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NRL Report 6171

Oxides on the Silver Electrode

Part 2 - X-Ray Diffraction Studies of the Working Silver Electrode

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ABSTRACT

Silver electrodes were examined in 20-50% KOH using a cell permitting simultaneous x-ray diffraction and electrochemical studies. Highly oriented smooth rolled sheet silver developed randomly oriented Ag on its surface during early cycles. Charge-discharge capacity increased to a maximum as surface area increased. AgO crystal size and amount formed varied inversely with charging current density with high charging rates giving tight coatings of small AgO crystals that limited further oxidation. Reactions took place initially at the outer surface of the electrode with oxidation to Ag_2O and AgO and reduction to Ag_2O and Ag occurring by formation of distinct crystals rather than by expansion or contraction of preexisting crystal lattices. Discharge capacity at the AgO/Ag_2O potential plateau depended more on surface area than on quantity of AgO. A slow discharge produced smoother Ag surfaces, lowering capacity of the next cycle. There was never evidence of a suboxide, oxidation state higher than AgO, solid solution, or alloy of oxygen and silver.

PROBLEM STATUS

This report concludes one phase of the problem; work on other phases continues.

AUTHORIZATION

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"Oxides on the Silver Electrode," C.P. Wales and Jeanne Burbank, NRL Report 5298, May 15, 1959

OXIDES ON THE SILVER ELECTRODE

PART 2 - X-RAY DIFFRACTION STUDIES OF THE WORKING SILVER ELECTRODE

INTRODUCTION

Investigation of the silver electrode in KOH solution is of interest since silver oxides comprise the positive active material of charged Ag-Zn and Ag-Cd storage batteries. It is therefore desirable to know the reactions and products occurring in alkaline solutions when oxidized silver electrodes are cathodically reduced, and when metallic Ag electrodes are anodically oxidized. In the present work an electrolytic cell was used that permitted x-ray diffraction examinations to be made of the working electrode during charge and discharge, instead of interrupting electrolysis and removing the electrode for x-ray examination as was done previously (1).

There is general agreement that Ag_2O having the Cu_2O type of face-centered cubic structure is formed at the first potential plateau when a silver electrode is anodically oxidized (charged) using constant current in alkaline solution. Although there have been claims that a silver suboxide may form on a silver electrode, its presence was not detected and indeed the existence of silver suboxide itself is quite dubious (1). When silver is anodized in KOH solutions, the potential rises to a peak after charging at the first plateau for sufficient time, and then monoclinic AgO forms at a second potential plateau. Finally, the potential rises again and oxygen evolution takes place. There have been unsubstantiated reports of higher oxides of silver, presumably containing trivalent silver, forming just before or during oxygen evolution. Some confusion has been caused by the report of Jones and Thirsk of what they believed was the x-ray diffraction pattern of AgO (2). Their pattern has since been shown to be that of the so-called silver peroxysulfate $Ag_7O_8SO_4$ and not AgO (1). The x-ray diffraction pattern for monoclinic AgO is well established now and has been given by Scatturin, Bellon, and Zannetti (3) and by Graff and Stadelmaier (4), among others.

Three additional oxides of silver have been reported recently. Tetragonal AgO, which appears to be a peroxide containing monovalent and divalent Ag, has a diffraction pattern closely resembling that of monoclinic AgO and was prepared by McKie and Clark through the action of ozonized oxygen on hot silver powder (5). Vol and Shishakov have reported that a silver peroxide having the NaCl type of cubic lattice forms when silver is heated in oxygen (6). A modification of Ag_2O having the CdI_2 structure has been obtained by Kabalkina and coworkers using high pressure and temperature (7). Only the face-centered cubic Ag_2O and the monoclinic AgO have been definitely established as being present on the silver electrode in alkali (1,8,10).

