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# ELECTROCATALYTIC REDUCTION OF NITRATE AND NITRITE AT NAFION-COATED ELECTRODES IN CONCENTRATED SODIUM HYDROXIDE SOLUTION

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The electrochemical reduction of nitrate ions in alkaline solution has been studied using various cathode materials and is the basis for a patent describing the conversion of nitrate into hydroxide ion in carbonate solutions[1-4]. Recently, Taniguchi et al.[5] have reported that certain well studied transition metal cyclic amine complexes, namely Co(III)-cyclam and Ni(II)-cyclam where cyclam is 1,4,8,11-tetraazacyclotetradecane, efficiently electrocatalyze the reduction of nitrate and nitrite to hydroxylamine at mercury electrodes. Here we report that the metal cyclam catalyst can be incorporated into a Nafion film electrode, and that the reduction of nitrate and nitrite proceeds efficiently at these electrodes in concentrated NaOH solution. Nafion is a perfluoroalkanesulfonated cation exchange material that has been widely used to immobilize redox couples at electrode surfaces[6], including electrocatalysis species[7].

## EXPERIMENTAL

Chemicals. The trans-[Co(III)(cyclam)$Cl_2$]Cl was prepared according to the literature procedure of Boenisch et al.[8] Certified A.C.S. grade reagent NaOH, $NaNO_2$ and $NaNO_3$ were used to prepare the solutions. Prepurified argon that was further purified by passage through a column of dispersed MnO on vermiculite[9] was used to remove oxygen from the solutions.

Nafion-coated electrodes were prepared by two procedures. In the

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first, electrodes were coated with a Nafion film by evaporation of 10-20$\mu$L of a commercial (Aldrich) 5 wt% solution using a hair dryer and then cycled through the Co(III/II)-cyclam couple in 1 M NaOH containing 5mM Co(III)-cyclam. The electrode was then removed from the solution containing the electrocatalyst, rinsed with distilled water and transferred to the solution under investigation. In the second method, an ethanol solution that was 2 mM in [Co(III)-cyclam($Cl_2$)]Cl was diluted with an equal volume of the 5 wt% Nafion solution. This solution was then used to coat the electrodes in the above manner. The latter electrodes tended to give greater sensitivity to nitrate, presumeably owing to the thinner coatings. Profilimetry on dry films cast on smooth glass substrates indicated that the films were quite rough with average thicknesses on the order of 100 to 300 nm.

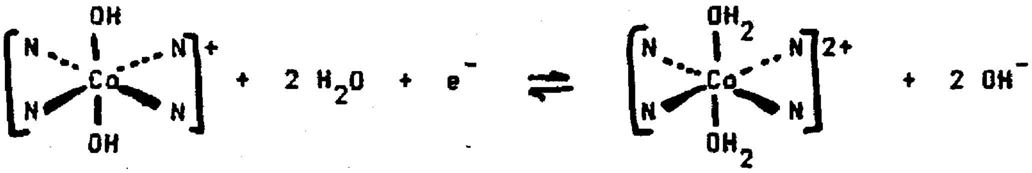
Hydroxylamine was determined quantitatively in solution using the spectrophotometric method of Dias et al.[10] The sensitivity of this method necessitated a ten-fold dilution prior to the color development step.

The substrate electrode for these studies was usually a gold disk (area: $0.032 cm^2$) that was lightly polished with 0.3$\mu$ lapping compound. For some experiments the gold surface was amalgamated by deposition of mercury before application of the Nafion solution. Equivalent results were obtained with either electrode substrate.

## RESULTS

Figure 1 demonstrates catalysis of the nitrate reduction at the Nafion-coated electrode. In Figure 1A is shown the cyclic voltammogram of the Co(III)-cyclam containing film in contact with 1 M NaOH; the $E_{1/2}$ is $-0.\overset{7}{\cancel{8}}4$V vs S.C.E. In solution the Co(III)-cyclam species exhibits a quasi-reversible one-electron wave at somewhat more negative potential than is seen for the Nafion film electrode. Furthermore, in the Nafion film the anodic segment of the wave is considerablely drawn-out, and as the potential is cycled , the peak currents decrease due to loss of Co complex to the solution. However, the response for the complex in the film persists for many cycles (more than 20) and the electrode remains active for nitrate reduction. Electrodes could be easily reactivated simply by coating with a new aliquot of Co(III)-cyclam containing Nafion.

