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THE
CHEMISTRY OF THE SECONDARY BATTERIES
OF PLANTÉ AND FAURE.



NATURE SERIES.

THE CHEMISTRY
OF THE 5-5-5-62
SECONDARY BATTERIES
OF
PLANTÉ AND FAURE.

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INTRODUCTION.

EIGHTY years ago Ritter constructed a secondary pile, and obtained from it a reversed current of short duration. Since that time many eminent scientific men have investigated the subject of voltaic polarisation, but it was the invention of the powerful cells of Planté, and the perception of how valuable an addition to the resources of electrical engineers a good secondary battery would be, that raised the subject to one of practical importance.

In the autumn of 1881, when many scientific men of ability were investigating the physical questions connected with the battery of Planté,

or the modifications of it introduced by Faure and others, the chemical questions remained un-attacked; while at the same time various difficulties arose in regard to its introduction into general use. It seemed to us, however, that a knowledge of the chemical reactions lay at the very foundation of the whole subject, and afforded the best hope of resolving some of these practical difficulties. Our former experience on copper-zinc and other couples enabled us to perceive that in the coating of lead peroxide in contact with metallic lead, and surrounded by dilute sulphuric acid, we had the elements of a very powerful local action. Our observations on this point, and on the formation of sulphate of lead, the existence of which seems not to have been recognised previously, were published in *Nature* on January 5th, 1882. That communication was followed by four others on March 16th, July 13th, October 19th, 1882, and April 19th, 1883, respectively. These are reprinted in the

present volume with such slight verbal changes as seemed necessary, and the addition of a few notes in further explanation of the experiments.

It may not be entirely out of place to refer to a popular misapprehension as to the nature of these batteries. It is somewhat unfortunate that they have been called "accumulators" or "storage batteries." There is a sense, no doubt, in which these names are applicable, but they seem to have conveyed the idea to some minds that any quantity of electric energy might be stored up in the leaden elements; whereas it is limited by the amount of chemical work which can be done on one or both plates. The name "secondary" also seems to have exaggerated in popular apprehension the difference between these and other voltaic arrangements. They are *secondary* in so far as they have been made by means of another voltaic arrangement or electric current; but when they are "formed" or "charged" they act in precisely the same manner as any other voltaic

battery; that is to say, their action is entirely conditioned by the chemical change that takes place between the binary liquid and one or both of the solid elements when these are brought into contact. When these chemical changes have come to an end the arrangement is no longer a battery, although it is capable of being made one again by an electrical current.

In looking over the very elaborate work of M. Gaston Planté, *Recherches sur l'Electricité*, we have been struck by the careful and minute observations of that philosopher. While he has not attempted to explain the chemical problems presented by his battery, he has noticed "the formation of a local couple between the oxidated surface and the subjacent metal." He has also observed that a gas is sometimes given off after the breaking of the primary current, or at first closing of the secondary current. He also remarked the fact, which is at first a very puzzling one, that "a secondary couple once discharged may yield

after a certain time, without being re-charged, residual charges analogous to those given by Leyden jars." He also remarked that when a secondary couple is discharged immediately after its removal from the primary circuit, there is observed, during the first few moments, a much higher electromotive force than that which is recognised as the normal force of the couple, and which he attributes to the existence of such products as peroxide of hydrogen. We believe that our inquiries have thrown light upon the nature of all these observations of Planté.

In conclusion we wish it to be borne in mind that our joint work has been of a purely scientific character, though we have not hesitated now and then to draw some conclusions that might bear on the best way of preparing or utilising a secondary battery.

THE
CHEMISTRY OF THE SECONDARY BATTERIES
OF PLANTÉ AND FAURE.

PART I.

LOCAL ACTION.

AMONG the important discoveries of late years few have claimed so much attention, or have been so full of promise for practical use, as the accumulator of Planté and its modifications. Our attention was very naturally directed to the chemical changes that take place in these batteries, especially as it appeared to us that there must be certain analogies between them and some actions which we had previously investigated. We propose in the first place to treat merely of local action.

It is well known that metallic zinc will not decompose water, even at 100° C., but we had found that zinc, on which copper had been deposited in a spongy condition, was capable of splitting up the molecule even at the ordinary temperature, oxide of zinc being formed and hydrogen liberated. If placed in dilute sulphuric acid, it started a very violent chemical action, sulphate of zinc and hydrogen gas being the result. We termed the two metals thus conjoined, the *copper-zinc couple*, and this agent was fruitful in our hands in bringing about other chemical changes which neither metal singly could effect. Electricians will readily understand the nature of this agent, and will recognise in its effects only an exaggerated form of what we are all familiar with under the name of *local action*. Now the negative plate of a Planté secondary battery is a sheet of lead, upon which finely-divided peroxide of lead is distributed. It is well known that the electromotive force of lead and lead peroxide in dilute sulphuric acid is nearly three times that of zinc and copper in

the same liquid. We were therefore induced to think that the plate must act in the same way as our copper-zinc couple. We found such to be the case. If a plate so prepared be immersed in pure water, the decomposition of the liquid manifests itself by the reduction of the puce-coloured peroxide to the yellow monoxide. There could be little doubt, therefore, that the lead peroxide couple, if we may call it so, would decompose sulphuric acid, with the production of sulphate of lead. This also was found to be the case.

As the destruction of peroxide of lead means so much diminution of the amount of electric energy, it became interesting to obtain some definite knowledge as to the rapidity or extent of this action.

