Electrochemistry of

Polymer-metal

Complexes

Paul V. Neilson

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

California Institute of Technology

1980

(Submitted September 1979)

To my Parents

and Friends

Acknowledgement

Abstract

Polymeric ligands, Polyethylenimine (PEI) and Chitosan, were
studied for possible applications in the modification of electrode
surfaces in relation to the three main goals:

1. metal ion scavenging

2. to find a system which catalyzes O_2 reduction

3. understanding of electron transfer in polymer-metal films.

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Introduction

The modification of electrode surfaces has been an area very actively researched lately. The advances which have occured since January 1978 include modification of carbon surfaces,[1-9] semiconductor surfaces,[10-17] metal surfaces,[18-20] others[21,22] and a review has appeared.[23] The field is past the early problems of getting anything to attach. More advanced studies such as electron transfer rates are now being investigated,[24-27] complemented by surface and interface studies.[28-42]

The types of molecules attached have also been varied considerably. Porphyrin systems,[1,6,19] dyes,[12,13] ferrocenes[11,18,25,26,43,44] and chlorophyll[17] are but a few of the systems which have been attached to electrodes.

A recent branch of modified electrodes, polymer coated electrodes, is undergoing the same history. At first, reports dealt with the attachment scheme itself. Now they deal with efforts such as applying these systems to catalysis[43-60] and even polymeric electrode materials have appeared.[61-63] These efforts have been paralleled by work on the characterization and catalytic activity of polymer metal systems. Systems such as Polyvinylpyridine,[64-69] polymethacrylic acid,[70-73] polyacrylic acid,[72,74-77] polybipyridine,[78-80] and others[81-85] with various metals have been studied.

It is hoped from these studies to prepare a polymer metal system in which the catalytic site is well defined, stable, and able to catalyze a useful reaction such as O_2 reduction.[86-90]

Nature is able to catalyze O_2 reduction effectively by enzymes which contain multiple metal centers in well defined arrangements which are stable. Polymers modified with binuclear or cluster metal complexes may be able to mimic this behavior (cf. polymer-heme complexes[91,92]). Polymer-single metal complexes are a good starting point for study.

Electron transfer studies will complement the O_2 reduction work in that structures are needed in which the electron transfer rate from the electrode to all parts of polymer-metal complex are optimized for high current density.

Cyclic voltammetry and chronocoulometry[93,94] will be the techniques of choice.

Chitosan

Chitosan is known for binding many metals and is under consideration for the removal of metal ions from waste water by the United States Department of Agriculture.[95-97] It is a polyglucosamine made by N-deacetylation of chitin. Its structure, as compared with other known biopolymers, is given below:[98]

CH_2OH
O
OH
OH
O Cellulose

CH_2OH
O
OH
NHCOCH_3
O Chitin

CH_2OH
O
OH
NH_2
O Chitosan
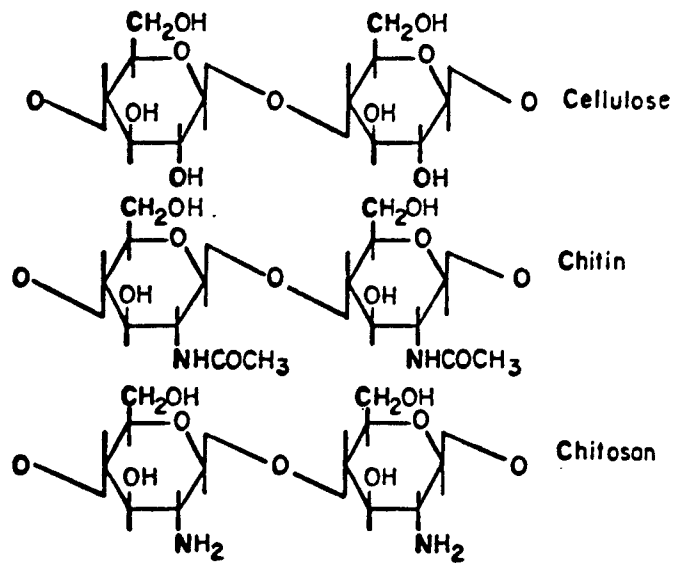
Chitosan is insoluble in water and a variety of other solvents, but is soluble in aqueous acid. Solutions of .05% or .1% chitosan in .1 M trifluoroacetic acid (HTFA) were used in the following experiments.

Basal plane pyrolytic graphite (BPG) electrodes were dipped in the acid-chitosan solution, rinsed with water, and then dipped into Fe^{2+} or Fe^{3+} (1mM as ammonium sulfates).

After rinsing, the electrode was placed in a cell containing only supporting electrolyte (1M NaTFA (pH ~5.7) or .1M HTFA) where the differential pulse and cyclic voltammograms were recorded. No firm evidence that there was iron or chitosan on the surface was observed. The main problem was that the electrochemistry of the iron complex used was very irreversible, as shown by 200 mV/sec cyclic voltammograms of the solutions below:

Solution	Anodic Peak Potential	Cathodic Peak Potential
2.17 mM Fe^{3+}	0.82	0.18
.1% chitosan, 2.21 mM Fe^{3+}	0.91	-0.09

The supporting electrolyte was .1 M HTFA.

Even after dipping the chitosan dipped electrode into NaOH solution, in the hope of forming insoluble chitosan on the surface, and then dipping it into Fe^{3+} solution, the electrode showed no iron waves in iron free supporting electrolyte. Pb^{2+} was also tried unsuccessfully.

Since one of the goals of this research is to find a metal-polymer complex which is easy to attach and maintain on an electrode, other systems were examined (vide infra).
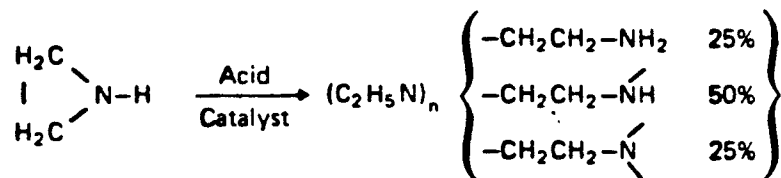
Polyethylenimine (PEI)

PEI is a good choice for possible attachment to graphite for a number of reasons. PEI can be chemically modified to produce polymer systems with many different characteristics for use as flocculants, adhesives, ion exchangers, and chelates. PEI and its derivatives form complexes with Cu, Hg, Ni, Cr, Co, Ag, Cd, Pb, Fe, and Zn.[95,99-101]
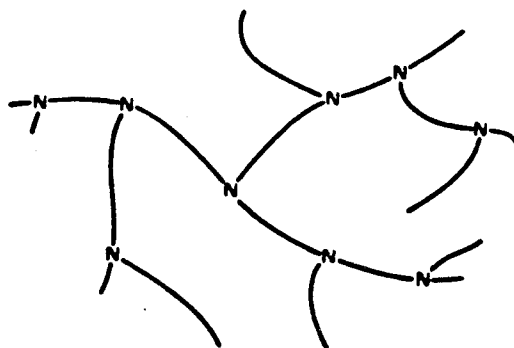
The ease of modification of the polymer is very important. The metal-PEI complex may have to be "fine turned" (redox potential and other properties) to be an effective catalyst. PEI is a very versatile polymer.

Properties of PEI

PEI is made by the following reaction:[99]

$$H_2C \diagdown N-H \xrightarrow[\text{Catalyst}]{\text{Acid}} (C_2H_5N)_n \begin{cases} -CH_2CH_2-NH_2 & 25\% \\ -CH_2CH_2-NH & 50\% \\ -CH_2CH_2-N & 25\% \end{cases}$$

As one can see it is highly branched and can be depicted as :

The PEI worked with had average molecular weights of 600 and 40,000. PEI (600) is an anhydrous liquid which is soluble in water (in all proportions) and other solvents such as DMF and methanol. The micro-analysis is given below:

	%C	%N	%H	Total
Calculated PEI(600)	55.8	32.5	11.7	100
Sample 1	50.5	31.5	11.2	93.2
Sample 2	52.4	32.2	11.4	96.0

Sample 1 and sample 2 are from the same bottle but were obtained about two months apart (sample 2 after sample 1). Whereas sample 1's bottle has been opened and closed many times, sample 2's has been opened only a few times. The discrepancy between them is almost certainly due to water absorption.

