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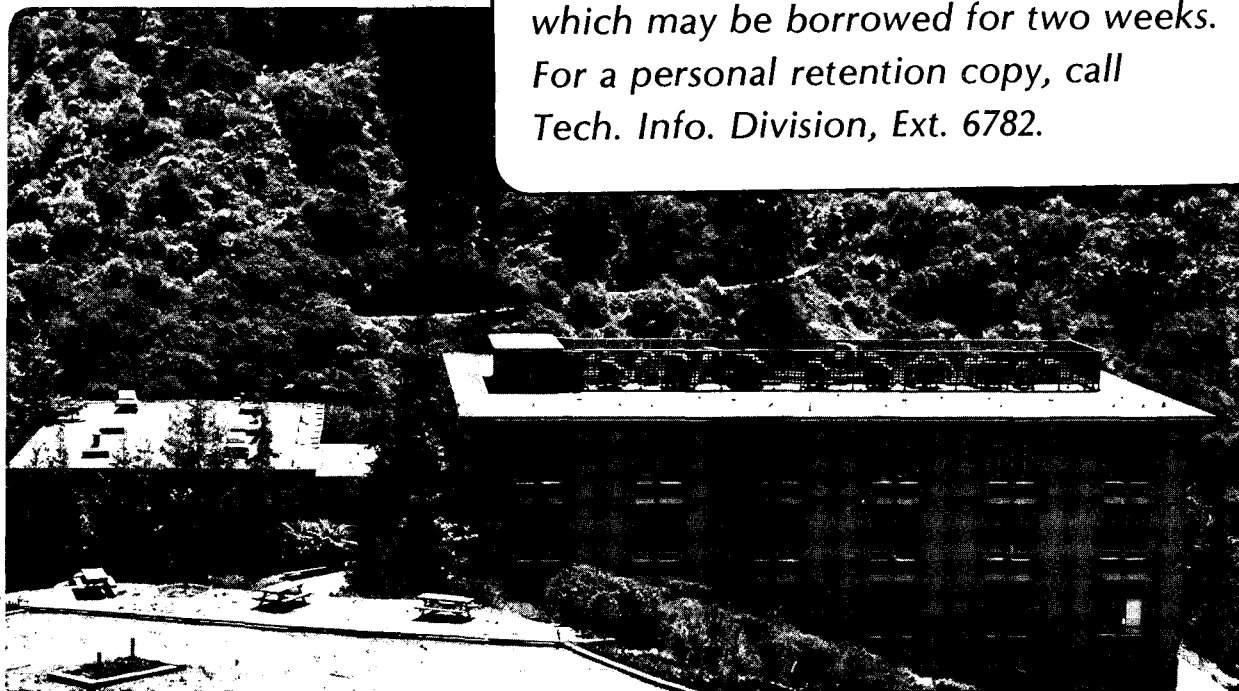
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P.N. Ross and H. Sokol

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I. ACETYLENE BLACK AND THE EFFECT OF COBALT CATALYZATION

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ABSTRACT

^{14}C labeling of acetylene black was used together with mass spectroscopic analysis of the gas evolved to determine the current efficiencies for oxygen evolution, carbon dissolution, and carbon gasification (to carbon monoxide). The current efficiencies were found to depend dramatically on potential, temperature and the presence of an evolution catalyst like Co_3O_4 . On uncatalyzed black, three regimes could be distinguished: I. - at potentials below 500 mV vs. Hg/HgO and temperatures below 50°C, carbon dissolution is the primary anodic process; II. - at 500-600 mV and 50°C or lower, carbon dissolution and oxygen evolution occur at equivalent rates; III. - above ca. 600 mV or above ca. 60°C oxygen evolution and gasification of the carbon to carbon monoxide are the dominant processes. Catalyzation with Co_3O_4 collapsed these regimes so that all three anodic processes are concurrent throughout the potential region of interest, and the overall rate of corrosion increased significantly. In addition, Co_3O_4 catalyzation caused the production of organic products (ca. 5% current efficiency) in a potential region where none is produced from acetylene black alone. The mechanism of action of Co_3O_4 on the acetylene black corrosion is not yet understood, but there is evidence that direct physical contact between the Co_3O_4 particles and carbon particles is not required to produce accelerated corrosion of the carbon.

INTRODUCTION

With the advent of dimensionally stable, metal oxide anodes for chlor-alkali cells, technological interest in the oxidation of carbon anodes (usually graphite) in caustic solution has waned. In the years when diaphragm cells with graphite anodes were the leading technology, there was a substantial body of literature produced concerning the corrosion of graphite accompanying chlorine evolution. This literature is reviewed in several places (1-4), the most recent being in the compilation of the electrochemistry of carbon by Randin (4). The literature on the corrosion of graphite anodes during oxygen evolution in chloride-free electrolyte is in comparison almost non-existent. Most of the work on graphite anodes for oxygen evolution has been in acid solution, and it is known that the corrosion processes for graphite change as a function of pH (5). Current technological interest in the use of graphite and/or carbon blacks in alkaline battery positives has revived interest in the corrosion processes of these materials in strongly alkaline chloride-free solutions. Graphite powder is used as a current collector and dispersion substrate for nickel electrodes (6), and various types of carbon blacks are of interest for use as catalyst substrates for bifunctional air electrodes (7). Acetylene black is widely used in primary batteries of both the alkaline and non-aqueous type, and is being examined as a catalyst substrate for air electrodes for a number of fuel cell and metal-air battery technologies. In none of these battery applications is the acetylene black intended to act as an active material for oxygen evolution, and in the primary batteries, oxygen evolution does not occur in normal use, so it is not surprising that very little research has been published on the corrosion of acetylene black in oxygen evolving electrodes. Yet the use of

acetylene black in a bifunctional air electrode is technologically attractive because of its very low cost relative to metal oxide materials, and the principle question concerning its use is the corrosion resistance.

It is a difficult matter to measure corrosion rates accurately in gas evolving electrodes. Standard electrochemical methods are not useful by themselves because the gas evolution is generally the predominant anodic process so the observed current is not representative of the corrosion processes. Electrochemical methods must be combined with other analytical tools which discriminate between the different anodic processes, at the least between oxygen evolution and all other processes, and in the ultimate each anodic process is measured independently. Historically, analysis of the anode gas composition for oxygen, carbon monoxide and carbon dioxide has been used together with standard electrochemical methods to obtain relative current yields for O_2 , CO and CO_2 . Examples of this approach are seen in the reports by Krishtalik and co-workers (8) on the corrosion of graphite anodes of the type used in chlor-alkali cells. The gas analysis method does not account for corrosion processes that produce solution phase species (soluble or insoluble), surface oxides, or intercalation compounds like "graphite oxide" (9). Other Russian work (10) on graphite anodes reported that the formation of water soluble products can be 30-40% of the current yield, and the total current yield of all reaction products (solution plus gas phase) was less than 100%, leading to the conclusion that some current (10-20%) passed in the formation of "graphite oxide." It is clear that if one is to determine the rate of corrosion processes by the rate of appearance of products the inventory of products must be complete. The prior work on graphite anodes suggests quantitative

solution analysis is imperative, including organic compounds that are not well-established. The approach we have taken in this work was to use ^{14}C acetylene black and quantitative radio-chemical techniques for analyzing the products in solution and a quadrupole mass spectrometer for analyzing products in the gas evolved. The ^{14}C technique has several advantages over conventional methods for the quantitative analysis of carbon in water: a) the lower limit of detection is ppb vs. ppm; b) the quantitative determination is absolute and relatively free of matrix or solvent effects; c) different types of carbon in the electrode can be discriminated against. The ability to label certain physical parts of a carbon electrode with ^{14}C was particularly useful in examining corrosion in the presence of evolution catalysts. The disadvantage of the ^{14}C labeling technique is that acetylene black is probably the only industrial carbon black that is made from a relatively pure feedstock (acetylene) that can be labeled, so the technique can not be extended to furnace blacks of technological interest. In order to make quantitative discriminations of inorganic (carbonate) from organic carbon in solution, we did develop a chromatographic procedure based on complete oxidation of organic to CO_2 . Our experience with this procedure indicated that with further development it is capable of making the quantitative determinations of the rate of production of carbonate ion and organics at the levels likely to be observed with industrial carbon blacks in future studies.

EXPERIMENTAL

^{14}C Radiotracer.— ^{14}C labeled acetylene black was supplied by Nuclear Research Chemicals with a specific radioactivity of 1.625 mCi/mg. The ^{14}C acetylene black was produced using the same commercial procedure for

Shawinigan Acetylene Black (Shawinigan Products Department, Gulf Oil Chemicals Company) but reduced to laboratory scale. Shawinigan Acetylene Black is made by continuous thermal decomposition of acetylene at 800°C in a retort. The retort is first heated to the decomposition temperature by burning the acetylene on introduction, then burning is discontinued and the acetylene continues to flow into the retort in the absence of air. Thermal decomposition occurs resulting in a flocculent black with a bulk density of ca. 0.019 g/cm³. ¹⁴C labeled acetylene black was produced by Nuclear Research Chemicals using the same procedure with ¹⁴C labeled acetylene gas. Since the quantity of ¹⁴C labeled acetylene black was quite small (2.59 mg), owing to its high cost and the fact that only a small amount is needed for radiotracer work, all the physical properties of the ¹⁴C acetylene black could not be compared to those of commercial Shawinigan black. Examination of the particle size, aggregate morphology, and microstructure by transmission electron microscopy (TEM) was the principal tool used to determine that the ¹⁴C labeled acetylene black was similar to Shawinigan acetylene black in its physical and chemical properties. The ¹⁴C black was blended with Shawinigan black using a two-stage procedure; i.) 0.59 mg ¹⁴C was liquid blended with 100 mg of Shawinigan using isopropanol and ultrasonic agitation; ii.) 10 mg of that blend was liquid blended with 100 mg of Shawinigan. The specific activity of the resulting blend was determined using a oxidizer method (Packard Model 306 Oxidizer) to be 1.4 ± .05 dpm/mg.

Catalyzation Procedure.—Both the ¹⁴C blend and the unlabeled Shawinigan black were catalyzed with cobalt oxide using an impregnation procedure. The cobalt content was prepared at a 20 w/o level assuming Co₃O₄ as the

final form. $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was dissolved in 1:1 methanol: water; the carbon black was dispersed into the solution with ultrasonic agitation; ammonium hydroxide was added to pH 11 to precipitate cobalt hydroxide into the carbon black. The impregnated carbon black was filtered from solution and air dried at 120°C for 24 hrs. Conversion of the cobalt to Co_3O_4 was confirmed by x-ray diffraction analysis, which showed only lines for this phase.

Cell and Electrode Design.—The electrochemical cell used in these studies is depicted in Fig. 1. It was essentially a standard glass H- cell modified for both gas sampling and solution sampling. The solution in the working electrode compartment was isolated from exchange with solution in the counter electrode compartment by cation- exchange membrane (Dupont Nafion 117) and from the solution in the reference by a thick ultrafine porous ceramic. Solution samples were drawn from the working electrode compartment through the rubber septum using a 100 μl syringe. The reference electrode was Hg/HgO and the solution was w/o KOH- 2 w/o LiOH. Some experiments were done without the lithium addition, and the presence of lithium did have an effect on the result so all the results reported here were obtained with the mixed electrolyte. The working electrode consisted of a carbon black- PTFE paste impregnated into a gold- plated tantalum mesh acting as the current collector. The paste contained 5 w/o PTFE solids (Dupont TFE-30B dispersion) mixed into the carbon black with 1:1 isopropanol:water, and was applied to the mesh by spatula followed by air curing at 320°C for ten minutes. The typical loading of a working electrode was 40 mg (ca. $10 \text{ mg}/\text{cm}^2$) of carbon black or catalyzed carbon black. The working electrodes were vacuum filled with electrolyte at room temperature

prior to use in the cell. The internal electrolyte volume in the working electrode was determined gravimetrically after emersion of the electrode and wiping the surface free of bulk electrolyte. The internal electrolyte volume was typically 2-3 $\mu\text{l}/\text{mg}$ initially, with an increase by as much as 100-200% on use in the cell (after extensive oxidation).

