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BRIEF

The behavior of a graphite electrode, chemically bonded with styrene by ^{60}Co irradiation, in neutral and acidic solutions, is described.

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ABSTRACT

Described is an electrode for ASV prepared by polymerizing and cross-linking the styrene impregnator to the graphite with γ-radiation from a 5000 Ci, ^{60}Co source. Electrodes prepared with this process have performed, anomaly-free, in neutral and slightly acid solutions for over 6 months. In acid solutions at pH 1-2, the electrode is viable for several days. Reasons for premature electrode failure in acidic solutions are offered and future areas of work are suggested.

INTRODUCTION

Anodic stripping voltammetry (ASV) in conjunction with mercury-plated, wax impregnated graphite electrodes (WIGE) is widely used to determine the trace metals amenable to the method in water. Trace organic ligands, primarily weak organic acids, in nature, generally accompany the sample. These ligands have sufficient complexing strength to totally mask lead and cadmium and to severely reduce the sensitivity with which copper is detected. To circumvent this problem, the sample is acidified to a pH of $\leqslant 2$ to effect ligand release. This, however, leads to problems with the stability of the electrode.

WIGE's are reasonably long lived -- perhaps 30 to 40 days -- when used exclusively in neutral or weakly acidic (pH $\geqslant 4.7$ acetate buffer) solutions. In contrast, in acidic solutions (pH 1 to 2), a WIGE will fail within a few days to a few hours of use depending upon the age of the electrode, as measured from the date of its impregnation, and its previous history of use. The longevity of a WIGE in any aqueous solution is dependent upon the type of wax employed. A critical discussion of waxes best suited as impregnators was given recently (1,2).

The onset of electrode failure in acidic solutions is portended by first a gradual decrease in its hydrogen over voltage characteristics which accelerates with each successive scan (1). This mode of electrode failure in acid precludes the analysis of Zn and compromises the utility of the method for Cd. For these difficulties alone, a search for the cause of electrode failure would be timely, for no investigator up to the present has offered a wholly acceptable explanation for the loss of hydrogen voltage. This difficulty also extends to glassy carbon (3).

It seems likely that if the answers to these problems were in the perview of electroanalytical chemistry alone they would have been resolved years ago.

The time is past due to meet this problem head on as a challenge, for the current interest in the analysis of the various environmentally important metals determinable with ASV has brought an influx of new-comers into the electroanalytical area who are ill-prepared to deal with all the idiosyncrasies the WIGE can exhibit. Solid electrode work is difficult enough for those skilled in the field; to the neophyte it can represent a very brutal initiation.

Rapid deterioration of WIGE's response in acidic solutions also precludes their use in continuous on-line monitoring applications and makes their use in field work less than ideal. In the laboratory, their use requires the often grudgingly given continuous attention of a skilled analyst. This problem has been the major drawback to our implementation of the all digital, field-model instrumentation described recently (4). It is rather important, therefore, to investigate the mechanism of electrode failure in acidic solutions, for only in this way can perhaps an acid-stable electrode be produced.

In an attempt to learn whether electrode failure is a recent phenomenon associated only with applications involving ASV, which would indicate involvement of mercury in the mechanism of electrode failure, or whether it had been recognized earlier in the development of the WIGE, a critical review of the literature was made. Failure of the WIGE has existed and was recognized virtually from the very inception of the use of graphite for voltammetric purposes (5,6,7). Mineral acids appeared to pervade the WIGE in a non-uniform manner with time (5). Further, neither wax nor polystyrene impregnation was useful in halting the ingression of mineral acids into the electrode (7). Surface polishing the electrode after each scan did provide a means of circumventing the problem in voltammetric applications (8), and was recommended in ASV applications (1); however, there is an attendant danger that the sample can become contaminated.

For example, we demonstrated in a recent intercalibration study of the analysis of lead at the sub-parts-per-billion level under clean-room conditions, that the simple act of polishing the electrode with filter paper could result in the spurious contamination of the 15-ml sample with as much as 0.6 ng of lead (9). Frequent re-polishing of the electrode, therefore, is not desireable in the laboratory and certainly not practical in field or remote ASV applications.

If, as was suggested by a recent worker, mineral acids pervade the WIGE along channels suggested to exist between the wax/graphite interface (10), maintenance of the electrode by polishing away the used surface immediately after each scan could be explained. And moreover, (if indeed this was the cause of failure) if the impregnator -- not necessarily wax -- could be chemically bonded to the graphite, then perhaps an acid-stable electrode could be developed.

The result of our efforts are graphite electrodes, impregnated with styrene monomer which is polymerized and cross-linked to the graphite with γ-radiation from a 5000 Ci, ^{60}Co source. These new electrodes have functioned flawlessly in neutral to weakly acidic solutions for well over six months. In acidic solutions, unfortunately, they exhibit little better stability than a freshly prepared WIGE. Their mode of failure in acidic solutions is different, however, and thus a new insight into the mechanism of failure is offered. Electrode failure appears to be the result of failure of the graphite itself.

Although we did not totally accomplish our initial objectives in this effort, the presented electrode should be of considerable use in areas of ASV and voltammetry not requiring the use of strongly acidic media. In view of its outstanding stability and longevity, it should find uses in on-line applications.

It is hoped that future workers will use this effort as a starting point and follow up with the use of surface analysis techniques such as electron spectroscopy and IR-reflectance to understand the surface chemistry which develops at the exposed graphite surface on potential cycling the electrode. A study of structural changes which occur at the graphite surface, especially in the presence of ferric chloride, should be of considerable interest. It seems likely, as of an outgrowth of these studies, graphite may serve as a substitute for platinum in some applications.