When the peroxide of lead on the metal is very small in quantity, its transformation into the white sulphate goes on perceptibly to the eye, but when the coating is thicker, the time required is, as might be expected, too long for this kind of observation. In one experiment,

following the procedure of Planté, we formed the peroxide on the plate by a series of seventeen charges and discharges, or reversals, each operation lasting twenty minutes, and the time was further broken up by seven periods of repose, averaging about twenty-four hours in length. After the last charge we watched the local action taking place, and found that the whole of the peroxide passed into white sulphate within seventeen hours. In another experiment the two plates formed according to Planté's method were immediately joined up with the galvanometer, and the deflection noted. They were then at once disconnected. After the repose of one hour they were joined up again, and another observation taken with the galvanometer. This was repeated several times, with the following percentage results :—

Initial strength of current	100
After 1 hour's repose...	97
„ 2 „	40
„ 4 „	14
„ 17 „	1.5

It results from this that during each of the

long periods of repose recommended by Planté the peroxide on the lead plate is wholly, or almost wholly, destroyed by local action, with the formation of a proportionate amount of sulphate. But this is not, as it would seem at first sight, a useless procedure; for in the next stage, when the current is reversed, the sulphate is reduced by electrolytic hydrogen, and, by a process which we explain when discussing the complete history of the reaction, the amount of finely-divided lead capable of being peroxidised is increased. That this is actually the case is shown by the following experiment. The peroxide formed on a lead plate by first charging was determined¹ and called unity; it was allowed to remain in a state of repose for eighteen hours, then exposed to the reverse current till completely reduced,

¹ This determination could not, of course, be made by direct analysis without destroying the plate; but was made from the amount of oxygen which was actually fixed by the lead. This was arrived at by placing a voltmeter in the circuit, and thus ascertaining how much oxygen was liberated by the electrolytic action. The amount of oxygen not fixed by the metal was also measured, and the difference between the two gave the amount which went towards making the peroxide.

charged a second time, the peroxide again calculated, and so on :—

Separate periods of repose.	Charge.	Amount of peroxide.
—	First	1'0
18 hours	Second	1'57
2 days	Third	1'71
4 „	Fourth	2'14
2 „	Fifth	2'43

Similar experiments were made with plates prepared according to the method of Faure. The peroxide was formed by reducing a layer of red lead (containing 51 grains to one square inch of metallic surface), and subsequently completely peroxidising the spongy metal so produced. In one series of experiments we left eight peroxidised plates to themselves for various periods and determined the amount of sulphate formed. This gave us the amount of peroxide consumed, as follows :—

Plate	I.	after 2 hours	7'2 per cent.
„	II.	3 „	15'1 „
„	III.	4 „	19'8 „
„	IV.	5 „	30'0 „
„	V.	24 „	36'3 „
„	VI.	7 days	58'3 „
„	VII.	11 „	67'3 „
„	VIII.	12 „	74'3 „

The experiment with the last plate was tested with the galvanometer during its continuance, as in the case of the plate formed by Planté's method, with the following percentage results :—

Initial strength of current	100
After 1 day's repose	92
" 3 " "	79
" 4 " "	34
" 5 " "	24
" 7 " "	11
" 9 " "	8
" 12 " "	1

It is evident from these observations that a lead-peroxide plate gradually loses its energy by local action. The rate naturally varies according to the circumstances of its preparation.

Two difficulties will probably present themselves to any one on first grasping the idea of this local action:—1. Why should a lead plate covered with the peroxide and immersed in dilute sulphuric acid, run down so slowly that it requires many hours or even days before its energy is so seriously reduced as to impair its value for practical purposes? In the case of the copper-zinc couple immersed in the same acid, though the

difference of potential is not so great, a similar amount of chemical change would take place in a few minutes. 2. In a Planté or Faure battery the mass of peroxide which is in contact with the metallic lead plate expends its energy slowly. How comes it to pass that if the same mass of peroxide be brought into connection through the first lead plate with another lead plate at a distance, it expends its energy through the greater length of sulphuric acid in a tenth or a hundredth part of the time ?

The answer to these two questions is doubtless to be found in the formation of the insoluble sulphate of lead, which clogs up the interstices of the peroxide, and after a while forms an almost impermeable coating of high resistance between it and the first metallic plate.

The following conclusions seem warranted by the above observations :—

In the Planté or Faure battery local action necessarily takes place on the negative plate, with the production of sulphate of lead.

The formation of this sulphate of lead is

absolutely requisite in order that the charge should be retained for a sufficient time to be practically available.

The rapidity of loss during repose will depend upon the closeness of the sulphate of lead and perhaps upon other mechanical conditions. These are doubtless susceptible of great modifications. We do not know how far they are modified in practice, but it is conceivable that still greater improvements may yet be made in this direction.

PART II.

THE CHARGING OF THE CELL.

THE procedure of Planté in forming his battery is at first sight extremely simple. He takes two coils of lead, separated from one another, and immersed in dilute sulphuric acid ; a current is sent through the liquid from one lead plate to the other, and the final result is that the one becomes covered with a coating of lead peroxide, while hydrogen is given off against the other plate. On the view that sulphuric acid merely serves to diminish the resistance, and so facilitate the electrolysis of water, the ready explanation would be given that the two elements of the water are simply separated at the two poles. But it seems more in accordance with the facts of electrolysis to suppose that the sulphuric acid,

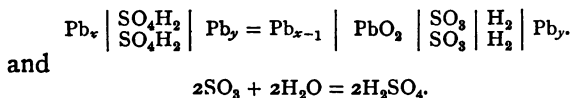
H_2SO_4 , is itself the electrolyte, and that the oxygen results from a secondary chemical reaction. As a matter of fact, if water be employed, no peroxide is formed, but only the hydrated protoxide, even though a current from twenty-four Grove's cells be made use of. The addition of a single drop of sulphuric acid to the water is enough to cause the immediate production of the puce-coloured oxide.

If we take two plates of lead in dilute sulphuric acid, and pass the current from only one Grove's cell, a film of white sulphate, instead of peroxide, makes its appearance on the positive pole, and the action practically ceases very soon. If, however, the current be increased in strength, the sulphate disappears, and peroxide is found in its place. In Planté's procedure, spongy lead and lead peroxide are indeed found on the respective plates. But, in consequence of the local action which takes place during the periods of repose, lead sulphate will be produced from the peroxide, and afterwards, in the course of the "formation," when the current is reversed, this

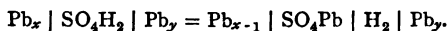
sulphate must be reduced to metallic lead by the hydrogen.

It may seem at first sight improbable that an almost insoluble salt of the character of lead sulphate should be decomposed under these circumstances. To test this fact by direct experiment, we covered two platinum plates with lead sulphate, immersed them in dilute sulphuric acid, and sent a current through. We found not only that the sulphate was reduced by electrolytic hydrogen, but that it was peroxidised by electrolytic oxygen. The white sulphate was, in fact, decomposed to a large extent at each plate, the positive being covered with deep chocolate-coloured peroxide, the negative with grey spongy lead.

