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THE STORAGE BATTERY.

by

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THE STORAGE BATTERY.

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 { Faure.
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III. General Theory.

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THE STORAGE BATTERY.

HISTORY.

The first storage cell was invented in 1801 by M. Gautherot but not until 1881 was it used to any extent. There is record of the application of a storage battery in England in that year. The first battery installed in this country was at a central station in Phillipsburg, Pa., in 1885 while 1889 marks the beginning of the general application of the storage battery in the commercial world. The storage battery or accumulator consists of two inert plates of metal or some oxide of metal placed in an electrolyte which is incapable of acting upon ~~them~~ chemically, until by the action of an electric current passed through the cell, the nature of the material on the plates is changed.

As a mark of the growth of the use of storage cells the following table might be of interest:

Year.	Growth in lbs.
1894	349,000
1895	1,112,000
1896	2,318,000
1897	3,607,300

This shows that about ten times as much battery was installed in 1897 as in 1894, three years before.

TYPES.

There are three types of cells which are of commercial importance; Plante', Faure and Alkaline.

The alkaline type of cell is not much used in practice today.

There are four advantages claimed for the Faure type of cell over the Plante', viz.,

1. They have less weight per unit of power.
2. Better retention of the paste or active material.
3. Provision for better contact between the supporting plate and active material.
4. Prevention of buckling.

It has been found in general practice that the storage of energy in an accumulator is from four to six watts per pound of battery. That is a battery weighs one hundred twenty-five to one hundred eighty-six pounds per horse power hour at its terminals, or if its available energy were all expended in gravitational work the average battery would lift itself through a vertical distance of two to three miles.

The Edison cell is one which has recently come into prominence. Its advantages are supposedly;- Absence of deterioration by work; Large storage capacity per unit mass: Capability of being rapidly charged or discharged without injury: Capability of withstanding the careless treatment of the ignorant attendant: Inexpensiveness.

This cell contains iron or iron gauze with super oxide of nickel immersed in an electrolyte composed of an aqueous solution of Potassium hydroxide. It weighs fiftythree and three tenths pounds

per horse power hour and is thus capable of lifting itself seven miles.

GENERAL THEORY.

As yet there is very little known as to the real combinations and reactions which take place in the storage cell. The general theory may be stated briefly thus:-

During discharge the active material of both plates is converted into lead sulphate, $Pb\ SO_4$, with the extraction of the Sulphion from the electrolyte and hence a reduction in its density. The reaction at the positive plate is supposed to take place in two distinct stages. First the $Pb\ O_2$ is reduced to $Pb\ O$ and then a mutual exchange takes place forming $Pb\ SO_4$ and H_2O . On charging the reaction is reversed, $Pb\ O_2$ is formed on the positive plates and Pb , metallic lead, on the negative while the $S\ O_4$ ion forms $H_2\ SO_4$ increasing the density of the electrolyte.

Some investigators believe that it is hydrated peroxide of lead, $H_2\ Pb_2\ O_5$, which forms at the positive plate, rather than $Pb\ O_2$.

USES.

Storage batteries are rapidly superceding primary batteries in the telephone and telegraph office and the modern electrical laboratory which has no storage battery is not considered as fully equipped.

In the cities of the eastern part of the United States the use of storage batteries is quite common in residences which are so far from the source of supply that too great a loss would be incurred in transmission, in office and business blocks where it is necessary to operate elevators and lights in parallel, and in buildings where power can be obtained at only one part of the day while it must be used at another.

But by far the most wide spread, as well as the most useful application of the storage battery is in connection with Street and Interurban Railway work. The practice is to install the battery in parallel with the generators and in series with a differential booster. This is a machine having two fields so arranged that when the line load is light the booster forces the generators to charge the battery, while when the line load is heavy the booster magnetization is changed and current is drawn from the battery.

Thus the battery becomes an automatic regulator taking all the fluctuations of the line and maintaining the generator load practically constant at the average. Thus it also permits of less expense of installation and operation for since generator capacity need be installed for only the average load, which is constant, the need of extra help in operating as well as extra idle generators is entirely done away with.

ABUSES.

There are a few important things to remember when dealing with a storage battery; first, never over charge, for after it is fully charged all the gases formed escape into the air and hence the energy used in liberating them is wasted. Second, never discharge the battery below 1.8 volts per cell; third, never place the plates in the electrolyte until ready to charge, fourth, never charge or discharge the battery at a greater rate than the maximum as given by the makers, and fifth, never allow the battery to stand discharged. If it cannot be fully charged give it what charge you can, even a partial charge is better than none at all.

As stated above the effect of over charging is a waste of energy for all the energy not used in the formation of lead peroxide

and spongy lead can not be gotten out of the cell on discharge. Hence, the efficiency is temporarily reduced.

If the cell is over discharged (below 1.8 volts with current flowing) the effect is an excessive formation of lead sulphate, $Pb SO_4$, which must be immediately removed by an over-charge. If however, the cell is only given the normal ampere-hour charge and an over discharge is persisted in the formation of $Pb SO_4$ which is not removed on charging soon becomes so thoroughly embedded in the plate that immediate and strenuous treatment must be given or the cell is ruined by sulphating. The effect of placing the plates in the electrolyte before charging current is ready for application is the same as that, of allowing the battery to stand discharged; the acid causes a slow separation of the active materials from the foundation plates.

By charging at an excessive high rate the formation of $Pb O_2$ is so rapid that it ~~does~~ not have time to distribute itself over the plate and any of several things may result the action ^{being} too rapid for proper distribution is liable to cover a part of the $Pb SO_4$ formed on the positive plate by the previous discharge and thus increase the liability to sulphating. Or it may cause the plates to buckle or bend. This buckling is the natural effect when if the plates are a little closer together at one point than another, too high a current, either on charging or discharging is used. The philosophy may be stated as follows: If two plates are quite close together at one point and a current is passed through the battery this current, tending to take the path of least resistance will concentrate itself at the point where it can get from one plate to the other through the least quantity of electrolyte; this concentration not only causes a reduction of the amount of current flowing between the plates where they are farther apart but a corresponding change in the chemical activity at these

various points. Thus, if the battery is being charged the formation of PbO_2 at the positive plate, being more rapid at one point than at the other the bulk of the plate at the point of more rapid formation will more rapidly increase and in accordance with the laws of physics the plate will bend at that point, as it bends the distance between it and the opposite plate, and hence resistance at that point is decreased and a still further increase in current density results, hence a more rapid formation of active material and a more rapid bending. Thus, excessive rates of charging will cause the positive plate to buckle but an excessive rate of discharge may cause a buckling of either positive or negative plate; the formation in this case being lead sulphate on both plates. If a plate starts to buckle it should receive immediate attention for the more it bends the more rapidly will it bend and very shortly it will be so far over as to touch the other plate and a short circuit results destroying the cell.

Data. First Charge.

