

## SOME STORAGE BATTERY PHENOMENA.

BY W. W. GRISCOM.

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It was with great hesitation that I ventured to accept your invitation to read this paper before a body of distinguished men, who are more or less masters of their own time and have devoted it, and dedicated themselves, to science and research, and it was finally with a view to enlisting your interest and assistance in the storage battery problem that I decided to lay before you some of the phenomena which have in turn baffled and instructed me, occupied my thoughts, and kept my faith from flagging during the ordeal through which the storage battery interests have passed.

The study of a complete curve of discharge of a storage battery (Curve III) discloses three rather sharply defined changes in  $P. D.$ , and after allowing for the effect of internal resistance, we find that the changes are those of the  $E. M. F.$

What is the reason for these changes? Which plate is responsible for them?

A microscopic examination of the negative (spongy lead) plate, disclosed metallic lead and what appeared to be one, or possibly two sulphates. The positive (peroxide) plate, however, showed spongiform crystals of very dark color, known as electrolytic peroxide; other comparatively large crystals of brilliant red, probably Frankland's red sulphate; others of yellow, probably yellow sulphate; and finally the better known white sulphate of lead.

The production of these diverse chemical forms must be attended by production of diverse potentials, and the  $E. M. F.$  of the battery is possibly a resultant with one or more chemical reactions predominating at various parts of the charge and discharge.

That there should be any change of E. M. F. during the charge or discharge of the battery, shows the complexity of the chemical actions, and as the changes are at times sudden, and at times gradual, uniform and invariable, it would seem to point to the conception that the E. M. F. is the resultant of three or more sets of chemical actions.

The material on the charged positive plate of the battery is

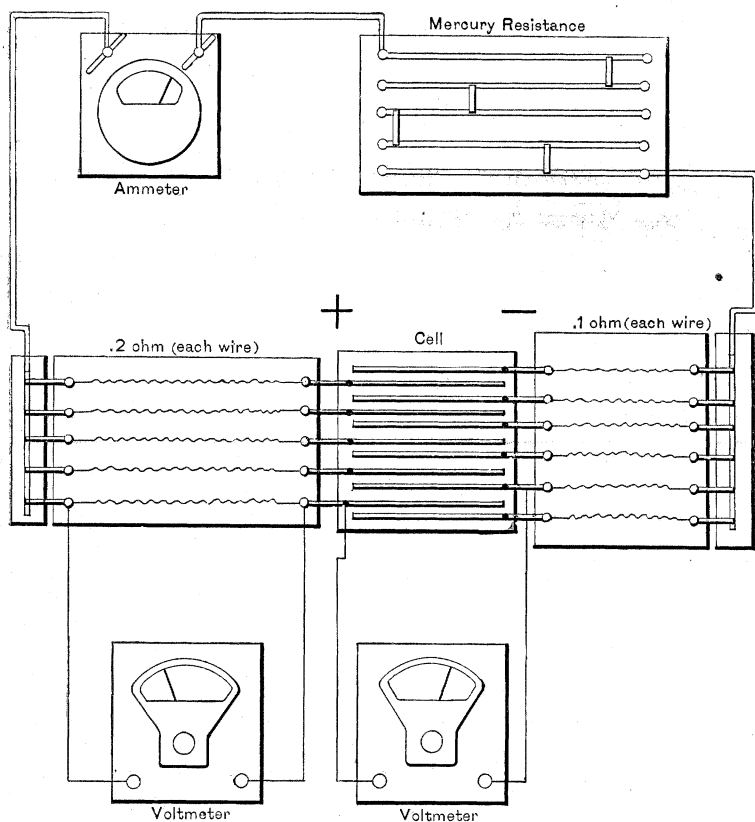


FIG. 1.

commonly called peroxide of lead, but it certainly differs from it both in its ability to generate electromotive force, and in its appearance, and Fitzgerald has pointed out that its composition corresponds to the hydrated peroxide of lead,  $H_2Pb_2O_5$ . He further intimates that a higher oxide of lead may be present, such as perplumbic acid,  $H_2Pb_2O_7$ . McLeod has told us how peroxide of hydrogen, ozone, and persulphuric acid are pro-

duced. Then there are the two new sulphates of lead and the various compounds of sulphuric acid and water. With this array of chemical products to assist our imagination, the wonderful curves of E. M. F. of a storage battery on charge and discharge become comprehensible. And the fact observed by Gladstone and Tribe that thirty-four per cent. more of oxygen was absorbed by the positive plate than could be accounted for by the production of  $PbO_2$  becomes explicable. It has probably been used in converting  $H_2Pb_2O_5$  into  $H_2Pb_2O_7$ . Their suggestion that it was absorbed by local action between the grid and the peroxide during charge is utterly untenable. There is no such action. And if there were, the grid would not last through a dozen charges.

The conversion of  $H_2Pb_2O_5$  into  $H_2Pb_2O_7$  would account for the abnormal rise of E. M. F. at the end of charge, and if it be assumed that the  $H_2Pb_2O_7$  is not stable, but yields ozone gradually, thus accounting for the odor of a freshly charged positive plate, it would account for the steady fall of E. M. F. on interrupting the charging current. The chemist will easily see the relation between these reactions, and the presence of peroxide of hydrogen and the continual evolution of oxygen from the positive plate, and the fact that a charged cell gradually loses its charge, maintaining for days a higher temperature than the air.

I am sorry that the time allotted me for the preparation of this paper did not admit of the preparation of curves showing the differences in temperature between certain plates of a cell and even between different parts of the same plate. Of course these changes, many of them, are very minute, and they are due to at least two causes, viz., the liberation or combination of sulphuric acid on the one hand, and  $C_2R$  on the other.

In order to study the progressive changes on either plates and to plot them out in a curve, it is merely necessary to choose a substance which produces a measurable electromotive force with the plates, independently of the electromotive force which is being produced by the two plates appertaining to the battery, but this substance must be one which is neither modified by the electrolyte nor by the minute current which it is required to produce for the voltmeter. The last is of more consequence than is generally understood, as a storage battery which has been over-discharged and which has been allowed to recuperate will, even if it be of large size, say of 350 ampere hours capacity, produce a deflection on a Weston voltmeter (of about 300 ohms),

which at first may be 1.75-100 volts and which will immediately begin to fall with a velocity quite appreciable to the eye. Many substances have been tried for such a test plate, as for example, zinc, carbon, platinum and copper, but nothing seems to be better than a well charged Faure or Planté couple of considerable dimensions. The use of such plates was first published by Mr. Crompton, although they have been used for years in my laboratories, and give concordant results.

It might be desirable, but it is not necessary to ascertain accurately the exact fraction of the total E. M. F. which is due to the plate under test. It is important, however, to know the rate of its change of E. M. F. while the cell of which it forms an individual part is discharging or charging.

Referring to the Curve III entitled Planté Cell, it will be observed that the negative plate maintains a nearly horizontal line, until the P. D. of the couple on discharge has fallen to 1.9 volts, while the positive plate maintains a curve almost parallel to that of the cell, showing that the characteristic curve on discharge of a storage battery with plates of nearly equal capacity is due mainly to the reaction in the positive plate.

At the end of the charge, however, the characteristic curve of E. M. F. is due to the negative, the rapid rise of its curve being nearly parallel to that of the battery, while the rise of potential of the positive is nearly a straight line, which, however, is gradually rising.

It should be noted that this curve is the true E. M. F. and is not dependent on the internal resistance of the cell, which reaches the maximum shortly after the 14th hour in this case, and remains quite constant during the remaining seven hours of the charge. But while the E. M. F. is not dependent on the internal resistance, the sudden changes in each curve are usually simultaneous, indicating a common cause.

It may be considered proven, therefore, that in a storage battery with plates of nearly equal capacity, the changes in the positive plate determine the characteristic curves of potential on discharge, and that the changes in the negative plate determine the characteristic curves of potential at the end of the charge.

A curious feature in charge is the intersecting of the curves of the positive and negative plate at several points. At the beginning of charge (Curve III) the two plates are at nearly the same potential,—the positive potential rises rapidly until it reaches

2.22 volts, when it begins to rise in a straight line strictly proportional to time. The negative on the other hand rises gradually until it reaches 2.18 volts, then it rises rapidly, intersecting the positive curve in  $14\frac{1}{2}$  hours and at 2.24 volts, and continuing to rise until it reaches 2.40 volts in  $16\frac{3}{4}$  hours, whereafter it remains constant for the five hours which the positive requires to reach the same potential.

To trace the history of a negative during discharge, (*vide* Curve I) it fell in five minutes .135 volts, in the next six hours .035 volts, in the following hour .250 volts and in 15 minutes more, 1.500 volts, showing less capacity than the positive plate. In half an hour after stopping discharge it recovered to 1.9 volts—jumping instantly on charge to 2.08 volts, and in 12 hours of charge arose only .05 volt. Of course the rate will not modify the general characteristics of the curve.

Within the working limits of charge or discharge, the negative did not vary over 2 per cent. of potential difference.

The history of the positive in this curve is not so satisfactory. Falling rapidly to 2.04 in ten minutes it fell thereafter in a gradual curve .115 volt during the normal time of discharge, a fluctuation of about 6 per cent. Ultimately the positive shows more capacity than the negative.