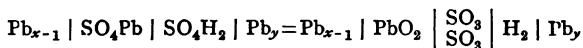
The reaction which takes place in charging a Planté battery may be viewed in two ways. The simplest may be thus expressed in the notation which we have employed in some previous papers. For convenience, the reaction is divided into two stages:—



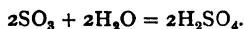
But it may be that lead sulphate is always formed in the first instance, and decomposed on the continuation of the current.



then



and



It seems not improbable that both these reactions may take place according to the varying density, or other circumstances of the current. The coating of peroxide interposes a great difficulty in the way of the further oxidation of the metallic lead. Hence Planté needs the successive periods of repose, to admit by local action of the formation of lead sulphate, and the oxidation of the increasing amounts of finely-divided lead thus brought into the field of action.

To obviate this waste of power and time, Faure covers both plates with red lead, and converts this into spongy peroxide and spongy lead respectively by the current. Now the first thing that happens, when the plates are immersed in

dilute sulphuric acid, is a purely chemical action. The minium suffers decomposition according to the formula—



But as both the lead sulphate and lead peroxide are insoluble, this change takes place mainly at the surface, and requires time to penetrate. Thus in an experiment performed with the object of testing this point the following amounts of minium were found to be converted into lead sulphate in successive periods of time :—

Time.	Minium changed into sulphate.
15 minutes ...	11·8 per cent.
30 „ ...	13·7 „
60 „ ...	14·6 „
120 „ ...	18·1 „

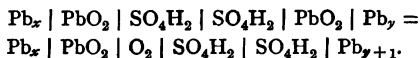
It is evident that in a Faure battery we are dealing with plates that consist of a superficial layer of mixed peroxide and sulphate of lead, the thickness of this layer depending upon the time during which the sulphuric acid has been allowed to soak into the minium.

It might happen, and we are told it has

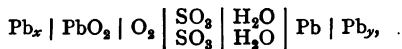
happened, that the amount of minium employed has been great enough to abstract all the sulphuric acid from solution, leaving only water. In that case water, of course, would be the electrolyte, and there can be little doubt that the lead plate might suffer oxidation in the manner which was described by us some years ago (*Chem. Soc. Journ.*, 1876) in a paper on "Phenomena accompanying the Electrolysis of Water with Oxidisable Electrodes." This paper detailed the results obtained on passing a current from one Grove's cell between two plates of the same metal immersed in pure water. We stated in the case of lead: "The positive electrode showed signs of slight oxidation, and the negative electrode a few small bubbles, in fifteen minutes; a slight cloudiness was then beginning to form, which afterwards increased; some oxide was found adhering in an hour; and afterwards grey metallic lead, which at the end of twenty-two hours was found to have stretched across to the positive electrode, forming a metallic connection which was so much heated by the passage of the voltaic

current that the liquid became warm." We are informed that such lead crystals have sometimes been found in Faure's cells.

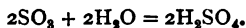
Supposing, however, that there is enough and to spare of sulphuric acid, the mixture of lead peroxide and lead sulphate presents a double problem. Were we dealing with peroxide alone it would be reduced on the one plate at the expense of two molecules of water or sulphuric acid, while at the opposite pole the oxygen would simply be liberated, the final result being:—



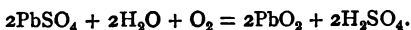
The intermediate stages are probably—



and



But as there is always lead sulphate present, this liberated oxygen is mainly used up in oxidating that substance, and it is evident from the following formula that it is theoretically sufficient to peroxidise the two molecules of sulphate—



These two molecules of PbSO_4 are obtained from one molecule of Pb_3O_4 (red lead), and it appears that two atoms of oxygen are sufficient to transform this into peroxide. But the corresponding amount of hydrogen (four atoms) by no means suffices to reduce a similar amount of what was once red lead on the other side, for in this case both the peroxide and the sulphate formed by the action of the acid have to be reduced. To accomplish this at least eight atoms of hydrogen will be necessary, and this will demand the electrolysis of an additional two molecules of water or sulphuric acid. It might therefore be expected, *à priori*, that the minium on the side to be oxidated ought to be twice the amount of that to be reduced.

In order to ascertain what is the real course of procedure, in charging a Faure battery, we took two plates of lead of equal size and covered each with a known weight of minium, which was found on analysis to be almost pure Pb_3O_4 . We passed a current of known strength, about one ampère, through the arrangement for many hours,

noting the amount of hydrogen gas which was liberated at the one pole, and the amount of oxygen liberated at the other.¹ From the data it was easy to calculate the amount of electrolytic hydrogen and oxygen utilised. We performed the experiment several times, varying the strength of the current and some other circumstances. The most complete result was as follows :—

¹ The pieces of apparatus employed in these experiments were the following :—(1) a battery of Grove's cells ; (2) a large glass vessel, used as a cell, containing the dilute sulphuric acid, and the two lead plates fixed on insulated supports ; (3) a voltameter to enable us to determine the actual amounts of the products of electrolysis liberated by the current in any given time ; (4) a galvanometer to indicate the strength of the current ; and (5) a resistance-box, by means of which the current might be maintained at a constant strength. Over each of the lead plates in the glass cell was supported a funnel leading into a long, graduated, glass tube filled with dilute sulphuric acid and set vertically. As the current passed and electrolysis took place, as much of the hydrogen and oxygen gases as was not absorbed at their respective lead plates rose into the tubes above them ; and the differences (corrected for temperature and pressure) between the amounts collected in a given time, and the amounts collected during the same time in the voltameter gave the amounts absorbed by the lead plates.

