NRL Report 6859

The Positive Plate of the Lead-Acid Cel
A Critical Review of Recent Literature

JEANNE BURBANK

Electrochemistry Branch
Chemistry Division

February 18, 1969

NAVAL RESEARCH LABORATORY
Washington, D.C.

This document has been approved for public release and sale; its distribution is unlimited.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
FOREWORD	1
INTRODUCTION	1
LEAD SULFATE	3
LEAD DIOXIDE	3
Chemical Characterization	3
Polymorphism	4
X-Ray Analysis of Mixtures	4
Resistivity	4
αPbO_2 and βPbO_2 in the Positive Active Material	5
The Reversible Electrodes	6
Cycling PbO_2 Electrodes	7
MECHANISM OF THE POSITIVE PLATE REACTION	7
GEOMETRICAL MORPHOLOGY	10
ANTIMONY IN THE POSITIVE PLATE	13
OXYGEN OVERVOLTAGE ON THE PbO_2 ELECTRODES	13
A SUMMARY LIST OF RESEARCH PROBLEMS	15
REFERENCES	17
APPENDIX — Essential Characteristics of the Lead-Acid Cell	21

ABSTRACT

Recent scientific literature on the positive plate of the lead-acid cell has been critically reviewed. The principal constituent of the plate is the nonstoichiometric oxide $PbO_{1.80-1.98}(OH)_{0.11-0.26}$ which under normal conditions behaves as a semimetal, the free electrons in the conduction band imparting a conductivity of 10^3 mho/cm. Two polymorphic crystal forms are known, and the electrochemical characterization of each has been investigated. The significance of the geometrical morphology and the function of Sb in the positive plate have been shown to be related: Sb acts to preserve the small particle size of the surface crystals that give high electrochemical capacity to the plate. O_2 overvoltage is different on the two polymorphs, and it is thought that the form having the lower overvoltage serves to prolong the life of the plates in overcharge tests.

In this review particular emphasis has been placed on relating the research findings to cell behavior and to pointing out areas where further work is required.

PROBLEM STATUS

This is an interim report on the problem; work is continuing.

AUTHORIZATION

NRL Problem C05-14
Project RR 010-01-43-4755

Manuscript submitted November 14, 1968.

THE POSITIVE PLATE OF THE LEAD-ACID CELL — A CRITICAL REVIEW OF RECENT LITERATURE

FOREWORD

The state of knowledge concerning the lead-acid cell has been greatly enriched in recent times by numerous scientific publications of research results. These contributions have not been reviewed in English, and it was suggested that a critical survey of this recently accumulated knowledge would make a desirable chapter for inclusion in the series "Recent Advances in Electrochemistry and Electrochemical Engineering," edited by P. Delahay and C. W. Tobias. In collaboration with others, the author was invited to prepare such a chapter, and this report is the critical review concerning the positive plate of the lead-acid cell offered as the author's contribution. This will be combined with similar reviews of other aspects of the cell by the other collaborators in a chapter intended to cover the lead-acid battery as a whole.

A review of this sort presupposes a knowledge of the essential characteristics of the lead-acid cell. For ready reference, a description of the cell is given in the Appendix, including the definition of terms used in this report.

INTRODUCTION

The thermodynamic reversibility of the lead-acid battery, established beyond all reasonable doubt, demands, of course, that the positive plate be reversible. The reaction at this plate may be written as

$$PbO_2 + 4H^+ + SO_4^{-2} + 2e = PbSO_4 + 2H_2O. \quad (1)$$

It has been shown that in strong H_2SO_4 the electrode behaves according to this equation, which is chemically very straightforward.

If the lead-acid cell were of purely scientific interest, further investigation of the reaction would be academic. But because of the practical importance of the cell and the ever increasing need for isolated power supplies, the positive plate, as one important aspect of the lead-acid battery, has received intensive study. These studies continue up to the present time, and a vast store of information has accumulated.

From a theoretical viewpoint, the reaction in Eq. (1) implies that every gram of PbO_2 should yield 0.224 amp-hr of electricity. In actual practice only 25 to 50% of this amount is normally available. Improving this efficiency is a research and development problem, and almost all investigations of the system are in some way connected with the practical goal of improvement in this performance.