The total fluctuation of the cell during the six hours after the first five minutes was 6 per cent. in discharge down to 1.9 volts. This was the fluctuation of the P. D., that is to say it was the fluctuation which would be noticeable to the engineer in practical service and included all changes due to internal resistance.

The usual construction of storage batteries—all the plates of one name being permanently fastened to one heavy conductor—has heretofore interfered with the study of the individual plates of a cell. To the end, therefore, of facilitating this investigation, the author constructed some cells with independent plates, connecting all those of one name to a common mercury trough, either directly or through intermediate resistances as in Figure 1.

The resistances were made such, that one ampere would give ten divisions on a dead beat galvanometer, and as each division could be divided by the eye into tenths, the current passing could be read within one-hundredth of an ampere. An independent ammeter and an adjustable mercury resistance were inserted and the total current kept constant. The cells tested in this way were of three types. The pasted cell of the Accumulator com-

pany, the chloride cell and the Planté cell. The object in testing a chloride cell was to ascertain whether the exceedingly good contact (produced by casting the grid around the active material while the latter was hard, and allowing the molten metal to contract upon it) would operate to lessen the somewhat remarkable variations in the behavior of all storage battery plates, but this was not the case. Neither was there any marked difference in the behavior of the Planté cell.

The following characteristic readings were obtained from the three types of cells at their normal discharging rates:—

## PLANTE CELL.

	AT START.		1 HOUR AFTER START.		2 HOURS AFTER START.		3 HOURS AFTER START.		6 HOURS AFTER START.	
	Amp.	Volts.	Amp.	Volts.	Amp.	Volts.	Amp.	Volts.	Amp.	Volts.
1	4.73	2.00	4.72	1.995	4.72	1.99	4.70	1.965	4.67	1.90
2	4.72		4.72		4.71		4.71		4.64	
3	4.71		4.71		4.70		4.70		4.72	
4	4.69	1.95	4.71	1.99	4.70	1.985	4.69	1.955	4.67	1.90
5	4.71		4.70		4.69		4.63		4.42	1.85
6	4.73		4.74		4.72		4.79		4.91	
7	4.75	2.005	4.77	2.003	4.74	1.995	4.81	1.985	4.96	1.956

## CHLORIDE CELL.

Positive.	AT START.		1 HOUR AFTER START.		3 HOURS AFTER START.		4 HOURS AFTER START.		6 HOURS AFTER START.		8 HOURS AFTER START.		Negative.
	Amp.	Volts.	Amp.	Volts.	Amp.	Volts.	Amp.	Volts.	Amp.	Volts.	Amp.	Volts.	
1	5.30	2.03 2.065	5.75	2.01 2.04	5.75	1.94 2.00	5.80	1.90 1.965	5.80	1.735 1.89	5.60	1.80 1.78	1 2
2	5.43	2.035 2.045	5.40	2.015 2.03	5.45	1.965 1.98	5.40	1.935 1.94	5.45	1.86 1.88	5.80	1.80 1.81	2 3
3	5.40	2.035 2.035	5.35	2.02 2.02	5.35	1.975 1.96	5.30	1.94 1.95	5.35	1.865 1.87	5.80	1.80 1.80	3 4
4	5.43	2.045 2.03	5.40	2.03 2.015	5.40	1.985 1.965	5.40	1.955 1.93	5.40	1.88 1.86	5.85	1.80 1.64	4 5
5	5.70	2.055 2.02	5.65	1.99 1.925	5.70	1.99 1.925	5.70	1.96 1.87	5.55	1.86 1.66	3.60	1.56 1.26	5 6

## PASTED CELL.

AT START.		8 HOURS AFTER START.	
Amperes.	Volts.	Amperes.	Volts.
6.00	2.035	6.00	1.77
5.93	2.025	6.15	1.79
5.90	2.024	6.125	1.795
5.89	2.021	6.05	1.78
5.92	2.025	6.025	1.78
5.92	2.02	5.85	1.74
5.95	2.022	6.10	1.80

The curious phenomenon was presented of variations of current amounting to 30 per cent. in plates manufactured rigorously alike, kept in parallel and subjected to like treatment during their previous life. In cases where the discharge is pushed below 1.8 volts I have observed even more serious differences amounting to a variation of about 225 per cent., one reading being 2.8 amperes, another 6.4 amperes for perfectly good new plates carefully treated.

And perhaps a still more curious fact was the differences of E. M. F. of the plates in the same cell discharging through equal resistances and connected finally in parallel to the same circuit—the E. M. F. ranging from 1.60 volts to 1.85 volts for neighboring plates in parallel in the same cell, at the same time. On interrupting the circuit at the end of the discharge of a cell, a considerable flow of current as might be expected passed from one plate into another and it was hours before the batteries reached equilibrium after the external circuit was open.

The discharge of one positive into its neighbor, was a rather unexpected result. It had been thought that if one plate had less capacity than its neighbor it would simply stop discharging at a certain point, but that its E. M. F. would always be equal to that of its neighbors and that therefore, no current would flow.

The explanation of the phenomenon appears to be that the deficient plate keeps on discharging at a lower rate than the perfect plate, and finally reaches a much lower point of discharge. On interrupting the current, the plate which has not been discharged so far, rapidly recovers a higher voltage than its neighbor and, therefore, discharges into it.

This effect must also take place in the different parts of any one plate, and may be a cause for the formation of peroxide on the surface of a negative plate after a discharge, a phenomenon

which I have never noticed, but which has been remarked by too many observers to be ignored.

The two outside negatives give more than their proportional amount of current on discharge, the current being actually less than on the other plates, the potential remains higher, and the discharge is therefore a little greater. This, in turn affects the positives next to them and these positives are usually the first to disintegrate in a carefully used cell. This fact was most noticeable in batteries used on the Eckington and Soldiers' Home Railway at Washington, where out of 45,000 positive plates, there did not occur a single instance of buckling, and yet the outside positives always showed greater disintegration than the others.

The tendency of one part of a plate or one portion of peroxide to discharge faster or slower than its neighbor, is one of the reasons which induced us to adopt the equi-potential methods of connecting up the several plates of the storage battery. It is to be noted that these phenomena occur to a serious extent only when the batteries are discharged below 1.95 volts of potential difference per cell.

The above tables afford the most complete proof of the irregularity of the chemical actions which produce the electromotive force of the battery. Now one plate is giving current, now another. And most remarkable of all, the different sides of the same plate exhibit differences of potential at their terminals which I can only attribute to differences of internal resistance, both in the electrolyte within the plates and in the porous active material itself.

The active material during charge and discharge is undergoing chemical change irregularly, not merely in the different plates, but in the different sides of the same plates, and as the active material is made up of large numbers of little pellets isolated from one another by the grid, the conclusion seems inevitable that one side of a given pellet is active to a different degree from the other side. It is not necessary to conceive that the E. M. F. generated on one side of a pellet is as different from the E. M. F. of the other side as would be indicated by the potential difference at the plate terminals. The more reasonable conception appears to be that the internal resistance of one side of a pellet is sometimes greater, sometimes less than that of the other side, varying with the unequal chemical action. But I cannot escape



the conclusion that there must be some real difference of potential and consequently local action—not merely between the parts of the grid, but between opposite sides of the same pellet or paste. This would account for the fact observed by Ayrton that a working cell is always above the temperature of the air—even when its own temperature is falling in discharge.

In 1890 Prof. Ayrton in his most valuable contributions to storage battery literature independently noticed the fall of temperature in a discharging cell, and published a curve which is reproduced in Fig. 2.

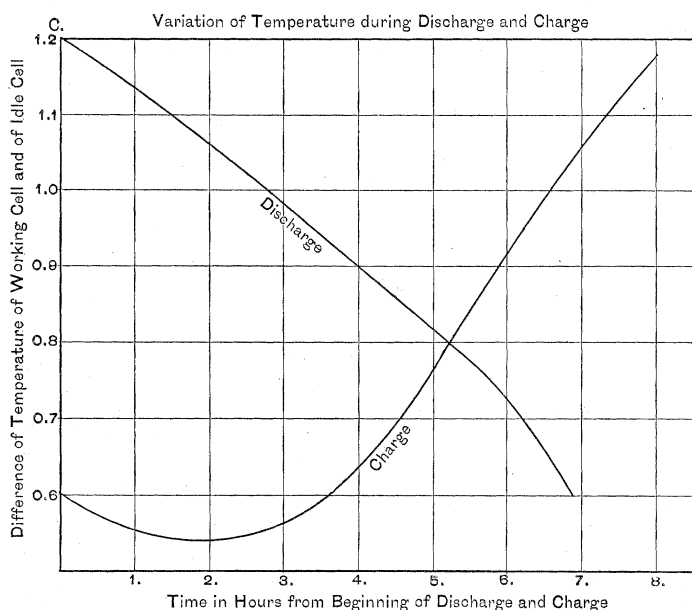


FIG. 2.