Time.	HYDROGEN.		OXYGEN.	
	Lost.	Absorbed.	Lost.	Absorbed.
hours.	c. c.	c. c.	c. c.	c. c.
1	Nil.	312	Nil.	156
2	"	318	18	141
3	"	306	48	105
4	"	300	66	84
5	"	300	72	78
6	2	313	90	67
7	5	295	87	63
8	3	312	96	61
9	6	303	93	61
10	21	297	99	60
11	37	273	99	56
12	101	220	105	56
13	150	158	105	49
14	195	132	105	58
15	210	92	100	51
16	228	90	106	53
17	225	85	100	55
18	270	66	108	60
19	264	51	108	49
20	270	50	111	49
21	273	43	114	44
22	270	30	114	36
23	276	30	114	39
24	297	21	123	36
25	309	9	126	33
26	270	18	120	24
27	300	18	132	27
28	309	11	138	22
29	321	15	141	27
30	318	15	147	19
31	300	6	135	18
	5,230	4,489	3,120	1,737

The amounts of hydrogen and oxygen capable of being absorbed by the materials on the plates were 4,574 and 1,294 c. c. respectively.

We read the indications of this table in the following way: At first, both the reduction and oxidation take place very perfectly, with little loss of either of the elements of water. The absorption of the hydrogen proceeds with little diminution, until by far the greater part of the lead peroxide and sulphate are reduced, but the last portions are very slowly attacked, probably because they are imbedded in a mass of reduced lead. On the side that is being oxidated it is otherwise: a considerable waste of oxygen soon shows itself, but nevertheless a continuous slow absorption of that element takes place long after the theoretical amount of it has been fixed. A very small amount of this excess is to be attributed, according to our experiments, to the oxidation of the metallic plate itself; but we attribute the greater portion to the local action which must be constantly going on between the peroxide and the lead plate with the formation of sulphate of lead, the sulphate in its turn of course being attacked by the electrolytic oxygen. Thus the excess of oxygen in the fifth column of the above table, 1737 as

against 1294 c.c., may be looked on as a measure of the local action which has taken place during the charging, and the figures in the lower portion as roughly indicating its progress from hour to hour. Local action will of course take place at first on the opposite plate, but it requires no more hydrogen to reduce two molecules of lead sulphate than one molecule of lead peroxide, and the possibility of local action gradually diminishes as the reduction proceeds.

All our other experiments told the same story as far as the absorption of hydrogen is concerned, but there are differences on the other plate. In one or two instances, not half of the theoretical amount of oxygen was absorbed. On searching into the circumstances on which this depended, we were unable to arrive at any other conclusion than that it was connected with the condition of the surface of the lead plate.

Experiments with a current of about two ampères showed that a larger quantity of both hydrogen and oxygen was fixed in a given time, but there was a larger proportionate loss, especially in the

case of oxygen. Experiments with a current of about half an ampère, on the contrary, gave a less rapid action, but a much smaller waste of force through the escape of free gas.

A complete study of the results of these experiments would be instructive, but the following comparisons may suffice to illustrate the points just mentioned. The theoretical amount of oxygen required for the red lead used is about 1,200 c.c., and the table shows the length of time in which 300, 600, and 1,000 c.c. were fixed by different strengths of current, together with the accompanying loss.

Strength of current.	Amount of oxygen stored.	Time.	Loss of oxygen.
Ampères.	c.c.	hours.	c.c.
2	300	1·5	174
1	„	2	18
$\frac{1}{2}$	„	3·8	15
2	600	4·1	617
1	„	5·5	249
$\frac{1}{2}$	„	7·6	47
2	1,000	13·9	3,081
1	„	12·2	900
$\frac{1}{2}$	„	16·0	400

In some cases we mixed the red lead with a little water, and allowed it to dry. In other experiments we mixed it at once with dilute sulphuric acid, but without finding any particular practical advantage.

The forming of a good secondary battery is a matter evidently depending upon very nice adjustment of conditions. It is but a few of these that we have carefully studied ; nevertheless, we feel ourselves in a position to make one or two suggestions in regard to the economic aspects of the question. It is evident that the energy stored up in a cell is determined mainly by the amount of peroxide present. This appears to be obtained with the smallest amount of waste when the current is not too strong ; in fact, in our experiments it was obtained when the density of the current was about $6\frac{1}{2}$ milli-ampères per square centimetre, calculated on the original surface of the lead plates.

There would seem to be no commensurate advantage in continuing the current after the oxygen has ceased to be absorbed pretty freely, because the presence of some unoxidised sulphate

of lead, although it increases the resistance, rather impedes than promotes local action.

On the other hand, however, it is necessary that the reduction of the minium on the opposing plate should be complete, for a mixture of lead peroxide and metallic lead would be peculiarly conducive to the production of lead sulphate, and thus increase the resistance ; while if any peroxide should escape destruction it would diminish the electromotive force of the cell.

It would appear probable, therefore, that the most economical arrangement would be obtained by making the red lead to be hydrogenated much smaller in amount than that to be oxidated. On trying the experiment with only half the quantity, we obtained a most satisfactory result as far as the charging was concerned. How far such an arrangement may be really desirable we consider more fully in treating of the chemistry of the discharge.

PART III.

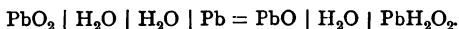
THE DISCHARGE OF THE CELL.

THE two plates of a Planté or Faure battery consist essentially of lead peroxide as the negative element, and metallic lead in a spongy condition as the positive. These are brought into communication with one another through the lead plates which support them, together with the connecting wire.

The lead peroxide reacts both with the lead plate that supports it, and with the lead on the opposite plate. At first sight, it might be expected that the reaction between it and the supporting plate would be the greater, as the space between them is so small, and the resistance of the intervening liquid in consequence almost inappreciable. The action is, indeed,

probably greater at the first moment, but, as explained in the first part, sulphate of lead is immediately produced, and that which lies at or near the points of junction, forms no doubt a serious obstacle to further local action, and admits of the lead on the opposite plate coming more fully into play.

If we consider *à priori* what is likely to be the reaction between lead peroxide and lead, with water as the connecting fluid, we should expect:—



On experiment this is found to be actually the case, yellow oxide appearing on the negative plate, and white hydrate on the positive.

If, however, the reaction takes place in presence of dilute sulphuric acid, the result will inevitably be sulphate on both sides, for even if oxide be first formed, it will be attacked by that acid. Of course this production of lead sulphate on each side might be expected gradually to produce a perfect electrical equilibrium. This, in fact, does take place under certain circumstances, but not under others. The reaction on the negative plate

is always of this character, as far as our analyses have shown. We have invariably found the deposit to consist of sulphate of lead mixed with unaltered peroxide. If, however, the cell be allowed to discharge itself rapidly, the lead on the positive plate is converted, not only into the sulphate, but, very partially, into lead peroxide. This is sometimes evident to the eye from the puce colour of the superficial layer, and we found also that this was confirmed by several chemical tests.