Solution Analysis.—100 μl aliquots were withdrawn from the working electrode compartment at periodic intervals (usually 30 min.) and put immediately into 5 ml of scintillation solution (New England Nuclear Atomlight NEF -968) and counted in a commercial scintillation counter (Tracor). Stirring of the solution in the compartment was accomplished by bubbling with argon; results from stirred and unstirred solution did not agree when the corrosion rate was above a certain level, so all the results reported here are for stirred solutions. Because of the requirement for gas flow, gas sampling and solution sampling were not simultaneous. Conventional (i.e. non-radiochemical) qualitative analysis of the solution was conducted to distinguish inorganic (carbonate) from organic corrosion products. The complete analysis procedure, shown in Fig. 2, was initially carried out in an apparatus built in our laboratory. However, it was found that the solutions did not contain any purgeable organic carbon, so the volatilization step was eliminated. Subsequently the organic/inorganic determinations were made in a single apparatus, a Dohrmann DC-80 Total Carbon Analyzer. Under certain conditions, the KOH solution became colored, and these solutions were analyzed colorimetrically with a UV/VIS spectrophotometer. Attempts were made to isolate and to analyze the colored product by GC-MS and proton NMR, but, as described later in the text, these were largely unsuccessful.

Gas Analysis.—Pre-purified argon was used as the diluent gas. The gas evolving from the electrode was accumulated in the space over the KOH solution, then sampled into a 10 ml gas sampling bulb using vacuum withdrawal. The sampling bulb was then isolated and transferred to a quadrupole mass spectrometer (Balzers QMG112) for analysis. Quantitative determinations of the composition of the gas (absolute partial pressures) were made using the calibration procedures described in the Appendix. The only gasses observed evolving from the solution were oxygen and carbon monoxide. All the carbon dioxide created anodically was apparently trapped in the electrolyte. The time required to accumulate an analyzable quantity of gas varied with potential, temperature, and whether the cobalt catalyst was present, e.g. from as much as 15 hrs. to as low as 30 mins. During this time, the electrode potential was controlled and the total charge passed was measured using a digital coulometer (PAR 179). The rate of gas evolution was calculated as an average quantity from the total moles of gas evolved and the collection time.

RESULTS

Microstructure Analysis by TEM.—Classical texts (11,12) on carbon chemistry refer to acetylene as having a "chainlike" structure and as more "crystalline" than most carbon blacks. At relatively low magnification, as shown in Fig. 3, acetylene black does appear to have a "chainlike" structure in that prime particles appear joined together in chainlike fashion so as to give a three-dimensional "fishnet" structure. However, at much higher magnification in a high resolution (<0.25 nm) TEM, the microstructure of acetylene black was seen to be very heterogeneous, and it is apparent that graphitic "chains" or "ribbons" characterize only a portion of the

total structure present. Therefore, while the characterization of acetylene black as being more crystalline (graphitic) than most carbon blacks is essentially correct, it is also the case that acetylene black has a significant portion of the carbon present in a disordered (lacking microcrystallinity) microstructure.

The ^{14}C labeled carbon black was indistinguishable from the Shawinigan acetylene black in terms of the microstructure observed by TEM.

TEM analysis also showed that the catalyzation of the acetylene black with Co_3O_4 resulted in macroscopically uniform dispersion of the oxide in the black but there was evidence of microscopic "clustering" of the oxide. A typical illustration of this "clustering" is shown by Fig. 3, in which the oxide prime particles (200-300 Å) have aggregated into certain regions of the black leaving other regions of black without Co_3O_4 . The characteristic dimensions of the catalyzed and uncatalyzed regions of black are ca. 0.1 μm , so that on the scale of 1 μm or more, the catalyzed black can be considered to be a homogeneous composite material.

Corrosion Rates for Acetylene Black.—A characteristic curve for the amount of carbon lost from the electrode into KOH solution as a function of time and potential is shown in Fig. 4. These data were always obtained in the direction of increasing potential following an initial (new electrode) "aging" period of 48 hrs. at 45°C, 450 mV vs. Hg/HgO.^a After obtaining data at one potential, the solution was drained and replaced with fresh solution before stepping the potential. The rate of weight loss to solution was calculated from the slope of the linear least squares fit of the

^aAll potentials in this paper are given versus an Hg/HgO in the same electrolyte at room temperature.

data. In some cases, such as at higher temperatures, or with Co_3O_4 present, there was clear evidence of an "induction period," as seen from the data in Fig. 5. These induction periods appear to represent a memory in the carbon, as after a step to either higher potential or higher temperature the dissolution^b rate remains for a period at the lower rate. Tafel plots of the dissolution rates are shown in Fig. 6. For the purposes of these plots, the dissolution rate was obtained from the steeper slope observed after the induction period. These data illustrate a further memory effect of much longer duration. The one set of rates were taken in the order of increasing potential and increasing temperature, then the temperature was reduced from 65°C to 25°C and the sequence repeated. The second set of data showed a lasting displacement to higher dissolution rates for the same potential and temperature. These memory effects show clearly how sensitive the dissolution rate of acetylene black is to the pre-treatment history, and makes it essentially impossible to determine an absolute (single-valued) dissolution rate for a particular potential and temperature. Therefore, the Tafel slopes in the plots in Fig. 6 probably do not have any significance relative to the mechanism for acetylene black dissolution. Rather, the potential dependence shown is the effect of increasing the potential on the quasi-steady-state dissolution rate.

The data shown in Fig. 6 are for the dissolution of the acetylene black into the bulk solution and do not contain the contributions from insoluble species or from partially soluble species that precipitate in the

^bFor compactness, the term "dissolution" refers to the oxidation of carbon to form dissolved species, or partially soluble or insoluble products which are solvent-extracted from within the electrode.

pores of the electrode, or from gaseous oxidation products. An extraction procedure was developed to analyze for precipitated product. After a run like that in Fig. 4 or 5, the cell was drained of KOH, replaced with an extraction solution, and left at open circuit potential while sampling from the solution. A typical extraction curve is shown in Fig. 7 for the extraction of carbonate using fresh KOH. In this case, the concentrate of carbonate in the pores of the electrode was the same as the concentration in the bulk solution. Extraction of organic was obtained using ethanol-water, but very little precipitated organic was extracted at any of the conditions in Fig. 6. Using the known solubility of KHCO_3 - K_2CO_3 in KOH (13) and the measured internal electrolyte volume in the electrode, one can calculate the amount of corrosion (as carbonate) required to cause precipitation in the electrode assuming no carbonate ion diffusion out of the internal region. The amount is surprisingly high; ca. 1 w/o loss is required to cause carbonate precipitation to occur even in the absence of diffusion into bulk solution. Since the typical data collection time for the rates given in Fig. 6 was ca. 5 hrs., only at the very highest dissolution rates ($>0.1\% \text{ hr}^{-1}$) would one expect to see any precipitated product in the electrode, and this was in fact the case. The extraction analyses did indicate that there was precipitated carbonate internal to the electrode in the 45°C and 65°C runs. The corrections to the dissolution rates for this contribution are shown in Figs. 8 and 9. Internal precipitation appears to account for the flattening of the potential dependence of dissolution rate in the 550-600 mV potential region at 45°C. It does not, however, entirely account for the negative potential dependence of the rates at 65°C.

Mass spectrometer analyses of the gas above the electrode indicated that only two gases were produced in significant quantity, oxygen and carbon monoxide. The CO_2 in equilibrium with the KOH solution in these experiments was at too low a partial pressure to be detected by our analyzer. There was no detectable evolution of CO at 25°C, but at 45°C, CO evolution was evident and at 65°C, it was substantial, as shown by the data reported in Figs. 8 and 9. Above ca. 600 mV at 45°C, CO becomes the majority corrosion product, which accounts for the apparent maximum in the dissolution rate observed by analysis of the solution. At 65°C, CO becomes the majority corrosion product at about 100 mV lower potential than at 45°C. When the gas phase and internal precipitate contributions are added to the solution phase analysis, the resulting Tafel plot at 45°C from 550-625 mV continues with approximately the same slope (ca. 130 mV per decade) as the low potential portion where carbonate was the only product. Above 625 mV the slope changes sharply due to the very different potential dependence for oxidation to CO than for dissolution to carbonate. The Tafel plot at 65°C after the gas phase and internal volume correction still shows behavior unlike that seen in the low temperature data. The relatively flat potential dependence of the total corrosion rate in the potential region of 400-500 mV may represent transport limitations, e.g. limiting diffusion of dissolved corrosion products out of the electrode and internal pH change, rather than nearly potential independent kinetics.

Qualitative analysis of the solution by the procedures in Fig. 2 indicated there was no measurable quantity (<10 ppm) of organic carbon in the solution at temperatures below 65°C. At 65°C, traces of organic carbon appeared at 550 mV and 575 mV, but the current efficiency for producing organic species was extremely low (<<1%).

In the potential region of this study, there are three anodic processes occurring, oxygen evolution, carbon dissolution, and carbon surface oxide formation. The latter is a pseudo-capacitance, while the former two are faradaic processes, so that, in principle, one can separate out the surface oxide formation from the other two by analysis of time dependence of the current response. The ^{14}C labeling and the mass spectrometer analysis enable the carbon dissolution and oxygen evolution rates to be determined independently, and from the simultaneous measurement of the total anodic current the current efficiencies for each anodic process can be calculated. The results at 45°C are shown in Fig. 10, and in Table I. The anodic current equivalent to a given rate of appearance of carbon product was calculated from Faraday's law assuming $4e^-$ per g-equiv carbonate ion, $2e^-$ per g-mol carbon monoxide, and $1.5e^-$ per g-equiv of carbon in organic form. The latter assumes that mellitic acid is the model for organic carbon in solution. Under the potentiostatic conditions used, when the potential was stepped to a higher potential the current increased sharply, then decreased to a steady-state potential and temperature. The time dependent current probably represents the surface oxidation process. Generally, the sum of the partial currents due to CO evolution, O_2 evolution and carbon dissolution was very close to the steady-state current, so that the contribution of the oxide formation process to the steady-state current was usually very small (<10%).

The effect of cobalt catalyzation on all the anodic partial currents was dramatic. The Tafel plots for the carbon dissolution rates are shown in Fig. 11. In comparison to the uncatalyzed results in Fig. 6, several changes due to catalyzation are apparent: i.) the rate of dissolution was much greater (factor of 2-3; ii.) the potential dependence at 25 and 45°C was about the same; iii.) the potential dependence at 65°C was very different. The change in potential dependence at 65°C reflects the preferential acceleration by Co_3O_4 of carbon dissolution processes that produced highly soluble organic species, as observed by the organic/inorganic qualitative analysis of the solution. The increase in organic product was even intuitively apparent by dramatic coloration of the solution, producing deeply colored reddish-brown solutions. At 65°C with fresh KOH solution in the cell, dark brown streaks could be seen streaming from the electrode upon the imposition of a potential of 550 mV! Gas evolution rates from the electrode were also increased, as seen by a comparison of Figs. 12 and 13. The oxygen evolution rates increased by more than an order of magnitude; the lower potential dependence probably reflects oxygen transport limitations at these higher evolution rates. The rate of CO evolution at low potentials (ca. 450 mV) was also increased by about an order of magnitude, but the rate at high potential (650 mV) was about the same. The nearly flat potential dependence of the CO evolution rate cannot be due entirely to transport limitations, as the transport limitations on oxygen evolution (which is evolving at a higher rate than CO) did not produce such flat potential dependence. It is more likely that there was a change in the distribution of anodic processes that occurred with increasing potential. In particular, the dissolution of carbon to soluble organic products was

found to increase suddenly when the potential was increased from 450 to 550 mV. This is reflected in the current efficiencies reported in Table I; at 450 mV there was essentially zero organic product but at 550 mV the rate of dissolution to organic was nearly equal to the rate of oxidation to carbon monoxide.

