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Feasibility of Microscopy for Investigating the Silver Oxide Electrode

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ABSTRACT

A study of the silver oxide electrode was made with the optical microscope, using methods that had previously proven successful for the lead-acid battery.

It was determined that Ag, Ag_2O, and AgO could be easily distinguished from one another in the polished section of the electrode without resorting to any etching or staining. Crystals of the three phases were also found to be of a size that made it feasible to follow crystallographic changes that occurred during the course of a discharge. Although considerable variations occurred in different areas of the same electrode, results were in agreement with previously obtained x-ray data.

PROBLEM STATUS

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

AUTHORIZATION

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FEASIBILITY OF MICROSCOPY FOR INVESTIGATING THE SILVER OXIDE ELECTRODE

INTRODUCTION

Optical microscopy has been successfully employed as one of the tools for solving problems connected with the lead-acid battery (1,2). In this connection special techniques were developed that have aided considerably in understanding the mechanisms of corrosion and crystallogenesis that occur in this system (3,4). By considering these results with the lead-acid battery, it seemed likely that microscopy could also be profitably employed in the study of the silver oxide electrode in alkaline solutions. This study could be a valuable addition to the work at NRL that has already been reported concerning the silver oxide electrode.

The instability of the silver oxide electrode at elevated temperature indicated that considerable difficulty might be experienced in preparing samples for microscopic study, since the techniques being used for the study of lead-acid batteries require heat for curing the plastic used in the impregnation of the samples. Without the impregnation, the porous electrodes could not be ground and polished successfully. In addition to decomposition of the silver oxides which might occur when the samples are heated, there might also be reaction between the silver oxides and the plastic before the plastic hardened or decomposition during the considerable period between the time the sample is obtained and is finally polished satisfactorily for examination. Both Ag_2O and AgO are known to decompose when heated and to have increasing rates of decomposition with increasing temperature (5). Since AgO, the more unstable of the two oxides, decomposes more rapidly when in alkaline solution (6), difficulty in washing the electrodes free from the KOH electrolyte might also cause problems.

A number of modifications were made in the technique previously employed to decrease the time between preparation and examination. Such modifications resulted in samples of somewhat poorer quality than had been previously obtained. The principal difficulties in the present experiment were the occurrence of scratches and of areas where incomplete impregnation by the plastic left cavities in the sample surface where it was sectioned. The scratches usually occurred within the cross-sectional area of the individual Ag particles, within which no detail appeared under the best conditions. The cavities occurred only in areas of actual pores and voids in the sample, so that they cannot be considered as artifacts. Nevertheless, they increased the difficulty of polishing and resulted in an unsightly appearance that added to the difficulty of interpretation. Both problems can be expected to disappear with increased experience.

The discharge of a well-cycled silver oxide electrode was selected for the first investigation for several reasons. Such an electrode was brittle and could be handled only with difficulty, thus representing the maximum problem likely to be encountered in applying the microscopic method. In addition, the electrode could have undergone considerable grid corrosion during the many oxidation-reduction cycles, and it was interesting to see if this corrosion also would be evident. Finally, during the discharge the silver oxide electrode underwent successive reduction from AgO to Ag_2O to Ag; thus, it could be determined at once whether these different phases might be identified individually and in combination.

This report deals with the methods used in the preparation of the samples for microscopic examination, a description of the type of instability that occurred in the samples, and illustrations of the kind of information that can be obtained concerning the silver oxide electrode. However, this report represents the results of a preliminary investigation which will be followed by a more thorough analysis in the future. The following observations are, therefore, indicative only of the possibilities inherent in a study of the silver oxide electrode.

EXPERIMENTAL PROCEDURE

Description of the Electrode and Its Electrochemical Treatment

The Ag samples described in this report were taken from a sintered Ag electrode which had a grid of expanded Ag sheet. The electrode had been manufactured commercially for use in a Ag-Zn storage battery that was designed to discharge at comparatively low rates and to require 1 or more hours for a complete discharge. Electrode dimensions were 41.5 by 38.0 by 0.8 mm. This sintered electrode was placed in a loosely fitting cell case, along with another sintered Ag electrode of the same size that served as the counter electrode. Both electrodes were wrapped with a treated cellulose separator to slow the diffusion of soluble Ag species. The cell contained an excess of 35% KOH solution and was kept at approximately 25°C.

Before samples of the electrode were removed for microscopic examination, the cell had been used to study the effects of various charge currents. Over a period of 23 months, the Ag electrode was given 218 complete charges to oxygen evolution, followed by complete discharges to -300 mv vs the Ag/Ag_2O reference electrode. Over half of the charges were done at the 20-hour current, with the remainder taking from 20 to 30 hours. The first 137 discharges were at the 20-hr rate, the following 45 discharges were at the 1-hr rate, and the remaining discharges were again at the 20-hr rate. The amount of sintered Ag on the new electrode corresponded to a theoretical capacity of 2.9 amp-hr. On the second cycle the actual discharge capacity of the Ag plate reached 78% of the capacity theoretically possible. Capacity fell to 51% of theoretical at cycle 9 and then slowly increased with additional cycling. The last 10 cycles at the 20-hr rate, before removing the first sample for microscopic examinations, gave from 61% to 64% of the capacity theoretically possible.

Four samples were obtained as follows from this electrode:

1. The first sample for microscopic examination was taken after the end of a constant-current charge at the 20-hr rate to oxygen evolution (point A of Fig. 1). The final electrode potential during the charge was 521 mv vs the Ag/Ag_2O reference electrode. The electrode had warped considerably after 218 cycles in the loosely fitting cell case, and the separator was in poor condition. The electrode was also quite brittle and crumbled and cracked when cut. A piece approximately 19 by 21 mm was cut from this charged electrode, and the remainder of the electrode was then returned to the cell. This first piece will be subsequently referred to as the charged sample.

2. The electrode was then discharged at what was calculated to be the 20-hr constant current for the amount of the electrode that remained. The discharge was interrupted as soon as the potential reached the Ag_2O/Ag plateau, -31 mv vs the Ag/Ag_2O reference at this discharge current (B of Fig. 1). It was estimated that approximately 23% of the capacity had been removed from the electrode at this point. At this time another approximately 19-by-21-mm piece was cut from the electrode, and this piece will hereafter be referred to as the 1/4-discharged sample. The remainder of the electrode was returned to the cell.

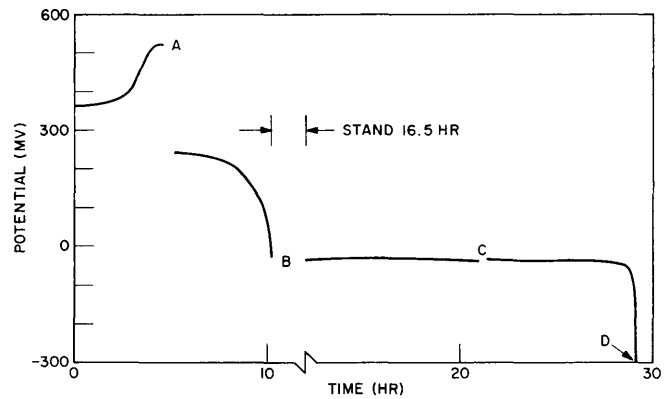

Fig. 1 - Potentials of sintered silver electrode at the end of charge and during the following discharge. The potentials are given with respect to the Ag/Ag_2O reference electrode. The letters A through D indicate four points at which samples of electrodes were removed for microscopic examination.

3. After the cell remained on open circuit for 16.5 hours, discharge was resumed at a lowered current that gave approximately the same current density as that used before removal of the sample. Discharge was continued until an estimated 65% of the capacity had been removed from the electrode. The potential was -38 mv vs the reference electrode at this point (C of Fig. 1). The current was again interrupted, and another sample of approximately the previous size was cut from the electrode. This piece will be hereafter referred to as the 2/3-discharged sample.

4. Discharge was resumed with current adjusted to give approximately the same current density as before. Discharge was ended when potential fell to -300 mv vs the reference electrode (D of Fig. 1). This final quarter of the electrode will be referred to as the discharged sample.

Preparation of the Samples for Microscopy

Each sample was handled separately to avoid delay in microscopic examination. Each was first put into at least four changes of distilled water to wash out the KOH solution. The sample was then placed in a 38-mm-diameter, 25-mm-deep cavity in an aluminum mold and held upright by surrounding it with Lucite pellets. The sample and mold were then inserted into a vacuum desiccator and vacuum-dried. To assist in the drying process, the mold and Lucite pellets were preheated to 40°C prior to the placing of the sample. The mold had a rather large mass and formed a sufficient reservoir to provide some heat throughout the drying process.

After drying and while still under vacuum, the sample was impregnated with a liquid polyester Marco MR-28-V, which had previously been well mixed with Accelerator "D" and MC-1 paste catalyst.* The impregnated sample was returned to atmospheric

*Material obtained from the Marco Chemical Corp., 1711 West Elizabeth Avenue, Linden, N.J.

pressure and transferred to an oven at 40°C for an 8-hr cure. After curing, a cross section of the sample was prepared which was ground successively on 120, 240, 400, and 600 silicon carbide abrasive and was finally wet-polished using Buehler Texmet as a lap* and Geoscience 9-micron boron carbide.† This procedure was followed by a dry-polishing on a sponge rubber lap charged with Linde 0.3-micron Alumina powder.‡

General Observations

The three phases Ag, Ag_2O, and AgO were quite distinct from one another and easily identified. When observed under bright-field vertical illumination in the manner employed for most metallographic specimens, the Ag had practically specular reflectance which was marred by some scratches. The reflectivity of either oxide was considerably less than that of the Ag but still sufficiently different in each case to make for easy identification. The AgO was the brighter of the two oxides. In polarized light the Ag was again the brightest-appearing constituent, and the Ag_2O was the darkest. Neither the Ag nor the Ag_2O exhibited polarization colors, but under crossed polars and with an interference plate the AgO showed strong color variation from one grain to another. The Ag_2O crystals also tended to be much smaller than the AgO crystals.