Based on the known $pK_a$'s of the diaquo <u>trans</u>-Co(III)-cyclam complex ($pK_1$ = 2.9 and $pK_2$ = 7.2[11]) and the pH dependence of the $E_{1/2}$ of the Co(III/II)-cyclam couple in solution (120 mV/pH for pH > ca. 7), the electrode reaction for the wave at ca. -0.8 V is written as follows.



(1)

The dicationic nature of the product of this reaction favors retention of the complex in the anion exchange Nafion film. (Note that the $-(CH_2)_n-$ bridges are omitted from the ligand structures in Eqn 1.)

Upon addition of low concentrations of nitrate to the NaOH solution, a nitrate dependent irreversible reduction wave appears at ca. -1.35 V. This wave is shifted by 200 mV from the position of the nitrate reduction wave that appears just before the background reduction of water at an unmodified mercury electrode in NaOH solutions. The wave is proportional to nitrate concentration over the range from $10^{-4}$ to $10^{-2}$M. At concentrations greater than $10^{-3}$M, the peak potential for this wave is strongly dependent on nitrate, shifting to negative potential at 60 mV per decade change in the $NO_3^-$ concentration.

The cyclic voltammetry of solutions of nitrate and co(III)-cyclam in NaOH is similar to Figure 1. In solution we have confirmed the result of

Tanganuchi et al.[5] that hydroxylamine, a six-electron reduction product, is the principal electrolysis product at mercury electrodes. (The mechanism of the solution electrocatalyzed reduction of nitrate and nitrite in NaOH is under study and will be reported separately.)

The Co(III)-cyclam containing Nafion modified electrodes responded to nitrite ions in a manner similar to nitrate. Figure 2 shows cyclic voltammograms of $NaNO_2$ in 1 M NaOH obtained at a Nafion-Co-cyclam modified electrode and Figure 3 shows the variation of the $NO_x^-$ (x = 1 or 2) reduction peak currents as a function of concentration. The slopes of the two lines in Figure 3 have the expected ratio for diffusion controlled reduction of nitrate and nitrite to hydroxylamine, six- and four-electron reductions, respectively.

A notable feature of these voltammograms of nitrite solutions is the clear appearance of an anodic wave at ca. -0.37V that appears to be due to *oxidation of a nitrite reduction product.* This wave is usually present in the cyclic voltammograms of nitrate as well, but it is larger and more evident for nitrite. For both nitrate and nitrite the Co(III/II) couple is not significantly influenced by the addition of the substrate.

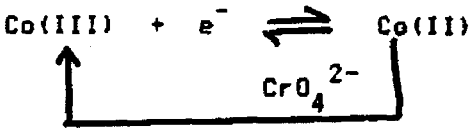
The peak at -0.37V is assigned to the oxidation of hydroxylamine based on the cyclic voltammogram shown in Figure 4, which was obtained at a Nafion-Co(cyclam) modified electrode in the presence of $1.0 \times 10^{-2}$ M $NH_2OH$. Although there are small waves in this region believed to be due to small equilibrium amounts of acidic Co(III/II) species, e.g. $Co^{3+/2+}$-cyclam, this wave appears to be due to the direct oxidation of $NH_2OH$ at the electrode surface. Interestingly, at high concentration of $NH_2OH$, there is a hint of a small wave at -1.35V which may be due to the electrocatalyzed reduction of nitrite formed in the oxidation. The wave at -1.0V in the voltammograms of the $NH_2OH$ solutions is also present at a bare Au surface and is assigned to a hydroxylamine oxidation product. These peak potentials and the cyclic voltammetric behavior is consistent the work of Rao and Meites who reported that the oxidation of $NH_2OH$ yielded NOH at mercury electrodes[12].

As expected for an uncharged species, the hydroxylamine oxidation current is attenuated by the Nafion film. For equivalent concentrations and the same sweep rate, the peak currents are in the approximate ratio of 1:0.06 at bare gold and Co-cyclam containing Nafion-coated electrodes, respectively. This ratio is not reproducible with the film casting techniques employed, however, and more careful experiments with Nafion coatings of controlled thickness are required before a conclusion can be made regarding a role for the Co-cyclam complex in the partitioning process.

## Effect of Added Chromate

A possible advantage of immobilizing the Co-cyclam catalyst in a Nafion film electrode is that negatively charged interferences might be excluded from the reaction site. An example is the chromate dianion which can oxidize intermediates and products of the nitrate reduction process, thereby thwarting the electrochemical destruction of nitrate. Accordingly, the effect of chromate on the cyclic voltammetry of nitrate at the Co-cyclam Nafion electrode has been examined. The qualitative features of the voltammetry as they pertain to the nitrate reduction will be described briefly.

At low chromate concentration, less than 0.02M, the cyclic voltammograms of nitrate are not markedly influenced by the addition of $CrO_4^{2-}$. Both the Co(III/II) wave and the nitrate reduction wave resemble those in Figure 1. At higher concentrations, however, more complex behavior is seen suggesting that chromate ion is not excluded from the modified electrode interface. Figure 5 shows typical voltammograms of the chromate/nitrate mixtures in 1 M NaOH. In the absence of nitrate, Figure 5A, some electrocatalysis of the chromate reduction, i.e. Eqn 2, is



$$\begin{tikzcd} \mathrm{Co(III)} + e^- \arrow[r, shift left] & \mathrm{Co(II)} \arrow[l, shift left] \arrow[l, bend left=60, "\mathrm{CrO_4^{2-}}"] \end{tikzcd} \qquad (2)$$

indicated by the increased cathodic peak current for the Co(III) reduction and the $(i_p)^c/(i_p)^a$ peak current ratio greater than unity. Upon addition of nitrate, the usual nitrate reduction and hydroxylamine oxidation waves appear, and in addition at high nitrate concentration (Fig. 5C), the Co(III/II) wave becomes dependent on the nitrate concentration. This result suggests that a reduced form of chromate generated in the diffusion layer at -0.8V by reaction with Co(II) can reduce nitrate ion. Significantly, the voltammograms indicate that although the redox chemistry is complex, nitrate is still reduced under voltammetric conditions in spite of the presence of chromate ion in solution.

## Conclusions

In strongly alkaline solution nitrate and nitrite ions are reduced to hydroxylamine at Nafion film electrodes containing Co(III)-cyclam complex ions. The presence of low concentrations of chromate does not change the voltammetric response suggesting that $CrO_4^{2-}$ is excluded from the catalytic sites in the Nafion film. At higher chromate concentrations, greater than ca. 0.02M, complex redox chemistry involving Co(II)-cyclam and intermediates or products of the nitrate reduction becomes significant.

