

# Charging the Silver Oxide Electrode with Periodically Varying Current

## II. Repeated Open-Circuit Periods

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### ABSTRACT

Sintered silver electrodes were oxidized anodically in 35-50% 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 d-c 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.

The discharge capacity of AgO electrodes is strongly influenced by conditions of the preceding charge (anodic oxidation). It has been shown that capacity of AgO electrodes can be increased by charging with a periodically varying current if pulses of charge current are added to the normal charging current using the proper conditions (1). 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. There may also be an increase in conductivity during a pulse if there is appreciable activation of the semiconductors Ag<sub>2</sub>O or AgO (2, 3). 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.

In general, both the total amount of AgO that forms on a silver electrode and the AgO crystal size vary inversely with the charging current density that is used (4). When charging storage batteries that contain silver electrodes it is often impractical to use rates requiring a day or more for completion, even though these low rates give a high 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 (4).

Capacity can be increased somewhat by putting a silver oxide 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 that had been manufactured for use in commercial silver-zinc storage batteries. The silver plaques were 30.5 x 63.5 x 0.8 mm or 41.5 x 38.0 x 0.8 mm. Neglecting the grid of expanded silver metal, the plaques had an average weight of 7.9 or 5.8g, respectively, for a theoretical capacity of 3.9 or 2.9 amp-hr. Porosity of unused electrodes, as determined by liquid absorption, was 50-56%. The silver plaques were wrapped in cellulose separator material of a type normally used in commercial silver-zinc cells. Similar silver electrodes were used for both the cathode and anode. 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. This 20-hr rate was taken as 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). This resulted in a charge input which was usually 101-102% of the following discharge. Discharges were done with a controlled constant current 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. All discharges used the 20-hr rate except where noted otherwise. The work was done at 25° ± 1°C.

Some charges by interrupted current were repeated with commercial silver-zinc secondary cells using 35 or 45% KOH. These cells were rated at 5 amp-hr, and each cell contained four silver electrodes. These electrodes were the same size as the test electrodes which had a theoretical capacity of 2.9 amp-hr. The test electrodes had been manufactured for use in this size of silver-zinc cell. The silver-zinc cells were charged to 2.05v and discharged to 1.10v using the 20-hr rate of constant current (as defined above). The electrolyte supplied with these cells was analyzed and found to be 45.0% KOH and 0.6% K<sub>2</sub>CO<sub>3</sub>. The "35%" KOH was prepared from reagent grade KOH. Analysis of this solution 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. In each of the four a particular length of charge and open circuit was repeated until strong oxygen evolution occurred. In one type, a cell was charged for 3 hr at the normal (20-hr) rate of constant current. This was followed by a stand period ranging from 12 min to 5 hr before resuming the charge. In the second type 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 1-15 min being the stand period. In the third type 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 0.5-6 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 d.c. were used. When stand times were under 1 min, a power source was

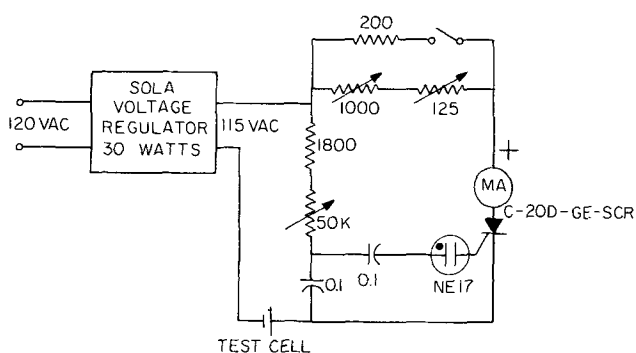


Fig. 1. Circuit for obtaining rectified a.c. with current interrupted for more than half of the a-c cycle.

used that had a recovery time of less than 50  $\mu$ sec for reaching the preset current value. For longer stand times, a d-c source having a recovery time of several seconds was used also. Half-wave and full-wave rectified a.c. were obtained from 60-cycle a.c. by typical rectifier circuits. Rectified a.c. in which the current flowed less than half of the a.c. 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 a.c. which consisted of approximately the last half of an a-c half-wave was called "quarter-wave rectified a.c." for simplicity. Current rose rapidly to a maximum value and then fell more slowly to zero, with no current flowing for  $\frac{3}{4}$  of the time (upper part of Fig. 2). Similarly the last quarter of an a-c half-wave was called "eighth-wave rectified a.c." (Fig. 2). Average current in these examples was 80 ma including the time in which no current flowed.

