider two here:

$$J = \frac{ZFr_o i_o}{RT\kappa_\infty} \quad \text{and} \quad N = -\Gamma(\tfrac{4}{3}) \frac{ZFr_o i_{lim}}{RT\kappa_\infty} \quad . \tag{2}$$

J can be regarded as a dimensionless exchange current density and N as a dimensionless limiting current density. Small values of J lead to a uniform current distribution; large values to a nonuniform distribution. Even for a small value of J, the distribution can be nonuniform if the current is large. Here one can use as a parameter the average current density made dimensionless in the same manner as J in equation 2. The value of N determines how large the dimensionless average current density can be without exceeding the limiting current. At the limiting current, the current distribution is uniform, but this mass-transfer effect loses force at currents only slightly below the limiting current.

The current density, whether it be the exchange current density, the limiting current density, or the average current density, is made dimensionless with the electrode radius r_o, the solution conductivity κ_∞, and other parameters over which there is little experimental control. Large disks and low conductivities promote a nonuniform current

distribution, and vice versa. For laboratory work on polarography and electrode kinetics, small disks and small reactant concentrations with an excess of supporting electrolyte can be used to ensure a uniform current distribution. However, in engineering systems involving electroplating, corrosion, etc., a nonuniform current distribution must be expected. Ohmic effects can lead to the following undesirable results:

1. Nonuniform deposition or dissolution.
2. Errors in kinetic parameters calculated with neglect of current nonuniformities.
3. Loss of control in analytical determinations. Harrar and Shain[8] give a lucid account of such an example in large cells.
4. Waste of current in cathodic protection in corroding systems.

Some numerical examples may be helpful. For $r_o = 0.25$ cm, $\kappa_\infty = 0.1$ (ohm-cm)$^{-1}$, $i_o = 1$ mA/cm^2, $Z = 1$, and $T = 298°$ K, the value of J is about 0.1. For small values of the average current density, this value of J implies a fairly uniform current distribution, but for an average current density of 0.1 A/cm^2, the current distribution will be nonuniform. However, for a value of $i_o = 40$ A/cm^2, the value of J is about 4000, and the current distribution will be nonuniform at all current densities (except very close to the limiting current).

As an example of the ohmic effect in corrosion studies, we might ask how large a disk electrode can be protected cathodically by a counter electrode at infinity, without waste of current. We assume that the disk is rotated, the flow is laminar, and the limiting current for the oxygen reaction is uniform.

The desired current distribution for cathodic protection is determined by the limiting current distribution for oxygen reduction. This results in a potential variation in the solution adjacent to the protected surface. The potential difference $\Delta\Phi_o$ between the solution adjacent to the center of the disk and that adjacent to the outside edge of the disk, for a uniform current distribution, can be obtained from reference 2 as

$$\Delta\Phi_o = 0.36338\ r_o i/\kappa_\infty \quad . \tag{3}$$

We want the electrode to have a potential between that necessary to prevent oxidation of the metal (say, -0.1 V vs. NHE) and that at which hydrogen generation begins (say, -1.0 V vs. NHE). This means that $\Delta\Phi_o$ should be no larger than 0.9 V. For a limiting current density of 10 mA/cm^2 and a conductivity of 0.04 $(ohm\text{-}cm)^{-1}$, the largest disk which can be cathodically protected is r_o = 9.9 cm.

The above equation can also be used for anodic protection of an electrode with active-passive kinetics. The potential of the electrode should be large enough to ensure that the surface is in the passive region and small enough to ensure that it is not in the transpassive region. Assume that this gives an allowed maximum of $\Delta\Phi_o$ of 0.5 V and that the current density in the passive region is 10^{-5} A/cm^2. Then, the largest disk which can be protected anodically corresponds to r_o = 5500 cm, again for a conductivity of 0.04 $(ohm\text{-}cm)^{-1}$. Equation 3 can also be used to guide the selection of conditions for constant-potential electrolysis.

