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Increasing the Discharge Capacity of a Silver Oxide Electrode by Charging with 60-Cycle Asymmetric AC

C. P. Wales

Electrochemistry Branch
Chemistry Division

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NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

The discharge capacity of sintered silver electrodes used in storage batteries was improved 40 to 50% when the prior charge was made by an alternating, rather than constant, current. Commercial Ag-Zn cells, under the same conditions, gave capacity increases of 15 to 25%. This improvement was obtained by charging the cells with 60-cps asymmetric ac, composed of two opposing half-wave currents 180 degrees out of phase and unequal in amplitude, as compared with charging by a constant current, both being at the 20-hr rate in 35% KOH at 25°C. Capacity depended on the proportion of charge and discharge components of the ac. Capacity improvements were smaller when net charge current was set at the 6-hr rate, when charge current was composed of 60-cps half-wave reverse current superimposed on constant charge current, or when the KOH concentration was increased. No significant improvement occurred when the charge with reverse current followed a series of discharges at the 1-hr rate.

PROBLEM STATUS

This is an interim report on one phase of the problem.

AUTHORIZATION

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INCREASING THE DISCHARGE CAPACITY OF A SILVER OXIDE ELECTRODE BY CHARGING WITH 60-CYCLE ASYMMETRIC AC

INTRODUCTION

An advantage of the silver oxide electrodes used in alkaline storage batteries is their ability to be discharged at high current densities. To obtain the full capacity of which the electrode is capable, common practice has been to charge it (anodically oxidize it) at a relatively low current density. Previous work at NRL has shown that when pulses of charge current are superimposed onto a steady charging current, the capacity of the subsequent silver electrode discharge can be greater than the capacity obtained by a constant current at the same rate (1). It has also been shown that when charge current is interrupted periodically throughout a charge, the result can be either increased discharge capacity or faster recharging (2). The present work was undertaken to see the effects of brief discharge periods during charges. The effects of relatively long discharges will be reported separately.

In the electroplating industry brief current reversal has been used for depolarization and for the periodic reverse current plating process. The effect of superimposing alternating current on direct current has been studied by a large number of investigators. A review of the earlier work was given by Halla (3). Some of the more recent work is covered by Rius, et al. (4), and the references cited therein. Many of these investigations have dealt with depolarization while gas was being evolved at inert electrodes.

The use of alternating current superimposed on direct current for recharging Leclanché primary cells without getting needles of zinc or large amounts of gas was proposed by Beer (5). In a similar way Romanov, et al. (6), used asymmetric ac for charging cells which contained zinc negative electrodes to prevent dendritic zinc from forming and causing damage. Romanov (7) reported several changes after asymmetric ac was used for charging pressed silver powder electrodes: the total capacity of the following discharge increased, and the AgO/Ag_2O potential plateau during discharge was shorter and at a lower potential than usual. The electrolyte concentration was not specified. Flerov (8) used sintered silver electrodes in 1.40-sp-gr KOH and found that if a sufficiently large ac is superimposed on the steady charging current, the AgO/Ag_2O discharge potential plateau can be eliminated completely, but in contrast to the results of Romanov (7), the total discharge capacity was unchanged. It has recently been reported that smooth silver electrodes in 10N KOH can give increased discharge capacity after oxidation by asymmetric ac under certain conditions as a result of increased surface area. (9)

EXPERIMENTAL PROCEDURE

Sintered silver plaques that were wrapped in cellulosic separator material were used for both the cathode and anode of the test cells. The plaques and separator had been manufactured for use in commercial silver-zinc storage batteries. The silver plaques were 41.5 by 38.0 by 0.8 mm. The sintered silver had an average weight of 5.8 g, not including the grid of expanded silver metal. This sintered silver weight corresponds to a theoretical electrode capacity of 2.9 amp-hr. The test cells contained an excess of

either 35% KOH or 50% KOH as the electrolyte and a Ag/Ag_2O reference electrode. All work was done at 25 ± 1°C.