EXPERIMENTAL PROCEDURE

The test electrode was a half-submerged rotating Ag disk 57 mm in diameter, mounted vertically in a cell designed for use on a horizontal circle x-ray spectrogoniometer (11). The method of mounting the disk covered its edge and back, leaving only one side to contact the electrolyte. X-ray diffraction patterns, using CuK_α radiation, were made from this side of the disk as it rotated out of the electrolyte. Initially the disk was cut from 0.25-mm-thick Ag of $99.99^+\%$ purity. This disk was not perfectly flat despite pressing, since it had been cut from a roll of sheet silver. Consequently the recording of the diffraction pattern

from this disk showed some variations with sample rotation because the sample surface was not all in the same plane. Disks cut from 1.6-mm-thick flat sheet Ag of similar purity removed this difficulty, and these were used for most of the work reported here. Satisfactory patterns have also been obtained from disks of sintered Ag cut from a storage battery electrode, but due to the porosity of this material the electrochemical reactions were not limited to one side, as was the case with sheet Ag.

A counter electrode of sintered Ag, wrapped in cellulosic separator material, faced the submerged part of the rotating specimen disk. The cell also contained a reference electrode of Ag/Ag_2O. Some work was done in 20% and 50% KOH, but the usual electrolyte was 35% KOH at 23° to 26°C, and this was used except where otherwise specified. Charge and discharge were carried out with a wide range of constant currents. The Ag sample rotated at 60 rpm and therefore the diffraction pattern was registered 0.25 second after the sample left the electrolyte, with the total time out of solution being 0.5 second. Current did not need to be interrupted during these x-ray examinations because the test Ag electrode was always partially submerged. This experimental arrangement permitted x-ray diffraction patterns to be made during charge and discharge of a working electrode simultaneously with electrochemical measurements and visual observations. The use of this cell lowered the possibility of an unstable crystalline compound being present but undetected by x-ray diffraction.

X-ray diffraction topography (12-16) was used to obtain information on the physical structure of the electrode surface without removing the specimen from the electrolytic cell. The parafocusing geometry of the spectrogoniometer is well suited for obtaining rapid topographs and the average exposure time was 20 minutes (16).

In the present preliminary work applying this technique to electrochemical deposits, dental film, mounted in a simple bracket, was held between the detector slit and the specimen (16). The film was approximately parallel to the plane of the detector slit and moved at the same rate as the sample during the scanning. The diffraction line of interest was scanned at 5 min per degree 2θ. Specimen rotation and the current were interrupted during the topographic exposures. The back of the mounting disk holding the electrode was scored so that topographs of the same area could be registered at different stages of charge and discharge. The photographic film was developed normally, and the topographs shown in this report are positive prints.

RESULTS

Before the initial anodic oxidation of the disks that were cut from smooth rolled sheet Ag, x-ray diffraction patterns showed strong preferred orientation: the (110) planes lying in the surface of the 0.25-mm sheet (Fig. 1) and the (110) and (100) planes lying in the surface of the 1.6-mm sheet. The initial charge produced first a thin layer of Ag_2O and then a thicker layer of AgO. Some randomly oriented Ag formed in the first discharge.

The highly oriented Ag substrate showed strongly through the randomly oriented oxide films in x-ray diffraction patterns made during early charge-discharge cycles. The amount of dendritic randomly oriented polycrystalline Ag present after discharge and the surface roughness of the Ag both increased gradually during the early cycles, and at the same time the amount of Ag visible by x-ray diffraction through the oxide film after charging to gas evolution gradually decreased. Capacity rose from its initial value of about 5 to 10 ma-hr and reached a maximum of about 65 to 75 ma-hr as the electrodes were cycled in 35% KOH, and a rough surface of dendritic polycrystalline Ag was produced. Although this Ag was in good electrical contact with the base Ag, it was easily broken from the surface. Randomly

Fig. 1 - X-ray diffraction topograph of the (220) reflection of the 0.25-mm sheet silver showing that the surface is mainly composed of grains in this orientation. Magnification 1.5X.

