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Crystallographic Changes During Oxidation (Charging) of the Silver Electrode

Part 2 - Oxidation Following Five Charge-Discharge Cycles at a Low Rate

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Previous Report in This Series

"Part 1 - Initial Oxidation of an Industrial Sintered Plaque," C. P. Wales and A. C. Simon, NRL Report 6701, May 3, 1968.

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ABSTRACT

The microstructures and morphology observed during the charge of a sintered Ag electrode that had received five slow charge-discharge cycles in 35% KOH solution differed considerably from those observed during the initial charge. The Ag particles in the discharged electrode with five prior cycles were larger and much more uniform in size than those in the unused electrode. The size of the voids between particles had also increased with cycling. After the electrodes were charged, the aggregates of AgO crystals were smaller in the cycled electrode and more widely spaced. Very little difference was noted in the forms of either Ag_2O or AgO crystals in the two cases, but considerably less of either oxide was formed during the sixth charge. The electrode capacity had declined as a result of the gradual change in structure.

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 2 -- OXIDATION FOLLOWING FIVE CHARGE-DISCHARGE CYCLES AT A LOW RATE

INTRODUCTION

The Ag electrode is one element of the Ag-Zn and Ag-Cd cell. During the oxidation of the Ag electrode the individual particles are first converted to Ag_2O and then to AgO. These phase changes are accompanied by marked changes in the structure of the electrode. The changes in structure and phase that accompanied the oxidation (or charging) of the Ag electrode were illustrated in a previous report (1). This was accomplished by removing portions of the electrode at intervals during the charging process, preparing these portions for microscopic examination by appropriate treatment, and recording the structure by photomicrography. In Ref. 1 the initial oxidation of a commercially prepared sintered Ag electrode was studied. In the present report a similar electrode is shown during oxidation following several cycles at a relatively low rate of charge and discharge, and the manner in which this cycling had altered the structure of the electrode is discussed.

The reason for this interest in the microstructure of the Ag electrode, and in the various oxidation states produced during the charge-discharge cycle, is to determine whether crystal morphology or aggregation is related to performance of the electrode. If a relationship can be established, it may be possible to determine and control the optimum structure for a given type of performance in order to improve the overall charge acceptance and capacity of this type of electrode. The investigation made to the present indicates that such a relationship does exist and that it can be evaluated.

PREPARATION OF THE ELECTRODE

The samples were taken from a commercially manufactured Ag electrode designed for use in a Ag-Zn storage battery intended for comparatively low-rate discharge, requiring 1 hr or more for a complete discharge. The electrode consisted of sintered Ag particles on a grid of expanded Ag sheet. Electrode dimensions were 41.5 mm wide by 38.0 mm high by 0.8 mm thick. The theoretical capacity of the electrode, based on the amount of sintered Ag present, was 2.9 amp-hr.

The electrode was charged and discharged between two parallel-connected counter electrodes of the same sintered Ag construction. All three electrodes were wrapped with treated cellulose separator. The cell containing these electrodes, which is described in Ref. 1, was constructed so that the electrode used as the sample could be removed readily from the separator for taking portions necessary for microscopic examination. The cell contained an excess of 35% KOH solution and was kept at approximately 25 °C.

The removable electrode was given five charge-discharge cycles according to the following procedure. Each charge was made at the constant current estimated to require 20 hr for a complete charge. A discharge was made at the same current as the previous charge. Progressively lower values of charge and discharge current were used as the electrode capacity gradually declined with cycling (Table 1). In the sixth charge the

Table 1
Capacity Changes During Cycling of the Silver Electrode

Cycle (number)	Current (ma)	Charge Capacity to Beginning of Ag_2O/AgO Plateau (amp-hr)	Discharge Capacity to Beginning of Ag_2O/Ag Plateau (amp-hr)	Total Discharge Capacity (amp-hr)
1	104	0.702	0.648	2.23
2	104	0.430	0.581	2.20
3	92	0.453	0.572	1.82
4	84	0.333	0.546	1.76
5	84	0.272	0.557	1.86
6	84*	0.265*	—	1.45†

*Compensated for removal of portions of the electrode.
†Estimated from charge capacity.

current was interrupted at the points indicated in Fig. 1, so that the electrode could be removed from the cell and a sample cut from the electrode. The remainder of the electrode was then returned to the cell and placed within the separator as before. When charge was resumed, current was lowered by an amount sufficient to compensate for the removal of each sample, so that current density on the remainder of the electrode was unchanged.

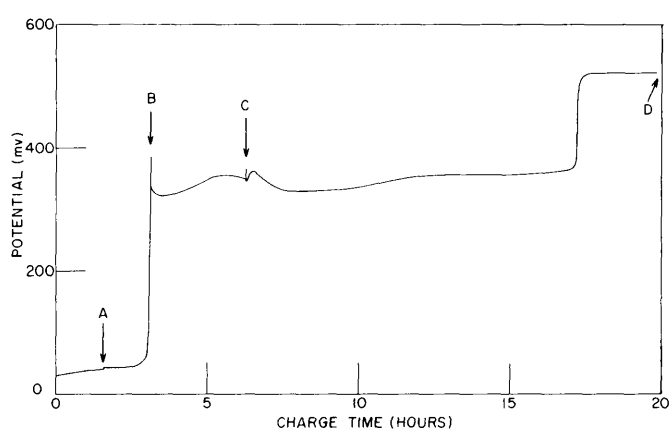

Fig. 1 - The potentials measured during the sixth charge of the sintered Ag electrode. The potentials are given with respect to the Ag/Ag_2O reference electrode and do not include open-circuit potentials while charge current was interrupted for sample removal. The letters A to D indicate the four points at which samples were cut from the electrode for microscopic examination.

For samples, approximately 19 by 21 mm, were cut from the removed electrode. The first sample (point A in Fig. 1) was taken when the electrode had received approximately half of the capacity that it would normally be expected to accept before the potential rose to the Ag_2O/AgO plateau. The surface of the electrode was a medium brown color, and even distribution of Ag was visible to the unaided eye where the interior had been exposed by cutting the sample from the electrode. At this point the electrode would be expected to consist of Ag_2O and a much larger amount of unoxidized Ag.

The second sample (point B in Fig. 1) was taken when the charge potential rose to the peak that marked the beginning of the Ag_2O/AgO potential plateau. The electrode was a uniform dark brown color on the surface, but when the sample was cut less Ag was visible in the interior than in the previous sample. At this point the electrode would be expected to contain the maximum amount of Ag_2O. The passage of additional current would result in the formation of AgO.

The third sample was removed at point C in Fig. 1, where the capacity accepted per unit area was estimated to be twice the capacity required to reach the potential peak (point B). The side of the electrode closest to the grid was the brown color of Ag_2O but about 2/3 of the other side was gray in patches. No Ag was visible to the unaided eye in the cut. At point C in Fig. 1 the electrode would be expected to contain some AgO that had formed from the Ag_2O already present at point B and some AgO from the additional Ag that had oxidized to Ag_2O between points B and C.

For the final sample the electrode was charged until strong oxygen evolution was occurring (point D in Fig. 1). The electrode had accepted less charge than anticipated; therefore, the charge current actually used was 12% larger than the true 20-hr rate for this charge. After oxygen evolution was occurring, the electrode would be expected to contain large amounts of AgO that were separated by a thin layer of Ag_2O from the Ag that had failed to oxidize.

The steps in the preparation of the samples for microscopic examination, and the difficulties experienced, have been covered in some detail in previous reports (1,2). For this reason only a brief description is given here.