As in the previous work (1,2) the constant current, which would result in a complete charge or discharge in approximately 20 hr, was arbitrarily taken as the standard, or normal, charge and discharge current. Since the test cells had a relatively constant average capacity after the first 10 charge-discharge cycles, the same current was used throughout the life of these cells, and corrections were not made for the deviations in charge-discharge time from 20 hr after the tenth cycle. Complete normal charges (using the 20-hr rate as defined above) alternated with complete charges which used one of the reversal conditions. Two types of charge current which had brief periods of current reversal were used. One type was obtained by taking a half-wave, rectified current derived from commercial 60-cps ac and superimposing this half-wave current in the discharge direction on a larger constant charge current. The waveform of this current is shown as B in Fig. 1. The second type was obtained by combing two half-wave, 60-cps rectified currents which were 180 degrees out of phase and which flowed in opposite directions through resistances of different values (D in Fig. 1). Both of these charge currents were types of 60-cps asymmetric ac with forward components larger than reverse components. Only one set of reversal conditions was used in any given charge.

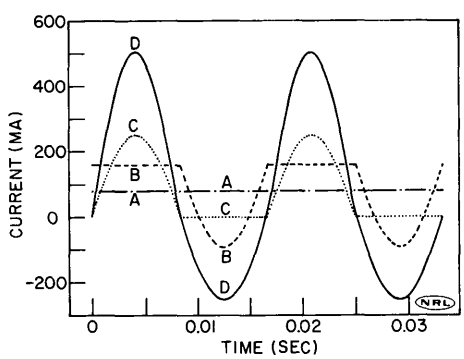

Fig. 1 - Comparison of constant current to several charge currents derived from 60-cps ac. For each example, the net charge current was equivalent in coulombs per unit time to a constant current of 80 ma. A represents constant current; B, constant forward current with half-wave, rectified ac superimposed in reverse direction; C, half-wave, rectified ac; D, half-wave forward current with half-wave reverse current superimposed 180 degrees out of phase with forward current. The ratio of forward component to reverse component was 2:1 for both B and D.

All charges were continued until oxygen evolution was occurring and potential stopped changing rapidly. This potential was about 510 to 530 mv positive to the Ag/Ag_2O reference electrode when the 20-hr rate of constant charge current was used. Constant current charge input was usually 1 or 2% greater than the capacity of the following discharge. After a charge was finished, a cell was immediately discharged at approximately the 20-hr rate of constant current to a final potential which was 300 mv negative to the Ag/Ag_2O reference. In a few cases a cell was discharged at the 1-hr rate to a final potential which was 500 mv negative.

To minimize variations in cell capacity the discharge capacities of the four normal cycles (20-hr constant current charge and discharge) that were nearest each discharge were averaged. This average was then taken as the normal capacity at that particular point in the life of a cell and is the capacity referred to whenever normal capacity is mentioned in this report. Capacity of each discharge was calculated as a percent of this varying average. Thus, the discharge capacity which followed a charge with current reversals could be compared to a value which was representative of actual cell capacity, regardless of changes in normal capacity over the life of a cell.

Some types of charge, which had current reversals and which resulted in increased test cell capacity, were tried with one model of a commercial silver-zinc secondary cell.

The commercial cells contained either 35% KOH or 45% KOH. Typical electrolyte analysis has been given earlier (2). Each commercial cell had four sintered silver electrodes of the same size as the test electrodes and five zinc electrodes. The silver electrodes limited cell capacity and gave a theoretical cell capacity of about 11.5 amp-hr, although the nominal-rated cell capacity, given by the manufacturer, was only 5 amp-hr. The silver-zinc cells were charged individually until cell potential reached 2.05 v. Complete charges at the 20-hr rate of constant current (as defined above) alternated with charges which had current reversals. The cells were discharged at the 20-hr constant current to 1.10 v. Since capacity of these cells varied from one charge-discharge cycle to the next, the 20-hr current was recalculated after each constant current cycle, and a different current was used for the following cycle whenever actual charge and discharge length had deviated greatly from 20 hr.

RESULTS

Before any charges with periodically reversed currents were tried, the cells were charged and discharged by the 20-hr constant current until capacity became relatively constant. During the first two charge-discharge cycles of a new test cell, capacity of the electrodes was often as high as 70% to 80% of the capacity theoretically possible for the silver active material. Then capacity decreased until, after 8 to 10 cycles, it became relatively constant in the range 45 to 60% of theoretical capacity, usually averaging 50 to 56% of the theoretical capacity in 35% KOH but about 10% lower in 50% KOH.

