NRL Report 6626

Identification and Characterization of Electrochemical Reaction Products by X-Ray Diffraction

JEANNE BURBANK
Electrochemistry Branch
Chemistry Division

December 20, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

This document has been approved for public release and sale; its distribution is unlimited.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
BACKGROUND AND EXPERIMENTAL METHODS	1
THE SILVER ELECTRODE	10
CONCLUDING REMARKS	14
REFERENCES	15

ABSTRACT

The application of x-ray diffraction methods to electrochemical studies is demonstrated by examination of the surfaces of polycrystalline solids by reflection diffractometry, operation of a cell designed for simultaneous x-ray and electrochemical studies, and the Berg-Barrett topographic technique. Silver anodes are used for illustrating the kind of information readily obtained by these methods: identity of crystalline reaction products associated with electrochemical phenomena, physical characterization of reaction mechanisms involving multiphasic coatings, distinction between large grains and preferred orientation, and estimations of coating thickness and crystal size.

PROBLEM STATUS

An interim report on the problem has been completed; work is continuing.

AUTHORIZATION

NRL Problem C05-14
Projects SF 013-06-06-4366
and RR 001-01-43-4755

Manuscript submitted August 16, 1967.

IDENTIFICATION AND CHARACTERIZATION OF ELECTROCHEMICAL REACTION PRODUCTS BY X-RAY DIFFRACTION

INTRODUCTION

The Theoretical Electrochemistry Division of the Electrochemical Society sponsored a symposium in May, 1967, at Dallas, Texas, on "Methods of Determining Structure and Characteristics of Surface Reaction Products." This report is a resume of the invited paper covering the application of x-ray diffraction methods (1). These techniques have been used for many years at this Laboratory in conjunction with electrochemical studies, and some of the results are cited to illustrate the applications of this analytical tool. It was the purpose of the presentation to describe the diffraction effects obtained from polycrystalline electrodes and electrochemical reaction products observed in situ, and to point out in familiar terms exactly what the diffractionist "sees" when he undertakes such a study. X-ray diffraction is a powerful analytical tool used for direct identification of crystalline materials, but in addition it can be used to further characterize surfaces and reaction products in rather unique ways. The amount of information obtained by skilled interpretation of the results is out of all proportion to the effort required for the experiments. Many excellent texts are available for introductory and advanced study, and just two of the very popular ones are cited here (2,3).

The diffraction of x-rays by crystals has been known since the discovery of x-rays, and there are many ways in which these effects are used. This paper is confined to a very limited area of this broad field, specifically to the study of polycrystalline masses making up electrochemical deposits and electrode surfaces.

Let us ask, what can x-ray diffraction examination tell us about the surface of an electrode? First of all, x-ray diffraction (XRD) will immediately tell us whether a material is crystalline, and, if so, it will identify the major solid crystalline phases (4). Small amounts of contaminants do not usually interfere with the identifications. XRD will show us changes in composition accompanying chemical or electrochemical treatment and will identify the reaction products. Using XRD, we can determine relative amounts of materials in mixtures (5) and the sequence of layers in laminated deposits. We can also estimate thicknesses of coatings even when they become so thin that their own crystalline character is no longer detectable (6). For the electrochemist concerned with deposition, dissolution, or alteration of solid phases on electrode surfaces this information is of fundamental significance and without it electrochemical measurements on a system are meaningless. Before he can advance the electrochemical aspects of his study he must first know the nature of his electrodes.

BACKGROUND AND EXPERIMENTAL METHODS

Most solid materials are crystalline; this means that the fundamental building blocks — atoms, ions, or molecules — are arranged with mathematical precision in the space occupied by each crystal of the solid. The manner in which the arrangement is accomplished and the spacing of the units with respect to each other are characteristic for each material. Most solids are polycrystalline; that is, they are a mass of contiguous individual crystals or grains, each one possessing the structure characteristic of the material but turned or twisted with respect to each other. Within each crystal the

building blocks are arranged in sets of parallel planes separated by fixed distances. Because these sets of interplanar distances are unique for each crystalline material, a solid may be identified by measuring these distances. To measure the small distances interference methods are used, and the very short wavelengths of x-rays are required.

Early in the history of x-rays, diffraction by crystal lattices was predicted, observed, and measured. These earliest observations were soon followed by the presentation of W. L. Bragg who greatly simplified the entire field of x-ray diffraction by recognizing the analogy of the laws of reflection of x-rays and the reflection of light by mirrors and diffraction gratings. The expression for the diffraction of x-rays by a set of parallel crystal planes, Bragg's law, is

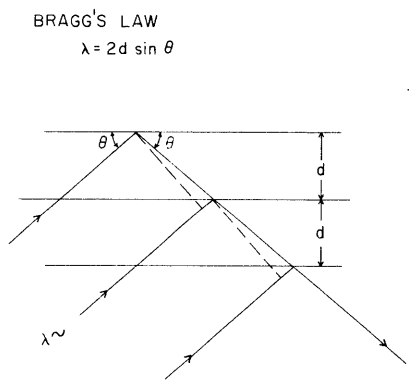
$$\lambda = 2d \sin \theta, \tag{1}$$

where λ is the wavelength of the x-rays, d is the interplanar spacing within the crystal lattice, and θ is the angle of incidence of the x-ray beam on the lattice planes.

The reflection of a light beam by a mirror may occur at almost any angle of incidence, and the angle of incidence equals the angle of reflection. In diffraction also the angle of incidence equals the angle of reflection but with this restriction the reflection will only occur at very specific angles where there is a whole number of wavelengths in the path difference for the ray traveling from one plane to the next parallel plane beneath it inside the crystal and back out to the surface. Under these conditions the reflections from a series of parallel planes in the crystal lattice give rise to additive reflections. When the crystal planes are tipped away from this specific angle, the path difference changes and becomes a fractional number of wavelengths; this results in destructive interference between rays reflected from the parallel crystal planes, and no diffracted beam emerges from the crystal. Bragg's law applies to each set of parallel planes within a crystal, of course, and the distances between the planes are characteristic for each crystalline material. Thus we obtain a distinctive set of "d" values, also called "lines," that when taken together specifically define a given crystalline material. This group of lines is called a diffraction pattern (Fig. 1). When we detect this pattern in a sample, it is undisputable proof of the presence of the given crystalline material. A collection of the standard diffraction patterns for thousands of crystals is available and is added to and revised each year (4).

