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# Crystallographic Changes During Oxidation (Charging) of the Silver Electrode

## Part 1 - Initial Oxidation of an Industrial Sintered Plaque

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## ABSTRACT

The Ag electrode has been studied during oxidation using the optical microscope. As a preliminary to other, more detailed experiments, the oxidation during the first charge of an unused sintered Ag plaque has been observed as Ag was converted first to $Ag_2O$ and then to AgO. The initial oxidation occurred on the smaller particles of Ag, and these were usually completely oxidized by the end of charge, whereas the larger Ag particles were left largely unconverted. The rate of reaction was quite unequal in different areas of the electrode. AgO crystals were larger than $Ag_2O$ crystals and may have blocked the surface in some areas. Both particle size of Ag and the formation of dense layers of AgO may have limited complete oxidation and may partially have been responsible for the inability of the electrode to produce the full capacity that was theoretically possible.


## PROBLEM STATUS

This is an interim report; work is continuing on the problem.

## AUTHORIZATION


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# CRYSTALLOGRAPHIC CHANGES DURING OXIDATION (CHARGING) OF THE SILVER ELECTRODE

## Part 1 — INITIAL OXIDATION OF AN INDUSTRIAL SINTERED PLAQUE

## INTRODUCTION

The Ag electrode forms one element of the Ag-Zn and the Ag-Cd storage batteries, which are important as high-rate and high-capacity power sources. The use of these batteries is limited by several factors, including the capacity decrease that often occurs as the batteries are used and the necessity to charge the batteries at a relatively low current if full capacity is desired. The reactions and products resulting from the cathodic reduction of silver oxide electrodes and the oxidation of metallic Ag electrodes in alkaline solution were identified previously by subjecting the electrodes to x-ray diffraction after removal from the cell (1) and by x-ray diffraction of an electrode in an electrolytic cell which permitted x-ray examination simultaneously with electrochemical oxidation and reduction (2). These studies have shown that, when a Ag electrode was anodically oxidized (charged) at constant current in an alkaline solution, there was a first potential plateau where $Ag_2O$ formed having the $Cu_2O$ type of face-centered cubic structure; this plateau was followed by a second potential plateau with the formation of monoclinic AgO. These studies also established that there was no evidence of a silver suboxide, an oxidation state higher than AgO, a solid solution, or an alloy of oxygen and silver.

The x-ray diffraction study made on highly oriented, smooth rolled sheet Ag also established that physical changes occurred in the electrode (2). The AgO crystal size and the amount of AgO formed varied inversely with charging current density, with the higher charging rates resulting in tight coatings of small AgO crystals that limited further oxidation. Reactions took place initially at the outer surface of the electrode with oxidation to $Ag_2O$ and AgO taking place with the formation of distinct crystals.

Following the reactions of an electrode by means of microscopic examination at various stages of the charge and discharge process can be of considerable value in understanding what processes occur, if the phases present can be identified. The x-ray diffraction studies referred to above have eased the problem of microscopic examination, since only the three phases — Ag, $Ag_2O$, and AgO — were expected to be present and needed to be identified in a microscopic study.

A preliminary microscopic examination of this system (3) has established that these three phases can be seen and differentiated from one another and that the crystals formed are usually large enough to be seen readily under the optical microscope. It is hoped that further study will lead to a correlation of crystallographic and morphological changes with such factors as charge acceptance and discharge rates. This study may suggest ways in which the crystallography can be modified to improve the performance of the batteries which use Ag electrodes.

The electrode that was used in the preliminary microscopic examination (3) had been cycled many times (218 cycles) before being removed for microscopic examination. This electrode had undergone considerable change in its structure because of corrosion of the Ag grid, repeated solution and reformation of crystals of $Ag_2O$ and AgO, and repeated electrochemical reduction of the oxides giving Ag in a different form from that originally present.

It was, therefore, considered desirable to begin the more thorough study of the electrode with unused sintered Ag plates, which had been obtained from a battery manufacturer. Using this material, the morphological changes could be followed from the first stage of oxidation to the last throughout repeated oxidation and reduction cycles.

This report covers the observations made during the first anodic oxidation of an unused sintered Ag electrode in KOH solution.

## PREPARATION OF THE ELECTRODES

The samples were taken from two electrodes which had been manufactured commercially for use in a Ag-Zn storage battery that was designed to discharge at comparatively low rates, requiring 1 or more hr for a complete discharge. The electrodes consisted of sintered Ag on a grid of expanded sheet Ag. The grid was much closer to one surface of an electrode than to the other surface. The electrodes had never been charged. Electrode dimensions were 41.5 mm wide by 38.0 mm high by 0.8 mm thick.

A piece of plastic 3.2 mm thick was made into a U-shape by cutting out a section larger than the width and height of an electrode. This plastic U was wrapped with five layers of treated cellulose separator to slow the diffusion of soluble Ag species. The top of the plastic U was open so that an electrode could be removed and reinserted without unwrapping the separator. Two other sintered Ag electrodes of the same size were also wrapped with the cellulose separator. These two electrodes were put on each side of a removable electrode in a cell and were connected in parallel to serve as counter electrodes. The cell contained an excess of 35% KOH solution and was kept at approximately 25°C.

The removable electrodes were charged individually at the current estimated to require 20 hr for a complete charge on the initial cycle. This current was 108 ma for an electrode before the first sample was removed. Current was interrupted at several points in the charge; the electrode was removed from the cell and a sample cut from the electrode. Then the remainder of the electrode was replaced in the plastic U that had been wrapped with separator. When the charge was resumed, current was lowered an amount sufficient to compensate for the removal of each sample so that current density on the remainder of the electrode was unchanged. Although the electrodes had never been charged before, experience with other electrodes of this size indicated a rough approximation of the total charge capacity to be expected and the approximate capacity that might be reached before the potential would rise to the $Ag_2O/AgO$ plateau. The charge capacity accepted by the two electrodes was not the same, however.

Four samples approximately 19 by 21 mm were cut from each removable electrode. Samples from one electrode were taken at points A, B, C, and E in Fig. 1, and samples from the other electrode were taken at points B, C, D, and E in Fig. 1.

One sample (point A in Fig. 1) was taken from an unused electrode before the first charge. The sintered Ag electrode was white, and one surface showed the diamond-shaped pattern of the expanded metal grid.

Samples were taken when both electrodes had received approximately half of the capacity they would accept before potential rose to the $Ag_2O/AgO$ plateau (point B in Fig. 1). One electrode was charged in fresh KOH solution and operated with a new cellulose separator. The surface of the sample from this electrode was still white, indicating unoxidized Ag, but the interior of the electrode exposed by the cutting was black. The second electrode was charged within a separator that had been used for 22 charge-discharge cycles and was in an electrolyte that had been used for seven cycles. The surface of the sample from this electrode was mostly an even gray color, with some

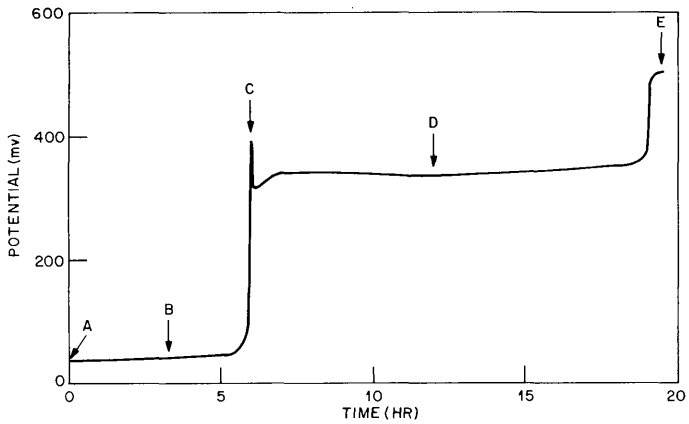


Fig. 1 - Curve showing typical potentials during the initial charge of a sintered Ag electrode. Letters A through E indicate the points at which samples were removed for microscopic examination. Potentials are given with respect to the $Ag/Ag_2O$ reference electrode.

white visible through the gray on the grid side. The interior of this sample, where exposed by the cutting, was an even gray color. Both samples had received the same ampere-hours of charge. Judging by the total charge capacity that other samples of these two electrodes accepted, the sample from the electrode charged in fresh KOH solution had received approximately 17% of the total capacity it would accept at the 20-hr charge rate before the potential rose to the oxygen evolution value, and the sample from the electrode charged in used KOH solution had received 14% of the capacity it would accept.

