

# Changing the Discharge Capacity of a Silver Oxide Electrode by Charging With Periodically Interrupted Current

C. P. WALES

*Electrochemistry Branch  
Chemistry Division*

October 19, 1966



**NAVAL RESEARCH LABORATORY**  
Washington, D.C.



## CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	1
RESULTS	2
DISCUSSION	10
CONCLUSIONS	13
ACKNOWLEDGMENT	13
REFERENCES	14

## ABSTRACT

Sintered silver electrodes were oxidized anodically in 35% to 50% KOH at 25°C, usually at the 20-hr rate, sometimes at faster rates. Length of charge plus open-circuit periods varied from 8 hr to 1/60 sec. A particular charge length and open-circuit length was repeated until oxygen evolution occurred. In 50% or 45% KOH this charge method gave either the same capacity as a constant dc charge or less capacity, but in 35% KOH the improvements averaged as high as 40% under certain conditions. Best results were obtained when the preceding discharges were at low rates.

## PROBLEM STATUS

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

## AUTHORIZATION

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

Manuscript submitted July 13, 1966.

## CHANGING THE DISCHARGE CAPACITY OF A SILVER OXIDE ELECTRODE BY CHARGING WITH PERIODICALLY INTERRUPTED CURRENT

### INTRODUCTION

The discharge capacity of AgO electrodes is strongly influenced by preceding charge conditions: the amount of AgO that forms and the AgO crystal size both vary inversely with the charging (anodic oxidation) current density (1). Storage batteries containing silver electrodes are best charged by a relatively low current, because this gives the largest discharge capacity per unit weight or volume. It is often impractical to charge at rates requiring a day or more for completion, even though these low rates give the highest capacity. As a compromise, sometimes a high charging current is used at first, followed by a lower current after potential begins to rise to the oxygen evolution value. This usually gives less capacity than if a lower current had been used for the entire charge, because the fine AgO crystals that form when using high current densities may make a tight coating on the electrode surface and limit further oxidation (1).

The capacity of AgO electrodes can be increased by charging with pulses of charge current added to the normal charging current, using the proper conditions (2). Polarization decreases during a short pulse of increased current, perhaps as a result of breaking or roughening the oxide film which covers the electrode. Thus the surface area increases and a larger amount of oxide can form before oxygen evolution begins. Also, there may be an increase in conductivity during a pulse if there is appreciable activation of the semi-conductors Ag<sub>2</sub>O or AgO (3,4). However, pulses of increased charging current must be short or else concentration gradients become so large that polarization increases greatly and resultant capacity is less than normal.

Since open-circuit periods allow time for concentration gradients to disappear, the capacity can be increased somewhat by putting an electrode on open circuit for a time, when charging potential approaches the gassing value. The present work was undertaken because it was believed that there may be benefit from periodically interrupting the charge current throughout a charge.

### EXPERIMENTAL PROCEDURE

The test cells contained sintered silver plaques (30.5 × 63.5 × 0.8 mm and 41.5 × 38.0 × 0.8 mm) that had been manufactured for use in commercial silver-zinc storage batteries. If the grid of expanded silver metal is neglected, the plaques had an average weight of 7.9 or 5.8 g respectively for a theoretical capacity of 3.9 or 2.9 amp-hr. Porosity of unused electrodes, determined by liquid absorption, was from 50% to 56%. The silver plaques, used for both the anodes and the cathodes, were wrapped in cellulosic separator material of a type normally used in commercial silver-zinc cells. The test cells contained an excess of 35% or 50% KOH.

A constant current which gave an average discharge length on the order of 20 hr following a charge using this same current was defined as the 20-hr rate of charge and discharge, called the standard or "normal" charge current. Charges were continued until potential stopped changing rapidly after reaching oxygen evolution (about 510 to 530 mv

positive to the Ag/Ag<sub>2</sub>O reference electrode). The result was a charge input which was usually 101% to 102% of the following discharge. The discharges were done with a controlled constant current at the 20-hr rate unless noted otherwise and ended at a final potential 300 mv negative to the Ag/Ag<sub>2</sub>O reference. Normal charges (as defined above) alternated with charges using interrupted current. The work was done at 25° ± 1°C.

Some charges by interrupted current were repeated with commercial silver-zinc secondary cells rated at 5 amp-hr containing four silver electrodes and using 35% or 45% KOH. The electrodes were the same size as the test electrodes which had a theoretical capacity of 2.9 amp-hr and which had been manufactured for use in this size of silver-zinc cell. The silver-zinc cells were charged to 2.05 volts and discharged to 1.10 volts using the 20-hr rate of constant current (as defined above). Analysis of the electrolyte supplied with these cells showed its composition to be 45.0% KOH and 0.6% K<sub>2</sub>CO<sub>3</sub>. The "35%" KOH electrolyte was prepared from reagent grade KOH, but an analysis gave 34.7% KOH and 0.9% K<sub>2</sub>CO<sub>3</sub>. When the electrolyte was used in the cells, the carbonate concentration probably increased from degradation of the cellulosic separators.

There were four types of charge regime using interrupted current, and in each of the four a particular length of charge and open-circuit was repeated until strong oxygen evolution occurred. In the first, a cell was charged for 3 hr at the normal (20-hr) rate of constant current followed by a stand period ranging from 12 min to 5 hr. In the second, the charge periods began every 60 min, with the cell being charged at the normal (20-hr) rate for periods ranging from 59 to 45 min and the remaining 1 to 15 min being the stand period. In the third, the charge periods began every 10 min, with the cell being charged at the normal (20-hr) rate for periods ranging from 9.5 to 4 min and the remaining 0.5 to 6 min being the stand period. The fourth type of charge was derived from rectified 60-cycle alternating current, using unidirectional currents that were equivalent in coulombs per unit time to either the 20-hr or 6-hr charge rate.

