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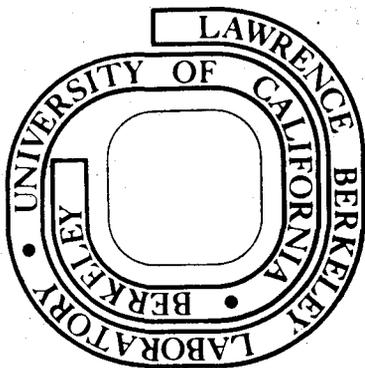
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CAUSE OF LOSS HYDROGEN-OVERVOLTAGE ON GRAPHITE ELECTRODES
USED FOR ANODIC STRIPPING VOLTAMMETRY (ASV)

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January 1975

BRIEF: Formation of oxides on the surface of graphite
ASV-electrodes, and not structure, is the cause of electrode
failure in acidic solutions. Mercuric-ion serves as an
oxidation catalyst.

ABSTRACT

Work with neutron-damaged graphites shows conclusively that structure is not the cause of ASV electrode failure. Mercuric and especially trace silver-ion strongly catalyze the oxidation of the graphite electrode surface with the result that graphite oxides are formed. Formation of carboxyl groups are the likely cause of loss of hydrogen overvoltage. Electrode behavior after treatment with vacuum ultraviolet light, diazomethane, lithium aluminum hydride, dimethylmercury, various amines, and propylene oxide is described.

INTRODUCTION

Electrode failure in acidic solutions has been a particular problem for us because our projects involve the estimation of the hydrogen-ion exchangeable lead content on clay particles and the ligand bound, hence, acid exchangeable lead in water samples after filtration through 0.45 μ Millipore filters or ultracentrifugation. Thus, we are forced to continually work with samples acidified to a pH > 1 but ≤ 3 . Since the lead content of the particle-free water samples is typically on the order of 0.04 to 0.08 ppb, amalgam accumulation times of 30 to 45 min and initial deposition potentials of -700 to -800 mV are not uncommon.

Taking into account the very small heights of the stripping peaks at such low levels of lead, any background measuring technique we might select will be very sensitive to small changes in the background current and in the hydrogen overvoltage (HOV) characteristics of the electrode.

Under these conditions of use, an electrode (a freshly prepared, wax-impregnated (1) or a new or refurbished styrene impregnated, ^{60}Co irradiated graphite electrode (2)) is usable only for a few hours or less depending upon the nature of the sample.

After an analysis, which consists of one scan on the sample alone followed by at least two additions of a standard lead solution, the wax electrode must be discarded or the styrene impregnated electrode must be buffed lest it lose its HOV during the next analysis. In either case, the new or refurbished electrode must be decontaminated by potential cycling it in an acidic solution before the next analysis, thus adding to the already lengthy analysis time and consequently foreshortening the life of the electrode.

These problems, in addition to those already set down in a previous paper (2), have led us to investigate the causes of HOV loss and subsequently the failure of electrodes used for anodic stripping voltammetry (ASV).

Briefly, acid failure of a wax impregnated electrode was characterized by a decrease in its HOV characteristics which accelerated with each successive scan and a concurrent decrease in sensitivity. Ultimately, as was evidenced with a photomicrograph, all the graphite at the electrode surface was ejected (1). Acid failure of the recently developed styrene impregnated, ^{60}Co irradiated graphite electrode, which for brevity will be designated as simply "electrode" or "graphite electrode" in the body of this report, was characterized by a continual loss of HOV with each successive scan (2). Long-term loss of graphite from the surface was not possible since it was chemically bonded to the styrene impregnator with radiation. This most recent work led us to believe that the common

knowledge -- pervasion of the acidic sample solution into the electrode along channels thought to exist between the graphite and impregnator (3) -- was incorrect. Graphite itself was somehow involved in the mechanism of failure.

ASV at impregnated, mercury plated, graphite electrodes is based upon the premises that the graphite substrate is inert and that the mercury is held in the form of droplets on the electrically conductive portion of the substrate by van der Waal's forces. The first premise is totally false; the second may be only partially true. These conclusions are drawn from experimental data presented in this report as well as from the existing literature. At this juncture, it is now possible, for the first time, to pinpoint the cause of electrode failure in acidic solutions.

At the conclusion of the previous report (2), we were convinced that structure was the overriding consideration in electrode stability. This is not so. Graphite extensively damaged with fast neutrons behaved no differently than did ordinary graphite. The cause of failure is the result of the formation of carboxyl groups on the surface of the electrode. These groups serve as a source of hydrogen-ion at the electrode surface.

Now that the existence of these groups and others are known it is possible to alter the character of the electrode surface with various reagents. These studies comprise the bulk of the report and lead to specific recommendations at the conclusion of this report.

EXPERIMENTAL

Instrumentation, Reagents, Materials. The electrochemical instrumentation and cell used in this effort were described previously (4,5,6). The hydrogen continuum vacuum ultraviolet source Model 630 was made by McPherson. It was attached to the sample vacuum chamber fabricated at this laboratory and was fitted with a LiF window.

Unless noted, all chemicals used were of reagent grade. The 0.1000 M HCl solution was prepared by dilution of a one-molar "Accurate" standard solution. Other standard acids were prepared by titration against sodium hydroxide which had been standardized against weighed samples of potassium acid phthalate to the phenolphthalein endpoint. All water used was distilled.

The following two reagents -- dimethylmercury and methylmercuric chloride -- are exceedingly poisonous and are thus mentioned separately from the above. At room temperature, the former is a very volatile liquid; the latter is a somewhat volatile solid. Neither reagent should be opened except in a fume-hood and precautions should be taken to avoid spilling them on the skin. Both are obtainable from Alpha-Ventron.

Diazomethane is an explosive, poisonous, yellow gas and thus should be synthesized only in a laboratory equipped with a good fume-hood and adequate shielding in the event of an explosion. The diazomethane was prepared from N-methyl-N-nitroso-p-toluenesulfonamide (Eastman #7066) (7), and was collected in dry diethyl ether at 0°C in an ice-bath. The ether solution was stored between uses in a freezer maintained at -28°C.

Lithium aluminum hydride was prepared as a slurry in diethyl ether (8). One should *always* test the ether used for the absence of water and peroxide (even if the ether container has been opened on the day of the experiment) by adding a *small* amount of reagent to a few milliliters of ether. Adding large amounts of reagent to a quantity of ether may result in a fire.

The propylene oxide was ordered from Eastman.

Graphite, grades U-2 and USP, were obtained from the Ultra Carbon Corporation in the form of 1/8-inch diameter rods. The reported ash content of the two grades was < 5 and < 0.1 ppm, respectively. Both had a density of 1.57 g/cm^3 . An elemental survey using x-ray fluorescence indicated an iron content of ~ 10 ppm for the U-2 specimen. No impurity elements were detected in the USP-grade material, and thus if they were present, they were present at less than the 2 ppm detection limit of the technique.

