[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Studies on Lead Oxides.[1] III. The Radioactive Indicator Method Applied to the Lead Storage Cell

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Introduction

In connection with the general program of storage battery research which has been in progress in this Laboratory for some time, it has been considered desirable to perform an experiment in which individual lead atoms could be "tagged" and their history thus followed throughout the course of the chemical reactions which they undergo during the operation of the lead storage cell. Since Th-B is a radioactive isotope of lead having a relatively short half-life, it was considered suitable for the proposed investigation.

The double sulfate theory originally proposed by Gladstone and Tribe in 1882[2] states that during discharge, lead dioxide is reduced to Pb^{++} which precipitates out as $PbSO_4$, and that the lead of the negative plate is oxidized to Pb^{++} which also precipitates as lead sulfate. The over-all reaction may be written

$$PbO_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4$$

Perhaps the most successful alternative proposal has been the "higher oxide" theory advanced by Fery.[3] He represented the over-all reaction as: $2Pb + H_2SO_4 + Pb_2O_5 \rightarrow Pb_2SO_4 + H_2O + 2PbO_2$, where Pb_2O_5 is supposed to be the anhydride of the acid $H_2Pb_2O_6$. He based his conclusions on (a) his own data concerning the variation in the weight of the plates on discharging; (b) the discrepancies in the data of other investigators concerning the amount of acid used on discharge; (c) chemical analyses of plates in which he claimed to have found compounds approximating Pb_2O_5 and Pb_2SO_4; (d) Rollet's analytical and electrochemical work which supports his contentions as to the existence of Pb_2O_5 and Pb_2SO_4 in the plates; (e) the fact that, after complete discharge, the positive plate is still composed largely of PbO_2, and (f) that sulfation of the plates could be avoided by prevention of the interchange of gases between plates by a partition. In spite of certain advantageous points of the Fery explanation, however, the preponderance of experimental and theoretical evidence is in favor of the double sulfate theory.

The double sulfate theory is supported by (a) a negation of other theories; (b) the fact that recent investigators have obtained values for acid consumption very closely approaching the theoretical in spite of the experimental difficulties; (c) the fact that X-ray evidence obtained by several investigators proves the presence of only PbO_2, $PbSO_4$, and Pb on the plates; and, (d) most convincing, thermodynamic considerations in which it has been shown that the double sulfate theory is the only one consistent with all of the data.

Admitting the double sulfate hypothesis for the over-all reaction, the mechanism of the chemical reaction at the plates, particularly the positive plate, still remains in doubt. Liebenow[4] assumes the existence of PbO_2^{--} in the solution from the reaction: $PbO_2 \rightarrow PbO_2^{--} + 2e$; PbO_2^{--} is then supposed to react with H^+ to give Pb^{++} and H_2O. It has been pointed out recently by Thompson[5] that, according to calculations from reasonable data, the PbO_2^{--} concentration in the solution is 4×10^{-53} mole per liter, or one ion in a volume 50,000 times that of the earth. LeBlanc[6] proposed an explanation which many authorities feel is the most reasonable so far. He assumed the hydrolysis of dissolved PbO_2 and subsequent ionization into Pb^{4+} to Pb^{++}, and the final precipitation of Pb^{++} as $PbSO_4$. Thompson has recently proposed a combination of the LeBlanc and the Liebenow theories.

In order to ascertain experimentally the intermediate steps in the mechanism of charge and discharge of plates the question of the migration of ions needs to be settled as a basis for future work. A substantial step in this direction was made by Seith[7] in 1928 when he used radio-lead (Ra-D) in the negative plate of a storage cell and followed the activity of the cell parts by means of an electroscope. He concluded that any

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[1] For the second paper in this series see Clark and Tyler, THIS JOURNAL, **61**, 58 (1939).

[2] Gladstone and Tribe, *Nature*, **26**, 251, 342, 603 (1882).

[3] Fery, *Bull. Soc. Chim.*, **51**, 1019 (1932).

[4] Liebenow, *Z. Elektrochem.*, **2**, 420, 653 (1895).

[5] Thompson, *Trans. Electrochem. Soc.*, **75**, preprint (1939).

[6] LeBlanc, "Lehrbuch der Elektrochem.," first edition, 1895, p. 222.

[7] Seith, *Z. Elektrochem.*, **34**, 362 (1928).

migration due to the passage of current was obscured by the natural exchange phenomena. The present work is essentially a reinvestigation of this problem with the improved methods now available.

Experimental

Geiger–Mueller Counting Circuit.—The Geiger–Mueller counting circuit used in these investigations is of the type now so common that no description is required.