The reversibility of the electrode is realized in practice by repeated cycles of the positive plate through many charges and discharges. But, sooner or later, there is an end to this operational reversibility, and the plate disintegrates. It may fail by grid corrosion, or, barring this failure, the active material itself may fail. Chemically, it remains the same, but it fails structurally or "wears out." Here again is a fruitful field

for investigation and one that is vigorously active at the present time. This structural breakdown is of a dual nature: the active material PbO_2 may soften and shed, losing interparticle contact and the ability to conduct electrons, or the plate may become hardened by deposition of excessively large $PbSO_4$ crystals that are not readily converted to PbO_2 on charging. These give rise to high electrical resistance and interfere with the normal functioning of the plate.

The overall operation of positive plates has been examined recently by Bode, et al. (1-3), using radioactive tracers and autoradiographs of the positive plates in new, operating, and failing cells. Sulfur and selenium replace each other isomorphously, and by the combination of the relatively low-grade radiation of ^{35}S and the more penetrating ^{75}Se, the deposition of $PbSO_4$ throughout the volume of the positive active material was determined. The geometrical distributions of charge and discharge were assessed, and the part played by the grid, the pasting processes, the rate of discharge, the cycling, and the separators were all examined in this definitive series of investigations.

Fresh positive plates initially showed localized charged and discharged areas which disappeared on cycling a few times. The heterogeneity was attributed to differences in the pressure applied during fabrication of the plates or to "overpasting." Following extensive cycling, shortly before the end of life, inhomogeneities in the distribution of discharge appeared again; this time they were attributed to the softening of the active material. A very small degree of warping of the plates also led to areas of uneven current distribution and to the isolation of active material.

Machine-pasted and machine-pressed plates were always more uniform than hand-pasted ones; however, unsymmetrically adjusted machines gave plates that were nonuniform. For example, these machines gave plates that initially discharged at the top but not at the bottom. Pressing with felt resulted in many isolated areas of PbO_2 that did not initially discharge, and plates pressed with webbing clearly showed the pattern of the weave in the autoradiographs of the discharged plate surface. Unpressed plates showed many localized areas of heavy discharge.

High- and low-porosity areas in separators were also visible in the distribution of discharge on the plate surfaces, revealed by the autoradiographs.

All these conditions disappeared after a few cycles and seem to have nothing to do with the service evaluation of the plates.

New plates frequently showed the grid bars as discharged areas in the autoradiographic examinations. This appearance was attributed to overpasting in these areas and to the proximity to the grid metal, which made it easy for these areas to carry the current on the first discharges. From about 10 to 75 cycles, the grid bars all remained "dark" in the radiographs; that is, the areas on and near the grid bars did not usually take part in the discharge. At the end of life, discharge again began to show along the grid-active material interface.

Very high discharge rates in dilute electrolyte caused local deposition of ^{75}Se on the grid. It was concluded that high-rate discharges in very dilute acid can result in actual reversal in local spots, because diffusion of acid into the interior of the plates does not keep up with current demand. At low current densities in normal battery-strength electrolyte, the active material cycled throughout the entire thickness of the plate in a fairly uniform fashion, not only at the plate surfaces.

It was also shown that the irregularities resulting from the pasting processes were present as differences in density in the interior volume of the paste.

Aside from the informative nature of the work, these findings are of extreme significance for the fabrication of dry-charged positives. The so-called dry charging is a process for producing a battery that is marketed in a dry state, the electrolyte being added at the time the battery is placed in service. These batteries are expected to retain sufficient starting power to give immediate performance without additional charge. From the above studies it is apparent that when the inhomogeneities present after formation are of sufficient extent, the inevitable additional losses accruing from the washing and dry-charge processing can render the plates unsatisfactory for this application. These same plates, given a few conditioning cycles, would have made satisfactory dry-charged positives.

The different aspects of the full and more detailed characterization of the positive battery plate and its reactions span many scientific disciplines. It is not possible to cover exhaustively here all published results; however, it is hoped that this discussion will serve to stimulate further interest and investigation to ultimately derive the maximum potentialities from this electrode system.

LEAD SULFATE

Of the two solid phases normally associated with the positive plate of the lead-acid battery, PbO_2 has received considerable attention, whereas $PbSO_4$ has been rather ignored as a significant phase. $PbSO_4$ forms in its normal crystal lattice of orthorhombic anglesite, readily identified by x-ray diffraction. It may deposit as very fine-grained material, or it may form large crystals that resist recharging, known as "hard sulfate" (4). Accumulation of significant quantities of this hard sulfate is normally associated with insufficient care in cell management and signals the end of life.