The explanation for at least a part of this phenomenon is simple. If, as we all know, the addition of sulphuric acid to water raises the temperature, it is natural to infer that the removal of the acid from the water will lower the temperature. The former occurs on charge, the latter on discharge.

This fall of temperature on discharge was first brought to my attention in 1887, when some of the cells of the Julien cars on Fourth Avenue, New York City, were reported to heat unduly, and the explanation offered was, that they were called on for increased currents on certain grades with unfavorable conditions of the tracks. As some of the cells did not heat I was not satis-

fied with the explanation, especially as the resistance of the cells, about .002 ohms, would only account for about  $1\frac{1}{4}$  heat units even on 100 amperes discharge which the cells produced at moments. I then investigated the question and found that the temperature actually fell even with heavy current, when the cells were in good order.

The potential of a cell is partly due to the degree of charge of the positive, and partly to that of the negative, and partly to the electrolyte. If a negative plate, taken from a fully charged cell indicating say 2.65 volts on the normal charging current, is coupled with a positive from a partly discharged cell, indicating say 1.9 volts on its normal discharge current, the E. M. F. of the combination will lie between the two. If the couple be removed to a stronger or weaker electrolyte, the E. M. F. will rise or fall accordingly. So that a measurement of the P. D. at the terminals of the cell is not an infallible indication of its condition of charge. If both plates are equally charged, the indication is most useful, but when as frequently happens in actual service, one plate is further discharged than the other the P. D. is deceptive.

The variations of specific gravity of the electrolyte are practically proportional to the ampere hours of useful charge or discharge—barring local action, short-circuiting, change of temperature, and a gradual sulphating of discharged positives when idle.

The variations of the internal resistance of a cell affords a valuable indication of the condition of its active material, and therefore of its degree of charge. These variations have been attributed to the varying porosity of the active material—the electrolyte becoming more and more excluded as the pores become clogged. But this explanation does not account for the odd but invariable nature of the characteristic curves of the internal resistance. If this were the true explanation, why does the curve fall rapidly in the early part of the discharge instead of rising? Why should it remain constant for the greater part of the useful discharge? Why should it suddenly rise to a great degree, and then fall in the middle of a prolonged charge? Why is the internal resistance less, instead of more, on a higher rate of discharge? These facts are not easily reconcilable with the clogging theory, and our knowledge of the chemical reaction is not sufficient as yet to afford a convincing explanation.

Experience shows that it adds greatly to the life of a cell, and brings other advantages to stop the charge at between 2.3 and 2.45 volts, and to stop the discharge at 1.90 or 1.95 volts, while a comparison of the accompanying curves of a cell will show that these potentials are reached shortly before, or during a sudden rise of the internal resistance.

A very curious misapprehension prevails among some battery people (in spite of the airing the subject has again and again received) to the effect that the negative plate has more capacity than the positive. If a cell be discharged at a high rate to 1.85 volts for example, the positive plate will show a much lower potential than the negative, and might therefore be deemed to be more discharged. If then the negative element be transferred to a freshly charged positive element, the negative will usually show a considerable additional capacity and this has been cited as a proof of the erroneous statement. But if the positive be similarly treated, it usually shows considerably greater capacity than the negative. This is especially the case with the Faure cell in Curve Ia in which the positive actually has 25 per cent. more volume of active material than the negative, and shows 45 per cent. more capacity; and is even so on a Planté negative which has as much active material as the positive, and yet the latter has nearly 10 per cent. more capacity.

The positive plate is usually made of greater capacity than the negative in order to prevent it from ever becoming discharged, to allow for its gradual loss of active material, but there are grounds for doubting the propriety of so doing. A negative plate ought never to be discharged so far as to drop after the first ten minutes, more than 1 or 2 per cent. in voltage, yet the temptation to do so with 45 per cent. excess of capacity in the positive is very great—with the result of causing shrinkage of the negative paste and a serious loss of capacity in the cell.

There is another action which goes on in storage batteries and presumably in other forms of electrolyte chemistry, which I have not seen explained, nor in fact described.

When the chemical reactions in an electrolytic cell are simple, as for example, decomposing sulphate of copper or sulphate of zinc, the amount of action is proportional to the ampere hours. But when the possible chemical reactions are complex as in a storage battery, the changes are governed by the potential difference as well as by the current, probably because one of the com-

ponents requires a different electromotive force to break it up from that required by another. A curious result ensues. Perhaps the current governs the amount of chemical action and the potential the kind. Our factory department reports that if a plate pasted with red oxide of lead is opposed to a plain lead grid in a "forming" bath, the formation of peroxide proceeds evenly and uniformly in the well known way. If it be opposed to a pasted negative the same result follows. But if it be opposed by another positive plate, a different action ensues, and the unformed plate cannot be properly converted to peroxide until the other positive has been completely reversed, and converted into a negative, thus raising the potential difference of the cell. In the Curve II it will be noted that at the time the potential of the piles suddenly rises, due to the sudden increase of the potential of the negative plate, there is at the same time a sudden increase of the internal resistance of that plate. This is, however, accompanied by a sudden and apparently sympathetic perturbation of the internal resistance of the positive plate, showing that some chemical change occurred in it, quite different from the usual action. This perturbation ceased as soon as the negative potential ceased to rise.

The purple color which is frequently observed in the vicinity of the peroxide plate has been variously attributed to the presence of gold, iron, manganese, etc. But as the phenomenon is observed anywhere and everywhere on the face of the globe, now in one cell, now in another, it seems more likely to be some unusual form of lead. The persulphide of lead is purple, and it may even be that the unstable elusive per-plumbic acid—if it really exists at all—is the source of the evanescent but beautiful tint. A freshly charged plate has a purplish slate color, very different from one that has been idle for a long while.

There are two other phenomena to which I will refer briefly in the hope that some members may be able to throw some light on their cause, viz: The sudden spontaneous discharge of a fully charged positive and the tendency to buckle away from the light, *i. e.* with a concave face toward the light. Wherever the tendency to buckle is great, as in treating Planté plates in some of the more rapid methods, I have observed that when a single positive is suspended freely a great distance from a negative in the center of a large jar, the buckling is invariably away from sun light. The plate may be turned around, it may be moved

quite close to one negative or the other, yet the buckling repeats itself invariably from the light. The plate may be straightened as you will, it may be left with a slight curve in the other direction, yet neither the natural differences of tension in the two sides of the plate, nor the increase or diminution of electrolytic action on either side has any influence in buckling compared, apparently with the action of direct sunlight.

It will be remembered that Prof. Ayrton in one of his valuable contributions to storage battery literature, commented on the theory of Mr. Crompton regarding the effect of light on the sulphating of the negative plate, and detailed an interesting experiment which although not conclusive, tended rather to confute this theory. Sir David Salomons remarked upon the effect of light on the glass cells causing them, he said, to crack. Altogether it would seem that storage batteries are devices which engineers would do well to keep in the dark.

The automatic discharge of the positive plate is a comparatively rare phenomenon. In my experience I have secured accurate data in only three instances. I am under the impression that Sir David Salomons, when by his courtesy I was enabled to examine his splendid private plant in 1886, mentioned this phenomenon, but I do not find it described in his book, and as it may not have recurred in his experience he may have felt some hesitancy in publishing it.

On one occasion a cell was reversed experimentally, and the reversing charge continued until 470 ampere hours or three times the normal capacity of the cell had been passed through it. The potential attained 2.41 volts on a low charging rate. The positive had the healthy dark color of electrolytic peroxide of lead and was freely gassing, showing that it was as fully charged as possible. The charging current was interrupted and the E. M. F. fell gradually to 2.12 volts in a perfectly normal way. In 35 minutes a curious seething sound attracted my attention to the battery, and I found it in a state of violent, almost explosive ebullition. The gas given off was pure oxygen in immense quantities. The temperature at the bottom of the cell had risen from 68° F. to 85° F. and at the top of the cell it reached 109° F. Fifteen minutes later the cell was quiescent, the voltage had fallen to .24 and the specific gravity from 1.157 to 1.123,—the lowest point which it had reached 470 ampere hours before. Two or three days later the E. M. F. was zero.

During the progress of the phenomenon and afterwards, the cell was examined carefully with the most minute care for any defect, short-circuit, or other irregularity and it was found to be in perfect order. A further charge of 876 ampere hours or about six times the normal capacity was given at a normal rate. On this charge as well as on the first reversal charge another curious effect was observed—the voltage rose in 15 minutes from zero to 0.18, in one minute more it jumped to 2.63. It then gradually fell to 2.01 in about 7 hours and thereafter gradually rose to 2.48. The discharge was normal to 148 ampere hours and presented a peculiarity of a fully charged cell, that is to say, the E. M. F. fell in two minutes from 2.05 on 30 amperes to 1.935 and then rose in a few minutes more to 1.94 volts, and then gradually fell the usual way.