EXPERIMENTAL

Instrumentation, Reagents, and Materials. The digital instrumentation used was described previously (11,12,13). Many of the reagents, the cell employed, and much of the materials used were the same as those described previously (1). The white-label grade styrene monomer purchased from Eastman is recommended. A commercial grade styrene obtained from Dow Chemical, Pittsburg, California was tried briefly. The methylmethacrylate was obtained from Rohm and Haas.

Impregnation, Irradiation, and Construction of the Electrode. Spectrographic rods, 12 inches in length, and 1/8 inch in diameter, obtained from the Ultracarbon Corp., were broken into 2 inch lengths. A length of graphite was placed in a 6-mm o.d. quartz tube sealed at the bottom. Attached to the open end of the tube was a quartz-to-Pyrex graded seal of the same diameter as the quartz. The open end of the tube was torch sealed to the vacuum system and the system was evacuated to $> 10^{-7}$ atm. The quartz tube was heated to 800°C with a small tube-furnace and the pumping continued to maintain the vacuum. After 4 hours, the heating was discontinued and the quartz tube placed in a Dewar of liquid nitrogen. The tube was isolated from the diffusion pump by turning a stopcock.

Styrene monomer, contained in a long necked flask and pumped free of dissolved gases and water, was connected to the system containing the quartz tube. The monomer was slowly distilled, freeing it of the inhibitor, into the graphite containing tube where it was frozen. When sufficient styrene had distilled, the distillation was discontinued, the styrene was melted to cover the rod, refrozen with liquid nitrogen; then the system was let up to 1.0 atm with helium. The exposed portion of the quartz tube was sealed employing an oxyhydrogen torch and removed from the vacuum system. On warming the tube to room temperature, the helium pressure in the tube was estimated to be 1.2 atm. The graphite-styrene containing ampuole was then transferred to the 5000 Ci, ^{60}Co source for irradiation.

After a 100-hr exposure, the tube was removed, the quartz was thoroughly cracked by gently squeezing in a vise, and the article was then placed in a Teflon beaker containing 48% HF. After the HF treatment, the tube was washed in distilled water. The quartz was chipped away using a small, steel spatula by inserting the tool in the cracks in the quartz made larger by the HF treatment.

A 1-cm piece of the quartz-free, styrene impregnated graphite rod was threaded with a 540-die, and screwed into the electrode holder described previously (1), then potted by dipping the electrode into molten Sonneborn 180M wax (1). After the wax was solidified, the end of the rod was exposed by rubbing it against #600 emery cloth. The electrode was polished by rubbing against a Whatman #541 filter-paper. The irradiated electrode is very hard, compared with wax electrodes, so heavy pressure is required for this final polishing step. The electrode is then ready for mounting in the electrode assembly.

Recommended Electrochemical Procedure. The same ASV procedure described previously was used, but with the new fabrication technique, buffing the electrode after each sample is unnecessary (1). This is qualified below.

RESULTS AND DISCUSSION

Impregnation of graphite ASV electrodes with wax is now practically a tradition; however, in a study of the effect of chemical bonding of the impregnator to graphite by irradiation, waxes could not be used. Waxes are very rapidly degraded in an intense radiation field. Plastics were selected as impregnators because they, like waxes, are generally inert, and some are not appreciably destroyed by radiation. The low viscosity characteristics of plastic monomers make them ideally suited for impregnation purposes.

The first plastic we studied was methylmethacrylate. It was distilled under vacuum, inhibitor free, onto a graphite rod in a Pyrex tube, which had been vacuum outgassed at room temperature. The tube was sealed under a pressure of 10^{-7} atm. On irradiating it in the ^{60}Co source, the plastic became viscous within 30 min and fully polymerized within 3 hrs. Plastic specimens left in the source for 3 hrs, 30 min exhibited the onset of radiation damage. Thin sections cut from the tubes and viewed end-on were dark green in color.

This first experiment was not successful. The population of free radicals seemed to be the greatest in the vicinity of the graphite rod. Polymerization contraction of the plastic was severe in this region of the tube. Vacuoles were sucked into the thickening monomer leaving, at random, portions of the rod unimpregnated. Vacuole formation was not surprising. As a general rule, plastic monomers contract by about 1/3 their molar volume or roughly 20% on being polymerized.

In the next experiments with methylmethacrylate, the tube was charged to $\sim$ 1.2 atm with helium to control vacuole formation. These experiments were more successful. Useable electrodes were obtained but they did not perform well in acidic solutions. Again, the graphite was ejected from the working surface on failure.

Perhaps, we thought, a three hour irradiation was too short a time to effect the required degree of radiation induced grafting of plastic to graphite. Since radiation is useful in polymerizing plastics only if the rate of polymerization is greater than the rate of degradation of the polymer, methylmethacrylate obviously could not be employed. Radiation degradation causes the evolution of CO_2 from the decarboxylation of the methacrylic acid and, on long exposure, the plastic becomes a chemically ill-defined liquid. For these reasons, a more radiation resistant plastic was sought.

Styrene has outstanding radiation resistance (14). Radiation causes cross-linking in it; it becomes hard and brittle and becomes brown in color, but it retains its structural integrity. Only a small amount of hydrogen is evolved on radiating styrene -- even after it is extensively damaged. In short, it was ideal for our studies.