Structurally, highly disordered graphite was prepared by exposing 2-inch lengths of U-2 grade material, previously vacuum outgassed at 10^{-7} atm for 12 hours at 800°C , in sealed quartz tubes to a beam of 15 MeV neutrons produced in a particle accelerator by the fusion reaction between 300 to 500 keV deuterium nuclei and tritium immobilized on a zirconium tritide target wheel. On the average, each 15 MeV neutron causes 21,000 carbon-carbon knock-on reactions in the graphite rods. The rods were exposed uniformly to the beam. In the most heavily damaged specimen, all the carbon-carbon bonds had been broken at least one time. Damage in subsequent specimens ranged downward from unity to only one carbon-carbon bond in 10^4 being broken.

Activity induced with fast neutrons is usually short-lived.

After a 50 hour "cooling off" period, the rods were essentially non-active.

After neutron irradiation, the rods were transferred to previously heated and vacuum outgassed quartz tubes, fitted with demountable stopcocks, in an inert atmosphere box. The tubes were connected, one at a time, to the vacuum-rack through the stopcocks, pumped down to 10^{-7} atmospheres at room temperature, chilled with liquid nitrogen, then previously outgassed styrene monomer was vacuum distilled onto the graphite. The quartz tubes containing the graphite and styrene were let up to 1-atm of helium at liquid nitrogen temperature, then sealed off with an oxyhydrogen torch. The samples were irradiated at least 100 hrs in the 5000 Ci, ^{60}Co source described previously (2).

Other styrene impregnated, ^{60}Co irradiated graphite electrodes used in this study were prepared as described previously (2).

Linde 0.3 μ alumina powder was used to polish the styrene impregnated electrodes. Initially, it was used sprinkled over filter paper but later it was found it could be used on hard-surfaced writing paper with better surface reproducibility and with negligible increase in contamination of the electrode surface.

Procedure. The *in situ* co-deposition of sample and mercury described previously (1) was used in this effort.

RESULTS AND DISCUSSION

The electroanalytical chemist has always considered graphite to have exceptionally good HOV characteristics in acidic solutions, exceeded only by those of mercury. When the HOV was lost (2), and in the case of the wax-impregnated electrodes, the surface graphite particles were ejected from the wax matrix (1), the electrode was said to have "failed". In our experience, this mode of failure was always exhibited regardless of form or manufacturer of the graphite used or the impregnator employed. Perhaps then, the electrode had indeed failed, or to take an unconventional position, perhaps graphite was simply exhibiting its true behavior.

Electrode failure is necessarily a subjective assessment. The magnitude of the background current can vary owing to variations in the density of the graphite used. Also, since the electrode used were hand-polished, variations in the macro- and microsurface areas are presented, hence variations in the observed background currents, were also possible. New graphite electrodes generally present an exceptionally flat background, therefore it is easy in a series of scans to detect the point in time at which HOV loss becomes a problem. This is illustrated in Figure 1A. Note the obliteration of the cadmium peak in Figure 1B as the failure of the electrode progresses. Also note the good reproducibility of the lead peaks despite the loss of HOV.

The results of our previous study strongly indicated that the cause of electrode failure lay with graphite itself. Considering the general properties of graphite, there appeared to be only two likely reasons for electrode failure -- lamellar compound formation (9,10) and/or formation of graphite oxides (9,10). The latter was initially totally discounted since the conditions required to synthesize graphite oxide border on the

Dantesque: it seemed unlikely that ASV would ever be attempted in boiling concentrated nitric acid or permanganate solutions, for example. The former seemed much more likely. Swelling of the graphite on failure and the acid penetration of the surface particles could be explained based upon lamellar compound formation.

Structurally, graphite, regardless of origin, form or product designation, at the unit cell level, is composed of a chemically bound, fused, extended hexagonal ring system which forms what crystallographers term the "a-plane" (10,11). The carbon-carbon bond distance is 1.415 Å. Weak van der Waal attractions between the parallel carbon sheets hold the crystallite together in such a way that the carbon atoms in alternate sheets are superimposable. The plane in which the carbon sheets terminate is called the "c-plane". The intersheet distance is 3.35 Å.

The weak interplanar attraction between the carbon sheets leads to unusual behavior. A host of common elements and simple compounds are able to tunnel into graphite via the c-plane to form interstitial or lamellar compounds (9). Lamellar compound formation can sometimes grossly alter the electrical properties of graphite and always its physical volume (for example, the formation of the IBr compound is accompanied by a volume increase of 300%). If it were the problem, the c-plane could be sealed or at least made very short by bombarding the graphite electrode with particles (11).

Fast neutrons were selected for this experiment because they are quite penetrating owing to their zero charge and thus cause homogeneous damage throughout the target specimen.

To test the HOV behavior of the most severely neutron damaged

graphite electrode with time, it was immersed in a stirred, thoroughly deoxygenated, 0.1 M HCl solution, a potential of -800 mV was imposed on the cell, and the electrode current-behavior was recorded or observed over a 16-hour period. Very little current charge was noted; most came in the first half hour. This was cause for optimism. The solution was then made 2 ppm in mercuric-ion and an ASV scan was made between -800 mV and +500 mV after a 5 minute amalgam accumulation period. On the second scan, HOV loss was noted and the loss increased with each successive scan. The electrode had failed. The same behavioral pattern was noted during subsequent experiments for conventional graphite. Thus, it was concluded that structural disorder had little or no effect on the loss of HOV. Similar results were later obtained in 0.1 M HClO₄ or HNO₃. Lamellar compound formation, at least with the acids tested or their anions, did not appear to be the cause of HOV loss.

In the following studies, 0.1 M acids were also used. The potential range scanned was from -1000 to +500 mV. The hydrogen discharge wave is irreversible and thus it was thought that earlier detection of HOV loss could be achieved at -1000 mV instead of at -800 mV normally used in our analytical work. Such proved to be the case.

The act of potential scanning alone did not seem to be responsible for the loss of HOV. Electrodes potential cycled for long periods of time in the absence of mercury did not lose their HOV. Only after mercuric-ion was added did HOV loss commence. This is in consonance with the above single potential study. If a new or refurbished electrode were taken, the onset of HOV loss at -1000 mV was delayed perhaps 30 to 45 min.

The effect of silver ion on the behavior of graphite electrodes was also briefly studied because silver interferes with the stripping behavior of copper (3) and its stripping peak potential location is virtually identical with that of mercury in all electrolytes tested. Also, silver has poor HOV characteristics (12). The silver study seemed particularly important since many workers use Ag/AgCl reference electrodes bridged to their test solutions in such a way that the sample can become contaminated with silver ion. Two scans are shown in Figure 2. A dramatic loss of HOV is noted in the second scan. Even though silver was very thoroughly stripped in several successive silver-free solutions at +800 mV, the HOV of the electrode was virtually the same in subsequent scans as that shown in the second scan.