After each sample was cut from the electrode, it was immediately put through several changes of distilled water to wash out the KOH solution. Following this the samples were drained of removable water and then dried as quickly as possible in a vacuum dessicator. After drying, the sample was impregnated with a self-curing resin. After the resin had hardened, the sample was cross-sectioned, and the sections were ground and polished to a condition suitable for microscopic examination.

DISCUSSION OF OBSERVATIONS

As in the previous reports a distinction will be made between microstructure and macrostructure. Discussion of macrostructure will be limited to those features that can be distinguished at the comparatively low magnification of 250X or less. This low magnification is not sufficient to observe the individual crystals but is important, because it revealed the changes in aggregation that took place, the appearance and disappearance of large voids in the active material, evidence of uneven reaction rates, and other features of interest. Microstructure, on the other hand, is used here to discuss the changes that could be seen in the individual crystals of the electrode, which usually required magnification well above 250X.

The Sample Charged to Half the Capacity of the Ag/Ag_2O Potential Plateau

Table 1 shows that the capacity which the electrode accepted during charge at the Ag/Ag_2O potential plateau (that is, before potential reached the peak that began the Ag_2O/AgO plateau) had decreased markedly with cycling. On the sixth charge this capacity was only about 1/3 as large as on the first charge. As a result of this decrease in capacity at the Ag/Ag_2O plateau, the sample taken at point A in Fig. 1 contained only about 1/3 as much Ag_2O as the samples that were charged to half the capacity of the Ag/Ag_2O potential plateau on the first charge cycle (1). The appearance of the Ag particles, following the five charge-discharge cycles at a relatively low current, was quite different in both macrostructure and microstructure from what was observed in the first charge of a sintered electrode of the same construction at a similar state of charge (1).

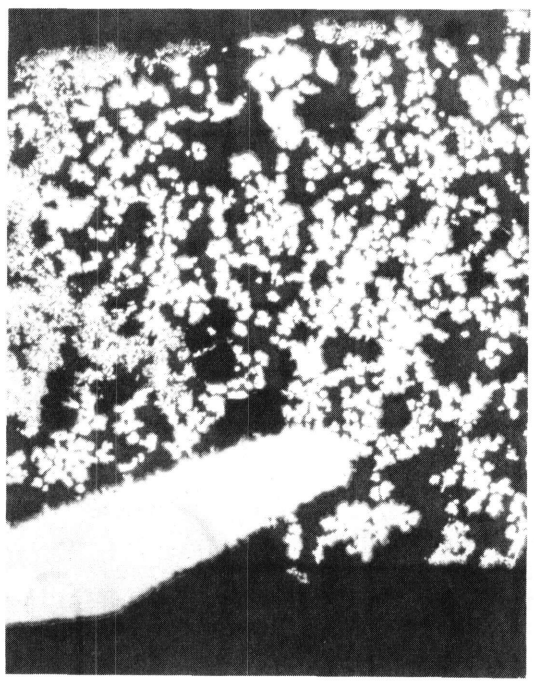

Fig. 2 - Low-magnification (100X) appearance of the electrode charged to point A of Fig. 1 after five charge-discharge cycles. Surfaces of the electrode are at the top and bottom of the photograph. The large white area at the bottom is a cross section of the expanded metal grid, and the white particles are Ag active material. The areas where Ag_2O had formed on these particles do not show at this magnification. The black areas are voids in the plastic (dark gray) that was used to impregnate the electrode. The lines forming squares indicate 238-μ separation in this and all other photographs that had an original magnification of 100X.

Macrostructure — The general type of macrostructure found in this sample is shown in Fig. 2. It should be emphasized that this and all subsequent photographs discussed in this report are of cross sections through the electrode and, therefore, also represent cross sections through individual crystals or through other particles of which the electrode is composed. In Fig. 2 the bright particles are the Ag that was produced by the electrolytic reduction of the oxide during the previous discharge. Some of the larger particles, however, were probably residual from the original sintered electrode, which was composed of a mixture of many particle sizes (Fig. 3). Some of the particles in the unused electrode were relatively large, but many were much smaller than the particles shown in Fig. 2 and were too small to be visible at 100X magnification. In Fig. 2 the large bright area is a portion of the expanded sheet Ag grid used as a support for the original sintered particles. The gray areas show the presence of the impregnating plastic and, therefore, represent former voids in the electrode which were filled by the impregnation. The black areas are also voids in the electrode, but in this case the plastic did not fill them, and actual holes appeared in the polished section at such points of

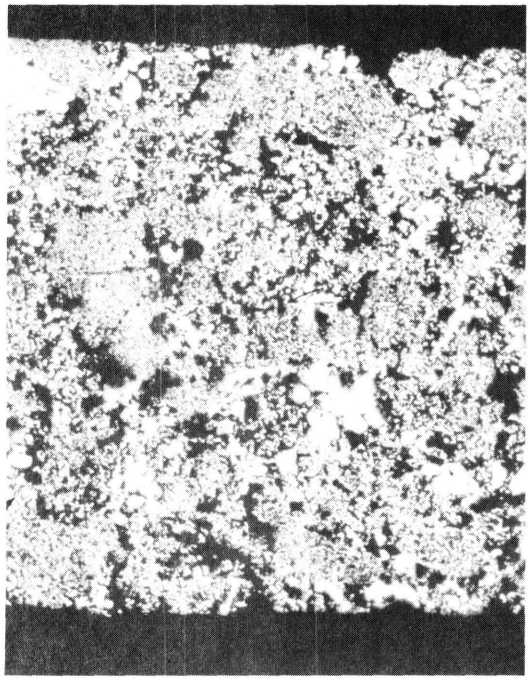

Fig. 3 - The structure of a commercially prepared sintered Ag electrode that had never been used. Ag particles (white) are present in a variety of sizes, and most particles are smaller than those shown in Fig. 2. The original magnification was the same as in Fig. 2.

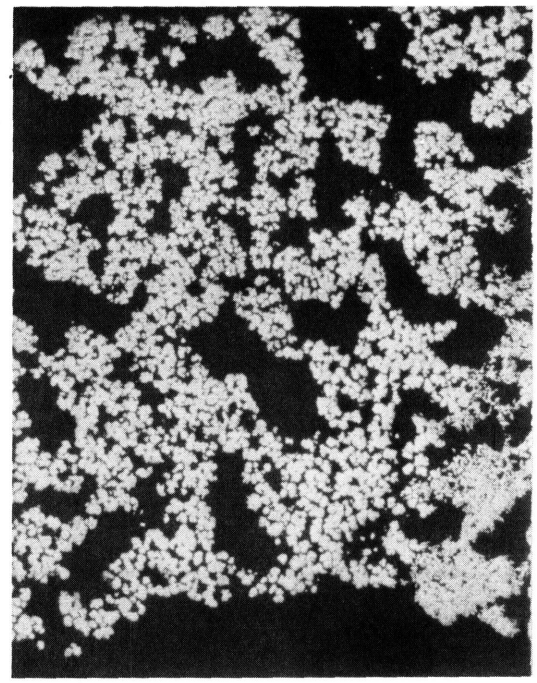

Fig. 4 - The structure of a discharged electrode that had been charged and discharged over 200 times. The electrodes shown in Figs. 2 to 4 all had the same original construction. Compare the Ag particles and void spaces shown here with those in Figs. 2 and 3. The original magnification was the same as in Fig. 2.

incomplete impregnation. Although the charge to point A of Fig. 1 produced some oxidation around the Ag particles, the small amount of Ag_2O cannot be detected at this low magnification (100X).

