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Submarine Storage Batteries
X-Ray Studies of Active Material

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SUBJECT

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BY

NAVAL RESEARCH LABORATORY

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NAVY DEPARTMENT

BUREAU OF ENGINEERING

Report on

Submarine Storage Batteries

X-Ray Studies of Active Material

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

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AUTHORIZATION

1. This problem was authorized by reference (a). Other references pertinent to this study are listed as references (b) to (e).

Reference: (a) BuEng let.SS/S62(7-30-D1) of 7 Aug.1935.
(b) Transactions, Electrochemical Society, 68, 268 (1935).
(c) "Applied X-Rays", G. L. Clark, New York: McGraw-Hill, 1932.
(d) NRL 1st end. SS/19 of 2 July 1932.
(e) NRL Report No. P-1254 of 24 March 1936.

STATEMENT OF PROBLEM

2. The object of this work is to investigate the application of modern X-ray diffraction methods which have been developed for studying the crystal structure of various materials in the active material of lead storage cells.

KNOWN FACTS BEARING ON THE PROBLEM

3. The active material in lead storage cells is initially made of a paste composed primarily of the several oxides of lead in various proportions. The type of oxides used and their proportions are determined by the individual manufacturers by empirical methods; and the optimum characteristics of the individual oxides, such as their particle size, crystal structure, etc., are determined empirically by the manufacturer of the oxides. Since the capacity characteristics of the final battery are so largely determined by the characteristics of the oxides from which it is made, a knowledge of the physical chemistry of these oxides is important for an understanding of and improvement in the action of the storage cell. Another important factor in determining the capacity of a lead storage cell is the process used in initially forming the active material. So far, the forming processes have been developed by purely empirical methods without an adequate appreciation of the physics and chemistry involved.

4. The common chemical methods are inadequate for a study of the battery oxides and formation methods, the effectiveness of which depends not alone on the chemical substances which are present but also on their physical structure - the particle size, whether the particles are crystalline or non-crystalline, whether or not the crystals are strained or distorted, etc.

5. The modern X-ray crystallographic methods are among the most powerful tools for a study of such problems. X-ray methods are in actual use by such manufacturers as the Delco-Remy Company of the General Motors Corporation (reference (b)) and the Prest-O-Lite Storage Battery Company.

THEORETICAL CONSIDERATIONS

6. The theory underlying the use of X-ray diffraction methods is given in several recent treatises of which Professor Clark's "Applied

X-Rays" (reference (c)) is most suitable.

NARRATIVE OF ORIGINAL WORK DONE AT THIS LABORATORY

7. The first significant use of X-ray methods in studying submarine storage batteries was made at this Laboratory by Dr. C. S. Barrett and reported in reference (d). This work was abandoned following the separation of Dr. Barrett from the staff of this Laboratory. The present work was done by Professor Clark and Mr. Schieltz in the laboratory of the Department of Chemistry, University of Illinois, under Contract N173s-2430, and is a continuation of the work reported in reference (e).

METHODS

(a) Preparation of Material

Positive Plate Formation Studies

8. For studying the formation of the active material in the positive plates, a small storage cell was constructed so that it could be mounted in an X-ray camera. The dimensions of the cell were calculated so that the plate-electrolyte volume ratio was the same as in a commercial cell. The plate under observation was made the center of the three plates in the cell.

Negative Plate Formation Studies

9. Analogously, a cell was constructed for mounting in the X-ray camera in which a negative plate was made the central of three plates. The X-ray camera was focussed on a region close to the grid rib.

Basic Sulphate Studies

10. The previous report having shown the importance of basic sulphates to the capacity and functioning of a storage cell, these studies were extended by preparing basic sulphates by a variety of new methods.

Studies of Positive Plate Material Near the Surface of the Grid

11. A rather old positive plate was obtained and broken apart for study in the X-ray camera. The camera was focussed on the material close to and surrounding the grid.

Study of the Antimony in Negative Plates

12. The negative plates from batteries which have been in use for some time were used in this study. These were examined by X-ray and optical spectroscopic methods.

Chemistry of Lead Oxides

13. Since a knowledge of the chemistry of the several oxides of lead is fundamental to an understanding of the manufacture and improvement of lead storage cells, a large number of various oxides (and basic sulphates

made therefrom) were prepared under a variety of conditions and analyzed by chemical and X-ray methods. The X-ray method enabled a study of the strain and distortion in the individual particles to be determined. Various mixtures and pastes made from the oxides were also prepared and studied.

Standing Tests

14. Further observations were made on the cells reported in the previous report which had been allowed to stand under various temperature conditions.

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

15. The interpretation of the X-ray diffraction photographs and other data obtained established the following facts:

Positive Plate Formation Studies

(a) The "green" plate was composed of lead oxides which showed a rather distorted lattice structure.
(b) As soon as electrolyte was added to the cell, finely divided lead sulphate was formed.
(c) Conversion of the lead sulphate into lead peroxide by the forming current starts at the surface of the grid and progresses radially outwards.
(d) With discharge, the conversion to lead sulphate starts on the surface of the plate and moves gradually inward. Such studies as these may be of considerable importance in determining the proper plate dimensions for various purposes.
(e) Complete conversion of the lead sulphate into lead peroxide is readily obtained.