Next let us consider an agglomerate of small crystals turned and twisted in all possible directions with respect to each other — a powder with random orientation of particles. This is a very common type of sample for x-ray diffraction specimens. When the powder is illuminated with the x-ray beam, some sets of planes in the little crystals will be in a position to reflect the beam, while others will not reflect at all. If this could be seen with the eye, the sample would look like a surface covered with small mirror fragments some of which reflect brightly toward the eyes, while others remain completely dark. The only way to make the dark ones light up is to move the sample, or the observer, or the light source so that every little mirror would come into the reflecting position. But in moving, the mirror grains that had been reflecting at first would flash off, different ones would reflect in turn, and the sample would glitter in the light.

In XRD we can use photographic film or radiation detectors (counters) to measure the positions and intensities of the reflections. Of primary interest in this report is the goniometric method which uses counters to register the line positions and intensities directly. In this technique, partially diagramed in Fig. 2, a polycrystalline mass with a relatively flat surface has some grains oriented so the crystal planes of each "d" spacing are parallel to the specimen surface. The sample is moved around an axis vertical to the plane of the drawing so the x-ray beam impinges at angles from grazing incidence to nearly 90°; during this motion all crystals lying with planes parallel to the surface will reflect in turn. As the specimen is rotated about its axis, the detector also moves



Ag

d	hkl	I
2.359	111	100
2.044	200	40
1.445	220	25
1.231	311	26
1.179	222	12
1.025	400	4
0.937	331	15
0.914	420	12
0.834	422	13

Fig. 1 - Bragg's law and the schematic representation of reflection from a set of parallel crystal planes. The path difference, indicated by the intersection of the dashed lines with the adjacent ray, must be a whole number of wavelengths in order that additive reflections will emerge from the crystal. The simple geometric proof of this law appears in introductory texts such as Refs. 2 and 3. The perpendicular distance between planes in the crystal is designated "d." A typical powder diffraction pattern is also shown for metallic Ag giving the values of "d," Miller indices hkl of the planes in the crystal having the given spacing, and the relative intensity I of the diffracted rays.

through an arc on a finely machined circle graduated in degrees. The angular positions of the reflections are recorded, and the corresponding "d" values calculated from Eq. (1). It is possible, but not usual, to have a specimen in which no grains lie with diffracting planes parallel to the surface. In this case it might be mistakenly concluded that the material is noncrystalline. Sometimes a sample is encountered in which almost all grains lie with the same plane parallel to the surface. These, of course, all come into reflection position simultaneously to give an unusually intense reflection, and the sample is said to exhibit preferred orientation. If the orientation is nearly complete, it is impossible to use the result for identification purposes because only one or two lines of the diffraction pattern will be registered. It is not possible to make a positive identification on this basis. On the other hand, much useful information can sometimes be obtained from such samples; frequently it is of greater significance to determine a preferred orientation in a surface reaction deposit than it is to verify the identification of an already known material.

When x-rays pass through materials, they are absorbed and the efficiency of the absorption is a function of the atomic structures of the elements. A particular x-ray wavelength may be highly absorbed or may pass through a given material with very little loss in intensity. Figure 3 shows a plot of the mass absorption coefficients of the elements for characteristic radiation from a copper x-ray target. These coefficients, available in reference tables (7), are used in calculating the efficiency of the diffraction to be expected from a sample. The true density of the crystalline material, the void space in the powder, and the elements present in the specimen combine to give the experimentally observed diffraction intensities. On the basis of these specific values for absorption the

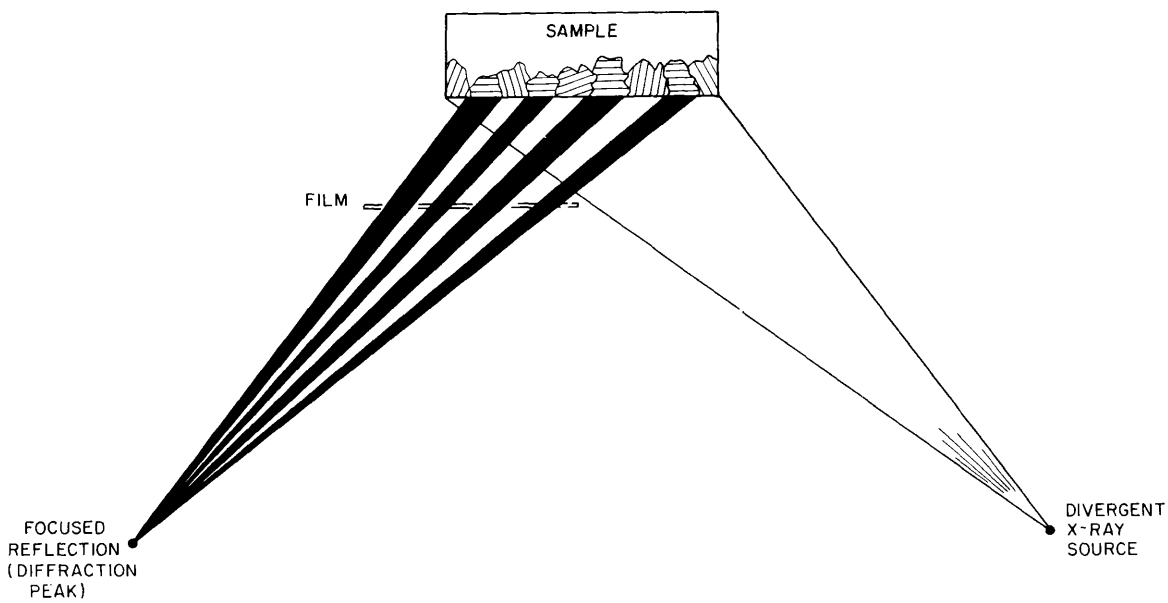


Fig. 2 - Schematic diagram of the principle of the diffractometric technique. The flat surfaces of the polycrystalline powder sample contain some grains with their crystal planes parallel to the surface. The x-ray beam will be reflected from these grains when the incident angle satisfies the Bragg equation given in Fig. 1. The diffracted rays from the individual crystals are shown in solid black in the diagram. For photographic registration making use of Berg-Barrett topography (13) photographic film is placed as close to the sample surface as possible and parallel to it. The individual reflections from crystals in the specimen surface will, under favorable conditions, be resolved.

measurements of surface film thickness (6) and quantitative analysis of mixtures (5) by XRD are performed.