Volts #2	Volts #5	Amp.	Amp. Hours
0.	0.	0.	0.
1.8	1.9	.8	.734
1.9	1.95	.75	1.317
1.95	1.97	.8	1.98
1.97	2.	.8	2.78
1.9	1.9	0.	2.78
1.95	1.97	.8	3.58
2.	2.	.8	4.18
2.02	2.05	.77	4.75
2.05	2.	.75	5.12
2.05	2.05	.75	5.49
2.08	2.08	.75	5.86
2.08	2.08	.75	6.43
2.	2.	.0	6.43
2.15	2.15	.8	7.13
2.2	2.18	.6	7.63
2.2	2.2	.7	7.86
2.05	2.05	.0	7.86
2.2	2.2	.8	8.19
2.18	2.2	.8	8.45
2.	2.	.0	8.45
2.2	2.2	.8	8.85
2.2	2.2	.8	9.05
2.2	2.2	.8	9.45
2.	2.	.0	9.45

Data. First Charge (con).

Volts #2	Volts #5	Amp.	Amp. Hours
2.2	2.2	.0	9.64
2.22	2.25	.75	10.02
2.25	2.25	.75	10.39
2.27	2.27	.75	10.85
2.25	2.25	.75	11.41
2.25	2.25	.75	12.16
2.08	2.08	.0	12.16
2.2	2.2	.75	12.23
2.25	2.25	.75	13.1
2.25	2.25	.75	14.16
2.25	2.25	.75	14.91
2.25	2.25	.75	15.54
2.	2.	.0	15.54
2.2	2.2	.75	15.72
2.25	2.25	.75	16.00
2.26	2.26	.75	16.62
2.25	2.25	.5	17.13
2.25	2.25	.5	17.45
2.25	2.25	.5	17.95

Decay on Open Circuit.

Time, Minutes	Volts #2 and #5.
0	2.25
10	2.15
15	2.13
22	2.12
30	2.1
40	2.05
60	2.

First Discharge of #2.

Volts	Amp.	Amp. Hours.
1.85	0	0
1.85	.75	.56
1.85	.75	1.12
1.84	.75	1.87
1.83	.75	2.62
1.81	.75	3.37
1.81	.75	3.93
1.805	.75	4.93
1.8	.75	6.18
1.8	.0	6.18
1.8	.75	6.37
1.83	.0	6.37
1.78	.75	6.68
1.77	.75	6.86

Data. Second Charge of #2.

<u>Volts</u>	<u>Amp.</u>	<u>Amp. Hours.</u>
1.85	0	0
1.95	1.16	.96
1.95	1.16	2.13
1.95	1.16	2.51
1.9	.0	2.51
1.97	1.15	2.7
1.98	1.15	2.99
1.98	1.15	3.95
2.	1.15	4.9
2.01	1.15	5.86
2.02	1.15	7.02
1.9	.0	7.02
1.99	1.15	7.12
2.01	1.15	7.21
2.02	1.15	7.5
2.03	1.15	7.78
2.05	1.15	8.74

Data. Second Discharge #2.

<u>Volts.</u>	<u>Amp.</u>	<u>Amp. Hours.</u>
1.85	.0	.0
1.84	1.1	.73
1.83	1.1	1.1
1.85	.0	1.1
1.82	1.12	2.22
1.81	1.12	3.34
1.8	1.1	4.44

Data. Third Charge #2.

<u>Volts</u>	<u>Amp.</u>	<u>Amp. Hours.</u>
1.88	.0	.0
1.98	1.2	1.2
2.05	1.2	3.
2.05	1.2	4.2
1.95	.0	4.2
2.15	1.25	6.7
1.94	.0	6.7
2.12	1.2	6.8
2.15	1.2	6.9
2.17	1.2	8.
2.2	1.2	9.1

Data. Third Discharge #2.

<u>Volts</u>	<u>Amp.</u>	<u>Amp. Hours.</u>
1.9	.0	.0
1.875	1.2	.3
1.875	1.2	.6
1.87	1.2	1.
1.85	1.2	2.2
1.83	1.2	3.8
1.81	1.2	4.8
1.8	1.2	5.1
1.8	1.2	5.2
1.79	1.2	5.5

Data. Fourth Charge #2.

Volts	Amp.	Amp. Hours.
1.9	.0	.0
1.99	1.2	.4
2.	1.2	1.6
2.	1.2	2.8
1.95	.0	2.8
2.08	1.2	4.9
2.01	.0	4.9
2.12	1.2	5.6
2.16	1.2	6.1
2.2	1.2	6.8
1.95	.0	6.8
2.15	1.2	7.0
2.2	1.2	8.1
2.2	1.2	8.4
2.2	1.2	8.8
2.23	1.2	10.
2.25	1.2	11.2

Data. Fourth Discharge #2.

Volts	Amp.	Amp. Hours.
1.875	.0	.0
1.86	1.25	.94
1.85	1.25	1.97
1.84	1.25	3.85
1.87	.0	3.85
1.85	1.25	4.06
1.84	1.25	4.47
1.8	1.25	6.55

Data. Fifth Charge #2.

Volts	Amp.	Amp. Hours.
1.84	.0	.0
2.	1.25	1.66
2.	1.25	2.92
1.95	.0	2.92
2.01	1.25	4.82
2.06	1.25	5.44
2.075	1.25	6.06
2.125	1.25	7.20
2.15	1.25	7.92
2.2	1.25	8.87
2.21	1.25	9.49
1.95	.0	9.49
2.2	1.25	9.80
2.	.0	9.80
2.22	1.25	10.84

Voltage Decay on Open Circuit. #5.

Time Minutes.	Volts.
0	2.24
1	2.2
2	2.16
3	2.14
4	2.13
8	2.105
17	2.075
21	2.07
24	2.065
29	2.055

Voltage Decay on Open Circuit. #5

Time, Minutes	Volts.
36	2.05
40	2.047
45	2.035
48	2.03
50	2.03

Internal Resistance During Charge American #12.

Amp. Hours	Resistance
0	.057
3	.05
9	.0433
11	.0416
13	.04
15	.0383
15.75	.038
17.25	.0366
18.5	.036
20.4	.035
22	.0343
24	.033
25	.05
25.5	.09

Data. Charging American #1.

Volts	Amp. Hours.
1.83	.0
1.9	1.25
2.	2.5

"Chloride Accumulator"

CAPACITY CURVE
#5

SHEET #10

RATE OF DISCHARGE

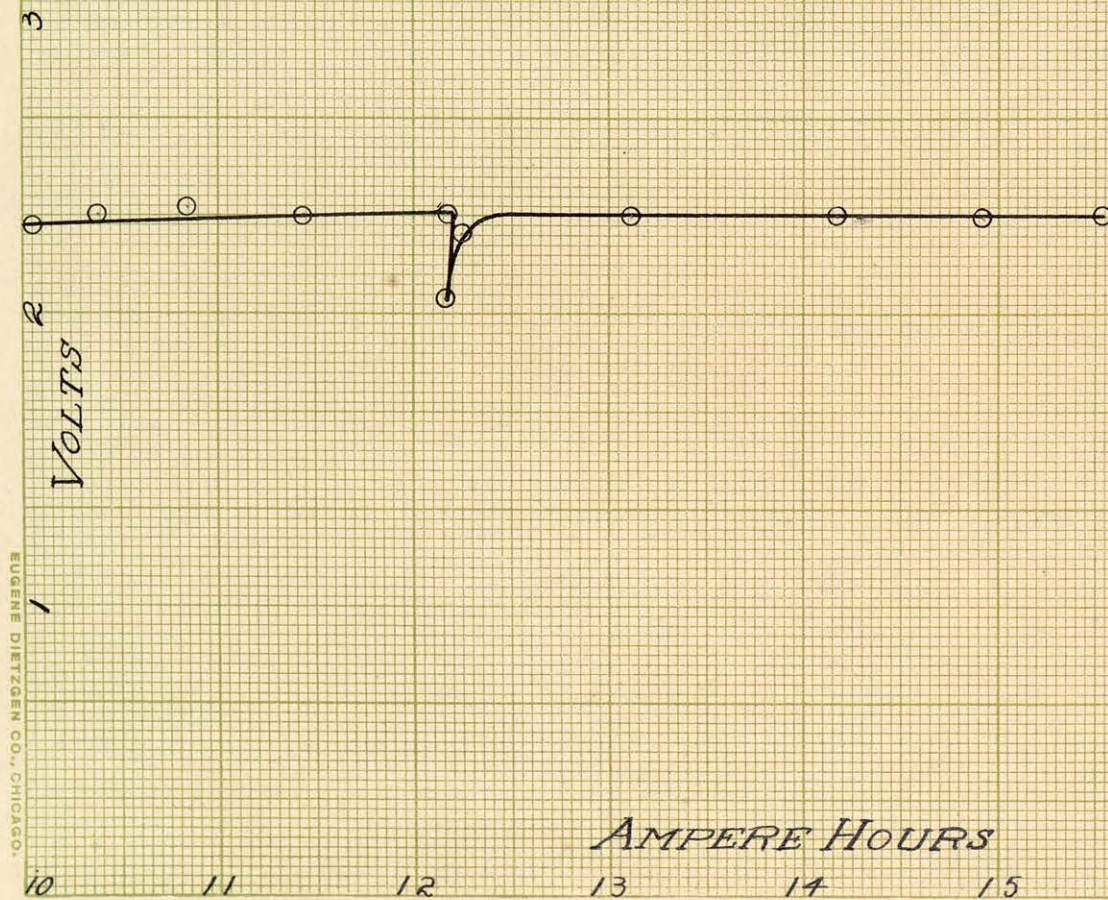
AMPERE HOURS

EUGENE DIETZGEN CO., CHICAGO.

.5 1 3 11 13 15 17 19 LCF-CAM



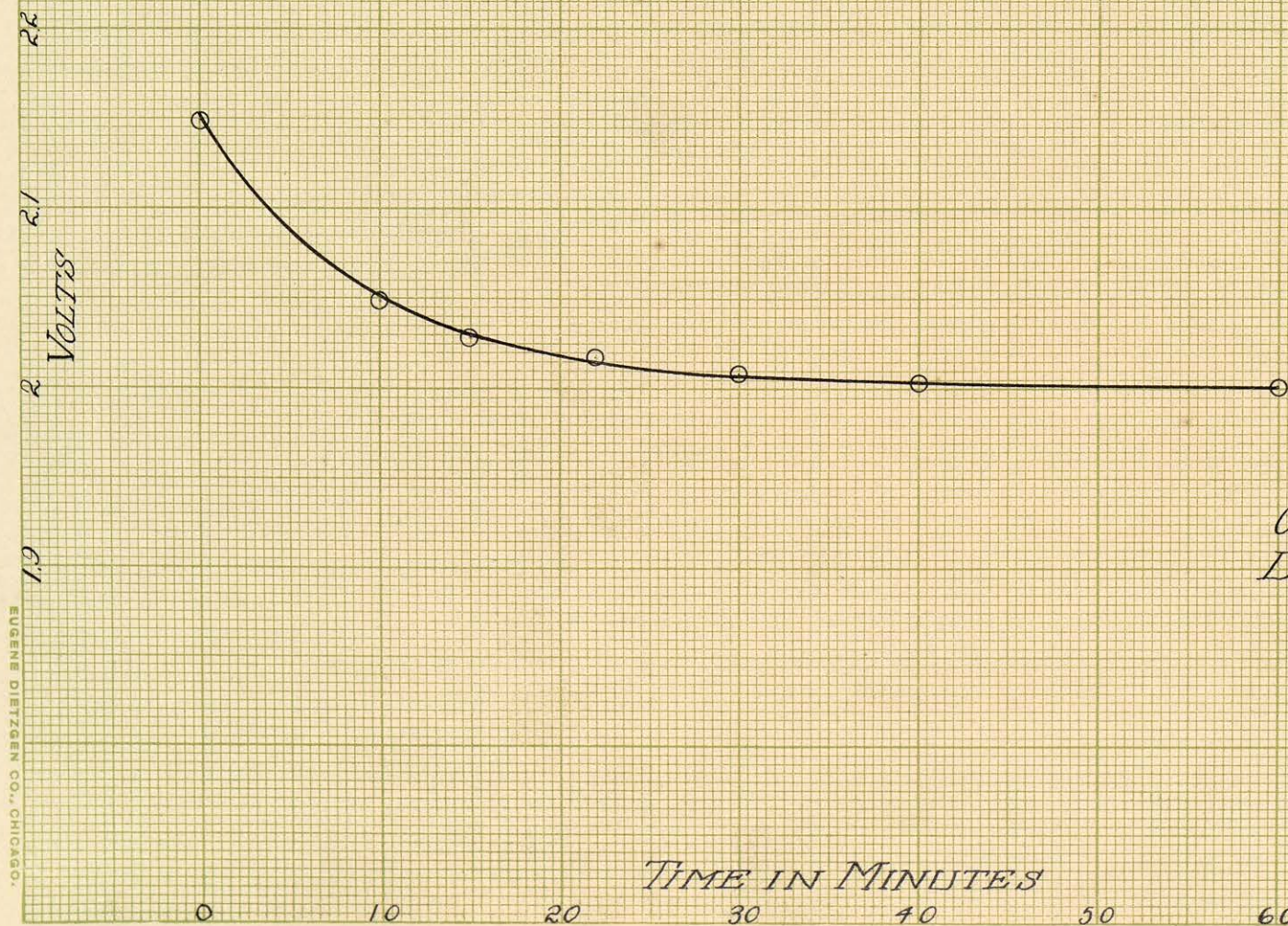
"Chloride Accumulator"