In the styrene experiments, quartz tube containers were employed. Pyrex suffers radiation damage and becomes brown in color. The color deepens with increasing radiation damage and is caused by the production of vacancy sites in the glass. Quartz suffers similar damage, but the color produced is a very pale lavender and becomes objectionable in intensity only after more than 100 hours of irradiation. Color judgment was essential in this work. Because the tubes were sealed, the only physical property we could use to evaluate the onset of radiation damage in the plastic was color.

In the first group of irradiations, the graphite rods were vacuum outgassed at room temperature. The polymerization of the commercial grade of styrene required over two weeks of irradiation. Although the behavior of the electrodes cut from these rods was very good, it was puzzling that such a long time was needed to effect polymerization -- unless the graphite was contaminated with free-radical scavengers or perhaps the commercial styrene was impure. Graphite absorbs a great deal of gas and water and it was thought that it might be the problem. Water is especially difficult to remove unless the graphite is heated (15).

In the next runs, the rods were heated at 800°C for times ranging from 4 to 12 hours under vacuum to promote outgassing. Little pressure change was noted after 4 hours. This is the minimum heating time suggested. An oily substance was collected during the heating in the liquid nitrogen trap stationed just before the diffusion pump. On exposure to air, this material evaporated on standing in the hood overnight. The nature of this substance is not known, but it came from the graphite. In the presence of the heat-treated rods, the Eastman styrene was polymerized in only 3 days irradiation time.

Polymerization was judged complete when, on inverting the sealed tube, no movement of the graphite rod occurred within 30 min. Irradiation was stopped when the plastic became yellow after 100 hours exposure.

Electrode fabrication was difficult. The styrene was not only chemically grafted to the graphite but also to the quartz tube. The tube and its contents were completely unitized. Cracking the quartz in a vise, treating with HF to open the cracks, and finally patiently picking away the quartz pieces was the best method we could devise to free the rod. Despite our best efforts, parts of the rod were lost in the tedious chipping operation. Total dissolution of the quartz with HF is probably a better approach, but this is a very slow process.

These cross-linked electrodes are very much harder than the wax electrodes and thus require much heavier pressure in the final polishing against filter-paper. The irradiated styrene electrodes are superior to any wax electrodes produced in this laboratory over the past two years. The electrodes have performed flawlessly in neutral to weakly acidic solutions for over 6 months. In acidic solutions, unfortunately, their stability is little better than that of a freshly impregnated wax electrode. Their failure mode is different from the wax electrodes, however. At no time have the graphite particles been sloughed off the working surface on failure. This important difference stems, of course, from the fact that the fact that the graphite particles are chemically attached to the styrene.

As with the WIGE, electrode failure is portended by a decrease in the hydrogen overvoltage characteristics. See photo-sequence in Figure 1. With continued use in acidic solutions, the cessation of the hydrogen wave moves to more positive values. Utility in the negative potential range is ultimately obliterated. Curiously, the electrode eventually comes to behave like a noble metal electrode. Hydrogen is evolved from its surface. Making the mercuric nitrate concentration much greater than the 2 ppm level suggested previously (1), is to no avail. Once the electrode has failed, it does not recover its initially high hydrogen over-voltage characteristics on being placed in a neutral solution.

Unlike the WIGE, however, the irradiated electrode can be restored to full service by repolishing. The affected surface is soft and is easily removed by rubbing it against filter-paper. Polishing is continued until it becomes difficult to mark the filter-paper. A refurbished electrode seems to have no chemical or physical memory of its ordeal.

It might be argued that electrode failure in acidic solutions was caused by the formation of micro-vacuoles in the styrene around the discrete macroparticles of graphite comprising the rod during irradiation. This might result from an insufficient gas pressure over the plastic during irradiation. However, experiments in which the quartz ampuole was charged with enough liquid argon before sealing, to give a pressure of 60 to 100 psig on being warmed to room temperature, produced electrodes of the identical character and quality as those produced under a slight positive pressure of helium.

The foregoing observations would seem to strongly implicate graphite, and graphite alone, in the electrode failure phenomenon, and thus preclude involvement of the impregnator or solution pervasion paths between the graphite and the impregnator.

To characterize the irradiated electrode, several voltammetric scans were made at various pH values in parallel with experiments conducted with freshly impregnated wax-graphite electrodes. The curves were virtually identical in shape. Only the traces for the irradiated electrode are shown in Fig. 2. The small wave observed for the scan in acetate buffer was also obtained with two different wax electrodes as were the other small anomalies shown in Figure 2. The chemicals employed were of reagent grade and no particular effort was made to purify them.

The longevity of the irradiated electrode coupled with its utility in both the positive and negative potential ranges should make it quite attractive for general voltammetric analysis and, in some instances, for on-line analysis.

The electrode exhibits none of the memory problems observed previously with old ceresin-wax electrodes (1). The ceresin electrodes generally had a strong chemical memory for several metals, mercury in particular, determinable with ASV. In contrast, the irradiated electrode exhibited none of these problems after almost 6 months of use. The following illustrates this. Curve A, Figure 3, is a mercury stripping peak obtained after a 5 min electrodeposition from an initially stirred, 0.1 M, neutral KCl solution. The solution was 2 ppm in mercuric ion. Immediately after the cessation of scan A, the potential was switched back to the starting potential and the scan rerun. See Figure 3, Curve B. The only evidence of mercury or calomel on the electrode is the very small bump barely discernable in Figure 3B and is the result of mercury accumulated during the scan. The current in the scan in Figure 3B is initially high and negative because the electrode was not permitted to come to equilibrium before the scan was restarted. The reduction wave for mercuric ion, inverted in the usual polarographic sense, is clearly shown.