Samples were taken from both electrodes when charge potential rose to the peak that marks the beginning of the $Ag_2O/AgO$ potential plateau (point C in Fig. 1). The surfaces of the electrode charged in fresh KOH solution were a chocolate-brown color, while the electrode charged in the used KOH had a surface that was black with some lighter streaks. The electrode in fresh KOH solution was then charged until the capacity accepted per unit area was twice the capacity required to reach the potential peak, and a sample was taken at point D in Fig. 1. The electrode surface showed irregular patches of gray.

For the final two samples, both electrodes were charged until strong oxygen evolution was occurring (point E in Fig. 1). When strong oxygen evolution began, the electrode in fresh KOH had been charged to approximately 71% of the capacity theoretically possible for the weight of the Ag particles present. The side of this electrode closer to the expanded metal grid still had some areas of two shades of gray, while the other side was mostly one shade of gray. Both sides of the electrode charged in used KOH solution were gray, with some variation in the shades of gray. This electrode had been charged to approximately 87% of the capacity theoretically possible.

The steps in the preparation of the samples for microscopic examination, and the difficulties experienced in the preservation of the polished samples, have been covered in some detail in a previous report (3). For this reason only a brief account is given here. After each sample had been cut from an electrode, the sample was immediately put in several changes of water to wash out the KOH solution. Then the sample was dried in a vacuum and, while still under vacuum, impregnated with a clear plastic. After the sample had been returned to atmospheric pressure, it was heated at 40°C for 8 hr to

cure the plastic. In the next steps the sample was cut into a cross section, ground, and polished. Then the sample was ready for microscopic examination.

## MICROSCOPIC EXAMINATION AND DISCUSSION OF THE OBSERVATIONS

The various changes that occurred during the oxidation of this electrode will be presented by first describing the changes observed in the macrostructure and then the changes observed in the microstructure. As used here, macrostructure refers to features that can be differentiated at relatively low magnifications, those below 250X. These features can show gross changes that occur, such as a change in the thickness, the apparent porosity, the color, or the reflectivity of the electrode. While individual crystals cannot be seen and individual phases cannot be differentiated at these low magnifications, it is still possible to tell whether the reaction is occurring uniformly throughout the electrode and to observe changes in the manner in which crystal growth tends to obstruct the openings in the active material.

At higher magnifications the true microstructure of the electrode can be observed. Provided that samples were taken at the correct points and that magnification was sufficient, individual crystals could be detected as well as changes that occurred in crystal form during the oxidation process and the metamorphosis from one form to the other. For practical purposes the limit of real magnification with the optical microscope is around 1400 to 1500X. Fortunately, the crystals observed so far on the Ag electrode have been of a size that can be seen at magnifications well within the practical range of magnification. The highest magnification used for photographs in the present work was 1600X (before reduction for reproduction). Although much higher magnification is easily obtained, it results in no increased resolution and is usually referred to as "empty" magnification. Other factors, such as flare, lack of contrast, and grain in the photographic film being used, cause problems that may result in a picture that is inferior to the actual view as seen by the eye.

The three phases — Ag, $Ag_2O$, and AgO — were quite distinct from one another and easily identified in the photographs. Metallic Ag was highly reflective in the polished samples and appeared as white or very light gray in the photographs; $Ag_2O$ appeared as dark gray and AgO as an intermediate shade of gray. The darkest color in the photographs was produced by the plastic with which the samples were impregnated.

### The Sample Before Being Charged

Macrostructure — For each sample discussed in Ref. 3, a composite picture was prepared from matched photographs of adjacent areas to give a panoramic view of a portion of the electrode at 100X magnification. This was necessary, since the macrostructure varied to such an extent that a photograph of a single small area was inadequate to record all of the structure variations that were present.

A similar panoramic view was prepared of each of the samples described in this report. Although the macrostructure of the samples of this series was much more uniform than that of the previous series, these panoramic views still proved extremely useful when making comparisons. The macrostructure of the sintered Ag electrode before being charged (point A in Fig. 1) of the present report was quite different from that found previously. An example of this difference can be obtained by comparing Fig. 2 with Fig. 3. Figure 2 shows the type of electrolytically produced Ag obtained from the reduction of the silver oxides after the electrode had received over 200 charge-discharge cycles. The appearance of the sintered and uncharged Ag electrode that was used in the present investigation is shown in Fig. 3. Both figures are at the same magnification and

similarly oriented, with the two surfaces of the electrode being shown at top and bottom of the photograph in Fig. 3. This would also be the case with Fig. 2, except that the cross section had become too wide to be entirely shown in the photograph at this magnification; thus, a surface is shown only at the bottom of the photograph. The sample shown in Fig. 2 was about 20% thicker than the new electrode, and this expansion may be an effect produced by the cycling.

Figures 2 and 3 both include a portion of the grid of expanded Ag sheet metal. The relative size of the grid section shown was not significant, as the apparent size depended both upon the angle of sectioning and the location in the Ag sheet where the cut was made. It was significant to compare the smooth and regular outline of the grid section in the new electrode (Fig. 3) with that of the grid section shown after over 200 charge-discharge cycles (Fig. 2). The latter grid had corroded during the cycling, and its outline had become very irregular. The original cross section of the grid had very probably been greatly reduced.

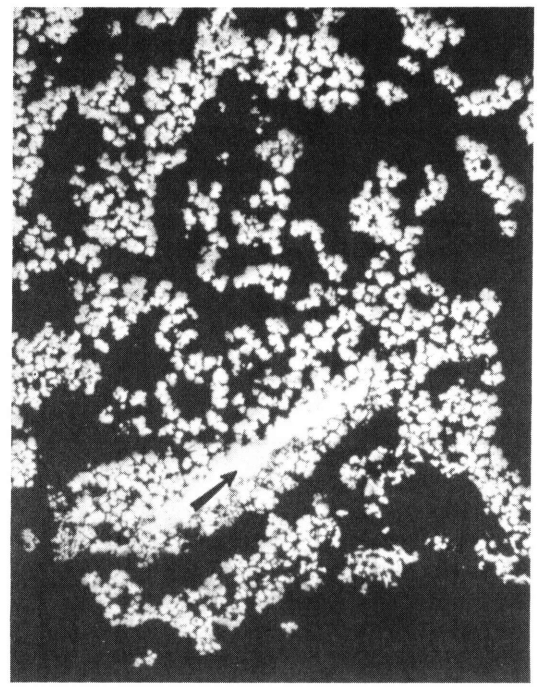

Fig. 2 - An example of the type of macrostructure found in a reduced (discharged) electrode after many cycles of charge and discharge. The electrolytically reduced Ag particles are granular in appearance but show an open distribution indicating unhampered access to electrolyte. The black arrow indicates the residue of a section of the expanded Ag sheet used as a grid (as seen in cross section). Lines forming the squares have a 238-$\mu$ separation in this and all other figures where the original magnification was 100X. This and all of the following figures are cross sections of the electrode.

It can be seen that the structure of the Ag making up the electrodes was quite different in the two samples. The Ag particles in the sample represented by Fig. 2 were large and granular in appearance and generally of a fairly uniform size. Each Ag particle looked as if it was more or less distinctly separated from the next, and the void space surrounding each group of particles was quite large. The particles were in contact with each other, however, in planes other than that of the cross section. In the sample illustrated by Fig. 3 the Ag was present in a wide range of sizes, with many of the individual particles too small to be visible at this magnification (100X) and with other particles larger than those shown in Fig. 2.

Although the material such as seen in Fig. 3 showed a high order of porosity at higher magnification, the major number of the voids were quite small and well distributed among the smaller particles of Ag. Electrolyte penetration was probably easier among the granular particles such as shown in Fig. 2.

While the proportion of large to small particles varied considerably in different areas of the unused sintered electrode, the general appearance of the macrostructure remained fairly uniform and comparable to that in Fig. 3. The really significant variations in structure were not seen until higher magnification was employed.