Titration of PEI(600) was also done. The titration in water can be seen in Figure 1. As one can see, PEI is a weak polybase. Therefore, the titration was performed using glacial acetic acid as solvent with $HClO_4$ in glacial acetic acid as titrant according to established procedure.[102] The nonaqueous titration is shown in Figure 2. The nonaqueous titration end-point is obviously good only to about 5% (probably too much water in polymer).
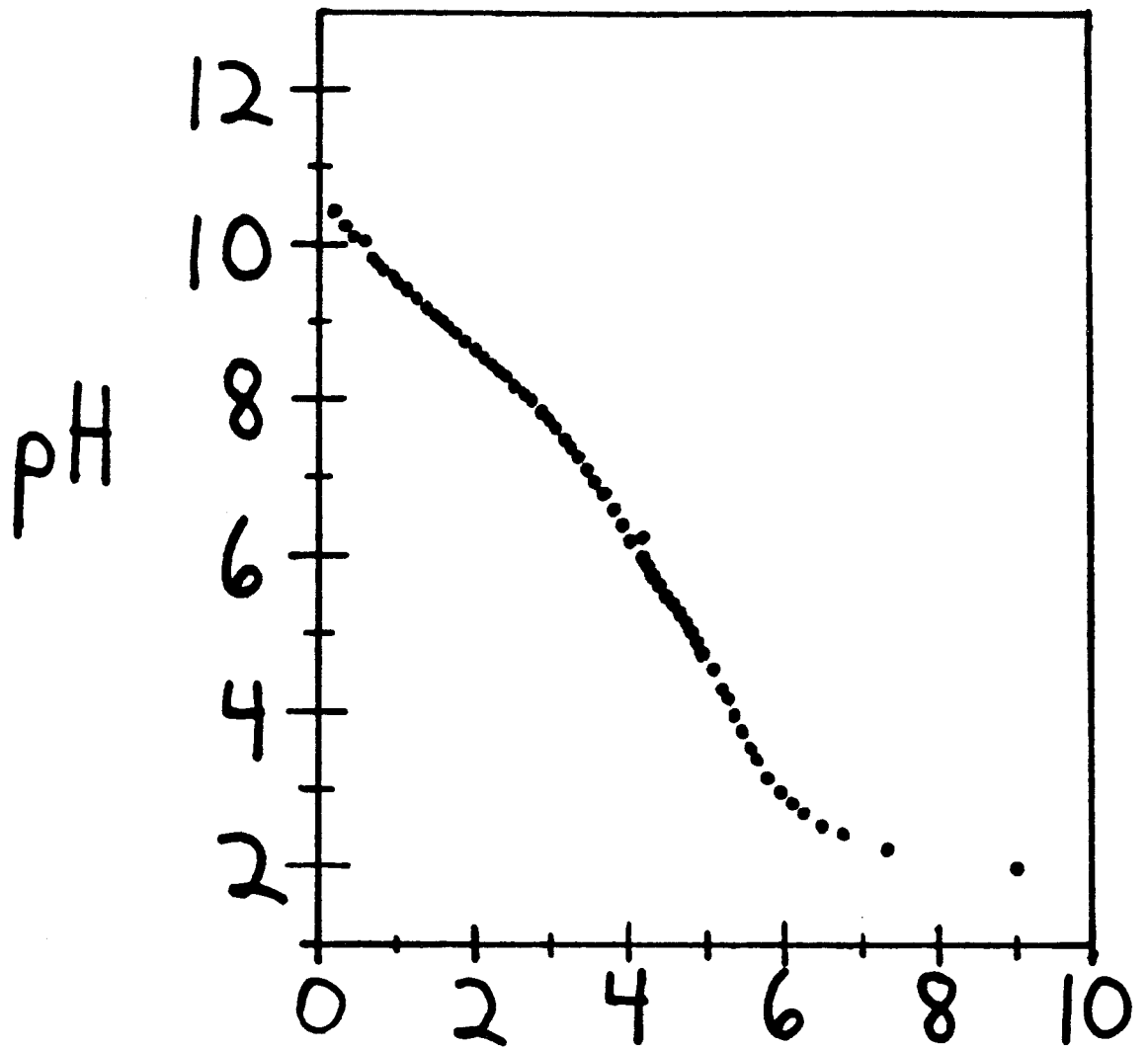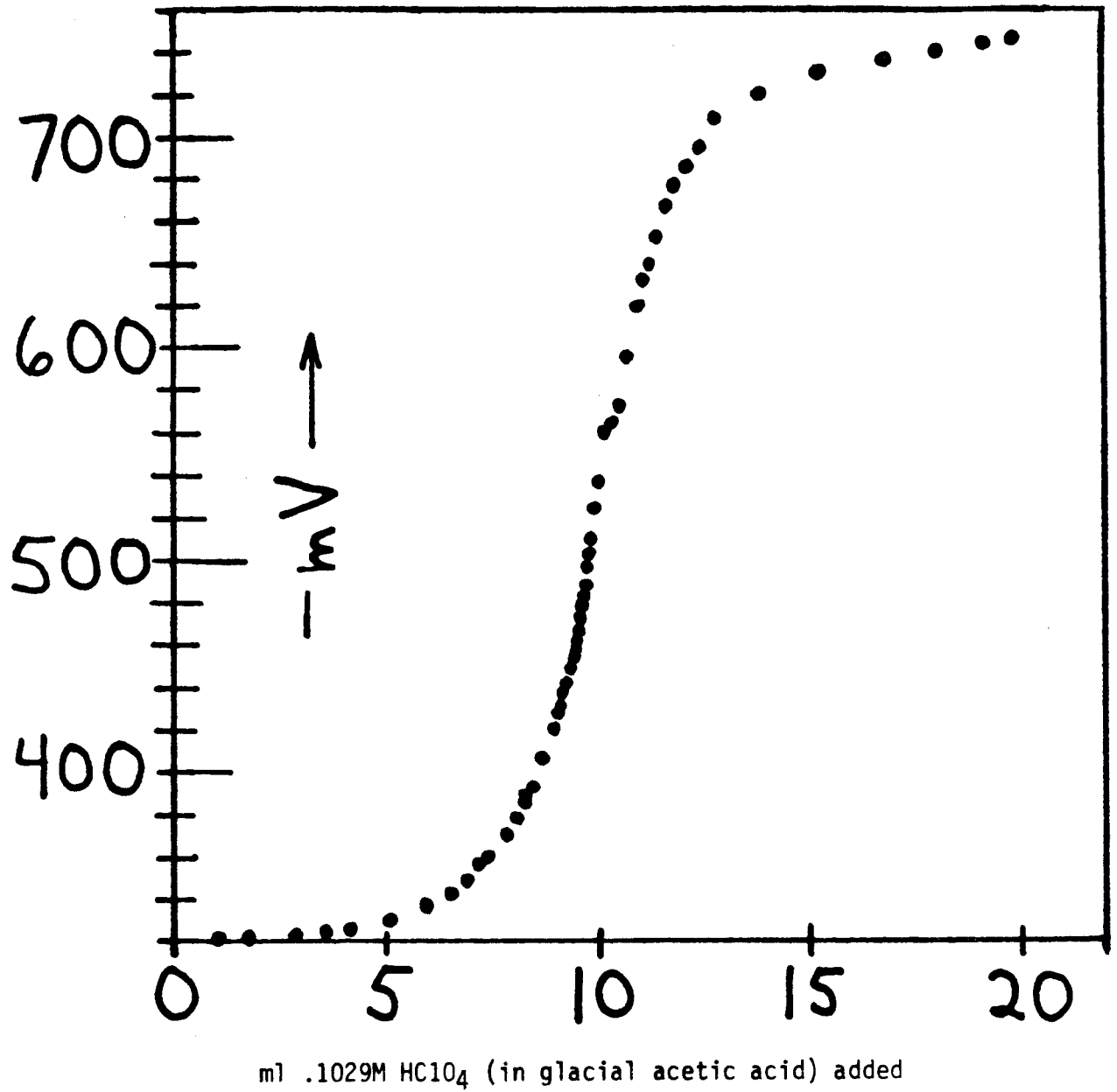
ml .0981M HTFA added

pH titration of .0342g PEI(600) in 10.00 ml
H_2O

Figure 1

ml .1029M HClO₄ (in glacial acetic acid) added

Potentiometric titration of 0.0611 g PEI(600) in 150 ml glacial acetic acid

Figure 2

Titration Analysis - (PEI-600)

$$\frac{g}{equivalent} \qquad 61.3 \pm 5\%$$

or

$$\frac{meq}{g} \qquad 16.3$$

The lab analysis may be reexpressed as:

Lab Analysis (PEI-600)

	Calculated	Sample 1	Sample 2
$\frac{g}{equiv.}$	43.1	44.5	43.5
$\frac{meq}{g}$	23.2	22.5	23.0

In other words, only about 70% of the nitrogens are titratable.

This is comparable to titration data in the literature and is probably, in part, attributable to the high charge density that PEI attains upon protonation.[99,105,106] (cf. Lab analysis 23 $\frac{meq}{g}$ - most resins only have about 4 meq/g). PEI and chitosan are cationic polyelectrolytes[106,107] and so are their metal complexes. Poly-electrolyte theory will therefore help in understanding their properties[108-112] (vide infra).

For comparison, PEI-40k's lab analysis is shown below:

	%C	%N	%H
PEI-40k	30.5	17.7	10.8
Calculated	27.9	16.25	11.4

PEI-40k is a 50% aqueous solution.

Cu - PEI Complexes

The visible spectrum of Cu^{2+} has one band at 630 nm with an extinction coefficient of 163 M^{-1} cm^{-1}. Nonogaki et al[113] found a band at 650 nm with an extinction coefficient of 180 M^{-1} cm^{-1}. However, experimental conditions were not clearly specified making comparison difficult. Cu^{2+} or PEI does not have a band in this region, making spectroelectrochemical measurements a possibility, although PEI-Cu^{2+} may have too low an extinction coefficient for the quantity on the electrode to be determined.