The styrene-impregnated electrode displayed none of the equilibrium problems reported for glassy carbon (16). The peak areas given in Table I are for consecutive scans made on the same 0.1 M KCl solution for lead at the 1-ppb level after a 7-min deposition time and were obtained by computer analysis of the data (1). The peak areas taken for the first scan with a refurbished electrode may be somewhat lower <u>or</u> higher than subsequent scans on the same solution. This is probably the result of gas being trapped in the micro-crevices or perhaps the flaking off of micro-particles produced in the polishing step.

This electrode shares in common with all other solid electrodes the problem of absorption of surface-active compounds. This problem might well be the limiting factor in the on-line application of ASV to flowing systems. For example, only trace amounts of sodium stearate has been found to be sufficient to completely inhibit the reduction of lead (10). Absorption of some other compounds also reduces sensitivity. In this laboratory, the analysis of a coastal water sample taken 2 miles west of San Pedro, California, anomalous results were obtained. After a few hours of use the electrode lost its sensitivity to lead. Concurrent with this sensitivity loss, a broad peak not assignable to any metal determinable with ASV appeared at potentials more positive than the mercury stripping peak. The problem disappeared after the electrode was gently polished against filter-paper. The growth of this broad peak is shown in the photo-sequence in Figure 4A. The concurrent decrease in the lead peak height is shown in Figure 4B. The users of ASV should be aware of this difficulty and its symptoms.

We have recently found that ozone is very effective and remarkably active in destroying naturally occurring organic compounds -- even in neutral solutions. It acts much more rapidly than uv-light. A brief report on this topic will be made in the near future.

In preparing graphite electrodes for ASV, the larger pores are sealed with the impregnating agent. Smaller pores, inaccessible to the impregnator, still exist, however, and might affect the long term stability of the electrode. The ratio of the molar volumes of styrene to water is only $\sim 6 : 1$. One way to seal these small pores is to damage the graphite by bombarding it with fast neutrons, protons, or a beam of heavy-ions. The ^{60}Co, γ-photon damage to the graphite used in this work is negligible. Particle bombardment induces cross-linking between adjacent graphite sheets and the formation of carbon interstatials -- primarily C_2 complexes (15). Surprisingly, as the damage becomes ever more severe, the apparent pore diameter, as measured by the gas absorption method, decreases. A plot of pore population against pore diameter peaks sharply at 20 Å in very heavily damaged graphites. Although the cavities produced in the graphite are large, the openings to the cavities are quite small. On annealing at 2000°C, the graphite reverts to its pre-irradiation density.

We now have particle damaged graphite and will report on this material in the near future.

In conclusion, the styrene impregnated electrode has more of the problems reported for the previous ASV electrodes, with the exception of the acid pervasion and absorption problems. Since styrene, unlike waxes, is a discrete chemical entity, inter-laboratory findings and electrode behavior could be more closely correlated if the use of this new electrode becomes widespread.

A ^{60}Co source was used in this work because it was available for extended and uninterrupted periods of time. Any ionizing radiation source of sufficient energy to penetrate the quartz tube and its contents should serve as well. This includes x-ray sources used in crystallography. Very large β-γ sources are available to the public for a nominal charge at the Isotope Division of the Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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Table 1. Effect of Repolishing on Reproducibility

Run No.	PEAK AREA, Counts
1	2.991 E + 03
2	2.970 E + 03
3	2.933 E + 03
1	3.216 E + 03
2	3.248 E + 03
3	3.171 E + 03

FIGURE CAPTIONS

Fig. 1. The onset of electrode failure in 0.01 M HCl (pH 2).

Conditions: 30 min amalgam accumulation time prior to each scan.

ΔE = 10 mV/step.

Δt = 800 msec/step.

Fig. 2. Voltammetric behavior of the ^{60}Co irradiated, styrene impregnated, graphite electrode at various pH values.

- a) 0.05 M borax buffer, pH 9.2
- b) 0.10 M $NaClO_4$
- c) 0.10 M acetate buffer, pH 4.7
- d) 0.10 M $NaClO_4$ + 0.01 M HCl, pH 2.0

Arrow denotes the direction of the potential scan vs SCE.