If the original structure shown in Fig. 3 is compared to the structure in Fig. 2, it can be seen that most of the smallest Ag particles had completely disappeared in five cycles and had been replaced by a larger granular sort of particle. Large granular Ag particles were also found in a discharged electrode that had received over 200 charge-discharge cycles, with the majority of the cycles having been done at the 20-hr rate for charge and discharge (Fig. 4). The electrode shown in Fig. 4 has been discussed in an earlier report (2).

On the very limited amount of evidence shown by comparison of Figs. 2, 3, and 4, and of other photographs made at the same time but not illustrated here, it would appear that the smaller Ag particles tended to disappear after only a few cycles at the relatively low charge-discharge rates used here. The granular particles of larger size which replaced them tended to form agglomerates with increasingly large spaces between the agglomerates. Although the particles found in the electrode represented by Fig. 4 averaged a somewhat smaller size than those of the electrode represented by Fig. 2, the size difference was probably not significant. The voids had become significantly larger with

repeated cycling, however. The change in pore or void size can be seen by comparing the compacted structure of the unused electrode (Fig. 3) to the structure with large voids obtained after five cycles (Fig. 2) and to the structure with larger voids obtained after many cycles (Fig. 4). The electrode that had received 218 cycles of charge and discharge also contained many areas where very small needlelike crystals could be seen (2). Areas of these very small crystals were unusual in the sample which had received only five cycles.

Microstructure — Although sufficient charge current had been passed to oxidize 9% of the Ag into Ag_2O, many of the individual Ag particles had little or no Ag_2O on their surfaces. Figure 5 shows an area at a magnification of 1600X where no appreciable thickness of oxide could be noted, although lack of reflectivity from the void areas indicated that the surfaces of these Ag particles must be covered with at least a thin film of oxide. The small Ag particles present in the unused electrode did not have convoluted surfaces, such as were present on these larger particles shown in Fig. 5. There were indications that Ag particles which remained unoxidized at the end of a charge served as nuclei for deposition of Ag as nearby Ag_2O went into solution during a discharge at low currents and the convoluted surfaces formed as the Ag particles gradually increased in size during the discharge (2).

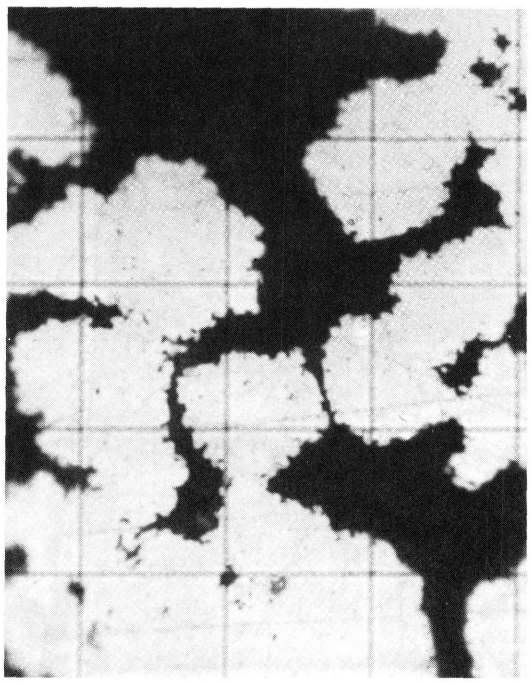

Fig. 5 - An area of the electrode shown in Fig. 2 where the Ag_2O coating was not visible on the Ag particles. The lines forming squares indicate 15-μ separation in this and all other photographs that had an original magnification of 1600X.

In contrast with Fig. 5, note the much more evident oxidation that had taken place upon the Ag particles seen in Fig. 6. Both pictures were made from the same sample but of different areas. Note that the particles in Fig. 6 are smaller than the particles shown in Fig. 5, where no appreciable oxidation had occurred. During the first charge of an unused sintered Ag electrode, oxidation occurred first at the surfaces of the smaller particles and did not appear on the surfaces of the larger particles until a later stage in the process (1). The present work shows that this observation continued to be true after the electrode had been cycled several times.

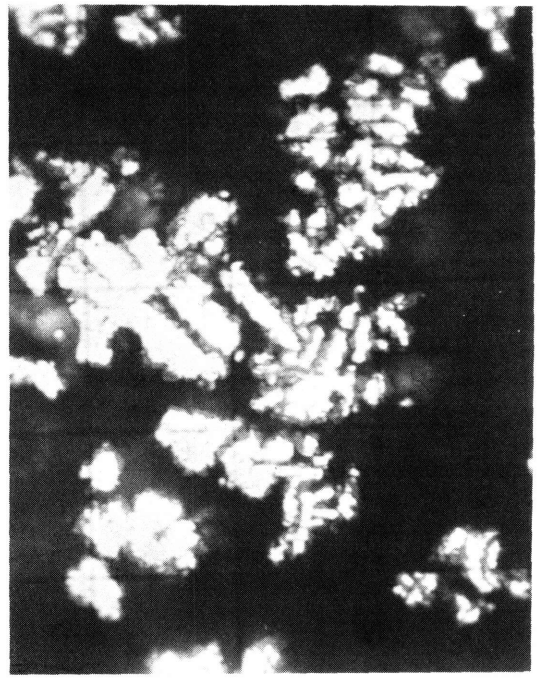

Fig. 6 - An area of the sample shown in Fig. 5 where the Ag particles were smaller and where Ag_2O (dark gray) had formed on the surface of the Ag particles (white). The original magnification was the same as in Fig. 5.

As a general rule the oxidation had proceeded very unevenly in various parts of the electrode. While this was due in part to the difference in rate of oxidation between small and large particles, it was also caused in part by other factors, such as unequal current distribution or differences in conductivity in different parts of the electrode. This was evident, since similarly sized particles in different areas of the electrode were oxidized to varying degrees. This varying degree of oxidation made it extremely difficult to make any visual quantitative estimate of the total amount of oxidation without resorting to particle measurement in a great many parts of the sample. Based on the charge ampere-hours, the amount of Ag_2O formed to this point should have been about 1/3 as much as was formed in electrodes charged to half the capacity of the Ag/Ag_2O potential plateau during the initial charge of an unused electrode (1). Figure 7 shows an example of the Ag_2O present at this point during the initial charge. Although the Ag particles in Fig. 7 resemble the particles in Fig. 6, the oxide layer on the particles was somewhat thicker and more extensive for the electrode shown in Fig. 7, as a result of having passed approximately three times as much charge current. Areas lacking appreciable Ag_2O were more common in the sixth charge, but the surface of this electrode reacted as readily as the interior, in contrast to the initial charge, where oxidation was inhibited at the electrode surface (1).

The Sample Charged to the Potential Peak that Begins the Ag_2O/AgO Potential Plateau

Macrostructure — The macrostructure of the sample charged to point B of Fig. 1 was not noticeably different from that of the sample charged to point A. This was to be expected, since the macrostructure was determined by the Ag particles. The amount of Ag_2O present had doubled but was still too slight to be noticed at such low magnification, as can be seen when comparing Fig. 8 with Fig. 2. These figures both show that grid corrosion had occurred during the five charge-discharge cycles. In the unused electrode the grids had smooth, regular sides, but Figs. 2 and 8 show grids with roughened, irregular sides.