FIRST CHARGE CURVE
CONTINUED

SHEET #2

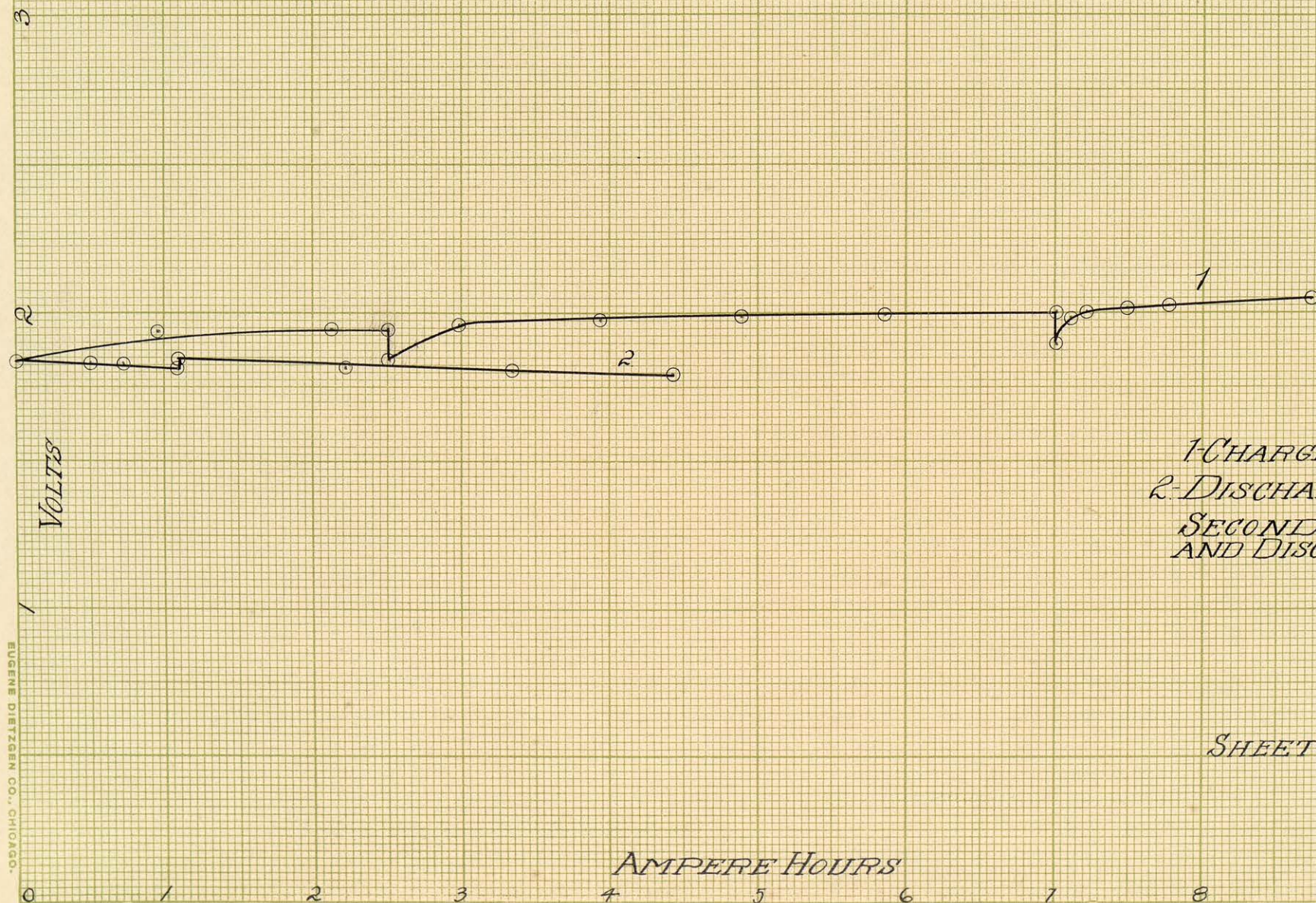
"Chloride Accumulator"



*CURVE SHOWING VOLTAGE
DECAY ON OPEN-CIRCUIT
#2.*

SHEET #3

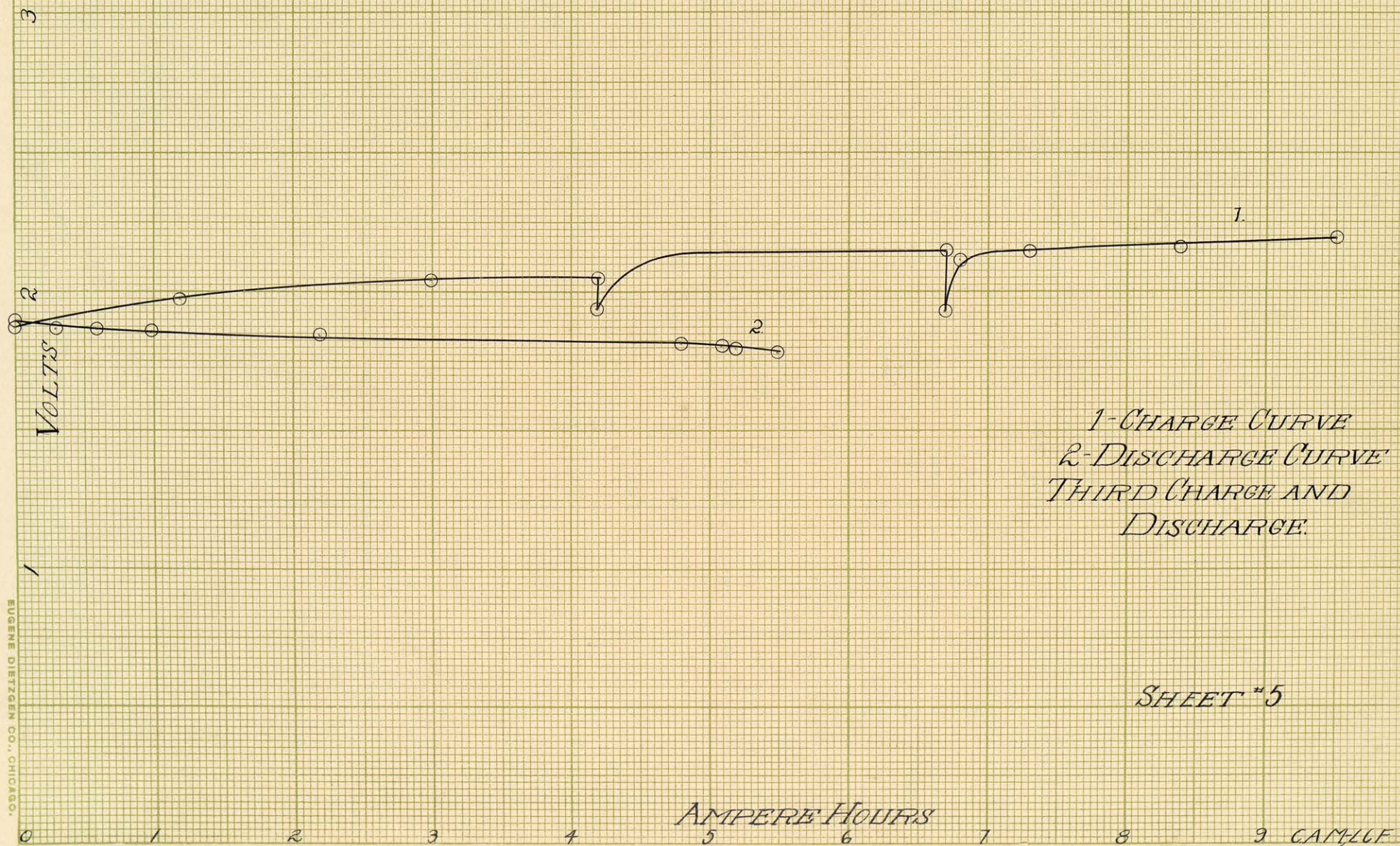
"Chloride Accumulator"



1-CHARGE CURVE
2-DISCHARGE CURVE
SECOND CHARGE
AND DISCHARGE

SHEET "4"

"Chloride Accumulator"

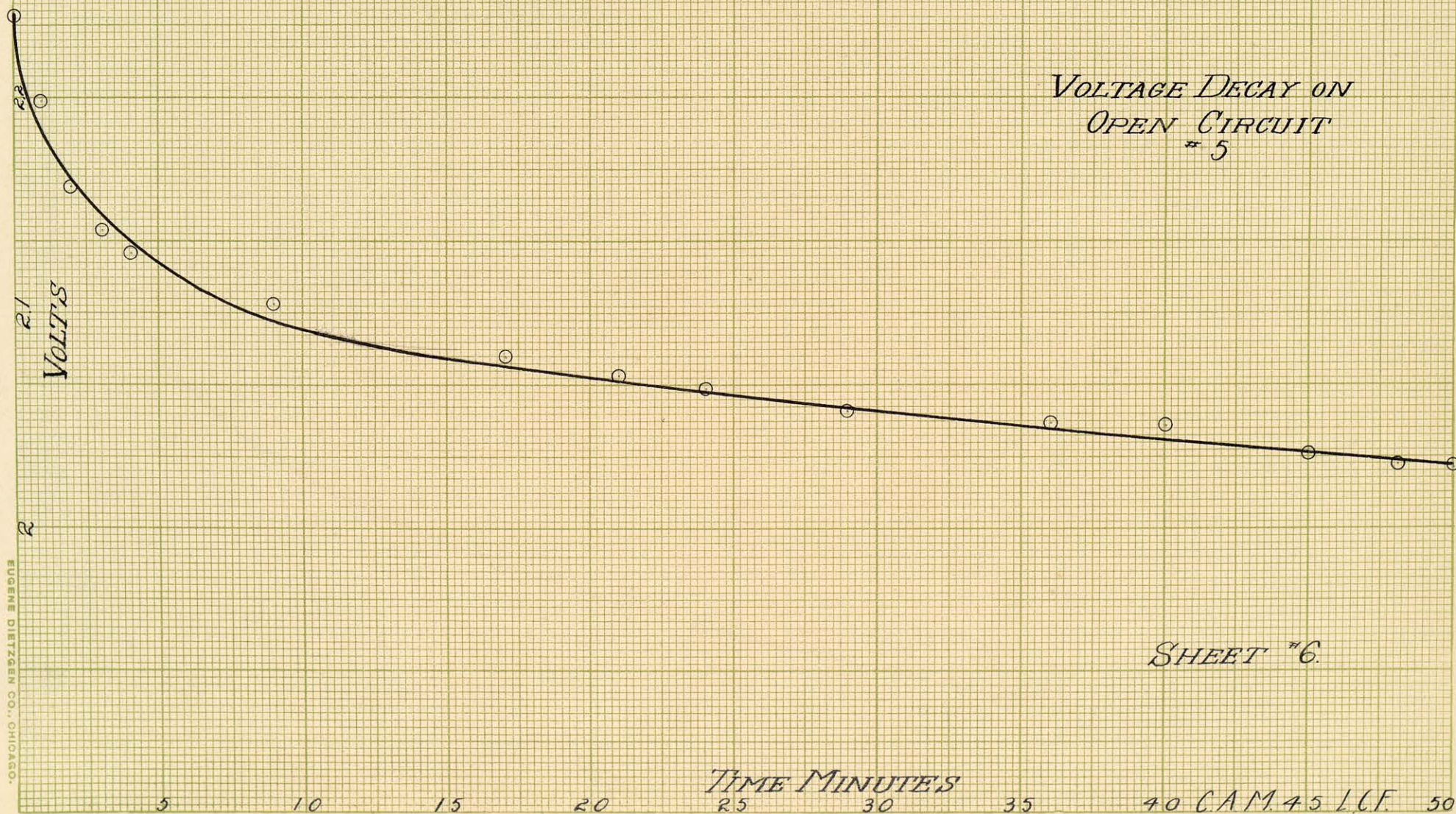


1-CHARGE CURVE
2-DISCHARGE CURVE
THIRD CHARGE AND
DISCHARGE.

SHEET #5

"Chloride Accumulator"

VOLTAGE DECAY ON
OPEN CIRCUIT
#5



SHEET #6.

"American Cell"