LEAD DIOXIDE

Chemical Characterization

Because PbO_2, a powerful oxidizing agent, is the major phase present in the charged positive plate of the lead-acid cell, it is of interest to define its chemical and crystalline form as well as possible. Complete chemical analysis of the material is very seldom performed, and, as a result, different preparations have a real and an apparent range of stoichiometries, which depend on the choice and extent of the analytical methods. It is generally accepted that the composition of this material lies within the limits

$$PbO_{1.80-1.98}(OH)_{0.11-0.26} \cdot$$

There are many analytical methods described for PbO_2, and the recent work of Bagshaw, et al. (5), is cited as an example of both analysis and synthesis of this compound. Further research on analytical methods would be of interest with a view to simplifying the total procedure.

The mistaken belief persists in some quarters even today that the crystal lattice of PbO_2 can be retained unchanged down to a stoichiometry of $PbO_{1.66}$. Examination of the scientific literature quickly reveals the source of this error, and the observation has been adequately refuted by the investigations of Bystrom (6), Katz (7), Butler and Copp (8), Anderson and Sterns (9), among others.

Polymorphism

There are two recognized polymorphic crystalline forms of PbO_2: the naturally occurring plattnerite with the rutile-type structure, known as βPbO_2 (10), and αPbO_2 with a columbite-type structure (11,12), which has not yet been found under natural conditions. In the scientific literature on these two materials, the prefixes α and β are sometimes used to designate the reverse phases, and it should be understood that β refers to the tetragonal and α to the orthorhombic crystal forms, respectively, throughout this discussion.

Several methods for the preparation of pure specimens of each polymorph have been described, and details of the procedures are given in the original articles (5,11,13,14). The polymorphic relationship between these two types of crystal structure has been shown for these as well as other pairs of oxides with analogous crystal structures (15-19). In the other oxide systems, the rutile-type structure generally is the high-temperature form, and the columbite type generally is the low-temperature structure. In the case of PbO_2, there is an anomaly in this relationship because αPbO_2 (columbite type) is the high-temperature, high-pressure phase, and βPbO_2 (rutile type) is the low-temperature, low-pressure form. Thus, orthorhombic αPbO_2 is metastable at normal atmospheric pressure and temperature. By analogy with the other oxide systems having the columbite structure as the low-pressure form, there may be a third, higher-pressure polymorph, as suggested by Kirkinskii (20). There is some experimental evidence for the existence of a third polymorph in the work of Ritchie (21) and Burbank (22,23); however, further research is required to fully define this third phase and its possible polymorphic relationship with the other two forms of PbO_2.

X-Ray Analysis of Mixtures

The relative amounts of polymorphic materials in mixtures are frequently determined by x-ray diffraction analysis. Dodson (24) was the first to use this method for αPbO_2 and βPbO_2. The technique is straightforward for many such mixtures, but in the case of PbO_2 from lead-acid battery positives, it presents certain problems. These problems arise from the small crystallite size, the lattice distortion, the preferred orientation, the superposition of diffraction peaks, and the internal absorption effects described by Fedorova, et al. (25,26), Bagshaw, et al. (5), and Kordes (14). Further investigation of x-ray techniques and specimen preparation methods for the mixtures would be of interest to determine the cause of the anomalies associated with the x-ray analysis. In standard mixtures of the two polymorphs, which contain measured amounts of each compound, the intensity of the diffraction pattern of αPbO_2 is weaker than it should be relative to the known amount of this phase present. Fedorova, et al. (25,26), attributed the abnormally low intensity to a coating over of the crystallites of αPbO_2 by the softer βPbO_2 during preparative grinding and mixing. On the other hand, it is possible that a recrystallization to the stable βPbO_2 takes place in the superficial layers of the metastable crystals of αPbO_2, perhaps initiated by the presence of crystals of the stable phase in the mixtures. This mechanism is certainly to be considered in the light of the findings of White, et al. (15), who could not preserve the α structure on quenching to room temperature and pressure in the presence of moisture.

Resistivity

PbO_2 is an intrinsic semiconductor; that is, it contains free electrons in the conduction band under normal conditions of temperature and pressure (27,28). These electrons impart metallic properties to the material, and it may best be considered a semimetal under normal conditions. Its low resistivity has been attributed to the O_2 deficiency of

the material; however, it has not been found possible to increase the electrical conductivity by removing additional O_2 from the lattice by heat treatment.