Electrochemistry, Cu^{2+} - PEI(600)

Cyclic voltammetry (CV) of the attached Cu^{2+}-PEI(600) is shown in Figure 3. CV shows ca. 5 μC of complex attached. The prominent anodic stripping wave ($Cu \rightarrow Cu^{2+} + 2e^-$) that one observes for Cu^{2+} solutions at .1 - .2 V (ca. 100 times as large as the waves of Figure 3), is not present in the Cu^{2+}-PEI CV on the BPG electrode. It is observed with 2.0 mM $CuSO_4 \cdot 5H_2O$/14 mM en, however. Cu^{2+}/en waves on BPG and HMDE are twice as big as Cu^{2+}/PEI waves (same concentration of Cu^{2+} and nitrogen) leading one to suspect that attachment to the polymer slows down the diffusion rate.

The electrochemistry of Cu^{2+}/en on HMDE is a quasi-reversible 1 electron process (60 mV peak separation at low scan rate - increases with scan rate). Selected $E_{1/2}$'s are shown in Table I. Cu^{2+}/PEI, however, shows widely separated anodic (plateau) and cathodic peak potentials as shown in Figure 4.
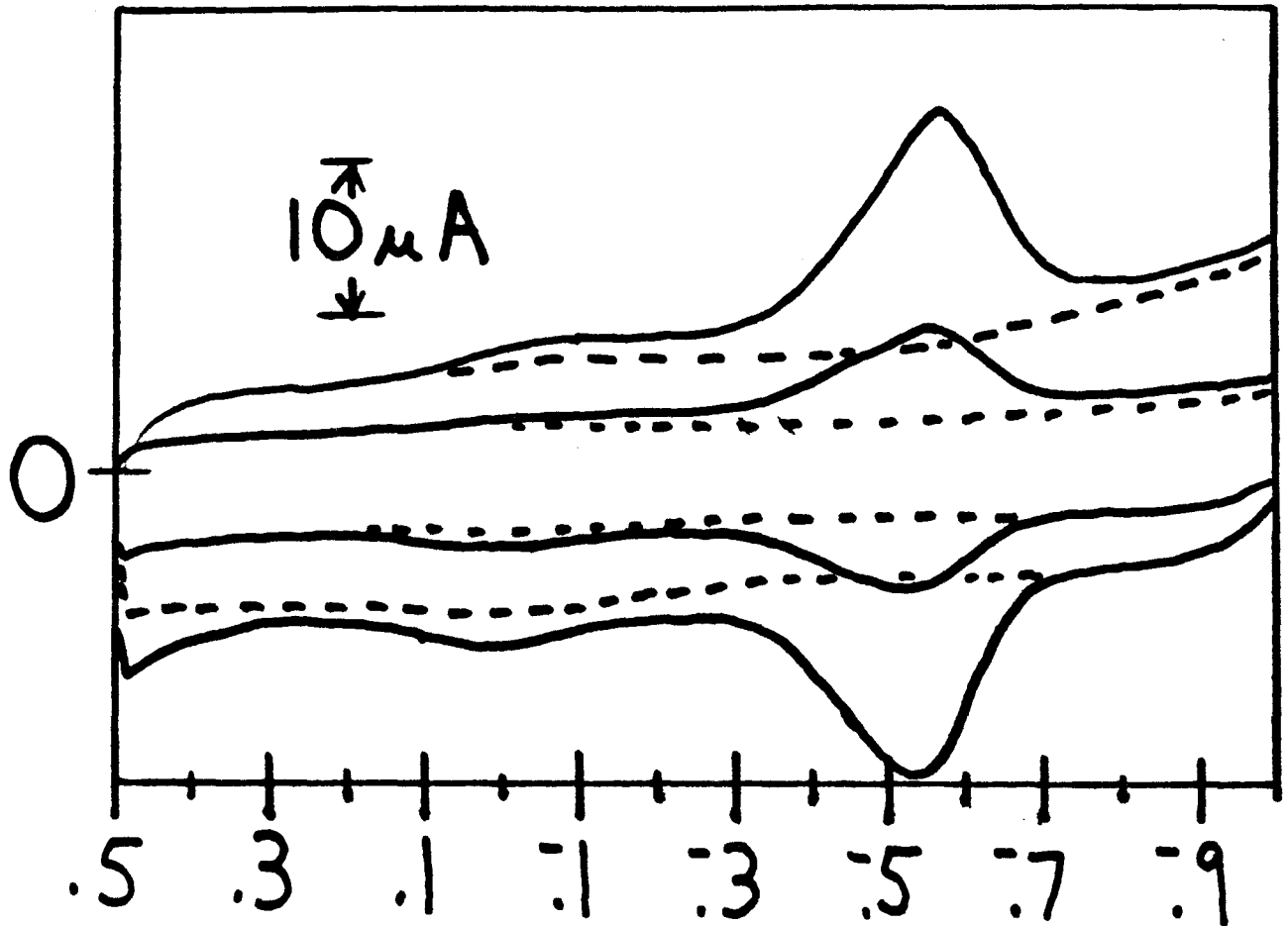
Volts vs SSCE

—— Cyclic voltammogram of a BPG electrode which has been dipped in a solution containing 2.15 mM PEI(600), 2.02 mM $CuSO_4 \cdot 5H_2O$ and 1M NaTFA for 15 minutes (ca. 14 Nitrogens per Cu^{2+}). The electrode was then rinsed with water and transferred to a solution containing only 1M NaTFA (pH = 7.9, rises to 8.4 at end) where the electrochemistry was done.
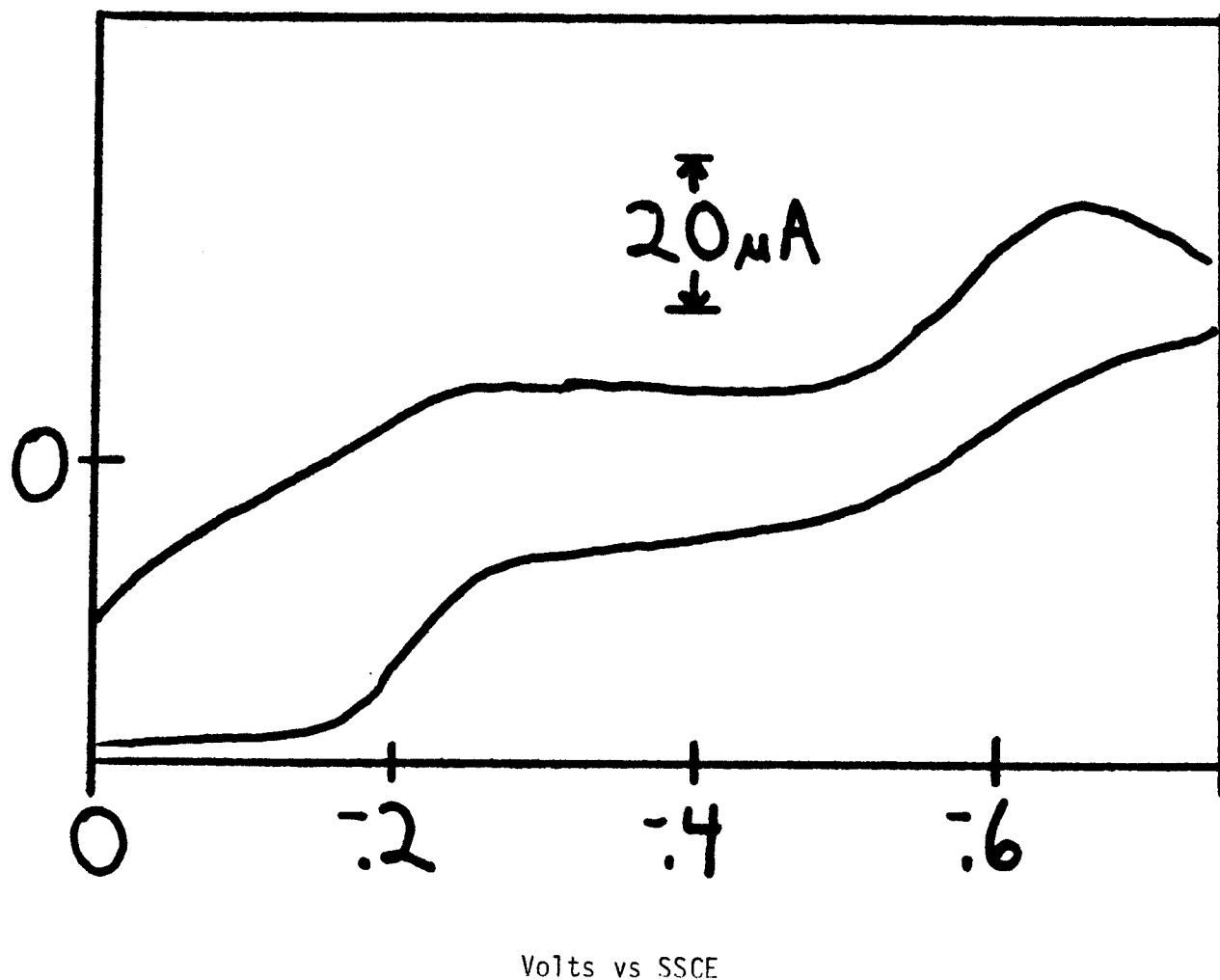
--- Background, 1M NaTFA only

Scan rates: outer curves, 500 mV/sec
            inner curves, 200 mV/sec

Figure 3

Table 1

Selected potential vs SCE

Reaction	E vs. SCE	Ref
$Cu^+ + e^- = Cu$	.271	114
$Cu^{2+} + 2e^- = Cu$	.093	114
$Cu^{2+} + e^- = Cu^+$	-.097	114
$Cu(en)_2^{2+} + e^- = Cu(en)_2^+$ (concentrations not specified)	-.63	114,115
$Cu(en)_2^{2+} + e^- = Cu(en)_2^+$ (1.07 M en, 23 mM Cu^{2+})	-.54	116

Cyclic voltammogram of a solution containing:

2.02 mM $CuSO_4 \cdot 5H_2O$

2.0 mM PEI(600)

1 M NaTFA

A hanging mercury drop electrode was used

pH ~ 10.6

500 mV/sec

Figure 4

Figure 5 shows a CV of the dipping solution of Figure 3. In spite of the fact that both Figures 3 and 5 have contributions due to adsorption and Figure 5 should have a contribution due to diffusion, also, both have about the same peak currents. The peaks of Figure 5 decrease slightly with cyclying. Figures 4 and 5 further support the hypothesis that the polymer coating is slowing down the diffusion rate.