Here, then, is the story of a complete automatic discharge of positive plates from the beginning of the preceding charge to the end of the following normal discharge. Was it because the peroxide formed only to a certain depth in a spongy lead and so densely as to exclude the electrolytes for a time, so that when the liquid at last penetrated the spongy lead a violent local action ensued? This would account for the heat, and for the fall of potential and of specific gravity, but would it account for the liberation of immense volumes of oxygen? I have frequently noticed the presence of considerable quantities of peroxide of hydrogen in electrolytes. Gladstone and Tribe have also remarked this substance, but intimate that they found it in minute quantities only. In some cases, however, I have observed it in very considerable amounts. Is it possible that this substance was present and exercised its well known property of liberating one atom of oxygen from peroxide of lead, and another atom of its own oxygen at the same time? This would account for all the phenomena, but what accounts for the peroxide of hydrogen in such an enormous amount, and why does it not always discharge oxygen from the peroxide? And finally is it possible that the continuous evolution of oxygen on the positive plate while the cell is idle is sometimes due to the presence of peroxide of hydrogen in minute amounts, and not merely to what has been called local action. I trust some of the gentlemen present will enlighten us on this point.

Perhaps the most striking peculiarity about the modern storage battery is the diversity of opinion among professional electricians,

as to its utility and commercial value. Men of the highest rank as electricians and engineers, are ranged on either side of the question. Men of affairs who have put them to a commercial test exhibit a like divergence of views. Men who have tried the storage battery for a year or two, have written about it in the most flattering terms, and have discarded it later. Men who have used accumulators ever since their introduction when they were much less efficient machines than now, continue to use them, and would under no circumstances be induced to part with them. Unmitigated praise on the one hand, and unmitigated contempt on the other. Broadly stated the European consensus of opinion, both technical and commercial, may be said to be in favor of storage batteries. The American view until now has been mainly the opposite. What is the ground for this wide discrepancy? Why is cautious conservative Europe so far ahead in the race? Why is America a laggard in the running?

The answer is not far to seek. Storage batteries are almost always an economical success abroad, while here they have been too often an economical failure in the past. And the reason is that the Europeans always demand a margin for safety, while the Americans, with less capital and keener competition, are tempted to sail too close to the wind.

A storage battery continually worked to its commercial rating is a commercial failure. A storage battery worked sufficiently within its capacity is invariably a commercial success.

It has been said of Watt that he pursued careful and exhaustive experiments upon the power of horses for all day work, and that he ascertained that the average power which they could maintain for ten hours was 22,000 foot pounds per minute, but in rating his engine he added 50 per cent. and called the horse power 33,000 foot pounds per minute, so as to make his new pumping devices more than satisfactory substitutes for horses. Would that storage battery people had been equally wise.

A battery's discharge should be stopped after its E. M. F. has fallen to 2 volts or at furthest to 1.9, unless it be desirable to draw upon its reserve. It should be understood that a full discharge, that is, to 1.8 volts is working a battery to the danger limit and is unadvisable for the following reasons:

- a. Regulation is troublesome.
- b. Efficiency is low.
- c. Dangerous molecular changes take place (as indicated by

changes of internal resistance and changes of electromotive force as well as occasional buckling.)

- d. Uneven plates discharge into one another after the circuit is interrupted.
- e. The life of the battery is diminished.

The writer has had occasion to watch with the closest scrutiny a considerable number of plants, aggregating perhaps some millions of plates. These batteries were rated like all reputable makes, well within their capacity in ampere hours measured by charging the battery to about 2.65 volts, and then discharging it until the potential difference was 1.8 volts per cell. Some batteries have been spoiled by bad management and neglect, and some by false economy or bad engineering at the very start; by eliminating these, there remain a very large number which were successful or were failures for no apparent reason. The utmost care was exercised at the factory. The constituent materials were analyzed as soon as purchased. Able engineers watched the processes of manufacture, but while the quality of the battery was improved until no flaw, mechanical, electrical or chemical seemed to remain, still an occasional failure occurred in actual practice and the cause eluded our search.

Finally by classifying the failures and successes, the truth dawned upon us. Wherever the battery was exhausted to its full capacity daily, its life did not exceed 500 discharges, but wherever it was worked within two-thirds of its capacity, complaints were unknown.

Exhaustive tests were undertaken and some curious phenomena heretofore unknown to the writer, were disclosed, and after some hesitation he concluded that they might be of interest to this society.

It is natural to ask why the rating should not be changed so that the owner of the battery would not be tempted to work it to the danger limit. It ought to be done, but in these days of close commercial figuring it would be difficult to sell a battery which appeared *ceteris paribus*, to cost 50 per cent. more than its competitors. However, the present rating is strictly accurate and has the sanction of custom the world over. It is only necessary for the engineer to remember to add 50 per cent. of the capacity as a factor of safety to his maximum load, just as he allows several hundred per cent. in calculating the strength of a bridge, or an axle.



This additional amount is not a dead loss in investment. It produces many countervailing advantages. It saves the necessity for regulation in most instances. It provides a very effective and safe reserve for cases where the charging apparatus breaks down and for many other cases, and it improves the actual efficiency of the battery which rises from about 80 per cent. to nearly 90 per cent. when used with a sufficient reserve. And for cases where it is necessary to maintain a constant difference of potential, such as electric lighting, it raises the efficiency much more, because in these cases the commercial efficiency must be rated not from the average point of electromotive force but from the lowest point to which the battery falls on discharge and when used in this way the P. D. drops only  $2\frac{1}{2}$  per cent. All the E. M. F. above the lowest point must be wasted in order to secure regulation, unless the troublesome method of regulating by the introduction of extra cells is adopted.

In circuits where this regulation is of no consequence as *e. g.* motor circuits for cars. all the E. M. F. is utilized in increasing the car miles per unit of energy.

In this connection it is perhaps worth while to call attention to a very common misapprehension on the part of engineers. A storage-battery for trolley systems or other central stations for the production and utilization of electricity has heretofore been regarded in this country as a very expensive addition to the plant. But this is not always the case. There are many opportunities for introducing storage-batteries as a part of the original plant without increasing the cost, as for example in cases where the maximum output is two or three times greater than the average output. In the tables here given I have taken Emery's figures for a basis for the steam plant.

#### 1,000 HORSE-POWER DIRECT SYSTEM.

Cost of steam plant.....	\$70,000 00
Electric plant, 750 kilowatts, at \$30.00 per kilowatt.....	22,500 00
	<hr/>
	\$92,500 00

#### 1,000 HORSE-POWER, STORAGE SYSTEM.

One-half steam plant.....	\$35,000 00
One-half electric plant (375 kilowatts) ...	11,250 00
1,500 kilowatt hours, accumulator capacity, at \$30 per kilowatt hour.....	45,000 00
	<hr/>
	\$91,250 00

Now that batteries are made in large units and in much more compact shape than formerly, with increased facilities for handling, it is to be hoped that the engineers in this country will begin to give the subject of their introduction more attention, especially as a cell having a capacity of twenty-four kilowatt hours occupies a floor space (exclusive of connections) of less than a square yard.

The points I have sought more particularly to lay before you are :

1. That the chemical reactions in a storage battery cell must be complex, in order to account for the curves of E. M. F., temperature, and internal resistance.

2. That the current and the E. M. F. of the component plates of a cell, and of each part of each plate, are constantly fluctuating, in spite of the fact that no source of electricity can compare with a storage battery for steadiness and constancy.

3. That by reducing the normal output of a battery by about thirty or forty per cent. the discharge can be mainly confined to one set of chemical reactions, thus prolonging the life of the battery.

4. That the negative and positive plates are apt to get out of step, therefore the battery should be given an occasional overcharge when necessary, but only when necessary to get them in line again.

It may fairly be said that none of these points are new. Only, instead of being mere opinions, accepted by one set of experts and rejected by others, they seem to me to be logical and inevitable deductions from the phenomena herein disclosed.

I desire to acknowledge the aid I have received in the study of these phenomena from my very competent laboratory assistants, as well as the accurate and fatiguing work, both night and day, kindly undertaken by two of them, Mr. Hugh Lesley aided by Mr. Norman Mellor, in making the measurements and plotting the curves herewith presented for your consideration.

## DISCUSSION.

DR. LOUIS DUNCAN:—In a paper which I had the pleasure of reading before the INSTITUTE some years ago, I described some experiments on some of the points brought out by Mr. Griscom, and I would like to say a few words about them. In the first place, with respect to the local action taking place in the plates, Mr. Weigand and myself made some investigation on this point, and found that the local action between parts of the same plate was very considerable under certain conditions. We found that when the cell had been very heavily discharged, that the chemical condition of different parts of a plug of active material was different, and a local action took place, which tended to make the plug uniform in its constitution, and this accounted for a part of the increased loss of energy when the discharge rate in a battery was high. Again I see that Mr. Griscom states that Professor Ayrton discovered the cooling of a storage cell on its being discharged. Mr. Griscom could not have read Professor Ayrton's paper carefully, or he would have noticed that Professor Ayrton himself attributes this discovery to myself and Mr. Weigand. We tried to explain the cooling effect by the taking of sulphuric acid from the solution, but this did not account for all of the cooling, and there must be some other cause for it. There is a considerable amount of energy given to a cell which is never given back again, but which results in the formation of compounds which are not reversed on discharge.