Aguf, Rusin, and Dasoyan (29) have recently determined the resistivity of both αPbO_2 and βPbO_2 and, by extrapolating to zero porosity, obtained the values $\rho_\alpha = 10^{-3}$ and $\rho_\beta = 4 \times 10^{-3}$ ohm-cm. In porous preparations of the two polymorphs, such as the positive active material of the lead-acid battery, the observed resistivities are functions of the particle morphologies. In the preparations examined, the area of interparticle contact of the β phase was larger because of its large surface area and needlelike form. The α phase occurred as larger particles of spheroidal shape with lower surface area, smooth surfaces, and, hence, lower area of interparticle contact.

αPbO_2 and βPbO_2 in the Positive Active Material

Both αPbO_2 and βPbO_2 may be present in positive plates of the lead-acid cell, although many plates contain only the β polymorph as far as can be detected by x-ray diffraction analysis. Bode and Voss (30) in 1956 first reported finding αPbO_2 in the interior portions of normal production plates. Dugdale (31) and Carey (32) have further examined its distribution throughout cross sections of plates, and their conclusions are shown schematically in Fig. 1.

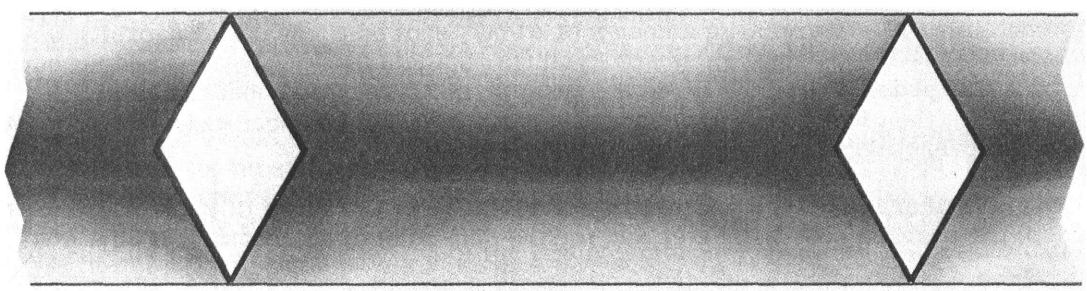

Fig. 1 - Schematic representation of the gradient of αPbO_2 throughout a positive plate cross section. The white diamonds correspond to sections through grid members. In those plates that contain αPbO_2, the outer central portions of the pellets are approximately 98% βPbO_2 with the αPbO_2 increasing in amount up to 46% at the central interior. Portions of the pellets near the grid bars also have a higher concentration of αPbO_2 (31,32).

Early x-ray diffraction examinations of positive active material (4,33,34) did not reveal the presence of αPbO_2, and the source of this material in modern battery plates is not well defined today. αPbO_2 has been variously suggested as arising from the oxidation of residual metallic Pb in the cured paste, high internal pH in the plate during formation, anodic oxidation of tetrabasic $PbSO_4$, the presence of Sb in the grid metal, topochemical oxidation $4PbO \cdot PbSO_4$ and acid starvation in the interior portions of the plate attributable to low porosity and dense packing (24,30,35-38). Still other mechanisms have been suggested. The most definitive work on this question is that of Ikari, et al. (39). In highly compressed pastes αPbO_2 was formed, and these investigators concluded that the chemical composition of the active material was not as significant in determining the phase of PbO_2 that would form on anodic oxidation as was prevention of access of acid into the interior of the plates. A dense coating of $PbSO_4$ on the plate

surface, a dilute-forming electrolyte, a high content of PbO in the paste, and highly compressed pastes all promoted the formation of αPbO_2. Increase in temperature also promoted formation of the α form.

If the original paste mix is essentially free of metallic Pb, there appears little likelihood of finding αPbO_2 in the finished plate. In curing pastes the residual lead is reduced to a very low value, less than 5% (40). Yet, it is estimated that plates can carry as much as 30% αPbO_2. If this originated from direct oxidation of metallic Pb in the paste, to obtain a final content of this value the cured paste would require a residual Pb content of approximately 28%. Dodson (24) has therefore discounted the possibility of free Pb in the paste as a source of the αPbO_2.

Interestingly enough, the conditions required for the development of αPbO_2 in the active material (24,39) are the reverse of the conditions promoting development of the α phase in anodic corrosion products of Pb and its alloys (41). Whereas the active material requires a high density of active material, a low concentration of forming acid, a high temperature of forming acid, and a low-forming current density, the formation of αPbO_2 as the major corrosion product on Pb and Pb-Sb, