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PROCEEDINGS

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V. " A new Form of Gas Battery." By LUDWIG MOND and
CARL LANGER. Communicated by LORD RAYLEIGH, Sec. R.S.
Received June 13, 1889.

In January, 1839, now over fifty years ago, Mr. (now Lord Justice)
Grove published the first notice* of his startling discovery—the gas
battery.   This he followed up in 1842, 1843, and 1845 by three
important papers†, two of which were read before this Society.

Since that time very little attention has been given by investigators
to the subject.   Papers by Schönbein,‡ De la Rive,§ Matteucci,‖
Beetz,¶ Gaugain,** Morley,†† Peirce,‡‡ Lord Rayleigh,§§ Figuier,‖‖
and Kendall,¶¶ and a few patents describing ingenious but imprac-
ticable suggestions for improved gas batteries, comprise the principal
contributions to the subject.

This is the more surprising as Grove had published a large number
of experiments leading, amongst other important results, to a complete
list of the voltaic relations of gases to each other and to other
substances, and had pointed out in his lucid manner the great
scientific interest attaching to the gas battery, which forms the
simplest instrument for generating electricity, possesses remarkable
constancy of E.M.F., and " exhibits such a beautiful example of the
correlation of natural forces."

Grove states that he never thought of the gas battery as a practical
means of generating voltaic power, but, nevertheless, he indicates
clearly in what directions improvements with this object should be
attempted, viz., by extending as much as possible the surface of
contact between the gases, the absorbent and the electrolyte.

We have been engaged for several years with investigations on gas
batteries, which fully corroborate Grove's view, but show that he, as

* Grove, ' Phil. Mag.,' vol. 14, 1839, p. 129.

† Grove, ' Phil. Mag.,' vol. 21, 1842, p. 417; ' Roy. Soc. Proc.,' vol. 4, 1843,
p. 463; vol. 5, 1845, p. 557.

‡ Schönbein, ' Poggendorff, Annalen,' vol. 56, 1842, pp. 135 and 235; vol. 58,
1843, 361; vol. 62, 1844, 220; vol. 74, 1849, 244.

§ De la Rive, ' Arch. d'Électric.,' vol. 3, 1843, p. 525.

‖ Matteucci, ' Comptes Rendus,' vol. 16, 1843, p. 846.

¶ Beetz, ' Poggendorff, Annalen,' vol. 77, 1849, p. 505; vol. 90, 1853, p. 42;
vol. 132, 1867, p. 460; ' Wiedemann, Annalen,' vol. 5, 1878, p. 1; ' Phil. Mag.,'
vol. 7, 1879, p. 1.

** Gaugain, ' Comptes Rendus,' vol. 64, 1867, p. 364.

†† Morley, ' Phil. Mag.,' vol. 5, 1878, p. 272.

‡‡ Peirce, ' Wiedemann, Annalen,' vol. 8, 1879, p. 98.

§§ Rayleigh, ' Cambridge Phil. Soc. Proc.,' vol. 4, 1882, p. 198.

‖‖ Figuier, ' Comptes Rendus,' vol. 98, 1884, p. 1575.

¶¶ Kendall, ' Roy. Soc. Proc.,' vol. 36, 1884, p. 208.

well as later investigators, overlook one important point, viz., the
necessity of maintaining the condensing power of the absorbent
unimpaired. We found that platinum black, the most suitable
absorbent for gas batteries, loses its condensing power almost com-
pletely as soon as it gets wet, and that it is therefore necessary for
our purpose to keep it comparatively dry. All attempts to attain this
with various constructions of the gas battery involving the use of a
liquid electrolyte failed. We have only succeeded by using an elec-
trolyte in a quasi-solid form, viz., soaked up by a porous non-conduct·
ing material, in a similar way as has been done in the so-called dry
piles and batteries.

In order to procure as large a contact as possible between the gases,
the electrolyte and the absorbent, and at the same time to obtain the
greatest possible duty out of a given quantity of the latter, we have
adopted the following construction :—

A diaphragm of a porous non-conducting substance, such as plaster
of Paris, earthenware, asbestos, pasteboard, &c., is impregnated by
dilute sulphuric acid or another electrolyte, and is covered on both
sides with thin perforated leaf of platinum or gold and with a thin
film of platinum black. The platinum or gold leaf, which serves as
conductor for the generated electricity (the platinum black being a
very bad conductor), is placed in contact at small intervals with
strips of lead or other good conductor in order to reduce the internal
resistance of the battery to a minimum. In place of the platinum or
gold leaf, fine wire gauze of the same metal or of carbon may be used.

The diaphragms so prepared are placed side by side or one above
the other, with non-conducting frames ·of pasteboard, wood, india-
rubber, &c., intervening, so as to form chambers through which the
gases to be employed (generally hydrogen and air) are passed, so that
one side of the diaphragm is exposed to the one gas and the other to
the other gas, and the spaces between the diaphragms are so con-
nected that these gases pass in contact with a number of diaphragms.

Of the numerous ways in which dry gas batteries can be con-
structed we will describe two. One of these constructions, suitable
for laboratory work, shown in fig. 1, consists of an earthenware
plate M, impregnated with sulphuric acid and cemented into an
ebonite frame R.

At a short distance from and all around the plate a copper wire A
is let into the ebonite frame. The earthenware plate is covered with
platinum leaf which has been perforated with a very large number
(1500 per square cm.) of small holes, and which extends over and is
in metallic contact with the copper wire. To protect the latter from
corrosion, and to avoid local action, molten paraffin is put over the
platinum leaf where it is in contact with the copper wire. Where the
platinum leaf is in contact with the earthenware plate it is coated by

Fig. 1.
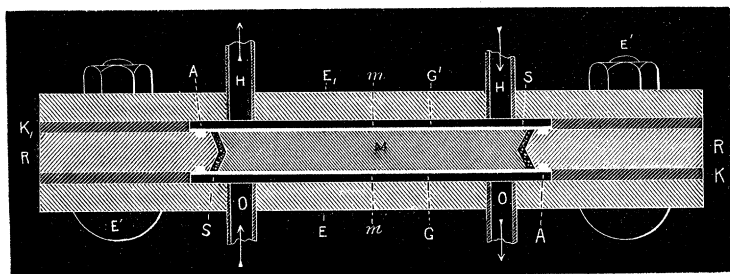
means of a brush with a very thin film of platinum black, which penetrates through the pores and holes of the platinum leaf, and thus comes into contact with the electrolyte. The frame R is fixed by means of screws between the two ebonite plates E, E', with two india-rubber frames K, K' intervening, thus forming two gastight chambers G, G', through which the gases to be used are let by the tubes O, O' and H, H'.

Fig. 2.
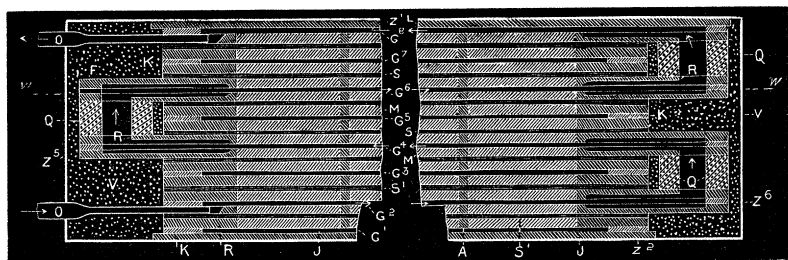
The second construction consists of a number of elements each of which is composed of two frames of lead and antimony consisting of a broad edge R, conducting strips A, and flaps F with holes and channels O, H, which form the inlets and outlets for the gases. These frames are coated with an insulating layer a of a mixture of gutta-percha, beeswax, resin, and paraffin. Between the two frames we insert a thin sheet S, prepared by coating a piece of cloth with plaster of Paris, and made impervious round the edges by the same insulating mixture, and then the open spaces formed by the conducting strips A are filled up with plaster of Paris mixed up with dilute sulphuric acid, so as to obtain an even plate. This is now coated with platinum leaf and platinum black in the same way as before described. A number of these elements are put side by side or one above the other, with non-conducting frames K of pasteboard intervening, so as to

Fig. 3.