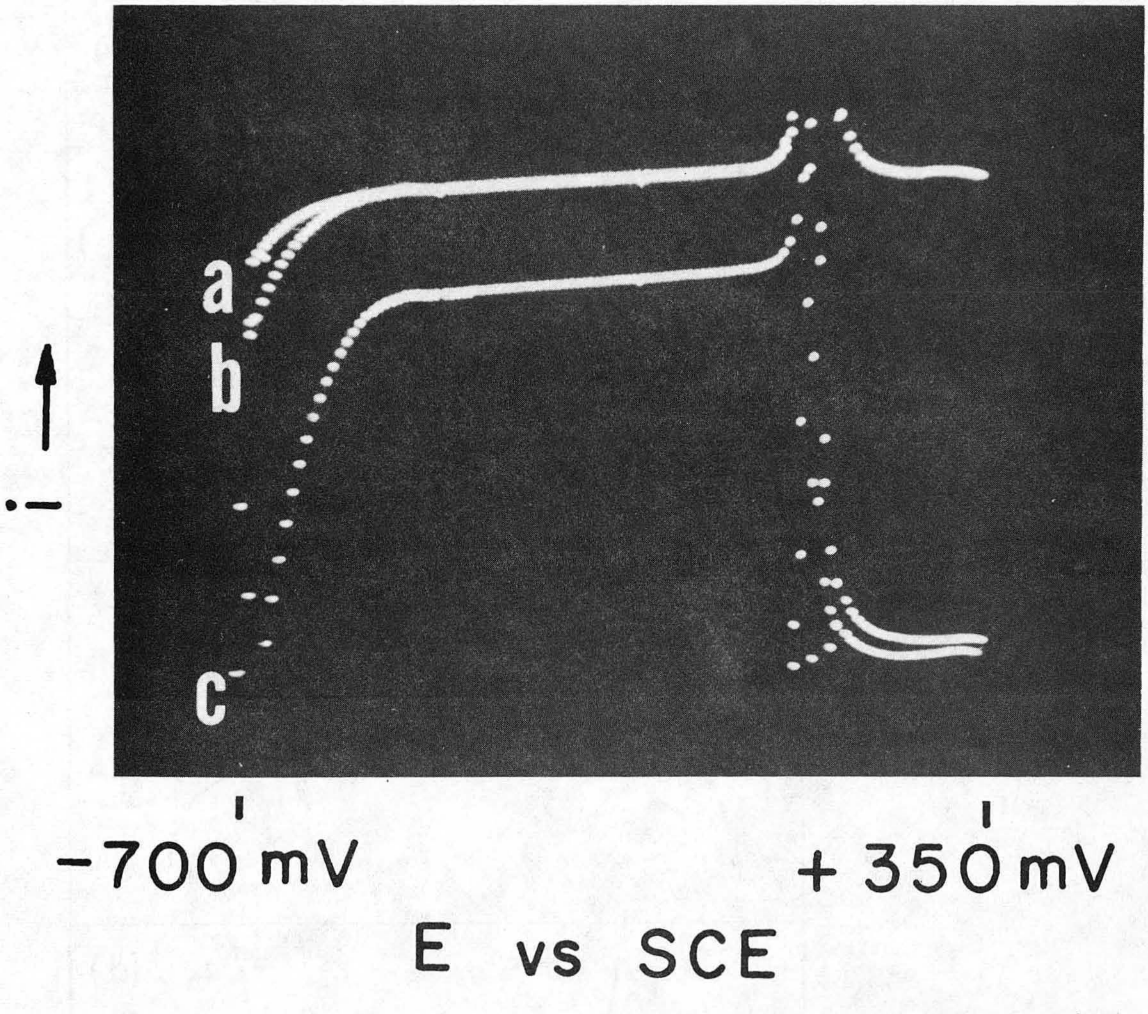
Fig. 3.A. Evidence against calomel formation at the irradiated electrode. (See text.)

B. 10-fold digital expansion of scan b of Figure 4A.

Fig. 4.A. Growth of an absorption peak. Each scan was made after a 30 min amalgam accumulation period.

B. Effect of the absorbed species on the lead peak height.

- a) lead peak in sample alone
- b) sample + 0.5 ppb lead spike
- c) sample + 1.0 ppb lead spike