Several sources of controlled dc were used. When stand times were under 1 min, a power source was used that had a recovery time of less than 50 μsec for reaching the preset current value, and for longer stand times, a dc source having a recovery time of several seconds was used. Half-wave and full-wave rectified ac were obtained from 60-cycle ac by typical rectifier circuits. Rectified ac in which the current flowed less than half of the ac cycle was obtained by using a silicon-controlled rectifier (Fig. 1). These forms of current were used rather than the customary square wave, because they were easily obtained and seemed more practical for possible widespread use.

Rectified ac which consisted of approximately the last half of an ac half-wave was called "quarter-wave rectified ac" for simplicity. Current rose rapidly to a maximum value and then fell more slowly to zero, with no current flowing for 3/4 of the time (upper part of Fig. 2). Similarly, the last quarter of an ac half-wave was called "eighth-wave rectified ac" (Fig. 2). Average current in these examples was 80 ma, including the time in which no current flowed.

## RESULTS

Before the periodically interrupted current was used, each new test cell was charged and discharged at the 20-hr rate of constant current several times until capacity stopped changing rapidly. The initial or second cycle often gave as much as 70% to 80% of theoretical capacity for the sintered silver, but the capacity dropped in the next few cycles. After about 12 cycles, capacity showed no further loss but varied irregularly, with the capacity of normal cycles in 35% KOH usually falling in the range 44% to 57% of theoretical capacity and averaging 50% to 55% of theoretical. In 50% KOH the capacity was usually in the range 36% to 48% of theoretical.

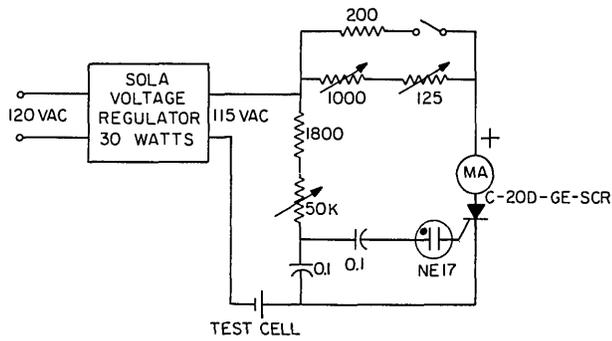


Fig. 1 - Circuit for obtaining rectified ac with current interrupted for more than half of the ac cycle

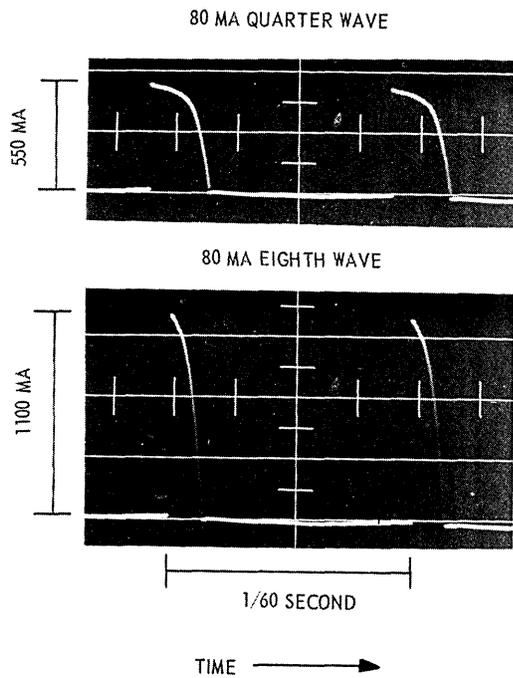


Fig. 2 - Oscilloscope traces showing the waveform of quarter-wave and eighth-wave rectified ac with approximate current calibration. Average current was 80 ma.

Variations in cell capacity were minimized by calculating the average discharge capacity of the four normal cycles (20-hr constant current charge and discharge) nearest to each discharge. This average was then taken as the "normal" capacity at that point in the cycle life of the cell, and capacity of each discharge was expressed as a percent of this normal capacity. These calculations also improved comparison between cells having different capacities. Normal capacity always means the average discharge capacity that was measured when using a constant current at the 20-hr rate for both charge and the following discharge.

Although capacity of individual normal cycles varied irregularly, 135 normal cycles in 35% KOH that alternated between the charges with repeated stands had a discharge capacity which averaged 100.1% of normal capacity and had a standard deviation of 7.1. The center half of these normal capacities fell in the range 96.1% to 103.4%. In 50% KOH there was less variation, the average of the discharge capacities of 27 normal cycles being 99.6% of normal capacity (standard deviation = 2.4) and the center half falling in the range 98.2% to 100.8%.

When stand periods followed each 3 hours of charge, most charge-stand combinations gave increased capacity in 35% KOH, and decreased capacity in 50% KOH (Fig. 3). The plotted points for 50% KOH were the average of two discharges and were very reproducible. In 35% KOH the plotted points were averages of three to seven discharges with individual capacities varying widely. For example, the 115.7% shown for 3-hr stands repeated every 3 hr in 35% KOH is the average of five discharges, divided between two cells, with individual capacities varying from 99.7% to 131.8% of normal capacity. Potentials of a charge having stand periods of 1 hr alternating with charge periods of 3 hr are given in Fig. 4.