Fig. 4.

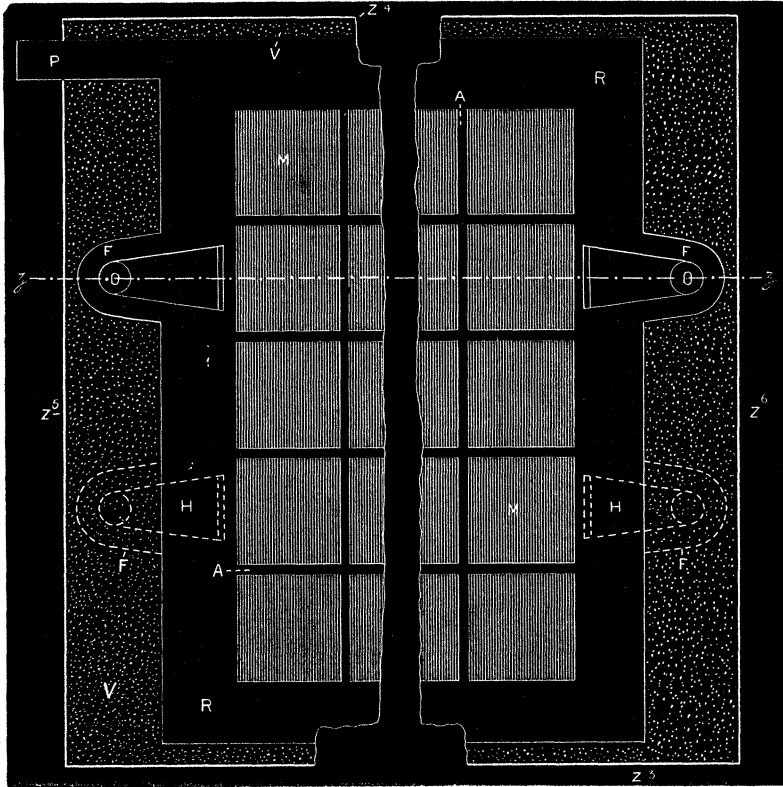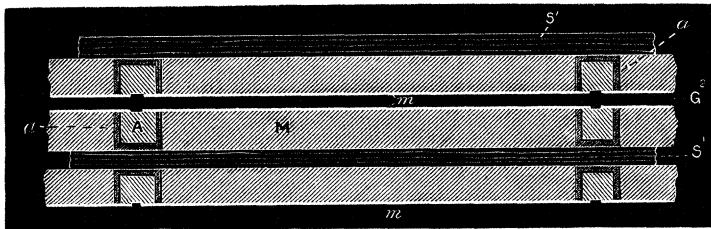form gas chambers G_1, G_2, G_3, which are connected by means of cork or rubber washers Q, so that the gases admitted by the pipes O pass through the whole series of chambers. The first and the last gas chamber are formed by an additional pasteboard frame intervening between the last plates and two plates of zinc Z_1, Z_2, extending beyond the battery plates, which hold the set together. The whole

set of plates is now coated on the four sides not covered by the zinc plates with a mixture of beeswax and resin, so as to obtain a block which is perfectly gastight all round, and the space V left between the two zinc plates is then filled up with plaster of Paris, so as to obtain one solid compact block with no openings except the entrances and exits for the gases. This is closed by four more zinc plates, Z_3, Z_4, Z_5, Z_6, which are soldered together so as to form a box.

The E.M.F. of this battery we found to vary considerably, according to the way in which the platinum black is prepared. The best and most regular results we have obtained from platinum black made by neutralising a boiling solution of $PtCl_4$ with Na_2CO_3, and adding this slowly to a boiling solution of sodium formiate. With this we obtain an electromotive force of 0·97 volt with the open circuit. The internal resistance varies considerably with the thickness of the porous plates, the amount of the electrolyte contained in these, and the surface of these plates. Plates of gypsum of 8 mm. thickness and 350 cm. surface gave an internal resistance of 0·02 ohm.