VARIATION OF
INTERNAL RESISTANCE
ON CHARGE

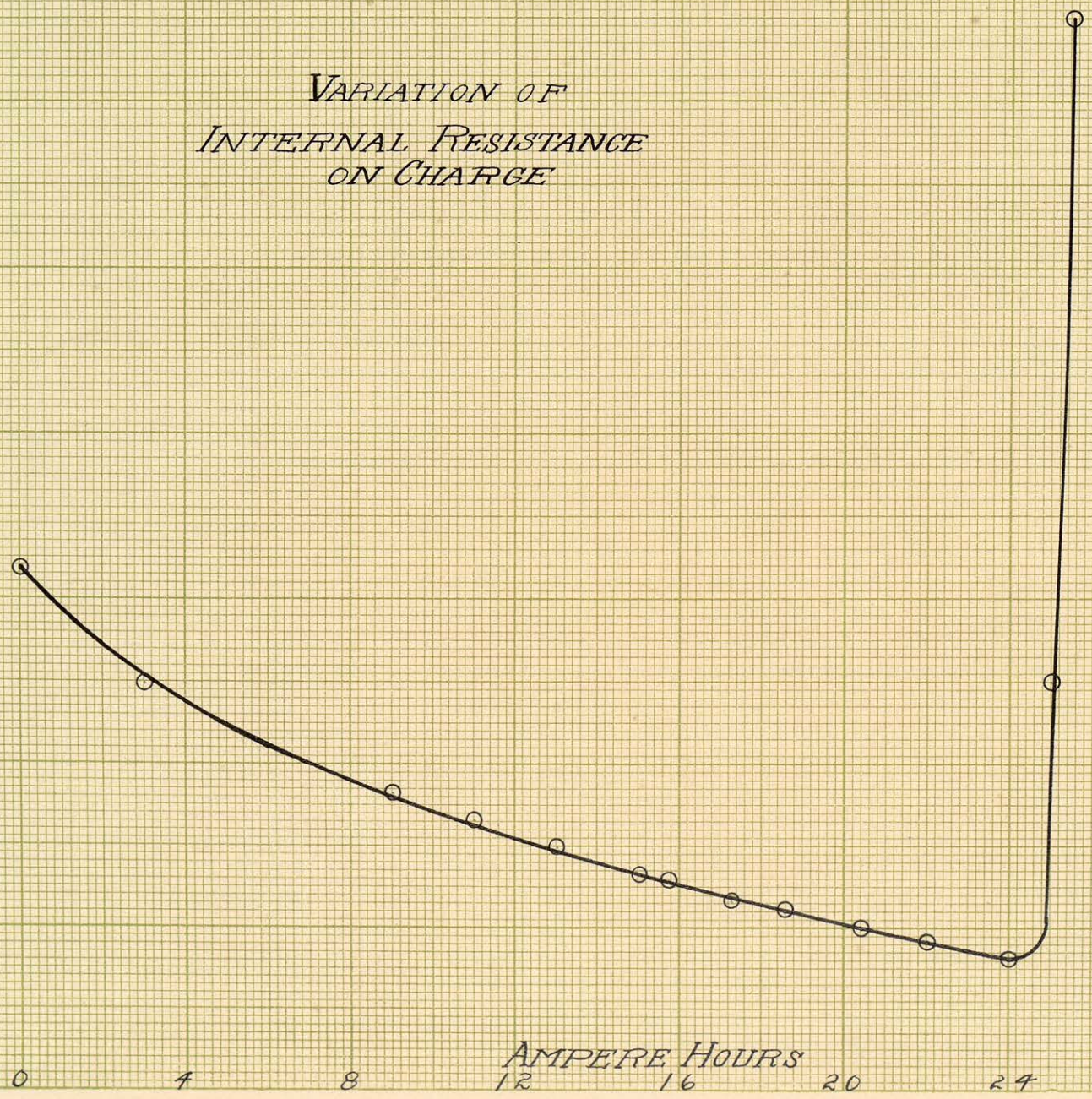
INTERNAL RESISTANCE

EUGENE DIETZEN CO., CHICAGO.

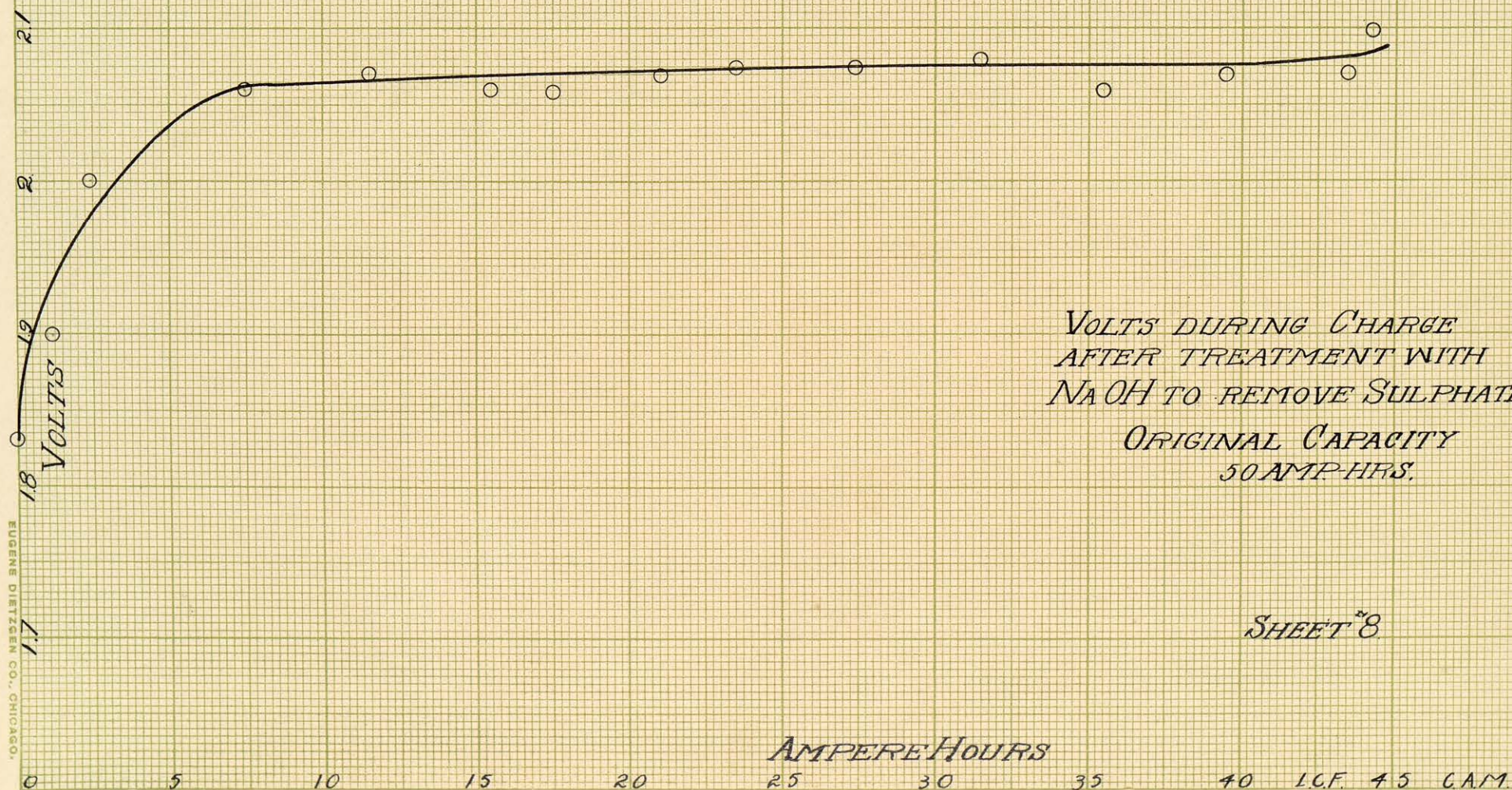
AMPERE HOURS

SHEET "I"

CAM-L.C.F.



"American Cell"



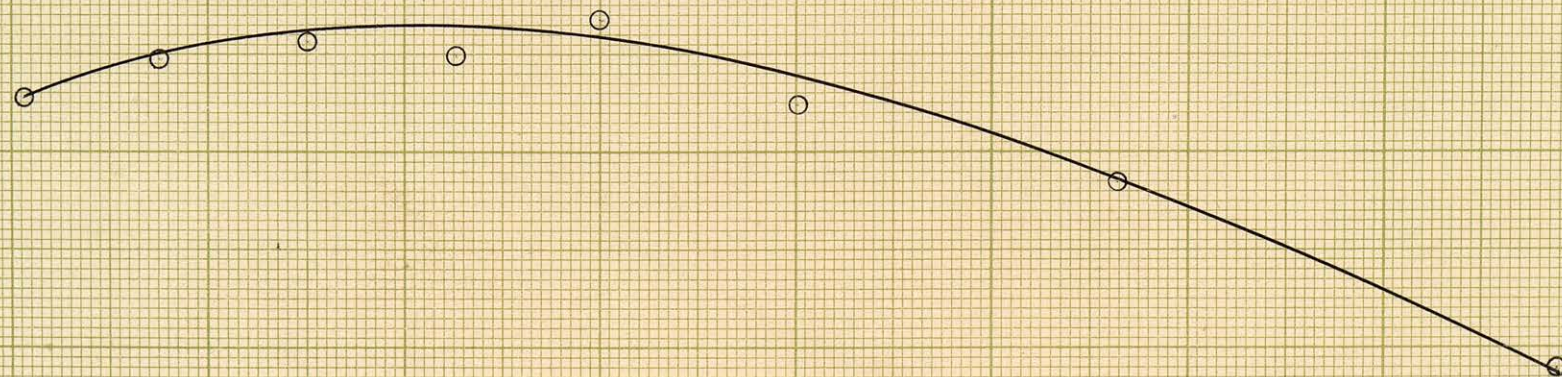
VOLTS DURING CHARGE
AFTER TREATMENT WITH
NaOH TO REMOVE SULPHATE
ORIGINAL CAPACITY
50 AMP-HRS.