The gamma ray tube is three cm. long and is made of nonex glass. The cathode is an oxidized copper tube with a fine tungsten wire anode down the center, and the tube is filled with an oxygen–argon mixture (10–90) at about 80 mm. pressure. The characteristic counting curve for this particular tube is fairly flat, suitable operating voltages ranging from 749 to 780 volts. For all measurements made in this experiment, the apparatus was operated at 760 volts. Voltage control was effected through the use of 1.5 volt dry cells as small increments, since the smallest voltage step possible with the "B" batteries alone is 22.5 volts.

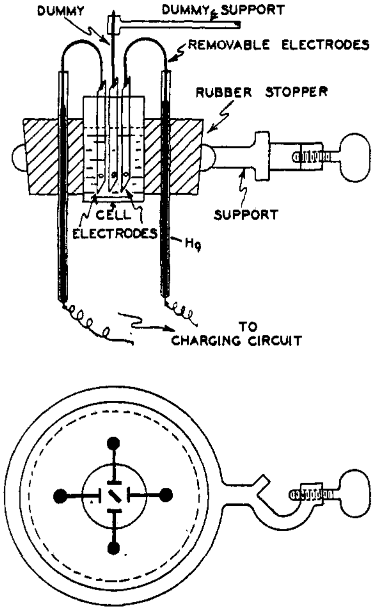

Fig. 1.—Storage cell.

The tube was connected through a 500 megohm resistor and a 5 mmfd. coupling condenser to the primary amplification unit consisting of a single vacuum tube stage. In such an arrangement, the electrical impulse allowed to pass the Geiger tube by the impact of an ionizing quantum is first amplified by the primary stage and then further amplified by the recording unit so that it has sufficient strength to operate the recording mechanism as well as a neon flash bulb for visual observation.

The Geiger tube was housed in a flat-topped cylindrical container made of lead 3 cm. thick, with a small hole in the top just over the tube. This furnished a convenient platform which made it possible to place the sample in exactly the same place with respect to the tube each time, and the thick lead shielded the tube from a great many fluorescent X-rays and scattered gamma rays. A glass rod pointer was firmly fixed in a permanent position to aid in placing the sample.

Charging Circuit.—The two questions to be answered by experiment are: (a) whether or not ions migrate from positive electrode to the negative or in the reverse direction, and (b) whether or not ions migrate through the solution from one part to another of the same electrode.

The procedure in the first case was merely to arrange positive and negative electrodes which could be readily removed and their activities measured. To accomplish the second objective, it was necessary to arrange two half electrodes for positive and two for negative which could be removed and measured separately, yet maintained at the same potential during the charging and discharging process. The cell with the four removable half electrodes is shown in Fig. 1. In order to be sure that the two halves of a single electrode were maintained at the same potential, the circuit shown in Fig. 2 was devised in which the current could be measured through any single half electrode or through the whole cell without interrupting the flow of current. It was possible to regulate the current so that the total flow was evenly distributed between the two halves of each electrode by means of variable resistances inserted in series with each half electrode. The small variable resistors used were of the radio volume control type. These were conveniently mounted on a fiber-board panel. It was found that, after some practice in balancing the cell, this could be done quite accurately and quickly. The cell usually stayed in balance for a considerable time, requiring a check-up only occasionally.

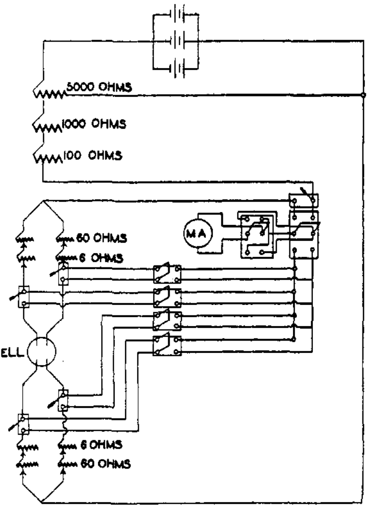

Fig. 2.—Charging circuit.

In addition to the four half electrodes, a dummy electrode, identical with the others and unconnected with the electrical system, was suspended in the center of the cell. Each electrode consisted of a 99.999% pure lead strip 35 × 4 × 1.5 mm. The active or inactive lead oxide paste was placed in a $^3/_{16}$-inch hole near one end of the strip, while a heavy copper wire lead was soldered onto the other end. The cell was a cylindrical glass container of about 10 ml. capacity.