Controlled potential electrolysis (CPE) was attempted using graphite cloth electrode since a large surface area electrode was required and mercury electrodes did not show the same behavior as graphite. The background current on graphite cloth was so large that no useful information was obtained.

Figure 6 shows the surface coverage, calculated by integration of the cyclic voltammograms, vs time behavior of the electrode of Figure 3. The PEI sample used has a small molecular weight (600), so it is not surprising that it falls off of the electrode rather rapidly.[117] Not shown in Figure 6 is the fact that this coverage **is potent1**al dependent. If a dipped electrode is held at +0.8 V, there will be no electrochemical response from this electrode, although an electrode held at +.5 V or -1.0 V for 30 seconds shows no significant loss of activity. Some degradation of the polymer at +0.8 V may have occurred. A 2.01 mM PEI (1 M NaTFA supporting electrolyte) solutions shows oxidation current at about +.6 V which supports this interpretation.

The polymer-metal complex may also be put on electrodes by dipping first into polymer solution and then into copper solution. However,

Volts vs SSCE
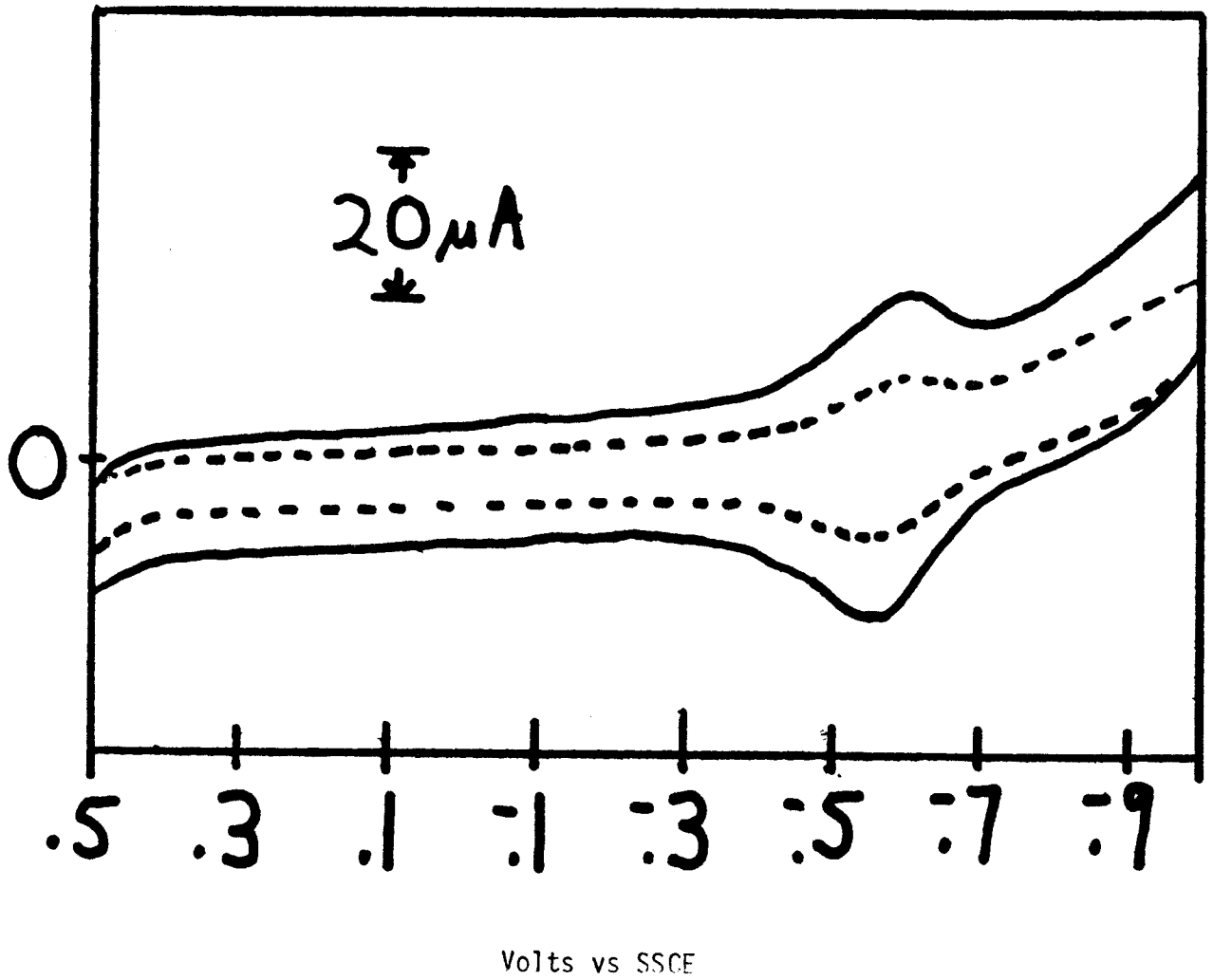
Cyclic voltammogram of a solution containing:

2.02 mM $CuSO_4 \cdot 5H_2O$

1.97 mM PEI(600)

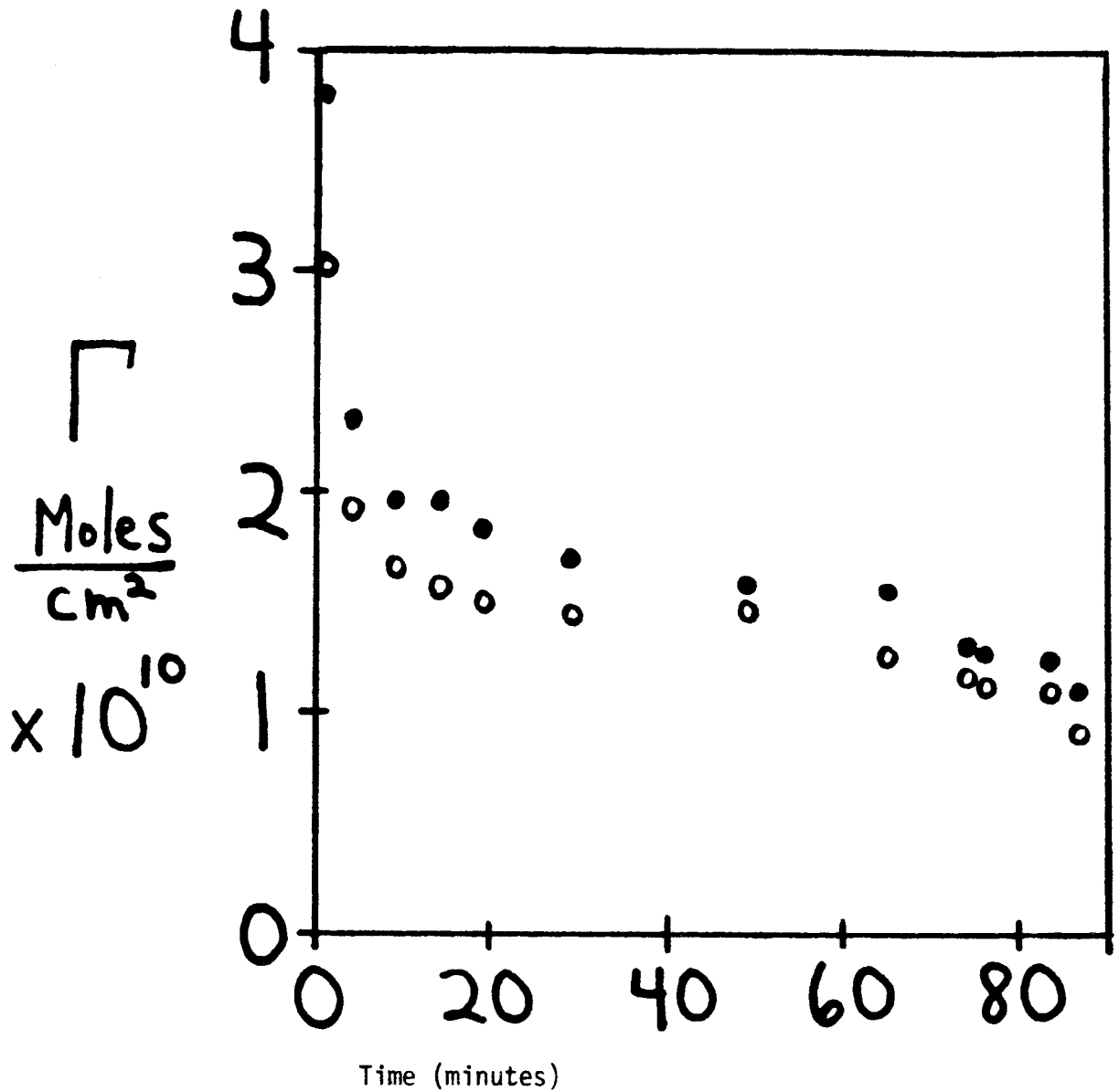1 M NaTFA

BPG electrode

———— 500 mV/sec

• • • 200 mV/sec

Figure 5

Surface coverage vs. time for the electrode
of Figure 5.