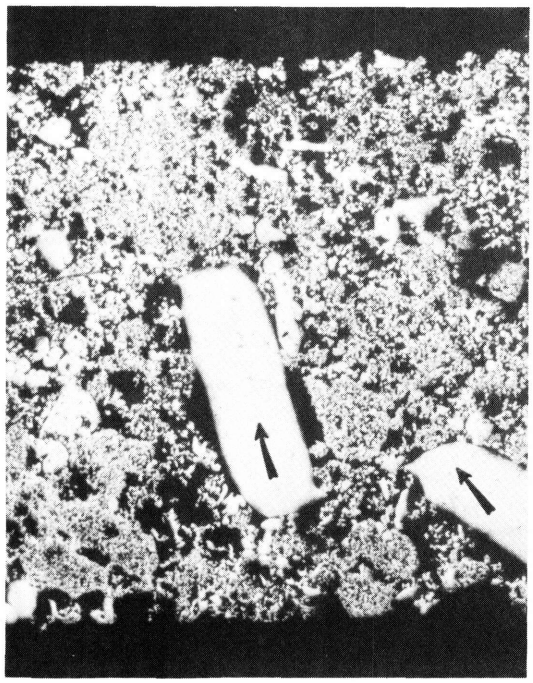

Fig. 3 - The original structure found in a commercially prepared, sintered Ag electrode. Although the structure seems to be less porous than that shown in Fig. 2, higher magnification showed that the porosity was actually quite high despite the fact that the Ag particles are much closer together than is the case in Fig. 2. Black arrows indicate portions of the Ag grid. The original magnification was the same as in Fig. 2.

Microstructure — When the magnification was increased to 250X, it was determined that a major portion of the Ag particles were quite small. The particles were much smaller than the granular particles (Fig. 2) found in the previous microscopic examination (3). Figure 4 shows that many of the quite small particles appeared to be enclosed together in an aggregate with a very definite outline. The boundary of this larger aggregate resembled in appearance and size some of the larger solid particles of Ag.

At the higher magnification of 800X (Fig. 5) the individual particles of Ag could be seen more clearly, and the agglomerates were found to be quite porous and to consist of individual particles with considerable variation in size and shape.

For comparison, Figs. 6 and 7 show at the same magnification (800X) the range of particle size and shape that was found in the electrolytically reduced Ag formed by discharge of the plate after 218 cycles. Although the size of the particles in Fig. 7 was even smaller than those shown in Fig. 5, the small particles were not very numerous in the electrolytically reduced sample with over 200 cycles, whereas most of the particles were small in the unused sintered electrode used in the present investigation.

### The Samples Charged to Half the Capacity of the $Ag/Ag_2O$ Potential Plateau

Samples were taken when both electrodes had received approximately half of the capacity that they would be expected to accept before the potential rose to the $Ag_2O$/AgO plateau (point B in Fig. 1). One sample had a white surface, indicating unoxidized silver, but the interior of the electrode exposed by the cutting was black. The second electrode to be prepared had a gray surface, probably the result of black $Ag_2O$ and white Ag both being present. After impregnation it was observed that the surface of the second sample had lightened considerably beneath the plastic layer, and a slight yellow discoloration was seen in the plastic surrounding the sample.

A number of additional electrodes were charged to this same point and beyond, and after various experiments the following observations were noted. When an electrode was charged at the $Ag/Ag_2O$ potential plateau until the surface became black and, after washing and drying, was immersed in the polyester resin used for impregnation, there was an immediate but very brief generation of gas bubbles, while the surface of the electrode usually assumed a white color almost immediately, indicating reduction of $Ag_2O$ to Ag. The same reaction was noted with or without the catalyst that was added to polymerize and harden the resin, but the reaction was slowed down if the resin was first subjected to a vacuum, presumably with the loss of a small amount of low-boiling constituent.

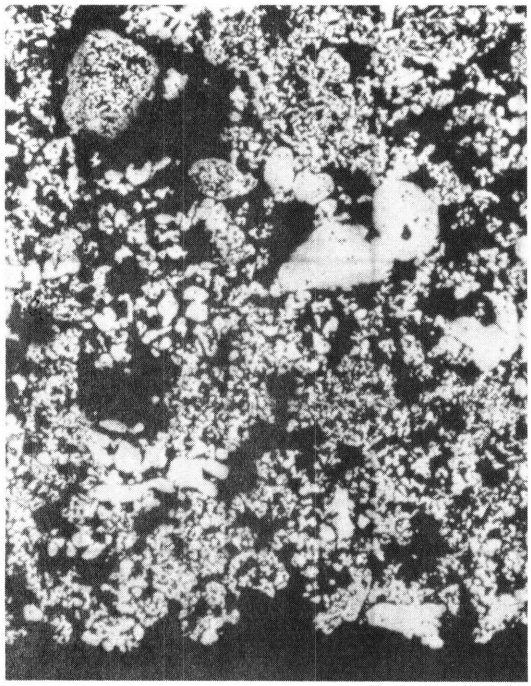

Fig. 4 - A portion of the unused sintered electrode of Fig. 3 at higher (250X) magnification, showing the manner in which the smaller particles of Ag had agglomerated into masses of larger size. Note the similarity in size and shape of these larger masses to the larger of the solid Ag particles that can be seen in parts of the photomicrograph. The dark background represents areas filled by the plastic and, therefore, also areas that were originally void in the electrode. Lines forming the squares have a 95-$\mu$ separation.

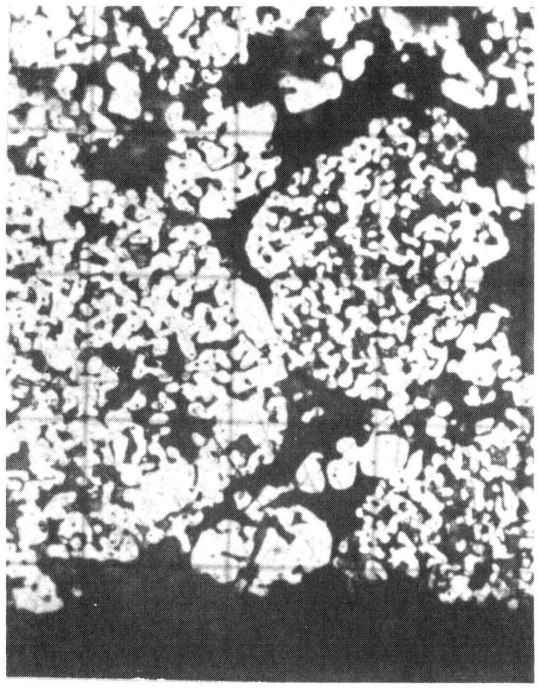

Fig. 5 - An area of the unused sintered electrode at even higher original magnification (800X) than Fig. 4. The Ag particles are, in general, small, very irregularly shaped, and in an assortment of sizes. The agglomerates are quite porous and the particles of which they are composed tend to create channels of rather small width and considerable complexity. Lines forming the squares have a 30-$\mu$ separation in this and all other figures where the original magnification was 800X.

The reaction took place only at the sample surface; the cut edges were not involved. If the white Ag surface that had been formed by the reaction with the resin was removed by scraping, the underlying material was found to be black and usually to remain black while in the liquid resin, although sometimes a slight lightening of the surface indicated a partial reduction of the $Ag_2O$. More heavily oxidized samples and those treated as above that had been allowed to remain in the dry state overnight either did not react when immersed in the resin or reaction occurred slowly during periods of more than 24 hr. Reagent-grade $Ag_2O$ was not appreciably reduced by the resin even after periods of immersion ranging up to 1 week, although the resin became dark brown. Observation of the oxidation process in several electrodes indicated that the interior usually became oxidized to $Ag_2O$ before the white disappeared from the surface.

It is evident from the above that some factor was different at the surface of the electrode. Whether this difference was merely that the oxide layer was very much thinner and more easily reduced to Ag or that there was for some reason increased activity

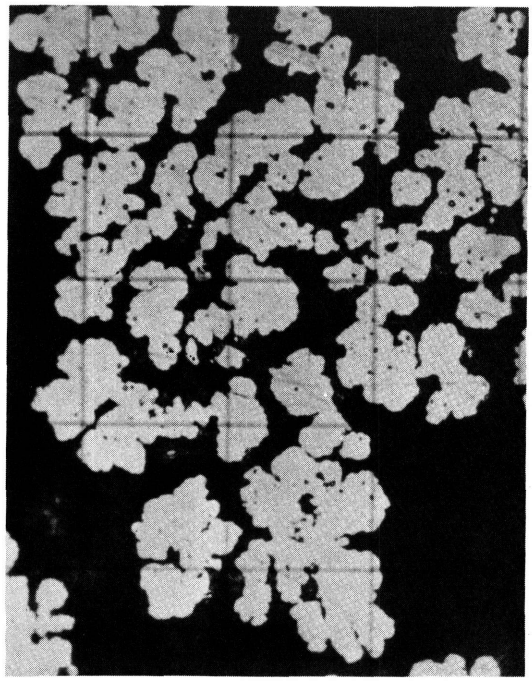

Fig. 6 - An illustration of the type and size of particles of Ag formed by electrolytic reduction after 218 charge-discharge cycles. Particles of this general configuration made up the major portion of the electrode. They should be compared with the Ag particles of Fig. 5, taken at the same original magnification (800X), and the Ag particles of Fig. 2.