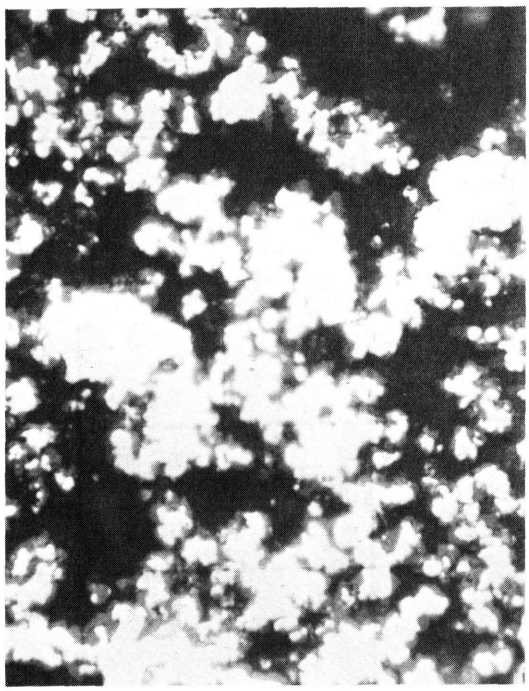

Fig. 7 - Ag_2O that formed on Ag during the initial charge of an unused electrode when the electrode was charged to half the capacity of the Ag/Ag_2O potential plateau. Compare with Figs. 5 and 6. The original magnification was 1600X.

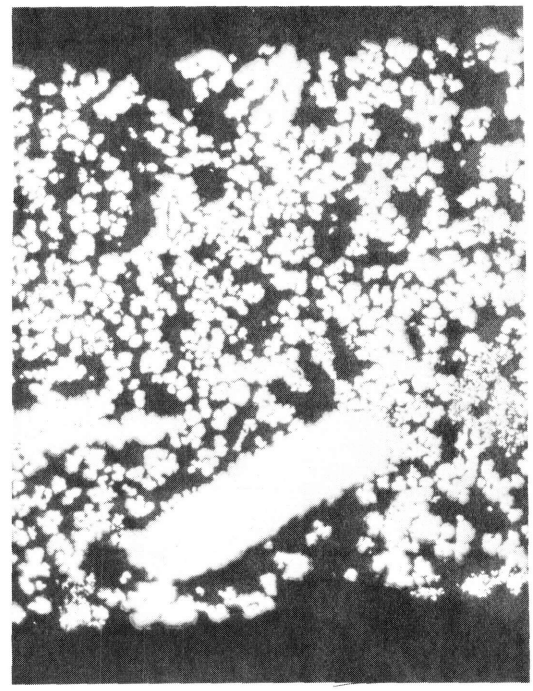

Fig. 8 - Low-magnification appearance of the electrode charged to point B of Fig. 1 after five charge-discharge cycles. A cross section of a grid is shown at the bottom. Compare with Fig. 2. The original magnification was 100X.

The macrostructure of Fig. 8 was quite different from that of an electrode charged to the potential peak during the initial charge (1). As shown in Table 1, during the initial charge of a sintered Ag electrode almost three times as much capacity was accepted before the potential reached the peak that begins the Ag_2O/AgO potential plateau as was accepted during the sixth charge. Figure 9 shows a sample taken at this peak during the initial charge of a sintered Ag electrode. The greater oxidation that occurred in the initial charge can be seen by comparing Fig. 9 with Fig. 8. The difference in the amount of Ag that oxidized before the potential reached the peak was probably due to the much smaller average particle size in the unused electrode and to the greater tendency of these smaller particles to oxidize.

Microstructure -- The microstructure of the sample charged to point B in Fig. 1 was similar to that seen in the sample charged to point A, except that oxidation to Ag_2O was much more evident. Figure 10 shows an area where the smaller particles have been oxidized to such an extent that crystals of Ag_2O are plainly visible at their surfaces. The large particle visible at the lower boundary of the photograph also had a quite definite layer of Ag_2O on its surface. In general, the larger particles throughout the sample now showed a definite layer of oxide along their surface. Figure 11 is representative of the appearance of the majority of the larger particles. However, areas could still be found where the larger Ag particles appeared to have undergone no change, except that a very thin layer of oxide must have been formed of sufficient thickness to darken their surfaces.

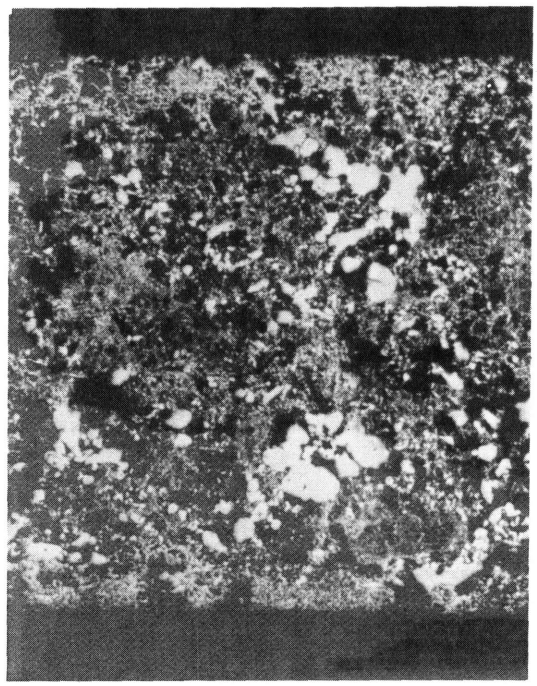

Fig. 9 - The appearance during the initial charge of a previously unused sintered Ag electrode when the potential reached the peak that begins the Ag_2O/AgO plateau. The charge current was at the 20-hr rate. The formation of Ag_2O had resulted in a considerable darkening of the sample. Compare with Fig. 8, which is at the same magnification but only contained approximately 1/3 as much Ag_2O.

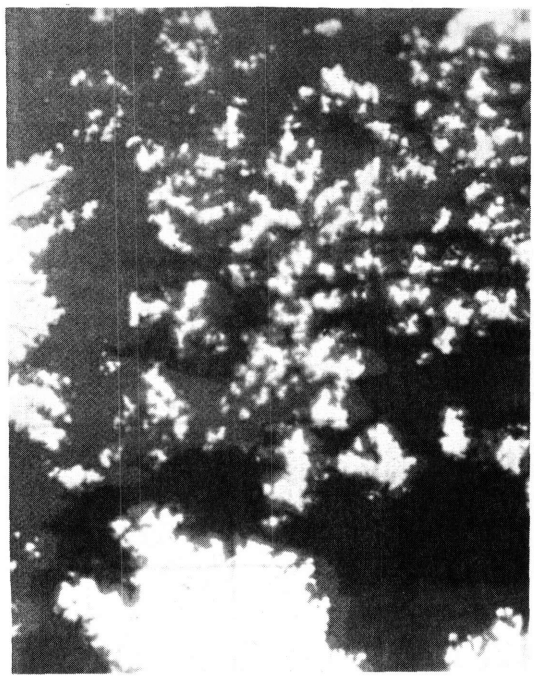

Fig. 10 - The microstructure of one area of the electrode charged to point B in Fig. 1 after five charge-discharge cycles. Most Ag particles are small in this area. Compare with Fig. 6, which was also at 1600X magnification.

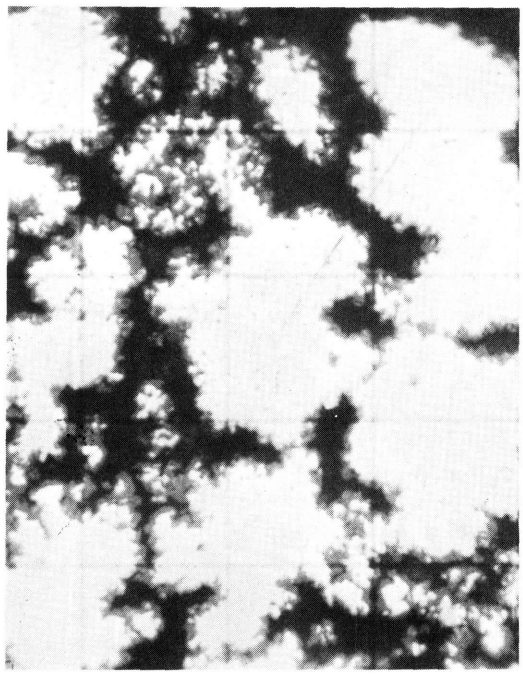

Fig. 11 - An area of the sample shown in Fig. 10 where many large Ag particles are present. Compare with Figs. 5 and 10. The original magnification was 1600X.