In Fig. 4 is shown schematically the diffraction method used for calculating surface film thickness. The x-ray beam traverses the coating material for a distance of $2t/\sin\theta$. The original uncoated electrode reflects the beam at a setting of θ with an intensity of I_0. As the coating forms on the surface the initial intensity I_0 will decrease in accordance with the absorption in the coating material

$$I_c/I_0 = e^{-2\mu\rho(t/\sin\theta)}, \tag{2}$$

where I_c is the intensity observed from the coated electrode, I_0 is the intensity observed from the coating-free substrate, μ is the mass absorption coefficient of the coating material, ρ is the density of the coating material, and t is the thickness of the coating in cm.

During coating formation it can be observed whether the intensity of each of the diffraction lines in the pattern of the substrate decreases at the same rate. If this takes place, the coating is depositing uniformly; on the other hand, if only certain lines of the substrate pattern decrease in intensity, it can be concluded that the deposit is taking place preferentially on these crystal planes. Similar considerations apply during removal of reaction products. Once a coating builds up to a certain thickness, the pattern of the substrate is obscured entirely, and coating thickness can only be defined as exceeding the appropriate value. Laminated coatings may be analyzed in the same way; each layer in turn may be considered the substrate and changes in intensity used to calculate the thickness of the outermost coating.

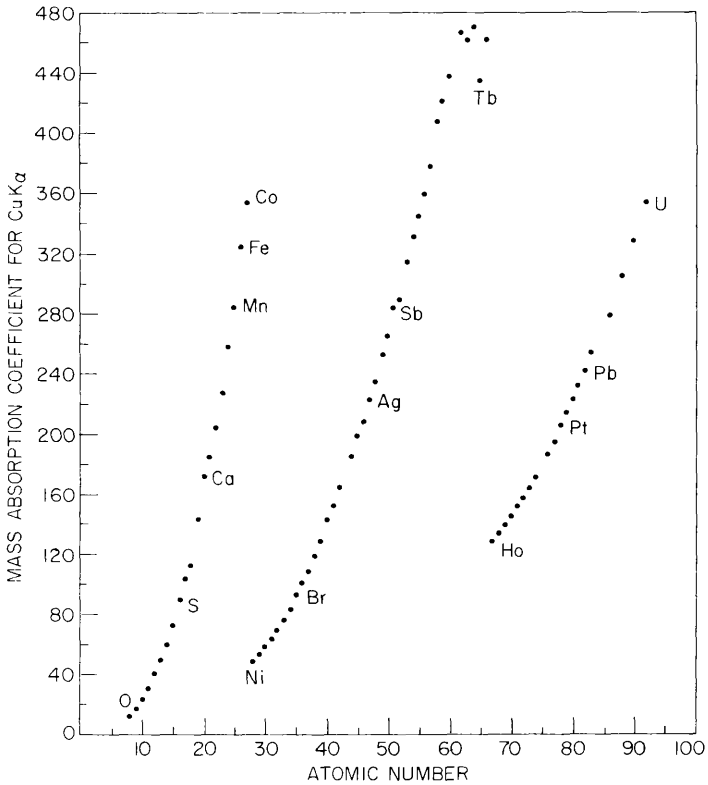


Fig. 3 - A diagram of the mass absorption coefficient for Cu K_α x-radiation of the elements with several of the more common metals indicated by chemical symbol. The absorption coefficient increases with the atomic number from O_2 to Co, then suddenly falls to a low value for Ni. This means that Ni is specifically transparent to the K_α radiation from a Cu target x-ray tube and performs as an excellent monochromatizing filter for this wavelength. Mass absorption coefficients for compounds are calculated on the assumption that the elements are present as a mixture. Thus a Ni compound may also serve as a satisfactory filter for Cu radiation. The mass absorption coefficients for the Ag oxides given in Table 1 were calculated from the individual coefficients of Ag and O.

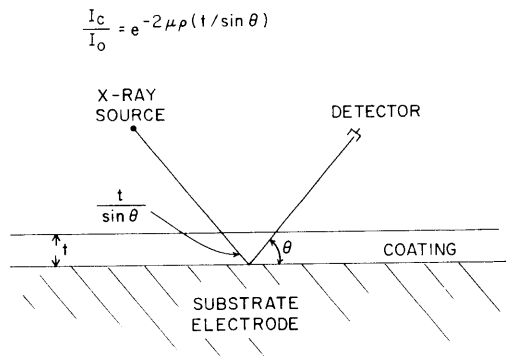


Fig. 4 - Scheme for measuring coating thickness by x-ray absorption. The intensity of the diffracted beam from the substrate is an exponential function of the coating thickness. This nondestructive method may be used to estimate the thickness of electroplated and other surface coatings.

But suppose a coating does not form as a uniform film. It may grow as dendritic or acicular crystals, absorbing some radiation but not covering the electrode uniformly. In this case the pattern for the substrate material continues to be detected when the apparent coating thickness (in electrochemistry this may be judged by coulometry) far exceeds the maximum limit. The relative intensities of the diffraction lines in these cases are more nearly like those obtained from mixtures of the powdered materials.

In mixtures of powdered crystalline materials each material behaves as though present alone, and the resulting diffraction pattern is a composite of the patterns from each pure phase. But, since the specimen is not a single material, the number of crystals of each phase present in the diffracting volume is a function of its concentration in the mixture. On the basis of these considerations x-ray diffraction can be used for quantitative analyses of powder mixtures. In most instances it is customary to make standard synthetic mixtures of the pure phases and establish nomograms for the analyses. The relation of the relative intensities of the diffraction lines from each material in a mixture is a linear function of concentration only in those cases where the mass absorption coefficients and densities of the compounds are very nearly the same, as in polymorphic forms of the same material. Thus the relative intensities for highly absorbing and poorly absorbing materials in a mixture will not be linear functions of their respective concentrations.