Higher charge currents in 35% KOH also could give beneficial results. When there were 3-hr stands after every 3 hr of charge at the 6-hr rate, the capacity averaged 90% of the normal 20-hr value and about 9 hr (total of charge time plus stand time) was required. This should be compared to the 83% of normal capacity that was obtained when using uninterrupted constant current at the 6-hr rate. When using 1-hr stands repeated after every 1 hr of charge at the 6-hr rate, a charge required about 13 hr (total) and 5 of these cycles gave an average 110.3% of normal capacity. When 1-hr charges at the 3-hr rate alternated with 1-hr stands, there was 83% to 93% of normal capacity obtained in about 6 hr.

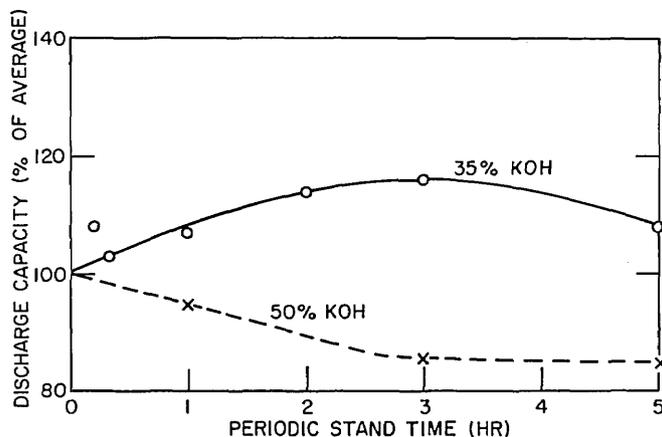
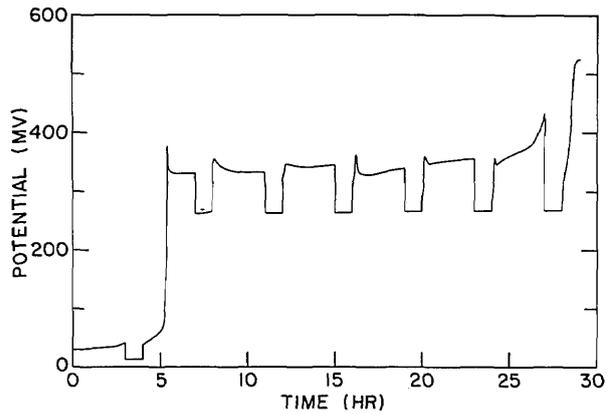


Fig. 3 - Change in discharge capacity following charges at 20-hr rate with stand periods after each 3 hr of charge. Plotted points are averages of several discharges.

Fig. 4 - Potentials during charge at 20-hr rate in 35% KOH with 1-hr stands after each 3 hr of charge. Potentials are given with respect to an Ag/Ag<sub>2</sub>O reference electrode.



The procedure using 3-hr charges was tried at the 20-hr charge rate with commercial silver-zinc cells (Table 1). Although results were not identical with test cell results, trends were similar.

Stand periods of 1 to 15 min repeated every 60 min during a charge gave discharge capacities that differed little from capacities following an uninterrupted charge at the 20-hr rate (Fig. 5). This type of charge was not tried in 50% KOH.

Table 1  
Effect on Commercial Silver-Zinc Cells of Stands After Each 3 Hours of Charge Using 20-Hour Charging Current

Periodic Stand Time (hr)	Average Discharge Capacity (%)	
	35% KOH	45% KOH
1	97.8 (4)*	96.3 (3)
3	114.2 (3)	99.8 (2)
5	105.8 (3)	95.9 (2)

\*Values in parentheses give the number of measurements made.

Stands repeated every 10 min during a charge could be beneficial or harmful, depending on conditions (Fig. 6). Although the averages fell close to a smooth curve, individual charges in 35% KOH gave widely varying capacity, particularly when using stands of 2, 3, or 4 min. There were six to nine charges for these three times and at least one of the following discharges varied more than 36% from each of these three averages (Fig. 6).

Selected portions of potentials that were measured during a charge having 2-min stands repeated every 10 min are given in Fig. 7. The first excerpt is at hour 4.33 as potential rose to the peak value that started the Ag<sub>2</sub>O/AgO plateau. Potentials rose to a maximum value in 0.4 to 0.8 min after the charge was resumed following most of the 2-min stands at the Ag<sub>2</sub>O/AgO plateau. After the third 8-min charge period at this plateau, stand potential fell to a minimum value in 0.2 to 0.3 min and then rose more slowly. This behavior continued throughout most of the charge after hour 5 (Figs. 7 and 8). There was a

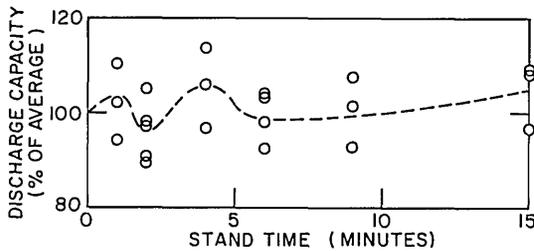


Fig. 5 - Discharge capacity in 35% KOH following charges at 20-hr rate having stand periods repeated every 60 min. The dashed line connects averages of plotted values.