## ACKNOWLEDGEMENT

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## FIGURE CAPTIONS

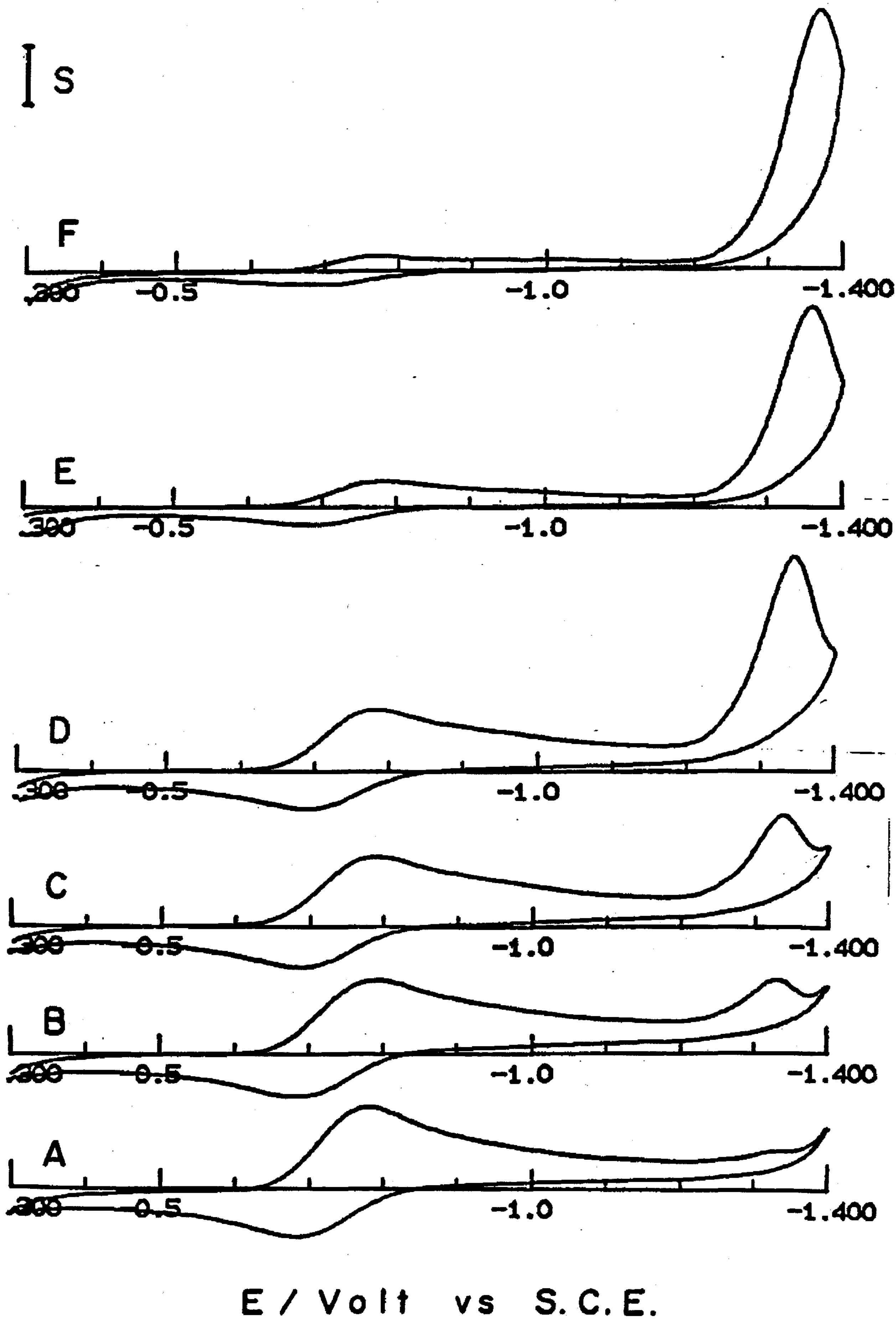
Fig. 1. Cyclic Voltammograms of Nafion/Co-cyclam Modified Electrodes in 1 M NaOH; sweep rate, 20 mV $s^{-1}$; A-F: 0.10, 0.50, 1.0, 2.0, 3.0, 5.0 mM $NaNO_3$; S = 1 μA(A-D), 2 μA(E), 2.5 μA(F).

Fig. 2. Cyclic Voltammograms of Nafion/Co-cyclam Modified Electrodes in 1 M NaOH; sweep rate, 20 mV $s^{-1}$; A-E: 0.10, 0.40, 0.70, 1.0, 5.0 mM $NaNO_2$; S = 5 μA(A-D), 40 μA(E).

Fig. 3. Variation of Peak Currents with Concentration for Reduction of $NaNO_3$ (open circles) and $NaNO_2$ (solid circles); sweep rate, 20 mV $s^{-1}$; Nafion/Co-cyclam Modified Electrode in 1 M NaOH.

Fig. 4. Cyclic Voltammogram of Nafion/Co-cyclam Modified Electrode in 1 M NaOH, $1.0 \times 10^{-2}$ M $NH_2OH$; sweep rate, 20 mV $s^{-1}$; S = 1 μA.