Alexander and Klug (5) have described the basis upon which the quantitative analysis of mixtures may be accomplished by XRD. The intensity of the diffracted beam is related to the characteristic absorption of each component of a mixture, and in the case of two components is expressed by the equation

$$\frac{I_1}{(I_1)_0} = \frac{x_1\mu_1^*}{x_1(\mu_1^* - \mu_2^*) + \mu_2^*}, \tag{3}$$

where I_1 is the intensity of diffraction from component 1 in the mixture, $(I_1)_0$ is the intensity of diffraction from pure component 1, x_1 is the weight fraction of component 1, μ_1^* is the mass absorption coefficient of component 1, and μ_2^* is the mass absorption coefficient of component 2.

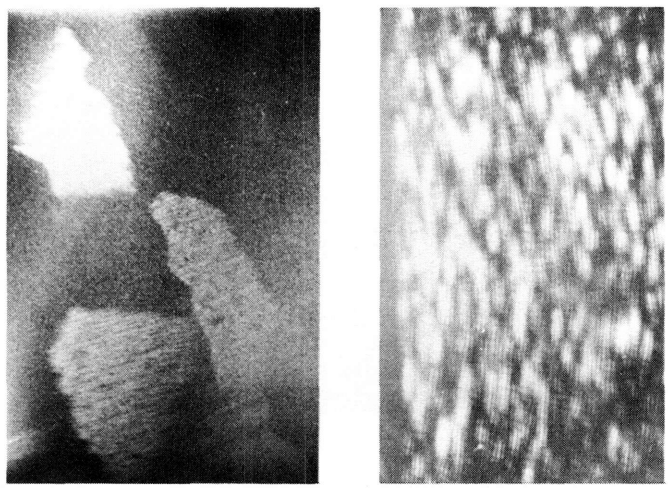
It is also possible under certain circumstances to estimate crystallite size and shape by XRD because the character of a diffraction line is a function of these. Recently this method has been used for measurements of grain size in metals. Although no examples of the application of this technique will be described in this report, it is mentioned here because it is an important application of XRD (2a, 3a, 8-10).

Qualitatively a material giving rise to a diffraction pattern characterized by broad rather diffuse lines is spoken of as having "poor" crystallinity, meaning that the crystals

are very small in size (usually less than 0.1μ), or that there is such a high degree of distortion in somewhat larger individual crystals that the lattice planes are tilted or displaced significantly with respect to each other causing the x-rays to reflect over a range of angles rather than at discrete well-defined Bragg angles. It is frequently possible to determine whether small crystallite size or lattice distortion is present in a sample by resorting to the technique known as x-ray diffraction topography.

As indicated above the diffraction "lines" are made up of myriad reflections from individual crystals. When a sample is very fine grained, the diffraction lines will be uniform in intensity, but if the crystals are larger, the lines will be spotty as they are resolved into individual reflections. This unique feature can be used to give valuable qualitative information regarding the nature of the reflecting crystals, and it can with careful experimental technique be further exploited with great profit, especially for examining the perfection of single crystals and grains (2b). For characterizing electrode reaction products the rather simple Berg-Barrett technique can be employed in conjunction with the diffractometric identification to establish qualitative descriptions of the nature of the crystals making up a surface or deposit. The method relies upon strategic placement of photographic film in the path of the diffracted x-ray beam. The fundamental concept is indicated schematically in Fig. 2. The individual reflections on the films may be examined at low magnification, and it is frequently possible to obtain images of individual crystals or grains such as seen in Fig. 5. This technique is known by several names, the most descriptive one being x-ray diffraction topography.

Splendid modern x-ray diffraction instrumentation is readily available at moderate investment, and in recent times methods for registering x-ray diffraction patterns have been greatly facilitated by use of the diffractometer. This instrument is a goniometer, simultaneously registering the angles at which x-ray reflections occur and their intensities. The x-ray machine in use for the electrochemical studies at this Laboratory is



a b

Fig. 5 - Berg-Barrett x-ray topographs taken by the method indicated in Fig. 2: (a) images of large grains in the surface of polycrystalline metallic Pb registered on fast dental film and (b) topograph of the surface of smooth rolled sheet Ag showing preferred orientation of most of the grains and elongation in the direction of rolling (vertical in the picture)

equipped with a horizontal circle goniometer to which an electrochemical cell has been fitted, permitting coordination of electrochemical treatment and x-ray diffraction examination (11). The electrode to be studied is a disk rotated half submerged in electrolyte, and the x-ray pattern is recorded from the top half of the disk face. The thin layer of electrolyte clinging to the surface absorbs some radiation; however as long as the rotation rate is constant this may be discounted as "background," and diffraction patterns of the electrode may be studied. The electrochemical treatment does not have to be interrupted during x-ray pattern registration, and it is feasible to make prolonged investigations, consecutively building up and removing the electroformed coatings.

The electrochemical cell shown in Fig. 6 has all parts made of Teflon except the screws, pulley, and the electrical contact system. An electrode of the specimen material, a disk 57 mm in diameter and up to 6 mm thick, is mounted vertically in the cell so that it is always partially submerged in electrolyte. The specimen disk is held tightly against platinum contact wires by a threaded retainer ring. The platinum contact wires pass through a hole in the drive shaft and are connected to a gold plated contact ring by a small screw. The moving contact is made through platinum leaf springs.

The x-ray beam passes above the cell case and is reflected from the upper portion of the rotating electrode, which is not submerged but remains wet with a film of electrolyte. A counter electrode faces the submerged part of the specimen disk in the same compartment of the cell. A reference electrode is placed in one of the other cell compartments where it does not shield the path of the x-ray beam. The rotation rate of the specimen disk is variable, and the time elapsing between total submersion and registration of the x-ray pattern may be quite short, limited only by the onset of splash. Diffraction patterns obtained from Pb and Ag anodes in the cell are shown in Fig. 7.