Silver, on a concentration-time basis, appears to be between 2 and 3 orders of magnitude as effective as mercury in causing deterioration of the HOV.

Once initiated, the extent of loss of HOV was solely a function of immersion time of the electrode in the acid solution. The process by which the HOV was lost was self-sustaining after the potential scan in which the loss began. This indicated to us a chemical involvement in the loss of HOV, especially in view of the fact that both test ions are weak oxidizers and interestingly, both function as addition catalysts in organic reactions involving carbon-carbon double bonds (13). Further, strong concentrated oxidizing agents such as cerate or permanganate after only a brief contact with the graphite electrode, brought about a marked loss in HOV, even in the absence of the above ions.

Even trace impurities in graphite can greatly increase its susceptibility to thermal oxidation (10), however, experiments in which HOV loss

measurements were compared in time for the two grades of graphite described above, no differences could be found.

In light of the above results, the considerable bulk of data on graphite oxides (9,10) was viewed with keen interest for it appeared that the oxidation of the electrode surface was the cause of HOV loss.

The graphite rods employed here are an agglomeration of discrete particles. Boehm views the surface of a crystalline solid as an extreme case of a lattice defect (14), capable of unusual reactivity. Hennig estimated that the edge carbon atoms of a graphite crystal had a reactivity some 20 times that of carbon within the basal planes of the crystal (15). Further, he demonstrated that all the oxygen uptake of a crystal after being cleaved several times occurred at the crystal edge or along the c-plane. Oxygen reacts with initially clean graphite at temperatures above -42°C to form oxygen containing functional groups (16).

Virtually every imaginable oxygen-containing organic functional group has been proposed to exist on the edges of graphite crystals (10). The most frequently suggested groups are the carboxyl, phenols, and quinones. Also suggested are the presence of ethers, peroxides, ester groups in the form of normal and fluorescean-like lactones, carboxylic acid anhydrides, and cyclic peroxides. Formation of graphite oxides is accompanied by the swelling of the crystallite c-planes and thus this promotes the disintegration of the crystallite. This could explain why the surface graphite particles are ejected from wax electrodes on failure (1). Swelling is particularly accentuated in the presence of several organic solvents (9).

Of all the foregoing groups, the ones capable of serving as hydrogen-ion sources at the electrode surface seem most likely to be the cause of HOV loss. These are, of course, the carboxyl and phenolic groups. Of the two, carboxyl groups seemed to be the most important because the pK_A values for aromatic acids are generally between 4 and 6, whereas, the pK_A values for phenols are usually around 9. The fact that new or refurbished electrodes possess initially high HOV characteristics which decay with use indicates that carboxyls are not initially present but rather are formed during the course of ASV scans in acidic solutions containing an appropriate catalyst or strong oxidizing agent.

The role silver plays in the oxidation of graphite is not clear. The addition of mercuric ions across carbon-carbon double bonds is well known, however, and the addition of mercuric salts to =CHR or =CR'R" compounds in water are occasionally and sometimes predominantly accompanied by oxidation and the formation of mercurous salt (17).

Phenols form one of the most easily mercurated classes of compounds (17), so it is likely that the graphite electrode surface becomes mercurated. If, however, polyhydroxylic phenols with ortho- or para-hydroxy groups are present on the graphite surface, they are not mercurated, they are oxidized with mercuric salts. This may well be the beginning of the formation of carboxyl groups on the electrode surface.

Although the foregoing suggested a need for intensive support in the area of surface analysis, such was not available at the time of this work. We were able to obtain a few analyses, however, and these were instrumental in determining the direction of our studies with chemical reagents.

Photoelectron spectroscopy (PES) was the first surface technique employed. The failed ASV electrode was made the anode in an evacuated electron spectrometer which was used to energy resolve the surface electrons ejected when the graphite surface was irradiated with the 1.487 keV (8.34 Å) aluminum x-ray line. For the first analysis, the geometric considerations were far from optimal. The spectrometer was designed to accommodate samples having a surface area of 1.1 cm². Since the electrode submitted had only 0.08 cm² surface area, it was necessary to irradiate it for more than 12 hours to accumulate a spectrum in the spectrometer data system. The C:O ratio was estimated to be ~ 10:1. Only C:O ratios can be reported. It was not possible to energy resolve among, and thus identify, the various oxygen containing functional groups.

For the next PES analysis, a much larger, 1 cm² electrode was fabricated from ¼-inch U-2 grade graphite rod. Before use, this electrode gave a C:O ratio of 1000:4.

The first electrode submitted gave some evidence of being radiation damaged because the potting wax and Lucite electrode holder were discolored. The HOV characteristics of the electrode were truly amazing. No hydrogen evolution was noted even at potentials in excess of -1.5 V in a solution of 0.1 M HCl containing mercuric ions at the 2 ppm level. The background current was virtually zero over the whole 2V negative potential range over which our instrument is capable of operating. Unfortunately, the electrode had virtually no sensitivity to metals determinable with ASV; the stripping peak for mercury at the 2 ppm was scarcely detectable. With continued use over a period of several days, the ASV sensitivity improved as the HOV deteriorated.

It appeared that a photochemical reaction had occurred but there is a dearth of information on organic photochemical reactions in the soft x-ray region, so it was decided to determine whether similar electrode behavior would be manifested after a 45 minute to 1 hour irradiation in the 1050 to 2000 Å vacuum ultraviolet region for which there is much more data. It was. See the photosequence in Figure 3. This behavior is reminiscent of that reported for glassy-carbon (18).

Surprisingly, vacuum ultraviolet light penetrates quite deeply into graphite. Figure 4 is a plot of the molar absorptivity coefficient versus wave length. Data for this plot were taken from reference (19).

It is quite difficult to make definitive assessments as to what occurs when the oxidized graphite surface is irradiated with ultraviolet light because oxidized graphite is a macro-molecule. Aliphatic acids exhibit primary photochemical reactions which are different from those found for the aromatic compounds (20). Substituent groups affect the photochemical path by which decomposition takes place. Further, secondary reactions (photochemical or free-radical) are also possible. Photochemical schemes for even simple molecules in the vapor phase can be extremely complex; it is unlikely, therefore, that a unique photochemical pathway can ever be presented for graphite. However, since virtually all chemical bonds are between 2 and 5 eV in energy and the energy of the vacuum ultraviolet light at 2000 Å is > 6 eV, considerable bond breakage must occur. Virtually all compounds absorb light in the 1050 to 2000 Å region.

Considering the difficulty with which an electrode is re-oxidized after ultraviolet treatment, even in the presence of oxidents, it is likely that highly inert alkane or perhaps phenyl groups are formed by migration

of the hydrogen ions to the carbon residue after removal of the carboxyl groups as CO_2 .

To facilitate matters, a need was developing for a process whereby new or refurbished electrodes could be oxidized rapidly and reproducibly, but in a controlled manner. Persulfate was reported to cause rapid electrode deterioration (21), and its reduction product, sulfate, was thought to be innocuous. Such was the case. At a level of 70 ppm $\text{S}_2\text{O}_8^{=}$ in 0.1 M HCl , HClO_4 , or HNO_3 solutions made 2 ppm in mercuric ions, the electrode, on potential cycling, could be made to fail within less than 15 minutes. The electrochemical behavior of the persulfate treated electrodes was indistinguishable from those that had been allowed to fail naturally. The artificially failed electrodes responded to the ultraviolet treatment in the same way as the naturally failed electrodes. If, however, an electrode was left in the oxidizing solution for several hours, the oxidized layer extended too deeply into the electrode to be effectively treated with the ultraviolet source.

Several successful efforts have been made in recent years to identify functional groups on the surface of graphite with attenuated total reflectance infrared spectroscopy (10). Two 1 cm^2 electrodes of the kind used in the PES experiments above were submitted to the infrared consultant. Before potential cycling, only bands between 2800 and 3000 cm^{-1} were detected and were indicative of alkanes. These bands were probably due to the presence of the ^{60}Co radiation damaged styrene. After potential cycling the electrode to the point of failure, in 0.1 M acid containing Hg^{2+} , an absorption band near 1700 cm^{-1} was detected indicating the presence of carboxyl groups.

The reaction of the various surface functional groups with group-specific reagents has been studied (22), but of course the electrochemical behavior of oxidized graphite after derivative formation has not. Since we were particularly interested in masking carboxyl groups, the most acidic function, we were practically limited to two reagents: lithium aluminum hydride and diazomethane. The first reagent is capable of reducing aliphatic and aromatic carboxylic acids to their corresponding alcohols (8). Diazomethane, in the absence of an acid catalyst converts only the carboxylic acids to their methyl esters (7).

The oxidized electrodes were reduced by immersing their surfaces in a stirred ether slurry of LiAlH_4 for up to 5 minutes. Figure 5 shows the scan of the oxidized electrode and again after the hydride treatment. After 15 to 20 minutes of use (after 3 to 4, 5 min ASV scans) in 0.1 M acid, 2 ppm in Hg^{2+} , the electrode behavior was virtually the same as it was before the hydride treatment. Evidently, the alcohols produced on reduction are highly susceptible to reoxidation. In view of the unusually high susceptibility of H and OH functions to oxidation when alpha to a benzene ring (23), the graphite alcohols must be related to benzyl alcohol. It should be noted too that benzaldehyde formed by mild oxidation of benzyl alcohol is also highly susceptible to further oxidation to benzoic acid (23).

Methylation of graphite carboxylic acids with diazomethane was not expected to impart a lasting increase in the HOV characteristics of oxidized graphite electrodes, because it had been reported that the methyl esters were readily hydrolyzed with dilute acid (22). Nevertheless, it was of interest to observe the electrode behavior after methylation.

Mindful that some mercuric species can be adsorbed onto the electrode surface, especially from HCl solutions (24), the electrode was oxidized by potential cycling it in 0.1 M HClO_4 made 2 ppm in Hg^{2+} and 70 ppm in $\text{S}_2\text{O}_8^{=}$. After oxidation, it was washed thoroughly with distilled water, dipped in 95% ethanol, next in 1:1 ethanol-ether, then finally ether alone before being dipped into the ethereal diazomethane solution. Methylation proceeded with the evolution of micro-fine bubbles of nitrogen at the graphite surface. Although the cessation of bubbling signaled the end of the reaction (generally 5 to 10 sec at 0°C), the electrode was left in the ethereal solution for 60 seconds.

The behavior of the electrode before and after CH_2N_2 treatment is shown in Figure 6A. The background current after methylation was very small over the potential range scanned. Data shown in Figure 6B are for scans taken two hours after the treatment; 16 hours later after the electrode had been soaked in an air saturated, mercuric containing 0.1 M HClO_4 solution over night, then 36 hours later. After being soaked an additional 6 days in the perchlorate-mercuric solution, the HOV was still judged sufficiently low to permit the detection of cadmium at or above the 1-ppb level. Note that the metals' sensitivity increases as the HOV decreases just as was described above for the uv irradiated electrodes. Also note the anomalous stripping peak for mercury in the initial scans.

The preceding results were entirely unexpected, but they could be duplicated.

On placing the above electrode in 0.1 M HCl made 2 ppm in Hg^{2+} , anomalous behavior was initially noted. See Figure 7. After making four ASV scans, the mercury stripping peak became very sharp, almost thorn-like,

as if it were the result of an adsorption/desorption process; and too, the HOV increased over that found in HClO_4 solutions.

Next, a new graphite electrode was oxidized but in the absence of mercury. After it was methylated, it was potential cycled in a 0.1 M HCl , 2 ppm Hg^{2+} solution. The HOV was lost in less than 10 min -- after the second 5 min ASV scan. This was the kind of behavior expected.

From the foregoing, some involvement of mercury in the improvement of the HOV was suspected. Diazomethane reacts with mercuric salts to form dimethylmercury (17). After oxidizing a new electrode as described above, about 5 μl of dimethylmercury was spitzered onto the graphite surface. A hard, almost glassine-like, surface coating was formed on evaporation of the excess liquid. Although the electrode was quite conductive, it had little sensitivity for the ASV determinable metals; but again, the HOV characteristics in 0.1 M acid were very good. See Figure 8. The dimethylmercury treated surface was so hard that buffing with emery cloth was required to remove it.

Dimethylmercury is reported to be easily cleaved with mineral acids to form the corresponding methyl-mercuric salt (17), however, such did not seem to be the case for the dimethylmercury coated graphite surface -- even after it was soaked in 0.1 M acid for days. If, however, the electrode were strongly cathodized in 0.1 M acid using a constant current source, the coating was gradually removed and concurrently the ASV sensitivity increased as the HOV deteriorated.

Treatment of the surface of a new electrode after oxidation with an alcoholic solution saturated with methylmercuric chloride did nothing to restore the HOV.

If, as was suggested by the foregoing data, that dimethylmercury was strongly adsorbed at the electrode surface, then perhaps other compounds would be also. If an amine could be found which strongly adhered to the surface, neutralization of the acidic surface groups would result and perhaps the ASV sensitivity would not be seriously degraded.

Of the amines investigated: pyridine, methylamine, ethylenediamine, o-phenylenediamine in ethanol, stearyl amine and aniline, only aniline gave the desired results. These amines were applied directly to the electrode surface. However, the improvement lasted for only a few potential cycles (~ 10 to 15 minutes) before it was desorbed into the solution or perhaps reacted with mercuric ions to give a derivative devoid of basic character (17). See Figure 9.

Brief but unsuccessful attempts were made to incorporate aniline in the impregnator and thus assure a continuing supply of amine at the electrode surface. For this, wax was used. The solubility of aniline in wax is so low that no beneficial effect could be sustained. Stearyl amine was soluble in molten wax but it served as a conduit for acid into the wax; the wax became swollen and ultimately crumbled to bits. Concurrent with the swelling, anomalous stripping behavior was noted. This approach did not appear to be fruitful and was discontinued.

One attempt was made to graft amine groups directly to the graphite with ^{60}Co irradiation. Graphite was vacuum outgassed as described above; liquid ammonia was condensed onto the graphite rod; the ampoule was sealed, then irradiated for 24 hours in the 5000 Ci ^{60}Co source at room temperature. After irradiation, the rod was vacuum impregnated with wax. The failure mode of this electrode was indistinguishable from that observed for

untreated wax/graphite electrodes.

Work with propylene oxide indicates that loss of HOV may stem in part from invasion of mineral acids into the interstices of the oxidized graphite crystallites. Previous workers have noted that it is extremely difficult to wash oxidized graphites completely free of mineral acid (10). Further, it has been demonstrated that the presence of salts aid in the uptake of acids by oxidized carbons (25). Alkene oxides are good scavengers for HCl. Epichlorohydrins are formed and the hydrochloric acid is consumed in the process. Electrodes oxidized in 0.1 M HCl-2 ppm Hg²⁺ solutions containing persulfate were treated by immersion in liquid propylene oxide for up to 5 minutes. The HOV was markedly improved but the improvement did not last. After immersion in the 0.1 M HCl-2 ppm Hg²⁺ solution for 20 to 30 minutes, the HOV deteriorated to its initial condition. The electrode response before and after treatment is similar to that shown in Figure 9 for aniline.

Some evidence was found which indicates graphite is not as impervious to mercury as it is generally thought to be. Mercury pervasion may be involved in the long term failure of graphite electrodes. In one of the first papers on pyrolytic graphite (26), the authors warned that it was of the utmost importance the c-plane of the crystal not be exposed to the sample solution, for in that plane, the graphite is permeable to aqueous solutions, molten salts, and even to metallic mercury. They attempted to fabricate a pyrolytic graphite electrode by sealing the graphite in a glass tube with epoxy-resin using mercury as the contact. The mercury found its way to the c-edge of the crystal. The electrode split apart. In our work, we have noted that the plated mercury can be

completely removed by wiping the electrode surface with tissue paper soon after the mercury has been plated. If, however, the electrode is plated, then set aside for several weeks, a small mercury stripping signal is observed until a millimeter or more of the electrode surface is buffed away.

The above presentation is by no means exhaustive but it does afford some insight into the causes of ASV electrode failure in acidic solutions. The finding that structure has no affect on the longevity of the electrode was surprising and required a complete reversal in the suppositions held at the outset of this work. It is sincerely hoped that other workers having free access to surface analysis instrumentation will study the graphite electrode more thoroughly than was possible for this report. Of particular interest would be spectroscopic surface measurements in the far infrared region to characterize the organomercuric compounds which are undoubtedly formed with oxidized graphite.

The foregoing work shows rather conclusively that it is generally disadvantageous to do ASV in acidic solutions and particularly in acidic solutions containing oxidents. Based upon several years of experience with ASV, if at all possible, it is better to work at pH values ≥ 3 and preferably on the pH interval between 4 and 7. Work in the low pH range will necessitate the frequent repolishing of the electrode, thus necessitating the frequent decontamination of the cell and electrode if lead is the metal of interest and especially if it is present at ≤ 0.1 ppb level. Workers who study chemical speciation will always be forced to work in acidic media, however, and will have to continually contend with the problems described in the introduction in addition to the problems of adsorption

described in a previous paper (2). Others who, as we are, are interested only in total metals bound to organic particulate matter or in filtered water samples may be benefitted by the new ozone oxidation methodology presently under development at this laboratory, because the natural pH of the sample is essentially unchanged after the oxidation. Also, naturally occurring organic compounds which cause electrode adsorption problems are destroyed.

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FIGURE CAPTIONS

- Figure 1A. Electrode behavior at the onset of failure. Note the progressive loss of hydrogen-overvoltage with each successive scan. Conditions: 0.1 M HCl, 2 ppm Hg²⁺. $\Delta E = 8$ mV/step, $\Delta t = 800$ msec/step. Amalgam accumulation time = 5 min.
- Figure 1B. 100-fold current expansion of the cadmium and lead stripping potential range of Figure 1A. Peak at left is cadmium. Peak at right is lead. Note the obliteration of the cadmium peak as the hydrogen-overvoltage deteriorates.
- Figure 2. Effect of trace silver on the hydrogen-overvoltage behavior of bare graphite. Lower trace: No silver added. Upper trace: Solution made 70 ppm in silver. Solution: 0.1 M HClO₄, $\Delta E = 8$ mV/step, $\Delta t = 800$ msec/step.
- Figure 3. Electrode behavior after irradiation in the vacuum ultraviolet region. Traces taken from top to bottom: 5, 15, 25, 35, 45 and 55 minutes after irradiation. Conditions: 0.1 M HCl, 2 ppm Hg²⁺. $\Delta E = 8$ mV/step, $\Delta t = 800$ msec/step, amalgam accumulation = 5 min for each trace.
- Figure 4. Plot of the molar absorptivity coefficient of graphite vs. wavelength. Assumption: density of graphite = 2.25 g/cm³.
- Figure 5. Electrode behavior before and after treatment with LiAlH₄. Upper trace: before treatment. Lower Trace: after treatment. Conditions: see those for Figure 3.

Figure 6A. Electrode behavior before and after treatment with CH_2N_2 .
Upper trace: before treatment. Lower trace: immediately after
treatment. Conditions: 0.1 M HClO_4 , 2 ppm Hg^{2+} , $\Delta E = 8 \text{ mV/step}$,
 $\Delta t = 800 \text{ msec/step}$, amalgam accumulation time = 5 min for each
trace.

Figure 6B. Electrode behavior after soaking in a 0.1 M HClO_4 , 2 ppm
solution for varying lengths of time. Traces taken from top to
bottom: 2 hrs, 16 hrs, 36 hrs, and 6 days after CH_2N_2 treatment.
Condition: see those for Figure 6A.

Figure 7. Behavior of six-day-old, CH_2N_2 treated electrode on being
placed in 0.1 M HCl solution. Conditions: see those for Figure 3.

Figure 8. Electrode behavior before and after treatment with $(\text{CH}_3)_2\text{Hg}$.
Upper trace: before treatment. Lower trace: after treatment.
Conditions: see those for Figure 3.

Figure 9. Electrode behavior before and after treatment with aniline.
Upper trace: after treatment. Lower trace: before treatment.
Conditions: see those for Figure 3.