The fact that the larger particles oxidized much more extensively between points A and B in Fig. 1 than they oxidized up to point A was another indication that the small particles reacted preferentially. Then, as charge potential gradually increased, the proportion of oxidation that took place on the larger particles increased. Although their convoluted surfaces gave these particles a relatively large surface area, complete oxidation of these large particles did not occur at the Ag/Ag_2O potential plateau, because oxidation was gradually hindered as the oxide layer thickened. The progressive decrease in the charge capacity that was accepted before potential reached the Ag_2O/AgO plateau (Table 1) probably represented an increase in size of the Ag particles that formed during the slow discharges. The Ag particles would probably not have grown as large if higher discharge rates had been used, because particle size varies inversely with current density (3).

The Sample Charged to Twice the Capacity of the Potential Peak

Macrostructure — Examination of the macrostructure of the sample charged to point C in Fig. 1 revealed that a definite change had occurred. Even at the low magnification of 100X used in Fig. 12, it can be seen that patches of the light gray AgO have appeared in some of the former void areas. This made the apparent porosity less as the crystals of AgO began to fill up the former voids. As in the previous electrodes investigated (1, 2), increased difficulty was experienced in impregnating the samples when AgO was present. The black areas near the center of the electrode shown in Fig. 12 were a number of unfilled voids in the plastic that impregnated the sample. Also shown is another example of grid corrosion.

Microstructure — Higher magnification showed that several phases were present simultaneously but distributed apparently at random in different parts of the electrode. In some parts of the electrode newly formed AgO crystals were present; these were separated from the remainder of the original Ag particles by a thin layer of Ag_2O (Fig. 13). The AgO crystals tended to form a dense and continuous layer around each Ag particle. Figure 13 can be compared with Figs. 5 and 11 but note that Fig. 13 is at a lower magnification. The convoluted Ag surface and the penetrating attack of Ag by Ag_2O that were visible in Fig. 11 were no longer as evident in Fig. 13, and the interface between Ag and Ag_2O had become much smoother. Pores between adjacent particles were beginning to be blocked as a result of the oxides occupying a greater volume than the metallic Ag. This made electrolyte penetration increasingly difficult, and concentration gradients would gradually increase as charge continued.

Although Fig. 13 is typical of some parts of the electrode, in other nearby areas the Ag particles were still surrounded only by Ag_2O, as shown in Fig. 14. Two features of Fig. 14 are especially noteworthy. The smaller Ag particles in this area had been almost entirely consumed in the formation of Ag_2O. Since this represented a considerably

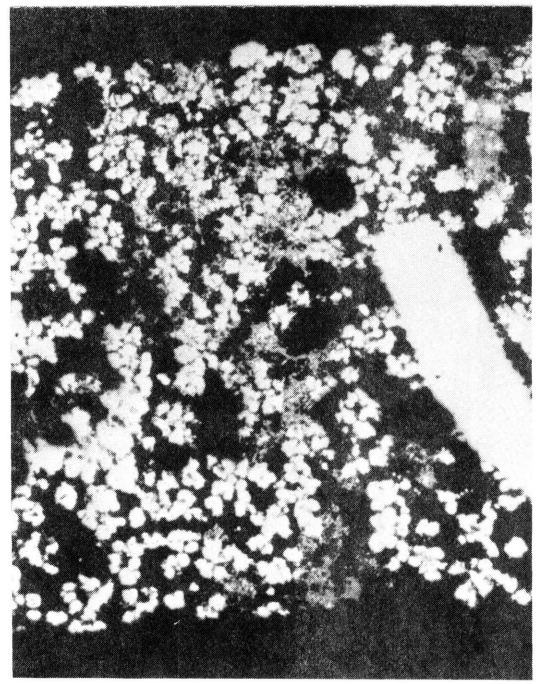

Fig. 12 - Low-magnification appearance of the electrode charged to point C of Fig. 1 after five charge-discharge cycles. Some patches of AgO have formed and can be seen as a few medium gray areas. Part of a grid is at the right. Compare with Figs. 2 and 8. The original magnification was 100X.

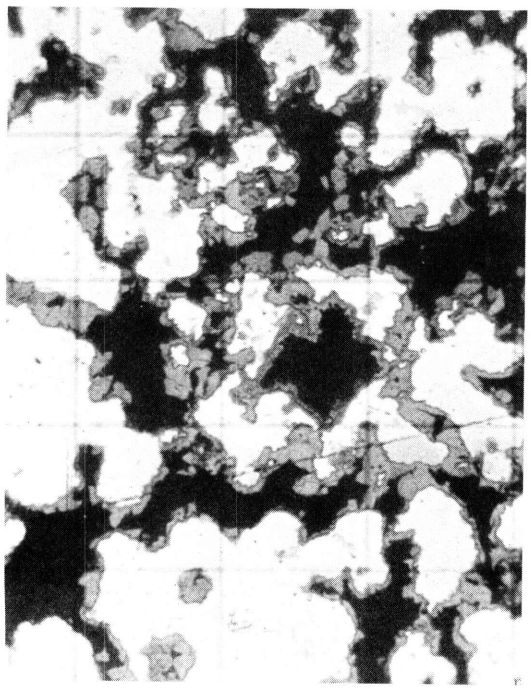

Fig. 13 - An area of the sample shown in Fig. 12 where large Ag particles predominated and where AgO had formed. The Ag appears here as the lightest shade, AgO as medium gray, Ag_2O as a darker gray in thin lines separating the AgO from Ag, and the impregnation plastic as the darkest shade. The lines forming squares indicate 30-μ separation in this and all other photographs that had an original magnification of 800X.

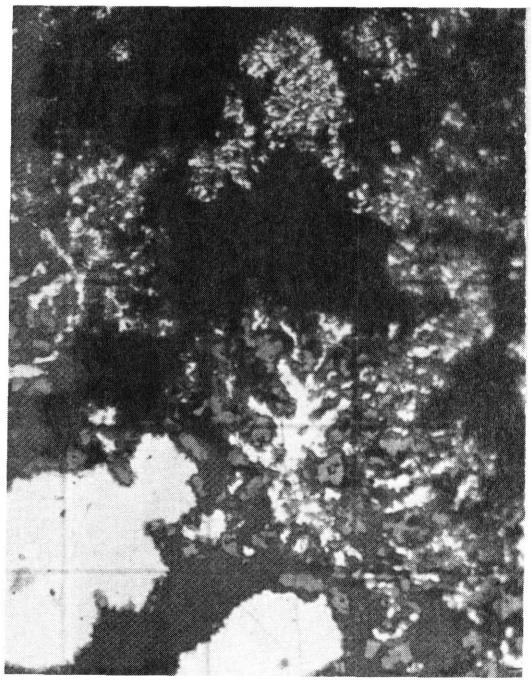

Fig. 14 - Another area of the sample shown in Figs. 12 and 13. In the areas at the top right of this photograph AgO had not formed, but formation of Ag_2O had continued. The original magnification was the same as in Fig. 13.

greater oxidation of the Ag than was observed in the sample shown in Fig. 10, it is reasonable to assume that the conversion of Ag to Ag_2O was continuing in this part of the sample, while other parts were being further oxidized to AgO. In the initial charge of a sintered Ag electrode the Ag_2O layers did not seem to thicken after the Ag_2O/AgO potential plateau had been reached (1). This difference may result from the greater amount of Ag_2O that had formed during the initial charge before AgO began to form. The other point to be noted in Fig. 14 is that despite the very advanced stage of oxidation of the smaller particles, the larger particles show very little more oxidation than was observed previously.