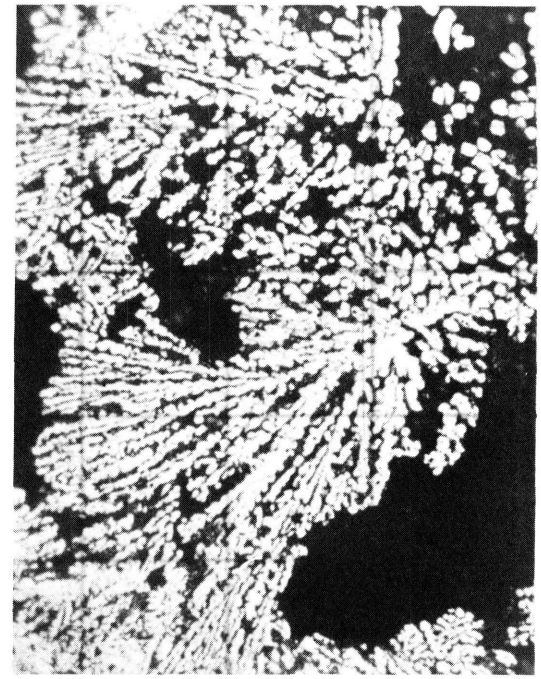

Fig. 7 - The smaller, needlelike crystals of Ag which formed in some areas of the same electrode as shown in Fig. 6. The size of these particles is close to those shown in Fig. 5, taken at the same original magnification (800X). Such areas as shown here were not numerous in the cycled electrode, however.

at this interface has not been determined. It was also evident that the polyester used for impregnation of the samples was not ideally suited for the purpose. Since nothing but the surface layer appeared to be altered even for much longer periods of immersion in liquid polyester than was the case in the impregnations, use of this polyester did not appear to invalidate observations other than some of those at the surface.

The samples shown in this report had already been impregnated with the polyester before the above observations were noted. Since that time, experimentation with epoxy formulations has discovered two epoxy formulations that cause no discernible reaction at the surface or elsewhere in the electrode; one of these has a sufficiently low viscosity to enable successful impregnation to be made. In other respects it is not as satisfactory as the polyester used previously and in the present investigation; other formulations will be tried before reporting further on a suitable impregnating agent.

Macrostructure — Both samples had received the same ampere-hours per unit area, and both were so nearly identical in microscopic appearance that they will be discussed as one. The macrostructure of these samples, charged to point B in Fig. 1, had not changed very much from that of the original uncharged sintered plate, as shown by Fig. 8. The most noticeable difference was the darkening of the macrostructure caused by the oxidation of the Ag particles. Approximately 24% of the Ag particles had been oxidized to $Ag_2O$; this oxidation caused considerable darkening of the samples.

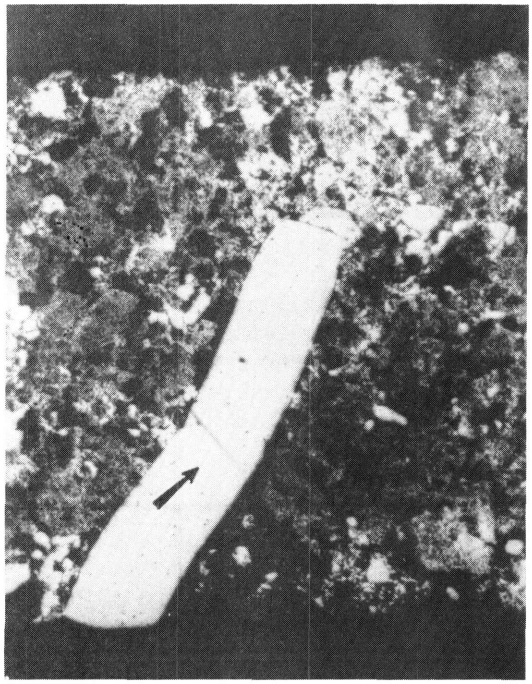

Fig. 8 - An illustration of the macrostructure found in the electrodes charged to point B in Fig. 1. Darkening of the electrode in some areas is the result of $Ag_2O$ formation around the smaller particles. It can be seen that the oxidation was not uniform, as some areas are much brighter than others. The black arrow indicates a portion of the grid. The original magnification was 100X.

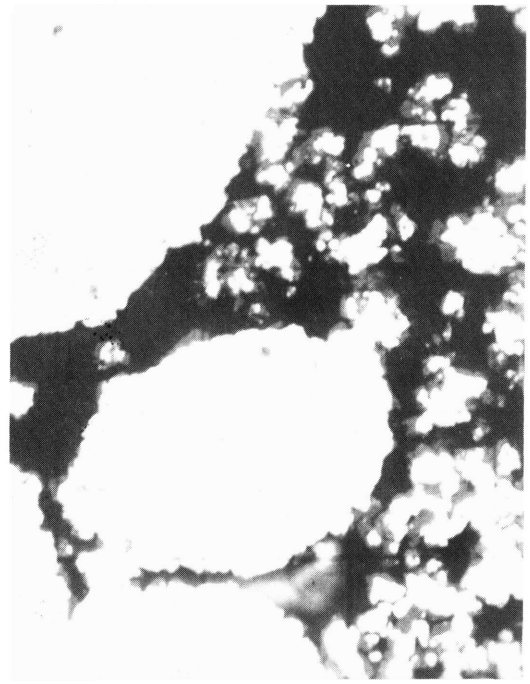

Fig. 9 - A portion of the sample shown in Fig. 8 but at 1600X magnification. Note particularly the comparatively greater oxidation that has occurred on the small particles of Ag. Lines forming the squares have a 15-$\mu$ separation in this and all other figures whose original magnification was 1600X.

Microstructure — At higher magnification (1600X) the individual particles of Ag could be seen more clearly, and it was found that the smaller particles were covered with easily discernible individual crystals of $Ag_2O$ as can be seen in Fig. 9. Figure 9 also illustrates that the smaller Ag particles were more reactive than the larger. The smaller particles were oxidized sooner and much more extensively than were the larger particles. The smaller particles did not react to the same extent in all parts of the samples. In a few areas the small Ag particles, like the larger, had very few $Ag_2O$ crystals on their surfaces. In other areas all of the smaller particles, and even some of the larger particles, were completely covered with $Ag_2O$ crystals.

In addition to the reaction being nonuniform throughout the central portion of both samples, no reaction at all appeared to have taken place along a clearly defined layer at each surface of one of the samples. Figure 10 illustrates this statement and represents the sample that had a white surface before impregnation with the polyester. One of the electrode surfaces is shown at the bottom of the photograph. In this photograph polarized vertical lighting was used so that all polished metal surfaces would normally appear dark except where fairly large scratches appeared. Occasional suitably oriented small surfaces just below the section surface also appeared as small white spots. If large areas of the surfaces below the level of the sectioning were bright, however, then

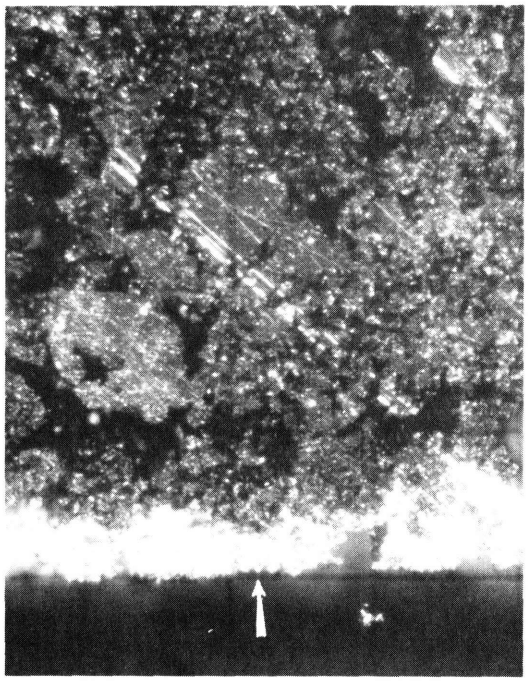

Fig. 10 - An area of the sample shown in Figs. 8 and 9 but near the surface of the electrode. The original magnification was 400X, and the light was polarized. Note the brightly reflecting layer at the surface (white arrow) that indicates the presence of unoxidized Ag particles. The white streaks diagonally across the picture are caused by scratches in the specimen. Lines forming the squares have a 60-$\mu$ separation in this and all other figures whose original magnification was 400X.

regardless of the orientation of subsurfaces the voids between the crystals would be seen as bright due to the random reflections from below the level of the section. Except at the electrode surface, however, these voids were dark, indicating the presence of a film of the dark oxide, $Ag_2O$. At the surface of the electrode, on the other hand, the reflection was so intensely bright that the area shown became overexposed in the photograph, and detail is lacking. This indicated that no $Ag_2O$ was present within the surface layer. The sample that had been gray on the surface before impregnation (probably indicating a thin or incomplete layer of $Ag_2O$ on the Ag) resembled Fig. 10 rather closely after impregnation, except that the white layer was not as thick or as well defined. The interaction of the polyester with $Ag_2O$ only in this surface layer and the resulting reduction of this $Ag_2O$ has already been discussed, and on this basis the surface layer of unoxidized Ag is explained for the sample that had been gray before impregnation.

The sharp demarcation between the particles that were oxidized and the particles that were not is shown for the sample (Fig. 11) which had an unoxidized surface before impregnation with the polyester. At the magnification of 1600X, at which Fig. 11 is shown, the brightness of the surface material below the level of the section was evident, even though unpolarized vertical illumination was used. The areas where the voids appear dark and where they appear bright correspond exactly to areas at the polished surface where the Ag particles were surrounded by visible $Ag_2O$ crystals and to where they were not. Note that there is no oxidation on one side of the line of demarcation and rather large $Ag_2O$ crystals on the other, with no evidence of any gradual transition. Even when the fact of chemical reaction between the polyester and $Ag_2O$ is accepted, the large size of the particles at the surface as compared to those surrounded by the $Ag_2O$ crystals indicates that the rates of electrochemical reaction were different on the two sides of the line of demarcation. Considering the briefness of the visible reaction between polyester and electrode surface, the resultant discoloration of the surrounding plastic caused by collodial Ag or dissolved $Ag_2O$, and the nature of the medium in which reaction occurred, it is unlikely that any large amount of $Ag_2O$, such as seen to the left of the picture, could have been reduced so completely to Ag with the original form and size.

Perhaps pressing or some other step in the manufacturing process resulted in changes in the surface layer that inhibited the initial oxidation of the surface. Since there was less surface oxidation on the electrode that was charged while using a new cellulosic separator and fresh KOH solution than there was when employing a used separator and used KOH, it is likely that dissolution of $Ag_2O$ was involved in some manner. To saturate the fresh

KOH solution contained in the pocket formed by the separator required approximately 0.13% of the total quantity of $Ag_2O$ that should have been formed by the charge to point B of Fig. 1, according to calculations based on the solubility of $Ag_2O$ in KOH solution (4). Additional $Ag_2O$ was probably consumed in reacting with the new cellulosic separator. Since Fig. 11 showed that Ag particles on the surface had not decreased in size, it was obvious that $Ag_2O$ had not formed evenly throughout the electrode and then dissolved at the surface layer.

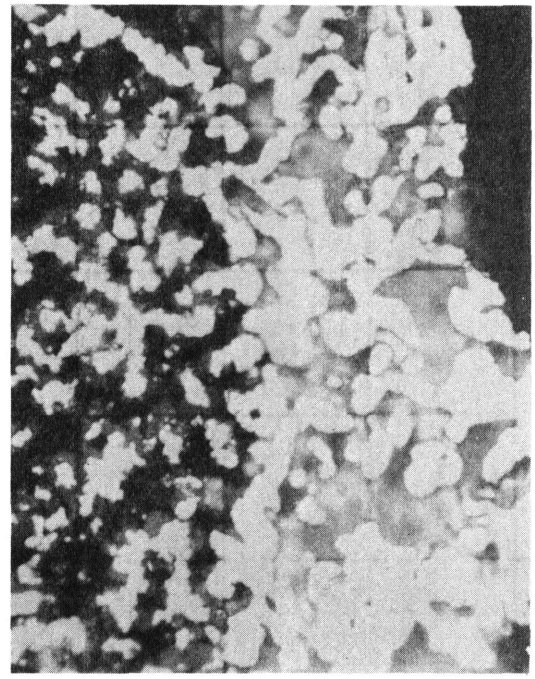

Fig. 11 - An illustration of the sharply defined boundary between oxidized and unoxidized particles that was observed in the samples charged to point B in Fig. 1. Here the original magnification was 1600X. Note the much larger Ag particles that appear to the right of the photograph and the sharp demarcation between particles with no oxide layer and those with a very heavy layer of $Ag_2O$ crystals.

### The Samples Charged to the Potential Peak that Begins the $Ag_2O/AgO$ Potential Plateau

Macrostructure — When the samples charged to the potential peak (point C of Fig. 1) were examined at a magnification of 100X, little if any difference could be detected between these samples and the samples that had been charged to point B of Fig. 1. The general appearance of an electrode charged to the potential peak is shown by Fig. 12. This photograph includes a portion of the grid and shows clearly that the grid was located toward one side of the plate, as was mentioned earlier. The granular appearance of the particles had increased slightly, but this was probably accounted for by the fact that each particle was surrounded by an increased layer of $Ag_2O$ and had thus become more distinctly separated from its neighbors visually.

Microstructure — The two samples charged to point C of Fig. 1 resembled each other closely. The only noticeable difference between these samples and samples charged to point B that was found when high magnification was employed was an increase in the amount of $Ag_2O$ present. In the central portion of the sample charged to point C almost all of the Ag particles were now encircled by $Ag_2O$ crystals, and the $Ag_2O$ layer that surrounded the smaller particles seemed thicker (Fig. 13). There still appeared to be more attack on the smaller Ag particles than on the larger particles, although at this stage definite $Ag_2O$ crystals could be seen along most surfaces of the larger particles and at some places even a somewhat penetrating type of attack (Fig. 14).

The layer of apparently unattacked Ag particles was still visible on the surface of the electrode but to a lesser extent than formerly. Compare Fig. 15 with Fig. 10. The surface of this sample had appeared dark brown after the charge to the potential peak. As seen through the plastic envelope the surface was still dark but not as dark as it had appeared before impregnation. It was found that as the charge given a sample before impregnation increased reactivity with the plastic decreased. Further examination of this sample revealed that reduction had taken place on a layer only a few particles in depth, and at many locations only the particles in the surface row were reduced. Under such conditions the dark background contributed by oxidized particles, seen through

Fig. 12 - The macrostructure found in a sample charged to the potential peak C in Fig. 1. Comparison with Fig. 3 reveals that the macrostructure in both cases is much the same. The original magnification was 100X.

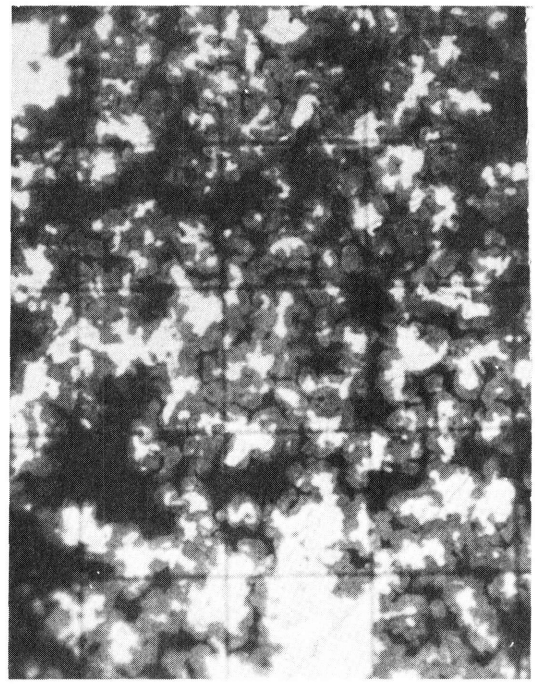

Fig. 13 - Appearance of the sample shown in Fig. 12 at 1600X original magnification. Compare with Fig. 9.

openings in the surface layer, gave the impression that the surface was still dark, although actually containing many reduced Ag particles.