XBB 7310-6105

Fig. 1

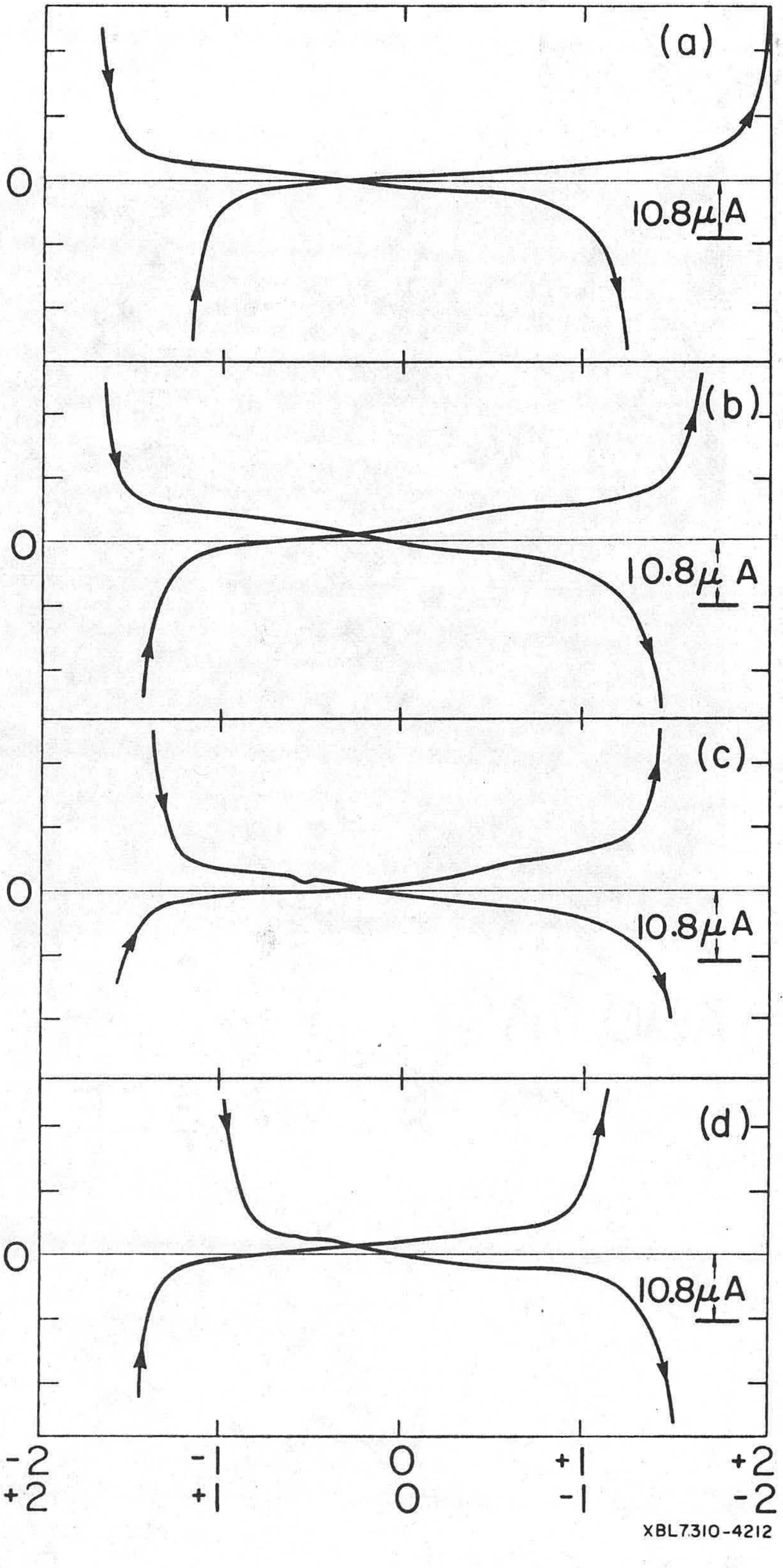