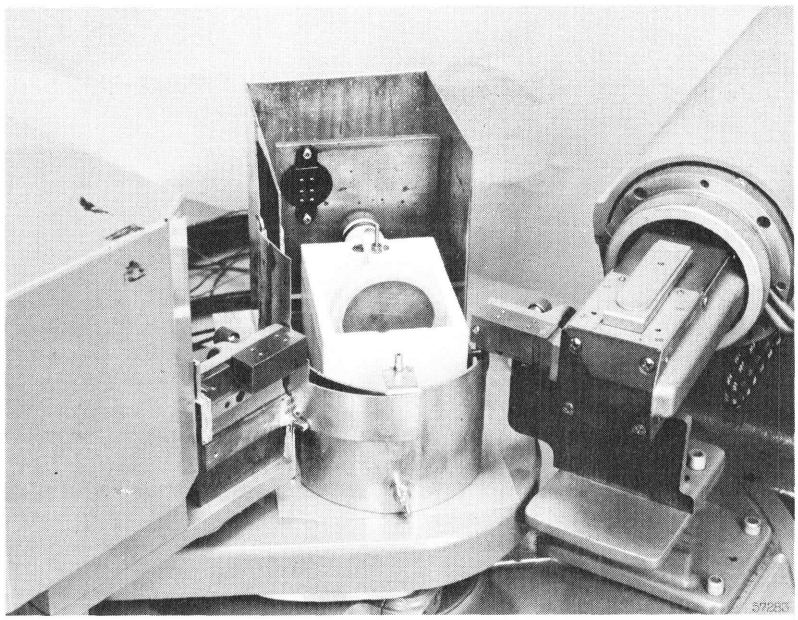


Fig. 6 - The electrochemical cell, in place on the x-ray machine, and the rotating disk electrode. The electrical connections for the counter and reference electrodes are made through the multiple plug on the rear plate. Part of the front x-ray shielding was removed for this photograph. The x-ray tube is at the right and the detector at the left.

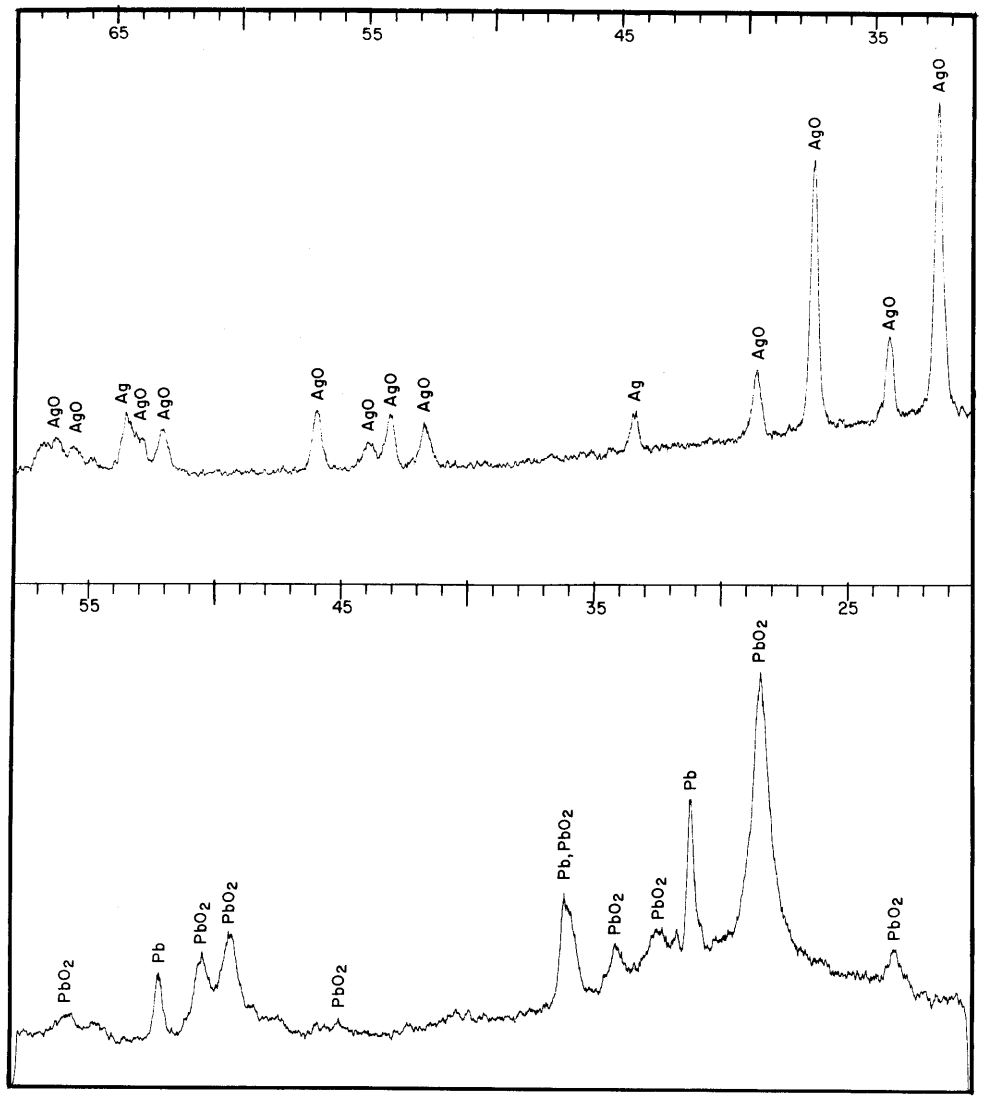


Fig. 7 - Diffraction patterns recorded during electrochemical treatment in the cell shown in Fig. 6. These are two patterns registered from Ag and Pb anodes in KOH solution. The pattern for AgO is very clear-cut, and the diffraction peaks are better defined than in the case of α PbO_2. This was usually true of the patterns obtained from the Ag electrodes. The differences in the background are particularly striking; that in the Ag case was close to a straight line, whereas anodic lead specimens usually showed broad bands such as that extending from the start of the pattern to 37°. The peaks of the lead pattern are broad because of the very small particle size of the deposits, and the broad band may indicate a considerable portion of the deposit is in an amorphous state. Electron microscopy has shown that anodic coatings on Pb are of very fine crystallite size, on the order of 0.1μ and smaller. Further work would be required to determine whether the broad band is caused by amorphous material or by lattice distortion. In these two patterns we have an example of what would be called "poor" crystallinity in the PbO_2 case when compared to the AgO pattern. On the other hand note that the pattern for the AgO does not have sharp, clear-cut peaks at the higher angles. For this reason when compared to a very well-crystallized material the AgO would also be called poor. Such designations are qualitative and comparative.