Figure 15 illustrates another feature of interest in this sample. As was already observed in Ref. 1, the AgO crystals at the surface of the electrode were smaller than the average size of AgO crystals elsewhere in the electrode. The surface AgO crystals shown in Fig. 15 had the additional difference of seeming to be more definitely oriented than AgO crystals were in the body of the electrode.

Still another point of interest is shown in Fig. 16. In this sample, for the first time, isolated crystals of AgO were observed. At the point where previous samples had been selected, the oxide formation was always so far advanced in areas where AgO predominated that the Ag particles were completely surrounded by AgO crystals. In Fig. 16 the individual AgO crystals can be seen attached to the Ag_2O layer that surrounded the Ag particle. These individual particles of AgO had grown to a considerable size at certain sites, while the remainder of the Ag particle had an unchanged layer of Ag_2O. From this it would appear that the AgO formed upon the surface of the Ag_2O rather than from the Ag_2O. As a matter of fact, the layer of Ag_2O appeared to be thicker under the AgO crystals than at other points. There also seemed to be a greater tendency for the crystals of AgO to form in sheltered recesses than at more exposed portions of the electrode. The AgO crystals definitely showed no preferential growth on points projecting outward from the general surface.

Since AgO patches were dispersed throughout the electrode apparently at random, the AgO had not formed preferentially in specific regions, such as near the grid or at the electrode surface. Although visually the AgO seemed concentrated on the surface farthest from the grid, microscopic examination of the cross section did not show any significant difference between the two surfaces. The formation of AgO in some regions and not in adjacent regions probably indicated difficulty in starting new nucleation sites. After AgO formed at some sites, the AgO tended to grow from these sites rather than to form new sites. Oxidation being concentrated in a few areas must result in high current density at these sites. High local current density and difficulty in diffusion through the oxide layer may explain, at least partly, why Ag electrodes must be charged at relatively low currents if full capacity is to be obtained.

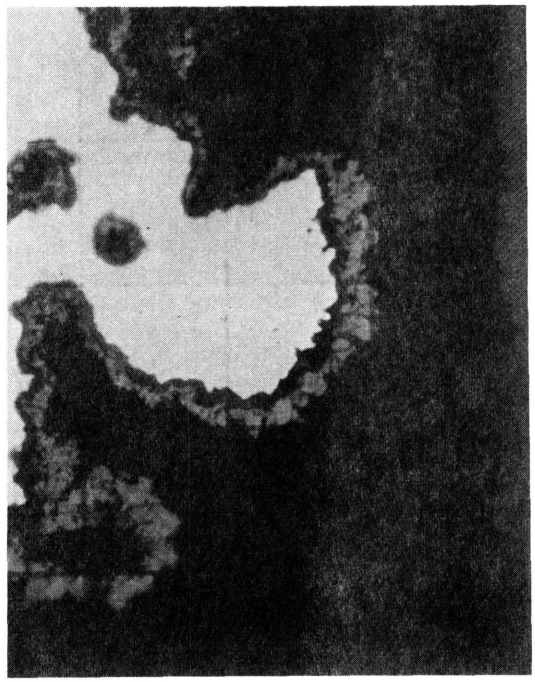

Fig. 15 - The surface of the sample shown in Figs. 12 to 14. AgO (medium gray) is separated from Ag (white) by a layer of Ag_2O (dark gray). The AgO crystals on particles at the electrode surface were smaller than they were below the surface. The original magnification was 1600X.

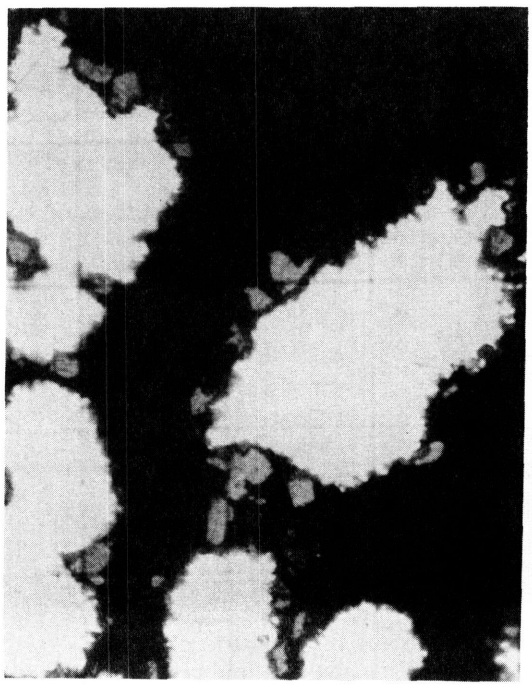

Fig. 16 - The area of the sample shown in Figs. 12 to 15 where isolated AgO crystals are present on the Ag_2O coating on large Ag particles. The original magnification was the same as in Fig. 15.

The Sample Charged to Oxygen Evolution

The sample was removed after charging until strong oxygen evolution had been occurring for over 2 hr, point D in Fig. 1. Although this electrode was charged at a relatively low current, the electrode had only accepted 50% of the capacity theoretically possible, or 2/3 as much capacity as was typical for the initial charges of similar electrodes (1). The capacity of the sintered Ag electrodes, when the 20-hr discharge rate was employed, usually decreased during the early cycles and became constant after eight to ten cycles. Table 1 shows the decreasing discharge capacity that was obtained in early cycles.

Macrostructure — The macrostructure of this sample was quite different from the structure of the samples taken early in the charge. As seen in Fig. 17, at the low magnification of 100X, the presence of AgO was quite evident, although Ag_2O was not visible at this magnification. It was somewhat surprising to observe that, despite the presence of the quite large AgO crystals, this sample seemed to have larger voids than did the earlier samples taken during this charge (Figs. 2, 8, and 12). There seemed to be a tendency for the AgO to form in tight clusters of crystals around the remaining large Ag particles. Since this electrode was kept at oxygen evolution much longer than was usual, it was possible that strong gas evolution had forced some of the smaller particles out of the channels. Figure 12 showed many more fine particles than were evident in Fig. 17.

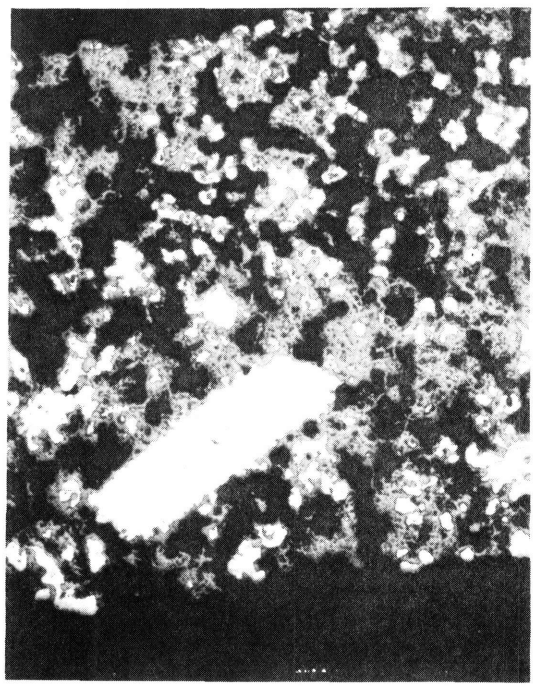

Fig. 17 - Low-magnification appearance of the Ag electrode charged to oxygen evolution after five charge-discharge cycles. Approximately half of the Ag has been converted to AgO. A cross section of the grid is at the bottom. Compare with Figs. 2, 8, and 12. The original magnification was 100X.