Capacity of the commercial silver-zinc cells also changed with use but not in the same way as the test cells. Thirteen commercial cells were used. Eleven reached a maximum capacity that was 68 to 79% of the theoretical value, and the other two reached 62% and 64%. The commercial cells which contained 45% KOH always gave the maximum discharge capacity after either the initial or second charge, but the cells which contained 35% KOH did not reach a maximum until charge 5 to 8. After reaching this maximum, the capacity of the commercial silver-zinc cells gradually declined during the remainder of their lives. Ten of the silver-zinc cells contained 45% KOH. These cells gave only 4 to 21 (an average of 11) charge-discharge cycles before they developed internal short circuits. A cell was discarded after it developed a noticeable short circuit, as evidenced by unsteady charging potentials and failure to reach 2.05 v during charge. The three commercial silver-zinc cells, which differed from these ten cells only in the electrolyte concentration of 35% KOH, did not develop noticeable short circuits and were still in good condition when work was completed, after having undergone from 23 to 53 cycles apiece.

Charge acceptance of a silver electrode could be increased over the amount obtained from a constant charge current if the electrode was charged with a constant current which had half-wave, rectified 60-cps ac, superimposed in the discharge direction (B in Fig. 1). When this type of current was used, with net current equivalent in coulombs per unit time to the 20-hr rate of constant charge current, a distinct increase in discharge capacity was obtained from the test cells which contained 35% KOH (Table 1). The improvement was insignificant, however, in 50% KOH or when commercial silver-zinc cells were used (Table 1).

Previous work has shown that a charge with half-wave, rectified ac (C in Fig. 1) can give a greater capacity to a silver oxide electrode than a charge with constant current (2). This work was extended by the use of half-wave rectified 60-cps ac in the charge direction combined with a smaller half-wave, rectified 60-cps ac in the discharge direction on alternate half-cycles (D in Fig. 1). Compared to results when constant current was used for a charge, this asymmetric ac gave relatively large capacity increases with the silver electrodes in test cells which contained 35% KOH and gave smaller, but definite, capacity increases with the commercial silver-zinc cells (Table 2). The effect of varying the ac

Table 1

Discharge capacity of silver oxide electrodes following charges with asymmetric 60-cycle ac obtained by superimposing rectified 60-cycle ac in reverse direction on constant charge current. The net charge current was equivalent to the 20-hr rate of constant current.

Magnitude of ac Components (multiple of 20-hr current)		Discharge Capacity (% of normal capacity)			
		Test Cells		Commercial Cells	
Forward	Reverse	35% KOH	50% KOH	35% KOH	45% KOH
1.0	0.0	100*	100*	100*	100*
1.5	0.5	119.5 120.0 129.3 123*	102.0 107.4 105*		
2.0	1.0	112.9 121.0 127.4 120*	100.9 101.8 101*	98.3 102.1 104.1 102*	99.3 101.6 109.3 103*
3.0	2.0	132.6 142.6 143.1 139*	99.2 107.1 103*	102.4 102.7 102.8 103*	103.3 105.3 104*

*Average.

frequency was not studied, but it is likely that capacity improvement depends, somewhat, on frequency, although frequency is probably not sharply critical.

The effective current, when using an asymmetric ac derived from commercial 60-cps ac, was the numerical value of the constant current which would produce the same quantity of electrochemical products as the asymmetric ac. The effective current could be calculated by taking the average (arithmetic mean) of the instantaneous ac values. The effective current was not the root-mean-square value of the ac (the numerical value of a constant current which would produce the same heat, or power, as the ac). It can be shown mathematically that the asymmetric current, obtained by combining two half-wave currents which flowed in opposite directions, had components which reached peak values approximately π times as large as constant currents that were equivalent in coulombs per unit time to these half-wave components (Fig. 1).