### Results

Each new test cell was charged and discharged at the 20-hr rate of constant current several times until capacity stopped changing rapidly, before charging with periodically interrupted current. The initial or second cycle often gave as much as 70-80% of theoretical capacity for the sintered silver. Capacity dropped in the next few cycles. After about 12 cycles

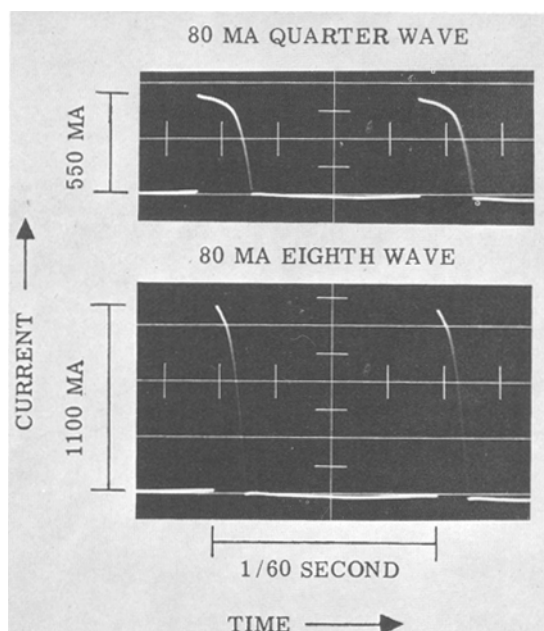


Fig. 2. Oscilloscope traces showing wave form of quarter-wave and eighth-wave rectified a.c. with approximate current calibration. Average current was 80 ma.

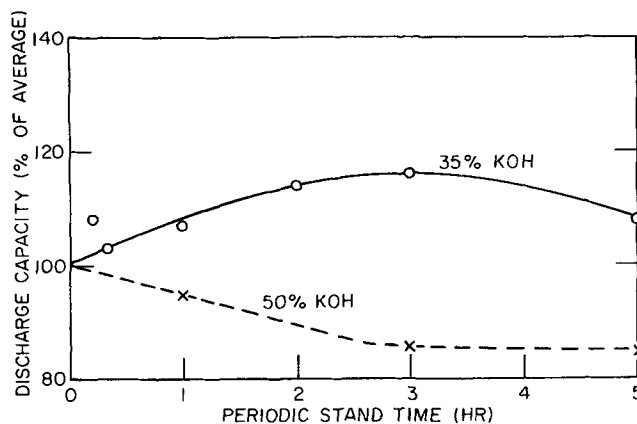


Fig. 3. Change in discharge capacity following charges at 20-hr rate with stand periods after each 3 hr of charge. Plotted points are averages of several discharges.

capacity showed no further loss but varied irregularly, with the capacity of normal cycles in 35% KOH usually falling in the range 44-57% of theoretical capacity and averaging 50-55% of theoretical. In 50% KOH the capacity was usually in the range 36-48% of theoretical.

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. Capacity of each discharge was expressed as a per cent of this normal capacity. These calculations also improved comparison between cells having different capacities. Throughout this paper the results are presented as being a certain per cent of normal capacity. 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 96.1-103.4%. 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 98.2-100.8%.

When stand periods followed each 3 hr 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 3 to 7 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 5 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 + 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

Table I. Effect on commercial silver-zinc cells of stands after each 3 hr of charge using 20-hr 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 brackets give the number of measurements made.

with 1-hr stands, there was 83-93% of normal capacity obtained in about 6 hr.

This charging method was tried at the 20-hr charge rate with commercial silver-zinc cells (Table I). Although results were not identical with test cell results, trends were similar.

Stand periods of 1-15 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.

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 6 to 9 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  $\text{Ag}_2\text{O}/\text{AgO}$  plateau. Potentials rose to a maximum value in 0.4-0.8 min after the charge was resumed following most of the 2-min stands at the

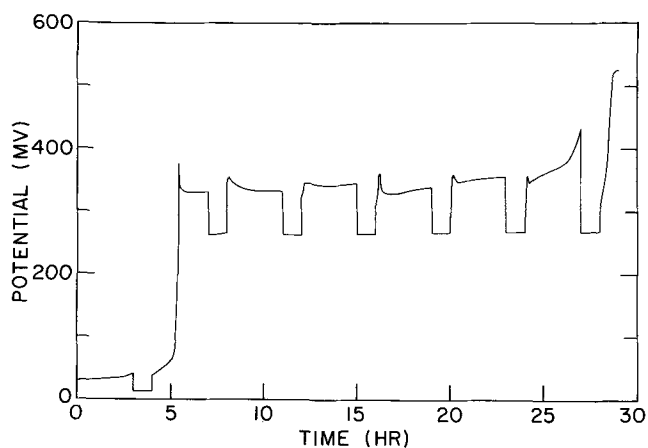


Fig. 4. Potentials during charge at 20-hr rate in 35% KOH with 1-hr stands after each 3 hr of charge. Potentials are given with respect to  $\text{Ag}/\text{Ag}_2\text{O}$  reference electrode.

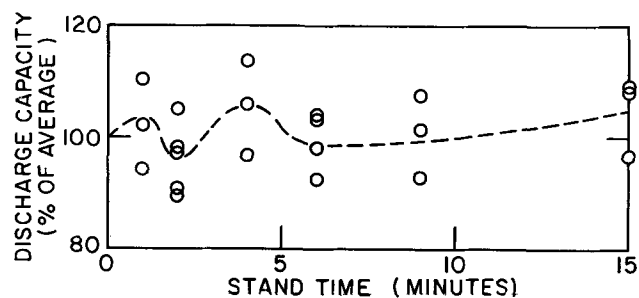


Fig. 5. Discharge capacity in 35% KOH following charges at 20-hr rate having stand periods repeated every 60 min. Dashed line connects averages of plotted values.

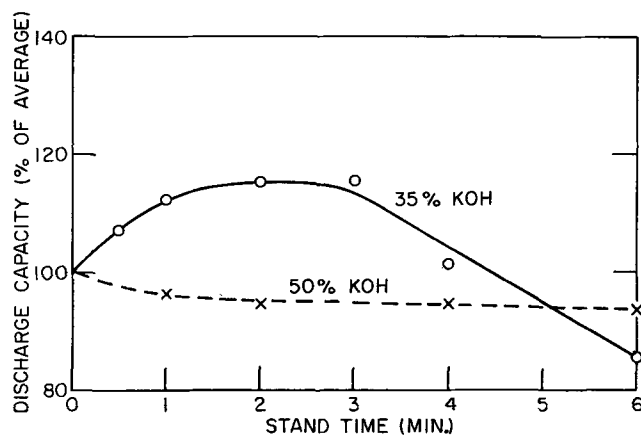


Fig. 6. Discharge capacity following charges at 20-hr rate having stand periods repeated every 10 min. Plotted points are averages.

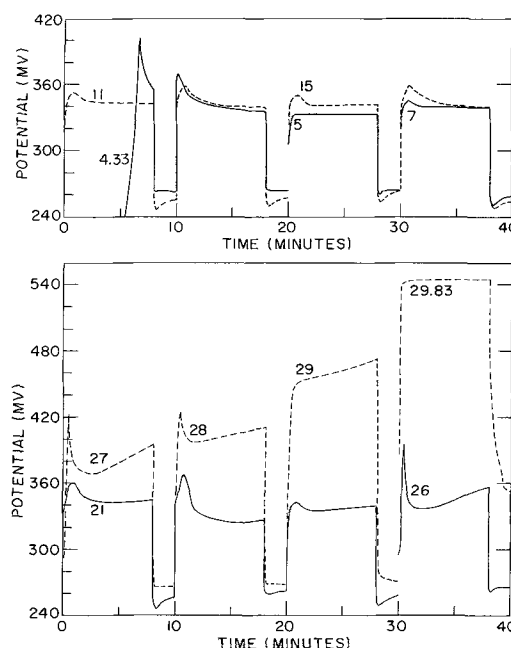


Fig. 7. Some brief excerpts taken from charge in 35% KOH having stand periods of 2 min every 10 min. Numbers indicate total elapsed time in hours at beginning of the particular 8-min charge excerpt that is shown. Lack of number indicates charge was continuous from previous stand shown. Potentials are given with respect to  $\text{Ag}/\text{Ag}_2\text{O}$  electrode.