The characterization studies of the structure of the catalyzed acetylene black had indicated that there was some clustering of the Co_3O_4 phase so that there are significant regions of the carbon that are not in contact with Co_3O_4 . To learn more about the degree of direct contact between Co_3O_4 and carbon black required for the catalyzation of the carbon corrosion processes, an electrode was fabricated from a mechanical blend of uncatalyzed ^{14}C acetylene black and unlabeled catalyzed acetylene black. Mechanical blending is unlikely to produce the degree of physical contact between the ^{14}C aggregates and the Co_3O_4 clusters achieved by solution phase impregnation. Therefore, if direct physical contact between Co_3O_4 and the carbon black particles were required for catalyzed corrosion, the mechanical blend should yield lower dissolution rates as measured by the ^{14}C method. As a comparison of the results in Figs. 11 and 14 show, this was not observed. The dissolution rates observed with the mechanical blend (Fig. 14) were the same (within the range of values observed for identical electrodes) as with the solution impregnated electrode (Fig. 11). It appears then that direct physical contact between the oxide phase and the carbon black aggregates is not required for enhancement of the corrosion process to occur.

DISCUSSION

One of the objectives of this study was to determine the individual rates of all the anodic processes occurring in an acetylene black electrode in the 450-650 mV potential region. The approach was to measure the rate of appearance of products of the anodic processes using a variety of techniques, and there remains the question as to whether all the anodic processes occurring in the electrode were accounted for. Techniques were developed to analyze for gaseous products, soluble products in the KOH solution, and partially soluble or solvent extractable products within the electrode. There are well-known anodic processes which do not produce products that would be seen by these techniques, in particular, the oxidation processes that form surface oxides or intercalation compounds like "graphite oxide" (14). An approximate measure of these processes can be obtained by comparison of the sum of the measured partial rates (as partial currents) with the observed total anodic current. This procedure has an inherent inaccuracy, as the product evolution rates require a finite sampling time whereas the anodic current is instantaneous and is changing during the sampling period. The resulting sums of the measured partial rates of oxygen evolution, carbon monoxide evolution, and carbon dissolution were generally less (ca. 90% of the total current) than the average values of the anodic currents observed over the time period for the partial rate determinations. But there are sufficient inaccuracies in the partial rate determinations that the relatively small differentials are probably not reliable measures of anodic processes like surface oxidation or "graphite oxide" formation. One can, however, reasonably conclude that these latter processes make a relatively minor (ca. 10%) contribution to the time-averaged anodic

current observed under potentiostatic conditions.

Due to the different potential dependence of each anodic process, the predominant anodic process changes as a function of potential (at constant temperature) and, due to different activation energies, the predominant process changes as a function of temperature at any given potential. In terms of potential dependence at low (<50°C) temperature, three regimes can be distinguished: i.) in the low potential region (450-500 mV) the predominant process is dissolution of the acetylene black to carbonate ion; ii.) in the 500-600 mV region oxygen evolution and carbon dissolution occur at equivalent rates; iii.) above 600 mV oxygen evolution and carbon monoxide evolution are the dominant processes. Elevation of the temperature at 65°C or higher preferentially accelerates the gas evolution reactions (for O₂ and CO) such that all three anodic processes occur at nearly equivalent rates at low potential. Carbon monoxide production was always commensurate with oxygen evolution, and was never observed in the absence of oxygen evolution, indicating that there is a good possibility that chemical oxidation of the carbon by evolving oxygen (or intermediates) may be occurring in addition to direct electrochemical oxidation. This was also indicated by the effect of Co₃O₄ on the CO evolution rate, particularly the results that showed that physical contact between Co₃O₄ and carbon was not necessary for enhanced oxidation. The results with the cobalt catalyzed acetylene black also suggest that CO evolution and organic formation are competing, and not parallel, reaction paths. This was evident from the observation that the appearance of significant quantities of organic product was always at conditions (potential and temperature) where the current efficiency for CO evolution was the lowest, e.g. Table I. It is not

mechanistically obvious why oxidation to CO and dissolution to organic would be competing reacting paths.

While the anodic processes of oxygen and carbon monoxide evolution appear to be coupled, there is no apparent coupling between oxygen evolution and dissolution to organic products. This is clear by comparison of the data in Table I, where high current efficiency for oxygen was not accompanied by measurable organic dissolution product. Also, in the case of the 65°C experiments with uncatalyzed acetylene blacks, the absolute oxygen evolution rates were about the same as with the catalyzed black at 45°C, yet no measurable quantity of organic appeared in the absence of catalyst. It seems clear that oxygen evolution is not a sufficient condition for organic product formation, and that cobalt oxide has a selective catalytic effect for the dissolution process to organics. We did not perform experiments designed to determine whether physical contact of Co_3O_4 and carbon aggregates is required for this catalysis as we did for the carbonate ion reaction. This determination could have been made by using ^{14}C detectors on the chromatographs in the organic carbon analysis, but our apparatus was not equipped with these detectors. Unfortunately, there are no results in this work that would help to elucidate the mechanism of the selective catalyzation of the dissolution of carbon to organic products.

We attempted some experiments designed to explore the relationship between the acetylene black microstructure and the corrosion rate, but these have not yet yielded definitive results. Because of the heterogeneous nature of the acetylene black microstructure, it might be expected that the corrosion rate might change (go down) with time as the more easily oxidized sites are used up. Also, if the different types of carbon in the black are

removed at different rates, one might expect to see the microstructure change by TEM analysis of corroded samples. However, it was clear from the TEM analysis that the scale of heterogeneity is fairly large, and that the amount of carbon loss required to see a significant change in either the structure or the overall corrosion rate could be as much as 30-40%. A ^{14}C acetylene black electrode was potentiostated in KOH solution at 550 mV, 45°C for 500 hrs., which resulted in a total weight loss (determined gravimetrically) of ca. 30%. This electrode was placed in the corrosion cell of Fig. 1 and the rates of the anodic processes measured. The absolute rates of all anodic processes were increased by factors of 1.5-2 times those for "new" acetylene black, but the current efficiencies were significantly changed, with the corrosion rates reduced relative to oxygen evolution. The TEM analysis on the corroded black was inconclusive in that we could not distinguish regions of the carbon that had been attacked preferentially. Apparently, the increase in surface area with carbon loss more than offsets the decrease in the rate per unit area resulting in a net increase in corrosion rate. The same effect was seen in the temperature cycling experiments shown in Fig. 6. After the measurements at 65°C, which resulted in a weight loss of about 20%, the dissolution rates at the lower temperatures were about a factor of 2 higher than before the 65°C measurements. It would seem that the difference in corrosion rate (per unit area) between the different forms of carbon in acetylene black cannot be very large, perhaps only factors of 2-3.

We were not able to identify the organic products of acetylene black corrosion, and, in particular, the nature of the deep reddish-brown coloration of the KOH solution. There is a long and interesting history related

to the observation and analysis of colored caustic solutions from the oxidation of graphite anodes in chlor-alkaline cells. Thiele (15), reviewed observations made in the 1930s on the oxidation of graphite in caustic solutions, and reported that a brown discoloration of the solution was observed with graphite oxidation, that "lampblack" carbon colored solutions more intensely than graphite, and that the brown product was probably humic acid. In the early 1940s, Heller (16) did a thorough analytical study to identify the source of color in caustic from chlor-alkali diaphragm cells. He found that when graphite anodes from these cells were soaked in water, a yellowish coloration developed, which left a dark brown residue upon drying. From this brown residue, Heller extracted a bright yellow crystalline compound which he concluded, from various property measurements, was pyromelletic acid chloroquinone. Janes and co-workers (17-18) at Union Carbide reported that caustic solutions prepared from the yellow crystalline material isolated by Heller had the same UV-Vis spectrophotometer spectra as chlor-alkali cell effluent, and concurred with Heller that this material was the source of color in caustic from diaphragm cells. They also reported that less graphitic raw materials for the anode like "lampblack" or "charcoal" gave increased coloration in cell effluent. However, further analytical study of Heller's yellow material by Wawzonek and Eftax (19) indicated this material was not a single compound but a mixture of mellitic acid, pentacarboxylchlorobenzene, tetracarboxylchlorobenzene and a material of unknown structure that is actually the source of color (!). Since this active period sparked by Heller's work, there has been very little further work on this subject. Some Russian work (10) reported isolating mellitic acid as one of the

organic products from graphite anode oxidation in 0.01 N Na_2SO_4 , but mellitic acid constituted only a fraction of the total organic product which was not otherwise identified. There appears to be no precedent in the literature for the specific catalyzation of the dissolution process to organic products, as we have observed in this work. It seems unlikely that progress can be made in understanding the mechanism of this catalytic effect until the chemical identity of the organic products can be established.

The practical consequences of the determinations of the partial rates of the anodic processes occurring in acetylene black electrodes made in this work could be significant with regard to the use of this material in alkaline batteries. There are two areas of discussion with respect to the practical application of these results. The first is a qualifying one, that care must be taken in applying these partial rates directly to practical electrodes. The rates of oxygen evolution, the current efficiencies in Table I, and the total anodic currents measured at any potential are influenced by the rate of oxygen transport from within the porous mass of the electrode. The rates measured here were for fully submerged electrodes containing only enough PTFE to bind the acetylene black together. Some experiments were done with a floating electrode containing ca. 20% PTFE so as to approximate the practical "gas diffusion" type structure (20), and the rates of oxygen evolution from catalyzed acetylene black, and the observed current density, increased several fold over that observed with the same material in a submerged electrode. This means the concentration of dissolved oxygen inside the submerged electrode was probably several fold higher than in the high transport rate gas diffusion electrode, so that the corroding action of evolved oxygen may be accentuated due to the transport effect. Also, in PTFE-bonded gas

diffusion electrodes, it is usually the case that all of the carbon is not wetted by electrolyte, so that the dissolution (via the direct electrochemical pathway) will not be as high as expected for fully wetted acetylene black. There will also be dry catalyst in a gas diffusion electrode, and oxygen and carbon monoxide evolving can react homogeneously with the dry carbon or dry catalyst to form gaseous carbon dioxide that may diffuse out of the electrode without being trapped in the electrolyte. The gas diffusion electrode might, therefore, be expected to give higher gaseous product to dissolved product ratios than reported here. However, due to the complexity of the interactions and the potentially compensating nature of some of these interactions, it is difficult to predict what the quantitative differences in the partial rates might be in a practical gas diffusion electrode from those reported here.

CONCLUSIONS

1.) Carbon dissolution to carbonate ion, gasification of carbon to carbon monoxide, and oxygen evolution are the predominant anodic processes in an acetylene black electrode at 450-600 mV vs. Hg/HgO in concentrated KOH. No evidence for the formation of a "graphite oxide" intercalation compound was found. The potential and temperature dependence of these anodic processes is different, so that there are various combinations of the three processes that are dominant at different conditions: i.) at potentials below 500 mV and temperatures below 50°C, carbon dissolution is the primary anodic process; ii.) at 500-600 mV and 50°C or lower, carbon dissolution and oxygen evolution occur at equivalent rates; iii.) above ca. 600 mV or above ca. 60°C at any potential above 450 mV, oxygen evolution and carbon gasification are the dominant anodic processes.

- 2.) Below 500 mV and 50°C, the current efficiency for oxygen evolution from acetylene black is sufficiently small that the total anodic current is essentially the corrosion current.
- 3.) In a cobalt oxide catalyzed acetylene black electrode, the current efficiency for oxygen evolution is increased several fold, but the rate of all three anodic processes is accelerated relative to the uncatalyzed black. In addition, cobalt oxide causes organic products to form at significant rates at conditions where only trace amounts are observed from uncatalyzed black.
- 4.) The cobalt oxide does not have to be in physical contact with the carbon black aggregates to produce an accelerating effect of the corrosion reactions. Accelerating the rate of oxygen evolution from within the electrode in itself causes accelerated corrosion of the carbon. It is probable that chemical oxidation of the carbon by evolving oxygen (or its intermediates) occurs in addition to direct electrochemical oxidation.
- 6.) The relative rates of the corrosion processes and of oxygen evolution are affected by the transport properties of the porous electrode. The relative rates in a practical gas diffusion type electrode may be different from those reported here.

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Table I. Current Efficiencies^C at 45°C.

<u>Potential</u>	Acetylene Black			
	<u>CO</u>	<u>CO₂ (CO₃²⁻)</u>	<u>O₂</u>	<u>Organic</u>
480	≈8	80	13	≈0
550	10	55	35	0
600	10	10	80	0
	Co ₃ O ₄ Catalyzed Acetylene Black			
480	18	18	64	≈0
550	6	15	74	5

^CBased on the sum of the partial currents and not the observed total current.

APPENDIX

Mass Spectrometer Calibration

The calibration procedure was based on the electrolytic generation of oxygen from KOH solution into the gas space above the solution, whose volume is maintained at a constant value. A nickel Exmet[®] working electrode was used to evolve oxygen at a constant rate by use of a constant current power supply. The quantity of oxygen in the argon is therefore known precisely, and a calibration curve of mass spectrometer peak ratio (oxygen to argon) versus quantity of oxygen (in coulombs) can be prepared, as shown in Fig. 15. Because oxygen is always present in low concentration relative to the argon, we chose the M/e = 36 peak of argon (the natural abundance of the 36 isotope is 0.337%) as the normalization factor. Water vapor in equilibrium with the KOH solution is present at partial pressures of 20-200 torr depending on temperature, so that the total pressure of the argon above the solution is a function of the solution temperature. A different calibration curve was therefore required for each solution temperature. The absolute calibration for carbon monoxide was obtained using the absolute oxygen calibration and observing the M/e-28:M/e-32 peak ratios for calibrated mixtures of oxygen and carbon monoxide (purchased from Matheson). As a check on this calibration, we computed the expected M/e-28:M/e-32 peak ratios from the quadrupole analyzer transmission function supplied by the manufacturer and tabulated ionization probabilities for O₂ and CO and found them to be in reasonable agreement ($\pm 5\%$) with the observed values.

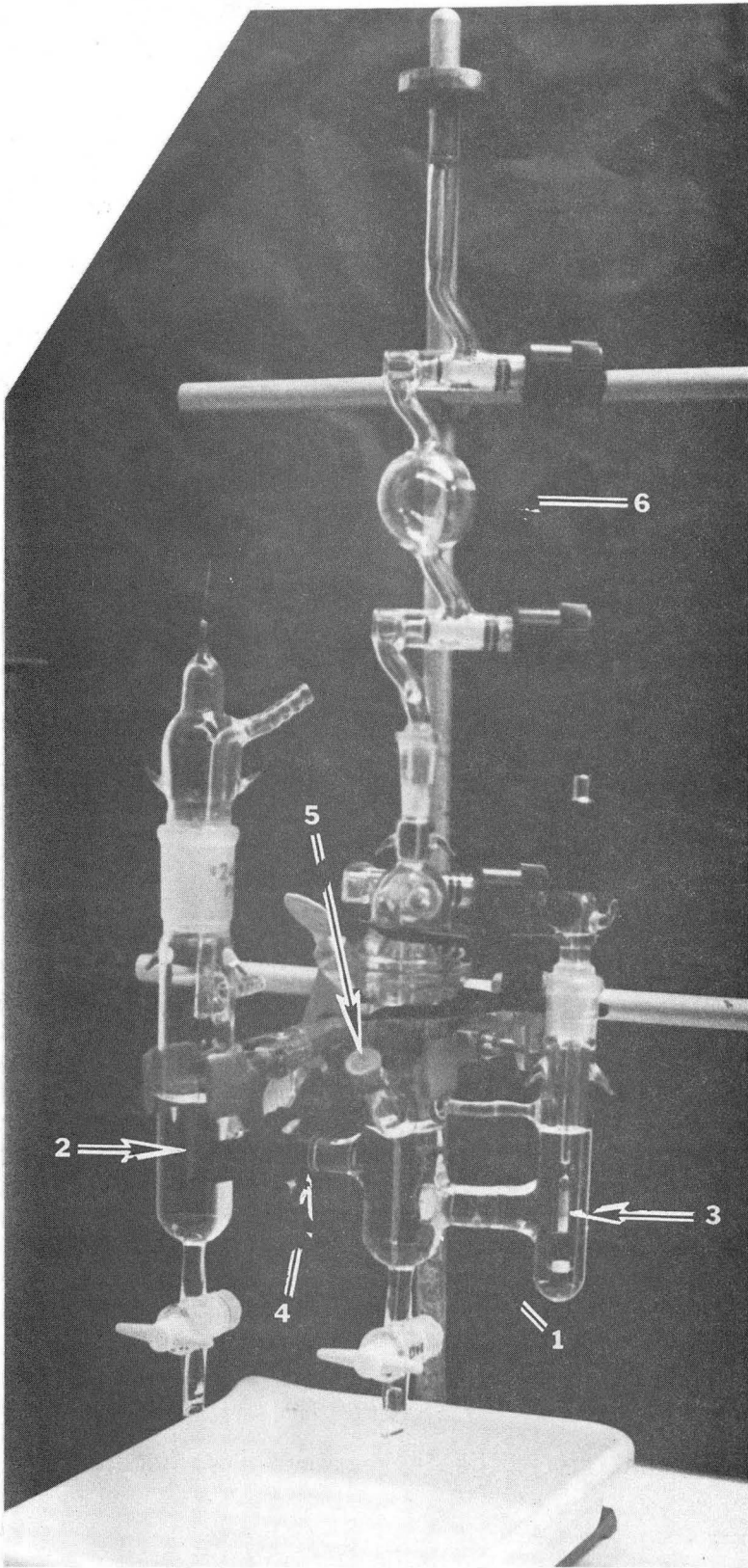


Figure 1. Three-chambered corrosion cell:
1-test electrode
2-Ni counter electrode
3-Hg/HgO reference electrode
4-Nafion membrane
5-septum for liquid sampling
6-gas sampling bulb

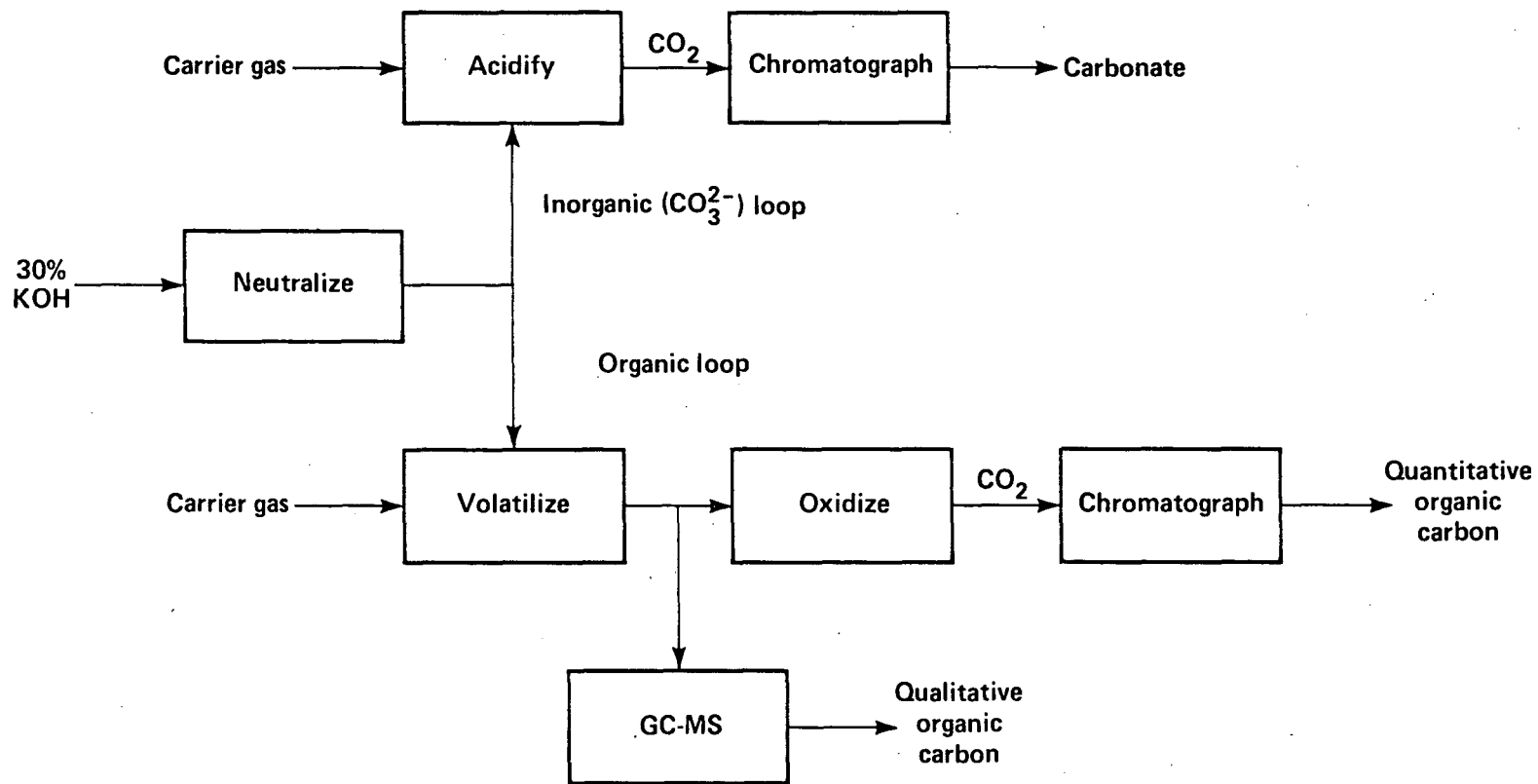


Fig. 2. Analysis of Soluble Corrosion Products.

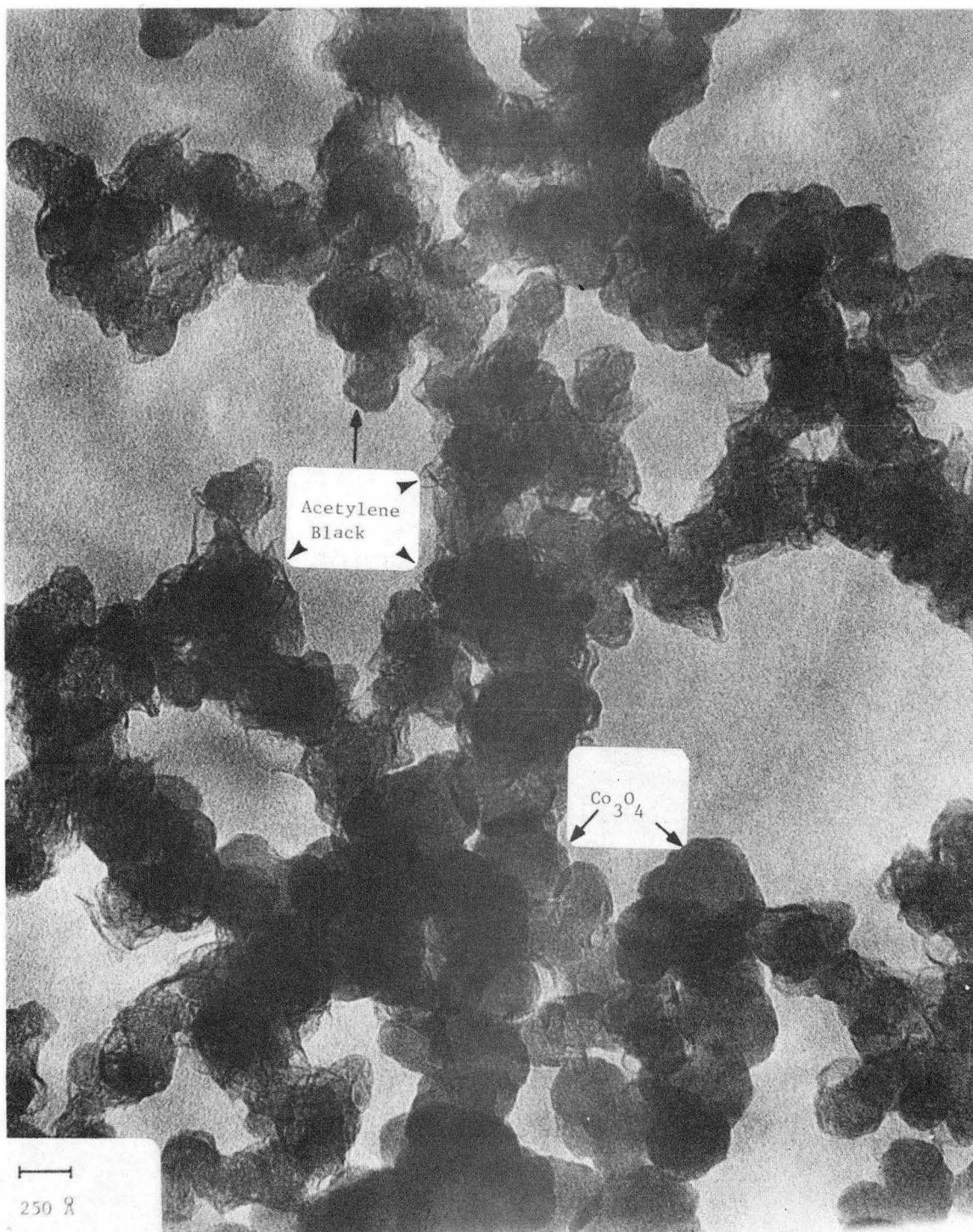
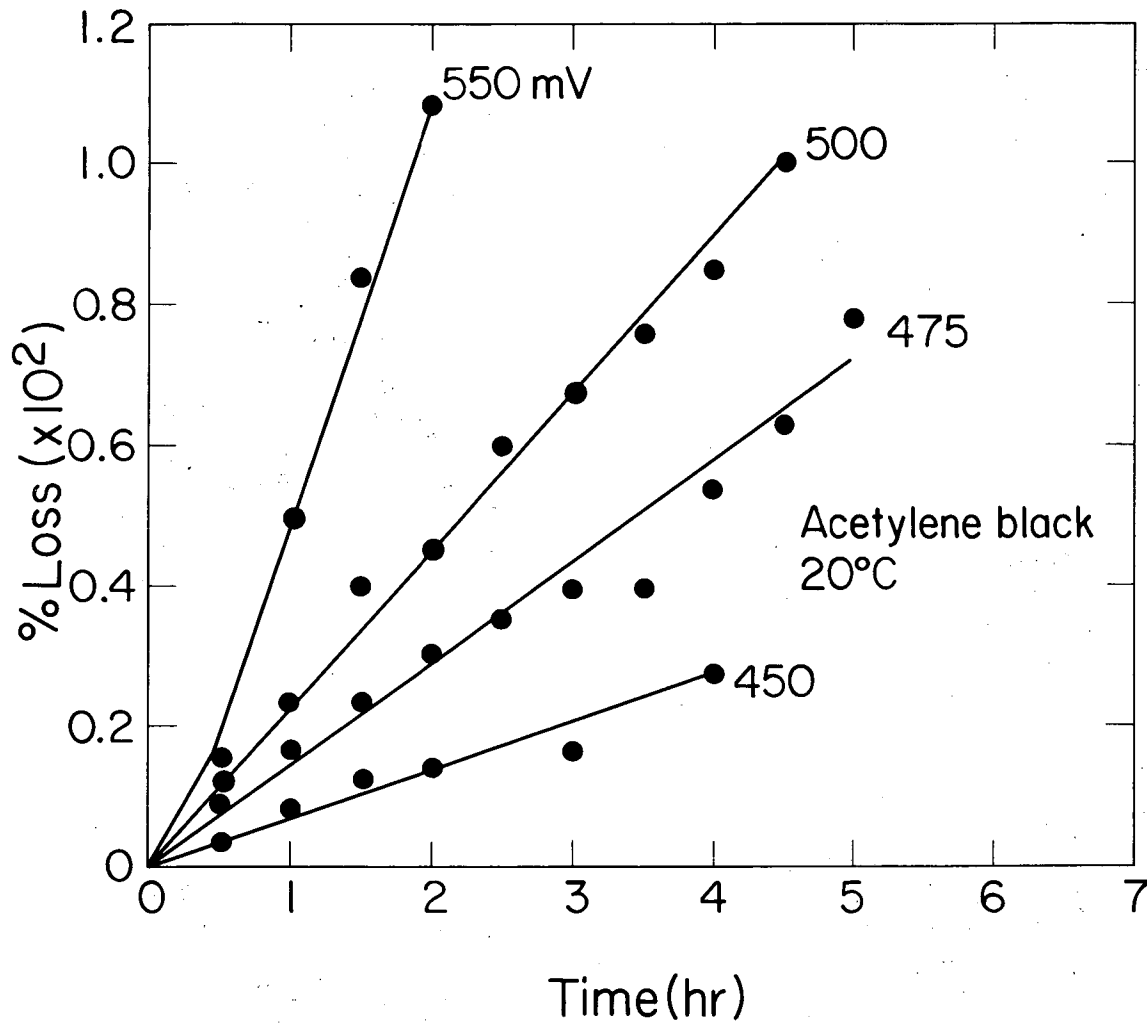


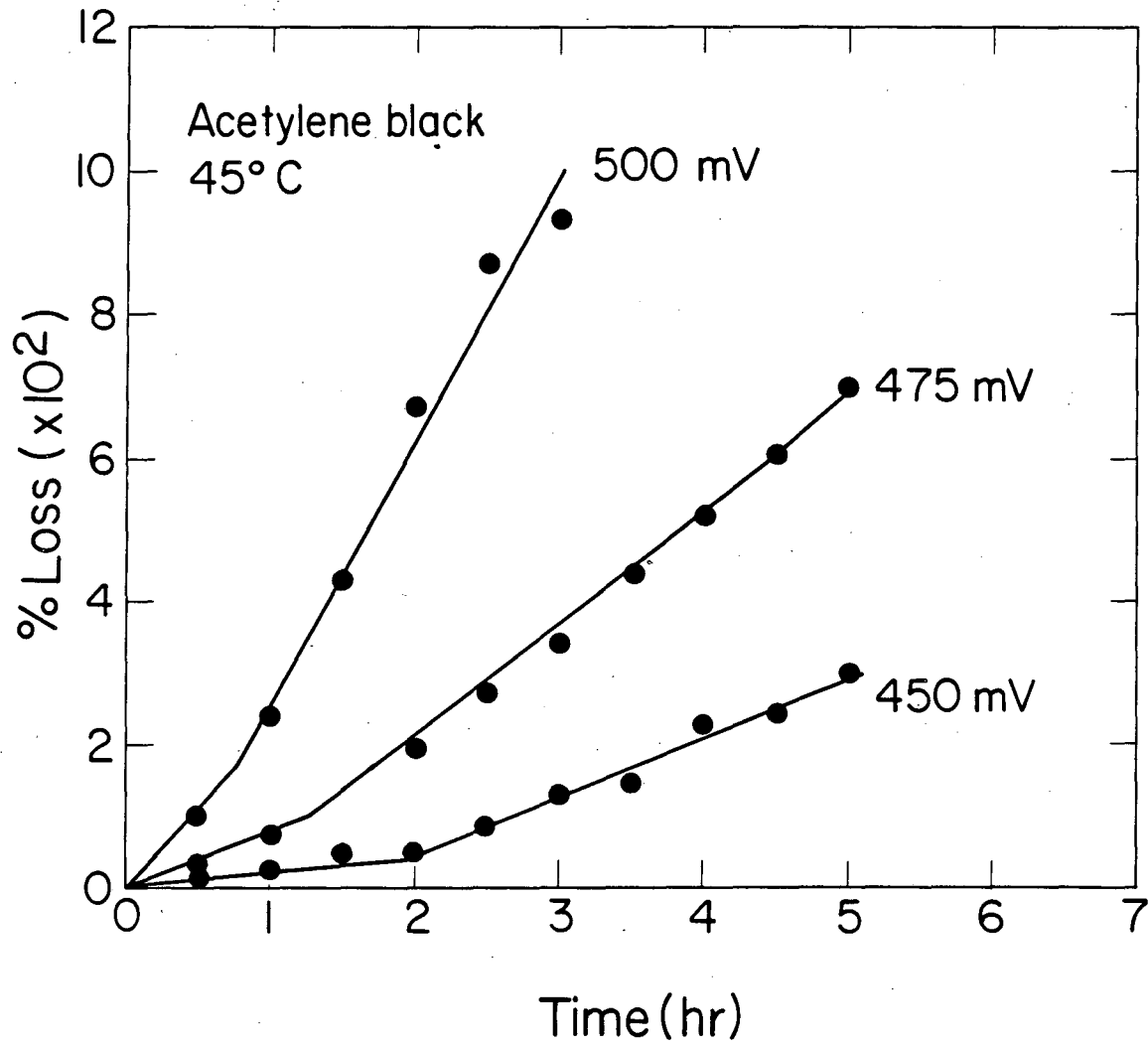
Fig. 3. TEM of cobalt oxide catalyzed acetylene black.

XBB 820-10445



XBL 836-2732

Figure 4. Quantity of carbon appearing in solution, expressed as a percentage of carbon initially in the electrode, versus time at a fixed potential.



XBL 836-2733

Figure 5. Same plot as Fig.6 at 45 C.