Capacity tends to decrease as charge rate increases. Figure 2 shows capacities obtained after complete charges of sintered silver electrodes at various rates of constant current, with the 20-hr rate taken as a reference point. Sixty-cps asymmetric ac of the type shown in D of Fig. 1 was tried at the 6-hr rate of charge using the test cells (Table 3). When the reverse component was low, there was little or no improvement over the capacity obtained following a constant current charge at the 6-hr rate (Fig. 2) or following a charge by a half-wave current at the 6-hr rate (Table 3, reverse component 0.0). Capacity of a charge at the 6-hr rate was improved when both components of the asymmetric ac were large.

This asymmetric ac was used at the 6-hr rate for a few charges of the commercial silver-zinc cells. The results resembled those shown in Table 3 except that improvement

Table 2

Discharge capacity of silver oxide electrodes following charges with asymmetric 60-cycle ac obtained by combining two half-wave currents which flowed in opposite directions and were 180° out of phase. The net charge current was equivalent to the 20-hr rate of constant current.

Magnitude of ac Components (multiple of 20-hr current)		Discharge Capacity (% of normal capacity)			
		Test Cells		Commercial Cells	
Forward	Reverse	35% KOH	50% KOH	35% KOH	45% KOH
1.0	0.0	123.7	99.5	101.1	97.4
		130.3	102.0	103.5	100.8
		132.6	101*	102*	99*
		129*			
1.5	0.5	140.9	99.3		
		149.6	103.4		
		145*	101*		
2.0	1.0	129.6	95.4	110.2	109.7
		149.0	100.2	114.6	111.5
		161.5	98*	120.5	111.7
		147*		115*	111*
3.0	2.0	147.8	90.1	121.6	101.7
		153.3	93.1	121.8	112.8
		160.2	92*	127.2	113.1
		154*		124*	109*
5.0	4.0	118.8		117.9	
		135.6		118.5	
		141.7		118*	
		151.2			
		137*			

*Average.

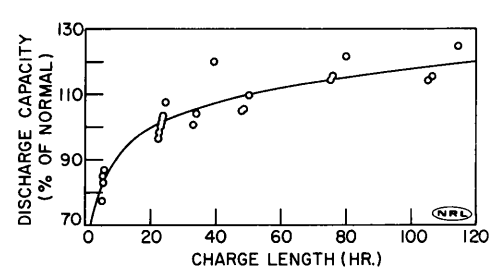

Fig. 2 - Dependence of discharge capacity of silver oxide electrodes on the rate of constant current used for charge. The electrolyte was 35% KOH at 25°C.

was not as large. For example, three charges at the 6-hr rate, which used 6 times the 20-hr rate for the forward component and 3 times for the reverse component, gave an average capacity in 35% KOH that was 96% of the normal, while a constant current at the 6-hr rate gave an average capacity that was 84% of the normal. In 45% KOH capacity was not this large but showed the same type of improvement. In 45% KOH charges at the 6-hr rate gave an average 81% of normal capacity with the same asymmetric ac and 69% of normal with constant charge current.

Table 3
Discharge capacity of silver oxide electrodes in 35% KOH, following charges with an asymmetric 60-cycle ac obtained from two half-wave currents 180° out of phase. The net charge current was equivalent to the 6-hr rate of constant current.

Magnitude of ac Components (multiple of 20-hr current)		Discharge Capacity (% of normal capacity)
Forward	Reverse	
3.0	0.0	69.2
		78.3
		89.8
		99.7
		84*
4.0	1.0	75.2
		75.9
		76.6
		99.5
		82*
5.0	2.0	76.4
		81.5
		95.0
		96.6
		87*
6.0	3.0	96.9
		101.6
		108.4
		102*
9.0	6.0	96.4
		107.9
		127.3
		111*

*Average.

Potentials of silver electrodes in the test cells are shown in Fig. 3 for a few of the discharges following charges which used 60-cps asymmetric ac at the 20-hr rate. The shape of the first discharge plateau was not completely reproducible. Potential of this plateau was noticeably lower after the forward component of the charge ac had been half-wave, rectified ac than after the forward component had been constant current. The first discharge plateau tended toward lower potentials as the forward and reverse components of the previous charge both increased, with net charge current remaining constant. These changes in discharge potentials, following a charge with asymmetric ac, were observed with commercial silver-zinc cells containing 35% or 45% KOH and with the test cells containing 35% KOH. In 50% KOH, however, the discharge potentials were the same as after a constant current charge.