The current obtainable from these batteries varies necessarily with the external resistance. It is possible to obtain 8 ampères from one such element, but the E.M.F. of the battery sinks at a very much more rapid rate than with constant batteries if a strong current is taken out, and the work done by the battery is not, as in constant batteries, at its maximum when the internal and external resistance are equal. Thus we found with a small battery of 42 sq. cm. surface and 0·36 ohm internal resistance the following results :—

R.	R_1.	P.	S.	E.	E_1.	D.	A.
0·360	0·30	0·265	0·883	0·62	0·58	0·04	0·236
,,	0·40	0·310	0·775	0·62	0·58	0·04	0·240
,,	0·70	0·430	0·614	0·67	0·65	0·02	0·263
,,	1·00	0·490	0·490	0·68	0·66	0·02	0·240
,,	2·00	0·605	0·302	0·72	0·71	0·01	0·219
,,	4·00	0·700	0·175	0·77	0·76	0·01	0·122
,,	8·00	0·780	0·097	0·81	0·81	0·00	0·075
,,	20·00	0·860	0·043	0·87	0·87	0·00	0·036

R.   Internal resistance in ohms.
R_1.   External resistance in ohms.
P.   Difference of potential at the poles.
S.   Strength of current in ampères.
E.   E.M.F. in volts, determined by the first deflection of the galvanometer needle 1 second after opening the circuit.
E_1.   Calculated E.M.F. in volts.
D.   Difference of E and E_1 = increase of E.M.F. during 1 second, showing rapidity of absorption of the gases with varying saturation of the platinum.
A.   Work done by the battery in watts.

These figures show that in the case of the battery experimented with the maximum of work was obtained with an external resistance of about double the internal resistance.

This result is probably due, as pointed out by Dr. C. A. Wright,* to the fact established by Favre† and Berthelot,‡ that the gases occluded or condensed by platinum black evolve less and less heat per unit weight of gas the more gas the platinum black had previously condensed.

The heat evolved by the condensation of the gases by the platinum black, or a certain portion of this heat, is in all probability lost for the production of the current; it follows that the more the platinum black is saturated the less energy will be lost by the condensation of the gases, and *vice versâ*. Now, probably the rate of absorption of gas by the platinum black will rapidly diminish as it is more and more saturated with gas, so that in order to maintain it saturated or nearly saturated only a moderate amount of current can be obtained from a given surface, while if it is kept far below the saturating point it will condense the gases very rapidly, and a very large current can consequently be obtained.

As a practical limit we prefer to work the battery with an E.M.F. with closed circuit of about 0·73 volt. This allows us to take from 2 to 2½ ampères (1·45—1·82 watt) out of an element with an active surface of 700 sq. cm., covered with 0·35 gr. of Pt leaf and 1 gr. of Pt black, which gives a useful effect of very nearly 50 per cent. of the total energy contained in the hydrogen absorbed in the battery.

We have found practically no difference in these results, whether we were using O and H or air and gases containing 30 per cent. to 40 per cent. of H, such as can be obtained by the action of steam or air and steam on anthracite, coke, or coal.

With a useful effect of 50 per cent., one-half of the heat produced by the combination of the H with the O is set free in the battery, and raises its temperature. By passing through the battery a sufficient excess of air, we can keep the temperature of the battery constant at about 40° C., and at the same time carry off the whole of the water formed in the battery by means of the gases issuing from it, so that the platinum black is kept sufficiently dry, and the porous plate in nearly the same state of humidity.

The E.M.F. of the open battery is very considerably below what it should be according to Thomson's theorem. The combustion of H and O should produce an E.M.F. of 1·47 volts, while we only obtain 0·97. It does not seem to us probable that this difference can be explained in the same way as the deviations from this theorem in a number of

* ' Phil. Mag.,' vol. 9, 1881, p. 169.

† ' Comptes Rendus,' vol. 77, 1873, p. 649.