I see that Mr. Griscom states that the theory held by some people that the decrease of the porosity of the plugs changes the resistance of the cell, is untenable. In the paper by Mr. Weigand and myself to which I have referred, we made some experiments on the porosity of plugs both when completely charged, and when discharged, and we found that they were much more porous when charged. We wanted to find why it is that a high rate of discharge is injurious to the battery, especially if it has been partly discharged, and also why the electromotive force of a cell drops faster when the battery is partly discharged than when it is fully charged. We found that when the discharge rate is rapid, acid is taken from the solution inside of the plug, thus, of course weakening the solution, which only gains acid again by diffusion from the outside. The diffusion decreases greatly as the battery becomes discharged, and when a certain strength of current is taken from it, the acid in the plug becomes greatly impoverished, and a phenomenon occurs which is mentioned by Gladstone and Tribe in their work on the storage battery. They found that when the solution reached a certain dilution the chemical action on the lead plates changed, and a different compound than peroxide of lead was formed, the plate being rapidly corroded. We came to the conclusion then, from our work, that a large part of the fall of electromotive force, and

the deterioration of batteries at high discharge rates was due to the weakening of the acid in the plug, and from our experiments on the rate of diffusion in the plug, we saw that both of these effects would be exaggerated as the battery was discharged, and the rate of diffusion was lowered. As the chemical action when the battery is partly run down takes place on the inside of the plug, the resistance will naturally be increased both by the greater distance from the support plate, and the decreased conductivity of the material through which the current must flow to the support.

There is one thing that seems to be particularly interesting, and that is the fact that plates in the same cell, after the discharge has taken place, will give a current between one another. Although the fact that local action takes place in the plate, has been observed before, yet I do not know of any experiments that have been made on the loss of energy due to currents between plates of the same name in the same cell.

There is another very interesting point in the paper, and that is the wonderful phenomenon of automatic discharge described by Mr. Griscom. I have never seen it take place, and I am very certain I cannot explain it.

MR. GRISCOM:—I would like to correct two misconceptions on the part of Dr. Duncan. I did not say that Ayrton whose unrivalled researches I have not only read but studied, was the first discoverer of the cooling effect of discharge, but that he independently discovered it and published the first curve showing the history of cooling on discharge. Nor did I mean to convey the impression that the clogging action of discharge had no effect whatever on the resistance of the cell, but that it was not the only influence at work. For the resistance varies in some parts of the charge and discharge in exactly the opposite way from that which would result from the clogging theory.

As to the irreversible electrolytic actions remarked by Drs. Duncan and Weigand, I can only say that I have heard of such actions very often since the Faure discoveries were published, but if the word "irreversible" be used in its absolute sense I have failed to find them—at least during the proper and legitimate use of storage batteries.

I entirely concur with Dr. Duncan regarding the importance of the researches made by himself and Dr. Weigand on the varying diffusivity of acid in the paste. Such researches give precision to our thoughts, and make us feel that some of our hypotheses, at least, are builded upon the rock.

[COMMUNICATED AFTER ADJOURNMENT BY MR. TOWNSEND  
WOLCOTT.]

Mr. Griscom's paper is a valuable contribution to the literature of the storage battery. In my opinion it is the best storage battery paper ever read before the INSTITUTE. In the paper Mr. Griscom offers explanations for a number of phenomena before unaccounted for, but he also presents a large number of phenomena for which he asks explanations from the other members. I am afraid that the desired information is not forthcoming. I say this because the theory of the storage battery is full of anomalies such as the following:

Take a strip of ordinary sheet lead which has been exposed to the air and become somewhat tarnished, cut it in two and place the halves in the ordinary battery acid and connect with a low reading voltmeter. In the majority of cases there will be a small E. M. F. shown, due to the minute differences in the oxidation (tarnish) of the two halves of the same strip. Now by carefully scraping the positive piece, the voltmeter may be brought to zero, after which a little more scraping will produce a deflection in the opposite direction.

This sensitiveness would seem to indicate that there was an exceedingly great propensity to local action in the storage battery, and it would also seem that a lead grid filled with peroxide would constitute a short-circuited couple with an E. M. F. of two volts or thereabouts and that when placed in the acid it would completely discharge itself in a short time.

That is not the case, however, as every one knows. In fact, if we take two perfectly clean pieces of lead which give no deflection on the voltmeter, and coat one with peroxide, even on one side the couple will give a considerable voltage, although it may be below two volts. That is to say, there is, apparently at least, no E. M. F. between the peroxide and the lead with which it is in direct contact, while between the peroxide and the lead with which it is connected through the voltmeter there is a very decided E. M. F.

The explanation of this appears to be that there is a strong tendency of the metallic lead and the peroxide to come to the same potential as soon as current begins to flow between them. There is probably a momentary current on immersing a peroxide grid, but it is probably only momentary, even if the grid remains apparently unoxidized. The fact that the voltmeter in the experiment just mentioned remains deflected for some time with two small strips of lead, would seem to show however, that an appreciable quantity of electricity passed before equilibrium is attained.

I am somewhat surprised at the results obtained by Mr. Griscom, in connection with the discharge of one plate into another which was at a low potential. So far as my experience goes, it

is rather contradictory to this. I have frequently seen an attempt made to divide the charge between two equal sets of cells, one of which was fully charged, and the other pretty well discharged. The result was always unsatisfactory. The tendency of the E. M. F. of a discharged cell to rise quickly above two volts as soon as recharge begins, would soon reduce the current to a trifling amount, so that the charges would not be even approximately equalized in any reasonable time.

The presence of peroxide of hydrogen in some cells but not in others, is another of the unexplained phenomena which are so frequently met in storage battery work. It may be possible or even easy to construct hypotheses to account for such irregularities, but what is wanted is demonstration and not speculation.

[REPLY TO MR. TOWNSEND WOLCOTT'S COMMUNICATION BY THE  
AUTHOR.]

Is Mr. Wolcott confident that the experiment which he details proves the existence of E. M. F. due to differences of oxidation? Is it not possible that it is due to occlusion of gases? I have found considerable differences of potential between two plates of chemically clean platinum, one of which had been exposed to the air, after being heated red hot, rather longer than the other.

If two pieces of platinum about one inch square be chemically cleaned, heated red hot and immersed in dilute sulphuric acid, they may be brought to the same potential by a little manipulation. If then one of them be removed again, cleaned, heated red hot and allowed to cool for a few minutes and then immersed in the electrolyte it will at the moment of immersion show a powerful deflection equal to over a milli-ampere. If, now, the same plate be taken out of the electrolyte again, cleaned, heated red hot and plunged while red hot in the electrolyte a very curious phenomenon will be noticed—the first deflection will be negative and immediately afterward the current will reverse and the platinum will resume its positive polarity.

It is hardly credible that the potentials are due to oxidations of the platinum. I am rather inclined to think that it occludes oxygen from the air and possibly it occludes an extremely minute portion of hydrogen when immersed red hot in the solution. It might, perhaps, be worth while for chemists to remember that platinum always absorbs oxygen from the air after being heated red hot and really to an appreciable extent—enough in fact to produce several milli-ampere seconds per square inch under the above circumstances. I have not given careful examination to the behavior of lead under these circumstances, but I must confess that I have not found so great deflections while using lead as I obtained with platinum.

I do not think that there is as much local action in a storage battery as has generally been supposed, if by local action is

meant an electrolytic effect due to the paste and grid. That local action must ensue with plain lead, coated with peroxide of lead when immersed in sulphuric acid is of course unquestionable, but the amount of action is limited to the oxidation of the metallic lead surface and that oxidation prevents further action to such an extent that positive plates which have been in use for eight years are not oxidized to a greater depth than  $\frac{1}{100}$  of an inch, provided the lead was of good quality and not full of minute holes. My own impression is that the loss of energy in a storage battery is due to a different kind of local action, to wit: that which is caused by the actual differences of potential of different parts of the paste and acid. This difference of potential may be due to different densities of acid in the pores of the active material, or it may be due to different degrees of oxidation of the active material, or it may be due to both factors combined.

[COMMUNICATED AFTER ADJOURNMENT BY SIR DAVID SOLOMONS,  
OF LONDON.]

I have been favored with an advance copy of Mr. Griscom's interesting paper, in which he does me the honor of referring to me in regard to one or two matters. I will, therefore, confine myself to saying a few words on my experience since the time alluded to in the paper.

It is quite true that the glass cells are very apt to crack in the sunlight. At first I thought this must be due to some chemical action upon the glass, but such, it would now appear, is not the case, for empty glass cells crack in the same way. Therefore, I conclude that the cause must be the unequal expansion of the glass, for I was unable to make pots, which had been very carefully annealed, crack in the manner described.

There can be no doubt that the positive plates in a section discharge themselves, if left at rest. There appears to be conclusive evidence upon this point. There are two causes for this: First, by the slight leakage which exists in every installation; and, secondly, a leakage in the cell itself apart from any local action which may take place, in consequence of the materials employed in building up a section, and this circumstance cannot be avoided, for all substances conduct in a greater or less degree. With due care and by the addition of caustic soda or sulphate of soda, I have been able to reduce the slow discharge in a very great degree. In all cases, where the battery is likely to be left at rest for considerable periods, great attention should be given to the materials employed for building up the section. Although this seems to be a common-sense proceeding, it is one often neglected.

[COMMUNICATED AFTER ADJOURNMENT BY MR. FREDERICK RECKENZAUN.]

While I had just missed the presentation of Mr. Griscom's interesting paper, on arriving at the Philadelphia meeting, I have since carefully perused its contents. Besides various striking points and suggestions, I note some features therein which appear to warrant discussion. First in their order are the curves and data giving observations on the P. D. of the positive and the negative plates, wherein the individual plates of another cell, which the author terms "test cell," as distinguished from the cell under test, have been used as the basis of measurement. Why Mr. Griscom should have adopted two separate standards, one for each plate under test, is not convincingly explained, but it is apparent, that this selection was not a fortunate one. Owing to the inconstancy of the standard cell (test cell) itself, as shown by its E. M. F. curve, the P. D. curves obtained for the separate plates actually represent the resultant values of two unknown and varying factors and not, as they purport, the specific potential variations of the plates under test. Nor could the latter be definitely deduced by allowing for the deviation, from a straight line, of the E. M. F. curve of the "test cell," because there is no evidence that the individual plate potentials of the latter varied alike. Such being the case, the characteristics obtained, necessarily become somewhat problematical.

In reference to the "continuation" discharge, (Faure cell) to which Mr. Griscom attaches special significance, it may be noted that the negative curve is decidedly odd, and the context rather remarkable for its omissions. The negative P. D. curve preceding the "continuation" discharge, if the compensation above referred to were made, would undoubtedly be nearer the horizontal than shown, and would be far from indicating a sudden, abrupt break to one volt, within the first five minutes of the continuation, and to almost zero in five minutes more; indeed, even taking the curve as it is, which represents the *sum* of the potential losses of both the standard and the plate under test, it forms an angle with the "continuation" curve which it would be idle to anticipate in an uninterrupted continuation of the discharge, and still more so in an interrupted one, as was the case, unless some very untoward accident or interference befell the plate. We are told that for the continuation test, the plates were separated and each opposed to freshly charged plates in fresh electrolyte. We are not told the specific gravity and temperature of the fresh electrolyte, which factors influence to some extent the E. M. F.; we are not told why fresh electrolyte has been used instead of the old one or one like it; nor are we told the period of rest that intervened. However, that their combined effect was considerable, and favorable to the positive plate, is shown by the curve for that plate, in view of which the negative continuation curve

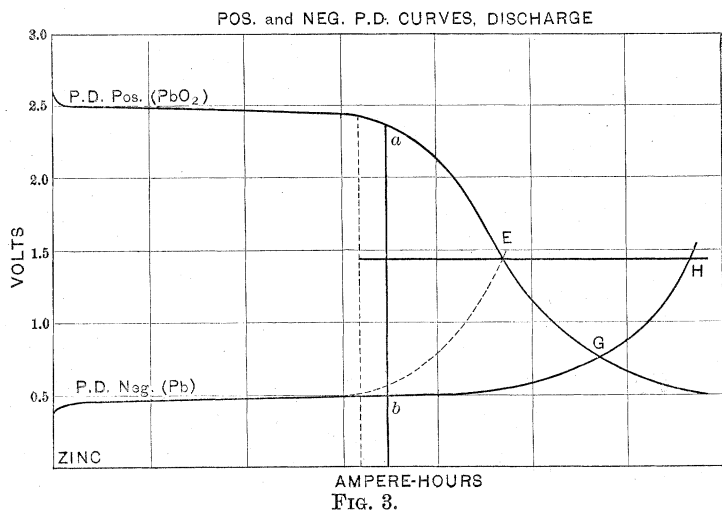


appears utterly incredible. Such a state of the negative, one might expect if it had been allowed to discharge, as by a short-circuit, or exposure to air, (followed by a momentary recuperation in the electrolyte) during the intermission. It may also be observed, by the way, that the "enlarged" continuation curves do not coincide with the smaller ones.

The charge curve (Faure cell) cannot lay claim to being illustrative of normal conditions, owing to the abnormal discharge (continuation) immediately preceding the charge, and which, of course, must have left its impress upon the plates, producing a corresponding influence upon the observations following. The electrolyte, too, differs here again, rising above its original specific gravity owing to the acid absorbed from the "fresh" electrolyte in which the discharge "continuation" had been effected. In fact, this gain in the electrolyte invites a comparison with the output of the continuation discharge. It should be approximately proportionate thereto, but it is not. Allowing equal formation of  $PbSO_4$  for positive and negative plates per ampere-hour of discharge, the amount of acid absorbed corresponds to one half of  $11 + 108$  ampere-hours (the respective extra discharge credited to the positive and negative plates) namely, 59.5 ampere-hours. The gain shown by the specific gravity curve, however, corresponds to 87 ampere-hours if the acid temperature had remained constant, but, as the temperature rose during the charge (temperature readings are omitted, only a rise of  $8^\circ$  F. for a certain period being quoted), and even if this had been all the rise occurring between the beginning of the discharge and the end of the charge, the gain in specific gravity would be equivalent to over 100 ampere-hours. The assumption that this difference between 59.5 and over 100 ampere-hours is due to a greater ratio of  $PbSO_4$  formation during the accounted-for extra discharge is not admissible, and the shape of the specific gravity curve of the discharge, as far as it goes, (for the extra discharge no specific gravity curve is given) would not in the least support it. Nor would it seem reasonable to suppose that the "fresh" electrolyte was so excessively strong that the portion of it that may have been conveyed by the plates made such a difference. So that this reminds again of the queer behavior credited to the negative plate on the continuation discharge. Altogether the curve tables seem but an imperfect basis for the conclusions built thereon in the context.

In regard to standards for taking the individual plate p. d's., it would seem beyond question that the use of a *single* standard, which is either electro-positive or electro-negative to *both* plates under test, would yield curves that bear a definite relation to each other, irrespective of any possible changes in its own potential. It would also facilitate the checking-off of observations, in-as-far as the distances between the two (p. d. positive and p. d. negative) curves obtained must correspond to the

independently measureable values of P. D. of the cell; and similarly with the respective E. M. F. values. Dr. Streintz, of Graz, Austria, in his extensive storage battery investigations (*Zeitschrift fuer Elektrotechnik*, Vienna, Vols. IX and XI.), has used zinc as a standard in observing the potentials of individual plates during discharge, and his results indicate that under proper conditions that metal is very satisfactory. This being the case, it is manifest that it will also lend itself to a variety of other lines of observations upon lead accumulators, including relative capacity tests of individual plates,—even to observations upon a complete reversal and its concomitant characteristics,—yet leaving a fair working margin between itself and the plates throughout all phases. And what is of no small advantage, the zinc standard affords a striking graphical illustration of the characteristics observed.



In testing the relative capacity of the plates, it is only necessary to discharge the cell in series with a larger cell (or two in an extreme case), in order to assist in overcoming the external resistance (wires, connections, ammeter, etc.) when nearing zero P. D. of the cell, as in the case of an ordinary zero test under a constant current, and beyond that point when the weaker plate or section, owing to its sluggish action, sets up a counter P. D. in the cell. The entire test can be made *without* removing the plates or electrolyte, or in any way interrupting the discharge or interfering with the proper conditions of continuation, and, consequently, without mutilation of the curves which are to tell the tale of the characteristics sought.

The accompanying Fig. 3 furnishes an example of the general shape of curves obtained by this method to and beyond the point

of the cell P. D. zero. The upper curve indicates the P. D. values of the positive plate ( $Zn-PbO_2$ ) and the lower curve those of the negative ( $Zn-Pb$ ), zinc being the zero or base line common to both. The two curves approach each other as the discharge proceeds, finally cross (as at G,) and deviate, if the discharge is forced toward reversal. Now, if a practical working limit of cell P. D. is prescribed or chosen (which should be well inside of the steep curvature of the weaker plate,) let special note be taken of the  $Zn-PbO_2$  value  $a$ , and the  $Zn-Pb$  value  $b$ , on *passing* that limit, because here really begins the comparison of the relative plate capacities. Then, if the positive and negative plates have the same capacity, zero cell P. D. (crossing of curves) will occur at a point (E) corresponding to  $(a + b) : 2$ , whereas, if either plate has an excess of capacity, the intersection will occur above or below that point; in the example given, the cell zero P. D. occurs at G. Thence the discharge is forced along until the P. D. of the stronger plate reaches the value  $(a + b) : 2$ , indicated by the letter H. *The difference between the relative capacities is expressed by the linear dimension E—H.* Upon reducing the capacity of the stronger plate accordingly, the new curve would more or less alter its shape at the assumed cell P. D. limit, and the latter for the same value would come somewhat further inside, as suggested by the dotted lines. The curves (for charge, discharge and complete reversal) obtained by this method will prove instructive in various ways, and their differences may suggest further investigation into structural and other features.