### The Sample Charged to Twice the Capacity of the Potential Peak

Macrostructure — The macrostructure of the sample that had been charged to point D in Fig. 1 was somewhat different from that of the samples with lesser charges. The reflectivity of the surface had changed in some areas, caused by the formation of a considerable number of the lighter colored AgO crystals. The previous fine texture, suggested by the presence of many very small Ag particles, had been replaced by a coarser texture as the many small voids became filled with AgO crystals. At the center of the sample, where the amount of AgO seemed greatest, there was a suggestion of a reticulate or cell-like structure, and the impression was obtained that porosity had been decreased. Most of these differences can be observed in Fig. 16.

Microstructure — At higher magnification it was found that changes in appearance of the sample charged to point D in Fig. 1 that were noted at low magnification were brought about because a large number of AgO crystals had formed around Ag particles and around the boundaries of voids. Although individual AgO crystals had not been discernible, the AgO crystals were large enough at low magnification to outline Ag particles and voids and thus change the general appearance as compared to previous samples. It could be

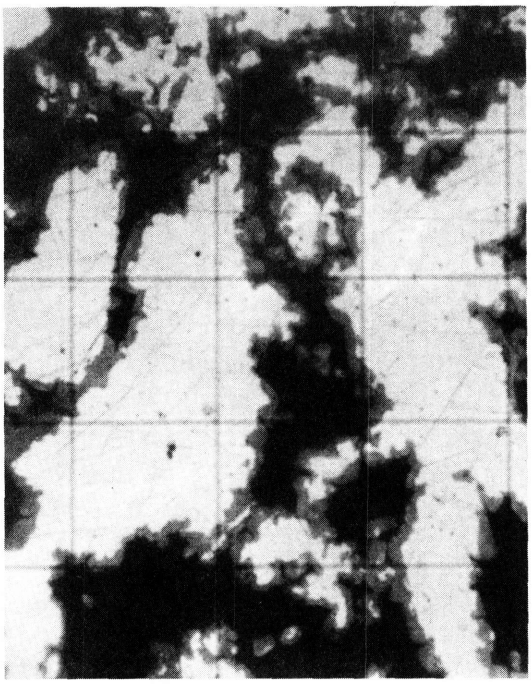

Fig. 14 - Another view of the sample shown in Figs. 12 and 13 and at 1600 X magnification but in an area of larger particles.

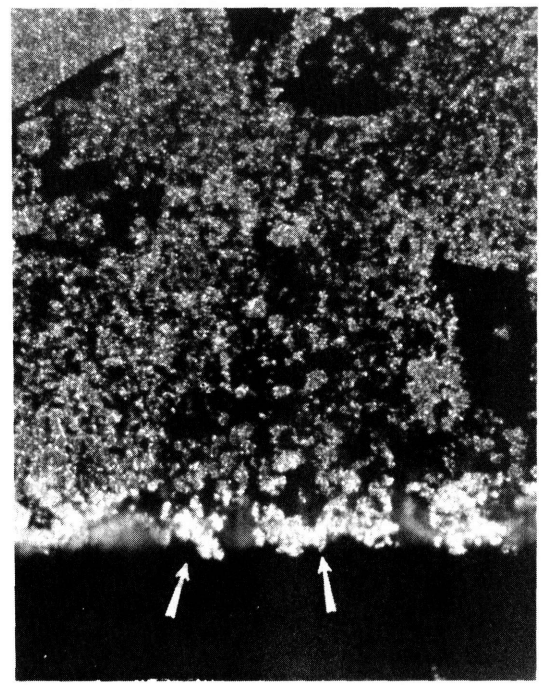

Fig. 15 - An area that includes the surface of a sample charged to the potential peak as seen by polarized light. Note that the brightly reflecting surface layer (arrows) is less intense and of decreased thickness as compared with Fig. 10. The original magnification was 400X.

seen at higher magnification that a large number of AgO crystals had formed at the surface and for a short distance beneath the surface. AgO crystals had also formed in the central portions of the electrode, but the intermediate areas between both surfaces and the center still consisted mostly of $Ag_2O$ crystals and Ag. Where AgO crystals were found, they had already grown to a considerable size and covered a considerable area. At the surface the AgO crystals seemed to be somewhat smaller than the average size, and in some surface areas AgO crystals were quite densely packed. This is shown in Fig. 17, where surface particles of Ag were covered with an appreciable deposit of AgO crystals of rather small size. The individual crystals are not visible in this figure. The AgO crystals were separated from the Ag surface by a thin layer of the dark $Ag_2O$.

Many of the internal cavities near the surface and at the center also had become completely or partially filled with AgO crystals (Fig. 18). The AgO crystals were usually fairly large and, except at the electrode surface, had rectilinear shapes. The AgO crystals usually appeared to have grown upon the $Ag_2O$ deposits. Often a fairly large area of AgO particles would occur next to a large area of Ag particles covered with $Ag_2O$ crystals but with no AgO present (Fig. 19). A much larger number of Ag particles were present in the areas of $Ag_2O$ particles than were present in the areas of AgO. Usually, but not always, a few small particles of Ag were still visible in the area occupied by the AgO. The lack of Ag in some areas indicated that all $Ag_2O$ that had formed at the lower plateau did not have to be oxidized to AgO before additional Ag could oxidize.

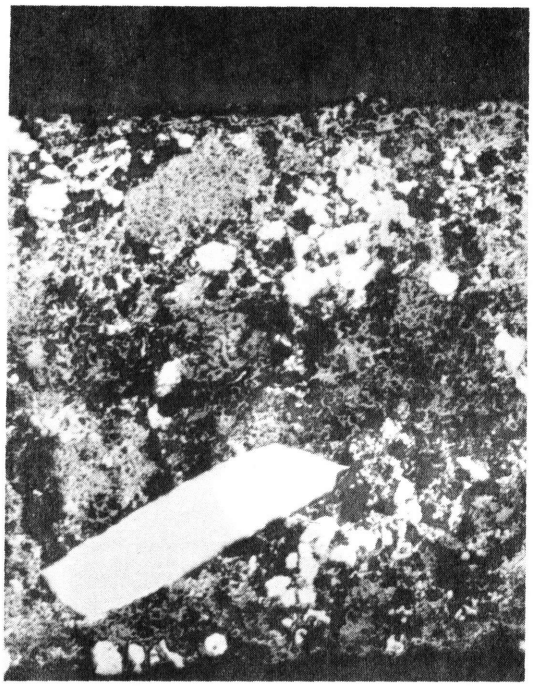

Fig. 16 - The macrostructure found in the sample that was charged to point D in Fig. 1. Compare with Figs. 3, 8, and 12. Note the change to a reticulate structure at the center of the section and the change toward a lighter shade as portions of the $Ag_2O$ become converted to less dark AgO. The original magnification was 100X.

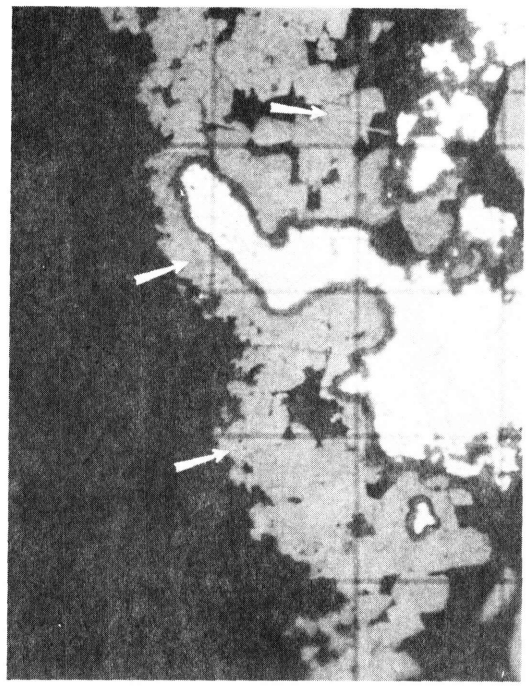

Fig. 17 - An area which includes the surface of the sample depicted in Fig. 16, at a magnification of 1600X. The photograph illustrates the manner in which the AgO crystals (white arrows) are separated from the Ag by a layer of the dark $Ag_2O$.