It is difficult to conceive how the reduction of the peroxide of lead on the one plate to oxide or sulphate, should be attended by a direct oxidation of lead on the other plate up to peroxide itself, as that would involve a reversal of the electromotive force. It is more easy to imagine that the peroxide results from the oxidation of sulphate of lead already formed, through the agency of electrolytic oxygen.

When this peroxide is formed on the positive plate, it is not difficult to foresee what must happen. A state of electrical equilibrium will be approached

before the peroxide of lead on the negative plate is exhausted. But the two sides are in very different positions with regard to local action. On the negative plate, the peroxide being mixed with a great deal of lead sulphate, it will suffer decomposition only very slowly through the agency of the supporting plate, but the lead peroxide on the positive plate, being mixed not only with lead sulphate, but with spongy metallic lead, will be itself speedily reduced to sulphate. Hence, on breaking the circuit, when local action alone can take place, the peroxide formed on the positive plate during the discharges will be destroyed much more easily than the original peroxide on the other plate. The difference of potential between the plates will be restored, and on connection the cell will be again found in an active condition.

Now it has been frequently observed that partially discharged accumulators do give an increased current after repose, that is, after the circuit has been broken and re-established. It remained for us to ascertain whether the chemical change above

described coincided in any way with the physical phenomena. For this purpose we prepared plates according to the method of Faure, and examined carefully the changes of electromotive force and strength of current, which took place during their discharge under known resistances, and the chemical changes that took place under the same circumstances.

We found that the initial electromotive force of freshly prepared cells was 2·25, 2·25, 2·21, and 2·31 volts, averaging 2·25, but that after standing for thirty minutes or so, or after being allowed to discharge for a few minutes, it was reduced to about 2·0 volts. We take this to represent the normal electromotive force of the arrangement of lead, lead peroxide, and dilute sulphuric acid, and believe that the higher figure obtained at the first moment is due to the hydrogen and oxygen occluded on the respective plates, and which either diffuse out, or are speedily destroyed.¹

We found, however, that in the discharge the electromotive force diminished in a manner that

¹ For further remarks upon this point, see p. 48.

depended upon certain conditions. Thus, in an experiment in which the external resistance was 1 ohm, and the internal 0.58 ohm, the E.M.F. sank in forty-five minutes from 2.25 to 1.92, but after being disconnected for thirty minutes, it was found to have risen to 1.96, and after eighteen hours' repose, it had actually risen to 1.98 volts. These observations were made many times in succession during the course of the experiment, which lasted six days.

With twenty times the external resistance, that is 20 ohms, the diminution of electromotive force was much slower; but after discharging for three days, the fall was more pronounced, and the rise on repose very apparent.

With 100 ohms resistance, the electromotive force varied very little for three days.

It is more difficult to obtain satisfactory chemical evidence of a quantitative character. It is clear that as chemical examination means the destruction of the substances, the same plate cannot be analysed in two consecutive stages. Nor can two plates be easily compared with one another,

although they have been formed under the same circumstances. Even the same positive plate, whether during or after discharge, presents to the eye very different appearances in different parts. To a certain extent we obviated this difficulty by cutting the plate in two longitudinally, analysing the one half at once, and allowing the other to repose for a given time before examining it for peroxide of lead.

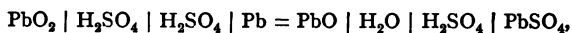
As to the estimation of peroxide in the presence of metallic lead, we finally adopted as the best method that of reducing it by means of oxalic acid, although we were not certain that the whole amount is obtained in this way, even though the solution be kept hot for a considerable time.

By this method many chemical examinations were made of the positive plate. The results are as follows:—First of all, when the external resistance did not exceed 20 ohms, the peroxide of lead was generally visible in patches, and its presence was demonstrated and approximately measured by various chemical tests. On repose, the quantity of this peroxide visibly diminished, and in the

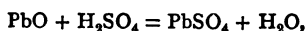
majority of instances the chemical analyses also showed a smaller amount. In all cases sulphate of lead makes its appearance early in the action, and gradually increases in quantity, becoming finally the only product of the discharge.

The deposit on the negative plate shows the presence of nothing but sulphate of lead in addition to the unchanged peroxide. At the conclusion of the action, we have always found more or less of the substance unaltered. Thus, as one instance, after a discharge lasting five days, and approximately complete, we found that only 68 per cent. of the deposit was lead sulphate.

We conclude, therefore, that the chemical action of the discharge is essentially what is expressed by the following theoretical formula :—



which oxide of lead in the presence of sulphuric acid becomes sulphate of lead, according to the equation—



the final result being sulphate of lead on both plates. This reaction is, however, sometimes complicated by the formation of a small amount of peroxide of lead on the positive plate. We believe this to be due to the oxidation of sulphate, an action which was explained in the preceding part.¹

Another conclusion has reference to the resuscitation of power observed on repose. This is not due to any purely physical action, but is a necessary consequence of the formation of PbO_2 on the positive plate. As sooner or later the result of the action becomes solely PbSO_4 , this temporary formation of peroxide does not seriously affect the quantity of electrical force that may be regained from the accumulator, but it does affect the evenness of its flow. The flow is more regular if the

¹ On the 1st of March of this year Professor Frankland read a paper at the Royal Society, in which he confirmed the reactions given in this and the preceding part. He expresses them, however, as the electrolysis of hexabasic sulphuric acid, in accordance with the views of Burgoin. We have looked into the evidence upon which these views are founded, but are not satisfied of its conclusiveness. We therefore prefer our original formulæ as involving a smaller amount of theory.

discharge be made slowly, but in that case the loss on the negative plate from local action will probably be greater.