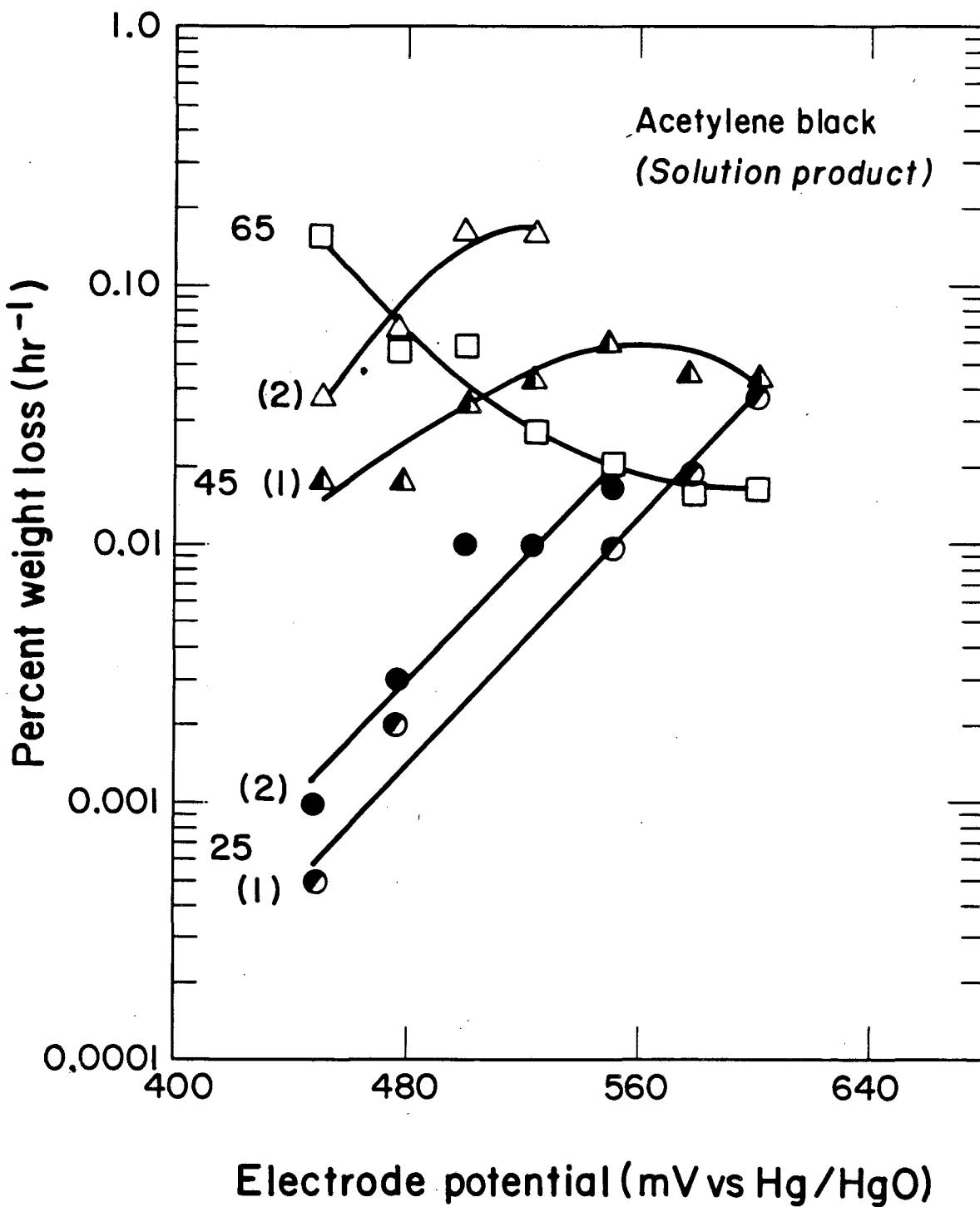
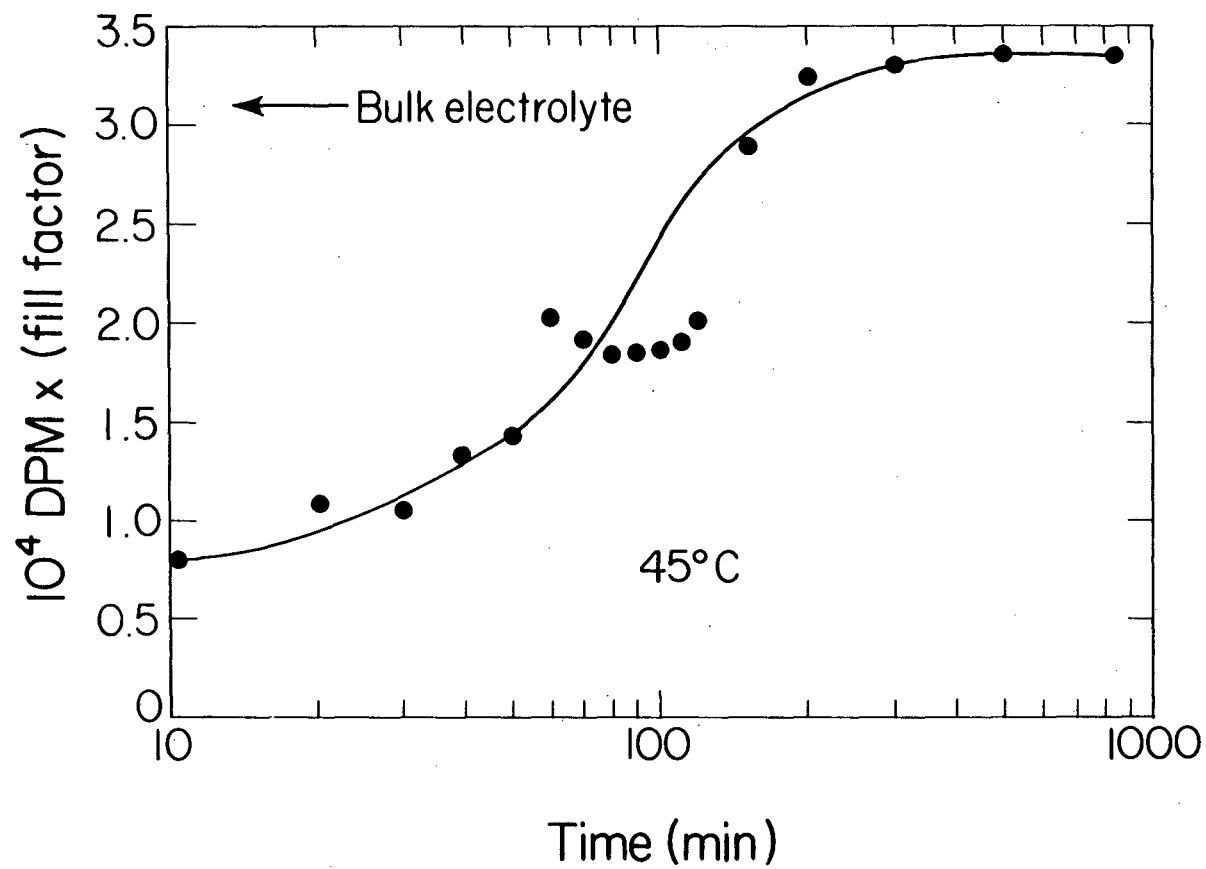


Figure 6. Rate of appearance of carbon in solution as a function of potential and temperature. (XBL 836-2741)



XBL 8212-4962

Figure 7. Extraction of carbon from solution within the porous electrode using fresh KOH solution.

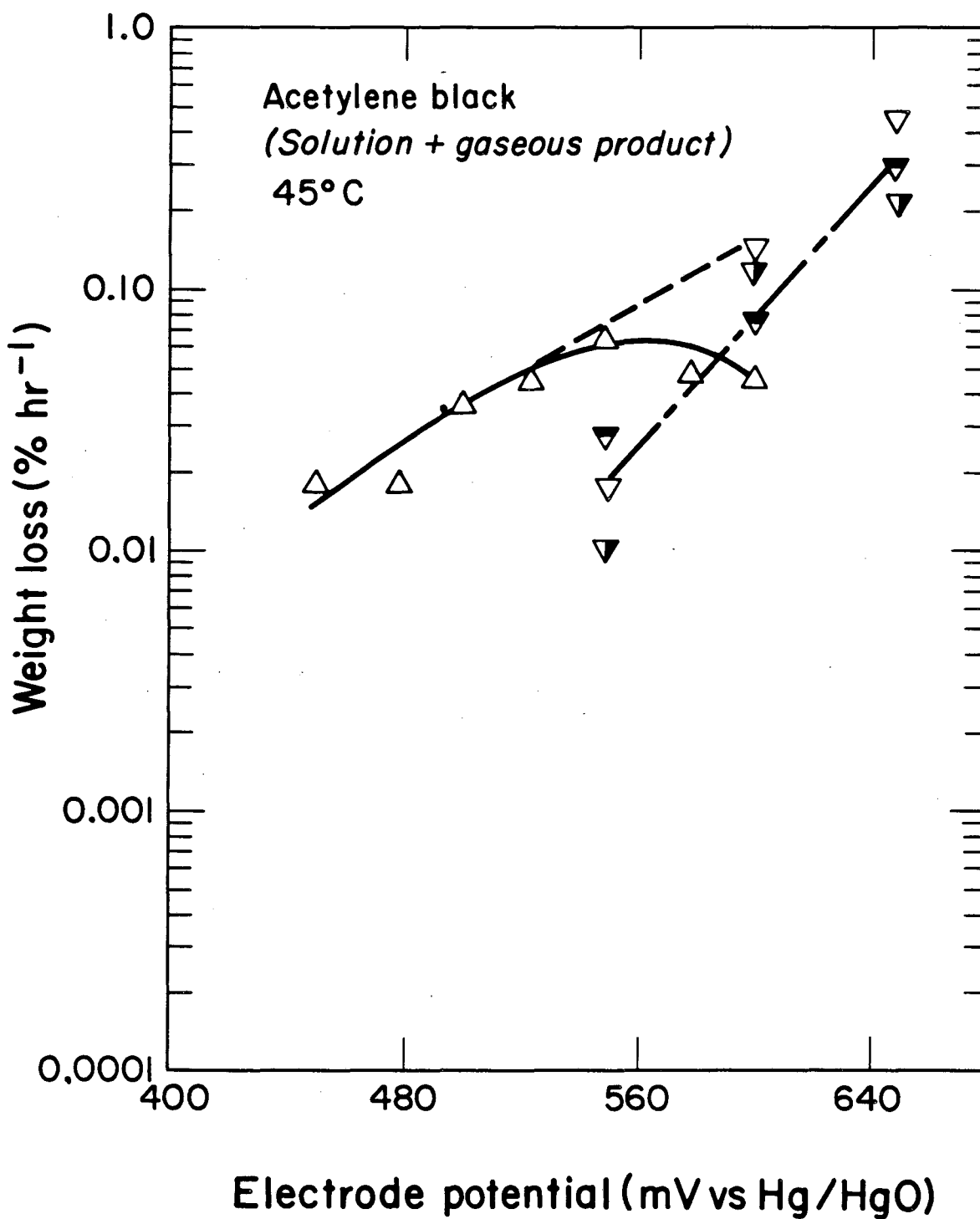


Figure 8. Contribution of carbon monoxide production to the total corrosion rate at 45 C. (XBL 836-2742)

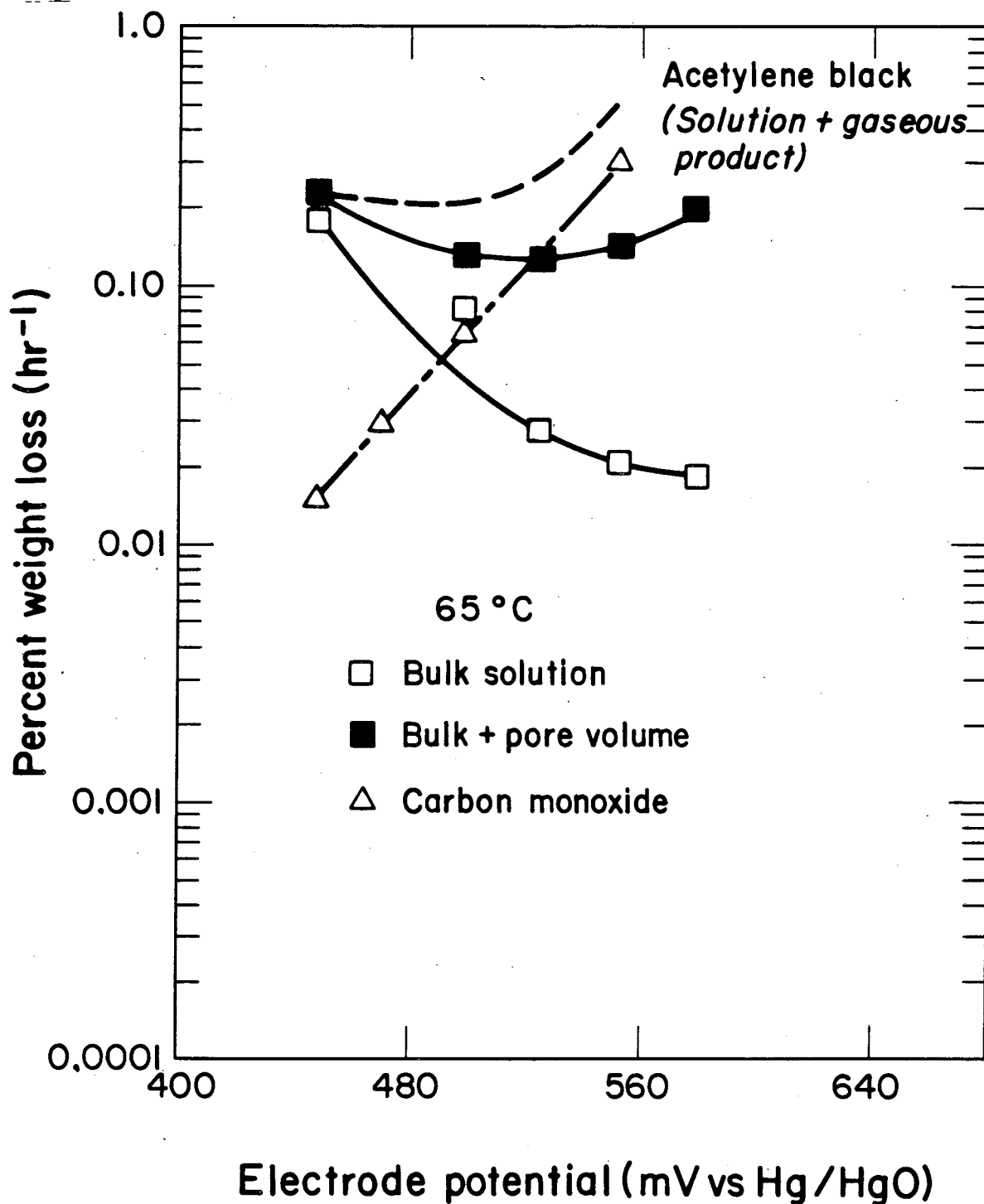


Figure 9. Contributions of internally precipitated carbonate carbon monoxide evolved to the total corrosion rate at 65 C. (XBL 836-2744)