In areas where the $Ag_2O$ was accompanied only by Ag (top of Fig. 19) it was observed that the $Ag_2O$ had the appearance of being made up of crystals which varied in size and shape along the surface of the Ag particles. The interface between the Ag and $Ag_2O$ was very irregular and seemed to be the result of unequal rates of growth among the various crystals of $Ag_2O$. A large $Ag_2O$ crystal was usually accompanied by a corresponding indentation in the Ag subsurface.

In areas where $Ag_2O$ was surrounded by the AgO (lower half of Fig. 19) the situation was somewhat different. The $Ag_2O$ which always enclosed a particle of Ag was in turn surrounded by a practically continuous layer of AgO crystals. In this case the $Ag_2O$ appeared to lose identity as separate crystals and instead appeared as a continuous and fairly uniform layer between the Ag and the AgO. The interface between Ag and $Ag_2O$ was fairly straight in the areas where AgO predominated, and sudden indentations along the interfacial surface were unusual, in contrast to areas where Ag and $Ag_2O$ alone were present.

The areas consisting of Ag and $Ag_2O$ without admixture of AgO were common, but as has already been said such areas were usually found about halfway to the center of the section and not very often at either the surfaces or the center. In most of these areas that lacked AgO no marked difference was noted from similar areas seen before any AgO

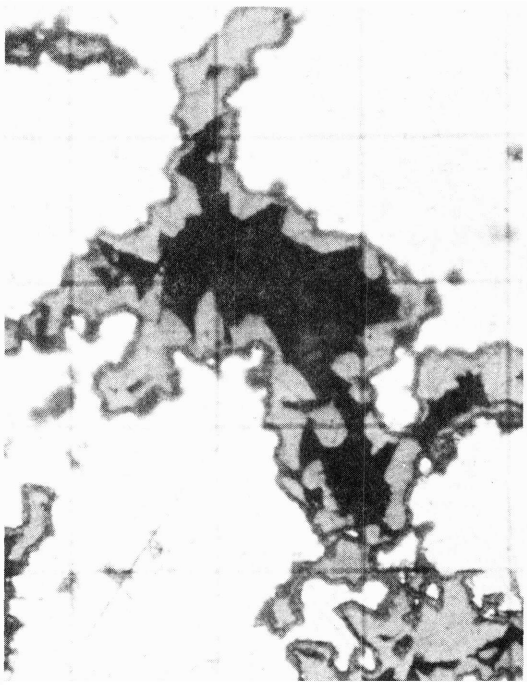

Fig. 18 - An illustration from the electrode charged to point D in Fig. 1, showing the internal cavities between large adjacent Ag particles and the manner in which these cavities have become partially filled with AgO crystals. It is possible that the growth of such crystals could block the internal channels of the electrode. The original magnification was 1600X.

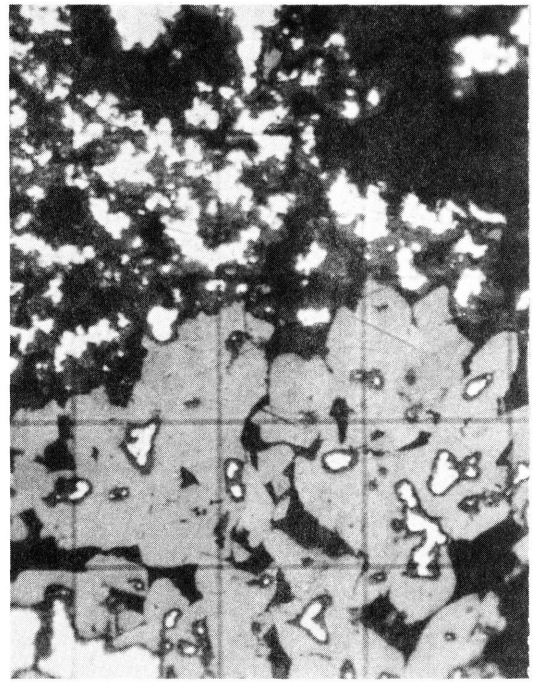

Fig. 19 - An example of the coexistence of areas of $Ag_2O$ (top) and of AgO (bottom) in the sample shown in Figs. 16 through 18. The original magnification was 1600X.

had formed, as in the samples charged to point C of Fig. 1. The amount of $Ag_2O$ deposited on the surface of the Ag particles, the number and size of the Ag particles and the thickness of the $Ag_2O$ deposits all appeared to be practically the same in the two cases. This similarity indicated that the increased charge given to the electrode as it charged from point C to point D of Fig. 1 had probably gone into the formation of AgO crystals at other areas.

## The Samples Charged to Oxygen Evolution

Macrostructure – The samples charged to oxygen evolution (point E in Fig. 1) resembled in macrostructure that shown at low magnification in Fig. 20. These samples had a more definite reticulate structure than was shown in Fig. 16 for the sample charged to point D in Fig. 1, and this structure now extended throughout almost the entire sections rather than being confined to the central portion of the electrodes. An observation of some concern was that in the 100% charged samples many of the large voids were open and unfilled with the impregnating plastic. This problem of the section not being completely impregnated with plastic seemed to occur only when large AgO crystals were present. Perhaps the large AgO crystals which had formed were able to block the entrance to many interior voids. Another possibility was that some of the AgO, like the

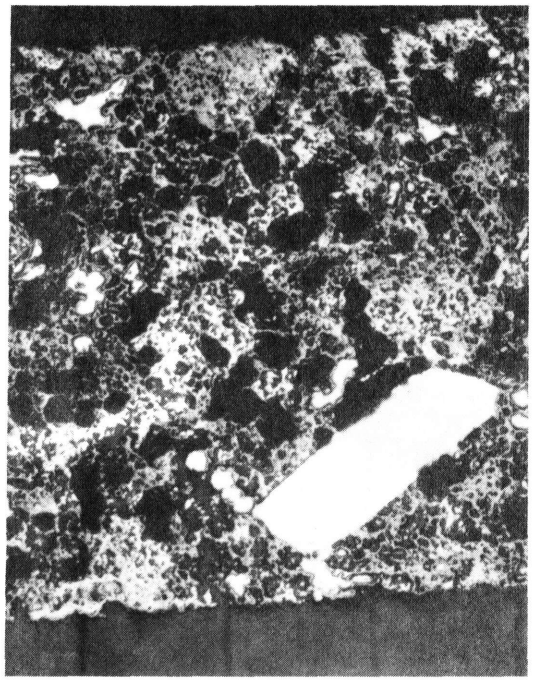

Fig. 20 - The macrostructure of an electrode that was charged to oxygen evolution. The very black areas of the cross section are holes caused by the incomplete impregnation of the electrode. Such holes correspond to pre-existent voids in the sample and appear similar in size and accessibility to nearby voids where impregnation was successful. Disregarding the actual holes, note the increase in reticulate structure that has occurred throughout the electrode and the general difference in appearance from Figs. 3, 8, 12, and 16, taken at the same magnification (100X).

$Ag_2O$ at the surface, had reacted with some component of the plastic and formed gas bubbles. This second possibility was less likely than for $Ag_2O$, since no reaction with the plastic was observed during the impregnation, and similar unfilled voids were not present in the 62% charged sample, although AgO was also present in that sample. A third possibility was that the gas evolution that had been observed to occur for approximately the first 5 min of washing had continued at a slow rate. The voids then would represent gas evolution that occurred between the time of impregnation and the time that the resin hardened.

Microstructure — Examination at higher magnification of the samples charged to oxygen evolution revealed that, while large particles of Ag remained, most of the smaller particles of Ag had disappeared. No areas were found where Ag and $Ag_2O$ alone were present. Figure 21 illustrates, as well as one photograph can, the general appearance of the electrodes charged to gas evolution. All of the remaining Ag particles were surrounded by a thin layer of $Ag_2O$ with no clearly defined crystal structure. This $Ag_2O$ was in turn surrounded by a more or less continuous structure composed of relatively large AgO crystals which tended to have rectilinear forms. Many of the former voids had become filled or partially filled with rectilinear crystals of AgO. In many areas of the samples the space was not as completely filled with AgO crystals as is shown in Fig. 21, and in other areas little or no Ag remained in the AgO. The structure of the electrodes charged to oxygen evolution was similar to the AgO areas in the sample charged to point D in Fig. 1. The structure of such areas has already been discussed.