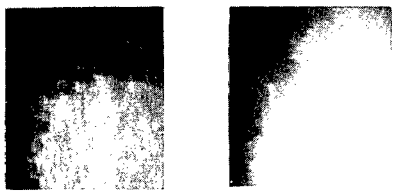
oriented Ag could also be obtained by abrading a smooth Ag disk with a fine polishing cloth before anodization, but this was not accompanied by any marked increase in discharge capacity, in contrast to the results when polycrystalline Ag was produced through repeated cycling.

There was never evidence of a suboxide, solid solution, or alloy of oxygen and silver during charge or discharge. Ag_2O lines gradually appeared in addition to the Ag lines of the x-ray diffraction patterns while dendritic randomly oriented Ag was charging at the Ag/Ag_2O potential plateau at a moderate current, for example the 12- to 24-hour rate. The diffraction lines for Ag did not broaden or shift as Ag_2O formed. The Ag_2O pattern had become moderately strong by the end of the Ag/Ag_2O potential plateau, and was about the same intensity as the metallic Ag pattern, which had decreased from its initial strength. The potential was usually 25 to 50 mv above the Ag/Ag_2O equilibrium during most of this plateau. Sometimes there was a secondary plateau at about 70 to 100 mv, after the electrode had charged about 30% of the normal amount of the Ag/Ag_2O plateau in 20% KOH. This secondary plateau was not observed in 35% or 50% KOH.

The AgO diffraction pattern could be detected when only a very small amount of AgO had formed, for example when the charge at the Ag_2O/AgO plateau was 0.3% to 0.5% of the total capacity. The Ag_2O pattern did not broaden or shift as Ag_2O was oxidized to AgO. The gas-evolution-potential plateau of the rotating electrode was about 0.1 volt lower than normal for O_2 evolution on AgO. This lower potential was an effect of rotating the electrode in and out of the electrolyte. Using a stationary electrode, the potential continued to rise for about 0.1 volt after the onset of O_2 evolution. Despite extensive gassing using various current densities, no pattern was ever observed that could be attributed to an oxidation state higher than AgO. The potential usually dropped rapidly to the Ag_2O/AgO plateau after a charge was terminated, but following very low rate charges the potential dropped more slowly than normal.

Low charging currents (1- to 10-day rates) resulted in a granular surface of light gray AgO. There was specular reflection from what appeared to be large crystal facets. The base Ag was greatly obscured or even undetected in diffraction patterns made after reaching oxygen evolution under these conditions. High charge currents (2- to 120-minute rates) gave a thinner coating of dark gray AgO having what appeared visually to be a much smoother surface (Fig. 2). Diffraction patterns of this AgO were quite poor, and the randomly oriented Ag produced through cycling was still detectable. Ag_2O was detectable after a moderate or high rate charge to gassing when using Ag that had developed the rough dendritic surface, but Ag_2O was not detected after low rate charges to gassing, or when using disks of smooth or sintered Ag. Oxides formed on a smooth Ag surface gave patterns of higher intensity than those obtained after the rough surface was developed. Strongest of all were the patterns from the sintered Ag disk.

Diffraction patterns were practically unchanged after an electrode was put on open circuit for 16 hours following a charge to 75% of capacity. After a fully charged electrode was on open circuit for 60 hours, the AgO pattern was slightly weaker but Ag_2O was not definitely visible. The self-discharge rate was obviously quite low.



(a) (b)

Fig. 2 - Topographs of the anodized 1.6-mm-thick electrode covered with AgO. Magnification 1.5X. (a) Topograph of the (200) and ($\bar{1}11$) planes of AgO after a 5-day charge. The coating is made up of individual crystals and appears granular. (b) Topograph of the same area following a fast charge. The coating is composed of a few individual crystals with much extremely fine-grained AgO not resolvable into separate particles under these conditions. Visually the deposit appeared smooth and uniform.