As to practical conclusions, we may note—I. Although as stated on page 24, the most economical arrangement for the initial charging of the cell is to "make the red lead to be hydrogenated much smaller in amount than that to be oxidated," yet, as foreshadowed at the same time, this arrangement is not desirable for the discharge of the cell. Nor is it for its subsequent charging, since, as will have been seen, the substances to be acted upon are now very different. On the negative plate there will be the sulphate of lead produced by the discharge, plus sulphate of lead produced by local action, together with more or less unaltered peroxide. On the positive plate there will be the sulphate of lead produced by the discharge, together with excess of lead, if any. Unless, therefore, the peroxide of lead unacted upon is allowed to be very considerable, the quantity of lead compound on the two sides

ought to approach equality. 2. Care should be taken that sulphuric acid is in sufficient excess to allow of there still remaining some of it in solution after all the available lead has been converted into sulphate. If it is removed and only water is present, an oxide or hydrate will be produced with probably some serious consequences to the cell.

PART IV.

THE FUNCTION OF SULPHATE OF LEAD.

WE have already frequently remarked on the formation of lead sulphate, and its importance in the history of a secondary cell.

In Part I. we showed that the local action that takes place at first energetically between the metallic lead and the adhering peroxide is gradually diminished by the formation of sulphate of lead.

In Part II. we stated that in the original formation of a Faure cell sulphate of lead is oxidated on the one plate and reduced on the other. We also described an experiment in which two platinum plates were covered with lead sulphate, immersed in dilute sulphuric acid, and placed in the circuit of a galvanic current, the result being

that "the white sulphate was decomposed to a large extent on each plate, the positive being covered with deep chocolate-coloured peroxide, the negative with grey spongy lead."

In Part III. we showed that on the discharge of a cell, lead sulphate is the ultimate product on both plates.

It might naturally be inferred from our previous statements that in the re-charging of a cell this lead sulphate would be oxidated on the one plate and reduced on the other, as in the original formation. This matter, however, has given rise to some controversy. All subsequent experimenters admit the *oxidation* of the lead sulphate, but Dr. Oliver Lodge could not obtain any reduction of it, when pure sulphate was employed.¹ Sir William

¹ A correspondence upon this subject is to be found in *Nature* of July 20, August 10, and October 19, 1882. Dr. Lodge also quotes experiments by Professor McLeod, and reverts to the subject in the *Engineer* of January 5, 1883. There are some interesting observations on the Chemistry of the Cell by Professor Herschel in *Nature* of April 6, 1882. The matter was also brought forward and discussed in a paper entitled "On Secondary Batteries, with special reference to Local Action," at the meeting of the British Association at Southampton on August 25, 1882; *vide* Report, p. 447.

Thomson also, when experimenting, with two platinum plates and layers of sulphate, obtained only a doubtful indication of reduced metal. The question as to whether the sulphate is reduced or not on re-charging a Faure cell is one of vital importance; for if the sulphate formed at each discharge accumulates on the positive plate it would clog up the space, and, what is perhaps worse, a fresh surface of the lead would have to be oxidated (or rather, converted into sulphate) at each discharge. Thus the positive plate will be continually corroded, and its life will be limited.

We have already replied to Dr. Lodge in *Nature* (vol. xxvi. p. 342), but we thought it desirable to repeat the experiment with the platinum plates especially with a view to determine whether the reduction was effected slowly or with any rapidity. We fastened 20 grms. of the white sulphate upon a negative plate by binding it round tightly with parchment-paper, placed it vertically in the sulphuric acid, and passed a continuous current of somewhat under an ampère. The hydrogen was at no time wholly absorbed—indeed the greater

part of it certainly escaped—but after the lapse of twenty-four hours, small patches of grey metallic lead became distinctly visible through the wet parchment-paper ; and these gradually spread in an irregular manner. At the end of ten days it was found that the whole of the sulphate, except a few small patches on the surface, was reduced to a grey spongy mass. Although there could be no reasonable doubt that this was metallic lead, a portion of it was tested chemically, and proved to be such.

It thus appears that the *reduction* of the pure sulphate of lead is an absolute fact, although it does not take place so easily as the oxidation.

In an actual cell the sulphate of lead is of course mixed with other bodies. Thus, in the formation of a Faure battery, the minium is converted by the sulphuric acid more or less completely into peroxide of lead and sulphate. We have already described an experiment in which 4489 c.c. of hydrogen were absorbed on a plate, the materials of which were capable of absorbing only 4574 c.c. if the whole of the sulphate as well

as the peroxide was reduced. In our note-book we have the particulars of four other experiments made in each case with the same, or nearly the same, amount of material, in which 4199, 4575, 4216, and 4387 c.c. respectively were absorbed, although perhaps in not one of these cases was the experiment continued until the action was absolutely complete. As, however, it may be objected that the amount of sulphate produced upon these plates was an unknown quantity, we have in a recent experiment treated the minium in the first instance with a considerable amount of sulphuric acid. This gave us a mixture which, on analysis, was found to contain 18.5 per cent. of sulphate of lead. This mixture, when submitted to the reducing action of a current yielded a mass of spongy lead that contained only a mere trace of sulphate.

As it seemed desirable fully to establish the fact that the sulphate of lead formed on the discharge of a cell is reduced in the subsequent charging, we took the quondam lead plate of a fully discharged cell, determined the proportion of sulphate to

unaltered spongy lead, and submitted it to the reducing action of a current. The amount of sulphate on the plate before passing the current was found to be 51 per cent., but, after the passage of a current of about an ampère for sixty hours, not a trace of it remained.

Hence it may be concluded that, during the alternate discharging and re-charging of a Planté or Faure cell, sulphate of lead is alternately formed and reduced on the lead plate, and that the plate itself is not seriously corroded. It would, however, appear desirable not to allow the whole of the spongy lead to be reduced to sulphate during the discharge, for two reasons, viz.: (1) because the supporting plate stands a chance of being itself acted on if there is not a sufficient excess of spongy metal; and (2) because the presence of this excess tends to facilitate the reduction of the sulphate.