Procedure.—It was at first suspected that, owing to the very small amount, about 5×10^{-6} g., of Th–B remaining in equilibrium with the Rd-Th, some complex method of separating the Th-B from the Rd-Th, perhaps one involving the use of dithizone, would have to be used. However, after trial and comparison of several more complicated techniques a far simpler and quite satisfactory method was then devised. A standard storage battery paste, previously tested, was utilized to prepare electrodes for all subsequent tests. The paste was spread in a thin layer on a strip of thin lead sheeting of suitable size, which was then exposed for two days to the thorium emanation. The activated PbO was then scraped off and made into a paste suitable for the preparation of an electrode. A possible objection to this procedure is that the radioactive lead isotope atoms are not present initially as oxide but as free metal. This, however, is considered to be of no real importance since most storage battery pastes, including the paste used in the present experiment, contain up to several per cent. of finely divided elementary lead.

Before the experiment was started, the active electrode was placed on a piece of filter paper and its activity measured, along with the background. Background measurements, made necessary by the presence in the laboratory of various weakly radioactive materials such as potassium, uranium, and thorium salts, and by cosmic rays were made for every determination. These background counts usually averaged between eleven and fourteen counts per minute. After the initial measurement on the active half-electrode, the cell was set up, the electrodes being permanently numbered and marked. The active half-electrode was always designated (see Table I) as number one, its mate as number two, and the two halves of the other electrode as numbers three and four. Exactly 5 ml. of sulfuric acid of sp. gr. 1.250 previously saturated with inactive paste was measured into the cell. A dummy electrode, as previously mentioned, was suspended in the middle of the cell. The cell was then started charging at five milliamperes. This value for the charging current was previously determined as approximately that which would completely charge the cell in about fifteen hours. The current through each half-electrode was adjusted, by means of the variable resistors, to exactly half the total. The point at which the cell was fully charged was simply estimated from the appearance of the positive plate, that is, the replacement of the light-colored paste of the pellet by dark PbO_2.

After the cell was completely charged, the half-electrodes were removed, washed with distilled water, and dried in air after removing most of the moisture by blotting with filter paper. Activity measurements were then made on all four of the half-electrodes, the dummy, and the electrolyte. Each count was of a minimum duration of ten minutes. After the measurements, the cell was again set up and the charge or discharge started as the case happened to be. The procedure was the same, whether after charge or after discharge. Complete experiments were run with the active paste initially in the positive, or the negative or the dummy electrodes in various stages of charge and discharge, after each of several cycles of charge and discharge, and after standing with no current passing. In some cases a completely charged or discharged half-electrode was removed from its cell and placed in fresh electrolyte with three other entirely new electrodes.

Because all of the numerous experiments lead to identical conclusions it would be profitless to present all of the data. Instead, Geiger counter measurements in a single experiment are presented in Table I as typical of all.

TABLE I

TYPICAL EXPERIMENTAL DATA WITH GEIGER COUNTER

Active material on negative (Pb) electrode no. 1 initially; no. 2 negative inactive; nos. 3, 4 inactive positive.

Specimen measured	Total hours elapsed	Total counts	Counts per min.	Cor. for coincident counts	Cor. for background	Remarks
Background	0	183	12.2	12.2	0	Initial
1 (NP)[a]		3686	307	339	327	count
1		8803	520	652	640	
Background	10	204	12.0	12.0	0	Cell not
1		5572	715	..	...	com-
1 (NP)		1200	173	183	171	pletely
2		162	11.8	11.8	−0.2	charged
3		108	9.8	9.8	−2.2	
4		218	12.8	12.8	0.8	
Electrolyte		298	21.3	21.3	9.3	
Dummy		273	10.9	10.9	−1.1	
Background	21	848	11.8	11.8	0	Cell
1		4386	338	379	377	com.
1 (NP)		519	86.5	92.5	80.7	pletely
2		134	13.4	13.4	1.6	charged
3		200	12.5	12.5	0.7	
4		145	10.4	10.4	−1.4	
Electrolyte		402	17.5	17.5	5.7	
Dummy		87	12.4	12.4	0.6	
Background	36	246	12.3	12.3	0	After
1		14461	688	..	...	discharge.
1 (NP)		394	30.3	30.3	17.9	Cell
2		125	9.6	9.6	−2.7	dead
3		707	12.2	12.2	−0.1	
4		181	12.9	12.9	0.6	
Electrolyte		444	31.7	31.6	19.3	
Dummy		238	12.5	12.5	0.2	
Background	58	164	10.9	10.9	0	After
1		3665	305	337	326	charging.
1 (NP)		296	37.0	36.9	26.0	Cell
2		104	13.0	13.0	2.1	charged
3		129	9.9	9.9	−1.0	
4		122	11.1	11.1	0.2	
Electrolyte		666	10.6	10.6	−0.3	
Dummy		206	11.4	11.4	0.5	
Background	68	178	11.9	11.9	1.0	After
1		2454	175	185	173	dis-
1 (NP)		110	15.7	15.7	3.8	charging.
2		111	11.1	11.1	−0.8	Cell
3		147	12.3	12.3	0.4	dead
4		115	11.5	11.5	−0.4	
Electrolyte		166	12.8	12.8	0.9	
Dummy		127	14.1	14.1	2.2	