For studies requiring the absence of air the cell may be enclosed in a balloon of plastic material to form a gas-tunnel in which a positive pressure of a special atmosphere can be maintained. Connections to the gas supply and to the source and detector slits can be made with elastic bands. Heating or cooling coils may be immersed in the electrolyte.

To make x-ray diffraction topographs of the specimen surface rotation must be temporarily halted. When fast dental film is used, exposure times may be very short, and some useful topographs have been obtained with as little as 30 seconds exposure. The back of the Teflon disk carrying the specimen is scored so that the same area of the specimen may be repeatedly examined by diffraction topography.

These electrochemical and x-ray techniques used in combination permit us to: (a) identify surface reaction products in situ; (b) determine the thicknesses of uniform coatings; (c) determine the relative amounts of individual components in mixtures; (d) estimate crystal size; (e) characterize the orientation of surface deposits and substrates; and (f) coordinate the surface deposits with the electrochemical potential and coulombic measurements. To illustrate these applications some results of studies on the Ag electrode will be described briefly (12-14).

THE SILVER ELECTRODE

When Ag is anodized in KOH solution, two potential arrests are normally observed before oxygen gas is evolved. These arrests have been associated with the growth of two different oxides on the metal surface, Ag_2O and AgO. During discharge of the electrode the oxides are reduced to metallic Ag. These reactions may be driven in both directions so that Ag performs well as the positive plate of a secondary cell:

$$2Ag + (OH)^- = Ag_2O + H^+ + 2e$$

$$Ag_2O + (OH)^- = 2AgO + H^+ + 2e.$$

These reaction products have all been identified by XRD (12,13). During anodic treatment of the Ag the initial coating formed is Ag_2O, which passivates the metal, and when the surface becomes covered with this oxide, only very low currents may be passed at the Ag/Ag_2O potential. In effect, the underlying Ag is protected by the oxide coating from further attack. If significant additional current is forced through the electrode, it becomes polarized to a second higher level where the second reaction takes place, the oxidation of Ag_2O to AgO. It is usually observed that more coulombs may be added at this potential than at the lower one, showing that in addition to oxidation of the coating of Ag_2O, further underlying Ag is also oxidized. Eventually the metal again becomes passivated, this time by the coating of AgO, and the continued passage of significant currents results in polarization to a still higher voltage where oxygen gas is evolved. During gas evolution little or no additional Ag is oxidized. In the reverse of this process, the discharge, relatively little of the capacity is usually drawn from the system at the higher voltage level of the Ag_2O/AgO reaction, the major portion of the discharge occurring at the lower voltage associated with the Ag_2O/Ag electrode. In the practical battery these facts mean that the major portion of the charge occurs at the higher voltage while the major portion of the discharge occurs at the lower voltage. This power imbalance is a distinct disadvantage in the operation of this plate.

In Table 1 are assembled some data for Ag and its oxides, useful in considering the detailed studies of this electrode. The mass absorption coefficients for the oxides for CuK_α x-radiation were calculated by assuming superposed monatomic mixtures. The specific volumes are of interest because, in cycling, the metallic Ag electrode undergoes

Table 1
Some Physical Properties of Ag and Its Oxides

	At Wt or Mol Wt (g)	Density (g/cc)	Molar or Atomic Vol (cc)	Vol per Gram Atom Ag (cc)	Mass Absorption Coef for CuK_α
Ag	107.88	10.50	10.274	10.274	223
Ag_2O	231.76	7.24	31.998	15.999	208.49
AgO	123.88	7.71	16.049	16.049	195.87

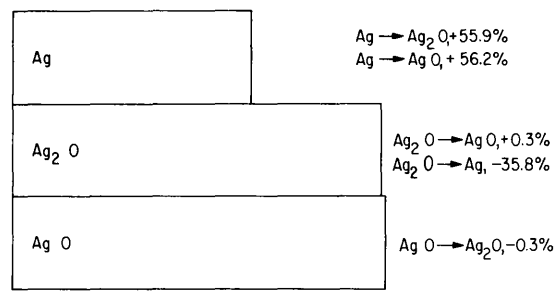


Fig. 8 - Diagram of the specific volumes of Ag, Ag_2O, and AgO indicating the relative changes to be expected upon charge and discharge of the electrode. The difference in volume between the two oxides is negligible, but there is a considerable volume difference between the metal and the oxides.

the changes in volume indicated by Fig. 8. The electrode has its maximum volume at full charge, whereas suitable counter electrodes would have maximum volume at discharge. These dimensional changes are probably important in the wearing of separator materials.

To illustrate the use of XRD for determining the mechanism of electrode processes the discharge of Fig. 9a, taken from Refs. 11 and 12, is cited. The previously cycled Ag electrode was charged at constant current coulometrically corresponding to a coating of AgO of 82,000Å thickness, assuming the area of the electrode was the apparent area. However using the mass absorption coefficient of AgO given in Table 1, Eq. (2), and the x-ray intensity data shown in Fig. 9a, we find that XRD shows an actual thickness of approximately 30,000Å. The ratio of these two figures is a measure of the surface roughness, which in this case of the Ag electrode is 2.75. This is a surprisingly low figure in view of the increase in electrochemical capacity of about 14 times developed by the cycling. This will be discussed further when the physical picturization of the Ag electrode is described.

At point P in the discharge shown in Fig. 9a XRD indicates that the electrode had become covered with an outer layer of Ag_2O; this point coincided with the fall in potential of the discharging electrode from the AgO/Ag_2O to the Ag_2O/Ag voltage plateau. It is obvious from the figure that a considerable amount of AgO remains on the electrode despite the fall in potential. Point P corresponds to about 19% of the coulombic capacity of the electrode. Again, using Eq. (2) and the data of Table 1, we find that XRD indicates a surface layer of Ag_2O approximately 8000Å thick. Subsequent discharge then proceeded by a most unusual mechanism: both oxides discharged simultaneously, but the diffraction data indicate that the AgO was discharging through an outer layer of Ag_2O with the constant thickness of 8000Å. On the other hand the growth of the metallic Ag crystals took place in the oxide layer in accord with the law of mixtures, Eq. (3), up to about 80% of the total capacity (Fig. 9b). Finally toward the end of discharge the intensity of the

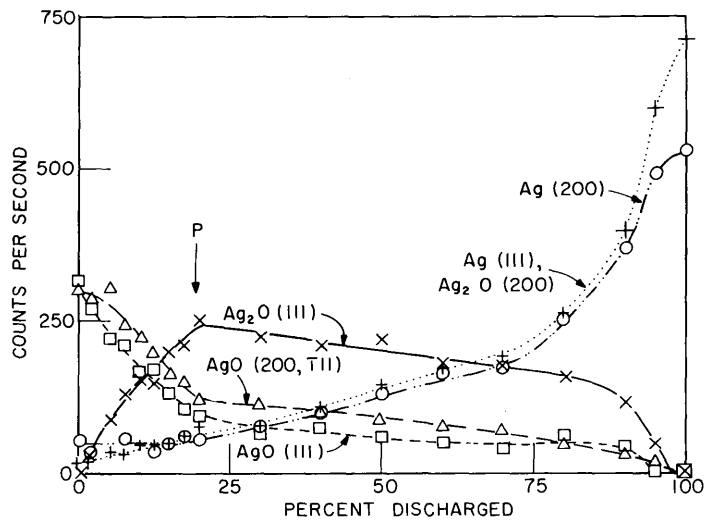


Fig. 9a - Intensities of the x-ray diffraction lines of the patterns of AgO, Ag_2O, and Ag plotted as a function of the percent discharge. The intensities of certain reflections only are shown as indicated. It is from the relative intensities of these diffraction lines that the discharge mechanism of the electrode may be interpreted according to Eqs. (2) and (3).

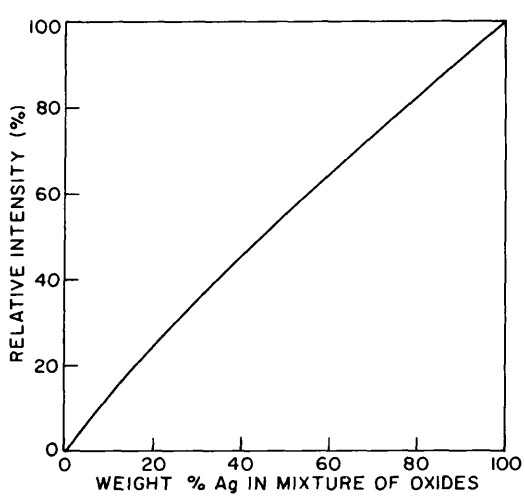


Fig. 9b - A plot of Eq. (3) showing the nearly linear relation of x-ray intensities characteristic for mixtures of Ag, AgO, and Ag_2O of varying composition. The plot of 9a shows that from about 19 to 75% of the discharge results in a mixture of Ag in the oxide mass.

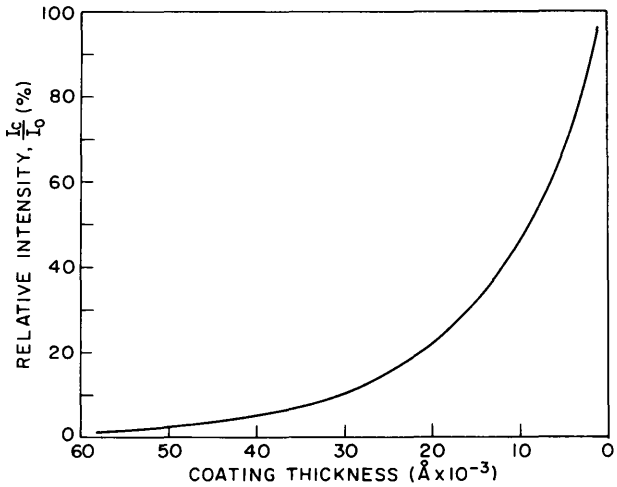


Fig. 9c - A plot of the removal of a coating of oxide from a Ag substrate showing the exponential relation of Eq. (2). This curve is similar to the final 25% of discharge shown in 9a where the intensities of the diffraction lines from the Ag substrate began to increase exponentially. In the initial 19% of the discharge, up to point P, the outer surface of the AgO coating was being covered by a layer of Ag_2O. It should be pointed out that if this were not the mechanism, at point P, the relative intensities of the patterns for AgO and Ag_2O would have been 4:1.

metallic Ag x-ray diffraction pattern increased exponentially, showing that at this final stage the discharge was also stripping away oxide coatings from underlying massive Ag in accordance with the coating law, Eq. (2) (Fig. 9c).

We can also establish a physical picturization of the discharge mechanism. It was possible to charge the original smooth Ag sheet to a depth of 6000Å, calculated on the basis of coulombs passed. If this is taken as the maximum depth of charge of a Ag surface, then the thickness observed by XRD of 30,000Å on the cycled electrode indicates that some mechanism has increased the thickness of the oxide by a factor of five. This could take place if the cycling developed a layer of spongy Ag on the electrode surface which when totally oxidized would produce a layer of oxide five times thicker than possible on a massive surface. In addition, those Ag crystals longer than 6000Å and with a cross section greater than 12,000Å would retain a core of metallic Ag after oxidation. A slow discharge would tend to grow larger Ag crystals and would lead to subsequent loss in capacity. This has been suggested as the cause of the observed fall in capacity of such plates following slow discharges (12).

It may be further concluded that the spongy Ag must be made up of particles close enough together to produce a coating having 2.75 times the apparent surface of the electrode. In other words, oxidizing the sponge gives rise to a smoothing of the surface by filling of valleys and congealing of adjacent grains of oxide. Inasmuch as the conversion of Ag to the corresponding quantity of oxide is accompanied by an expansion of 56% in volume (Table 1 and Fig. 8) such a process is to be expected. These effects are illustrated schematically in Fig. 10.