Detection of the Current Distribution

Various methods are conceivable for detecting a nonuniform current distribution on a rotating disk electrode. Direct measurement of the deposit thickness has been used with success by Marathe and Newman.[9] Irene Sun, at Berkeley, has sectioned a radioactive deposit on a disk electrode, and autoradiograms of radioactive deposits have been made by Jordan and Finston.[10]

Albery and Ulstrup[5] have measured collection efficiencies at the ring electrode of a ring-disk system with a view toward detecting a nonuniform current distribution on the disk electrode. If the current density is higher near the edge of the disk than at the center, then the collection efficiency at the ring should be higher than that calculated with the assumption of a uniform current density on the disk. A quantitative comparison of theory and experiment is made difficult by the fact that a current to the ring will accentuate the nonuniformity on the disk. Nevertheless, the results of Albery and Ulstrup show a lower measured collection efficiency. This conflict led us to repeat the experiments, as described in the next section. Bruckenstein and Miller[11] have also treated this conflict, coming to conclusions similar to ours.

It would be more straightforward to use the ring-disk system as a sectioned electrode for the purpose of measuring the nonuniformity of current distribution. In this application, the ring and the disk would be held at the same potential so as to function as a single electrode to the parts of which the current could be measured separately. Since this is a classical method of measuring current distributions, we have assessed in a separate paper[12] the error which might be introduced

by the nonzero gap between the ring and the disk. Experimental measurements are also reported for this technique.

Angell, Dickinson, and Greef[13] have measured the potential distribution near a rotating disk electrode. In order for such measurements to detect a nonuniformity of current distribution on the disk, measurements would have to be made quite close to the electrode itself, as shown by the theoretical potential profiles along the disk axis (see figure 1). McIntyre and Peck[14] have developed an interrupter technique and applied it to the measurement of the ohmic potential drop at a rotating disk electrode. Although the ohmic potential drop to the center of the disk can vary by 27 percent depending on the uniformity of distribution of the same total current,[2] an interrupter technique will ideally measure the ohmic potential drop corresponding to the primary current distribution, independent of the actual current distribution prevailing before interruption of the current.[15]

Ring Collection Efficiencies for the Bromide-Bromine System

Albery and Ulstrup[5] have reported the results of experiments with a ring-disk assembly to test critically the predictions of current distribution on a disk electrode. The disk was operated at a given current as an anode, oxidizing bromide to bromine, which was then reduced back to bromide at the ring. The nonuniform current distribution on the disk should produce a concentration of bromine at the edge of the disk which is higher than that expected from the average current density. This should result in a higher current on the ring (or a higher collection efficiency) than that predicted by Albery and Bruckenstein.[16] In other words, bromine produced near the edge of the disk has less chance to