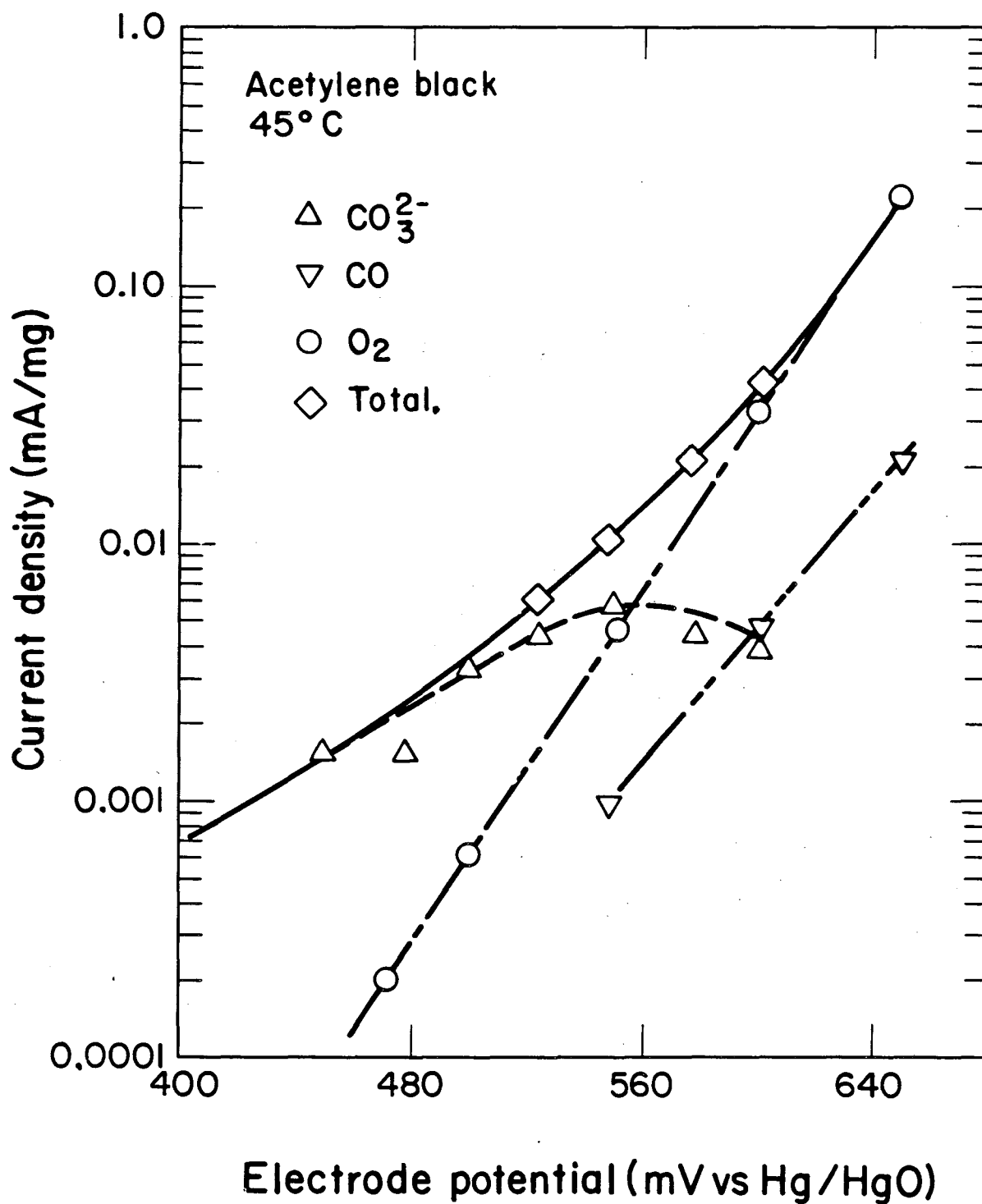


Figure 10. Partial anodic currents for oxygen evolution, carbon monoxide evolution, and carbonate ion formation and the total anodic current at 45 C. (XBL 836-2739)

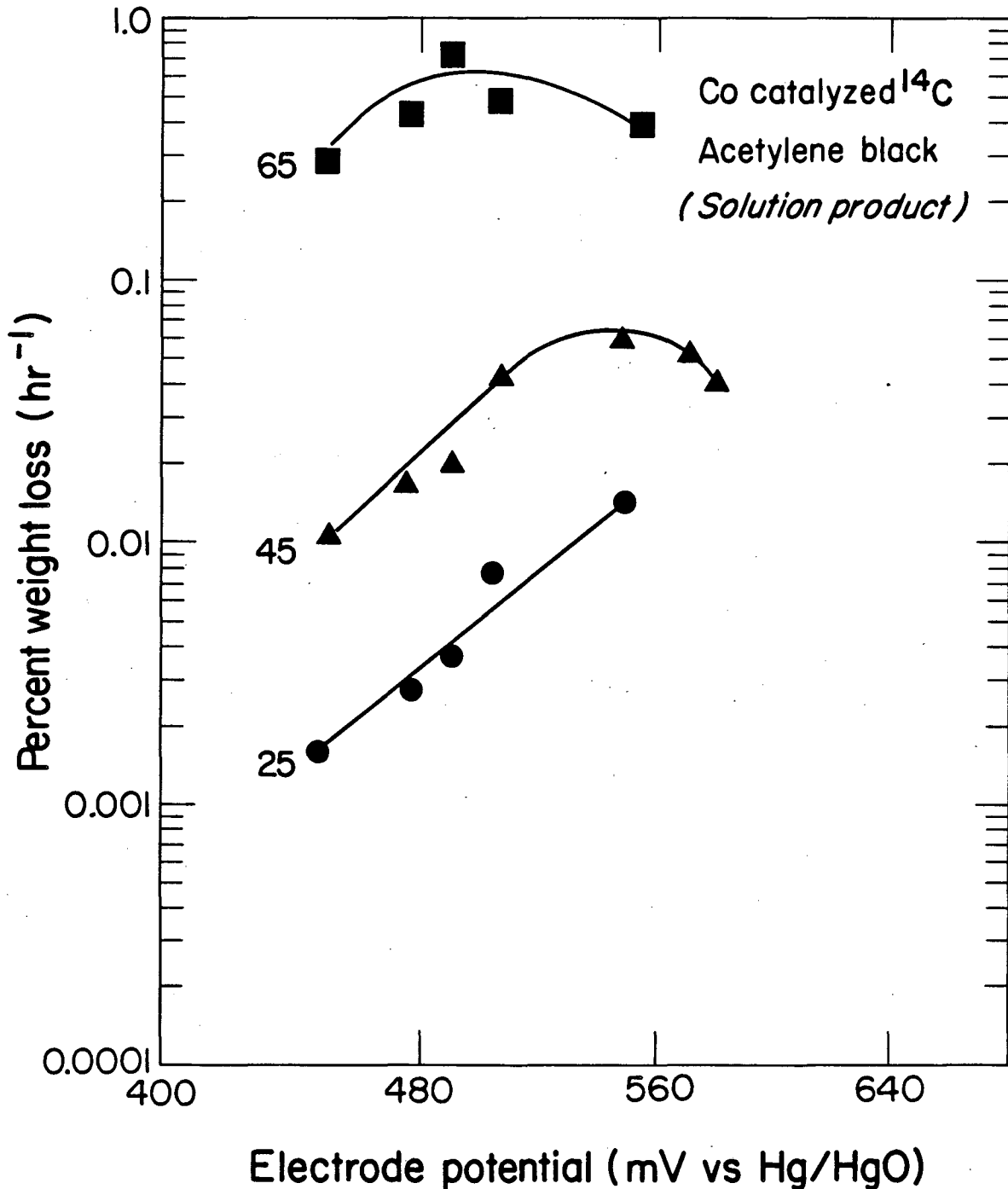


Figure 11. Cobalt oxide catalyzed ^{14}C labelled acetylene black dissolution rate as a function of potential and temperature. (XBL 8212-4961)

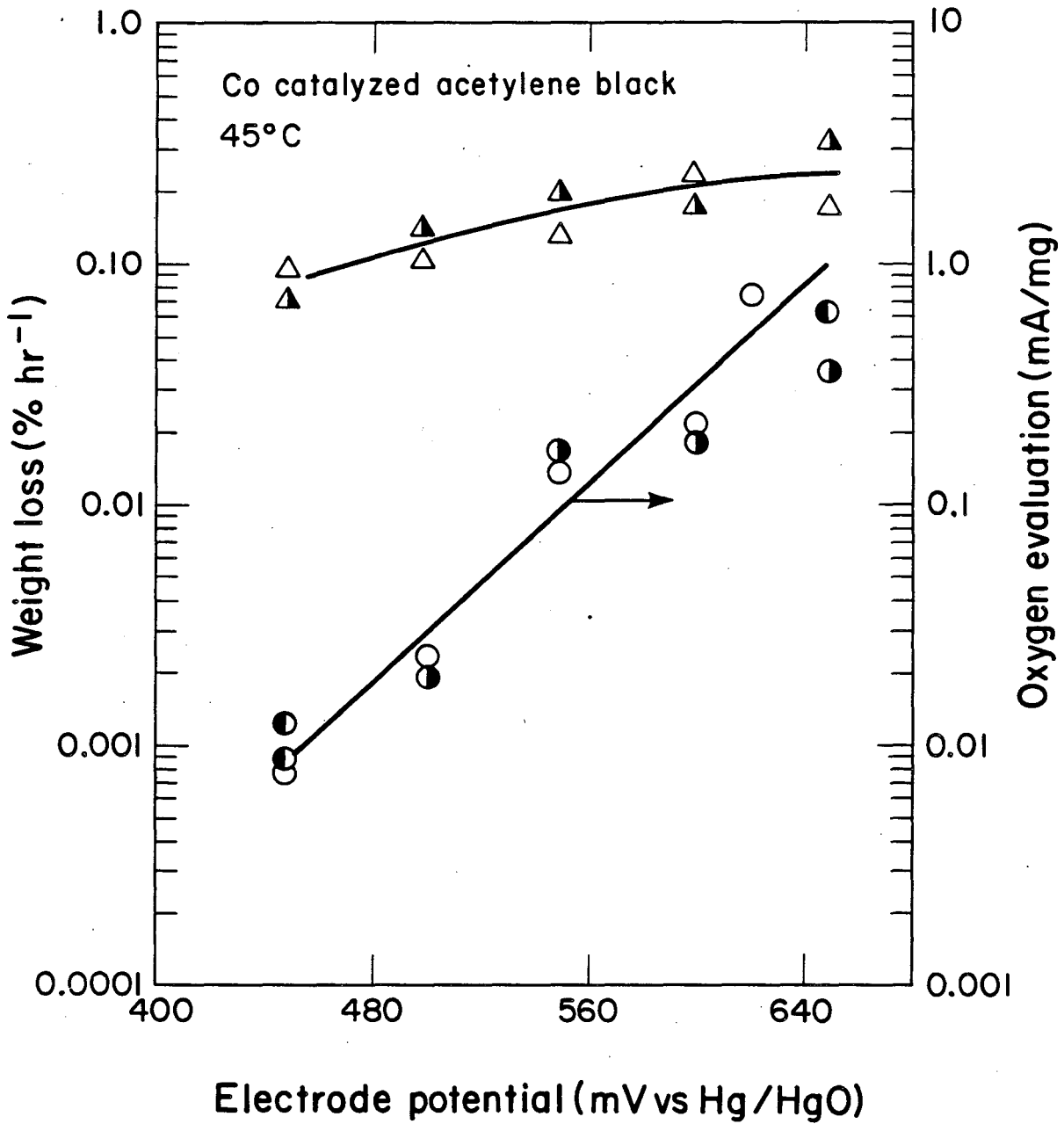


Figure 12. Rates of gas evolution from catalyzed acetylene black at 45 C as a function of potential.
(XBL 836-2734)