● cathodic scan

○ anodic scan

The electrode is on open circuit between scans.

Figure 6

this procedure shows the importance of the Cu^{2+}/PEI ratio. Figure 7 shows the effect of dipping a PEI coated electrode into a concentrated solution of $CuSO_4 \cdot 5H_2O$. This behavior may be readily understood by examining Figure 8. An electrode dipped into base (NaOH) and then into a Cu^{2+} solution (Figure 8) shows the same waves as Figure 7.

If variable concentrations of dipping PEI solutions are tried, broad waves centered around -.49 V show up which last as long as Figure 3's waves. This may be due to a variable number of ligands bound to Cu^{2+}.[118]

If pH 1 supporting electrolyte is used no electrochemistry will be observed. The complex is destroyed by strong acid as expected from complex stability constant data in the literature [119-124] for PEI, ammonia, ethylenediamine or tetren.
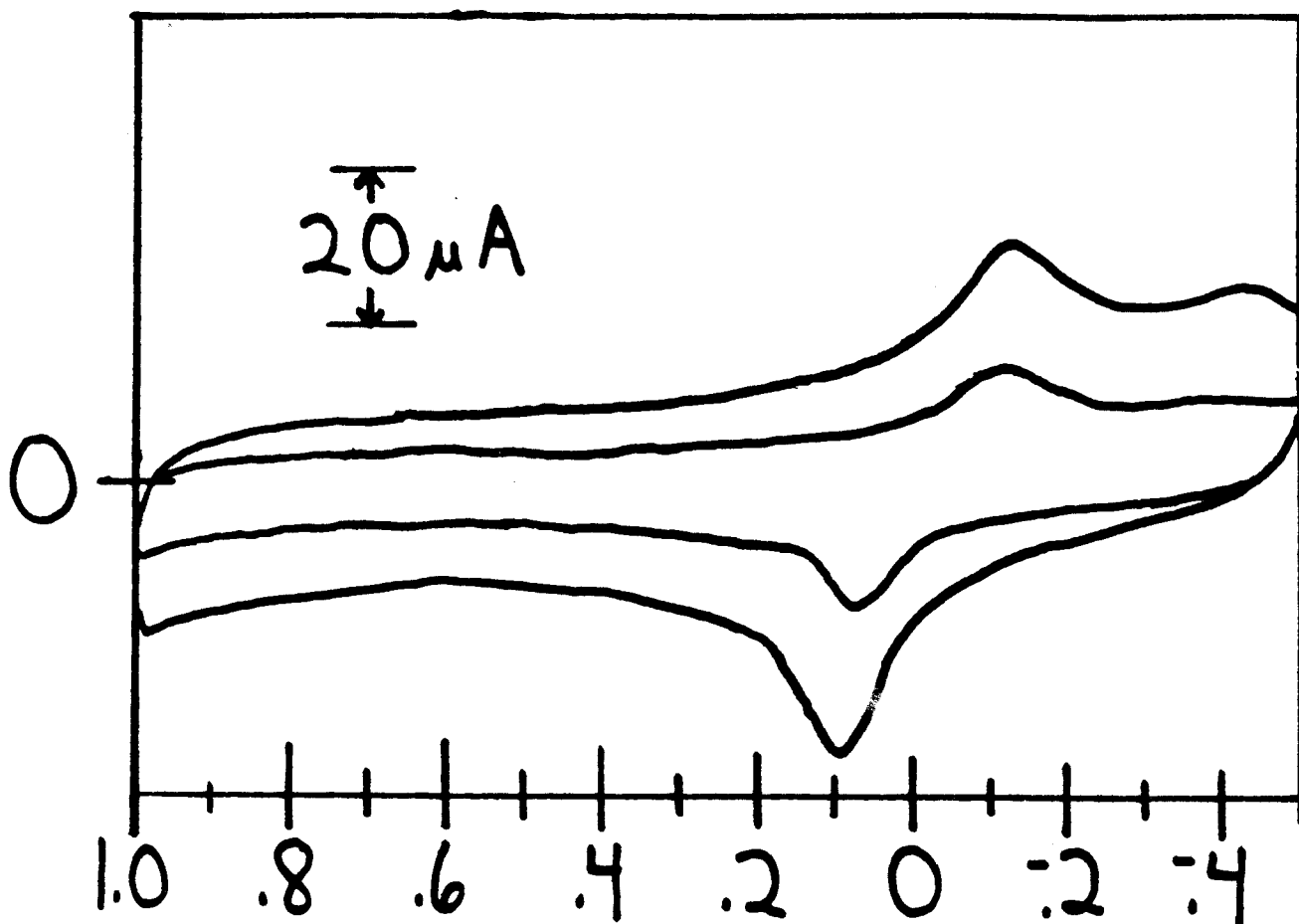
Volts vs. SSCE
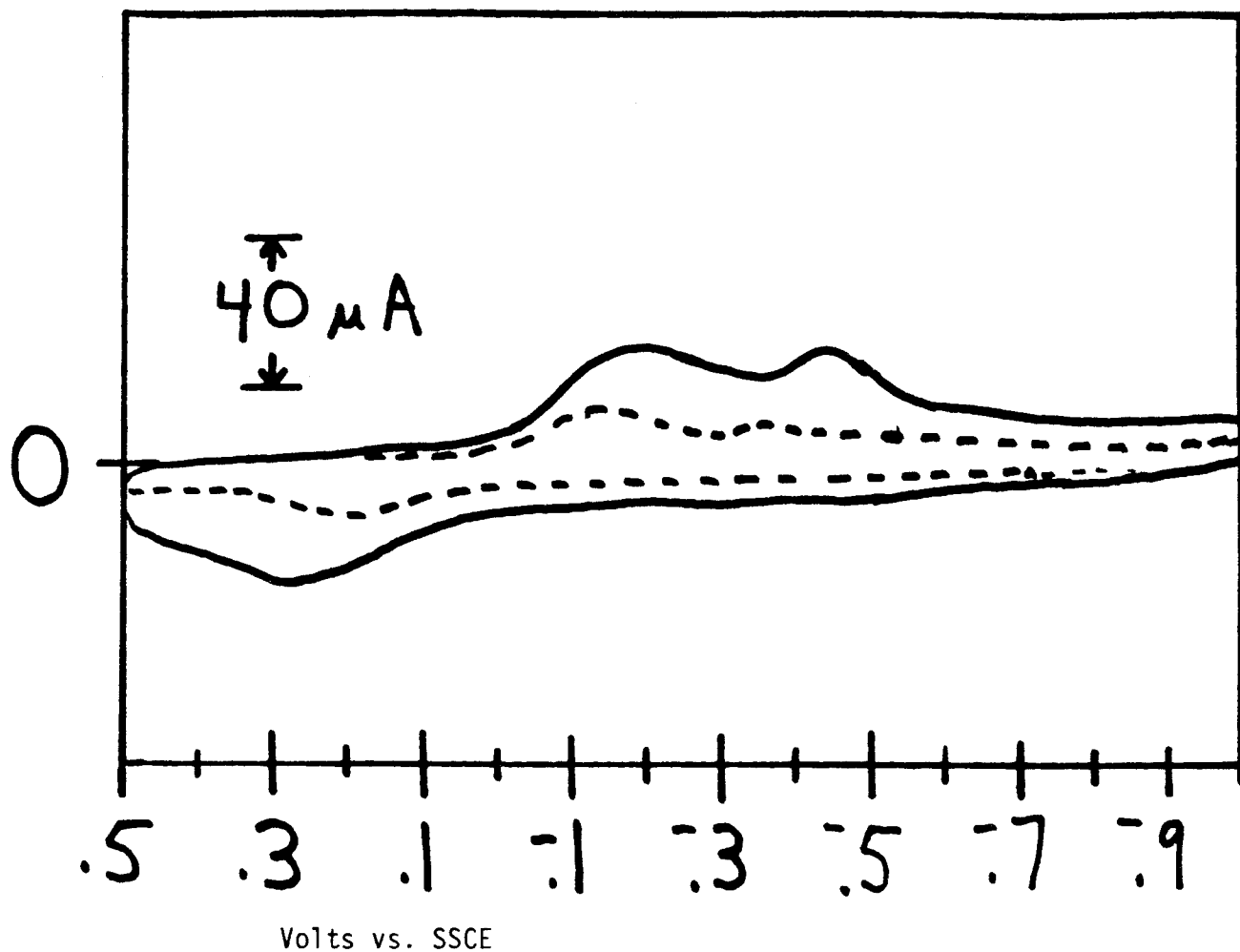
Cyclic Voltammograms of BPG electrode which has been soaked 15 minutes in a solution containing 2.01 mM PEI (600) (and 1M NaTFA), then soaked in a solution containing .1M $CuSO_4 \cdot 5H_2O$ (pH = 4.27). The electrode was then rinsed and transferred to a 1M NaTFA supporting electrolyte where electrochemistry was done.