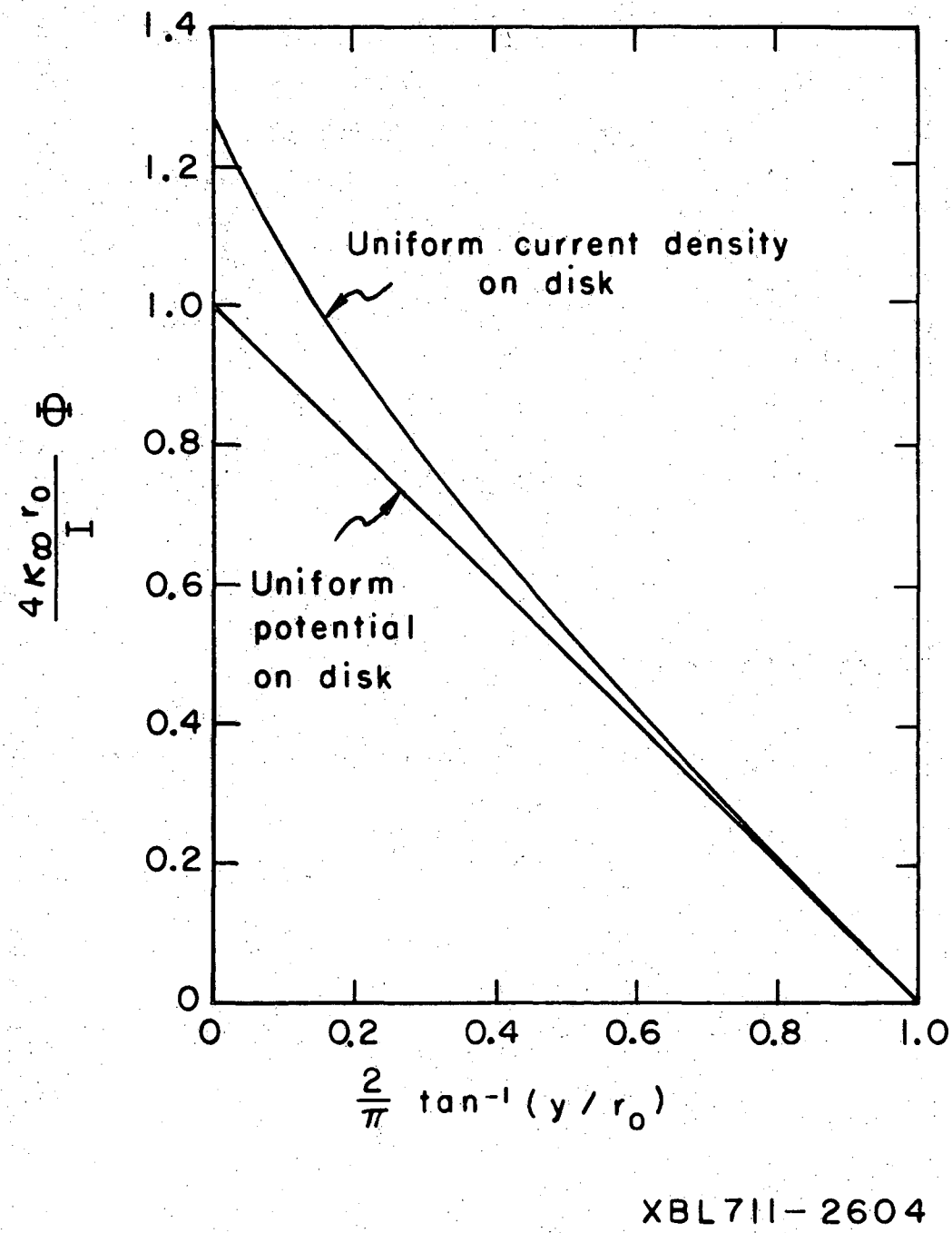

Figure 1. Potential distribution along the axis of the disk.

diffuse away and not react at the ring. In contrast, Albery and Ulstrup report a lower current on the ring.

Three effects might complicate the interpretation of these results:

1. Operation of the ring cathodically enhances the nonuniformity of the current distribution on the disk and should lead to a still higher collection efficiency.
2. The ohmic potential drop may have been large enough in some of the dilute solutions to obviate the limiting-current measurements on the ring, that is, the ring may not have been at limiting current at the potential of its operation. This possibility is difficult to assess theoretically since the placement of the reference electrode is not indicated in the work of Albery and Ulstrup.
3. Kinetic complications on the disk might have resulted in the production of less bromide than was supposed.

For the rotating ring-disk system described below, calculations were made of the ohmic potential drop between the ring and the reference electrode, with the ring operating at limiting current. The results of Newman[2] and of Nanis[17] were used for the calculations. It was found that the ohmic effect was too small, and in the wrong direction, to be of importance for the concentrations used in the measurements reported below.

Since the importance of the last possibility could not be determined from the data reported by Albery and Ulstrup, the measurements were repeated. The solutions were NaBr and $HClO_4$ in water. The ring, disk, and counter electrodes were made of platinum. The dimensions of

the ring-disk assembly (RD1) were: r_o = 0.442 cm, r_1 = 0.504 cm, and r_2 = 0.621 cm. The calculated collection efficiency was 0.340. The ring and disk were imbedded in epoxy, and the overall radius was 1.27 cm. The reference electrode probe (Luggin capillary tip) was placed in the plane of the disk at r = 2.27 cm. A Regatran constant-current power supply maintained a constant disk current. A Wenking potentiostat and voltage-ramp generator were used to measure the limiting current curves on the ring. Currents were determined by measuring the potential drop across precision resistors. The vessel containing the solution and electrodes was open to ambient air, and was at ambient temperature (23 $\pm$ 2°C). The ring-disk assembly was rotated at 1550 revolutions per minute.

Polarization curves for the ring, which were typical of those obtained in the more concentrated solutions, are shown in figure 2. The limiting current plateau is broad and well-defined. It can be seen that the ring current at +400 mV (vs. SCE) could be taken as the limiting current, for these solutions and the reference electrode placement used here. At decreased concentrations, especially that of $HClO_4$, the region between attainment of limiting current and onset of reduction of oxide on the platinum is more narrow.

Additional data for several different concentrations are reported in Table 1. The measured collection efficiency is greater than that calculated for all but three entries in the table. The departure from the calculated value of the collection efficiency is greater than the experimental error (~1%) and is indicative of a nonuniform current distribution. These results should be contrasted with those of Albery and Ulstrup who found good agreement between measured and calculated efficiencies.