Negative Plate Formation Studies

(f) The "green" plate was composed almost entirely of the basic sulphate $4PbO \cdot PbSO_4$.
(g) When electrolyte is added, fine grained lead sulphate is formed immediately.
(h) Free lead appeared after 5 hours of formation; this was due in part to the proximity of the region studied to the grid rib.
(i) Standing over a period of 40 hours produced a considerable amount of lead sulphate on the surface of the lead.
(j) The grain size of the lead sulphate increased rapidly over a period of several days (during which the forming process was continued).
(k) With cycling, grain growth of the lead was very noticeable (35 cycles).

Basic Sulphate Studies

(l) The results previously reported were continued; namely, only three basic sulphates were formed irrespective of the method of preparation. They are:

$4\ PbO \cdot PbSO_4$
$3\ PbO \cdot PbSO_4$
$2\ PbO \cdot PbSO_4$

Studies of Positive Plate Material Near the Surface of the Grid

(m) Surrounding the grid of the old positive plate there was found a scaly substance which X-ray examination proved to be lead sulphate with a large proportion of highly distorted lead dioxide. Between this scale and grid proper, there was found a thin grayish film which was essentially lead sulphate. This film presumably serves to decrease the corrosion of the grid by formation during the life of the cell.

Study of the Antimony in Negative Plates

(n) The X-ray and spectroscopic studies showed that antimony is present in appreciable amounts throughout the entire negative plate. Various depths of the plate exhibited approximately the same proportions of antimony.

Chemistry of Lead Oxides

(o) The results of the studies of the chemistry of the lead oxides are embodied in Table 1. The chemistry of lead compounds is quite complex and changes in the conditions of manufacture and of formation of lead cells therefore have an important effect on the capacity of the final batteries.

Standing Tests

(p) The examination of the cells which had been allowed to stand since last year showed the following:

Positive Plates

(1) Distortion was found on the inside of plates which in pronounced cases was accompanied by the formation of a new compound.
(2) Grain size in the plates increased with time.
(3) Lead sulphate was more pronounced and of larger particle size on the surface of the plates.
(4) In general, standing at room temperature seems to have produced slightly larger particle size, especially when the plates were in the lead sulphate state. Conversion from sulphate to dioxide was easy and complete.
(5) When the original distorted oxide was completely destroyed by discharge, distortion seems to have disappeared on charging.

Negative Plates

(1) There was a noticeable increase in particle size.
(2) Negative plates are much slower in conversion by charging from the sulphate than are the positive plates. It is doubtful if all the sulphate is ever removed, since lead sulphate forms whenever sulphuric acid is in contact with lead.
(3) Charged cold cycled plates showed more and larger grained lead sulphate on the surface, and still more in the interior.
(4) Discharged plates that had been cold cycled were much slower in taking a charge than were those that stood at room temperature.

(b) Opinions

16. It is considered that the present work demonstrates the value of X-ray diffraction methods in the manufacture and use of storage cells. The correctness of this opinion is proved by the fact that at least two large manufacturers of storage batteries (General Motors Corporation and Prest-O-Lite Company) are actually using X-ray methods. It is considered that the X-ray methods should be used by manufacturers in the following ways:

1. Research on and development of new cell types.
2. Research on and development of new methods of making battery oxides.
3. Standardization of manufacturing processes in producing oxides.
4. Control of manufacturing processes in producing oxides.
5. Research and development of expanders.
6. Standardization and control of manufacture of expanders.
7. Research and development of new pasting processes.
8. Standardization and control of pasting processes.
9. Study of pickling and drying processes.
10. Study of grid alloys.
11. Research and development of formation processes.
12. Control of formation procedure.
13. Study of operation and maintenance of storage batteries.
14. Diagnosis of failures and troubles.
15. Tests of foreign and domestic competitive products.

(c) Recommendations

17. It is recommended that the Bureau of Engineering attempt to induce the manufacturers of storage cells to make use of the X-ray diffraction methods in the development of submarine storage cells having higher capacities than those at present obtainable.

Table 1
Chemistry of Lead Oxides

Sample	Method of Preparation	Chemical Analysis	X-ray Analysis Pb_3O_4	X-ray Analysis PbO_2
1	Chemically Pure PbO_2, commercial	$PbO_{1.917}$		All
2	PbO_2 prepared with chlorine	$PbO_{1.729}$		"
3	PbO_2 distorted sample	$PbO_{1.85}$		"
4	PbO_2 distorted sample, boiled with water	$PbO_{1.85}$		
5	Chemically Pure Pb_3O_4, commercial	$Pb_3O_{3.88}$	All	None
6	Pb_3O_4 treated with HNO_3, 1:1, cold	$Pb_3O_{4.03}$	"	"
7	" " " " 1:1, boiled 1 hr.	$Pb_3O_{4.07}$	"	"
8	" " " " 1:2, cold	$Pb_3O_{4.28}$	"	"
9	" " " " 1:2, boiled 1 hr.	$Pb_3O_{4.48}$	Nearly All	(Strongest line, (faintly visible.
10	" " " " 1:3, cold	$Pb_3O_{4.63}$	" "	(Strongest line (more pronounced.
11	" " " " 1:3, boiled 1 hr.	-	" "	(5 strongest lines.
12	" " " " 1:4, cold	-	Mixture	
13	" " " " 1:4, boiled 1 hr.	-	None	All clear pattern.
14	" " " " 1:8, cold	$PbO_{1.86}$	"	All. Very diffuse pattern
15	" " " " 1:8, boiled 1 hr.	$PbO_{1.93}$		All. Clear pattern