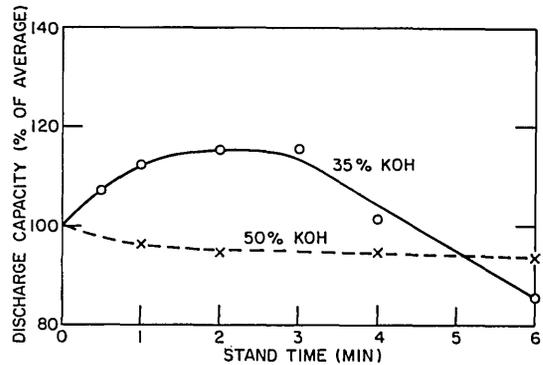


Fig. 6 - Discharge capacity following charges at 20-hr rate having stand periods repeated every 10 min. Plotted points are averages.

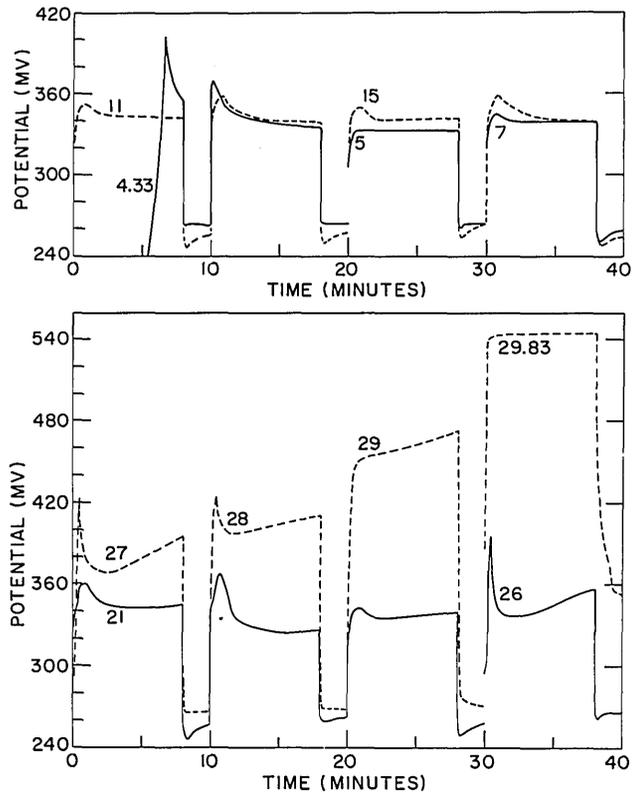
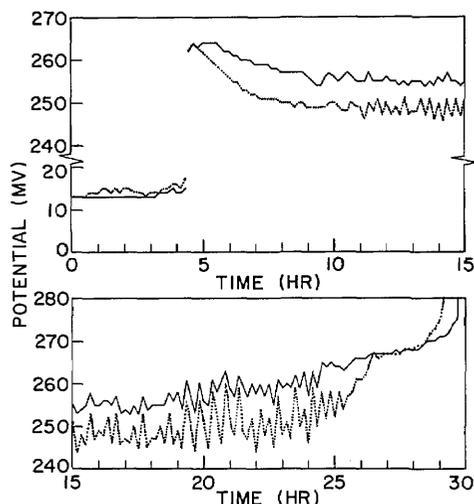


Fig. 7 - Some brief excerpts taken from charge in 35% KOH having stand periods of 2 min every 10 min. Numbers indicate the total elapsed time in hours at the beginning of the particular 8-minute charge excerpt that is shown. The lack of numbers indicates the charge was continuous from the previous stand shown. Potentials are given with respect to an Ag/Ag<sub>2</sub>O electrode.

Fig. 8 - Open-circuit potentials after standing 0.25 min (dotted line) and 2.0 min (solid line) during charge shown in Fig. 7



marked tendency for the charge and stand potentials to be relatively low during one 10-min period but higher the next, beginning about hour 11. This is shown more clearly in the 20-min excerpt at hour 15 (Fig. 7). After the electrode was two-thirds charged, the potential patterns usually repeated themselves every 30 min instead of 20 min (hour 21—Figs. 7 and 8).

The same type of charge in 50% KOH gave potentials that were more steady. Until the electrode was half charged, potentials in 50% KOH lacked a maximum when charge was resumed following the brief stands. After the electrode was half charged, there was a small maximum in charge potential following the brief stands, but this maximum was usually less than 10 mv. Stand potentials did not show a minimum in 50% KOH, but did fall to increasingly lower values as the charge progressed until the electrode was 80% charged. This charge in 50% KOH gave a capacity slightly below normal. Six-minute stands repeated every 10 min in 35% KOH, a charge that gave relatively low capacity, had similar weak maxima in the charging potentials.

Two-min stands every 10 min were also tried when using the 6-hr charge rate in 35% KOH. Two cycles gave an average 98% of normal (20-hr rate) capacity, instead of the 83% average obtained using constant current at the 6-hr rate. This charge was tried with the commercial silver-zinc cells at the 20-hr rate, but it gave no significant change in capacity.

A charge current that was interrupted 60 times per sec resulted in improved capacity when using 35% KOH, but had no particular effect in 50% KOH (Table 2). Included in Table 2 are normal constant-current cycles that alternated with the cycles using rapidly pulsating charge current derived from 60-cycle ac. Although there was variation in capacity during the life of the cells, the variation did not conceal the beneficial effects that could be obtained, even when actual discharge capacity was considered. This is shown in Table 2, where discharge capacity is given both in terms of average normal capacity at a particular point in the cycle life of the cells and also as a percent of capacity that was theoretically possible for the sintered silver of the six test electrodes that were used here.