‡ ' Annales de Chimie,' vol. 30, 1883, p. 519.

abnormal voltaic batteries have lately been explained by Chroustchoff and Sitnikoff,* viz., by the Peltier effect, which would probably not be different for the combinations HPt,SO_4H_2 and SO_4H_2,PtO ; nor do the causes by which Herroun† explains this deviation appear to us to be applicable to the gas battery. It seems more probable—and what we have stated above respecting the rapid loss of the E.M.F. when taking out larger currents favours this view—that this loss of energy is to some extent due to the heat given out in the condensation of the gases by the platinum black.

Favre‡ found the heat given out by the condensation of 1 gram of H by platinum to vary from 23,000 to 13,000 calories, and concluded that this condensation was analogous to the condensation of carbonic acid by carbon, a purely capillary action. He did not determine the heat of condensation of oxygen.

Berthelot§ found the heat of condensation of H by platinum to vary per gram of H condensed from 17,000 to 8700 cal., and concluded that the H formed two distinct combinations with the platinum, the first taking place with a disengagement of 17,000 cal., and then combining with another equivalent of H with a disengagement of 8700 cal.

Berthelot also attempted to determine the heat given out by the absorption of O by platinum, which gas he found to be absorbed only in very small quantities, so that he could not determine the caloric effect with any amount of certainty; but he calculates it from the figures he obtained at at least 17,000 cal. for 8 grams of O. But these figures would lead to a much larger loss of energy than we find actually to take place. According to Berthelot, the condensation by platinum of 1 gram of H and 8 grams of O produces 25,700 to 34,000 cal. We obtain in the battery out of 34,187 cal. (resulting from the combination of 1 gram of H with 8 grams of O) 23,512 cal. as electricity, thus losing 11,666 cal. We are engaged upon an investigation of this rather difficult subject, with a view to further elucidating its effect upon the gas battery.

The fact that PdH, which, according to Favre,‖ is formed with an evolution of only 4150 cal. per 1 gram of H (a figure which agrees fairly well with that obtained by calculation from the tension of PdH), produces, if opposed to PtO, a smaller E.M.F. than PtH, has also to be considered in studying this question.

Using Pd black on gold foil opposed to Pt black on Pt foil in our battery, we found the E.M.F. $PdH,H_2SO_4,PtO = 0·91$ volt, as compared to 0·97 volt for PtH,H_2SO_4,PtO.

* 'Comptes Rendus,' vol. 108, 1889, p. 987.
† 'Phil. Mag.,' vol. 27, 1889, p. 209.
‡ 'Comptes Rendus,' vol. 77, 1873, p. 649.
§ 'Annales de Chimie,' vol. 30, 1883, p. 519.
‖ 'Comptes Rendus,' vol. 68, 1869, p. 1525.

In the hope of throwing some light upon the question of the disappearance of energy in the gas battery, we have determined the E.M.F. of the following combinations by means of a block of plaster of Paris impregnated with sulphuric acid, one end of which was covered with platinum foil and platinum black and arranged so that it could be exposed to H or O, while the other end was plunged into a beaker which contained the liquid electrolyte and the electrode which we wished to examine.

	Found.	Theory.	Difference.
PtH,H_2SO_4,PtO	$= 0\cdot97$ volt	$= 22,512$ cal.* instead of $34,178$ cal.†—	$11,666.$
Zn,H_2SO_4,PtO	$= 1\cdot77$ volt‡	$= 41,078$ cal. instead of $53,043$ cal. $-$	$11,965.$
Cd,H_2SO_4,PtO	$= 1\cdot425$ volt‡	$= 33,171$ cal. instead of $44,928$ cal. $-$	$11,767.$
Cu,H_2SO_4,PtO	$= 0\cdot70$ volt‡	$= 16,245$ cal. instead of $27,978$ cal. $-$	$11,733.$
$PtH,H_2SO_4,CuSO_4,Cu$	$= 0\cdot31$ volt	$= 7,194$ cal. instead of $6,200$ cal. $+$	$994.$
$PtH,H_2SO_4HNO_3,C$	$= 1\cdot19$ volt	$= 27,617$ cal. instead of $29,175$ cal. $-$	$1,558.$
PtO,H_2SO_4,HNO_3,C	$= 0\cdot22$ volt.		