Scan rates: ——— 500 mV/sec

••••• 200 mV/sec

Figure 7

Volts vs. SSCE

Cyclic voltammograms of BPG electrode which has been soaked for 15 minutes in .1M NaOH and then for 15 minutes in Cu^{2+} solution and then transferred to 1M NaTFA (pH = 7.7) supporting electrolyte where electrochemistry was performed.

Scan rates: Outer curves   500 mV/sec
                 Inner curves   200 mV/sec

The electrode was rinsed with water and blotted dry between each step.

Figure 8

Electrochemistry, Cu^{2+}-PEI(40k)

Since Cu^{2+}-PEI(600) fell off the electrode rapidly (cf. Figure 8), PEI of higher molecular weight was used. Figure 9 shows a CV on a BPG electrode dipped into PEI(40k) and then into Cu^{2+}. The symmetric wave is very similar to the waves produced when the same procedure is used with PEI(600). The Cu waves produced for the PEI(40k) are longer lived than the waves for PEI(600). More electroactive Cu is found on the electrode surface with the higher MW polymer although the amount is still not reproducible. It is for the above reasons that PEI(40k) was used in the O_2 and H_2O_2 reduction work.

O_2 and H_2O_2 Reduction - Cu^{2+}-PEI(40k)

Figure 10 shows that Cu^{2+}-PEI(40k) does indeed catalyze O_2 reduction by about 200 mV (Figure 10 only shows first scans - subsequent scans are smaller). An electrode dipped in a solution of 1 M NaTFA/ 10 mM borate/5 mM Cu^{2+} also shows a 200 mV shift, however. This may be due to some kind of Cu-hydroxide species on the electrode surface. Whatever it is falls off after the catalysis experiment, whereas not as much Cu^{2+}-PEI(40k) falls off.

Figure 11 shows that Cu^{2+}-PEI(40k) also catalyzes H_2O_2 reduction. Cu^{2+}-PEI(40k) also falls off after this experiment. Haas et al[155] find that peroxide oxidizes PEI which is accompanied by some chain degradation. Since the intermediate of the reduction of O_2 is presumably a peroxide species, both fall offs may be rationalized as peroxide decomposition of the polymer. This obviously makes Cu^{2+}-PEI unattractive as a O_2 reduction catalyst. See for example 125-139.
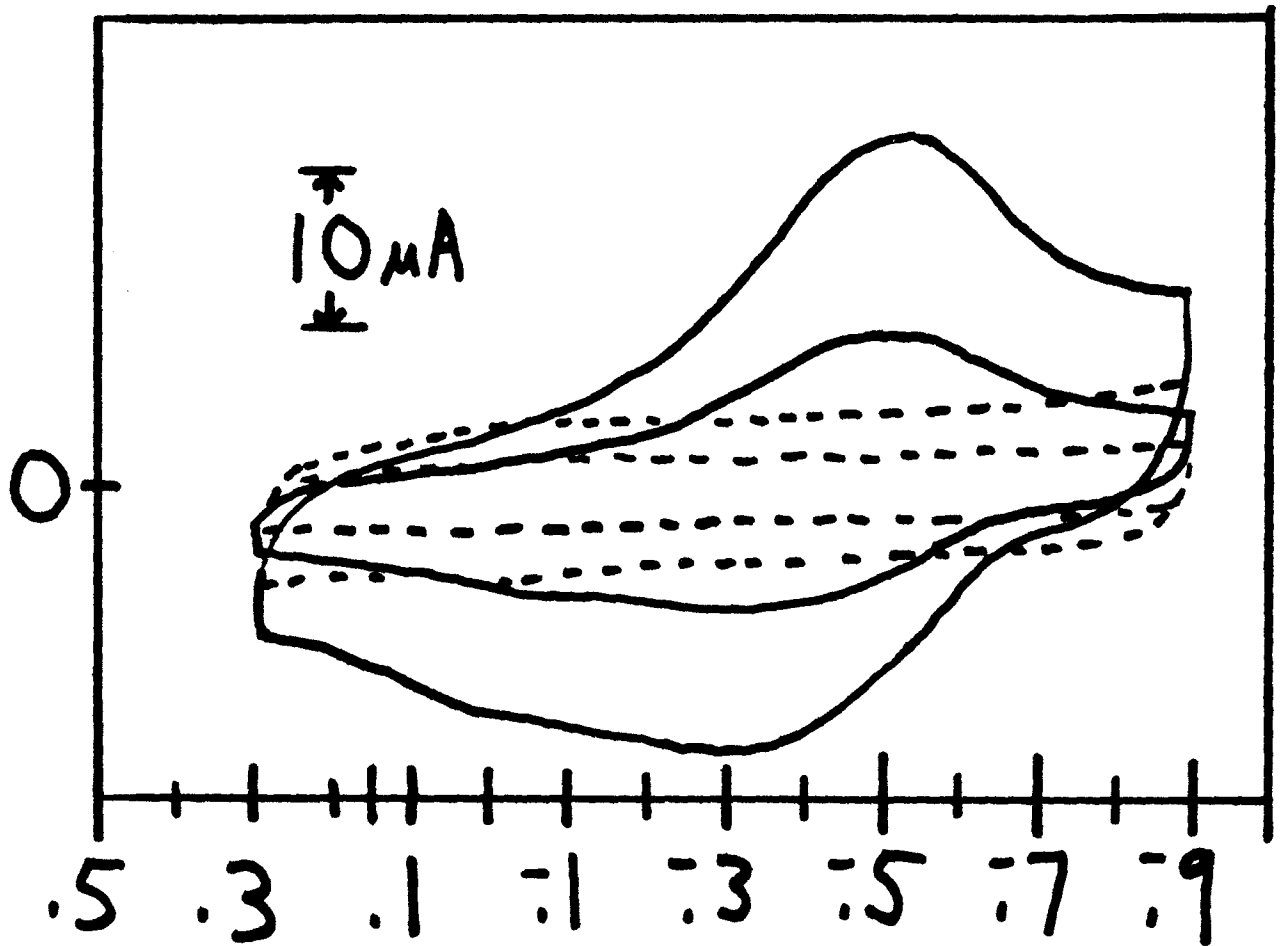
Volts vs SSCE

━━━ CV of a BPG electrode which has been soaked for 18 minutes
in a solution of .6533 g PEI(40k)/25 ml H_2O and then
soaked for 15 minutes in a solution of 2.61 mM $CuSO_4 \cdot 5H_2O$/
1 M NaTFA and then transferred to a solution containing
1 M NaTFA/10 mM borate.

━ ━ ━ dipped in PEI only.

[inner curves: 200 mV/sec]
[outer curves: 500 mV/sec]