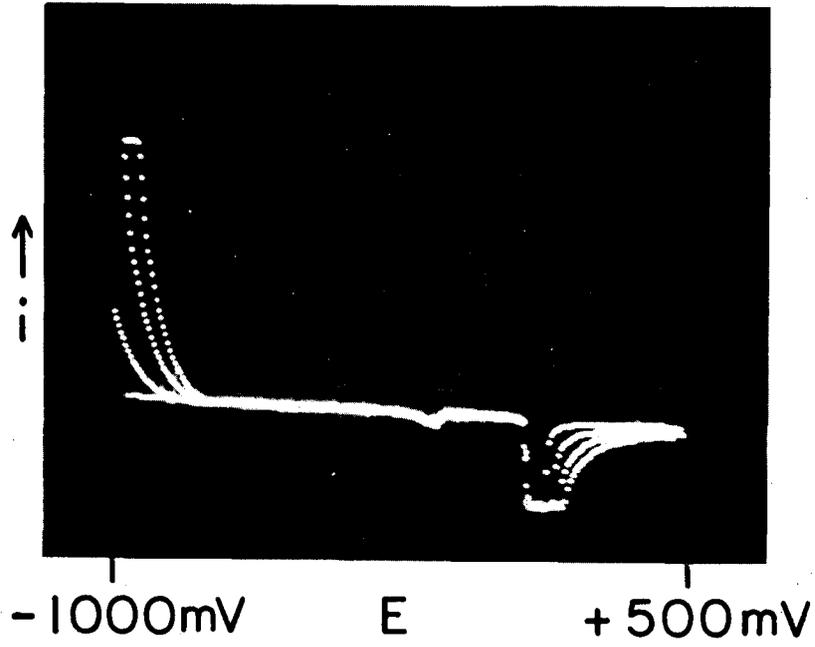
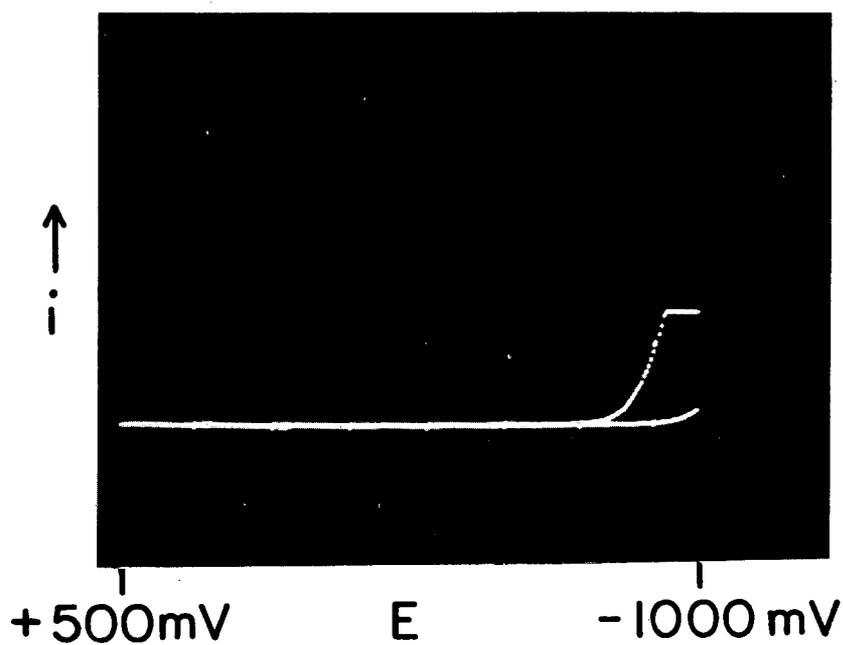


Fig. 1b

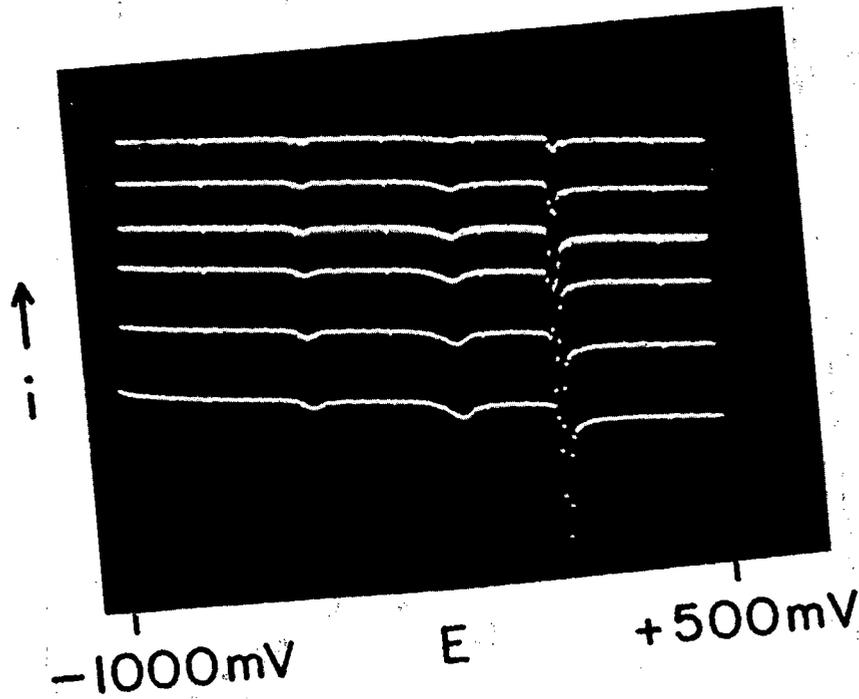
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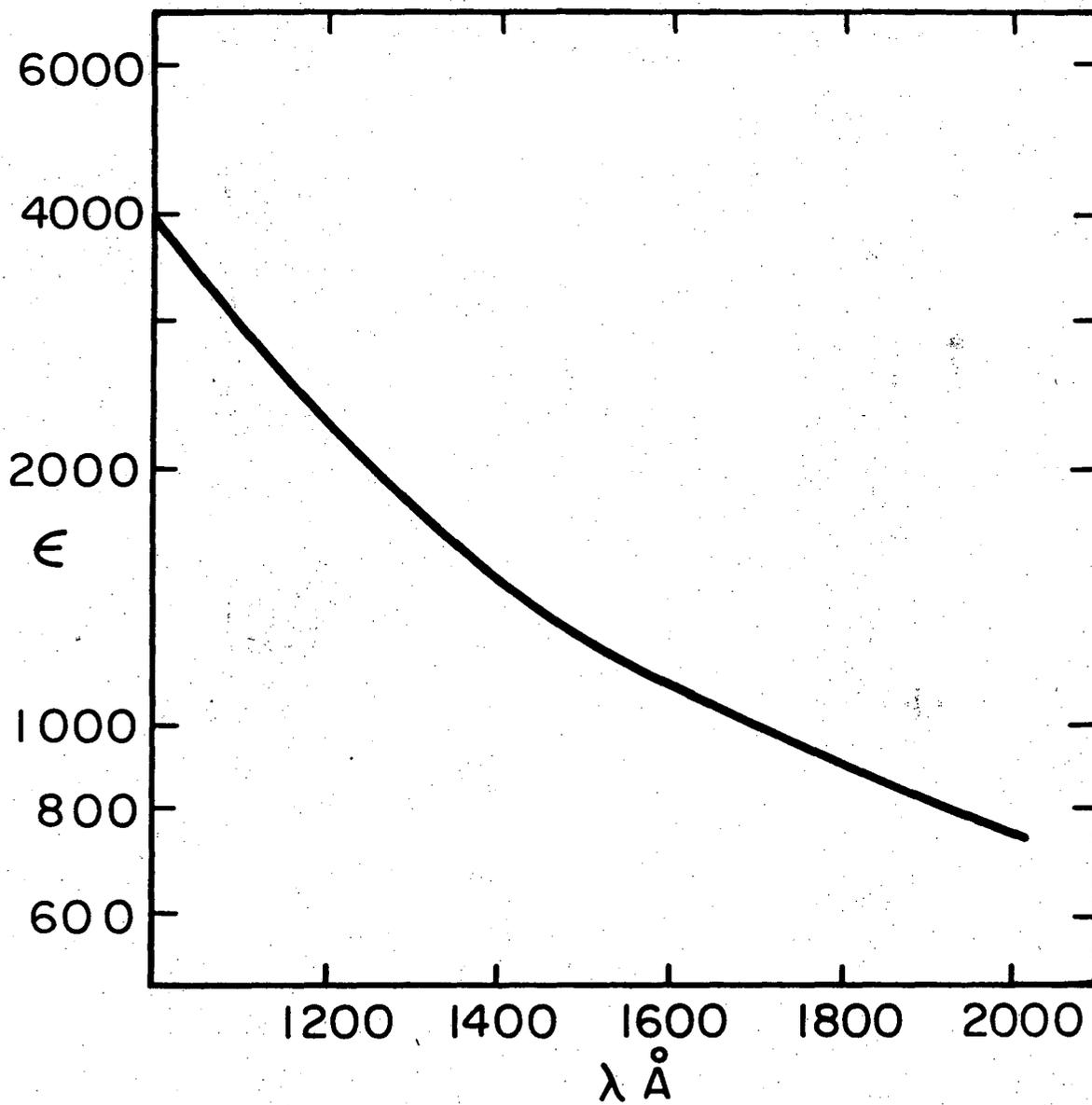
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Fig. 2