SHEET "8"

AMPERE HOURS

"Chloride Accumulator"

100
80
60
40
20
% EFFICIENT



EFFICIENCY CURVE
#2.

SHEET #9

HOURS CHARGE

1

3

5

7

9

11

LOF-CAM 13

"Chloride Accumulator"

CAPACITY CURVE
#5

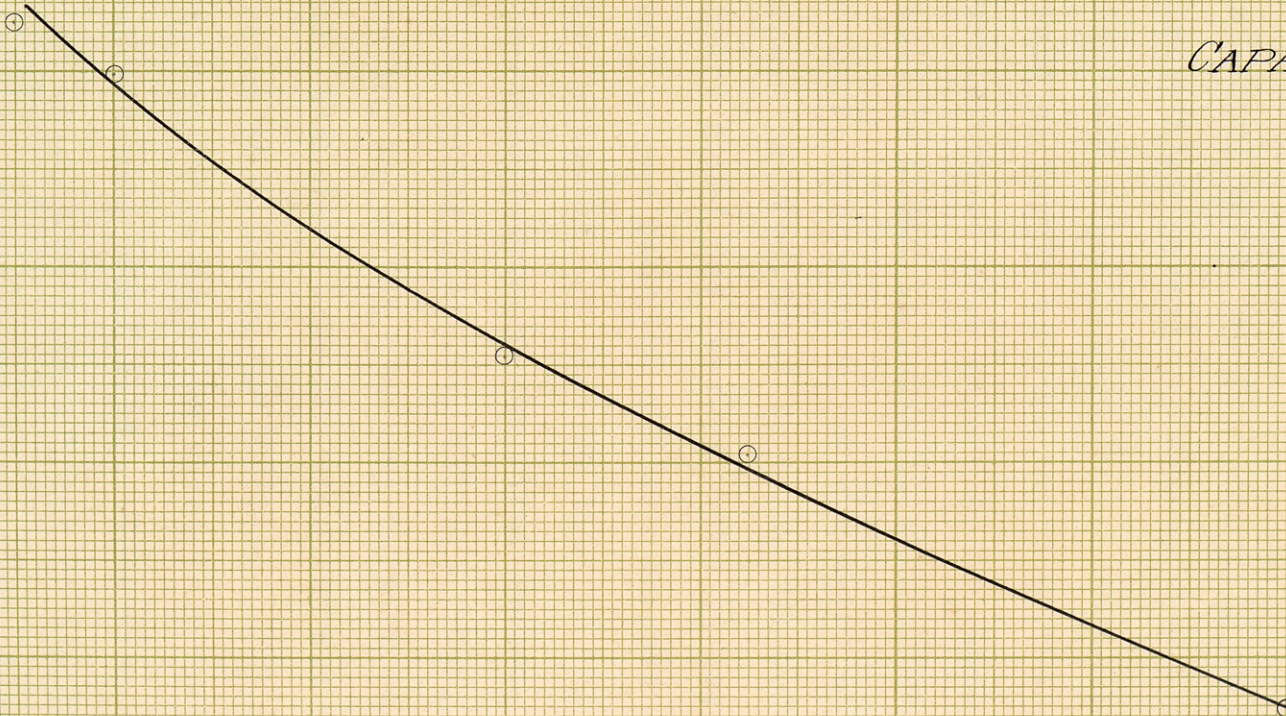
SHEET #10

RATE OF DISCHARGE

AMPERE HOURS

EUGENE DIETZEN CO., CHICAGO.

5 1 3 11 13 15 17 19 LCF-CAM



Data Charging American #1. (con

Volts	Amp. Hours.
2.05	3.3
2.06	7.5
2.07	11.5
2.06	15.5
2.06	17.5
2.07	21.
2.075	23.5
2.075	27.5
2.08	31.5
2.06	35.5
2.07	39.5
2.075	43.5
2.1	44.25

Efficiency Data #2.

Time Charge	% Eff.
1:05	86
2:00	90
3:00	91.4
4:00	90.
6:20	85
5:00	94.5
8:22	77
11:30	57.8

Capacity Data #5.

Rate of Discharge	Amp. Hours. Discharged.
.5	10.25
.6	10.
1.	8.55
1.25	8.05
1.8	6.75

DISCUSSION.

First Charge.

When a cell is first received from the makers it should be given a charge of about twice the full capacity in ampere hours but at a rate much lower than normal. This is the finishing touch of the forming process and greatly adds to the durability of the plates. Following this rule as nearly as time would permit we charged a number of chloride accumulators of 12.5 ampere hours capacity eighteen ampere hours. The result is shown in Curve 1, sheets one and two.

The E. M. F. rose from 0. at the start to 1.9 volts at one ampere hour charge. It continued to rise, but more slowly, until a charge of 2.8 ampere hours was reached where it was cut off, it being the noon hour, and in one hour the voltage dropped to 1.9. When the current was again turned on the voltage rose as the ampere hours increased, but more rapidly than in the first period. So all along the curve there are breaks where the voltage drops. These are due to lapses of time during which the charging current was cut off. It will be noted, however, that each time the charging was resumed the rise at first was more rapid than during the corresponding time of the preceding period. The discharge curve on sheet 1 is seen to be a straight line gradually approaching the X axis. Comparing this curve with the discharge curve on sheet 4 we find a break in the latter. This is caused by the stopping of discharge for a time, during which the PbSO_4 distributed itself exposing more PbO_2 to be reduced. This action would of itself raise the E. M. F.

The cells tested would not stand at 2 volts on open circuit but after each charging interval the voltage dropped to about 1.97. This is the point at which the discharge curve starts.

Decay of Voltage on Open Circuit after Charging.

As the charging current nears the limit of the capacity of the cell the voltage begins to show a tendency to rapidly rise, as does also the internal resistance. This tendency to rapidly rise is caused by the presence of combined gases near the plates. If now, the cell having been fully charged, the circuit is broken and readings of the E. M. F. are taken at intervals of, at first, not more than one minute, later (after about ten minutes) the interval should be increased, it will be found that within the first two or three minutes the pressure will fall very rapidly. Then the decrease becomes more gradual and after a period of about an hour, readings taken thirty minutes apart are identical, that is the E. M. F. has reached the limit of its decrease on open circuit.