Contrary to original expectations, the various phases appeared to remain fairly stable when entirely within the embedding medium. At the interface between the impregnating plastic and the outer surface of the electrode, however, there was some indication of a slight reduction of the silver oxides before the plastic hardened. After the plastic had hardened, there was no reaction between the oxides and the plastic. Where exposed at the polished surface, however, the system was subjected to a slow, but continuous, change. Except for tarnishing, the exposed Ag of a reduced electrode appeared to remain unchanged. This observation was also true of an electrode consisting entirely of Ag and Ag_2O. Electrodes containing AgO and residual Ag were the greatest problem. At the earliest time that examination could be made, a narrow band of Ag_2O was found to be intermediate between Ag particles and AgO. When the sample was first sectioned, this band was so narrow that rough polishing or microtoming did not give sufficient detail to be positive of its width, but there was little doubt that an intermediate layer was present. In the time taken to reach a fairly good polished condition after sectioning, which was roughly 2-3 hours, the line of Ag_2O was broadened to a point where it was easily visible at 1600X magnification. Under continued polishing or standing the line continued to broaden, and eventually this Ag_2O layer had become very uneven in extent and had spread over a considerable area of the original AgO crystals. Nuclei of Ag_2O also began to form in parts of the AgO material where no Ag appeared to be present. While the polishing may have contributed to this reaction, the rate at which the sample was altered was much higher when allowed to stand than when kept under continuous polishing.

The most surprising feature was that the original appearance was again restored when the sample was ground down with 400- and 600-mesh silicon carbide papers and then repolished. This restoration would indicate that the major instability was in or near the surface layer and was triggered by atmospheric components, because the materials used in polishing appeared to be unreactive toward the sample.

For most purposes of examination these slowly occurring changes offered no great difficulty. The sample could be examined with oil-immersion lenses without any appreciable reaction so that an upper limit of about 1600X magnification was possible. One hundred times magnification was about the lowest magnification at which significant

*Buehler Ltd., 2120 Greenwood St., Evanston, Illinois.
†Geoscience Instruments Corp., 110 Beekman Street, New York, N.Y.
‡Crystal Products Dept., Linde Co., 2065 U.S. Route 22, Union, N.J.

detail could be observed without resorting to the use of a stereo wide angle or dissecting type of microscope. If the observations were first made at the higher magnifications and then at the lower, no problem existed in determining the original crystallography and general structure, since a practically unchanged sample was present for 3-4 hours for photography or comparison, and in this period change could be detected only at the highest magnification, as has been previously mentioned. The period of examination may be extended to several days or even weeks by repeated regrinding and repolishing. It would appear that during such a period change occurring within the impregnated specimen was insignificant and that transition took place only in the surface layers.

OBSERVATIONS RELATING TO THE DISCHARGE PROCESS

Observations Made at Low Magnification

The most immediate observation made in connection with the discharge of the plate was the overall gross change in appearance. This gross change includes the obvious change in color which occurred as the AgO was converted to Ag_2O and then to Ag but refers in particular to the changes in what might be called the macrostructure of the electrode. These macrostructure changes could be observed by changes in the texture and porosity of the sample cross section, by changes in crystal structure, by volume changes, and by the appearance and disappearance of various phases.

While the detailed effect of these various changes could best be observed at high magnification, the gross overall effect of such changes was visible at fairly low magnification. But even at fairly low magnification it was difficult to include a sufficient area of the plate to show the many variations that occurred in different areas of the same electrode.

For this reason a series of photographs were taken in sequence as the field was serially changed, and the resulting photographs were then matched and arranged as a composite picture to give a panoramic view of the cross section. Such a composite was extremely useful in comparing electrodes from one set of conditions with another, although requiring considerable effort to prepare. The individual photographs making up the composite were taken at 100X, and although only a portion of the sample was included, the resulting composite was about 80 cm long and, therefore, unsuitable for reproduction here. The principal types of structure are illustrated here by the use of individual photographs from among those used in the preparation of the composite.

Charged Sample – Figures 2 and 3 show the appearance of portions of the cross section made of the charged sample. While the magnification is not sufficiently high to see the individual crystals, several features assist in understanding the photographs. The impregnating plastic had a lower reflectivity than either the silver oxides or the metallic silver and thus comprises the dark background matrix. The few very dark spots that appear in the photographs either represent the residue from deep scratching or small holes left by entrapped air bubbles or incomplete impregnation. The brightest areas, which are numerous in Fig. 3 but scarce in Fig. 2, represent the metallic Ag that remained at the end of the charge, while the intermediate gray areas represent AgO. While some Ag_2O was present around the Ag particles, it represented areas too small to be seen at this low magnification. Areas of the AgO appear as large clumps which also seem to be interconnected by isthmuses of the same material.

Figure 3 includes a small section of the expanded sheet Ag grid that supported the active material. After the over 200 cycles of charge followed by discharge to which this electrode had been subjected, the grid showed severe electrochemical attack and considerable conversion into the oxide. This condition was typical of the grids in this electrode. It is interesting to note that the metal/oxide interface was quite irregular, indicating

penetrating attack and that the number of residual Ag particles was quite large in the vicinity of the grid as well as in other areas that were at considerable distance from such a continuous conducting path.

All of the photographs taken as 100X show almost a full cross section through the plate and usually include one of the electrode surfaces at the bottom of the pictures. Thus one of the original surfaces of the electrode is shown at the bottom of Fig. 2 and the other surface is just out of view at the top. There was no appreciable difference in oxide distribution between the surface facing the counter electrode (at the top of Figs. 2 and 3) and the other surface. There was, however, considerable variation between different areas of the electrode. Some areas contained a large amount of residual Ag, as in Fig. 3, while others almost completely lacked such particles, as in Fig. 2.

One-Fourth-Discharged Sample — Figures 4 and 5 are from the 1/4-discharged sample and, in general, show a considerable difference in appearance from the charged plate. There was again evidence of a very nonuniform structure from different areas of the electrode. In some locations the material seemed to be unchanged from that shown for the charged sample (compare with Figs. 2 and 3). In other areas it will be seen that the material had assumed a much more open texture or that it appeared darker because of an admixture of

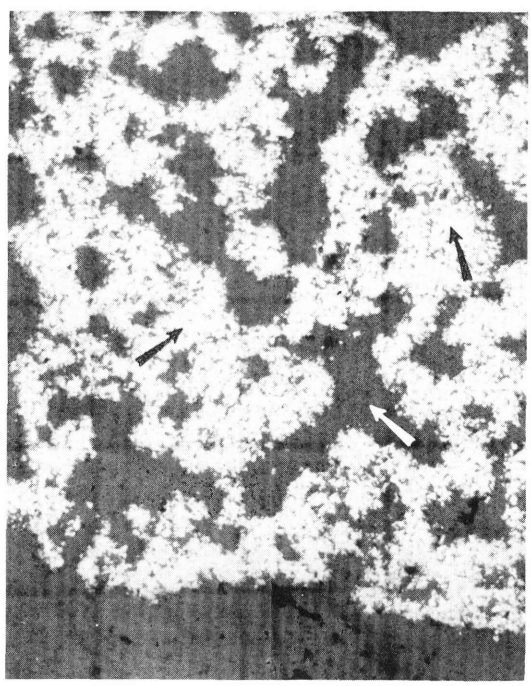

Fig. 2 - Appearance of the charged sample at 100X magnification in an area of low residual Ag. The dark areas (white arrow) represent large voids filled with a plastic of low reflectivity. Gray-toned areas (black arrows) represent AgO crystals interspersed with small voids filled with plastic. Note the overall open structure of the plate and the large number of internal voids of fairly large size. A small number of very black spots represent defects in plastic impregnation or in polishing. Lines forming the squares indicate 238-micron separation.

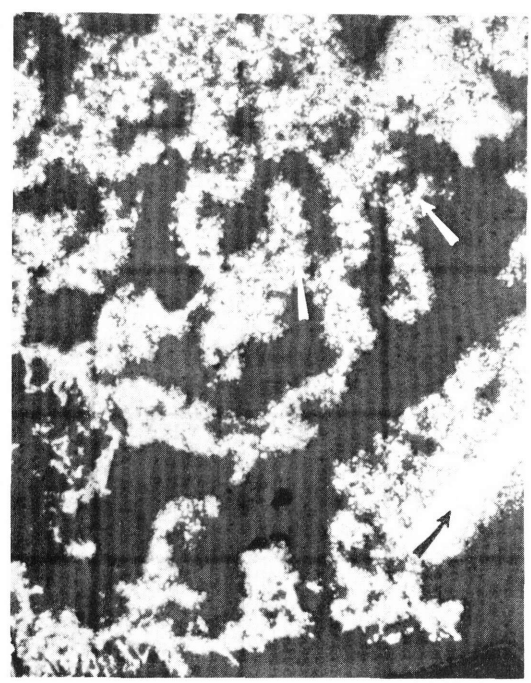

Fig. 3 - Another area of the same sample as Fig. 2 but one containing large amounts of residual Ag. Small, very light areas represent residual Ag particles (white arrows) and the large light area (black arrow) is part of the Ag grid. Magnification was the same as in Fig. 2.