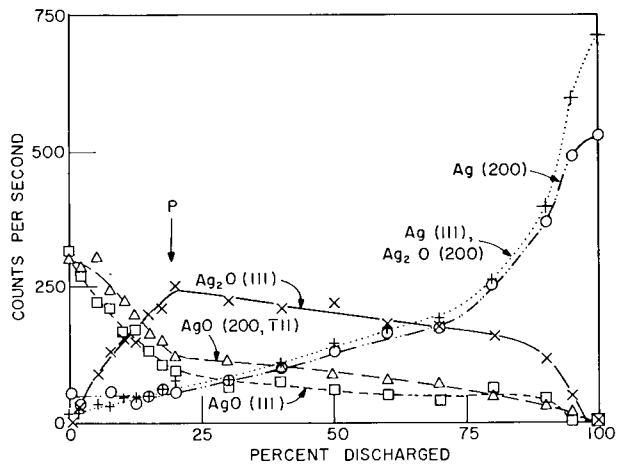
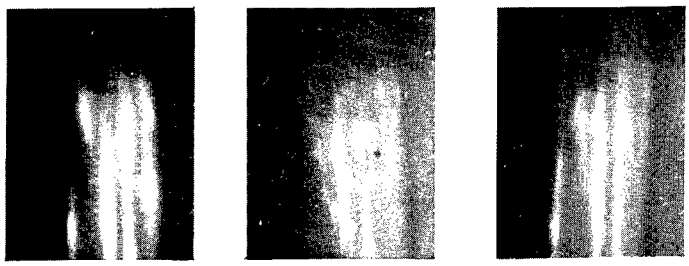


Fig. 3 - Change in intensity of x-ray diffraction peaks during continuous discharge of AgO in 35% KOH. The end of the first discharge plateau is indicated by P.

Ag_2O could be detected quite early in a discharge. It appeared to form first at areas that were the last to charge, where the AgO was thin. When using disks that had developed the rough dendritic surface, AgO was present in diffraction patterns until very near the end of discharge (Fig. 3). The first 2.5% of the discharge of Fig. 3 was done at the 40-hour rate following a charge at the 18-hour rate to oxygen evolution. X-ray diffraction patterns were made every 0.5% of discharge in this initial period, but for clarity not all the points were included on Fig. 3. Current was increased to the 10-hour rate after the electrode was 2.5% discharged, and when 20% discharged, current was increased to the 2.5-hour rate. The Ag_2O/Ag potential plateau was reached after the discharge was 19.2% complete and is indicated by P. Total capacity of this discharge was 70.3 ma-hr. Diffraction peaks for the (002) and (202) reflections of AgO showed the same trend as the two AgO peaks plotted in Fig. 3, but with intensities about half as strong. The (220) reflection of Ag had peaks about 20 to 80 counts per second stronger than the (200) peaks shown.

X-ray diffraction at the end of a discharge showed only metallic Ag, although at times small spots of Ag_2O could be seen visually. Rapid discharges (2 hours or faster rate) gave very good randomly oriented polycrystalline Ag patterns despite the speed of reduction. Slow discharges gave poorer Ag diffraction patterns having increased amounts of highly oriented Ag visible (Fig. 4). The charge-discharge cycles following a slow discharge had less than normal capacity. Capacity could be restored by a low rate charge that required several days to reach gas evolution.



(a) (b) (c)

Fig. 4 - X-ray diffraction topographs of the (220) reflection of the 1.6-mm-thick Ag electrode taken after complete discharge in several different cycles. Rolling direction vertical. Magnification 1.5X. (a) After cycling and immediately following a 2-hour discharge. The elongation of the grains in the rolling direction and a banded structure are visible. Some randomly oriented silver was present. (b) The same area immediately following a 20-minute-rate discharge. The oriented substrate is largely obscured by the randomly oriented fine grained silver dendrites. (c) The same area following a 40-hour-rate discharge. The large grains of the substrate are reappearing. Some randomly oriented silver was present.