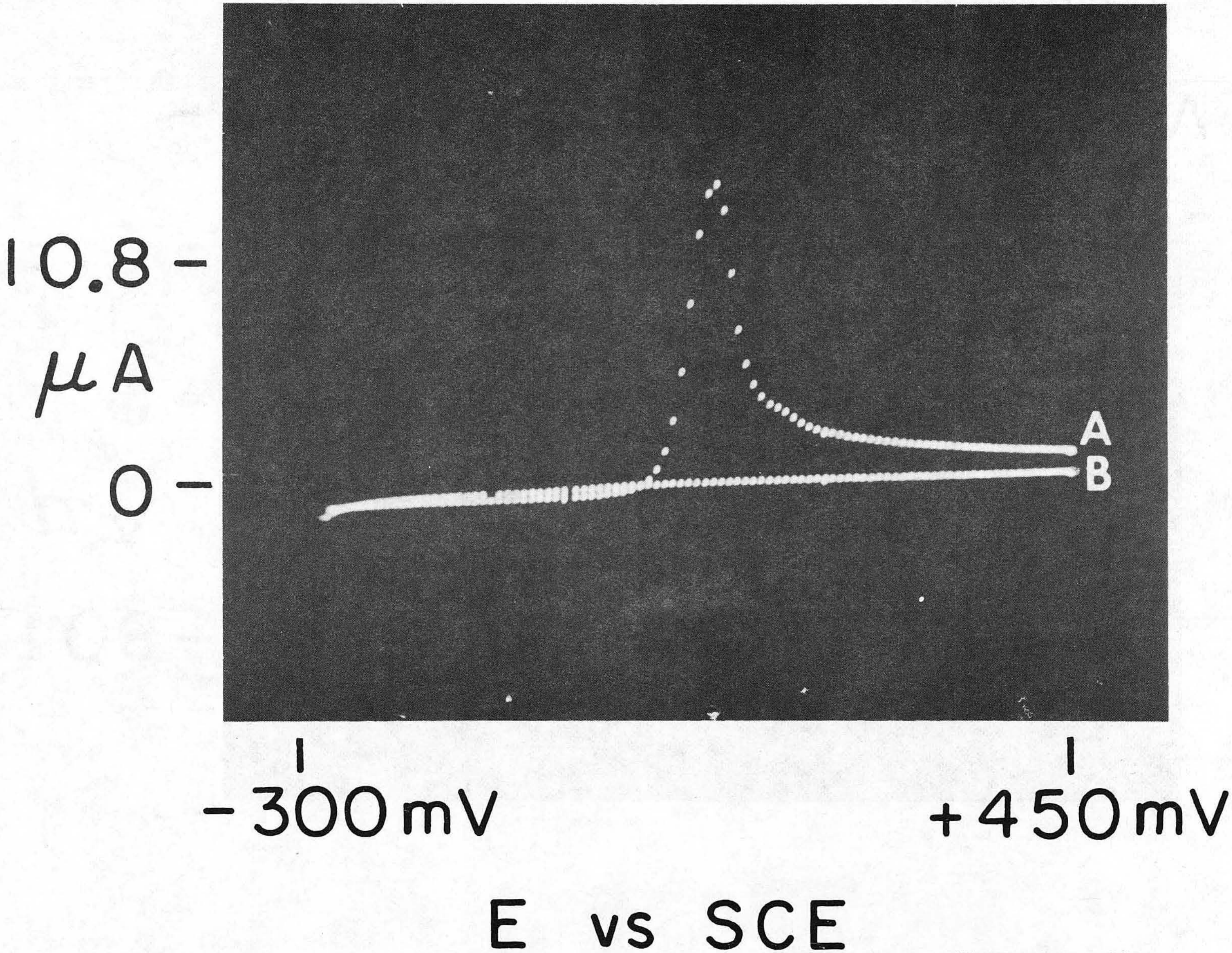
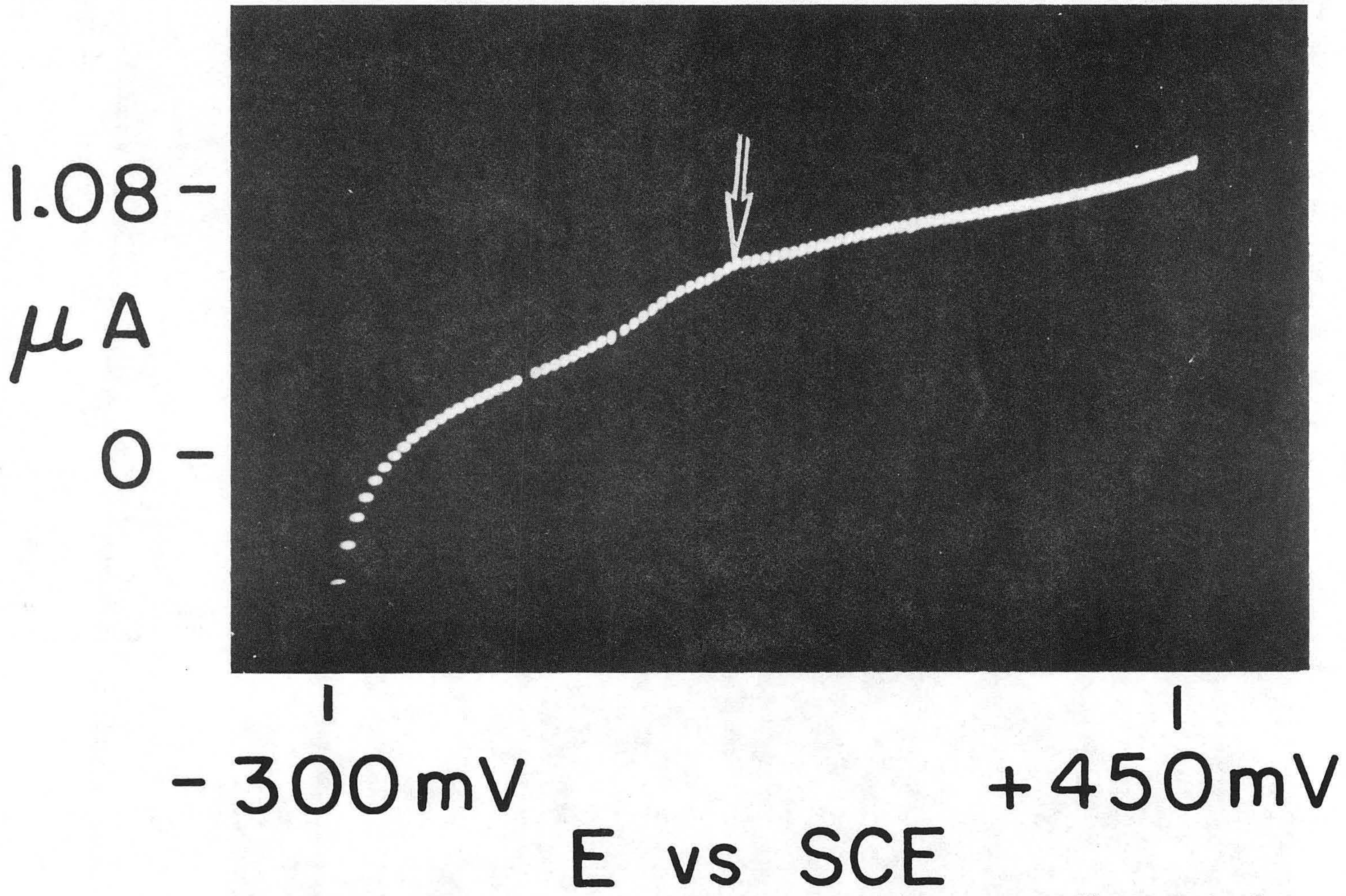