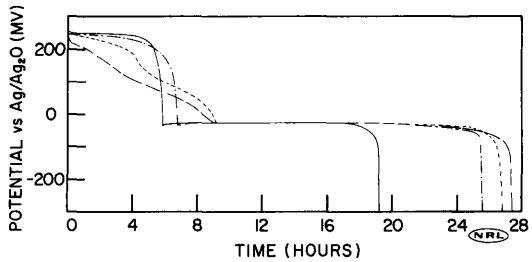

Fig. 3 - Constant current discharges of silver oxide electrodes in 35% KOH. Net current of previous charge was at or equivalent to 20-hr rate of constant current. The solid line represents discharge after constant current charge; the dash and dot line, after half-wave, rectified 60-cps ac charge; the short dash line, after charge by 60-cps asymmetric ac with constant forward component of 3 times the 20-hr rate and half-wave reverse component of 2 times the 20-hr rate; the long dash line, after charge by 60-cps asymmetric ac, with half-wave forward component of 3 times the 20-hr rate and half-wave reverse component of 2 times the 20-hr rate.

It was noted that interruption of the reverse current component for a few seconds resulted in different charge potentials after current was resumed. The net charge current was increased by interrupting the reverse current component. The net charge current fell back to the normal value after resuming the reverse current, but charging potentials became lower than they were before the interruption. This drop in potential was similar to the potential drops observed after pulses of charge current were added to a constant charge current (1). These results suggest that the beneficial results of the two types of charge might be combined, but this was not pursued further.

As already mentioned, cycles with normal charges alternated with cycles having reversals. Sometimes, for no apparent reason, a constant current charge at the 20-hr rate gave a capacity that differed rather widely from the normal capacity. It seemed likely that these differences could be a result of changes that had occurred during the preceding cycle, in which charge current had been reversed. The current composed of two half-wave, rectified currents (D in Fig. 1) was the charge current most likely to be followed by a 20-hr constant current charge-discharge cycle which had unusual capacity. There was, nevertheless, no increase or decrease in capacity following a constant current charge which correlated consistently with this or any other of the charges with reversals.

For the results that have already been given, capacity was measured at the 20-hr discharge rate. There were also three series of charge-discharge cycles in which fully charged silver electrodes were discharged in 35% KOH at the 1-hr rate. Each series consisted of 13 to 45 consecutive, complete discharges at the 1-hr rate following completion of charges at the 20-hr rate. The first discharge at the 1-hr rate gave slightly less capacity than was obtained at the 20-hr discharge rate. As charges at the 20-hr rate and discharges at the 1-hr rate were repeated, discharge capacity gradually increased for 5 or 6 cycles and often exceeded normal capacity. The length of the AgO/Ag_2O potential plateau decreased during the first few discharges at the 1-hr rate until, finally, the AgO/Ag_2O potential plateau no longer appeared on discharge. At the same time the Ag/Ag_2O charge plateau was becoming longer until it reached approximately 1.6 to 2.1 times its normal length, with almost 50% of the charge taking place at the Ag/Ag_2O plateau. The final potential of the oxygen evolution plateau gradually increased in this period.

After charges at the 20-hr rate and discharges at the 1-hr rate became relatively reproducible, charges were tried under some of the reversal conditions that had proved most beneficial earlier. These conditions no longer increased capacity significantly. For example, the test cells were charged with currents of the types shown in B and D of Fig. 1, having the ratio 3:2 for charge component to discharge component, with net charge current equivalent to the 20-hr constant current, but capacity of the subsequent discharge of the test cells at the 1-hr rate was only 100 to 102% of capacity following a constant current charge.

After resuming the 20-hr discharge rate, it was noted that the electrode had not discharged completely at the 1-hr rate. Ten to 30% additional capacity could be removed at the 20-hr rate following a discharge at the 1-hr rate. Normal cycles revealed several changes from conditions before the series at the 1-hr rate. Capacity had increased 15 to 40%, and the AgO/Ag_2O discharge plateau was only 1/3 to 2/3 its normal length. Capacity declined to approximately its former value in 10 cycles. The length of the AgO/Ag_2O discharge plateau is given in Fig. 4 for normal cycles before and after discharges at the 1-hr rate. As this plateau gradually increased, the amount of charge that took place at the Ag/Ag_2O plateau gradually decreased back to its former value.