Charge-discharge efficiency was usually in the range 95% to 102% when using 35% KOH, but was only 70% to 80% in 20% KOH. This contrasted with results reported earlier in which only 0.5% loss was found in 20% KOH (17) and no loss in 35% KOH (18) when using Ag electrodes wrapped with semipermeable separator material. Most of this loss was probably due to Ag going into solution during charge. Black particles that precipitated out of the 20% KOH were identified as metallic Ag.

DISCUSSION

There were several changes in characteristics of the Ag electrode with cycling: charge-discharge capacity, surface roughness, and amount of randomly oriented Ag all increased to a certain extent. The capacity increase was caused by the increase in surface area and did not appear to represent either actual increase in oxidation depth or an effect of oxidizing randomly oriented Ag instead of highly oriented Ag. A medium or slow rate discharge produced more highly oriented Ag and less capacity on the following cycle than did a rapid discharge, but this loss in capacity was due to a smoother surface resulting from a larger crystal size and epitaxial deposition after using the lower discharge currents, rather than to an effect of Ag orientation.

The relative line intensities of the diffraction patterns indicated that there were fewer (111) planes in the reflecting position following medium or slow rate discharges. In these cases the (200) and (220) reflections became relatively more intense. This could be the result of several morphological configurations:

1. After a slow discharge there could be fewer but larger crystals of dendritic silver which masked the oriented substrate less completely, and a fast discharge could give rise to more numerous smaller dendrites;

2. There could be preferred growth of dendrites in a fast discharge with their (111) planes parallel to the electrode surface. In a slow discharge the preferred growth directions could be [110] and [100]; or

3. In a slow discharge the reduced silver could be growing epitaxially on the substrate, accompanied by less dendritic randomly oriented deposition.

Using x-ray diffraction topography it was possible to choose which of these mechanisms was responsible for the differences in the diffraction patterns. Figure 4 shows three topographs taken from approximately the same area of the totally discharged 1.6-mm disk after several different cycles. Figure 4a shows large silver grains of (110) orientation after a 2-hour-rate discharge; Fig. 4b shows a random deposition obtained after a 20-minute discharge; and Fig. 4c shows the reappearance of more highly oriented material following a 40-hour-capacity discharge. After this slow discharge the original grains of the substrate are reappearing indicating that the deposition is taking place epitaxially onto the original crystals in the metal surface. In Fig. 4b the substrate grains are only partially visible, having been obscured by the random growth produced by a rapid discharge. It thus becomes clear why the discharge capacity of the electrode is lower and why there is a change in the diffraction pattern of the Ag immediately following prolonged discharges. The surface area of the deposited Ag is less, and the Ag appears to be plated out epitaxially on the substrate to some extent.

From this preliminary application it is apparent that the technique of x-ray diffraction topography can be used profitably on polycrystalline samples and serve as an aid in clarifying the physical mechanisms of electrodeposition under favorable conditions. This technique is a useful tool for augmenting and confirming conclusions based on the normal diffraction patterns. Especially in those instances where similar diffraction effects may arise from several different causes, topographic studies may permit selection of the correct alternative. One particularly outstanding advantage of x-ray diffraction topography in this study was the fact that it was nondestructive, and the topographs were registered without removing the electrode from the cell or otherwise disturbing the experimental setup. Other methods of examination such as electron or optical microscopy which could have yielded the same information, would have necessitated interruption of the electrochemical studies and a change in or total loss of the specimen.