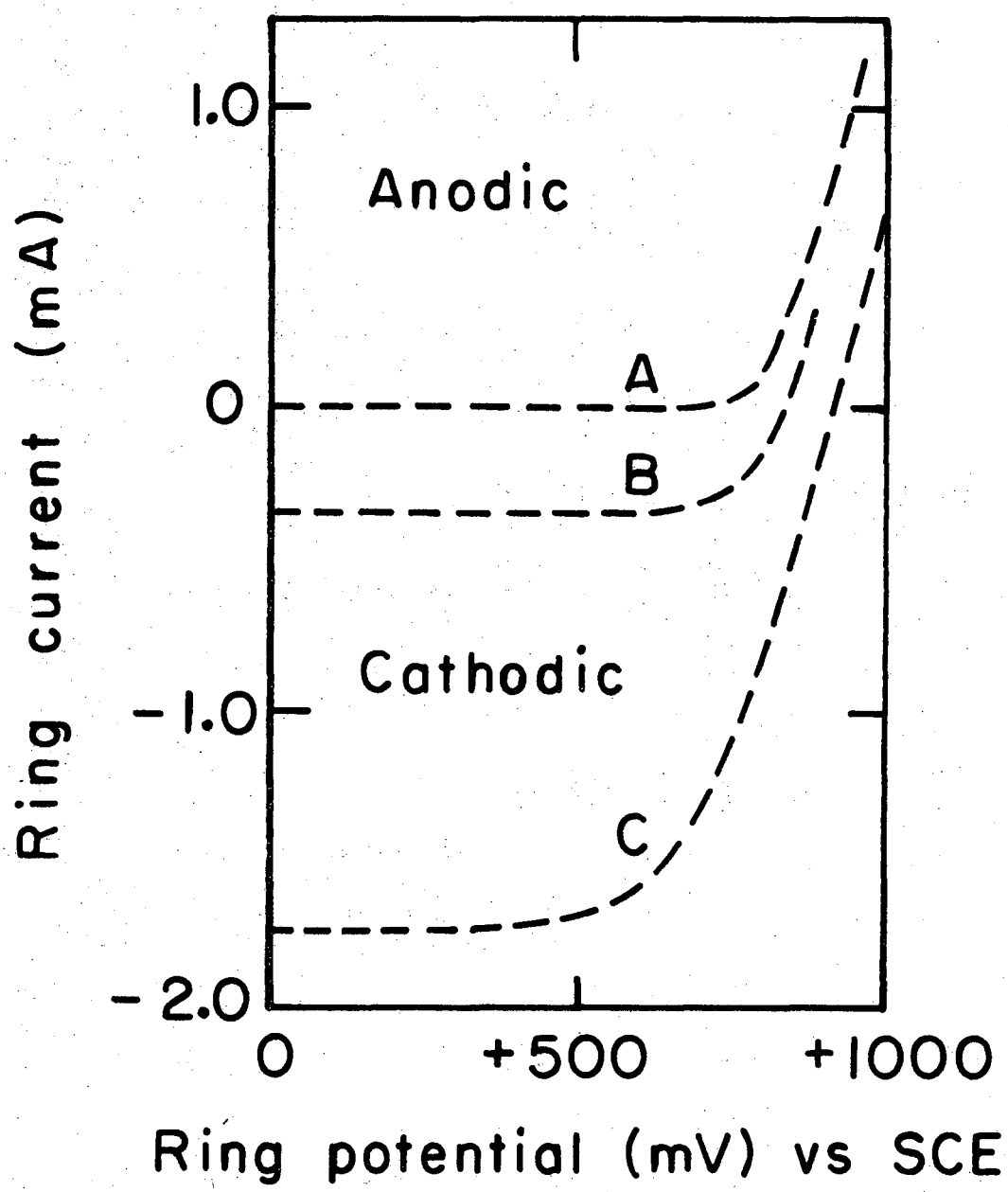

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Figure 2. Potential scan curves for the ring for a solution compositon of 0.1 M NaBr and 0.01 M $HClO_4$.
Curve A: Zero disk current.
Curve B: 1.0 mA disk current.
Curve C: 5.0 mA disk current.

Table 1. Collection efficiencies for NaBr-$HClO_4$ systems.