A few typical potentials drawn from oscilloscope photographs of a quarter-wave charge are given in Fig. 9. Here, the average current was the 20-hr rate, but peak current was about 7 times larger. (See the upper part of Fig. 2 for the waveform.) The same types of charge current were used at the 6-hr rate (Table 3) and using commercial silver-zinc cells (Table 4).

Table 2  
Effect of 20-hr Charges Using 60-cps Pulsating Current

Type of Charge Current	35% KOH			50%KOH		
	Normal*	Theor. †	No. ‡	Normal	Theor.	No.
Constant dc	99.8	48.6	22	100.1	41.4	12
75% constant dc with 25% superimposed half-wave rectified ac	108.4	54.7	3	-	-	-
50% constant dc with 50% superimposed half-wave rectified ac	140.2	65.8	3	103.2	43.8	2
Full-wave rectified ac	123.2	57.3	6	99.1	40.9	2
Half-wave rectified ac	128.9	59.0	3	100.8	41.2	2
Quarter-wave rectified ac	131.0	65.9	4	95.0	40.1	2
Eighth-wave rectified ac	125.9	64.8	5	101.4	42.6	2

\*Normal: average discharge capacity given as a percent of normal capacity.

†Theor.: average discharge capacity given as a percent of theoretical capacity.

‡No.: number of measurements.

Fig. 9 - Some potentials during quarter-wave charge at 20-hr average current in 35% KOH. Potentials are given with respect to an Ag/Ag<sub>2</sub>O electrode. The different curves are: A, half charged at Ag/Ag<sub>2</sub>O potential plateau; B, 1/8 charged at Ag<sub>2</sub>O/AgO plateau; C, 7/8 charged at Ag<sub>2</sub>O/AgO plateau; and D, while strong oxygen evolution occurred.

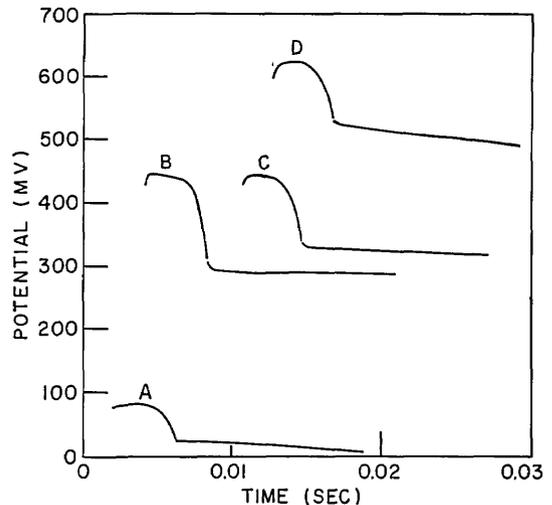


Table 3  
Capacity Following Charges at 6-hr Rate Using 60-cps Pulsating Current Compared to Capacity Following Constant Current Charges at 20-hr Rate

Type of Charge Current	Average Discharge Capacity (%)	
	35% KOH	50% KOH
Constant dc at 6-hr rate	83.3 (4)*	67.9 (6)
50% constant dc with 50% superimposed half-wave rectified ac	95.1 (3)	58.6 (2)
Full-wave rectified ac	83.0 (3)	57.8 (2)
Half-wave rectified ac	82.4 (3)	66.3 (2)
Quarter-wave rectified ac	99.0 (3)	53.7 (2)
Eighth-wave rectified ac	97.2 (3)	55.8 (2)

\*Values in parentheses give the number of measurements made.

Table 4  
Effect on Commercial 5 amp-hour Silver-Zinc Cells of 20-hour Charges Using 60-cps Pulsating Current

Type of Charge Current	Average Discharge Capacity (%)	
	35% KOH	45% KOH
Constant dc	101.6 (6)*	100.4 (5)
50% constant dc with 50% superimposed half-wave rectified ac	107.0 (2)	98.9 (2)
Full-wave rectified ac	96.6 (2)	103.9 (2)
Half-wave rectified ac	102.3 (2)	99.1 (2)
Quarter-wave rectified ac	108.0 (2)	104.0 (2)

\*Values in parentheses give the number of measurements made.

During a discharge following a normal charge at the 20-hr rate, 26% to 32% of the capacity was obtained before reaching the  $\text{Ag}_2\text{O}/\text{Ag}$  potential plateau. The same proportion was obtained after a charge with repeated stand periods, with but few exceptions. The proportion of discharge at the upper potential plateau was often 5% to 10% longer than normal, following charges having stands of 2 or more hr after each 3 hr of charge. After charging with the various forms of rectified 60-cycle ac at the 20-hr rate, the discharge at the upper plateau was at a lower potential and the proportion was usually 5% to 10% smaller than normal. Capacity obtained at this plateau had not increased as much as total capacity had increased: the discharge capacity at this plateau was practically unchanged following a charge of 50% constant current with 50% superimposed ac, although total discharge capacity was considerably increased. This resulted in the proportion of discharge being about 20% to 25% less than the normal proportion.

For one series of cycles, a cell was charged at the 20-hr rate and was then discharged at the 1-hr rate, instead of the 20-hr rate. The initial discharge at the 1-hr rate gave a capacity that was about the same as normal capacity, but upon repetition the capacity of discharges at the 1-hr rate was increased by an average of 10%. Under these conditions, full-wave rectified ac or repeated 8-min charges followed by 2-min stands gave about the same capacity at the 1-hr discharge rate as did constant current charges. Quarter-wave rectified ac gave about 5% additional improvement in discharge capacity.