Fig. 5. Cyclic Voltammograms of Nafion/Co-cyclam Modified Electrodes in 1 M NaOH, 0.04 M $CrO_4^{2-}$ Solution; sweep rate, 20 mV $s^{-1}$; A-C: 0.40, 1.6, 2.8 mM $NaNO_3$; A-C: S = 0.50, 1.00, 10.0 μA.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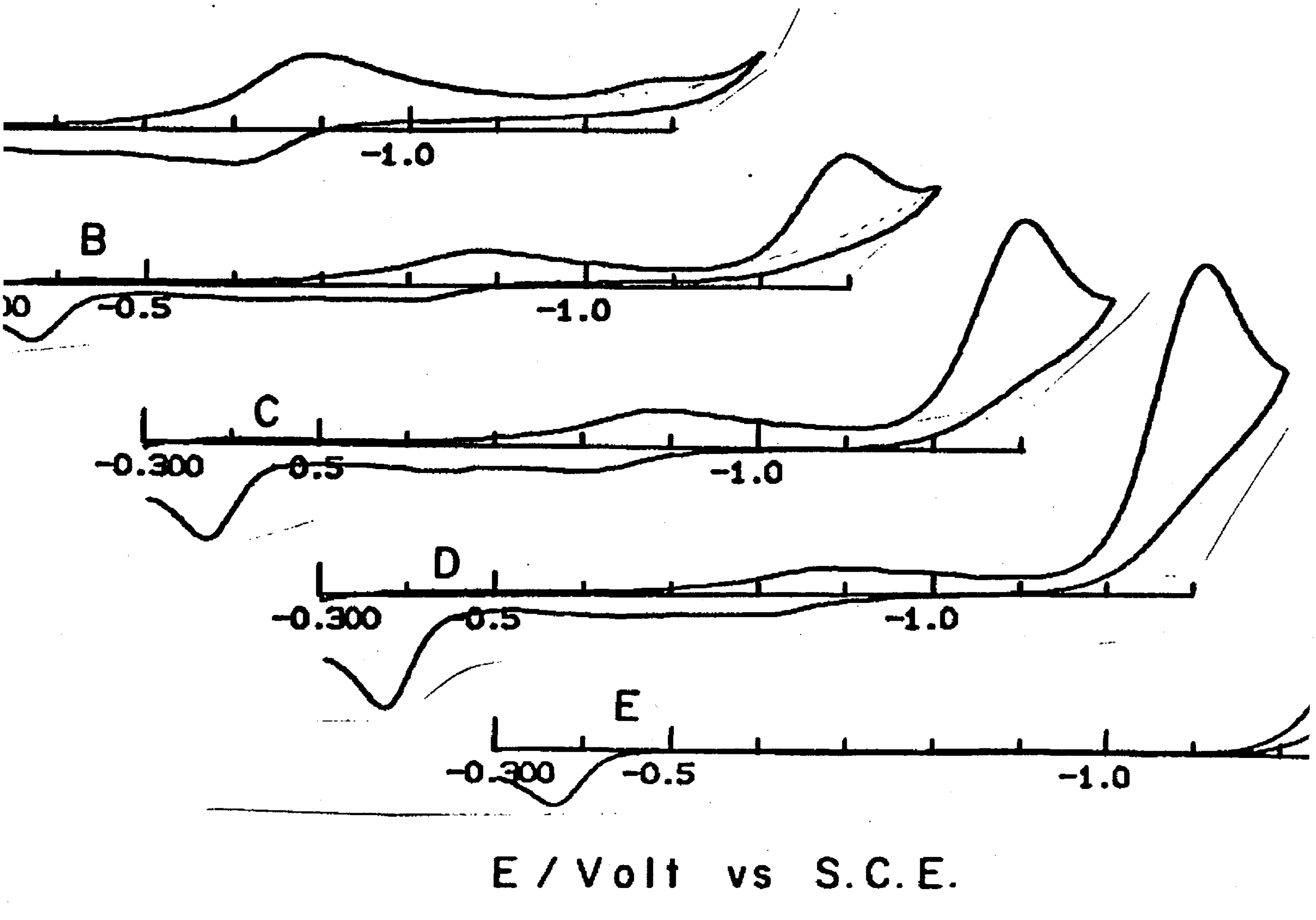