The amount of oxides that were present after charging increased with cycling, as indicated both by rising capacity and by Ag from the substrate gradually becoming weaker in x-ray patterns made during the initial cycling. Weaker diffraction patterns were obtained from the oxides after cycling, despite a 5- to 10-fold increase in quantity, due to the great increase in surface roughness. The more porous surface absorbed and scattered the x-ray beam, resulting in less efficient diffraction. Surface roughness may be the cause of detecting Ag_2O at the end of some moderate or high rate charges after building up capacity, but not detecting Ag_2O in the thin films during the initial cycles of the smooth surface. Patterns of the rough surface, recorded from a porous mass of dendrites or spheroidal particles, may have viewed a greater effective cross section and thus given more intense Ag_2O patterns than a thin Ag_2O film on a smooth base could give. An alternative possibility was that roughness affected current density over the surface and deeper crevices were not charged as efficiently, with the result that Ag_2O remained on the electrode when charge current was high, but not when the charge required at least 12 hours for completion.

Ag_2O and AgO had random orientation regardless of whether they were formed on randomly or highly oriented Ag. Ag_2O formed as distinct crystals on the Ag surface and not through a gradual expansion of the Ag lattice as oxygen entered. A gradual expansion of the lattice was to be considered possible since both Ag and Ag_2O have a face-centered cubic lattice, but if this were the true mechanism of formation, the diffraction lines for Ag

should have broadened or shifted, with a progressive expansion of lattice parameters from metallic Ag to Ag_2O. Similar evidence showed that oxygen did not gradually distort or expand the Ag_2O crystal lattice in forming AgO, but AgO formed in its own definite crystal lattice. Finding AgO after charging 0.3% to 0.5% at the Ag_2O/AgO plateau indicated that initially AgO must be forming on the surface of the electrode next to the solution. The amount of AgO present at this point was less than that necessary for detecting one component of a mixture by x-ray diffraction, and this amount of AgO would not have been detected if it was distributed throughout the Ag_2O or forming at the Ag/Ag_2O interface.

Assuming that AgO formed initially from Ag_2O and that no Ag was oxidizing simultaneously, the amounts of AgO and Ag_2O should be equal when the quantity of charge current exceeded that required to reach the beginning of the Ag_2O/AgO potential plateau by 50%. This was true, judging by the relative strengths of the Ag_2O and the AgO diffraction patterns. This measurement was only sufficiently accurate to indicate that at least most current was oxidizing Ag_2O in this period, since a few percent of the current could have oxidized Ag without it being detected. When the quantity of charge current was twice that required to reach the Ag_2O/AgO plateau, the Ag_2O pattern had become quite weak, but Ag_2O still being present indicated that additional Ag had oxidized by this point. It was calculated that 15% to 40% additional metallic Ag oxidized after reaching the Ag_2O/AgO plateau in typical low or medium rate charges.

The AgO coating obscured the base Ag much more at the end of a charge than did Ag_2O at the end of the Ag/Ag_2O plateau, even when the 15% to 40% additional oxide is considered. This may indicate a greatly increased thickness of AgO compared to Ag_2O. Yoshizawa and Takehara (10) reported an oxide layer 1.5μ thick after oxidizing to the end of Ag_2O formation (electrode approximately 1/3 charged) and a layer 8μ thick after oxygen evolution (10). Since the base Ag was obscured to a large extent when heavy films of AgO were on the electrode, some Ag_2O may also be present at the Ag/AgO interface under these conditions, but masked by the AgO coating.

Charges at the 4- to 10-day rate were the most effective for oxidizing the Ag base, and for building capacity up to the maximum reached by cycling. After dendritic randomly oriented Ag had been formed on the base Ag, low rate charges appeared to oxidize this polycrystalline Ag completely. The total amount of AgO and its crystal size both varied inversely with the charging current density. The best diffraction patterns were obtained after charging with medium currents, for example 12- to 24-hour rates. This was probably the range of current densities giving the optimum particle size for x-ray diffraction. Oxygen evolution appeared to perfect crystallinity when using medium rates of charge, perhaps by perfecting the lattice or by changing the particle size.