$\text{Ag}_2\text{O}/\text{AgO}$  plateau. After the third 8-min charge period at this plateau, stand potential fell to a minimum value in 0.2-0.3 min and then rose more slowly. This behavior continued throughout most of the charge after hour 5 (Fig. 7 and 8). There was a 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 Fig. 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



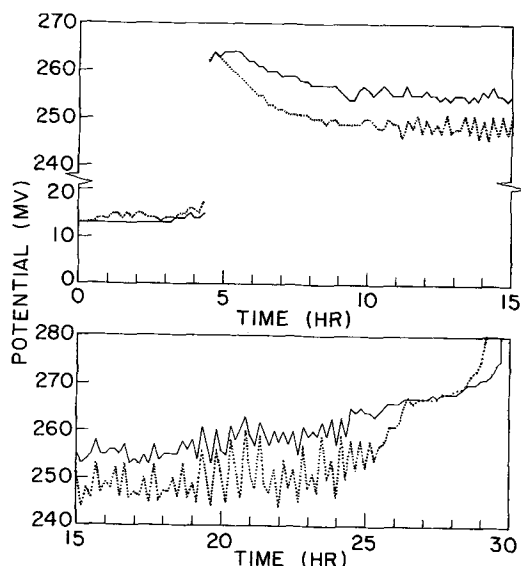


Fig. 8. Open-circuit potentials after standing 0.25 min (dotted line) and 2.0 min (solid line) during charge shown in Fig. 7.

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-minute 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 a sec resulted in improved capacity when using 35% KOH, but had no particular effect in 50% KOH (Table II). Included in Table II are normal constant current cycles which alternated with the cycles using rapidly pulsating charge current that was derived from 60-cycle a.c. 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 II 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 per cent 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. The average current was the 20-hr rate, but

Table II. Effect of 20-hr charges using current pulsating 60 cps

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

Normal means average discharge capacity given as a per cent of normal capacity. Theor. means average discharge capacity given as a per cent of theoretical capacity. No. means the number of measurements made.

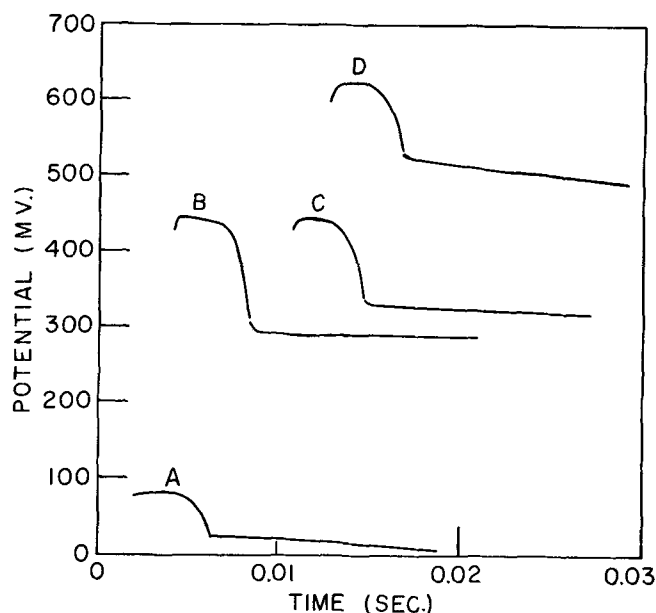


Fig. 9. Some potentials during quarter-wave charge at 20-hr average current in 35% KOH. Potentials are given with respect to Ag/Ag<sub>2</sub>O electrode. A, half charged at Ag/Ag<sub>2</sub>O potential plateau; B, 1/8 charged at Ag<sub>2</sub>O/Ag plateau; C, 1/8 charged at Ag<sub>2</sub>O/AgO plateau;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

peak current was about 7 times larger. This current wave-form was shown in the upper part of Fig. 2. The same types of charge current were used at the 6-hr rate (Table III) and using commercial silver-zinc cells (Table IV).