This decrease, as shown on curve sheets 3 and 6, may be accounted for by the same explanation given for the rise of E. M. F. and resistance at the end of charge. That is, when the circuit is first broken after charging there are present in the cell large quantities of hydrogen and oxygen which are unable to combine with either the electrolyte or plates or possibly forming H_2SO_4 . This unstable compound, if formed, rapidly breaks down leaving sulphuric acid and oxygen which latter is given off. As the breaking down action goes on the E. M. F. falls proportionally, but as it goes on it becomes slower and slower in operation. Thus the E. M. F. will fall rapidly at first and become more nearly constant as the surplus amount of gases decreases.

INTERNAL RESISTANCE.

Wishing to know the exact relation of internal resistance to the amount of ampere hours charge, we proceeded thus. Taking the

E. M. F. of the cell on open circuit immediately on breaking the circuit., make circuit and read the drop across the cell with current on. Now since the drop is due to E. M. F. and internal resistance $E - E$ is evidently the drop due to resistance. Divide this by the current flowing and we have R . Now below a certain point the resistance of H_2SO_4 decreases as the specific gravity increases. Hence, we should expect that as charging progresses R . decreases. This we found to be true, as shown by the first part of the curve on sheet 7. But when the point of full charge is reached the formation of uncombined gases has a tendency to insulate the plates from the electrolyte. If the formation of free gas produces this insulating effect more rapidly than the resistance due to change in the density of the electrolyte decreases the combined effect will of course be a rise in R . This, too we found but the sudden rise after such a gradual decrease can only be explained by saying that in this instance the current was not decreased and the evolution of gas increased the insulation of the plates much more rapidly than the increase of density decreased the resistance of the electrolyte. The curve as shown might lead one to believe that R . would be a good indication of the condition of the cell, but we found that the curve given could not be duplicated on any other cell. All other attempts gave a crescent shaped curve with about the same rapidity of increase at the end of charge as that of decrease at the beginning.

Treatment for Sulphating.

When a cell is subjected to continued over discharge without the accompanying over charge to overcome its evil effects the effect is a formation of lead sulphate, $Pb SO_4$ which so thoroughly embeds itself in the plates as to resist all efforts ordinarily used

to remove it. Then it is that an immediate remedy must be at hand.

Treadwell in his "Storage Battery" recommends as a remedy for sulphating, over charging. In several instances we tried this method and the result was without exception void of success. It may suffice where the cell is not too badly sulphated if the current used in charging is less than the maximum of the cell so as to permit of an even, thorough action throughout the plate. But the cells under our observation being treated in this way were evidently beyond hope of redemption by this method. In hopes of finding some way of bringing them up to usual voltage we short circuited one for twenty-four hours and then charged it, making the negative plate the positive and positive negative, that is a discharging current was forced through it. After it had run thus for eight hours the direction of current was reversed for ten hours, but the effect was only an excessive discharge and when the current was passed in the proper direction for charging the E. M. F. could not be brought above 1.6. Another cell of the same type and capacity was treated thus; The acid was removed and a strong solution of sodium hydroxide, Na OH was placed in the cell. With the plates in this solution a charge was given the cell. The result was a rise of voltage from 1.25 to 2, and the solution during charge changed from alkaline to acid with evolution of a very light gas. Investigation was immediately made and it was found that Na OH became Na SO₄ or H₂ SO₄ while on the positive plate Pb were formed. The result sought had been obtained.

The electrolyte was removed and H₂ SO₄ placed in the cell and charging current turned on. The charging curve obtained was normal (between 1.8 and 2.3 volts) and the cell, when turned over to the laboratory gave excellent service.

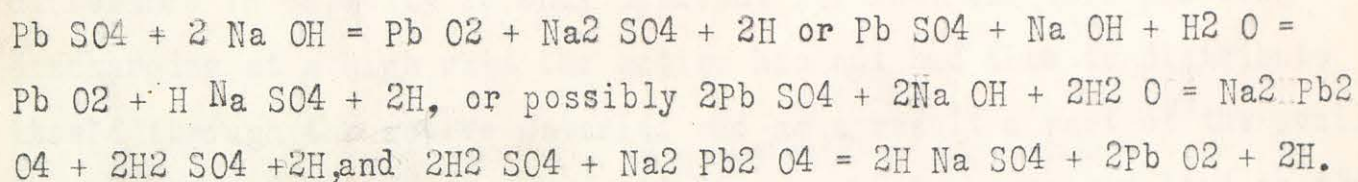
Immediately the cell which had been discharged so low by

the other treatment was treated in same manner with Na OH and the result was all that could be desired. The voltage of the cell rose to normal and the alkaline solution rapidly changed to acid and when more Na OH was added this, too, was overcome and an acid solution obtained. When this solution was removed and H₂ SO₄ took its place this cell also acted normally and afterwards gave good service in the laboratory.

Other cells were then brought out. One had been badly sulphated and then left standing for a year. It was given a charge with Na OH and then with H₂ SO₄ and the charging curve obtained is shown on sheet 8. Another had been standing dry for eighteen months with both plates entirely covered with Pb SO₄. In this one we used a solution of Potassium hydroxide instead of sodium hydroxide with equally good results. The reactions are the same except that potassium is substituted for sodium.

The effect of placing the plates in a bath of Na OH or KOH was tried but without results. The reaction in the cell when charging with Na OH (or KOH) as the electrolyte is supposed to be as follows:

At the Positive,



Analyses showed nothing of the presence of Na either in the electrolyte or on the plate but as the samples were taken at different times the condition of the cell may have been different.

Efficiency.

The efficiency of a cell is found to vary with different

amount of charge. Thus ~~we found that~~ a cell of 12.5 ampere hours, charging capacity was given a charge of 1.32 amperes for one hour and five minutes and then discharged to 1.8 volts and it was found to give out eighty-six per cent of the ampere hours put in. At a two hour charge it was ninety per cent efficient. And thus the curve was found to rise to about ninety-three per cent at five hours charge after which it falls, being seventy-seven per cent at eight hours and twenty two minutes charge and fifty-eight per cent at eleven hours thirty minutes. All charges were at a 1.32 ampere rate. An efficiency of eighty-five per cent for a six hour and twenty minute charge was probably a little low for this point was obtained after the cell had been overcharged one and one-half hours.

Capacity.

If the cell is discharged at different rates the amount (ampere hours) it is capable of giving out before its potential falls to 1.8 is found to vary. Thus when discharged at a .5 ampere rate the capacity of the cell under test was 10.25 ampere hours. At .6 amperes it was 10 ampere hours. At 1 ampere the capacity was 8.55 ampere hours and for 1.8 amperes the capacity is only 6.75 ampere hours. This difference in capacity is only apparent for when the cell has been discharging at a high rate the action has not had time to distribute itself through the active material and as a result a part of the available Pb O₂ on the positive as well as a part of the spongy lead on the negative plate is covered by PbSO₄ and further chemical action thus prevented. In proof of the theory that the low capacity is only apparent we may cite that if after a high rate of discharge has brought the voltage to 1.8 if the cell is allowed a short period of rest a considerable amount of energy may still be obtained from it at a lower

rate of discharge. Or if after a high discharge the cell is again charged it is found that only the amount taken out plus the usual amount to account for internal losses must be put in to restore it to full charge.