Solution Composition	Total Disk Current (mA)	$-I_r/I_d$
0.1 M NaBr	0.1	0.350
0.1 M $HClO_4$	1.0	0.345
	5.0	0.360
	10.0	0.350
0.01 M NaBr	0.01	0.350
0.01 M $HClO_4$	1.00	0.353
0.001 M NaBr	0.005	0.350
0.1 M $HClO_4$	0.010	0.350
	0.020	0.340
	0.030	0.340
	0.040	0.350
	0.050	0.350
	0.100	0.350
	0.050	0.354
0.001 M NaBr	0.010	0.340
0.01 M $HClO_4$	0.012	0.360
	0.050	0.360
	0.10	0.355
0.0001 M NaBr	0.02	0.350
0.1 M $HClO_4$	0.03	0.350

However, the more interesting systems are the dilute solutions in which Albery and Ulstrup found the anomalous collection efficiencies. More specifically, for a solution of 10^{-3} M $HClO_4$ and 3.3×10^{-3} M NaBr, they found lower than expected ring currents for disk currents above a certain level (current density not known since the disk radius was not specified). To investigate the possibility that these results were caused by kinetic complications on the disk, disk polarization curves were measured for different preparations of the surface. Typical results are shown in figure 3.

Curves 1 - 4 were obtained in a solution of 10^{-3} M $HClO_4$, 10^{-3} M NaBr, with RD1, and in the sequence numbered. Curve 1 was taken after the ring-disk had been freshly buffed on a metallographer's wheel — our usual preparation. The run (and each subsequent run) was started at +500 mV (vs. SCE) and swept at 156 mV/min to more positive potentials, with simultaneous measurement of the disk current. Immediately after curve 1 was obtained, the potential was returned to +500 mV, another sweep was started, and curve 2 was obtained. The difference in the two was caused by the different state of the platinum surface in the two runs. This was confirmed by: (1) prereducing the disk at -100 mV(vs. SCE) for 1.5 minutes before curve 3 was taken, and then; (2) preoxidizing the disk at +2500 mV (vs. SCE) for 1 min before curve 4 was obtained. Finally, a curve was obtained after the disk had been prereduced at -100 mV (vs. SCE) for 5 minutes, and the results were identical to curve 3.

Similar investigations at concentrations of 10^{-2} M $HClO_4$ and 10^{-3} M NaBr revealed that the inhibition of Br_2 production on a <u>preoxidized</u> surface was much less important than for the above system. With a lower