Figure 9
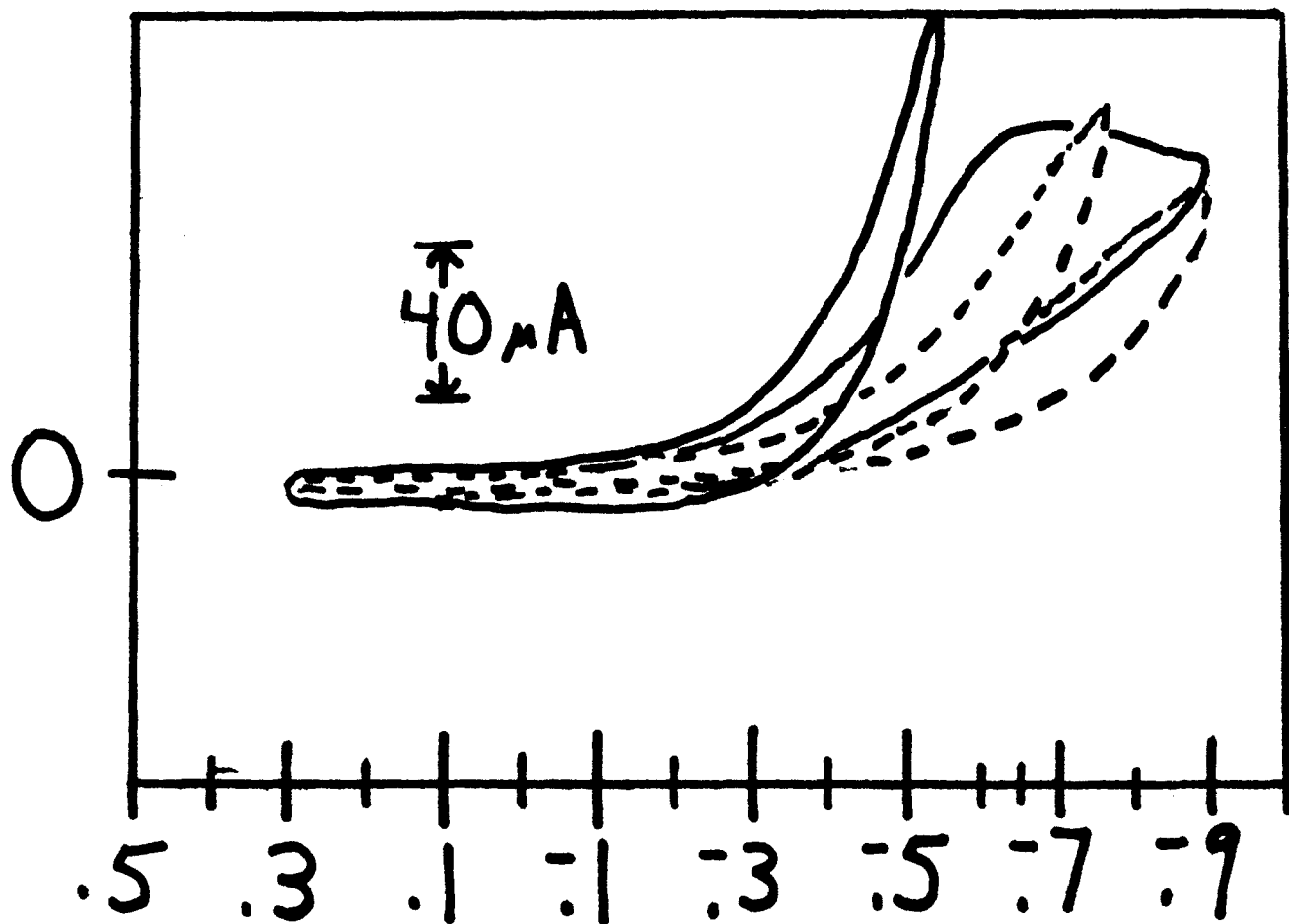
Volts vs SCE

CV (first scan) of O_2 saturated solution with the
BPG electrodes of Figure 9.

━━━ Cu^{2+}/PEI(40k)

●●●● PEI(40k) only

upper curves   500 mV/sec
lower curves   200 mV/sec
   (200 mV/sec solid curve
   not shown from +.3 -
   -.3 due to overlap with
   dashed curves)

Figure 10

Volts vs SCE
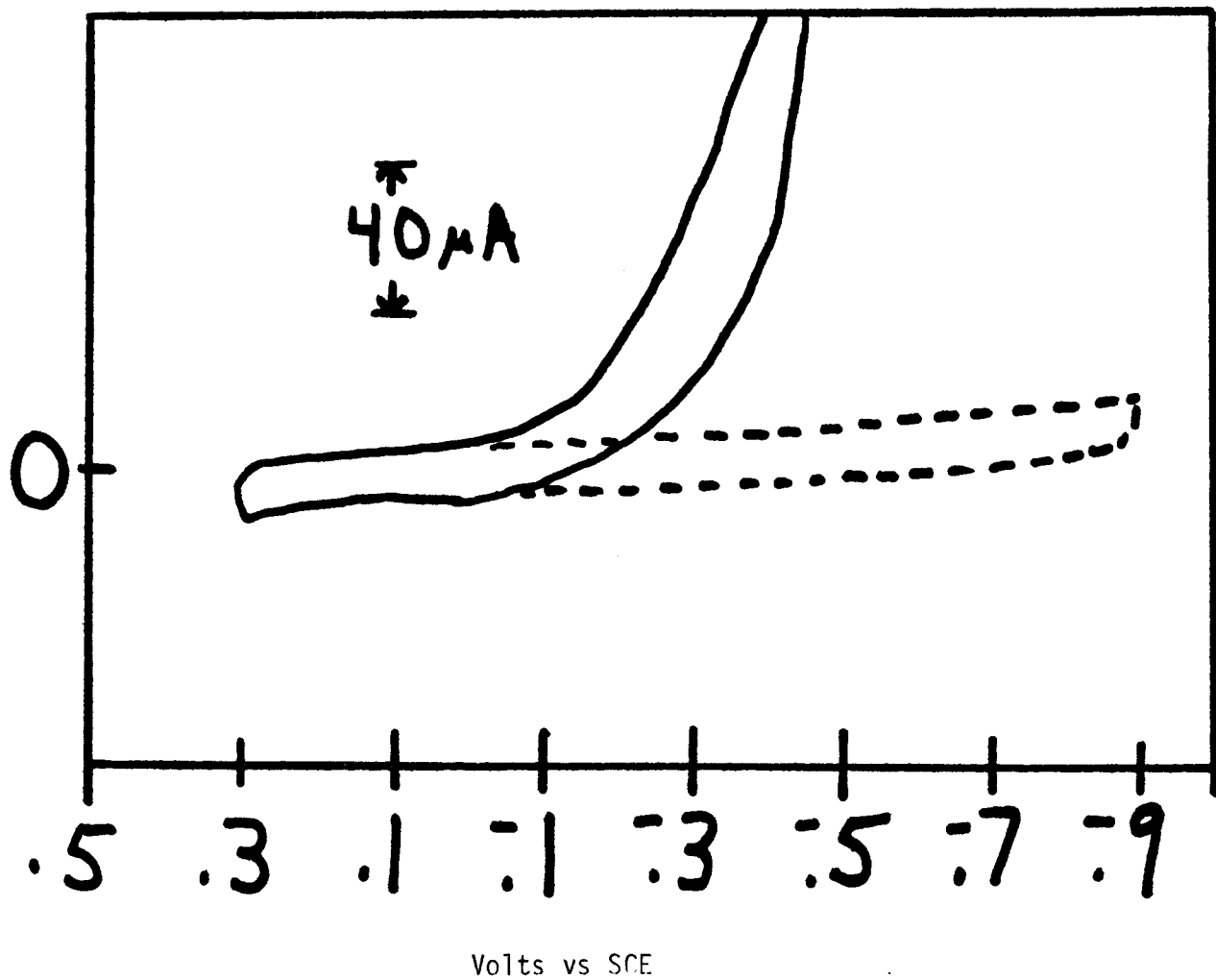
BPG electrode soaked for 27 minutes in PEI(40k)
and then for 15 minutes in Cu^{2+} (see Figure 9).

PEI(40k) only

Solution:

    1 M NaTFA/10 mM borate

    20 mM H_2O_2

    pH = 8.1

Figure 13

Summary of Cu^{2+}-PEI

PEI was found to scavenge Cu^{2+} from solution and the resulting Cu^{2+}-PEI was found to catalyze O_2 and H_2O_2 reduction, although PEI was unnecessary for catalysis of O_2 reduction.

Evidence was presented to suggest that PEI slowed down the diffusion rate as compared with en.

Co-PEI

The cobalt(II) complex of PEI was also tried using mainly PEI(40k). PEI(40k) was found to scavenge Co^{2+} from solution. Pickup of Co^{2+} from a 1 mM solution of Co^{2+} by a PEI(40k) coated electrode is complete after about 20 minutes. Increasing the concentration of Co^{2+} from 1 mM to 5 mM and then to 10 mM has no effect after the initial 20 minutes. Figure 12 shows a result of a PEI(40k) coated electrode in 1 mM Co^{2+}. The waves are very stable. There is virtually no decrease after 4 hours. If this electrode is taken out of solution and dried and then retried 2 days later in Co^{2+} free supporting electrolyte, the same waves are observed, although smaller. These waves are also very stable - very little decrease is observed after 6 hours. CV of a solution of Co^{2+} with an uncoated electrode is equivalent to background over Figure 12's scan ranges. An electrode which has been dipped into base (NaOH) and then into Co^{2+} solution also shows no waves in this region unlike Cu^{2+}.