We have already shown that sulphate of lead is produced by the local action that takes place between the peroxide and its supporting lead plate during repose. The same local action also takes

place during the charging of the plate, as was pointed out in our second communication, and this sulphate is, in its turn, attacked by the electrolytic oxygen. In this way the absorption of oxygen in forming the negative plate ought never to come to an end. In order to see whether this was the case, we allowed an experiment to continue for 115 hours, although the main action was over in about forty hours. For the last two days of the experiment, the amount of oxygen absorbed was pretty constant, being about 9 c.c. per hour, which is equivalent to 0.24 grms. of sulphate of lead formed and oxidated. The whole charge on the plate was forty grms. of peroxide. This local action also takes place during the discharge, as is evidenced by the sulphate of lead formed on the negative plate always exceeding in amount that formed on the positive plate.¹

Through this local action taking place during the formation of the cell, during repose, and

¹ For details of the experiments from which these conclusions were drawn, see Appendix.

during the discharge, the lead plate which supports the peroxide must be continually corroded more and more; and it is doubtless due to the insolubility of the sulphate formed that the destruction of this kind of secondary battery is so materially retarded in practice.

PART V.

I. INFLUENCE OF STRENGTH OF ACID.

IN Part II., when treating of the charging of the cell, we pointed out that in the electrolysis of dilute sulphuric acid between lead electrodes, two totally different reactions might be obtained. The positive metal becomes thinly coated with lead sulphate when the current employed is of small density, but with lead peroxide when the density of the current is of greater magnitude. This latter action is, of course, what takes place in the ordinary formation of a Planté battery. The chemical change, therefore, which goes on at the positive electrode is to a certain extent dependent upon the strength of the current. It appeared also of both theoretical and practical interest to determine whether the chemical change was also influenced by the strength of the acid

employed. Our experiments consisted in passing a current of uniform strength, about 1 ampère, between electrodes of lead, 12 square inches in size, in varying strengths of sulphuric acid, and estimating in each case the amount of oxygen fixed by the positive electrode. We determined this for successive five minutes of time, and as such actions are not always very uniform, we made in each instance more than one experiment. The results are given in the following table :—

Strength of acid.	Expt.	Percentage of oxygen fixed.				
		First 5 mins.	Second 5 mins.	Third 5 mins.	Fourth 5 mins.	Total.
1 to 5	I.	38·1	28·6	28·6	33·3	128·6
	II.	39·5	30·2	25·6	30·2	125·5
1 to 10	I.	43·4	38·7	29·2	34	145·3
	II.	44·1	39·3	29·3	34·9	147·6
1 to 50	I.	48·3	39·6	35·3	22·4	145·6
	II.	46·2	43·9	23	30	143·1
	III.	54	40	35·3	35·5	165
1 to 100	I.	42	38·3	33·9	29·5	143·7
	II.	42·4	40	37·8	35·5	155·7
	III.	51·1	44·2	34·9	34·9	165·1
1 to 500	I.	46·6	32·6	27	27	132·6
	II.	46·4	27	27	18	118·4
1 to 1000	I.	90·6	81·1	76·4	57·5	305·6
	II.	90·8	77	72·3	63·1	303·2

It appears from this that the strong sulphuric acid (1 to 5) is not quite so favourable to the action as the more dilute (1 to 10), but that between this latter proportion and 1 to 500 there is no great difference in the amount of oxygen fixed, and therefore of corrosion of the plate. The appearance of the plate in every instance indicated the formation of only lead peroxide. With sulphuric acid diluted with 1000 parts of water, the amount of oxygen fixed, and therefore of corrosion, was at least doubled, while the chemical action was very different. On parts of the electrode, streaks of a mixture apparently of the yellow and puce-coloured oxides were seen. On other parts a white substance formed and was easily detached, falling in clouds into the liquid. Where this latter action took place, the plate was visibly the most corroded. This white substance gave an analysis SO_4 equivalent to 73.6 per cent. of lead sulphate, suggesting the idea that it was a basic sulphate of the composition $2\text{PbSO}_4, \text{PbO}$, which would require 73.1 per cent. As the peroxidation of the lead is required, and

the corrosion of the plate is to be avoided as much as possible, it is evident that this extremely dilute acid must be avoided. It has already been shown that if the sulphuric acid is entirely removed from solution, as sometimes happens in an accumulator, the lead is simply converted into the hydrated protoxide, and therefore corroded without any good effect.

2. FUNCTION OF HYDROGEN.

In the formation of a secondary cell, after the complete reduction of oxide or sulphate to metallic lead, bubbles of hydrogen gas are seen to escape from the lead plate. It has been assumed that a portion of this element is occluded by the lead, or in some other way enters into association with it, and it has been supposed that this hydrogen compound may play an important part in the subsequent production of electromotive force. It therefore appeared desirable to obtain experimental evidence as to whether hydrogen is so absorbed. The process we adopted for this purpose was founded upon the observation

of Graham that hydrogen associated with palladium reduced ferri- to ferro-cyanide of potassium, and that generally in the occluded condition the element was more active chemically. We had previously ascertained that hydrogen associated with other elements, as platinum, copper, and carbon, was capable of reducing potassium chlorate to chloride. This method seemed to give trustworthy results, and therefore we applied it in this instance. As the result of several trials, however, we found that the amount of hydrogen associated with the reduced lead was almost inappreciable. Small as this quantity is, however, it is by no means impossible that it may be the cause of the exceedingly high electromotive force observed for the first few moments, on joining up a completely-formed cell immediately after its removal from the circuit of the charging current. This, however, may be due, as Planté imagined, to the gaseous hydrogen itself. The principal if not the only function of the hydrogen of the water or sulphuric acid is therefore that of reducing the lead compounds.

By a totally different process Prof. Frankland has very recently come to the same conclusion as ourselves in regard to the exceedingly small amount of occluded hydrogen.

3. EVOLUTION OF OXYGEN FROM THE PEROXIDE PLATE.

Planté noticed a small escape of gas from the negative plate of his cell immediately after its removal from the influence of the charging current. This he attributed to a decomposition of water by means of local circuits between the peroxide and the subjacent lead plate in contact with it.

The explanation given by us of the local action which goes on at the negative plate does not account for the escape of any gas—either oxygen or hydrogen. We therefore thought it of interest to ascertain the nature, and if possible the origin, of the gas noticed by Planté.

We found that the escape of gas from a Planté negative plate was very slight, and soon ceased ; but we observed that it became much more

pronounced when the temperature of the electrolytic liquid was raised. In order to get a sufficient quantity of the gas for examination, we prepared a negative plate according to the procedure of Faure, and then heated it in dilute acid, with an arrangement for collecting the gas as it was evolved. The amount of gas was still very small in comparison with that of the peroxide, but a sufficient quantity was collected to enable us to ascertain that it was oxygen. We next heated some of the electrolytic peroxide apart from the lead plate, and again noticed a similar evolution of gas, which was also found to be oxygen. This shows, therefore, that it was not a result of local action.