The drop in temperature of a discharging cell, alluded to by Mr. Griscom, is a result dependent upon very low internal resistance and moderate current. Under opposite conditions the opposite result, namely, a rise in temperature, will occur. Mr. Griscom's explanation of the cooling effect may help to explain the heating effect also. There are two opposing functions in discharging a storage battery, which do not bear a fixed relation to each other; the chemical (or cooling) effect being *proportional* to the current (as is also the absorption of sulphuric acid, referred to by Mr. Griscom), whereas the heating effect varies as  $C^2 R$ . Thus, while the cooling effect may predominate under favorable conditions, upon increasing  $C$ , a point will be reached where the two factors balance and beyond which heat will ensue. This balance point, of course varies with different types and sizes of storage batteries. In Prof. Ayrton's temperature tests, alluded to by Mr. Griscom, the cell temperature, though remaining above that of the surrounding air, fell slightly below that of an idle cell, wherein the heating was due to some local action (possibly the same two functions, with their relative magnitude reversed. Dr. Duncan and Mr. Weigand<sup>1</sup> mention

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1. TRANSACTIONS vol. vi., p. 217.

having observed a temperature reduction in some cases, and a rise in a number of others, the data on which indicate favorable conditions in the latter direction. My own observations were also of both kinds, and numerous; especially have I noted a marked rise when discharging at such an excessive rate as to produce lively gassing at the plates, which was accompanied by a marked increase in the internal resistance. Again, in cases where a number of cells were confined within a close space affording little or no ventilation, (as in an electric launch, etc.,) even a slight initial rise would have a cumulative effect, to a noticeable extent. These observations were made on cells in good condition.

On page 312 the author refers to "a very curious misapprehension" prevailing "among some battery people" to the effect that the negative plate exceeded the capacity of the positive, and then proceeds to prove the contrary by reference to tests, the shortcomings of which have been pointed out above. As a matter of fact both conclusions are unwarrantably broad. In view of the diverse types that are on the market, it must be observed that the relative capacity of the plates is as the manufacturer chooses to make it. It depends upon structural features, upon the relative size and thickness of the plates, the relative proportion of "active material" contained therein and the quality, condition and distribution of the latter, each of which factors, if varied itself, will produce different results. In some accumulators the positive and negative plates are made exactly alike up to the point of final "formation," and in most of these, when in good working order, the negative plates have a considerable excess in capacity, owing, no doubt, to the spongy lead being capable of more thoroughly undergoing the chemical change than the peroxide. Dr. Frankland (Royal Society, 1890) remarked that "only half as much material seems to be necessary for the negatives as for the positive plates." Messrs. Gladstone and Tribe made similar observations. Prof. Ayrton<sup>1</sup> suggests an explanation why in the E. P. S. (pasted grid) type "it is necessary to employ nearly twice as much lead peroxide as is actually needed for the chemical action." Some manufacturers have as much as ten years ago recognized the difference and accordingly made the positive plates thicker than the negatives, and, although Mr. Griscom doubts the propriety of so doing, his company also follows that practice. I have myself made careful tests of the comparative capacities of plates and materials, extending over some years, and found a considerable difference in the oxides of different makers, their capacities ranging (with grid plates  $\frac{1}{4}$  inch thick), under like conditions, from 1.4 to 2.5 ampere-hours per ounce of red lead in positive plates, and (with similar grids) from 2.75 to 3.25 ampere-hours per ounce of litharge contained in

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1. *Inst. Elec. Eng.*, London, 1890.

negative plates, in all these cases putting double their amount of active material opposite them, to ensure maximum output of the samples with the usual working p. d. limit, at a uniform current. Among a variety of tests to determine the relative capacity of plates working together, I have made a series of experiments calculated to yield the most direct results for practical purposes, as follows: I prepared 3 cells, each containing 4 negatives and 3 positives; size  $7\frac{3}{4} \times 9\frac{3}{4}$  inches; thickness, all positives  $\frac{1}{4}$  inch; negatives, in one cell  $\frac{1}{4}$  inch, second cell  $\frac{3}{16}$  inch, third cell  $\frac{1}{8}$  inch;  $\frac{1}{4}$  inch grids being planed down to the respective thicknesses for the second and third cell. The oxides used were of the best quality available (the litharge being specially manufactured for storage battery purposes.) The cells were worked daily for several weeks, under normal conditions, and the net results, briefly stated, were, that the cell in which the negatives were reduced to one half their thickness and the amount of litharge therein to 38 per cent. of that contained in the  $\frac{1}{4}$  inch negatives, yielded an output only 16 per cent. less than cell 1. (The reason for only 38 per cent. and not 50 per cent. of litharge being in the  $\frac{1}{8}$  inch plates was in the perforations being tapered.) The object of this experiment was to find how thin a negative would answer for a given positive with the materials used, without undue sacrifice in the capacity of the cell, and the results obtained approximately correspond with theoretical deductions. Generally speaking, the results do not vary exactly with thickness, volume and weight, but many other minor points, as above indicated, necessarily contribute in determining them; the subject is too intricate to be broadly covered by either Mr. Griscom's implied conclusions or the one he undertook to refute.

I concur with Mr. Griscom in his views on the success of storage batteries in Europe, and their lack of success in this country. Other points of comparison suggest themselves, among which are the generally greater day load of central stations in this country, due largely to a more general use of motors, which tends to make the use of storage batteries a somewhat less pressing object, and further, the entire absence, until recently, of large, substantial and durable types of cells suited for central station purposes. While in Europe central station types have been given the utmost attention by manufacturers, with corresponding success, American storage battery manufacturers, on the other hand, have largely endeavored to cope with that alluring subject: storage battery traction—unfortunately with but little success—and neglected to cater to the central station field with types especially adapted to that class of work.

[REPLY TO MR. FREDERICK RECKENZAUN, BY THE AUTHOR.]

Some of the points made by Mr. Reckenzaun show that my paper requires a little further elucidation:—

First. Mr. Reckenzaun says that the text is rather remarkable for its omissions with respect to the curves. I did not pretend

to give a complete analysis of the curves, which, by the way, are perfectly normal, but only to use some features of them to illustrate my paper.

Second. He states that I adopted two separate standards, one for each plate under test, and states that owing to the inconstancy of the standard cell, (test cell), the P. D. curves for the separate plates actually represent the resultant values of two unknown and varying factors.

Now this appears to me to show a little tendency—

“ \* \* \* \* \* to divide  
“ A hair 'twixt north and north-west side.”

The total discharge of the “test cell” during the 300 or 400 readings represented by the curve did not exceed  $\frac{1}{2000}$  part of its capacity. Therefore, there was no change appreciable to my instruments in the E. M. F. due to the amount of discharge. Similarly, the current was about  $\frac{1}{500}$  of the ordinary discharge rate of the plate, consequently there was no appreciable modification in the readings due to the discharge rate. The total variation of the “test cell” in discharge is, as shown by the curve, about  $\frac{1}{70}$  of the total variation of the cell under test, say .03 volt, of which about .01 volt was due to the negative and .02 volt to the positive. And this variation, which Mr. Reckenzaun is pleased to call “inconstancy,” is due entirely to the specific gravity and temperature of the electrolyte. The advantage of using this plan is evident. Inasmuch as the temperature and density of the electrolyte affect the “test cell” and the cell under test equally, and inasmuch as the “test cell” and the cell under test are of the same nature, this plan enables us to eliminate the effect of the change of temperature and of average density from those curious changes going on in the plates which it was my endeavor to lay before the INSTITUTE.

Third. Later on in Mr. Reckenzaun's communication he appears to recommend the use of a single standard and refers to the investigations of Dr. Streintz, of Gratz, Austria, who used zinc. I have also used zinc in past years, but abandoned it on account of its solubility in the electrolyte, its tendency to deposit during charge on the negative plate and the false effects due thereto and for other reasons. It is true that by using separate cells and by taking precautions to prevent the intermingling of the electrolytes, it is not impossible to obtain important results with the use of a single standard, but unfortunately it is necessary to make an exhaustive and complete research into the various behaviors of the single standard in the presence of a varying electrolyte and a varying storage-battery plate, before it is possible to be sure that curves with any single standard represent anything but the misleading resultants of unknown and varying factors.

On the other hand, by using for the test cell, well-charged storage-battery plates, which have been allowed to stand until

they have reached a stationary E. M. F. you obtain fixed and invariable and scientific results because you obtain the loss of potential which is due purely and simply to the plate under test. It is as though you measured the difference of potential due to the changes in that one plate while the opposing plate had undergone no change from the beginning.

The use of single standards will not do this. They give simply a comparison which is not only uncertain in its nature, as explained above, but which has no relation to the real use of storage batteries.

Fourth. It does not appear whether Mr. Reckenzaun or Dr. Streintz is responsible for the method which he advises for testing the relative capacities of the plates of a storage-battery. The idea of forcing a current for this purpose through a battery which has ceased to be active whether through the exhaustion of one or both of the plates, is, to say the least, open to criticism. If the negative plate, for instance, becomes exhausted first, as usually happens, forcing a charge through it means charging it in the reverse direction so that you have the anomaly of a negative plate charged, or still worse, partially charged as a positive opposed to a positive in the same cell. The experiment, of course, is interesting; in fact, I have no doubt that this very thing frequently occurred in former practice, in the dark ages of storage-batteries, when cells frequently got exhausted by short-circuits and buckling, were straightened and cleaned again, and put in service only half charged. Buckling and short-circuiting are happily things of the past, but Mr. Reckenzaun's method would yield an interesting study of the behavior of a battery when treated in the best manner to ensure its destruction.