[a] NP refers to a *new position* of the specimen further away from the ionization chamber than the usual distance on the lead shield; this was done in order to provide more accurate data with the slower count in case the results indicated removal of lead isotope atoms to other parts of the cell.

Results and Conclusions

For very precise work it would be necessary to apply a correction to the activity measurements obtained from Th-B-containing materials, because of the fact that the products of the disintegration of Th-B are themselves highly radioactive. The results of these experiments, however, are such that the application of such a correction is unnecessary and would have little meaning. It is sufficient to use the radioactivity purely as a qualitative indicator. In none of these experiments was there any measurable activity for any of the half electrodes except the one in which the active paste was originally introduced, or for the dummy. In all cases the electrolyte showed some increase in activity, but upon allowing to settle to the bottom of the cell, or filtering or centrifuging it was found that all of the radioactivity resided in a slight amount of sludge in suspension from the "shedding" or crumbling of the lead oxide–sulfate pellets in the electrode.

One experiment was designed primarily to give some indication of whether or not PbO_2 is appreciably soluble in the electrolyte, since one of the modern theories postulates the existence of the Pb^{4+} ion in the solution. No activity was noted for the electrolyte when a completely charged, active plate was placed in fresh sulfuric acid, either after standing or after discharging.

Another experiment was intended to determine whether lead ions would be transferred to the electrolyte and to the other electrode by simple exchange with no current flowing. No activity was noted, either for the electrolyte or for the inactive electrode. These experiments show that Pb ions from the electrodes do not exist in the electrolyte, either from a charged or uncharged plate, with or without the flow of current.

Summary

1. The problem of the migration of ions in the lead acid storage cell has been studied by means of the radioactive indicator method, using a Geiger–Mueller counter to measure quantitatively the radioactivity of the cell parts at intervals during the operation of the cell. Thorium-B, a radioactive lead isotope, was used as a tagged lead atom.

2. No migration was detected, either from positive to negative, from negative to positive, or from one part of a plate to another part of the same plate through the electrolyte. Since the method is an extremely sensitive one, this is believed to establish, as a basis for future considerations, the fact that there is no migration of lead ions through the solution in a lead acid storage cell.

3. The above conclusion is in accord with the Gladstone–Tribe theory of double sulfation, and it is unfavorable to the LeBlanc theory which states that the positive plate reaction takes place with the formation of plumbic ions as an intermediate product.

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Studies on Lead Oxides.[1] IV. Polymorphic Transitions by Grinding, Distortion and Catalytic Activity in PbO

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Several investigators have reported the transition yellow, orthorhombic PbO → red, tetragonal PbO by abrasion and pressure but no mention has been made of the fact that the product so obtained was an active, or distorted one. Clark and Tyler[2] found, for active lead monoxides obtained by other methods, a characteristic X-ray pattern with some lines greatly broadened, increased catalytic activity, and increased heat of solution. It was thus decided to make a quantitative study of the same type on the distorted product obtained by grinding in an effort to correlate extent of grinding with distorted properties and to see how it compares with distorted PbO prepared by other methods.

Grinding Apparatus.—Since it was hoped that the experiment on the production of active PbO by grinding could be made quantitatively, every effort was made toward this end. It was found that a ball mill of the conventional cylindrical type gave uneven grinding due to the inability of the balls to reach the material which became packed in the angular junction of wall and cover. To avoid this non-uniformity of sample, the ball mill shown in Fig. 1, in which the inside surfaces of the two end-pieces were spherical rather than flat, was designed and built. To further aid in the grinding of all of the material, a few short steel rods, pointed on both ends, were placed in the mill for the purpose of gouging out caked material from

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[1] For the third paper in this series, see Clark and Rowan, THIS JOURNAL, **63**, 1299 (1941).

[2] Clark and Tyler, *ibid.*, **61**, 58 (1939).