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Fig. 3

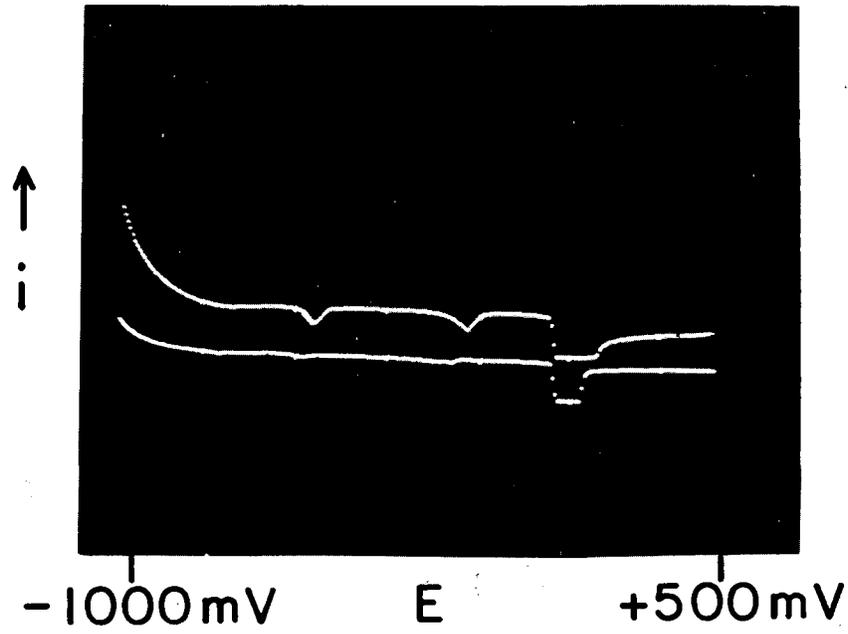


XBL751-2056

Fig. 4

0 0 0 0 4 2 0 2 7 1 0

-31-



XBB 751-447

Fig. 5

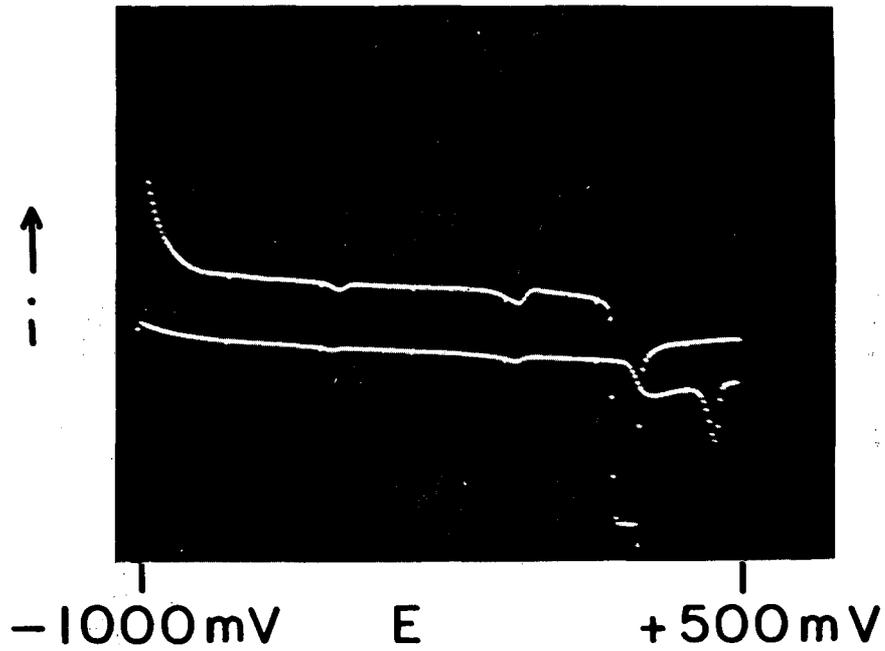


Fig. 6a

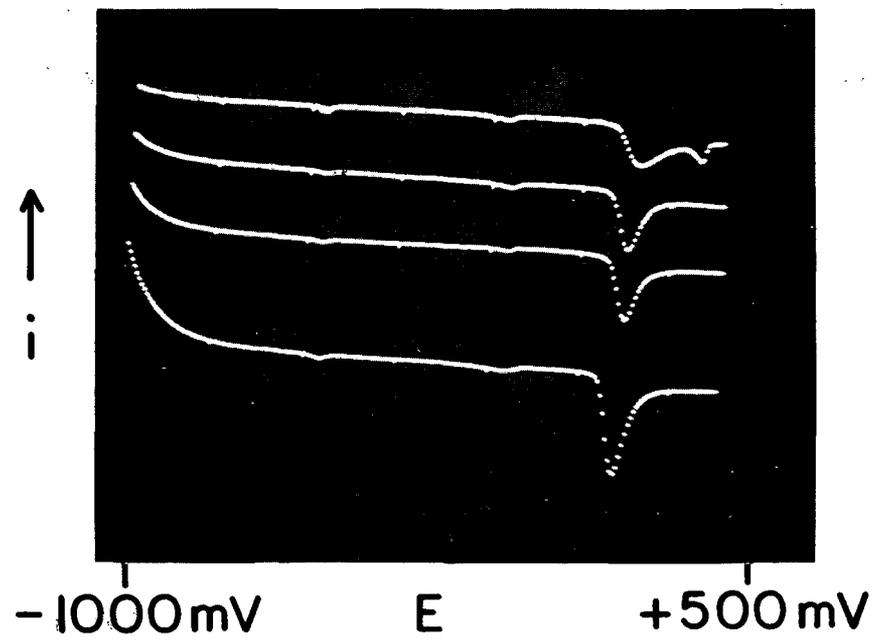
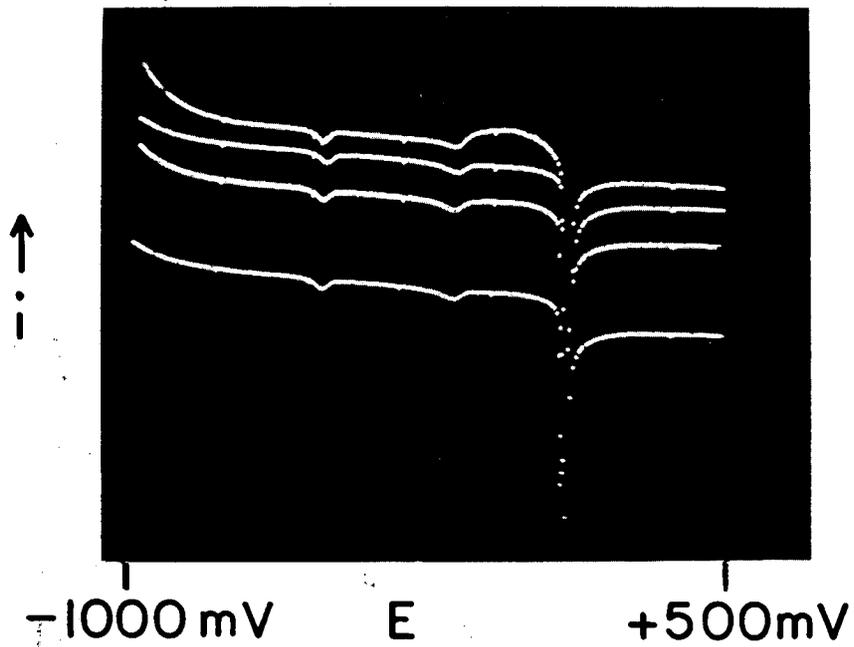