## DISCUSSION

The experimental results showed that significant improvements in capacity were possible through the use of repeated open-circuit periods during charge when using 35% KOH as the electrolyte. The largest capacity increases were obtained by using a rapidly fluctuating current, with or without stand periods (Table 2). All of the rapidly pulsating currents tried at the 20-hr rate improved capacity in 35% KOH. There was no marked change in capacity when stand length and pulse current both increased, with net current remaining equivalent to the 20-hr rate (Table 2). Superimposing a charge current that was pulsating 60 times per sec onto a constant charge current, the smoothest type of current used except for constant current, could give a large improvement. This type of current is related to that used earlier, in which current was increased for a few seconds every 10 to 60 min and an increase in capacity up to 30% to 40% was obtained (2). Lack of improvement in 50% KOH was also noted in this earlier work.

Constant current at the 6-hr rate gave only about 5/6 of normal capacity in 35% KOH, but close-to-normal capacity could be obtained by using rapidly pulsating currents (Table 3). Here again a relatively large improvement resulted from superimposing a charge current that was half-wave rectified ac onto a steady charge current. Benefits at the 6-hr rate of charge were less in proportion than they were at the 20-hr rate.

Comparison of Figs. 3, 5, and 6 showed that neither stand length nor charge length nor ratio of these lengths determined whether or not a particular charge-stand combination was beneficial. A disadvantage to some of these types of charge with repeated stands was that total charge time increased greatly. Higher capacity was not just an effect of this increase in total charge time. Charging at the 6-hr rate with 1-hr stands after every hour of charge required only two-thirds of normal charge time but gave 10% more capacity than a normal charge. Charging at the 20-hr rate with charge periods of 3 hr alternating with stands of 3 hr required approximately the same total time as the 40-hr rate of uninterrupted constant current but averaged about twice as much capacity improvement, comparing both types of charge to a normal charge. The use of low charging currents may be preferable for some applications, however, because the following discharge will have a shorter AgO/Ag<sub>2</sub>O potential plateau and thus give a more constant discharge potential. Although more AgO is present after charging with a low current than is present after using a high current, the surface area is smaller when the oxide is formed slowly and is covered more rapidly with Ag<sub>2</sub>O during a discharge (1). Therefore, the discharge shows less capacity at the AgO/Ag<sub>2</sub>O potential level even though total discharge capacity has increased. This initial potential plateau lasted 17% to 25% of the total time for a discharge immediately following a 40-hr charge, and 7% to 16% when discharged immediately following an 80-hr charge. As mentioned earlier, 26% to 32% was obtained following a 20-hr charge or most charges using stand periods.

The wide scatter of individual measurements in 35% KOH that were averaged for the points shown in Figs. 3 and 6 indicated that all factors were not under control. If all factors could be controlled consistently, there is possibility of an improvement larger than that shown by these figures, because many individual measurements were much better than the averages. The scatter could not be attributed to different cells or to whether a measurement was made early or late in the cycle life of a cell.

Potentials gave an indication of electrode conditions. When stands repeated after 3 hr of charge or stands repeated every 10 min were used, the largest capacity followed a charge showing strong potential maxima soon after many of the open-circuit periods at the  $\text{Ag}_2\text{O}/\text{AgO}$  plateau. A charge lacking these maxima, or having but slight maxima, gave only normal capacity. When a silver electrode is oxidized anodically with constant current, the potential rises sharply to a maximum value after the silver surface is covered with  $\text{Ag}_2\text{O}$ . The first reaction following this potential peak or maximum is  $\text{Ag}_2\text{O}$  oxidizing to  $\text{AgO}$ . Little or no additional silver oxidizes until a large part of the  $\text{Ag}_2\text{O}$  has oxidized (1,5). With some charge-stand combinations the open-circuit potentials began to have a minimum value as the charge continued to form more  $\text{AgO}$  (Figs. 7 and 8). The potential minimum tended to reach increasingly lower values as the  $\text{AgO}$  layer thickened for approximately the first half of this type of charge (Fig. 8). These potential minima were probably the result of nonuniform distribution of oxygen and silver in the oxide layer (6).

When the electrode was about one-third charged using 2-min stands every 10 min, potential patterns began to be repeated every 20 min (hour 11—Figs. 7 and 8). The low stand potential and the following high charging potential both indicated that ion movements were retarded under these conditions, following which a change must have occurred that decreased concentration gradients in the electrode. It is believed that the oxide coating cracked, allowing the electrolyte to penetrate nearer to the silver, which decreased the concentration gradients in the oxide layer. Decreased concentration gradients were indicated both by the lowered charge potentials and by the potentials of the next stand being nearer to equilibrium values, close to values measured earlier when only a small amount of  $\text{AgO}$  was present. The process was repeated as the film built up again. It is likely that development and removal of concentration gradients in the electrode were also at least partly responsible for the potential maxima observed after stands of 1 to 5 hr. These comparatively slow changes within the electrode probably did not take place to any great extent when using current pulsating 60 cps because of the short time between successive current pulses.