There is evidence of the polymer "gumming up" the electron transfer. Integration of Figure 12's waves shows about 10 μC of charge on the surface whereas chronocoulometry of the same electrode shows about 30 - 50 μC of charge over a blank BPG electrode (which shows 20 - 40 μC) for a 700 sec cathodic step. Figure 13 shows the CV of $[Co(en)_3]Cl_3$ with excess en on BPG electrode. The same solution shows reversible behavior on HMDE electrode (linear current vs (scan rate)$^{1/2}$). A 2 mM Co^{2+} and 2.3 mM PEI(600) (pH = 10.5) shows no waves on BPG. No catalysis of O_2 or H_2O_2 reduction by Co-PEI(40k) was observed.
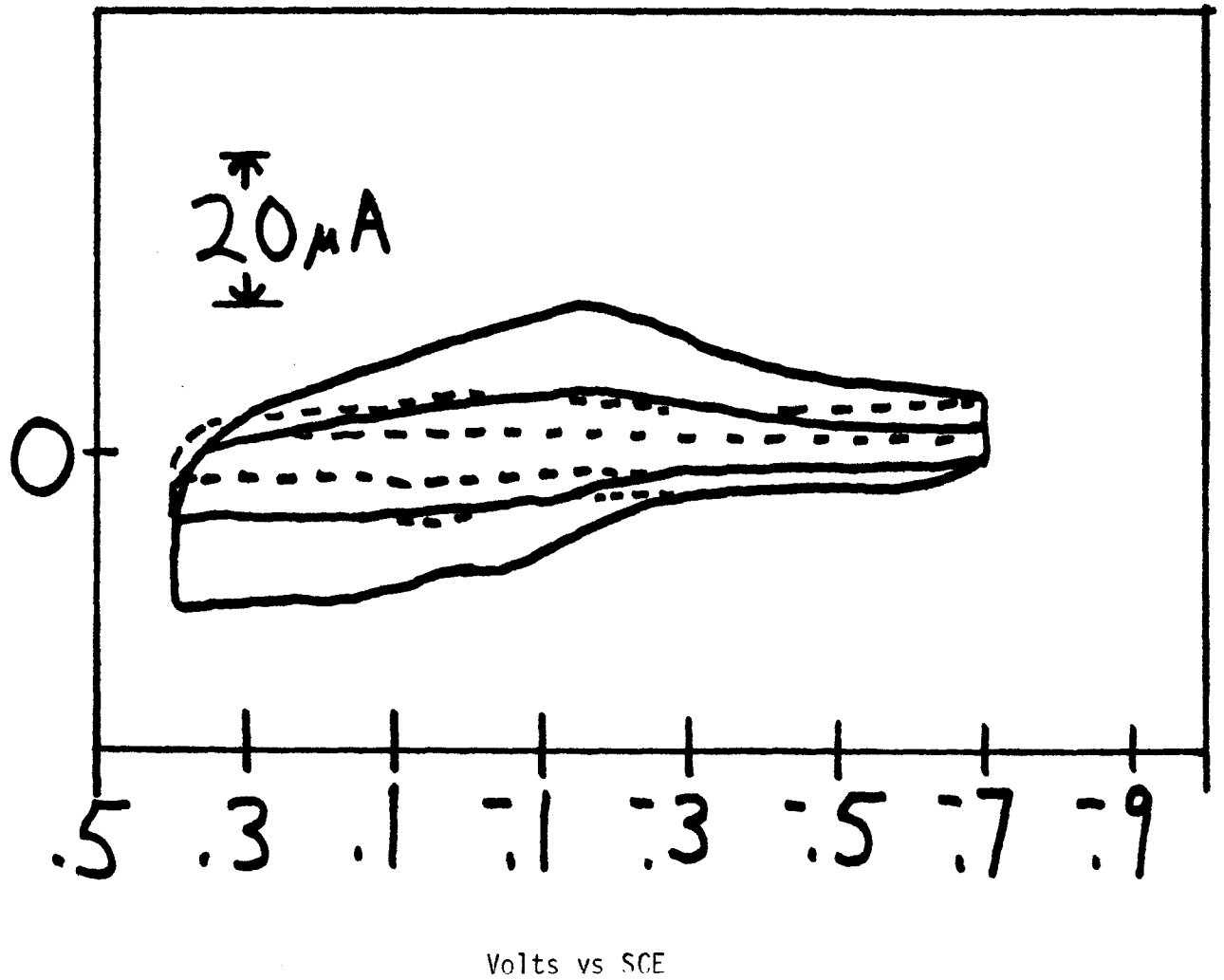
Figure 12

BPG electrode which has been soaked in a solution
containing .6533 g PEI(40k)/25 ml and immersed in a
solution containing 1 M NaTFA/10 mM borate/1 mM Co^{2+}
where CV was then performed.
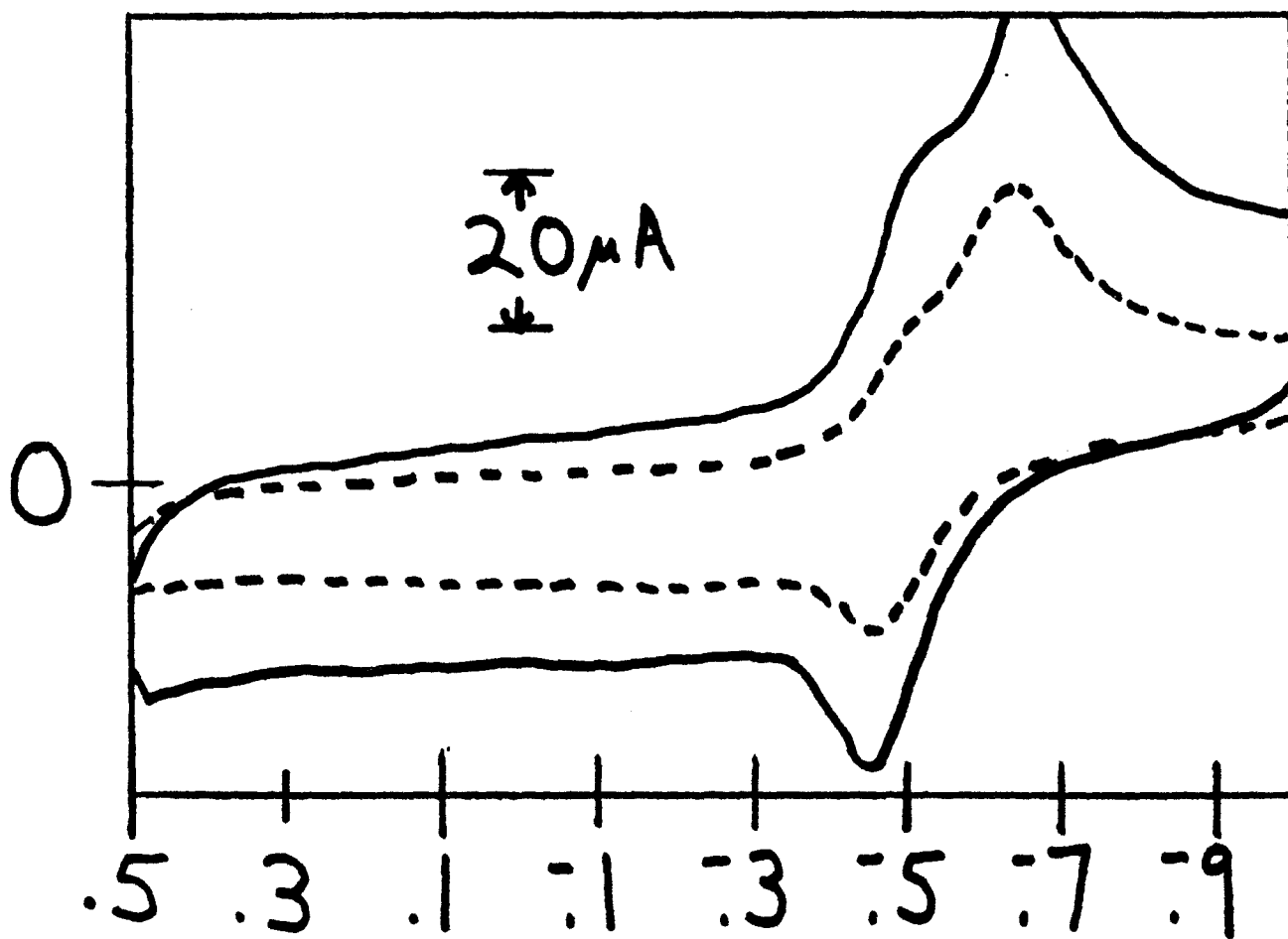
Volts vs SSCE

CV of a solution containing:

1.01 mM [Co(en)$_3$]Cl$_3$

11 mM en

1 M NaTFA

pH = 11.05

━━━ 500 mV/sec

●●● 200 mV/sec

Figure 13

Experimental

Reagents

Reagent grade chemicals such as $CuSO_4 \cdot 5H_2O$ (Mallinckrodt), perchloric acid (Baker), acetit anhydride (Mallinckrodt), ferric and ferrous ammonium sulfate (Mallinckrodt and Baker respectively), cobaltous sulfate (Baker), and acetic acid (Mallinckrodt) were used as received.

PEI(600) (Polyscience) and PEI(40k) (Cordova Chemical - 50% solution) were also used as received.

Trifluoracetic acid (MCB) was used as received. NaTFA was prepared by neutralizing HTFA with 50% NaOH solution.

Borate buffer was prepared from $Na_2B_4O_7 \cdot 10H_2O$.

Electrochemistry was performed on solutions which were degassed by passing argon through hot copper turnings (ca. 450° C) and then distilled again before use or passed through a Barnstead deionizer.

Apparatus

Cyclic and differential pulse voltammetry was performed by a PAR model 174 A polarographic analyzer with a Houston Instrument 2000 x-y recorder.

Potentiometric titrations were carried out with a Leeds and Northrup model 7664 pH meter.

An Orion model 701 A digital pH meter was used for pH titrations. The usual 3 electrode cell was used.

A Cary model 14 UV-visible spectrometer was used for visible
spectrum measurements.

Electrode Preparation (BPG)

Pyrolytic graphite disks were drilled out of a small block of
graphite (Union Carbide Corp., Parma, Ohio) which had the basal planes
oriented parallel to the main face of the block. These disks were
sealed in heat shrinkable polyolefin tubing (Alpha Wire Co.) and onto
glass tubing. Mercury was used for electrical contact to the disk
and copper wire for the connection to the external circuit.

Whenever a clean electrode was needed, an electrode as described
above was cleaved with a razor blade.

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