The surfaces of the electrodes taken to oxygen evolution also resembled similar AgO areas of the sample charged to the point D in Fig. 1. This can be seen by comparing Fig. 22 to Fig. 17. The layer of AgO crystals along some of the Ag particles that were exposed at the surface of the plate still seemed to be composed of much smaller and more densely packed crystals than was the case in the interior of the sample.

The samples that had been charged until oxygen was evolving strongly had received 100% of the usual charge capacity for the first charge of these sintered Ag electrodes, but the samples had only accepted 71% and 87% of the charge capacity theoretically possible for the sintered electrodes, and fairly large amounts of unoxidized Ag still remained (Fig. 20). The only differences noted between these two samples was that the sample which had accepted 87% had less Ag remaining and had slightly less void space.

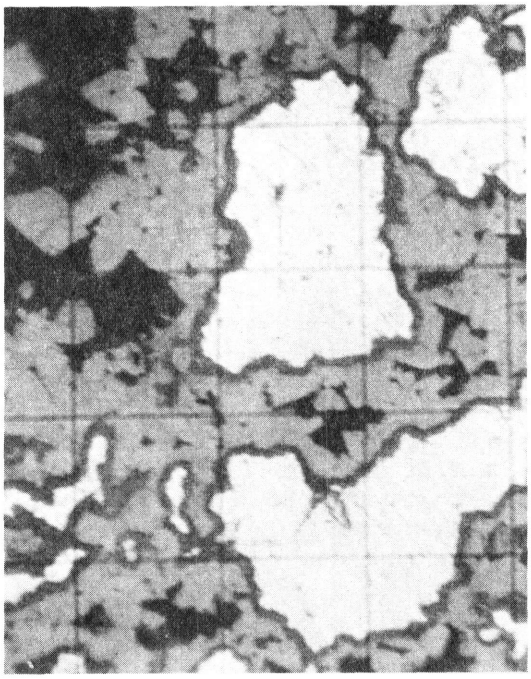

Fig. 21 - Appearance of the sample charged to oxygen evolution, at the original magnification of 1600X. Note that each Ag particle is still surrounded by a dark layer of $Ag_2O$ and that the remaining space between the Ag particles is nearly filled with the large crystals of AgO (light gray).

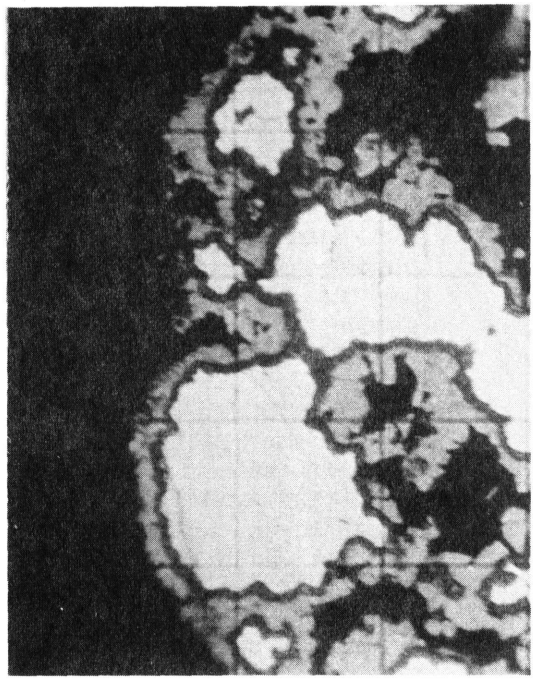

Fig. 22 - An example of the appearance of the AgO crystals at the surface of the sample charged to oxygen evolution. Note that the surface layer of AgO appears to be continuous and that these crystals did not assume the rectilinear forms noted elsewhere in the electrode. The original magnification was 1600X.

The microscopic examination indicated several factors which probably contributed to the failure of some Ag particles to oxidize completely to AgO. One factor was that when AgO crystals formed during a charge, the surface and many of the internal cavities became partially or completely filled with the AgO crystals, as was shown in Fig. 18. If these AgO crystals blocked some of the internal channels, additional oxidation of the surrounding area could be limited. Another factor was the particle size of the Ag. The smaller Ag particles oxidized in preference to the larger particles and to a greater depth. This was illustrated in Figs. 9 and 14. As the charge progressed and many of the smaller Ag particles were completely converted to AgO, the charge current must have been gradually concentrated more and more at the large Ag particles which remained. Both an increasing local current density and the increasing thickness of oxides on the remaining Ag particles probably resulted in potential gradients increasing within the electrode, until oxygen evolution became the main reaction taking place, and oxidation of the remaining Ag ceased to occur in significant amounts.

## SUMMARY

Unused sintered Ag electrodes were compared to a sintered Ag electrode that had been charged and discharged over 200 times in 35% KOH. The unused electrodes had a

more uniform structure, although the size of Ag particles included smaller and larger particles than were found in the used electrode. The particles had clumped in the used electrode, which resulted in removal of the smallest particles and increased the porosity by creating larger voids. The largest Ag particles and the Ag grid had become smaller after cycling, apparently as a result of irregular and sometimes penetrating surface oxidation.

During the early part of the first charge of a previously unused electrode, the surface of fine Ag particles in the electrode tended to be oxidized to $Ag_2O$ in preference to the surface of large particles, and fine particles tended to be oxidized to a greater depth at any given time. While the electrode was charged at the $Ag/Ag_2O$ potential plateau, the depth of the $Ag_2O$ coating on the Ag particles increased. When the end of the $Ag/Ag_2O$ potential plateau was reached, most Ag particles had been encircled with $Ag_2O$ crystals. The $Ag_2O$ coating consisted of separate crystals which varied in size and shape. The interface between $Ag_2O$ and Ag was very irregular, probably as a result of unequal rates of $Ag_2O$ crystal growth. During most of the charge at the $Ag/Ag_2O$ potential plateau there were clearly defined layers at the electrode surface which contained little or no $Ag_2O$, probably the result of the initial formation of $Ag_2O$ being inhibited near the electrode surface. Electrical conductivity must have been good within the electrode, because oxidation did not tend to occur preferentially at or near the grids.

After potential rose to the $Ag_2O/AgO$ plateau, AgO crystals formed at the surfaces and at the center of the electrode before forming in the intermediate areas. AgO did not form in some areas until near the end of the charge. In areas where AgO predominated in a partly charged electrode, relatively few Ag particles were present, and these particles were always enclosed by a thin layer of $Ag_2O$. This $Ag_2O$ was surrounded by a practically continuous layer of AgO crystals. AgO crystals tended to fill cavities near the surface and perhaps blocked internal channels.

In some areas AgO crystals covered the surface of an electrode completely. The layer of AgO crystals at an electrode surface was composed of crystals that were much smaller and more densely packed than were the AgO crystals in the interior. The AgO crystals tended to have rectilinear shapes, except at the electrode surface, and grew to considerably larger size than the $Ag_2O$ crystals.

By the end of a charge all areas contained AgO. Most of the smaller Ag particles had disappeared; the Ag particles which remained were coated with a thin layer of $Ag_2O$, and this layer was surrounded by AgO crystals.

One cause for sintered Ag electrodes failing to charge to the capacity that is theoretically possible may be the presence of large Ag particles in an electrode, because small particles charged more readily than large ones. Another factor may be the growth of dense layers of AgO crystals which can limit oxidation of the remaining Ag and $Ag_2O$.

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13. ABSTRACT

The Ag electrode has been studied during oxidation using the optical microscope. As a preliminary to other, more detailed experiments, the oxidation during the first charge of an unused sintered Ag plaque has been observed as Ag was converted first to $Ag_2O$ and then to AgO. The initial oxidation occurred on the smaller particles of Ag, and these were usually completely oxidized by the end of charge, whereas the larger Ag particles were left largely unconverted. The rate of reaction was quite unequal in different areas of the electrode. AgO crystals were larger than $Ag_2O$ crystals and may have blocked the surface in some areas. Both particle size of Ag and the formation of dense layers of AgO may have limited complete oxidation and may partially have been responsible for the inability of the electrode to produce the full capacity that was theoretically possible.

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|---|---|---|---|---|---|---|
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| Oxidation – Reduction | | | | | | |
| Charging | | | | | | |
| Ag | | | | | | |
| $Ag_2O$ | | | | | | |
| AgO | | | | | | |
| Microstructure | | | | | | |
| Silver anode | | | | | | |
| Batteries | | | | | | |

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