Figure 17 also gave another example of attack at the grid. Apparently the surface of the grid was oxidized during each charge and then the oxide was reduced to Ag on the following discharge, but the reduced Ag did not all deposit back on the original sites. This oxidation and reduction process gradually decreased the thickness of the grids. The grids of the electrode which had received over 200 cycles had been severely attacked, and their outline had become very irregular (2).

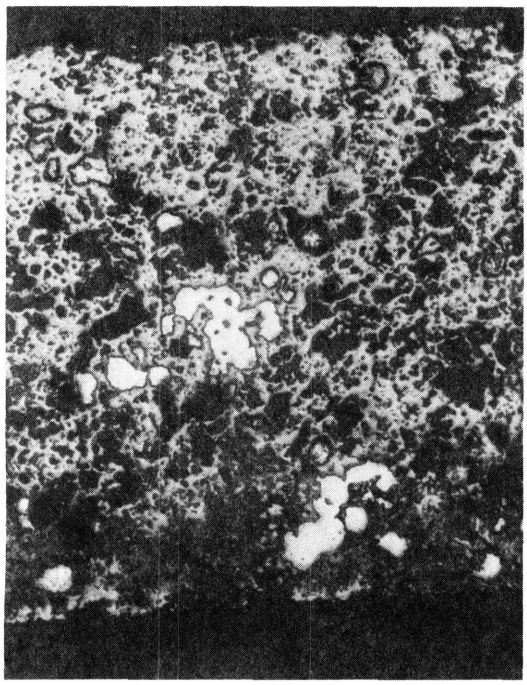

Fig. 18 - The appearance of a sintered Ag electrode after the initial charge to oxygen evolution. Note the large amount of AgO present as a result of the electrode having accepted 87% of the charge capacity theoretically possible. Compare with Fig. 17, which was at the same original magnification.

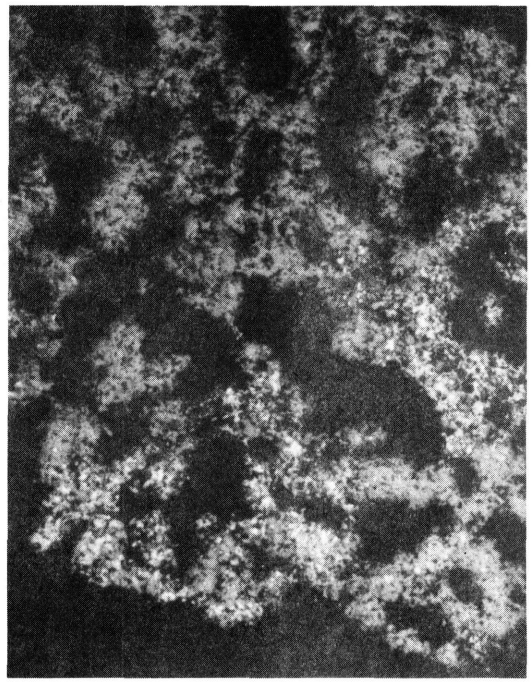

Fig. 19 - The appearance of an electrode charged to oxygen evolution after 218 charge-discharge cycles. Compare with Figs. 17 and 18, which show at the same original magnification similar electrodes earlier in their cycle life.

When a sample obtained at the end of the first charge of a sintered Ag electrode (Fig. 18) is compared with the sample charged to oxygen evolution after five charge-discharge cycles (Fig. 17) and with a sample charged to oxygen evolution following 218 charge-discharge cycles (Fig. 19), it can be seen that progressive changes in the structure occurred during the life of an electrode. The electrode gradually changed from a closely joined mass of AgO crystals with numerous small voids (Fig. 18) to a more and more open structure of large voids surrounded by apparently isolated clumps of AgO crystals, within which there seemed to be very little porosity (Figs. 17 and 19). Expansion within the electrode, when Ag oxidized to Ag_2O and then to AgO, blocked some of the channels and may have caused the electrode to become thicker with cycling. Then, as the large clumps of AgO were reduced during discharge, the tendency seemed to be for Ag to form in groups of particles, with the result that large voids occurred adjacent to the particles.

Microstructure — The microstructure of the sample charged to gassing after five prior charge-discharge cycles was noticeably different from a similar sample charged to gassing on the original charge. Figure 20 at 800X magnification shows the type of structure found in the present sample. Every area of AgO crystals had formed as a dense and not very thick layer around large Ag particles. Comparison of Fig. 20 to Fig. 13 shows that AgO thickness had increased as the charge progressed. No areas were found where Ag_2O and Ag alone were present. Figure 21 shows at the same magnification the structure found in a sample after the first charge to gassing. The growth of AgO had

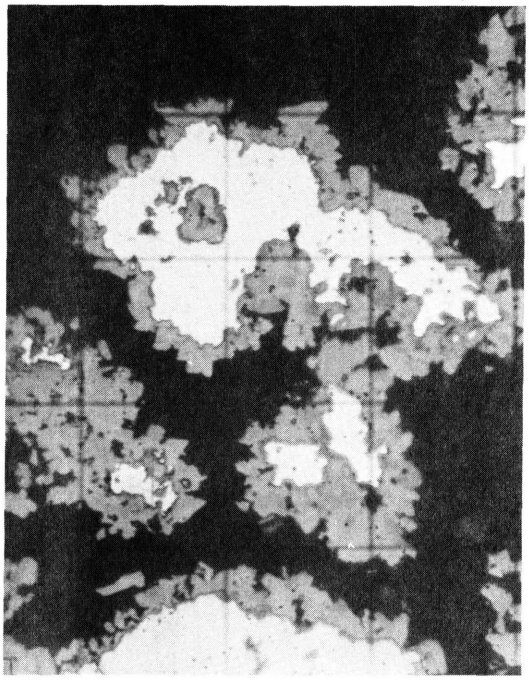

Fig. 20 - The appearance of typical AgO coating on Ag particles in an electrode charged to oxygen evolution after five charge-discharge cycles. A thin dark line of Ag_2O separates AgO from Ag. The original magnification was 800X.

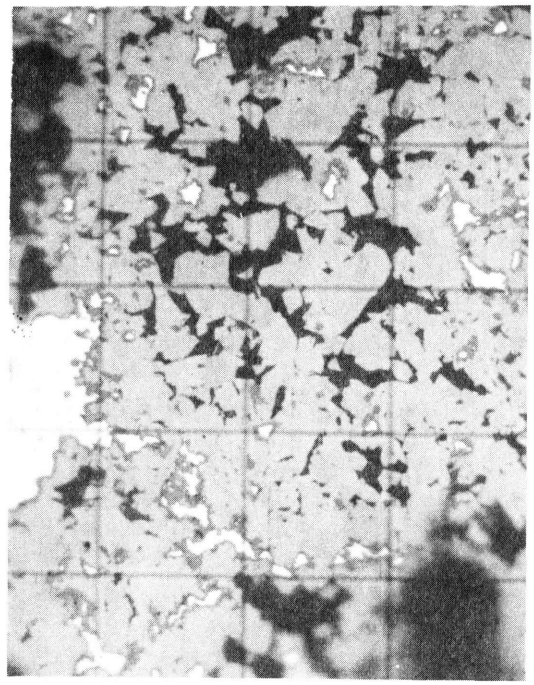

Fig. 21 - AgO that formed after the first charge of a sintered Ag electrode. Compare with Fig. 20 at the same original magnification.

been much more extensive on the first charge and gave the appearance of having attacked the Ag particles to a greater depth. Probably more AgO formed on the first charge, because a large proportion of the Ag particles in the unused electrode was small. Although there was expansion as the small particles were converted to AgO, cracks tended to remain in the AgO coatings. These cracks or channels permitted electrolyte penetration in many AgO areas until near the end of the charge; thus, many of the Ag particles could be oxidized completely or almost completely (Fig. 21). When Ag particles had grown larger after several cycles (Fig. 20), less oxidation was required to cover the large particles with an AgO layer that limited access of electrolyte to the Ag, even though the space between these large Ag particles was not filled.