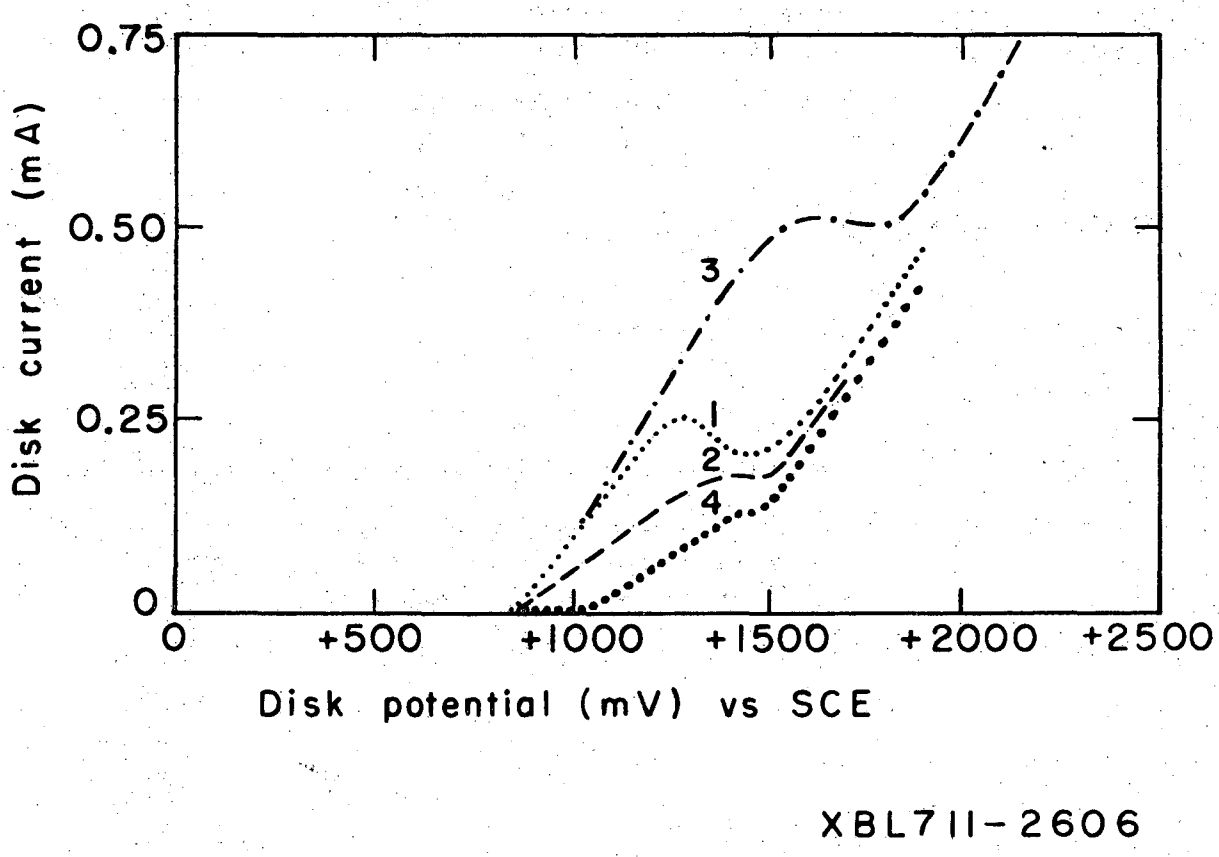

Figure 3. Disk polarization curves in 0.001 M NaBr - 0.001 M $HClO_4$.
Curve 1: Freshly buffed.
Curve 2: Run immediately after 1.
Curve 3: Prereduced @ -100 mV for 1 min.
Curve 4: Preoxidized @ +2500 mV for 1 min.

concentration of $HClO_4$ (10^{-4} M, 10^{-3} M NaBr) however, it was not possible to obtain a current due to Br^- reduction of more than 0.12 mA (total disk current), no matter how much the disk had been prereduced. These observations reveal the limitations of concentration and surface preparation which are appropriate for measurements of collection efficiency with this system. One may conclude that: (1) bromine evolution on the disk is affected by the surface preparation, i.e., is inhibited by oxide on the platinum; and (2) a reproducible surface may be obtained by prereduction of the disk. Similar inhibition effects have been obtained recently for the Cl^- - Cl_2 system.[18]

The influence of the preparation of the disk surface on the collection efficiencies in dilute solutions is demonstrated by the results in Table 2. For preoxidized platinum disks, these results are qualitatively in agreement with those of Albery and Ulstrup. Presumably, the extra disk current on a preoxidized surface (above that required to produce the Br_2 detected on the ring) goes to produce oxygen which is not reduced on the ring in the potential region scanned. However, prereduced platinum shows a striking difference, i.e., the collection efficiency is constant up to the disk limiting current. This indicates that all the disk current is going to produce Br_2, which is then detected on the ring.

We conclude that the results obtained by Albery and Ulstrup reveal the state of oxidation of their platinum disk rather than any shortcomings of the treatment of Newman.[2] Proper measurement of collection efficiencies for this system provides support for Newman's results. A recent paper by Bruckenstein and Miller[11] reports measurements in general agreement with the present results.

Table 2. Surface treatment effects on collection efficiency in NaBr - $HClO_4$ systems.

Solution Composition	Total Disk Current (mA)	$-I_r/I_d$	Disk Treatment
0.001 M NaBr	0.01	0.330	Prereduced @ -100 mV for 1 min
0.001 M $HClO_4$	0.02	0.330	"
	0.03	0.330	"
	0.05	0.340	"
	0.10	0.340	"
	0.25	0.350	"
	0.30	0.340	"
	0.40	0.330	"
	0.25	0.120	Preoxidized @ +2500 mV for 1 min
	0.40	0.075	"
0.001 M NaBr	0.01	0.340	Prereduced @ -500 mV for 1 min
0.0001 M $HClO_4$	0.03	0.330	"
	0.05	0.330	"
	0.10	0.330	"

Conclusions

Nonuniform current distributions on a disk electrode may be detected in several ways. Of these, the method of measuring the deposit thickness on the disk, and the technique of using the ring-disk system as a sectioned electrode are probably the most straightforward. The collection efficiency method, proposed by Albery and Ulstrup,[5] is not as simple to interpret, but may be used to provide qualitative evidence for nonuniform current distributions. Experimental data have been reported here which support the predictions of theory[2] and should be contrasted with the data of Albery and Ulstrup.[5]

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