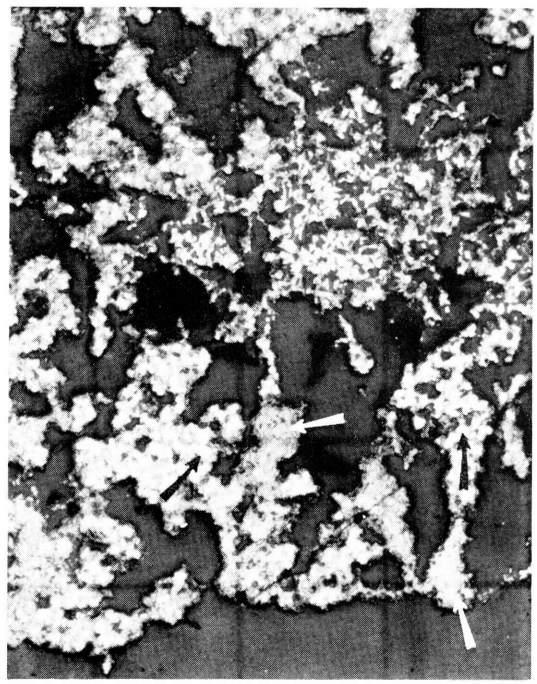

Fig. 4 - An area from the 1/4-discharged sample. Shown here are residual Ag particles which were not converted to oxide in the previous charge (black arrows). Other sections of the illustration contain very little Ag but consist of a mixture of AgO with Ag_2O (white arrows). Lines forming the squares indicate 238-micron separation, and the original magnification was 100X.

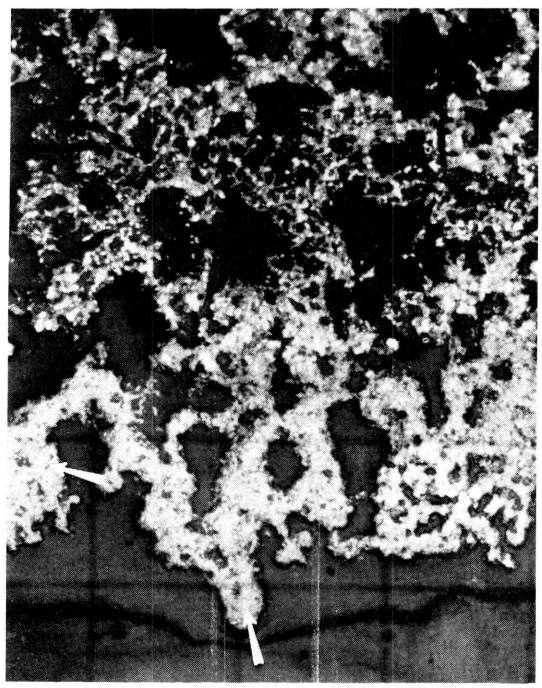

Fig. 5 - An area from the 1/4-discharged sample which contains a large portion of the original AgO (white arrows), similar to that seen in Figs. 2 and 3. Note the light color which indicates that there has been very little conversion to Ag_2O. Also note the almost complete absence of Ag particles in these areas. Magnification was the same as for Fig. 4.

Ag_2O. Examination of the composite picture of this sample at 100X showed that a preponderance of the apparently unchanged material appeared to be on the outer portions of the electrode, while the greatest change appeared to take place in the interior. This sample also showed an unusual number of voids which had not been filled by the impregnating plastic after the impregnation, and these voids were concentrated near the center of the electrode.

Two-Thirds-Discharged Sample — Figures 6, 7, and 8 are representative of the appearance when the plate was about 2/3 discharged. As previously, the reaction appeared to be at different stages of evolution in different parts of the electrode. In some areas, as in Fig. 6, the material consisted almost entirely of Ag_2O with a small admixture of AgO. In other areas it was evident that reduction had proceeded much further, and in such areas there had been almost complete reduction to Ag (Fig. 7). Figures 6 and 7 represent adjacent areas with the right border of Fig. 6 being the left border of Fig. 7. Figure 8 shows an area surrounding the expanded sheet Ag grid. The grid was still surrounded by a mixture of AgO and Ag_2O, while there had been a very definite reduction to Ag in other areas. Figure 8 was typical of most areas of this sample in having oxides mainly at the interior and Ag near the surface. The counter electrode was on the side that is at the top in Figs. 6 to 8.

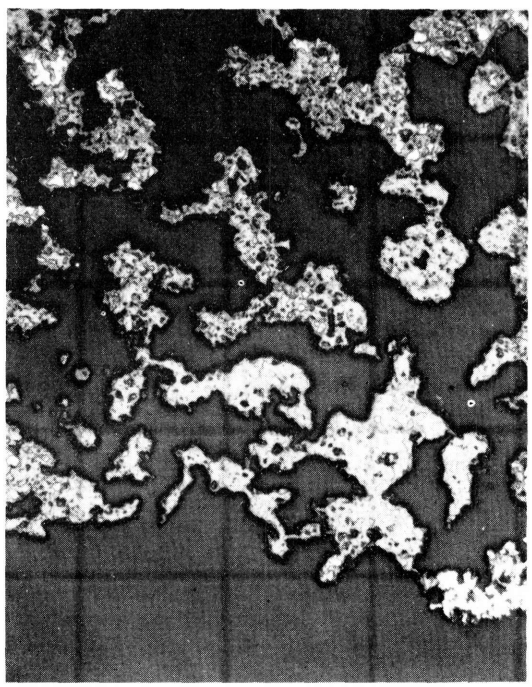

Fig. 6 - An area from the 2/3-discharged sample. In this area the major portion of the material appeared to be Ag_2O. There was very little Ag or AgO present. Lines forming the squares indicate 238-micron separation, and the original magnification was 100X.

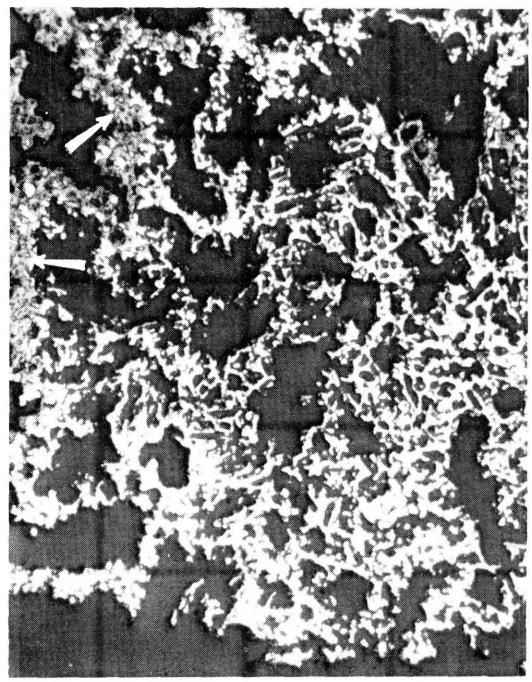

Fig. 7 - An example of a completely different structure and phase in another portion of the same sample as represented in Fig. 6. Here the major constituent was newly reduced Ag with a small amount of Ag_2O (white arrows) appearing at the edges of the picture. There was no AgO found in this area. Examination at a much higher magnification exposed the presence of a small amount of Ag_2O scattered through the central area that here appears to be entirely composed of Ag. Magnification was the same as in Fig. 6.

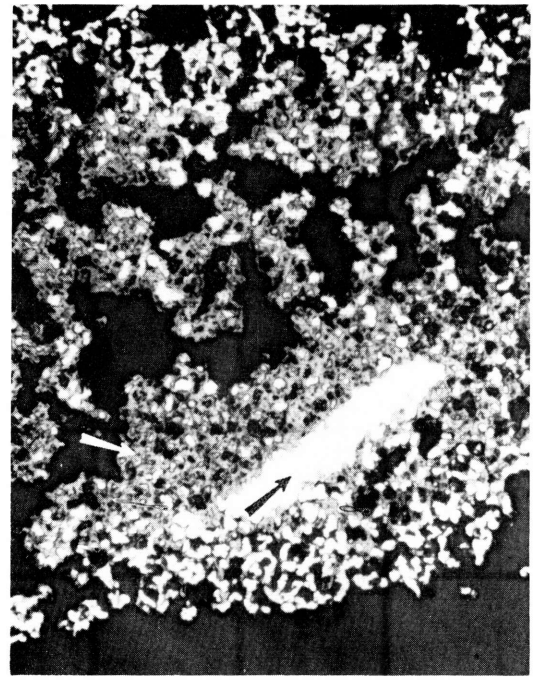

Fig. 8 - Another area of the same sample as shown in Figs. 6 and 7. Here the major constituents appeared to be Ag_2O and Ag. Note the large amount of Ag_2O (white arrow) in the vicinity of the Ag grid (black arrow) and the relatively greater amount of Ag at the surface of the electrode (shown at the extreme top and bottom of the photographs). AgO was not visible at this magnification (same as Fig. 6), because it was present for the most part in small areas too small to resolve.