An additional factor during the long stands was formation of a thin  $\text{Ag}_2\text{O}$  film on the silver as a result of the reaction between silver and  $\text{AgO}$  (4). During short stands the formation of  $\text{Ag}_2\text{O}$  was not appreciable, but when charge was resumed after 1-hr stands, potential often did not rise to a peak immediately (Fig. 4) as it should have done if the maximum were caused entirely by  $\text{Ag}_2\text{O}$  resistance. The reaction between silver and  $\text{AgO}$  can result in slightly deeper oxidation and slightly increased capacity. Benefit would be limited, because the reaction rate probably decreased as the  $\text{Ag}_2\text{O}$  film thickened and separated the reactants. In earlier work,  $\text{Ag}_2\text{O}$  was not definitely visible to x-ray diffraction, even after a 2-1/2-day stand of a charged electrode, although x-ray diffraction patterns of  $\text{AgO}$  had weakened in this time (1). It should be noted that  $\text{Ag}_2\text{O}$  was more likely to form deep in the electrode where silver was available than at the electrode surface, where  $\text{Ag}_2\text{O}$  could be detected more readily by x-ray diffraction.

It is unlikely that enough  $\text{Ag}_2\text{O}$  was formed in the longer stand times used in these charging methods for the  $\text{Ag}_2\text{O}$  to cause sufficient resistance to account for the entire potential rise. If there were a high internal resistance due to  $\text{Ag}_2\text{O}$ , there would be a large potential gradient in the electrode as current passed. Although grid or terminal potential could be quite high, the surface potential would not be expected to rise beyond the potential necessary for oxidation of  $\text{Ag}_2\text{O}$  to  $\text{AgO}$ . But potentials rising to the oxygen evolution value have been observed after long stands (3). It may be that as conducting paths to the surface are formed, when a charge is resumed after very long stands, concentration of charge current along these conducting paths allows the surface to reach the gas evolution potential. Oxidation of  $\text{Ag}_2\text{O}$  and oxygen evolution could then take place simultaneously until potential fell as more or better paths to the surface are formed.

A more important factor to be considered is changes in AgO crystallinity under the different charge conditions. It has been established that there is an exchange of oxygen between a KOH solution and AgO (7). It would not be surprising if there is also an exchange between dissolved silver and AgO. These exchange reactions would allow perfection of the AgO crystallinity and smoothing of the surface when time was sufficient, such as during long stand periods or during low-rate charges. Thus true current density following a long stand would be higher at the surface of the electrode, and the increased current density could account for high charge potentials as well as the low discharge potentials that have been observed at the AgO/Ag<sub>2</sub>O level after very long stands. Results in 50% KOH, although not improved by a charge with repeated stands, usually were much more reproducible than in 35% KOH. This was probably at least partly caused by physical differences between the AgO coatings that formed on silver in 35% KOH and the coating in 50% KOH. Perhaps AgO crystallizes in a physical form in 50% KOH that retarded passage of oxygen through the AgO. There is no reason to assume that a cubic AgO forms initially and that this AgO converts to monoclinic AgO at low current or during long stands as has been suggested (3). Monoclinic AgO can actually be detected quite soon after anodic potential reaches the Ag<sub>2</sub>O/AgO plateau (1), and the compound originally reported as cubic AgO has since been shown to be a different material (5).

The most important cause of increased capacity in the charges that were beneficial was believed to be an increased surface area. Increased surface area allowed more AgO to be formed during a charge before slow diffusion through the AgO caused sufficient polarization that the potential rose to the oxygen evolution value. When the charging potential increased to a relatively high value after a stand, oxygen from the surface layers could penetrate deeper into the oxide layer under the influence of the high charging potential, thus oxidizing silver that was under the oxide coating.

There is a large expansion when a certain quantity of silver is oxidized to an equivalent amount of Ag<sub>2</sub>O. There is only a slight additional increase in volume when Ag<sub>2</sub>O is oxidized to an equivalent amount of AgO. If the reactions take place entirely in the solid state, with each single crystal of Ag<sub>2</sub>O changing into a single crystal of AgO, then an oxide film may also be broken by distortion of the crystal lattice. Two cell dimensions expand, one contracts, and one angle changes as a face-centered cubic crystal of Ag<sub>2</sub>O is oxidized to monoclinic AgO. Expansion of the crystal lattice as AgO formed from Ag, most likely through Ag<sub>2</sub>O as an intermediate, probably cracked the oxide coating which covered the electrode and allowed electrolyte to penetrate nearer to the silver under these conditions. The increased porosity resulted in decreasing current density and decreasing concentration gradients within the oxide layer. For this reason the charge potential fell to its lowest value in the same 8-min period that had the highest potential (for example, see the curve at 21 hr 10 min in Fig. 7).

Thus the potential drop after the maximum was probably caused by breaking of the smooth oxide layer and, after long stands, also partly caused by oxidation of resistive Ag<sub>2</sub>O to AgO. If the drop in potential were merely the result of activation of the semiconductors Ag<sub>2</sub>O (4) or AgO (3), conditions after activation would be the same as they were before interrupting the current and there would be no reason to expect increased capacity after a series of potential maxima, but the best discharge capacity usually followed charges that showed irregular potentials. It is proposed here that the capacity increase was mainly the result of deeper oxidation of the silver, caused by breaking of the surface as AgO formed below the electrode surface.

The increased amount of oxide that formed when using current pulsating 60 cps in 35% KOH was probably also the result of surface area increasing as the oxide film on the electrode broke or roughened when current was high. Stresses may be set up as a result of fast formation of the oxide film or layer and then be relieved by cracking. Stand time was not important or even necessary when using these rapidly pulsating currents (Tables 2 and 3). Current, high for only a brief time, prevented harmful formation of large

concentration gradients, such as would have occurred if current had remained high for longer times. Charges at the 6-hr rate were less beneficial than charges at the 20-hr rate because the faster charge resulted in larger concentration gradients in the electrolyte and smaller crystals of AgO were formed (1). Both of these effects could limit further oxidation.