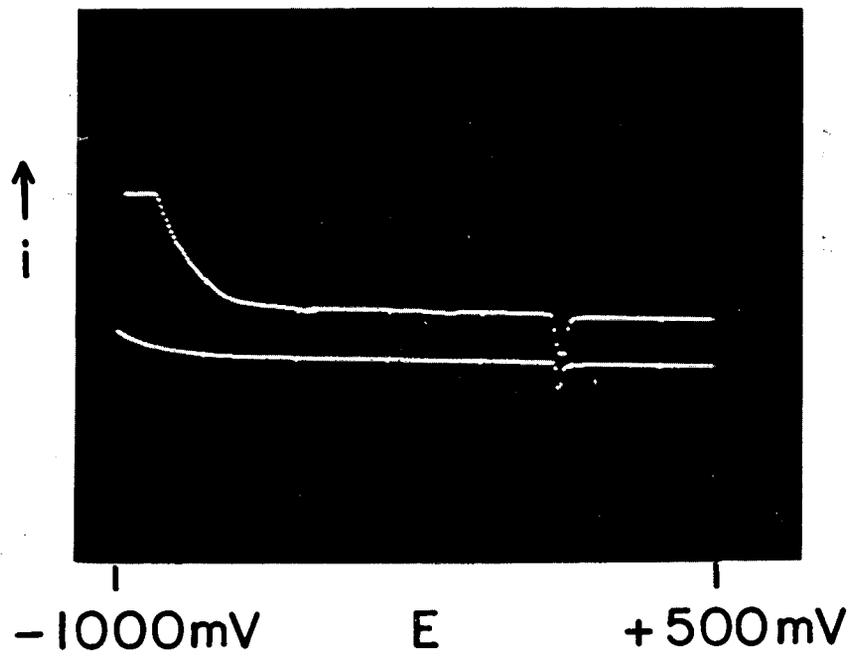


Fig. 6b



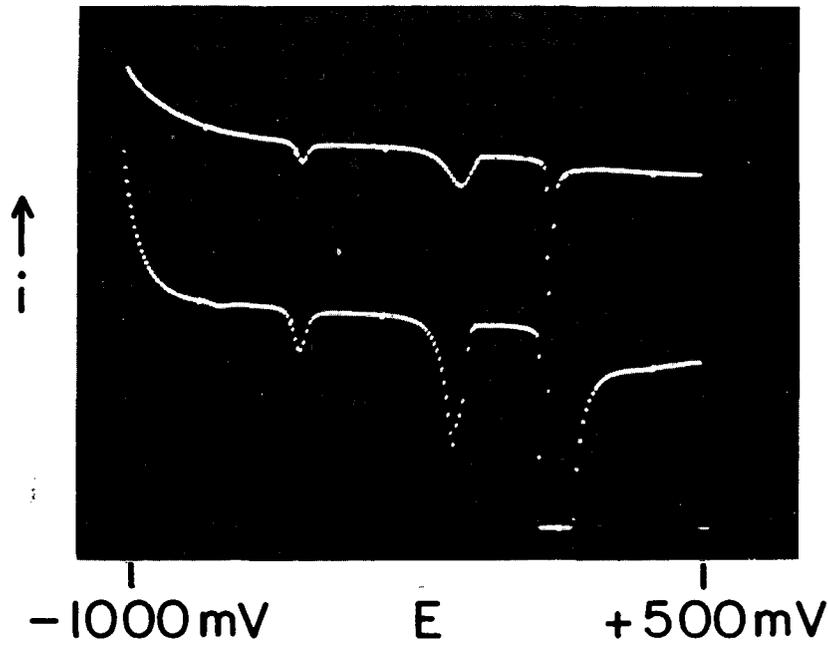
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Fig. 7



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Fig. 8



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Fig. 9

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