In Fig. 22 a portion of the same sample shown in Fig. 20 is represented at the higher magnification of 1600X. This picture reemphasizes the relatively small size and limited extension of the AgO crystals in the charged sample that had been cycled five times. Another feature that may be of significance was the limited width of the Ag_2O layer that separated the Ag from the AgO. While the width of this layer seemed to vary from sample to sample, and even in various parts of the same sample, it was less prominent here than in any sample observed to this time and, in addition, seemed to be of constant thickness throughout the sample. For the sake of comparison Fig. 23 shows an area at the same magnification taken from the sample that had been charged to gassing on its initial charge. Note that AgO crystals were larger and more extensive here than in Fig. 22 and that the layer of Ag_2O that separated the Ag from the AgO was somewhat thicker. These figures both show the characteristic angular shapes that AgO crystals usually assume, as was noted earlier (1).

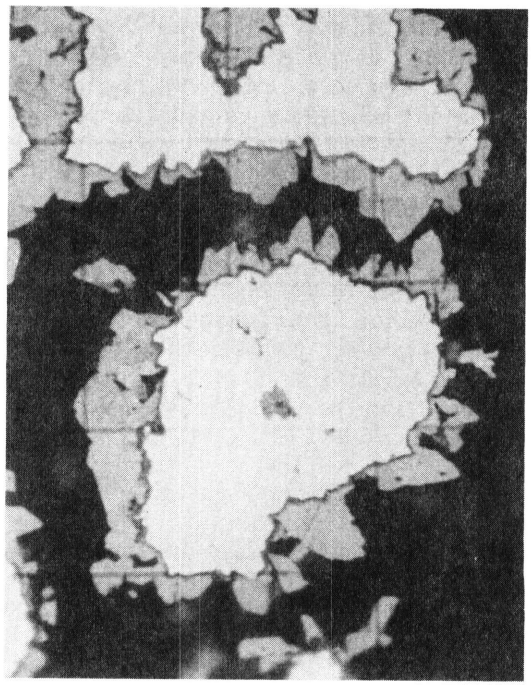

Fig. 22 - Higher magnification view of the oxide coating on Ag particles in the sample shown in Figs. 17 and 20 when charged to gas evolution after five cycles. A thin dark line of Ag_2O separates AgO from Ag. The original magnification was 1600X.

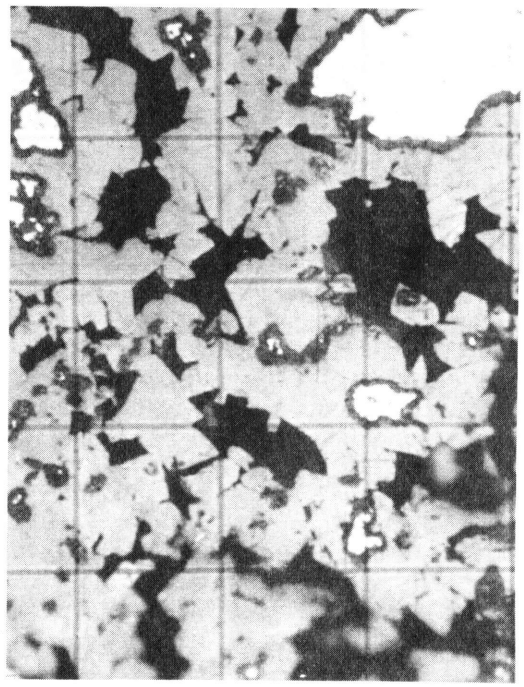

Fig. 23 - Higher magnification view of the oxide coating on Ag particles in the sample shown in Fig. 21 at the end of the initial charge of this electrode. Note that the layer of Ag_2O between the Ag and AgO is thicker here than in Fig. 22. The original magnification was 1600X.

SUMMARY

Samples were removed from a Ag electrode during a charge and were examined by optical microscopy. A study was made of the way that the structure of an unused sintered Ag electrode had been altered after five cycles at the 20-hr rate of charge and discharge in 35% KOH solution. Comparison was also made with the structure of an electrode that had been cycled over 200 times.

In an unused electrode the grids had smooth, regular sides, but after five cycles the grids had roughened, irregular sides. After 200 cycles, much of the grid had disappeared, and the outline of the remainder had become very irregular. The change probably resulted from penetrating attack at some sites during charges and deposit of Ag at other sites during discharges.

The original sintered electrode had contained Ag in a wide range of particle sizes, but by the time that the electrode had cycled five times most small Ag particles had been replaced by larger particles. Little further change in average particle size took place with 200 additional cycles. The larger particles tended to form agglomerates, and at the same time the void space between particles increased. Particle size probably had increased as Ag was deposited slowly during low-rate discharges.

During a charge the oxidation to Ag_2O took place preferentially on the smaller Ag particles that were present in the electrode, and oxidation took place unevenly in different areas of the electrode. By the time that the potential rose to the peak that begins the Ag_2O/AgO potential plateau, all small Ag particles and most larger ones had a definite Ag_2O layer on their surfaces. The amount of Ag_2O that formed before the potential rose to this peak decreased during the first few cycles and by the sixth charge was only about a third as large as on the initial charge, probably the result of the average particle size of the Ag increasing in this period.

When the electrode was charged at the Ag_2O/AgO potential plateau, at first AgO formed only in scattered areas of the electrode, while in other areas apparently Ag_2O continued to form. AgO tended to form dense, continuous layers around each Ag particle and was always separated from the Ag by a thin layer of Ag_2O. It appeared that AgO formed on the surface of Ag_2O rather than from the Ag_2O. AgO seemed to form preferentially in sheltered recesses and not on points projecting outward.

At the end of the initial charge of a sintered Ag electrode, the AgO was present in many areas as a closely joined mass of crystals with numerous small voids. By the end of the sixth charge the AgO was present as a dense but not very thick layer around large Ag particles, with the AgO and Ag arranged in clumps adjacent to large voids. Capacity of the electrode had declined as a result of the gradual change in structure, because large Ag particles did not oxidize as completely as small particles.

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13. ABSTRACT

The microstructures and morphology observed during the charge of a sintered Ag electrode that had received five slow charge-discharge cycles in 35% KOH solution differed considerably from those observed during the initial charge. The Ag particles in the discharged electrode with five prior cycles were larger and much more uniform in size than those in the unused electrode. The size of the voids between particles had also increased with cycling. After the electrodes were charged, the aggregates of AgO crystals were smaller in the cycled electrode and more widely spaced. Very little difference was noted in the forms of either Ag_2O or AgO crystals in the two cases, but considerably less of either oxide was formed during the sixth charge. The electrode capacity had declined as a result of the gradual change in structure.

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Microstructure						
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