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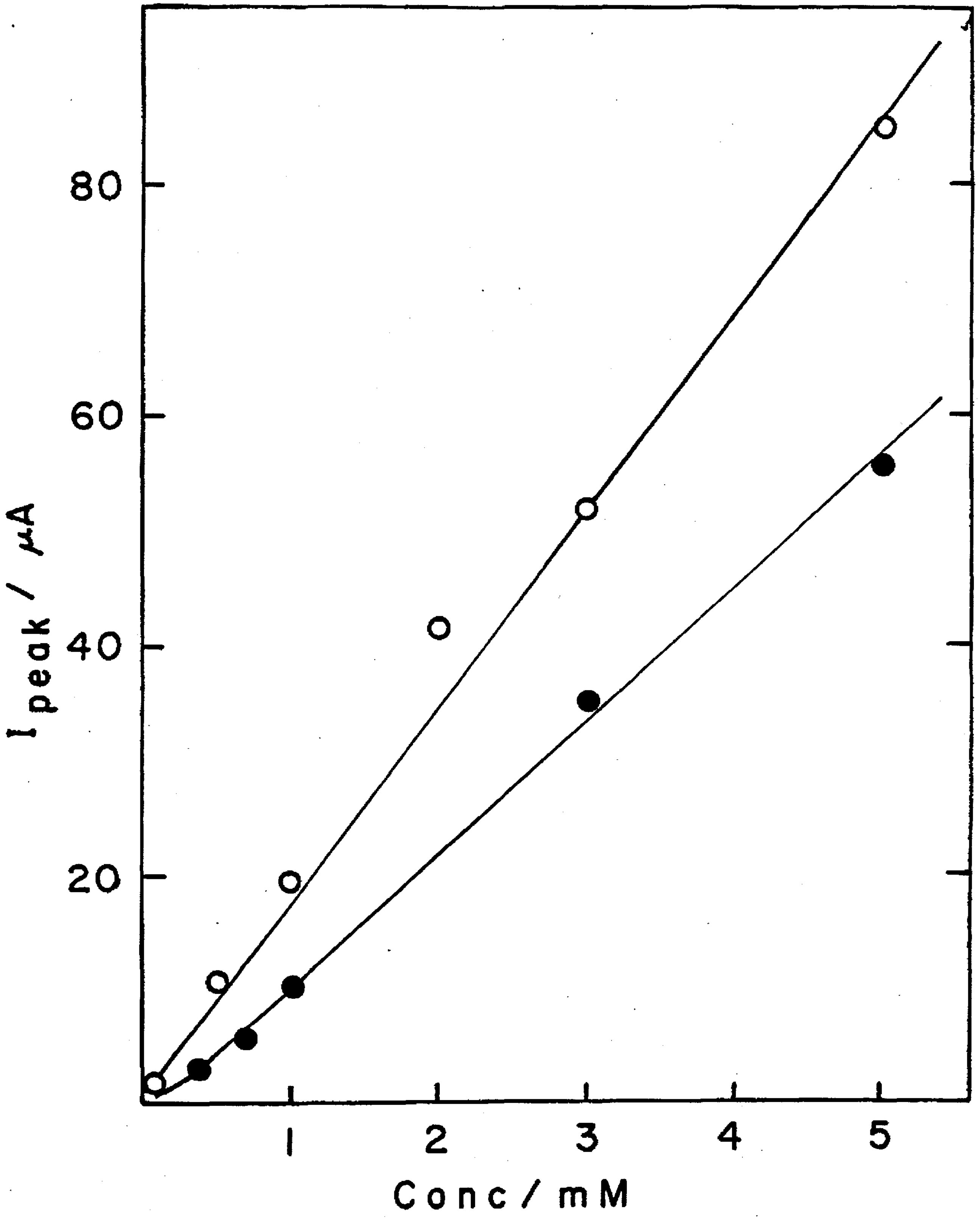
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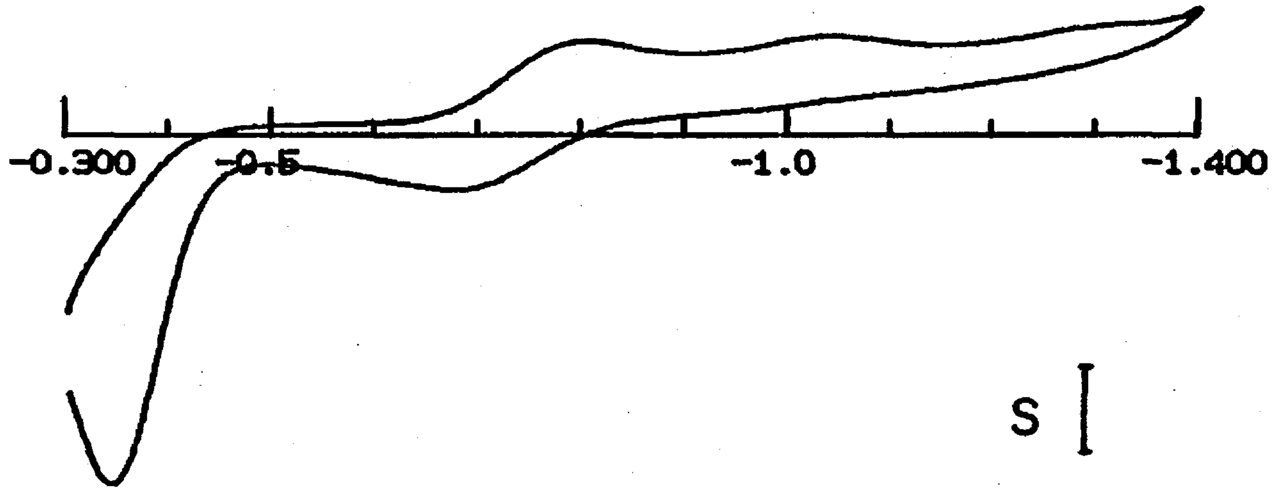