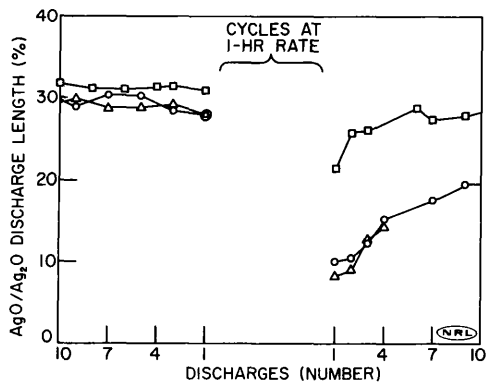

Fig. 4 - Percent of discharge that took place before Ag_2O/Ag potential was reached after charges at 20-hr rate in 35% KOH at 25°C. Results are given for discharges at the 20-hr rate immediately before (at left) and immediately after (at right) a series of 13 (□), 22 (△) or 45 (○) complete discharges at the 1-hr rate.

DISCUSSION

Earlier work has shown that it is possible to increase the charge acceptance of a silver electrode in 35% KOH as much as 40% over the normal value if, during a constant current charge, the current is increased for only a few seconds after every 10 to 60 min of charge (1). Charge acceptance can also be increased by approximately the same amount if the electrode is charged by a rapidly pulsating, unidirectional current (2). An even larger improvement can result in 35% KOH from the use of an asymmetric ac for the charge current. Table 2 shows that capacities more than 50% larger than normal could be obtained by charging with a 60-cps asymmetric ac composed of two half-wave currents. Capacity increases were smaller, however, when silver electrodes were charged in 35% KOH by an asymmetric ac which was obtained by superimposing a half-wave, 60-cps current in the discharge direction on a larger constant charge current (Table 1). This difference is not surprising because a half-wave charge current without reversal gave approximately 29% more capacity than a constant charge current (Tables 1 and 2, reverse component 0.0). When forward and reverse half-wave currents were combined, a part of the beneficial effect of reversal was obtained, in addition to the benefit from the rapidly pulsating charge current. Note that the waveform when a half-wave, 60-cps reverse current was superimposed on a constant charge current, was rather different from the waveform of the current obtained by combining two opposing half-wave currents (B and D in Fig. 1). The current reached much larger forward and reverse values for the same net charge current when the two half-wave currents were used.

Compared to a normal charge with constant current, several changes were observed during a charge with asymmetric 60-cps ac. The Ag/Ag_2O potential plateau was shorter than normal, the Ag_2O/AgO plateau was longer than normal, and the potential rise to the oxygen evolution plateau was slower than usual. The rapidly fluctuating current was, of course, accompanied by fluctuating cell potentials. As the silver electrode became more completely charged, its potential could exceed the oxygen evolution potential while the charge component of the ac reached its maximum value, particularly when a large charge

component was used. Part of the current consumed in gas evolution resulted in a lower current efficiency than the efficiency which was obtained with a constant charge current. One can speculate that charges with asymmetric current could shorten cell life, especially if the components of the current were large with respect to the net effective current. This effect was not observed, but the experimental method (alternating normal charges with charges having current reversals) would somewhat mask a shortening of life if the harmful effect was weak.

After commercial silver-zinc cells which contained 35% KOH were charged with asymmetric ac composed of two half-wave currents, their discharge capacity was markedly larger than the capacity obtained from commercial cells by the other charge methods (Table 2). This type of asymmetric ac also gave an increased capacity with commercial silver-zinc cells which contained 45% KOH. Although the capacity increase was relatively small, it was the only time that the commercial silver-zinc cells which contained 45% KOH showed a definite improvement when charged with periodically varying current. The test cells which contained 50% KOH did not give significantly increased capacity after a charge with either type of asymmetric ac. This outcome was consistent with the previous results; cells containing 50% KOH always lacked the improvement which could be obtained in 35% KOH by charging with a varying current (1,2).

In addition to the increased capacity, another notable change that was observed following a charge with 60-cps asymmetric ac was the tendency for potentials to be lower than usual in the early part of a discharge (Fig. 3). The proportion of the total discharge that took place before potential reached the Ag_2O/Ag plateau remained approximately the same as it had been following a normal charge. As mentioned earlier, the potential of the initial discharge plateau was lower following a charge with asymmetric ac which had large forward and reverse components than it was following a charge at the same net current which had smaller components. These results suggested that if sufficiently large forward and reverse components had been used, the initial potential plateau would disappear, as has been reported to occur (8). The discharge rate was defined by the 20-hr rate following a constant current charge. Therefore, discharges actually lasted closer to 30 hr after the charges which gave greatly increased capacity (Fig. 3). The initial potential plateau will decrease as discharge current increases and disappear at sufficiently high current. If a higher discharge rate had been used following the asymmetric ac charges which had large components, it is likely that the initial plateau would have disappeared at a much lower discharge current than would be required for it to disappear following a normal charge.

Tables 1 and 2 give results obtained by using the 20-hr rate of current. Marked improvement in capacity could also be obtained in less time. As a general rule, the capacity of a secondary cell will decrease as charge rate increases (10). A silver electrode, charged in 35% KOH with constant current at the 6-hr rate, gave a discharge capacity which averaged 83% of the normal capacity (Fig. 2). Table 3 shows that this capacity was not significantly different from the 84% average obtained when the electrodes were charged at the 6-hr rate with 60-cps half-wave, rectified ac (waveform C in Fig. 1). Previous work has shown that close to 100% of normal capacity could be obtained at the 6-hr rate when a silver electrode was charged with unidirectional current that flowed 1/4 or 1/8 of the time, with 60 periods of current flow per sec (2). By charging at the 6-hr rate with asymmetric current type D in Fig. 1, which had a sufficiently large reverse component, capacity was obtained which exceeded the normal capacity and was 1/3 greater than the capacity obtained by a constant current at the 6-hr rate (Table 3). Although slow charges with this asymmetric ac gave a larger capacity than rapid ones, a rapid charge with asymmetric ac is valuable if it is important that charge time be small.

It is believed that the increased capacity that occurred when the silver electrodes were charged with a 60-cps asymmetric ac was mainly the result of the transient high charge currents. As mentioned earlier, the asymmetric ac reached high peak values, particularly when the ac was composed of two half-wave currents. The peaks in charge

current were closely followed by peaks in potential. When charge potential reached a maximum, possibly the AgO coating cracked as a result of expansion as oxides formed below the electrode surface. Cracks in the oxide coating would allow the electrolyte to penetrate nearer the metallic silver. Crystal lattice dimensions indicate that there is a large expansion of the crystal as metallic silver is oxidized to Ag_2O. There is only a slight additional increase in volume as Ag_2O is oxidized to AgO, but the lattice is distorted as dimensions change in going from face-centered-cubic to monoclinic crystals. Another possible, but less likely, factor was that cracking may have resulted from stresses set up by the rapid formation of oxides when the forward current reached peak values. The reverse current tends to relieve stresses. Although cracking would decrease concentration gradients within the electrode and allow more silver to oxidize, cracking could have the disadvantage of isolating some of the oxidized silver from good electrical contact with the conducting grid.

Lowered conductivity and differences in the microstructure of the active material probably account for a discharge following an asymmetric ac charge having less of an initial potential plateau than usual. Conductivity improved after silver began to form during discharge (11). At the end of a normal charge which followed several charges with asymmetric ac, potential tended to rise slower than usual. Both this slow rise and the low potentials in the early part of a discharge following an asymmetric ac charge may indicate that some of the active material was in poor electrical contact after asymmetric ac charges. The active material would not oxidize during a charge at a particular current until potential rose sufficiently to overcome internal resistance. The potential rise at the end of a charge became more rapid when the constant current charge was repeated.

The briefness of the periods of high current when asymmetric 60-cps ac was used prevented unduly large concentration gradients from forming in the electrolyte. Large concentration gradients can limit the amount of oxidation during a charge at a high current density. This effect is greatest in very concentrated KOH, where the mobility of the hydroxyl ion becomes most limiting. Therefore, when high currents were reached with 60-cps asymmetric ac charges, capacity was always lower in 45% and 50% KOH than it was in 35% KOH for the same current (Tables 1 and 2).

The differences between results with the commercial silver-zinc cells and the test cells were probably due mainly to different concentration gradients. It is doubtful that the presence or absence of zinc was important. The commercial cells were tightly packed and had a limited amount of free electrolyte. This setup should result in concentration gradients near the electrode surface being larger in the commercial cells than they were in the test cells at the same current density. Therefore, the commercial cells showed less improvement after a charge with reversals than the test cells showed.

The lack of improvement when discharges were done at the 1-hr rate was consistent with results reported earlier. After a series of discharges at the 1-hr rate, a silver electrode gave a relatively high percent of the capacity theoretically possible. Under these conditions a charge with repeated open-circuit periods, which usually resulted in improved capacity, gave only about the same capacity as a constant current charge (2), because the form of silver in the electrode varied with the rate of reduction (12). Fast reduction of the silver oxides resulted in smaller crystals of silver, and rapidly produced silver probably had a larger number of imperfections. These smaller crystals could be charged more readily. Therefore, a charge following several fast discharges can have more capacity than a charge following a slow discharge. The observed gradual increase in capacity during a series of cycles with fast discharges indicated a progressive decrease in particle size of the silver active material. The small particles had a larger surface area, and more Ag_2O formed before charge potential rose to the Ag_2O/AgO plateau.

The high oxygen evolution potential at the end of a charge, following discharges at the 1-hr rate, indicated that resistance under these conditions was higher than usual. This

resistance could be a result of the finer particles being in poorer contact with each other because a larger than usual proportion of silver had been oxidized. Resistance becomes more important at high rates of discharge. The oxide particles with poorer contact were not all reduced before discharge potential dropped to the cutoff value. Capacity was probably limited more by incomplete reduction than by charge acceptance during discharges at the 1-hr rate. It was likely, therefore, that the form of charge current was less important under these conditions than under slow discharge rates. When the slow discharge rate was resumed, particle size increased during the next few cycles, as indicated by the gradually declining capacity and by the potential plateaus gradually recovering their former proportions.

CONCLUSIONS

Charge acceptance was increased markedly, under certain conditions, when current was reversed periodically during a charge. Highest capacity was obtained after a charge by an asymmetric 60-cps ac composed of two opposing half-wave, rectified currents 180 degrees out of phase, with the reverse component two-thirds as large as the forward component. When test cells containing 35% KOH were charged with this current at the 20-hr rate, one-half more capacity could be obtained than the capacity which resulted from a constant current charge at the same rate. This ac used at the 6-hr rate gave one-third more capacity than a constant current at the same rate. When commercial silver-zinc cells containing 35% KOH were charged with this asymmetric ac, they gave less improvement than the test cells but more capacity than they gave with other charge methods. Improvement decreased with increasing KOH concentration. A discharge following an asymmetric ac charge which gave improved capacity showed less AgO/Ag_2O potential plateau than usual, probably as a result of lowered conductivity. The charges with periodic reversals were not effective in increasing capacity after a series of discharges at the relatively high current of the 1-hr rate. Under these conditions capacity was probably limited more by incomplete reduction during discharge than by charge acceptance.

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13. ABSTRACT

The discharge capacity of sintered silver electrodes used in storage batteries was improved 40 to 50% when the prior charge was made by an alternating, rather than constant, current. Commercial Ag-Zn cells, under the same conditions, gave capacity increases of 15 to 25%. This improvement was obtained by charging the cells with 60-cps asymmetric ac, composed of two opposing half-wave currents 180 degrees out of phase and unequal in amplitude, as compared with charging by a constant current, both being at the 20-hr rate in 35% KOH at 25°C. Capacity depended on the proportion of charge and discharge components of the ac. Capacity improvements were smaller when net charge current was set at the 6-hr rate, when charge current was composed of 60-cps half-wave reverse current superimposed on constant charge current, or when the KOH concentration was increased. No significant improvement occurred when the charge with reverse current followed a series of discharges at the 1-hr rate.

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