During a discharge following a normal charge at the 20-hr rate, 26-32% of the capacity was obtained before reaching the Ag<sub>2</sub>O/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 5-10% longer than normal following charges having stands of 2 or more hours after each 3 hr of charge. After charging with the various forms of rectified 60-cycle a.c. at the 20-hr rate, the dis-

Table III. Capacity following charges at 6-hr rate using current pulsating 60 cps compared to capacity following constant current charges at 20-hr rate

Type of charge current	Average discharge capacity, %	
	35% KOH	50% KOH
Constant d.c. at 6-hr rate	83.3 [4]	67.9 [6]
50% constant d.c. with 50% superimposed half-wave rectified a.c.	95.1 [3]	58.6 [2]
Full-wave rectified a.c.	83.0 [3]	57.8 [2]
Half-wave rectified a.c.	82.4 [3]	66.3 [2]
Quarter-wave rectified a.c.	99.0 [3]	53.7 [2]
Eighth-wave rectified a.c.	97.2 [3]	55.8 [2]

Values in brackets give the number of measurements made.

Table IV. Effect on commercial 5 amp-hr silver-zinc cells of 20-hr charges using current pulsating 60 cps

Type of charge current	Average discharge capacity, %	
	35% KOH	45% KOH
Constant d.c.	101.6 [6]	100.4 [5]
50% constant d.c. with 50% superimposed half-wave rectified a.c.	107.0 [2]	98.9 [2]
Full-wave rectified a.c.	96.6 [2]	103.9 [2]
Half-wave rectified a.c.	102.3 [2]	99.1 [2]
Quarter-wave rectified a.c.	108.0 [2]	104.0 [2]

Values in brackets give the number of measurements made.

charge at the upper plateau was at a lower potential and the proportion was usually 5-10% shorter 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 a.c., although total discharge capacity was considerably increased. This resulted in the proportion of discharge being about 20-25% 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 on repetition the capacity of discharges at the 1-hr rate was increased by an average of 10%. Under these conditions full-wave rectified a.c. 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 a.c. 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 II). All of these rapidly pulsating currents that were 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 II). Superimposing a charge current that was pulsating 60 times per second 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 10-60 min and an increase in capacity up to 30-40% was obtained (1). 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 III). Here again a relatively large improvement resulted from superimposing a charge current that was half-wave rectified a.c. 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 Fig. 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 this smaller surface is covered more rapidly with Ag<sub>2</sub>O during a discharge

(4). 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 17-25% of the total time for a discharge immediately following a 40-hr charge, and 7-16% when discharged immediately following an 80-hr charge. As mentioned earlier, 26-32% 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 Fig. 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 nor to whether a measurement was made early or late in the cycle life of a cell.

Potentials gave an indication of electrode conditions. When using stands repeated after 3 hr of charge or stands repeated every 10 min, the largest capacity followed a charge showing strong potential maxima soon after many of the open-circuit periods at the Ag<sub>2</sub>O/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 Ag<sub>2</sub>O. The first reaction following this potential peak or maximum is Ag<sub>2</sub>O oxidizing to AgO. Little or no additional silver oxidizes until a large part of the Ag<sub>2</sub>O has oxidized (4, 5). With some charge-stand combinations the open-circuit potentials began to have a minimum value as the charge continued to form more AgO (Fig. 7, 8). The potential minimum tended to reach increasingly lower values as the AgO layer thickened, for approximately the first half of this type of charge (Fig. 8). The 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 Fig. 7, 8). The low stand potential and the following high charging potential both indicated that ion movements were retarded under these conditions. Then a change must have occurred that decreased concentration gradients in the electrode. It is believed that the oxide coating cracked, allowing electrolyte to penetrate nearer to the silver, and this 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 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 1-5 hr. These comparatively slow changes within the electrode probably did not take place to any great extent when using current pulsating 60 times per second because of the short time between successive current pulses.

An additional factor during the long stands was formation of a thin Ag<sub>2</sub>O film on the silver as a result of the reaction between silver and AgO (3). During short stands the formation of Ag<sub>2</sub>O was not appreciable. 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 Ag<sub>2</sub>O resistance. The reaction between silver and AgO can result in slightly deeper oxidation and slightly increased capacity. Benefit would be limited because the reaction rate probably decreased as the Ag<sub>2</sub>O film thickened and separated the reactants. In earlier work Ag<sub>2</sub>O was not definitely

visible to x-ray diffraction even after 2½ days stand of a charged electrode, although x-ray diffraction patterns of AgO had weakened in this time (4). It should be noted that Ag<sub>2</sub>O was more likely to form deep in the electrode where silver was available than at the electrode surface where Ag<sub>2</sub>O could be detected more readily by x-ray diffraction.