The very poor diffraction patterns obtained after quite high charge rates were due to small AgO crystal size (Fig. 2) and in addition the AgO lattice may have been highly distorted. After charging the Ag electrode to oxygen evolution using a high current and then lowering the current, there was only a little further charge acceptance. AgO diffraction patterns remained poor, and the discharge capacity was less than if the low current had been used throughout the charge. The small AgO crystals made a more uniform coating and were more interlocking than the larger crystals obtained with slower charge rates. Thus OH^- or O^{--} could not penetrate this tight AgO coating readily and further oxidation was limited. Nevertheless, AgO of small particle size may be better in a primary or storage battery because the increased surface area may result in less polarization and improved electrical contact.

X-ray diffraction patterns indicated that Ag_2O formed as distinct crystals during discharge and not by gradual shrinking of the AgO lattice. Ag_2O formed initially on the surface of the AgO as was indicated by visual observations and its early appearance in the patterns. A discharge reached the Ag_2O/Ag potential plateau after Ag_2O covered the

electrode surface. Although only Ag_2O could be seen visually on the surface, diffraction patterns often showed AgO too (Fig. 3). Ag did not trap any oxides during a discharge. When using the Ag electrode that had developed a rough surface, after Ag_2O had formed on the outer surface of the protrusions the discharge could then proceed from the inner surface outward, with relatively little Ag forming on the surface at first. Thus the diffraction patterns would continue to show Ag_2O until close to the end of discharge (Fig. 3). Smooth electrodes discharged more evenly.

It has been recognized that the discharge following a very slow charge exhibits an unusually short AgO/Ag_2O potential plateau, although the total discharge has a very large capacity. Explanations offered for this short plateau include assuming that the depth of oxidation was greater when charging with a low current due to AgO slowly reacting with base Ag. The resultant charged electrode then would have much Ag_2O in it, and Ag_2O would cover the surface after a relatively short discharge (17). As already mentioned above, however, no Ag_2O was detected after low rate charges. The slower fall in open circuit potential to the AgO/Ag_2O plateau, following a low rate charge, could be another indication of little or no Ag_2O being present. Under these conditions Ag_2O must form before the AgO/Ag_2O potential was obtained. On the basis of the work reported here it is now believed that the unusually short higher potential plateau during discharge under these conditions resulted from having a coating of large AgO crystals on the electrode. Less Ag_2O needed to be formed to cover the AgO since the large crystals had a smaller surface area. Therefore, the potential fell to the Ag_2O/Ag plateau during a discharge after relatively little AgO was reduced to Ag_2O, even though an unusually large amount of AgO was present. Another indication of a small surface area following a very slow charge was that the AgO plateau was entirely lacking during a rapid discharge; potential fell to a minimum at first and then rose to the Ag_2O/Ag plateau. Conditions differed when using a high rate charge, as then small AgO crystals formed having a large area, although a smaller total amount of AgO was present. It took longer to cover this surface with Ag_2O on discharge. The electrode contained considerably less AgO by the time the Ag_2O/Ag potential plateau was reached, and the lower plateau was relatively short.

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13. ABSTRACT

Silver electrodes were examined in 20-50% KOH using a cell permitting simultaneous x-ray diffraction and electrochemical studies. Highly oriented smooth rolled sheet silver developed randomly oriented Ag on its surface during early cycles. Charge-discharge capacity increased to a maximum as surface area increased. AgO crystal size and amount formed varied inversely with charging current density with high charging rates giving tight coatings of small AgO crystals that limited further oxidation. Reactions took place initially at the outer surface of the electrode with oxidation to Ag_2O and AgO and reduction to Ag_2O and Ag occurring by formation of distinct crystals rather than by expansion or contraction of preexisting crystal lattices. Discharge capacity at the AgO/Ag_2O potential plateau depended more on surface area than on quantity of AgO. A slow discharge produced smoother Ag surfaces, lowering capacity of the next cycle. There was never evidence of a suboxide, oxidation state higher than AgO, solid solution, or alloy of oxygen and silver.

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Anodic coatings							
Charge-discharge capacities							
Oxidation	KOH electrolyte						
Reduction							
Ag_2O							
AgO							
Ag							
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