Discharged Sample — Figures 9 and 10 show the principal features of the sample after it had been discharged at the 20-hr rate to -300 mv vs the Ag/Ag_2O reference electrode. This potential was equivalent to an endpoint of about 1.2 to 1.3 v for a Ag-Zn cell, assuming a typical Ag-Zn cell with an excess of zinc. Since a small amount of additional capacity could have been removed if the discharge had ended at a lower potential, there was no doubt that traces of the oxide still remained. However, the only visible phase at this magnification was metallic Ag. In some areas, as for example one such as shown in Fig. 9, the Ag appeared to have a granular appearance, while at other locations it appeared as very finely divided dendritic needles (indicated by white arrows). Areas, such as the ones indicated by arrows in Fig. 10, where the material had a much coarser needlelike structure, were also characteristic of this sample.

Observations at High Magnification

Many of the statements made up to this point require acceptance with considerable faith, as the photographs used in the previous illustrations do not individually convey as much information as has been implied here. More definite information can be obtained from a study of the electrodes at much higher magnification, but in such a study the macrostructure already described must still be kept in mind.

Charged Sample — Figure 11 represents the appearance of the fully charged sample at 1600X. The very light colored areas represent residual particles of Ag that had not been converted to oxide. These particles appear to be relatively large. Surrounding each Ag particle was a continuous layer of dark material which is apparently Ag_2O. The very large rectilinear crystals, shown in a lighter tone of gray were composed of AgO. These crystals were not as large as they appear in Fig. 11. Under polarized light the individual grains become distinguishable by different polarization colors, and it was found that what at times may have appeared to be one large crystal as viewed by vertical illuminations under normal light would, in fact, consist of as many as three or four smaller crystals when viewed by polarized light. Even when using normal illumination,

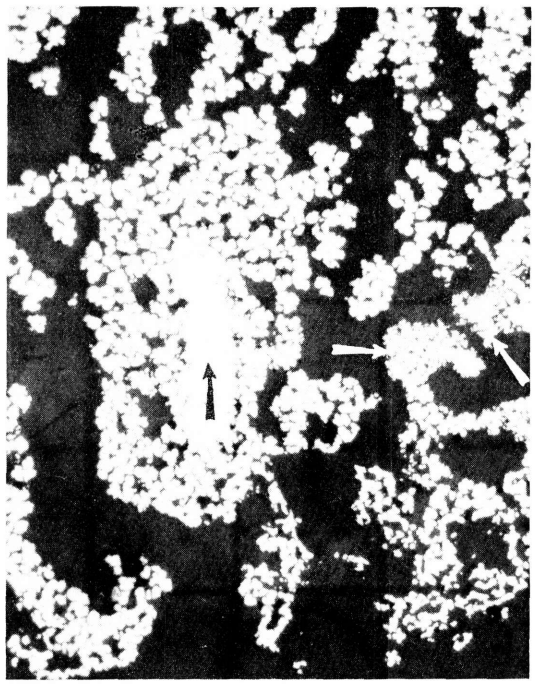

Fig. 9 - Cross section through the sample which had been discharged. The area shown was near a grid member (black arrow). Note that the grid appears to be completely surrounded by a rather dense agglomerate of large, granular-appearing Ag particles. Much smaller dendritic needlelike Ag crystals appear in other areas (white arrows). Lines forming the squares indicate 238-micron separation, and the original magnification was 100X.

Fig. 10 - Illustration of a third common form of dendritic Ag particle in the discharged sample. These particles (white arrows) were also aciform-type crystals but much coarser and less close-packed than those seen in the bottom of the figure (black arrows). Magnification was the same as in Fig. 9.

there was some evidence of difference in reflectivity or the presence of grain boundaries within the larger crystals, but this difference was lost in photography and reproduction.

As was mentioned at the beginning of the report the thickness of the dark Ag_2O layer surrounding the Ag was found to increase with increasing time from the original preparation of the sample, and it is possible that the layer shown was much thinner or even nonexistent at the time that the charge was completed. However, it was also found that in the same sample and at very nearly the same time of examination the thickness of this Ag_2O layer varied. This variance is illustrated by Fig. 12, taken very nearly at the same time as Fig. 11 but representing a different area of the sample. It seemed to be generally true that the dark layer surrounding very small particles was somewhat thicker than the dark layer surrounding larger ones. In any case, in the charged electrode the only Ag_2O found was surrounding the remaining particles of Ag. Where Ag was present, Ag_2O was also evident, and where Ag was absent, only AgO appeared. This observation is shown by comparison of Figs. 13 and 14, which were taken at 400X. An area where residual Ag was absent, except for a few scattered particles, is shown in Fig. 13. It will be noted that the dark Ag_2O occurred only at the surface of such particles. In Fig. 14, on the other hand, the entire area was filled with residual Ag particles, including the quite large portion of the supporting grid. Every particle was found to be surrounded by

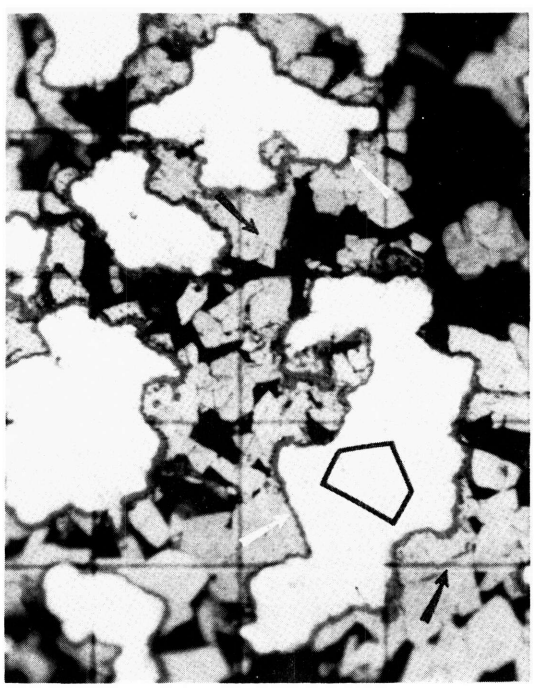

Fig. 11 - View of residual silver particles (open arrow) surrounded by a dark layer of Ag_2O (white arrows) in a charged plate. The larger AgO crystals appear as an intermediate shade of gray (black arrows). Note that, while coverage of Ag particles by Ag_2O layer was complete, some breaks occur where the Ag_2O layer was covered by AgO crystals. Lines indicate about 15-micron separation, and the original magnification was 1600X.

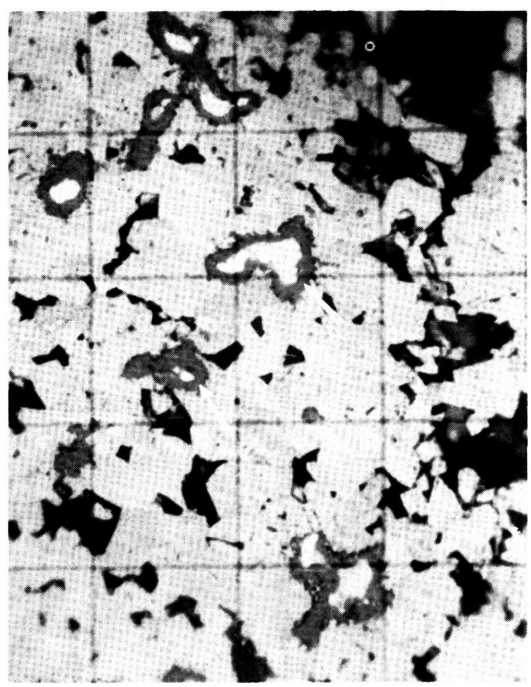

Fig. 12 - Illustration of the difference in thickness of Ag_2O layer on different portions of the same sample. The conditions were the same as for Fig. 11. Residual silver particles were much smaller here, but Ag_2O layers (white arrows) appeared to be thicker. Note the rather dense and impervious layer formed by the AgO crystals.

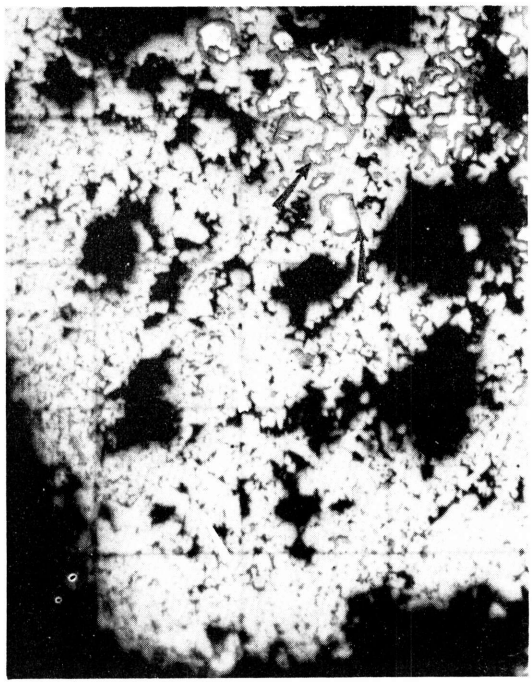

Fig. 13 - An illustration of the charged sample in an area containing very little residual Ag. Note that the only dark Ag_2O which appeared had formed around the Ag particles in the upper right corner of the picture (black arrows). The portion of the sample without Ag particles appeared to consist entirely of AgO (white arrows). Lines represent about 60-micron separation, and the original magnification was about 400X.