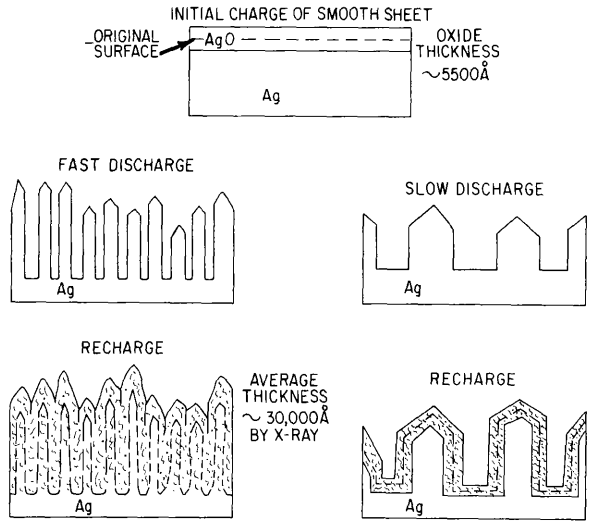


Fig. 10 - A schematic diagram of the Ag sheet electrode and the mechanism for the development of the capacity by formation of filamentous Ag crystals that can become totally oxidized on cycling. The original smooth sheet was oxidized to a depth of 6000Å. This could be increased to a depth of 30,000Å by cycling. The surface of the oxide was only 2.75 times the apparent area of the electrode because of the filling in of valleys and congealing of adjacent grains of the oxide. This may be explained as a result of the 56% volume expansion accompanying the conversion from Ag to AgO. It has been shown that capacity loss follows a slow discharge. This has been attributed to a loss in surface area of the reduced Ag. Slow deposition normally gives rise to large crystals as diagramed in the figure. The contours of the original Ag surface are shown as dashed lines, and the oxide coating as the stippled area.

The coulometric increase of 14 times in electrode capacity is in remarkably good agreement with the measurements of the coatings by XRD. The increase of 5 times in depth of oxide and 2.75 times in area corresponds to an increase of 13.75 times in capacity, within 2% of the measured coulombic capacity.

CONCLUDING REMARKS

The observations described in this report were made from recorder traces of the diffraction patterns of the operating electrode, rotating in the Teflon cell. The values are therefore statistical in nature; the counter response is statistical. Since the x-ray beam scans many grains of the oxides and base Ag on the rotating electrode, the registration can with some confidence be said to be truly random (2c). The precision of the measurements reported here would be expected to be approximately ±3% and could have been improved by scaling the intensities; nevertheless the agreement to within 2% of the coulometric measurements indicates that the actual data are in fact better than this anticipated precision.

REFERENCES

1. Burbank, J., Extended Abstracts I-6 of the Theoretical Electrochemistry Division, Electrochem. Soc. 5:74 (1967)

2. Barrett, C.S., and Massalski, T.B., "Structure of Metals," 3rd ed., New York: McGraw-Hill, 1966

   a. p. 155 ff

   b. p. 418 ff

   c. p. 133 ff

3. Klug, H.P., and Alexander, L.E., "X-Ray Diffraction Procedures," New York:Wiley, 1954

   a. Chapter 9

4. "Powder Diffraction File," Am. Soc. Test. Mater., Phila.

5. Alexander, L., and Klug, H.P., Anal. Chem. 20:886 (1948)

6. Friedman, H., and Birks, L.S., Rev. Sci. Instr. 17:99 (1946)

7. Internat. Tabellen z. Bestmg. v. Kristall., Vol. 2, Berlin:Borntraeger, p. 577, 1935

8. Ebel, H., Z. Metall. 56:560 (1965)

9. Ebel, H., and Effenberger, E., Z. Metall. 58:20 (1967)

10. Vorob'ev, G.M., and Kotova, L.I., Ind. Lab. USSR 32:820 (1966); Translation 32:1006 (1967)

11. Burbank, J., and Wales, C.P., J. Electrochem. Soc. 111:1002 (1964); "Electrolytic Cell for X-Ray Diffraction Studies of Electrode Phenomena," NRL Report 6050, Mar. 1964

12. Wales, C.P., and Burbank, J., J. Electrochem. Soc. 112:13 (1965); "Oxides on the Silver Electrode Part 2-X-Ray Diffraction Studies of the Working Silver Electrode," NRL Report 6171, Oct. 1964

13. Wales, C.P., and Burbank, J., J. Electrochem. Soc. 106:885 (1959); "Oxides on the Silver Electrode," NRL Report 5298, May 1959

14. Burbank, J., and Wales, C.P., Extended Abstracts J-1 of the Battery Division, Electrochem. Soc. 12:102 (1967)

This page intentionally left blank.

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

IDENTIFICATION AND CHARACTERIZATION OF ELECTROCHEMICAL REACTION PRODUCTS BY X-RAY DIFFRACTION

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on the problem.

5. AUTHOR(S) *(First name, middle initial, last name)*

Jeanne Burbank

6. REPORT DATE December 20, 1967	7a. TOTAL NO. OF PAGES 20	7b. NO. OF REFS 14

8a. CONTRACT OR GRANT NO. C05-14 b. PROJECT NO. SF 013-06-06-4366 c. RR 001-01-43-4755 d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6626 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research and Naval Ship Systems Command) Washington, D.C. 20360

13. ABSTRACT

The application of x-ray diffraction methods to electrochemical studies is demonstrated by examination of the surfaces of polycrystalline solids by reflection diffractometry, operation of a cell designed for simultaneous x-ray and electrochemical studies, and the Berg-Barrett topographic technique. Silver anodes are used for illustrating the kind of information readily obtained by these methods: identity of crystalline reaction products associated with electrochemical phenomena, physical characterization of reaction mechanisms involving multiphasic coatings, distinction between large grains and preferred orientation, and estimations of coating thickness and crystal size.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
X-ray diffraction						
Reflection diffractometry						
Polycrystalline solid surfaces						
Electrochemical reaction products						
X-ray diffraction topography						
Bragg's law						
Silver anodes						

DD FORM 1 NOV 65 1473 (BACK) (PAGE 2)

GPO 934-438

Security Classification