It is unlikely that enough Ag<sub>2</sub>O was formed in the longer stand times used in these charging methods for the Ag<sub>2</sub>O to cause sufficient resistance to account for the entire potential rise. If there were a high internal resistance due to Ag<sub>2</sub>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 Ag<sub>2</sub>O to AgO. But potentials rising to the oxygen evolution value have been observed after long stands (2). 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 Ag<sub>2</sub>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 (2). Monoclinic AgO can actually be detected quite soon after anodic potential reaches the Ag<sub>2</sub>O/AgO plateau (4) 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 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 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 (3) or AgO (2), 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 times per second 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 II, III). Current being 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 (4). 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 60 times per second (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 II, III). 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 (4). 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.

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## The Photogalvanic Disruption of Cuprous Oxide Films on Copper

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### ABSTRACT

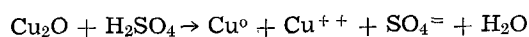
The cuprous oxide film normally present on copper is disrupted by photogalvanic action. Partial illumination of an oxidized copper surface in an electrolyte results in reduction of the cuprous oxide to metallic copper in the illuminated areas and oxidation and dissolution of the cuprous oxide in the unilluminated areas. The disrupted film is believed to lead to an observed increase in corrosion rate of copper in an illuminated salt-spray cabinet.

It is well known that a photovoltaic effect characteristic of a p-type semiconductor can be observed on cuprous oxide (1-5). Since the oxide layer on mildly oxidized copper consists essentially of cuprous oxide, it is not surprising that there have been numerous reports of the effect of light on the corrosion of copper (6-10). In general, light has been found to accelerate the corrosion of copper, although it has been shown recently that the rate of initial growth of the oxide film is decreased by light under certain conditions (11), while the dissolution of cuprous oxide to cupric ions is promoted by light.

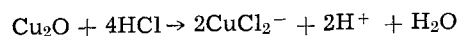
When the oxide film becomes relatively thick (200Å), it serves to some extent as a protective film against further corrosion. We have found that the effectiveness of this film is greatly decreased by light if the oxide coated surface is covered by a conducting solution. The purpose of this paper is to describe the photogalvanic reactions which take place on oxidized copper surfaces to disrupt the continuity of the oxide film. Using a simple salt-spray corrosion test, the effect of light on the oxidation rate of copper was also evaluated.

### Experimental

Because copper is a relatively noble metal, the oxide can be removed from the surface by acid dissolution without appreciable attack of the metal. If a dilute acid such as 2M H<sub>2</sub>SO<sub>4</sub> is used, only half of the copper in the cuprous oxide film is dissolved as a result of disproportionation



Although this method has been used for oxide film analysis by previous investigators (12), it was felt that total dissolution of the oxide film with concentrated hydrochloric acid would be more suitable for our purposes. In this case the acid dissolves all of the cuprous oxide with formation of the anionic chloride complex



In either case, care must be taken to exclude atmospheric oxygen which would cause further oxidation and dissolution of the metal. Cupric oxide is dissolved by either method, and, therefore, the latter method can be considered an analysis for total oxidized copper, while the former method would result in an ambiguity if the oxide film contained an unknown amount of cupric oxide. The oxide film on copper treated at 300°C for about 10 min has been shown to be essentially all cuprous oxide (13). Analysis of equal areas of an oxide film prepared under these conditions by both the dilute sulfuric acid and concentrated hydrochloric acid dissolution methods resulted in twice the concentration of copper in the hydrochloric acid solutions, thus verifying the self-consistency of the two methods.

Analysis for copper in solution was done spectrophotometrically after formation of the tetraethylene pentamine complex as outlined in the literature (14).

The copper corrosion samples were ASTM B-133 pure copper (99.9+%). Other chemicals used were all reagent grade. Ordinary household tungsten filament incandescent lamps were used for illumination.