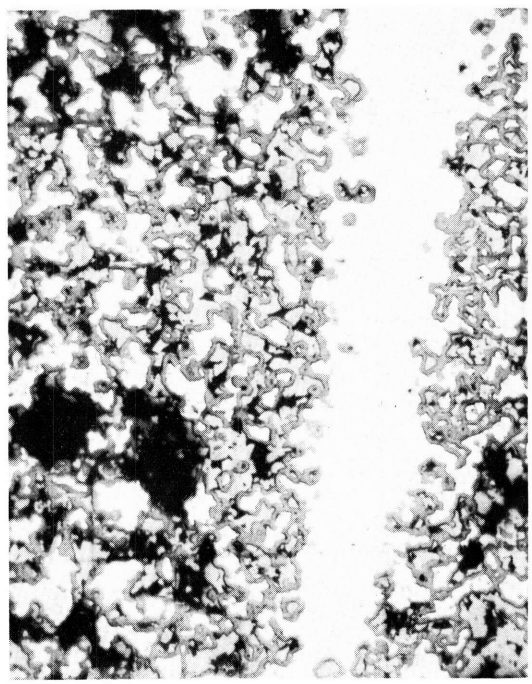

Fig. 14 - Same sample as seen in Fig. 13 but here showing an area with a large number of residual Ag particles and a portion of the grid. Note particularly that each Ag particle (white) was surrounded by a Ag_2O layer (dark) which separated it from the AgO (light). Magnification was the same as for Fig. 13.

a fairly uniform layer of the dark Ag_2O. It should also be noted that the attack on the grid metal had been very penetrating and in many cases appeared to have caused complete encirclement of areas at the surface of the grid.

The condition of the surface layer of the charged sample is shown in Figs. 15 and 16. A considerable number of unoxidized Ag particles remained in the surface layer. Although crystals of AgO extended right up to the surface and rather effectively filled the spaces between Ag particles, the outer surfaces of the Ag particles were practically bare, as indicated by the short arrows in the photographs. Such Ag surfaces were actually covered by a very thin oxide film, not sufficiently thick to be detected in the cross section, but thick enough to make the Ag surfaces nonreflective since the particles were not surrounded by a bright halo when viewed by polarized light. As discussed in more detail subsequently, such a halo is indicative of a clean, metallic surface. As mentioned earlier, there were some indications that perhaps the plastic had reacted slightly with the oxides on the original surface of the sample. Further work will be done to determine whether the bare surfaces actually represented the original electrode condition or were the result of reaction with the plastic.

As can be seen in the figures, the layer of Ag_2O that was between the Ag and AgO was of comparable thickness in all photographs of this sample except where the Ag on

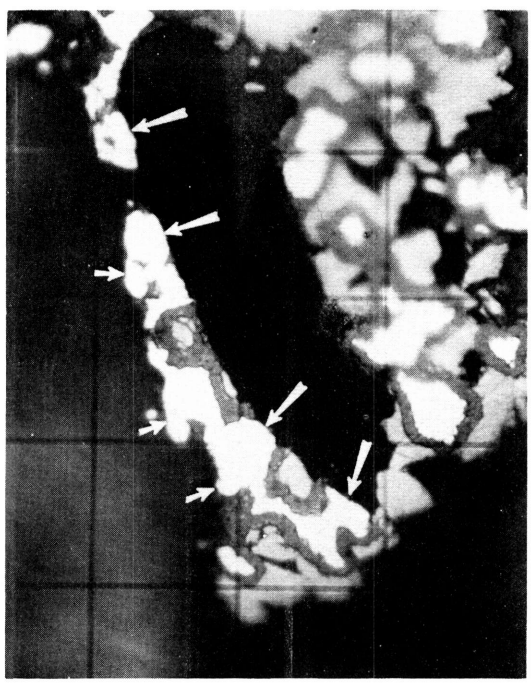

Fig. 15 - An example of the lack of Ag_2O or AgO formation in some areas of the surface layer of the charged sample. Note the apparently unattacked Ag surface where it was exposed at the surface of the sample (short arrows) and at the surface of the interior cavity (long arrows). Lines indicate about 15-micron separation, and the original magnification was 1600X.

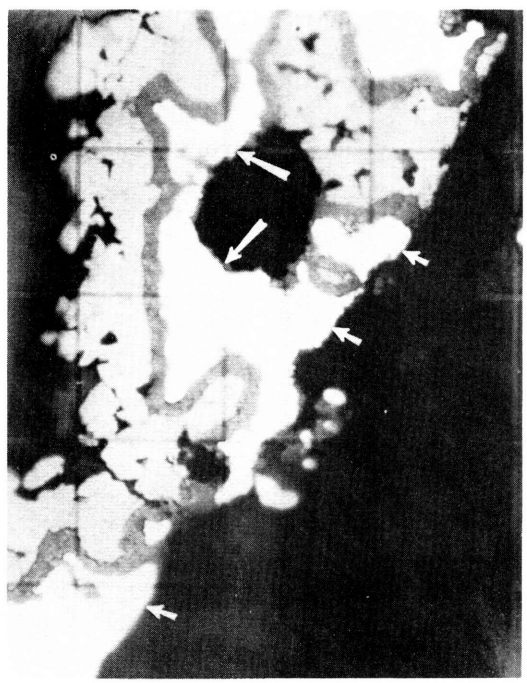

Fig. 16 - Another view similar to Fig. 15. Note again the lack of attack on Ag at the surface (short arrows) and in the interior void very close to the surface (long arrows). Magnification was the same as in Fig. 15.

which it normally formed was exposed at the actual surface. At such points there was very little evidence of either Ag_2O or AgO. The available surface of the plate was carefully scanned, and very few exceptions to the above observation were detected.

One-Fourth-Discharged Sample — Considerable difference was noted between the fully charged and the 1/4-discharged samples. The amount of Ag_2O appeared to have increased considerably, and instead of being present only as a narrow layer around each Ag particle that had remained at the end of the charge, the Ag_2O was now found to be a quite appreciable phase in certain areas of the sample, although other areas were much as they had been in the previous sample. It was noticed that areas containing residual Ag particles were more likely to show this increased Ag_2O than were the areas that contained no residual Ag. This difference is shown by a comparison of Figs. 17 and 18. Figures 17 and 18 should also be compared with Figs. 11 and 12, and such comparison will indicate a much increased proportion of Ag_2O in the present sample. The reminder should be made, however, that many portions of the 1/4-discharged sample still remained that had the same appearance as that of the charged sample. This again emphasized that various portions of the plate did not react simultaneously.

Figures 14 and 19 are also comparable, both being at the same magnification and both showing an area including a grid section. It was interesting that the only remaining AgO to be found in Fig. 19 was in the immediate vicinity of the grid.

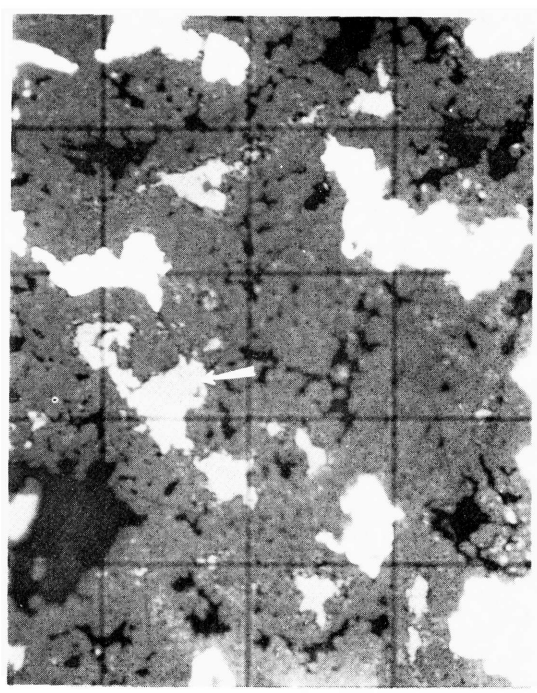

Fig. 17 - Appearance of the sample after being 1/4 discharged. Note that dark Ag_2O predominated in the area included here, although patches of AgO, such as shown by the arrow, were still present. Lines indicate about 15-micron separation, and the original magnification was 1600X.

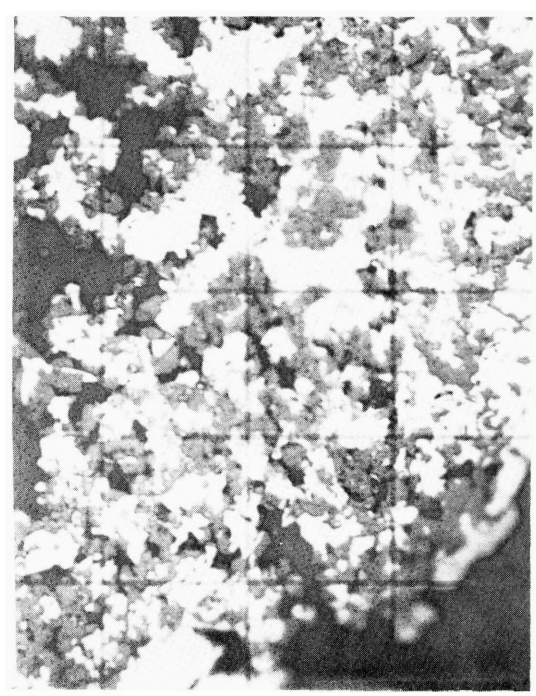

Fig. 18 - Another area of same sample as shown in Fig. 17 but one where residual Ag particles were absent. Note in this case the much larger total amount of the light AgO and the more widely dispersed and smaller quantity of dark Ag_2O. Lines indicate about 15-micron separation, and the original magnification was 1600X.