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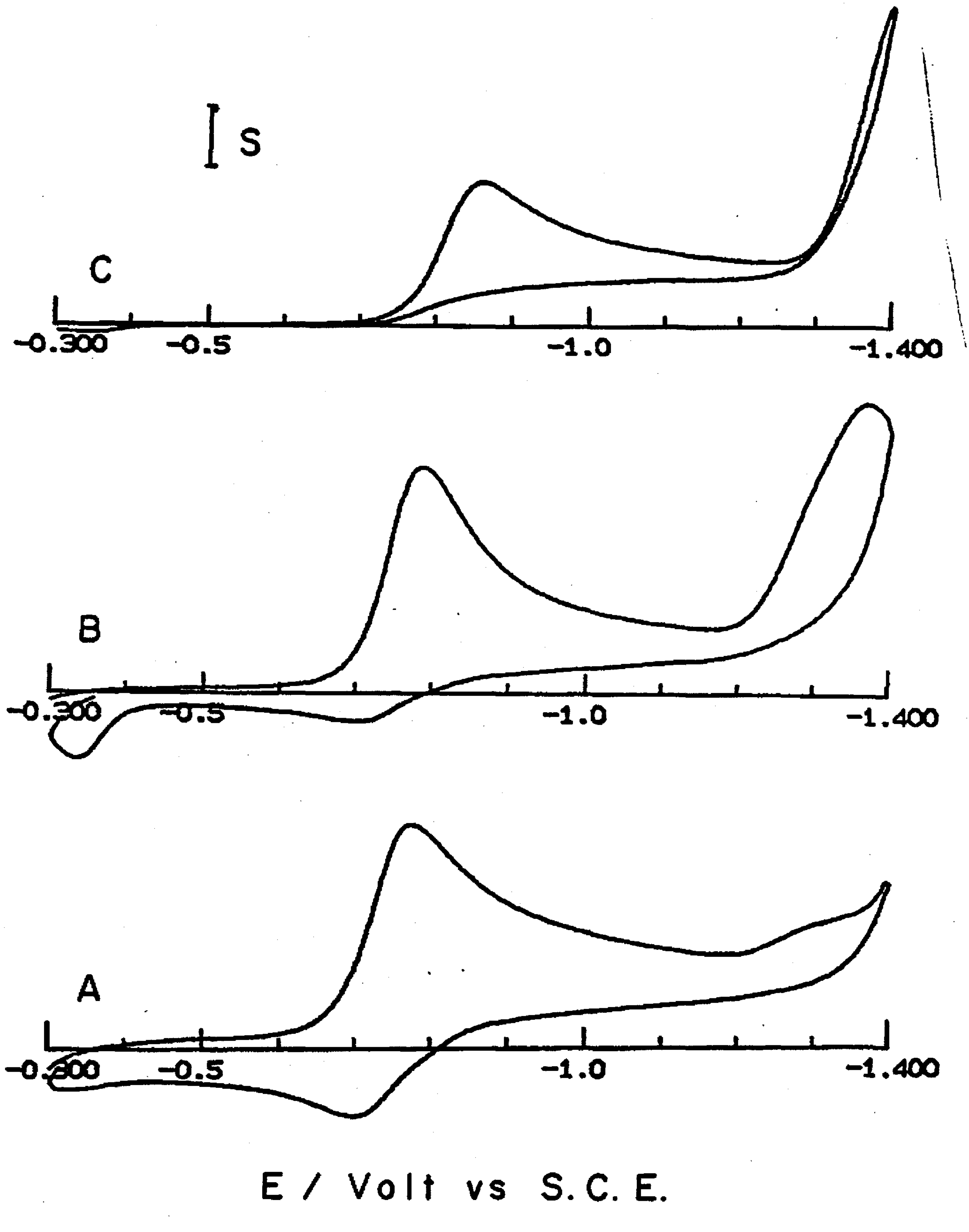

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