These figures show that the loss of energy is very nearly the same per equivalent of O consumed, when PtO is used as the negative electrode, whether PtH, zinc, cadmium, or copper is used as positive electrode, and also that PtH with copper in copper sulphate, or carbon in nitric acid, as negative electrodes, gives nearly the theoretical E.M.F. It would thus seem as if the loss of energy in the gas battery occurred on the PtO electrode; but the question is undoubtedly a complicated one, and requires further study before an explanation of it can be attempted.

This battery differs from all other gas batteries in showing all the characteristics of polarisation after it has been at work for some length of time. It loses within an hour from 4 to 10 per cent. of its E.M.F. As the chemical processes taking place at the electrodes could not explain this, we had to look out for its cause in another direction, and found it to be the transport of the sulphuric acid from the O to the H electrode, resulting in the acid becoming gradually more concentrated on the positive side and weaker on the other, which we have established by analysing the gypsum scraped off below the platinum leaf at both sides. Probably this difference of concentration of the acid sets up a counter-current. In order to counteract this disturbing influence and to keep the current constant, we interchange the gases in the battery from time to time, say once an hour, so that the current goes in an opposite way through the porous diaphragm, and transports the sulphuric acid back. This necessitates,

* 1 Daniell $= 25,065$ cal. $= 1\cdot08$ volts.

† Calculated from Thomsen's data ('Thermochemische Untersuchungen') divided by 2, so as to refer to $O = 8$.

‡ Wright and Thompson found $1\cdot75, 1\cdot5$, and $0\cdot78$ respectively ('Roy. Soc. Proc.,' vol. 44, 1888, p. 182).

where constant currents are wanted for a longer period, the working
of a number of elements or batteries connected by means of a com-
mutator in such a way that one element or battery will always be out
of the circuit, and have its gases changed, and be replaced in the
circuit at the moment when the next element or battery is switched
out for the same purpose.

In using, in place of sulphuric acid, a solution of sodium chloride
as electrolyte, we found, after working the battery for some time,
sodium hydrate on one side and HCl on the other side of the battery,
and have been able to determine in this case the polarisation to be
equal to 0·54 volt, which very nearly accounts for the difference
between the E.M.F. of the open battery and the E.M.F. calculated
according to Thomson's theorem.   The E.M.F. of PtH,NaClAq,PtO
we found equal 0·86 volt, which, added to the polarisation of
0·54 volt just mentioned, gives a total of 1·40 against the theoretical
figure for H, O = 1·47.   By changing the gases after the polarisation
was fully established, the battery showed an E.M.F. of 1·39 volts.

This observation, as well as the determinations of Peirce,[*] of the
E.M.F. of gas batteries with the same gases and different electrolytes,
shows that the electrolyte also has considerable influence upon the
E.M.F.

We hope by further investigation to arrive at assigning their
proper value to the various causes affecting the E.M.F. of gas
batteries.

VI. "Contributions to the Chemistry of Storage Batteries.
No. 2."   By E. FRANKLAND, D.C.L., F.R.S.   Received
June 18, 1889.

Under this title I communicated to the Royal Society, in February,
1883,[†] the results of some experiments on the reactions occurring
during the charging and discharging of a storage cell. I showed that
no appreciable part of the storage effect was due to occluded gases,
as had been previously suggested by some chemists and physicists;
but that the act of charging consisted essentially in the decomposi-
tion of lead sulphate whilst the discharge was produced by the re-
composition of this salt.

The establishment of these, as practically the only reactions going
on in a storage cell, enabled me to prescribe a very simple method by
which the charge in any cell could be ascertained; for as sulphuric
acid is liberated during the charging and absorbed by the active
material of the plates during discharge, the amount of charge could

* 'Wiedemann, Annalen,' vol. 8, 1879, p. 98.
† 'Proceedings of the Royal Society,' vol. 35, p. 67.