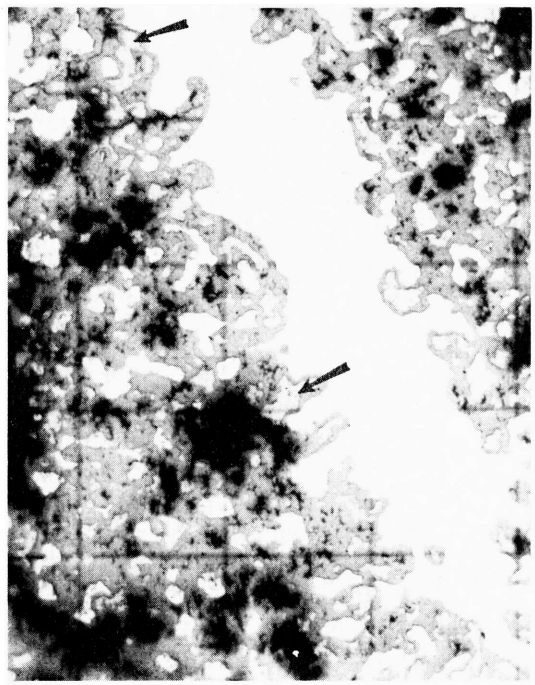

Fig. 19 - View of portion of grid and surrounding area of the 1/4-discharged sample. Note the penetrating attack on the grid, and also the presence of AgO in areas immediately adjacent to the grid (black arrows). Also compare with Fig. 14 to note the much greater amount of Ag_2O in this illustration. Lines indicate 60-micron separation, and the original magnification was 400X.

Two-Thirds-Discharged Sample — When the examination was shifted to the 2/3-discharged sample, several additional features of interest were noted. This sample continued to show diversification in the degree of reaction. Areas of newly nucleated Ag, such as shown in Fig. 20, could be found throughout the sample. Such an area is shown at higher magnification in Fig. 21. Figure 22 shows adjacent areas that were obviously in different stages of reduction. The upper right corner of the illustration shows an area where reduction had proceeded completely to Ag particles that were much larger than the newly nucleated Ag particles and had quite a different appearance. Neither oxide was present in this area. The lower left portion of Fig. 22 shows a site that was predominately Ag_2O but which also still contained small isolated patches of AgO. The larger particles shown in Fig. 22 differed not only from the very small Ag crystals shown in Figs. 20 and 21 but also from the Ag particles that remained residual at the end of the charge process (Figs. 11–14). In Fig. 23 two of the types of Ag particle are shown for comparison at a magnification of 1600X. The upper particle, which appeared as a result of the electrolytic reduction of Ag_2O, was nearly circular in shape, although its circumference is greatly convoluted. Growth of a large Ag particle was usually accompanied by a partial or complete disappearance of oxide from its immediate vicinity. The other large Ag particle shown in the lower part of Fig. 23 had a shape that is not easily defined but which can best be distinguished from the upper type of particle by its angularity, irregular outline, and by the fact that the oxide material in its vicinity remained undisturbed.

In general more areas of reduced Ag, free of remaining oxide, appeared near the surface of the electrode than near the center in the 2/3-discharged sample. Proximity to the grid of the electrode did not appear to offer any advantage in the reduction process. This observation is illustrated by Fig. 24. In this photomicrograph a considerable amount of Ag_2O can be seen in immediate contact with the grid, while at a further distance a considerable portion of the oxide has disappeared.

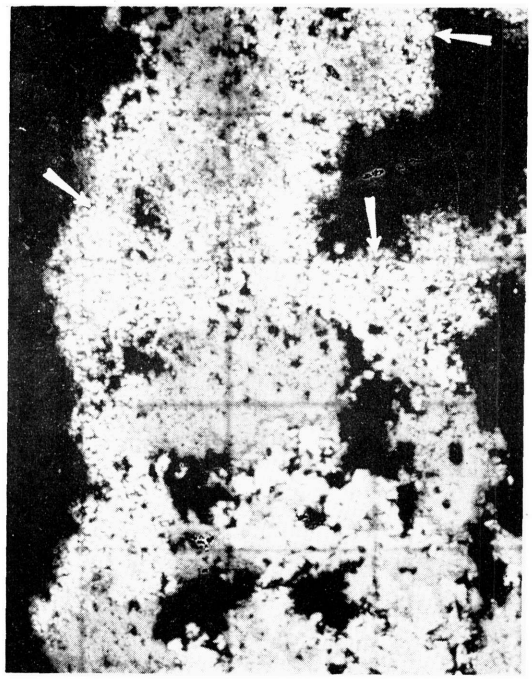

Fig. 20 - View of an area in the 2/3-discharged sample which contained numerous Ag nuclei (arrows), as well as sites of both Ag_2O and AgO. The original magnification was 400X.

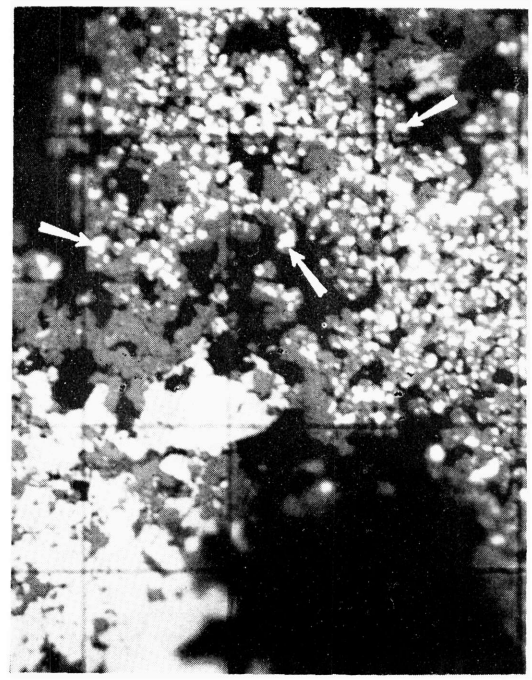

Fig. 21 - Ag nuclei (white arrows) in 2/3-discharged sample at higher magnification. Note Ag_2O which surrounded the Ag and nuclei-free area at lower left center which consisted of Ag_2O and AgO. Lines indicate separation of 15 microns, and the original magnification was 1600X.

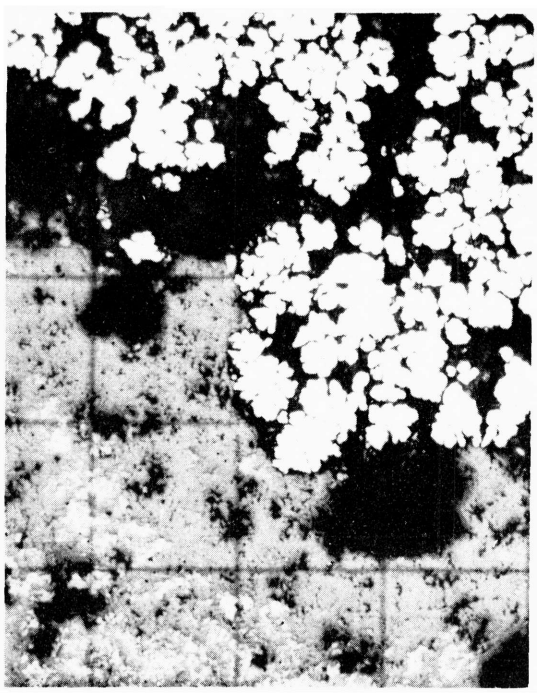

Fig. 22 - View of the 2/3-discharged sample. The area shown consisted of three phases. In upper right portion was electrolytically reduced Ag, free of either oxide. In lower left of center was an area with no Ag but consisting for the most part of dark Ag_2O. However, small patches of the lighter AgO may be seen at the bottom of the picture. Lines indicate 60-micron separation, and the original magnification was 400X.

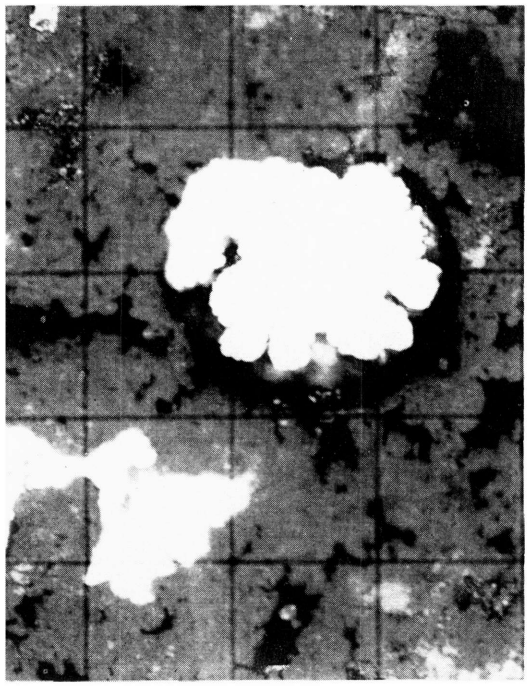

Fig. 23 - Comparison of Ag particle newly formed by electrolytic reduction in the 2/3-discharged sample (upper) and Ag particle left residual from the previous charge (lower). Note the oxide-free cavity surrounding the newly formed particle. The original magnification was 1600X.