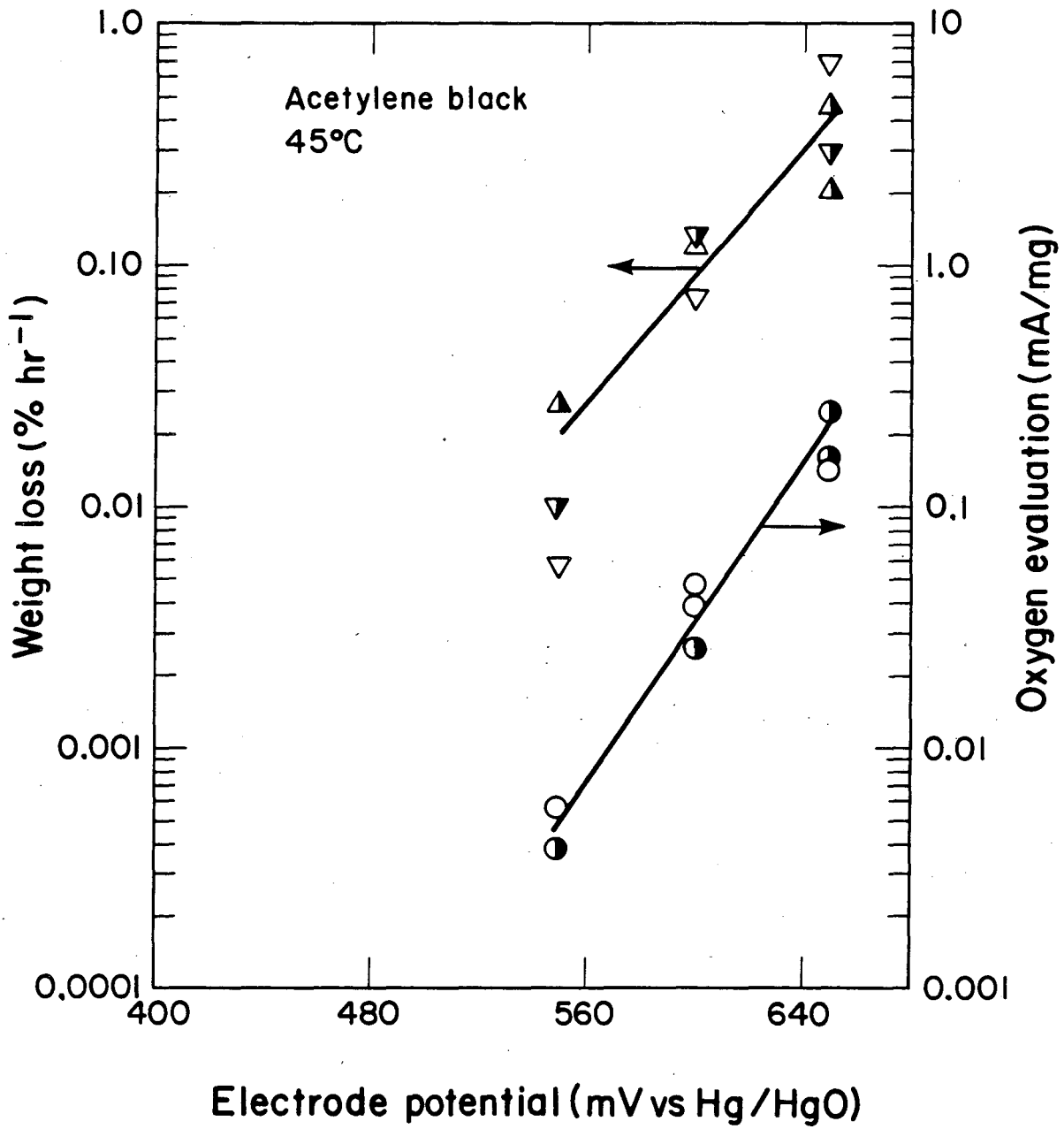


Figure 13. Rates of gas evolution at 45 C from uncatalyzed acetylene black as a function of potential. (XBL 836-2740)

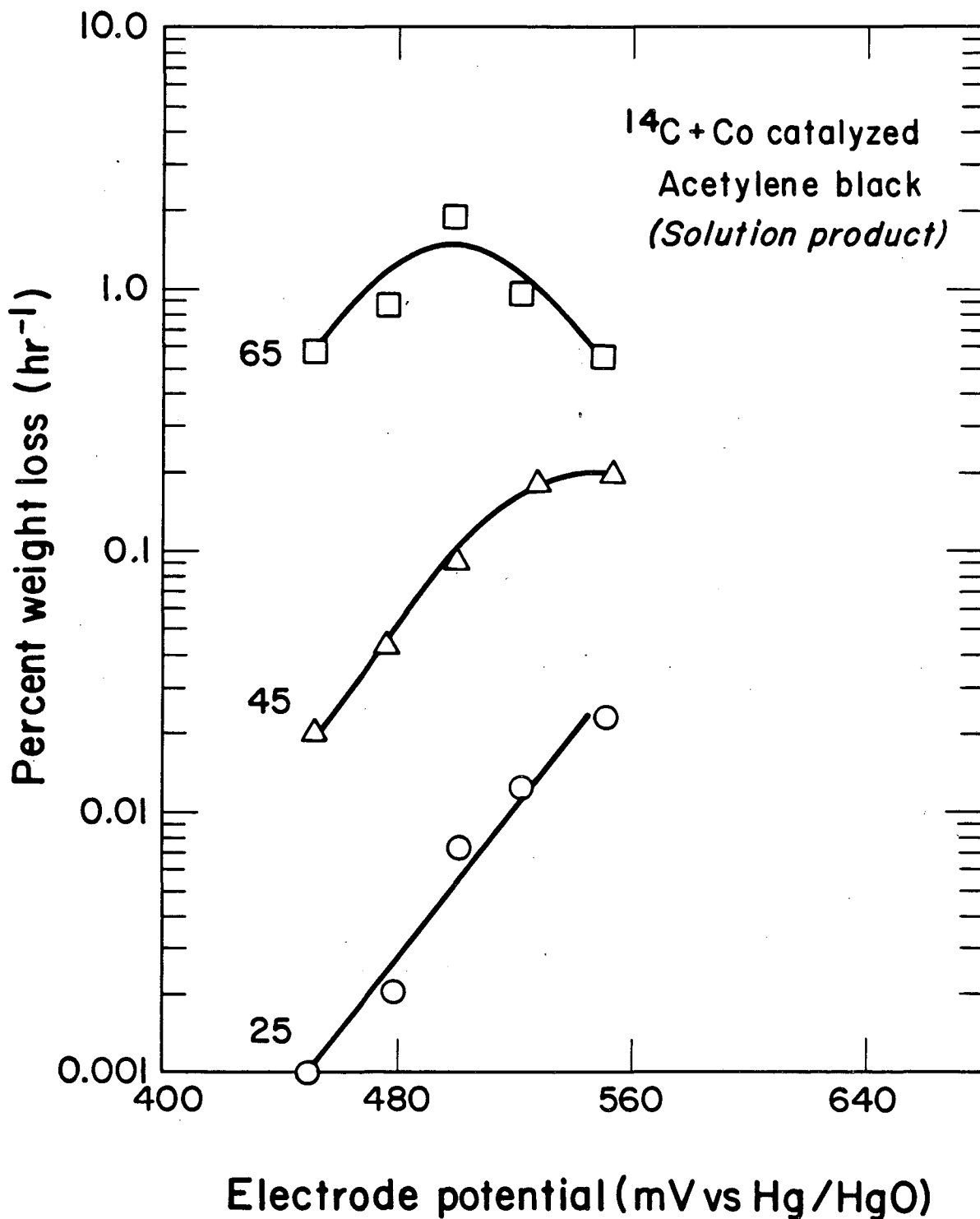


Figure 14. Rates of dissolution for a mixture of ^{14}C acetylene black with catalyzed unlabelled acetylene black. (XBL 836-2743)

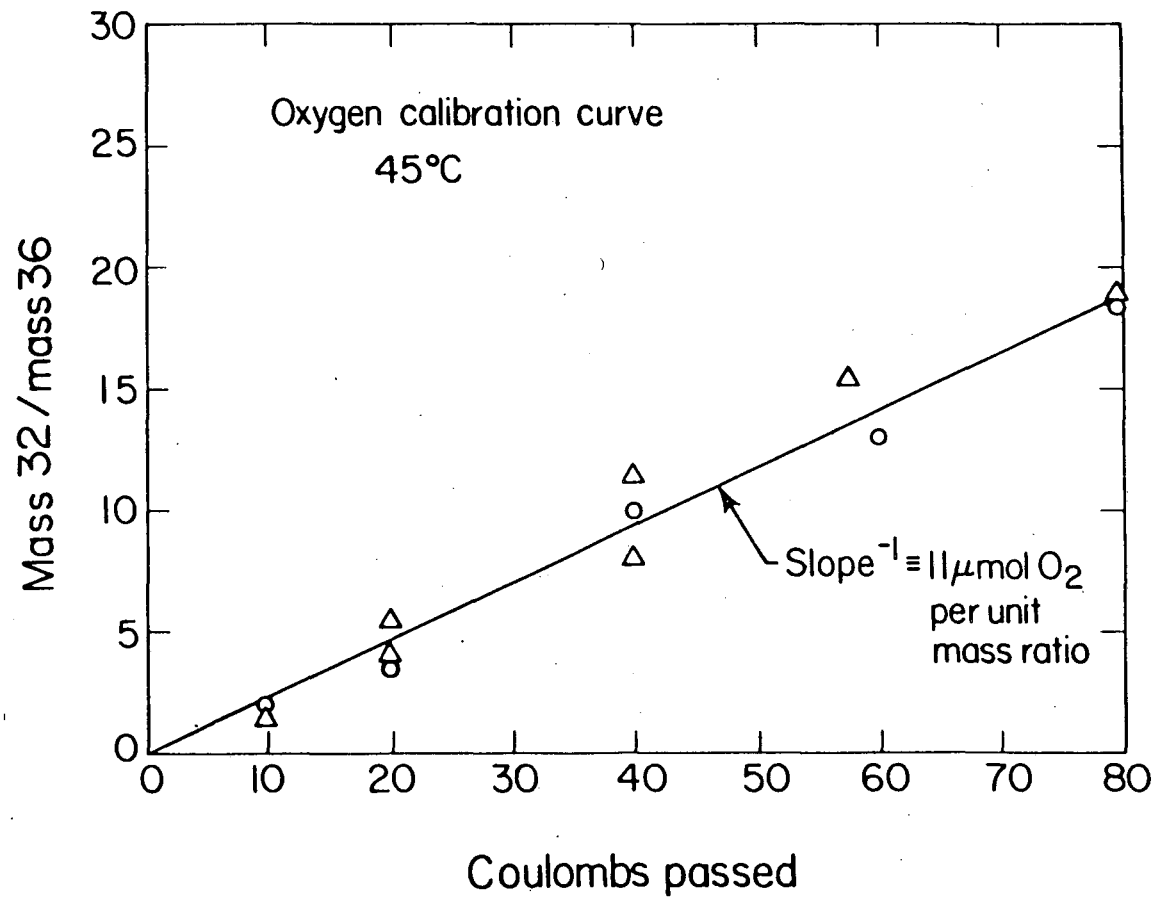


Figure 15. Mass spectrometer calibration curve for absolute determination of oxygen in argon dilute gas above the electrolyte. XBL 836-2735

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