The gas has generally some odour of ozone, and, on testing the dilute acid between the plates of a Planté cell, we always found traces of something that bleached permanganate of potassium, and which might be either ozone or peroxide of hydrogen.

The origin of the gas noticed by Planté may be easily attributed to the oxygen which always

passes off in quantity from the peroxide plate during the process of "formation." It is only necessary to suppose that some of this becomes condensed on the peroxide, and is gradually eliminated from it when the surrounding conditions are changed. But the matter is capable of another explanation. If peroxide of hydrogen be really formed in the liquid, it will exert its well-known influence on higher oxides, namely, that of reducing them and itself at the same time. As a matter of fact, if peroxide of lead is dropped into peroxide of hydrogen, oxygen is evolved.

4. TEMPERATURE AND LOCAL ACTION.

Planté has recently pointed out that an elevation of temperature facilitates the formation of his secondary cell (*Comptes Rendus*, August, 1882). The character of the chemical changes which take place at the negative plate led us to think it exceedingly probable that this increase in the rate of formation arose from an augmentation in the amount of local action. Experiment showed such to be the case. Pairs of similar negative

plates on Planté's model were allowed to remain in repose at 11° C. and 50° C. respectively, and the formation of the white sulphate was visibly more rapid at the higher than at the lower temperature. The same is also true with negative plates prepared by Faure's process. Thus we found that two similar plates kept in repose for an hour, the one at 11° C. and the other at 50° C., formed by local action 2.6 and 7.4 per cent. of lead sulphate respectively. On two other plates the proportions were 7.6 and 9.5 per cent. respectively. These observations of course by no means exclude the idea that an increase of temperature may also facilitate the other chemical changes that take place in the formation of a lead and lead-oxide cell.

APPENDIX.

APPENDIX.

THE experiment referred to on page 42 was made in the same manner as that on page 19. The results of the observations were as follows:—

		H evolved (in Voltr.).		H absorbed.		O evolved (in Voltr.).		O absorbed.
1st hour	...	160	...	160	...	80	...	78
2nd „	...	185	...	185	...	92·5	...	88
3rd „	...	150	...	150	...	75	...	71
4th „	...	170	...	170	...	85	...	79
5th „	...	170	...	170	...	85	...	79
6th „	...	175	...	175	...	87·5	...	78
7th „	...	180	...	180	...	90	...	79
8th „	...	170	...	170	...	85	...	74
9th „	...	185	...	185	...	92·5	...	70
10th „	...	175	...	173	...	87·5	...	58
11th „	...	200	...	197	...	100	...	69
12th „	...	180	...	176	...	90	...	57
13th „	...	185	...	181	...	92·5	...	42
14th „	...	168	...	164	...	84	...	31
15th „	...	175	...	171	...	87·5	...	34
16th „	...	175	...	169	...	87·5	...	30
17th „	...	165	...	158	...	82·5	...	25

	H evolved (in Voltr.).	H absorbed.	O evolved (in Voltr.).	O absorbed.
18th hour ...	183	173	91·5	28
19th ,, ...	185	173	92·5	27
20th ,, ...	183	169	91·5	26
21st ,, ...	185	167	92·5	29
22nd ,, ...	180	153	90	20
23rd ,, ...	180	145	90	20
24th ,, ...	180	119	90	17
25th ,, ...	168	110	84	19
26th ,, ...	173	102	86·5	18
31st ,, ...	185	35	92·5	14
41st ,, ...	177	0	88·5	11
54th ,, ...	190	0	95	10
67th ,, ...	183	0	91·5	7
78th ,, ...	224	0	112	12
90th ,, ...	220	0	110	10
95th ,, ...	216	0	108	8
103rd ,, ...	223	0	111·5	9
115th ,, ...	213	0	106	6

In the above table the amounts of hydrogen and oxygen absorbed were calculated as before by means of the hydrogen evolved in the voltmeter during the same period. The oxygen evolved was calculated from the hydrogen, and is placed in the table in order to render the fifth column more clearly intelligible. After the twenty-sixth hour, though the action of the current continued without interruption, intervals

of about half a day were allowed between the observations. These, however, as before were made for an hour at a time, so that each line of the second portion of our table is strictly comparable with each line of the first, though the whole covers an additional period of nearly four days. It will be seen that the results are in accordance with those previously obtained. The hydrogen was *completely* absorbed during the first nine hours, and *almost* completely for some ten hours longer. Its absorption then began to rapidly fall off. At the end of the twenty-sixth hour the volume absorbed amounted to 4,255 c.c., and for some hours afterwards at least there was a small absorption still going on, probably enough to make up the theoretically possible amount of 4,500 c.c. On the opposite plate the absorption of oxygen was never perfect; but the loss became gradually greater and greater. Although at the end of twenty-six hours the amount of oxygen actually absorbed (1,246 c.c.) about equalled what was requisite to peroxidise the whole of the minium, the absorption still went on, and did not exhibit

any signs of ever coming to an end. A small amount was found to be continuously absorbed as long as our experiment lasted. Taking the amounts shown in the fifth column as fairly representing the action, it may be calculated that the oxygen absorbed from the twenty-sixth to the end of the 115th hour was 901 c.c. ; which of course, if our interpretation be correct, implies a large amount of action between the peroxide and its subjacent lead plate.

Our best observations on the amount of sulphate formed on the negative and positive plates respectively, were made with the experiments on page 30, the material on each plate after the discharge was analysed, and gave the following percentages of sulphate of lead :—

	1 Ohm.	20 Ohms.	100 Ohms.
Negative plate... ..	33·0 p. c.	30·7	35
Positive ,,	28·8 ,,	20·0	26

The formula of decomposition during the discharge would of course require the same amount of sulphate of lead on each plate. Some experiments were also made to determine whether the

local action was in any way diminished by the co-existence of the discharge. We failed, however, in getting good quantitative results, but fully assured ourselves that during the first ten minutes the double action was taking place.

THE END.

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