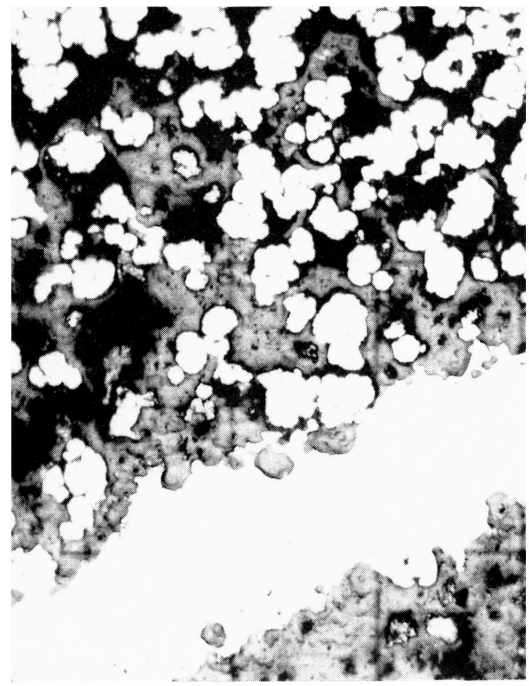

Fig. 24 - Illustration of the large amount of Ag_2O remaining in the vicinity of the grid for the 2/3-discharged electrode. Note that most of the Ag particles appeared to have the characteristics that indicated that they had been formed in this reduction and that most were surrounded by at least a small oxide-free area. Lines indicate spacing of 60 microns, and the original magnification was 400X.

Discharged Sample — Figure 25 is a magnified view of an area of Fig. 9 at the site of the grid cross section. At this magnification it can be seen that although the particles had a somewhat granular appearance, they also had very rough and convoluted surfaces as evidenced by their very irregular cross section. Since the impregnating plastic was transparent, these particles could be examined for a short distance below the surface by slowly advancing the microscope fine-focusing control. From this technique it was determined that these grainlike crystals were joined in a network similar in structure to that which would be formed by dendritic growth, but it was also possible that such an apparent network was actually the result of individually growing crystals contacting one another in the process of growth. Since the actual surfaces of such grainlike crystals were found to contain many small crystals of quite regular form, it was also possible that these grainlike structures were aggregates of much smaller crystals, but these aggregates were not visible in the cross sections of the granular crystals.

A point is illustrated in connection with the completely reduced Ag dendritic crystals that will be of value to note in this and subsequent examination. The question is often asked as to whether an oxide layer that is quite thin can be detected by these sectioning techniques. The answer is, of course, that only an oxide layer of considerable thickness can be seen in such cross sections unless resorting to the very special technique of low-angle sectioning. In the case of Ag, however, the pure electrolytic form has a brilliant

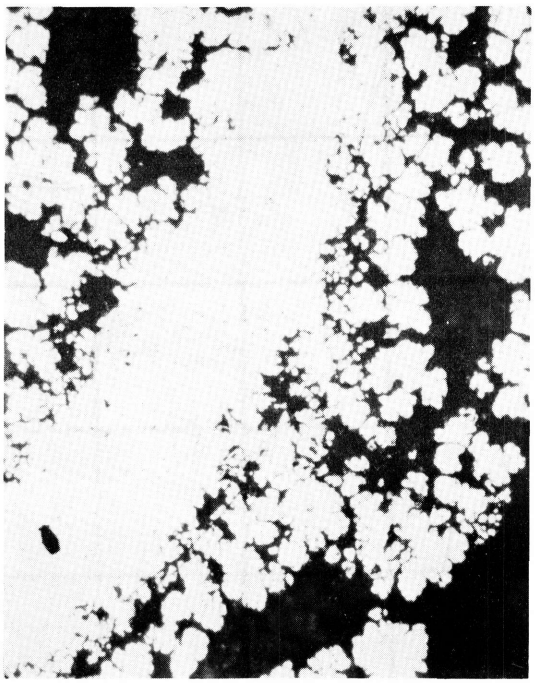

Fig. 25 - A view of the discharged sample which shows a further magnification of a portion of the grid seen in Fig. 9. Note that both large and small granular particles of Ag appeared together and in the vicinity of the grid. Lines represent 60-micron separation, and the original magnification was 400X.

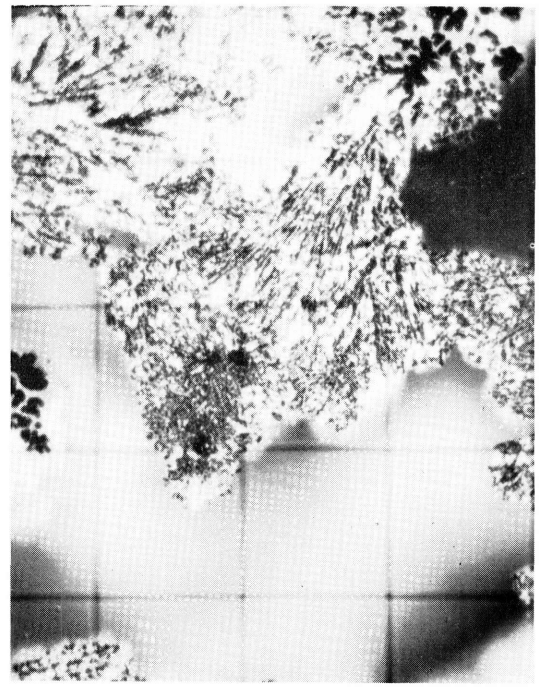

Fig. 26 - An example of the appearance of the discharged sample when using polarized light. Note the reflectivity of the underlying Ag, indicating the complete absence of an oxide film. Lines represent 60-micron separation, and the original magnification was 400X.

white surface, and when polarized illumination is used, the light penetrating the surface of the plastic is reflected back from lower surfaces of the Ag as a brilliant halo in which sectioned crystals stand out starkly (Fig. 26). In such a case as Fig. 26 shows, the brightness of the reflected light indicated that no substantial amount of oxide could be present, although traces of Ag_2O were seen in other areas of the sample, and at some points crystals of appreciable size were found. In areas where the Ag was covered with even a very thin layer of oxide, the tendency to reflect light from surfaces buried in the plastic was lost, and the area surrounding the sectioned crystals remained dark under polarized light. When bright-field vertical illumination was used and the light was unpolarized, most of the reflections were from the sectioned surface of the Ag, so that this distinction between areas with and without an oxide film could not be made (Fig. 27).

Examination of these Ag particles at higher magnification revealed nothing of additional interest, as they seemed to be solid, with very few internal voids and showed no internal structure with the method of polishing that was used. The sections of the Ag particles were not etched, as the external rather than internal structure seemed to be of the greater importance. Actual external surfaces could often be viewed below the surface of the plastic, and although they could not be seen clearly nor be photographed with any success, these external surfaces definitely were made up of very small crystals of Ag having a regular habit of growth.

DISCUSSION

Although the electrode samples which contained AgO were unstable, the changes in the samples occurred so slowly that microscopic examination was quite practical. If a sample was examined at high magnification immediately after polishing and then at lower magnification, as described above, the effects of the amount of Ag_2O gradually increasing could be kept at a minimum. Since the increase in Ag_2O first appeared where thin Ag_2O layers separated particles of metallic Ag from AgO, and since the growth of Ag_2O seemed to be at the expense of both Ag and AgO, there was little doubt that the Ag_2O was a product of the reaction $Ag + AgO \rightarrow Ag_2O$. It has been shown by x-ray diffraction (7) and by potential measurements (8) that this reaction will take place when a Ag electrode is partially charged and then allowed to stand. Since the reaction between AgO and Ag took place chiefly, and perhaps entirely at a surface of a sample that was exposed to the atmosphere and not in the interior of the sample, it is likely that some atmospheric component or components promoted the reaction. Moisture in the atmosphere may be the component responsible, since it has been reported that the reaction between AgO and Ag is much slower when they are dry than when they are wet (9).

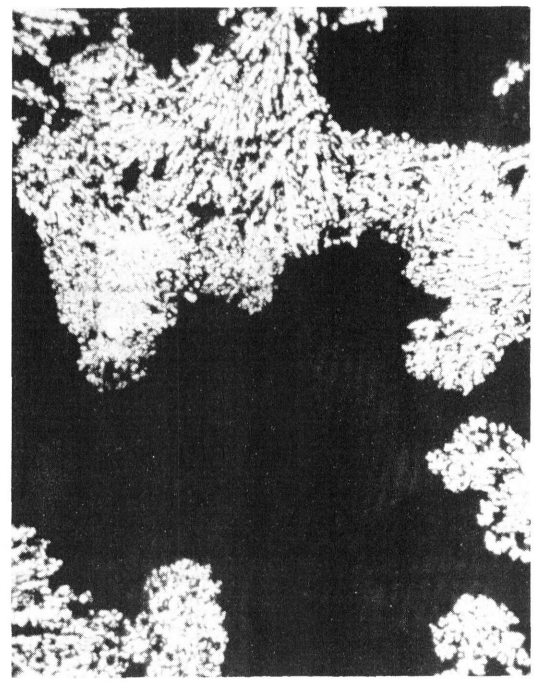

Fig. 27 - An example of the appearance of the same area shown in Fig. 26 when viewed by vertical illumination without polarization. Same magnification was used as in Fig. 26.