Fig. 2



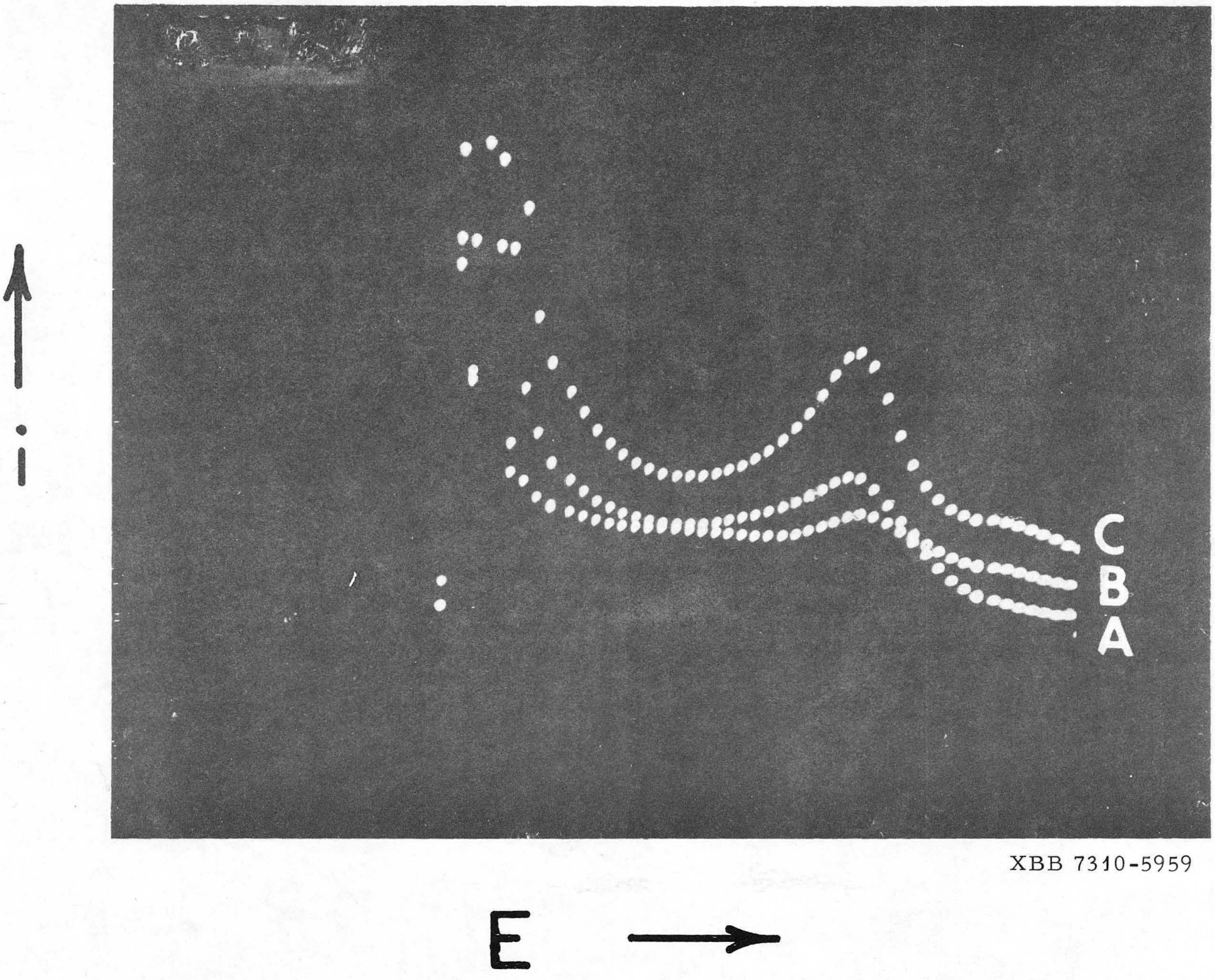
XBB 7310-5960

Fig. 3a



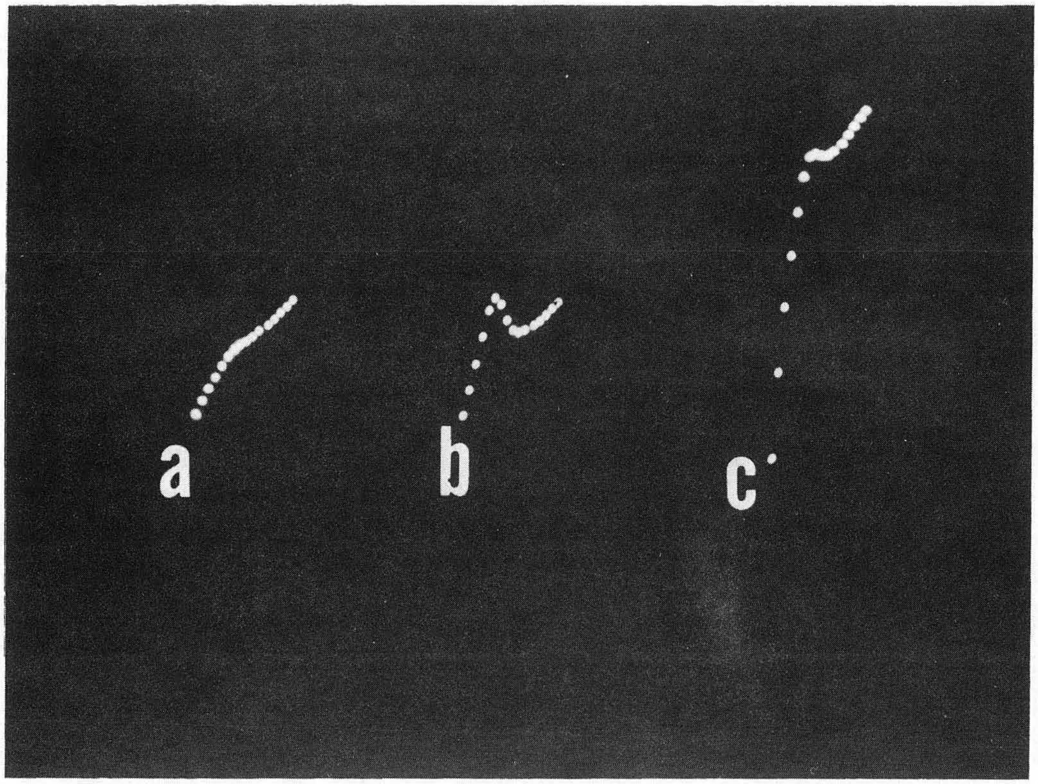
XBB 7310-5957

Fig. 3b



XBB 7310-5959

Fig. 4a



XBB 7310-6106

Fig. 4b