The mobility of the hydroxyl ion is an important factor in the oxidation process (8); lack of hydroxyl ion at the electrode can seriously impair charges. This can occur in concentrated KOH solution, or when using high current densities, or at low temperatures. A combination of these is more harmful than any one singly. For example, capacity decreased more rapidly with increasing charge current in 50% KOH than it did in 35% KOH (9). Thus one would expect that a current pulsating at 60 cps (and momentarily reaching higher current densities than a normal charge) would not necessarily give as good results in 50% KOH as it does in 35% KOH, especially when using faster charges (Tables 2 and 3). The limited amount of free electrolyte in the commercial silver-zinc cells, due to tight packing in the cell cases, probably resulted in increased concentration gradients in the electrolyte near the electrode surface compared to test cell conditions. This may be the reason for the commercial cells usually not showing the improvement that test cells showed, but no experimental work was done to prove this.

As mentioned earlier, the rate at which a cell was discharged in 35% KOH had a large effect on the results of a charge using pulsating current. It has been shown that a charge following a high-rate discharge gave more capacity than a charge following a low-rate discharge because of differences in chargeability of the forms of silver that resulted under these conditions (1). Therefore, when a cell was given a series of complete discharges at low current density, capacity tended to decrease at least to a point. If a cell was then given a series of complete high-rate discharges, capacity tended to increase back toward the original value. As a result of this, although a single discharge at the 1-hr rate might give less capacity than the preceding discharge at the 20-hr rate, after several discharges at the 1-hr rate (and recharges at the 20-hr rate) the capacity increased to a value larger than it was after a series of discharges at the 20-hr rate. Charge acceptance at the Ag/Ag<sub>2</sub>O plateau had doubled, but charge at the Ag<sub>2</sub>O/AgO plateau was only 90% of its normal length. Under these conditions, where the capacity was high already, a constant current charge gave about the same capacity as the pulsating charges.

Several phenomena were involved in the results reported here, and no single explanation will adequately cover them all. Further work is obviously necessary for a more definitive explanation and will be undertaken after determining the effect on capacity of current reversals during a charge. In particular a microscopic examination of the electrodes at various steps in the different types of charge is expected to be useful.

## CONCLUSIONS

The charge methods described can be beneficial or harmful, depending on specific conditions. Faster charges or greater capacity after slow charges could be obtained by these charging methods. Results in 35% KOH were always better than in 45% or 50% KOH. The charge methods worked best when a cell had previously been discharged at low currents.

## ACKNOWLEDGMENT

The author wishes to thank Mr. C. H. Presbrey, Jr., for technical advice and assistance in adapting and setting up the circuitry used in part of this investigation.

## REFERENCES

1. Wales, C.P., and Burbank, J., *J. Electrochem. Soc.* 112:12 (1965)
2. Wales, C.P., "Increasing the Discharge Capacity of a Silver Electrode," *NRL Report 5912*, Apr. 2, 1963; *J. Electrochem. Soc.* 111:131 (1964)
3. Flerov, V.N., *Zh. Prikl. Khim.* 36:1980 (1963)
4. Dalin, G., and Stachurski, Z., "Aging of Silver Oxide Zinc Primary Batteries," *New York Meeting of the Electrochemical Society*, Oct. 1963
5. Wales, C.P., and Burbank, J., *J. Electrochem. Soc.* 106:885 (1959)
6. Yoshizawa, S., and Takehara, Z., *J. Electrochem. Soc. Japan* 31:91 (1963)
7. Rozental, K.I., and Veselovskii, V.I., *Zh. Fiz. Khim.* 35:2670 (1961)
8. Dirkse, T.P., *J. Electrochem. Soc.* 106:920 (1959)
9. Wales, C.P., *J. Electrochem. Soc.* 108:395 (1961)

## DOCUMENT CONTROL DATA - R&amp;D

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

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2 a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>	
		2 b. GROUP	
3. REPORT TITLE CHANGING THE DISCHARGE CAPACITY OF A SILVER OXIDE ELECTRODE BY CHARGING WITH PERIODICALLY INTERRUPTED CURRENT			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) This is an interim report on the problem.			
5. AUTHOR(S) (Last name, first name, initial) Wales, C. P.			
6. REPORT DATE October 19, 1966		7 a. TOTAL NO. OF PAGES 18	7 b. NO. OF REFS 9
8 a. CONTRACT OR GRANT NO. NRL Problem C05-14		9 a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6460	
b. PROJECT NO. SF 013-06-06-4366			
c. RR 001-01-43-4755		9 b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Office of Naval Research and Naval Ship Systems Command), Wash., D.C. 20360	
13. ABSTRACT Sintered silver electrodes were oxidized anodically in 35% to 50% KOH at 25°C, usually at the 20-hr rate, sometimes at faster rates. Length of charge plus open-circuit periods varied from 8 hr to 1/60 sec. A particular charge length and open-circuit length was repeated until oxygen evolution occurred. In 50% or 45% KOH this charge method gave either the same capacity as a constant dc charge or less capacity, but in 35% KOH the improvements averaged as high as 40% under certain conditions. Best results were obtained when the preceding discharges were at low rates.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Alternating current Direct current Electric discharges Electrodes Silver compounds Storage batteries Electrolytes Zinc Oxides						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.