The sintered Ag electrode used in this work was quite porous. Although the pores varied greatly in size, the plastic impregnating agent penetrated readily into the small pores, and even at high magnification no areas were found into which the plastic had failed to penetrate (see Figs. 12 and 17 for examples). This complete penetration indicated that both large and small internal cavities were interconnected and extended without interruption to the surface of the plate. The voids that were found in the plastic near the center of the 1/4-discharged sample (Figs. 4 and 5) could not be explained, in view of the very open and porous nature of the electrode and the fact that plastic had penetrated into the pores in which voids were found. Large voids were only found in this one sample. If the voids in the plastic had been the result of gas evolving from the oxides either from decomposition of the oxides or from a reaction between the plastic and the oxides, the voids would have appeared as small bubbles on the surface of the active material and should have been more widely distributed throughout the electrode.

It was obvious that particles of active material which appeared to be isolated (for example, see the cross sections shown in Figs. 6, 7, 9, and 10) were actually in electrical contact with the rest of the electrode. As can be seen in the figures, the particles that appeared to be isolated reacted simultaneously with areas in which the active material was obviously touching. The connections for the particles must have been above or below the plane of the cross sections.

Figures 2, 3, 6, and 7 show that having only one side of the Ag electrode face the counter electrode did not limit the reaction to that side or even favor that side strongly. The similarity between the two surfaces of the electrode probably resulted from both the high porosity of the sample and the relatively low current density used for charge and discharge. If a sufficiently large current density had been used, it is likely that the reaction products would have been concentrated on the electrode side that faced the counter electrode. Under the conditions used, however, there was much more difference between adjacent areas of a sample than there was between the two surfaces of a sample.

The reactions taking place at the grid during discharges can be studied at low magnification by comparing Figs. 3, 8, and 9 or at higher magnification by comparing Figs. 14, 19, 24, and 25. It was obvious that the various reactions did not necessarily originate at the grid. At the end of a charge there was a large amount of unoxidized Ag in the vicinity of the grids (Figs. 3 and 14). When the electrode had been discharged to the Ag_2O/Ag potential, there was still AgO remaining near the grids (Fig. 19). When the electrode had been 2/3 discharged and a large amount of Ag had formed from the oxides, there was no evidence of concentration of this Ag at the grid (Fig. 8). These results indicate that many areas of the plate were in good electrical contact with the grid, even though they do not appear in the figures to be in contact. Although much grid corrosion had occurred, there was no evidence that the usefulness of the electrode had been impaired by this corrosion. Reactions seemed to be more hindered at the grid than elsewhere. Few regions of the electrode had as large an area of relatively close packed particles as the regions near the grids. Density or comparative lack of porosity near a grid may hinder the movement of oxygen between the active material and the bulk of the electrolyte during charge and discharge. If concentration gradients built up in the electrolyte near the grid, the reactions would be expected to take place with more difficulty there.

Charged Sample

When Ag is oxidized anodically in alkaline solutions, the final oxidation product is AgO. The large amount of residual Ag that remained at the end of a charge was not surprising. The discharge capacity had indicated that only 61 to 64% of the capacity theoretically possible was actually being obtained under the conditions used. Although some Ag had been lost from the electrode, as indicated by reaction with the cellulosic separator and by the fine precipitate of Ag in the cell, only a small proportion of Ag was lost. Therefore, one would expect a large amount of Ag or of both Ag and Ag_2O to remain on the charged electrode. The photographs agreed with the results of x-ray diffraction which showed that the surface of a charged sintered Ag electrode had only AgO and Ag (7). X-ray diffraction of sheet Ag also showed only AgO and Ag at the end of most charges, although some Ag_2O was detected after a moderate or high rate charge when using sheet Ag that had developed a rough surface (10).

One-Fourth-Discharged Sample

The discharge reaction in the period before the discharge potential of a silver oxide electrode reaches the second plateau is the reduction of AgO to Ag_2O. This period was between A and B of Fig. 1. It was, therefore, expected that the sample from the 1/4-discharged electrode would show a large increase in the amount of Ag_2O, a corresponding decrease in the amount of AgO, and no change in the amount of Ag. Comparison of Figs. 17 to 19 with Figs. 11 to 14 showed the large increase in Ag_2O and decrease in AgO that was expected. Similar results have been obtained by x-ray diffraction (7,10). Apparently, those areas of AgO that had Ag remaining at the end of the previous charge were reduced in preference to areas that had no metallic Ag. The reason for this preference may be that the regions with Ag were also the regions with some Ag_2O remaining at the end of a charge. During discharge this Ag_2O promoted formation of additional Ag_2O in these

places. As a result there were still areas which were predominantly AgO after the discharge potential reached the Ag_2O/Ag plateau (Fig. 5). The great variation between different areas indicated that it was possible that a single sample might not be representative of the whole electrode.

Two-Thirds-Discharged Sample

Two reactions were expected to occur as the electrode discharged from point B to point C on Fig. 1. In this period Ag would form from the reduction of Ag_2O, and a part of the remaining AgO would be reduced to Ag_2O (7,10). Microscopic examination verified these reactions and showed that the 2/3-discharged electrode was composed largely of Ag and Ag_2O with a small amount of AgO present. When the electrode was removed from the cell for cutting the sample, it had been noted that the electrode side that had faced the counter electrode was white, indicating complete reduction to Ag, while the other side was not completely white except near the grids. Microscopic examination of the sample did not indicate any particular difference between the side of the electrode that faced the counter electrode (top of Figs. 6 to 8) and the other side. Reduction to Ag had taken place to approximately the same depth on both surfaces. Most of the newly reduced Ag was at or near the electrode surface, although there were some areas where Ag extended from one side of the electrode to another (Fig. 7). It was interesting that even after the electrode was 2/3 discharged, an area immediately adjoining newly formed Ag still contained a large amount of AgO and had as yet developed no reduced Ag particles (Fig. 21).

As noted above, in addition to the very small Ag particles which probably were newly nucleated, much larger Ag particles were also present (Fig. 23). While these large particles could conceivably have originated from areas such as that shown in the upper part of Fig. 21, it seemed more likely that the large particles were produced by a different mechanism. Facts which supported this belief were that very few of the small particles were coexistent with the larger particles, the areas where the two forms occurred had general differences, and the larger particles had a more open distribution. It was concluded from a study of samples that the very fine aciform crystals, such as are shown in the upper part of Fig. 21, originated in areas like the ones shown in Fig. 18 in which there were few, if any, Ag particles remaining at the end of the previous charge. The larger, more granular-appearing Ag crystals seemed to form where Ag particles were residual from the charge. It was generally noted that where the large granular type of Ag particle appeared, the angular residual particles disappeared. It is suggested, without other confirmation, that these larger granular particles grew around or upon the residual Ag particles. The residual Ag probably formed a convenient nucleus for the deposition of Ag by reduction. In areas without residual Ag particles from the previous charge, new nuclei would be necessary, and this requirement may account for the very small aciform crystals in such areas. A supporting observation was that small, faceted crystals of Ag appeared on the outer surfaces of the granular type crystals. This observation indicated a slow and uniform deposition.

The cavity that largely surrounded the growing Ag particle shown in Fig. 23 illustrated the fact that metallic Ag occupies less volume than Ag_2O and indicated that the oxide went into solution before it deposited as Ag. Note that the upper Ag particle of Fig. 23 retained angularity at the upper left where it appeared to contact the oxide and that the residual Ag particle at the lower left did not contact the electrolyte. This observation suggested that reduction of the oxide did not take place where the oxide coated the Ag tightly and that electrolyte must be present for the reaction to occur.

Discharged Sample

At the end of a discharge, the silver oxides had been almost completely reduced to metallic Ag. Oxides were not detected visually or by x-ray diffraction (7,10). Although

traces of oxide remained, for all practical purposes the electrode could be considered to consist of Ag alone. The reason for all of the various modifications of Ag structure found in the discharged electrode could not be readily determined, since their evolution was not traced through the various stages of reduction. From the study of the composite panoramic view of the electrode, it seemed that the granular type of Ag generally appeared near grid members and the very small dendritic needlelike or aciform crystals tended to be developed near or at the surface of the plate (Fig. 9). Some Ag having the needlelike structure appeared to surround cavities that were sufficiently rectilinear to suggest that these cavities may have been the former site of crystals of regular habit (Fig. 10), although no crystals of this type were detected. The type of particle shown by the black arrow in Fig. 10 was less common and when found was usually in the central area of the sample. The angular form of Ag particle, the only form observed at the end of a charge, had entirely disappeared by the end of a discharge. It was assumed that as the oxide covering was gradually reduced, the electrolyte penetrated to all of these residual Ag particles and then reduction took place on their surfaces and their shape changed as they grew. The size and form of the Ag particles must have a large effect on the ease of their oxidation during the following charge. The small particles probably react more readily than larger particles, and it is likely that the largest particles will fail to oxidize completely during the next charge and will tend to be perpetuated.

CONCLUDING REMARKS

This progress report has shown that the silver oxide electrode can be studied profitably by the use of microscopy. Further work is obviously needed for a full explanation of the phenomena reported here. Additional reports will be made on studies of the physical state of the silver electrode under various conditions of charge and discharge.

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13. ABSTRACT

A study of the silver oxide electrode was made with the optical microscope, using methods that had previously proven successful for the lead-acid battery.

It was determined that Ag, Ag_2O, and AgO could be easily distinguished from one another in the polished section of the electrode without resorting to any etching or staining. Crystals of the three phases were also found to be of a size that made it feasible to follow crystallographic changes that occurred during the course of a discharge. Although considerable variations occurred in different areas of the same electrode, results were in agreement with previously obtained x-ray data.

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Ag						
AgO						
Ag_2O						
Batteries						
Microstructure						

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(PAGE 2)

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