Fifth. Mr. Reckenzaun says in reference to the continuation of the discharge of a Faure cell, that, "if the compensation above referred to were made," the curve would undoubtedly be nearer the horizontal than shown. I think there is no reason for this conclusion of Mr. Reckenzaun. The continuation of the discharge was made with fresh plates of the *L* type, the capacity of which was many times in excess of the remaining capacity of the cells under tests,—so much so, in fact, that there was no appreciable falling off in potential on the part of the larger plates, and the curve of the test cell was therefore omitted as superfluous.

Sixth. The fall of temperature on discharge is a difficult thing to explain. Unfortunately for Mr. Reckenzaun's explanation, the cell will sometimes indicate a rise of temperature and sometimes a fall under what appear to be, externally, at least, exactly the same conditions. I am not inclined to believe that such an eminent scientist as Professor Ayrton could have made an error due to local action in an idle cell, as Mr. Reckenzaun insinuates. And in this connection, as against his theory that there is a marked rise of temperature whenever there is "a marked in-

crease in the internal resistance," I will remind him of the tests which were made under his supervision in our Newark laboratory in 1887. In one of these tests, the cell was discharged at the rate of 40 amperes to 1.8 volts. The records show that the temperature of the cell fell .9° F., and at the time when the cell reached 1.8 volts, its temperature was actually .4° below that of the air, and yet, as everyone knows, the internal resistance of the cell under those circumstances was at least double its average internal resistance, and the current remained constant at 40 amperes. This seems to be in direct contradiction of Mr. Reckenzaun's theory.

To be sure, such a test, crudely made in a factory laboratory, has not the weight of a test made by Professor Ayrton, assisted by competent electricians and checked by all the skill and resources of a trained scientist for the express purpose of instructing the scientific world. But when the test conforms to Professor Ayrton's results, it seems entitled to at least as much weight as some other crude tests which differ from these results.

In Professor Ayrton's experiment he found that the heat produced by  $C^2 R$  amounted to 3,456 calories, whereas the heat loss due to the cell cooling down amounted in some cases to 12,000 calories—three or four times as much. Furthermore, the heating due to  $C^2 R$  in a given cell does not vary directly as the square of the current, because, the internal resistance diminishes as the current increases, and what is still more curious, the E. M. F. itself appears to increase.

Mr. Reckenzaun talks of experiments in which an excessive discharge rate increases the r. r. He must have been using cells of extremely faulty design, or else he must have made his measurements after the cell had exceeded its proper working capacity for the discharge rate, or else he based his statement on guesswork instead of experiment. I have never known of such a case.

Seventh. Mr. Reckenzaun devotes some space to what he calls the "queer behavior" of the negative plate in the continuation of the discharge of the Faure curve and proves that it is "queer" by an argument based upon certain apparent behaviors of the electrolytes as shown by the curves. The facts are not as Mr. Reckenzaun assumes. The relative proportions of electrolyte were not the same in the charge and discharge, and there is consequently no relation between the actual measurements of the specific gravities in charge and discharge. The specific gravity curves are absolutely independent of one another, and if used for purposes outside of my paper should be studied independently.

The "queer behavior" which so impressed him, is what always takes place in the complete discharge of a negative plate of good construction and the fact that some electricians did not know of this "queer behavior" was perhaps a sufficient reason for me to



mention it. The fact is only "utterly incredible" to those who are too credulous of outworn theories, and who will not venture to subject them to actual test.

His explanations, that there might have been short-circuits, or unsuitable electrolyte, or undue exposure of the negative to air, display a singular idea of scientific tests. It may be proper to inform him that such infinite precautions hedge about laboratory work of this nature that none of these things could occur. Moreover, the negative, even if exposed to air, does not lose any capacity whatever until it begins to heat; and after it has heated, it does not recuperate to two volts, or more, but behaves like an entirely different material with a much lower electromotive force. I think all the voltage readings are correct within two-tenths of one per cent.; any possible errors in any of the curves are in one direction, so that what I particularly desired to set forth, to wit, the relation between the curves, is accurately shown.

Eighth. Mr. Reckenzaun takes it very hard that I should have said that a very curious misapprehension prevailed among some battery people to the effect that the negative plate exceeded the capacity of the positive, and he then points out alleged shortcomings of the curve upon which he appears to think I based my statement. Of course, I did not rely on any one experiment, but upon many hundreds of tests. If Mr. Reckenzaun wants to attack them by repeating the tests under the same conditions, I shall, of course, have no objection; but I must protest against having my curves demolished by faulty dialectics based on errors of fact.

I am surprised that Mr. Reckenzaun should not have known that the negative plate in all usual and commercial storage-batteries of good design has less capacity than the positive, and that the curve at the end of discharge for both plates is for a considerable space a nearly vertical line,—the loss of a volt in five or ten minutes being of usual occurrence. His method of testing the relative capacities of the plates is roundabout and the results have evidently misled him. The simplest ways are the best. My usual method is to place one plate between two others of several times its capacity and discharge it to exhaustion. In this way its curve is purely its own curve, practically unaffected by anything but the electrolyte, and the insignificant loss of potential of the larger plates. Care is taken to maintain the electrolyte at the proper density. A similar curve is made of the other plate and any changes of proportions which may be desirable are calculated from the curves.

Ninth. The citation which Mr. Reckenzaun attributes to Dr. Frankland in support of what appears to be his theory, to wit: "only half as much material seems to be necessary for the negative as for the positive plate," was made by an anonymous writer in the *Electrical Review*, of London, of August 22d, 1890, in an article referring to Dr. Frankland and not by Dr.

Frankland himself. It would not be astonishing, however, if Dr. Frankland had assumed this to be true, as did many other scientific gentlemen at that time; but experiments of Crompton, Anthony Reckenzaun, Drake and Gorham, which I have confirmed myself, show that it is not true. The original idea obtained currency, I believe, because in the original formation of a battery it took twice as much energy to form a given weight of negative element as it did of positive element, and it was then supposed that on discharge after formation, the chemical processes were reversed; but such is not the fact.

Tenth. His reference to the *Journal of the Institution of Electrical Engineers*, 1890-1891, containing Professor Ayrton's papers, is fortunate, for it contains a refutation of the very theories which he is endeavoring to support by it. In the discussion following one of Professor Ayrton's papers, Mr. Reckenzaun's brother gave a clear and logical explanation of the causes which made it difficult, if not impossible, to furnish a durable negative plate with more capacity than the positive, and told why the positive plate in the E. P. S. form of battery always showed after the cell was discharged, the presence of a large amount of lead peroxide. The reason he gives for the latter effect is that the negative plates become exhausted too soon, in other words had too little capacity, and so left the positive plates only partially exhausted and consequently with a large excess of peroxide. This explanation, I think, is at least partially true, inasmuch as the negative plate in the principal batteries of the world, when new and in good condition always becomes exhausted first.

I ought, perhaps, to add that I referred to commercial batteries of usual types and in good condition, and not to the abnormal types which occasionally make their appearance in the market with excessively large pellets of active material, the centers of which gradually grow inactive.

In this connection, I am sorry that Mr. Reckenzaun was not more specific in alleging an error in the "enlarged" continuation curves. I fail to find it. Both curves were made directly from the notes of the tests.

Eleventh. The experiments which Mr. Reckenzaun performed for us and which he relates in his paper, viz: the ones where he reduced the thickness of the negative plates and obtained 84 per cent. output with 38 per cent. of negative active material, are also explained by Mr. Reckenzaun's brother in the discussion before the Institution of Electrical Engineers three or four years ago; in a word, a greater proportion of the spongy lead was active in the thin plate than in the thick plate.

Twelfth. Mr. Reckenzaun's curve, which he says has the "general shape of curves obtained by" his "method," reached me after writing the above. I am at a loss to tell from his cautious language, whether the curve was purely hypothetical, or whether it was the result of the actual measurements of a round-

about method. In either case, it suits his argument in appearance, and is an admirable proof of the danger of using any but direct methods of ascertaining scientific facts. There is only one safe way of ascertaining the relative capacities of positive and negative plates and that is by measuring them independently. Any other way until checked by a direct method may involve misleading and unknown factors.

Mr. Reckenzaun's curve, (with zinc standard), shows an easy slope for one-fifth of the total discharge to zero on the part of the negative, and for one-third on the part of the positive. Such a thing never occurred in a normal storage battery discharge. During the latter part of complete discharge, the E. M. F. of each plate is always on a mad rush to perdition—measured not in hours, but minutes or seconds. His curve is not representative of the behavior of a well designed cell in normal discharge, nor even of the worst commercial cell which has ever come under my notice. Nevertheless, the curve is of a novel nature, and if not purely hypothetical may open the field in curious and unexplored directions.

I do not recall at present any other point of importance in my paper which Mr. Reckenzaun has attacked. I would like to add, however, that such frank, direct and pointed criticism as he has made, is always useful as tending to give precision to our ideas. Eventually, of course, the truth on whichever side it may be, will prevail.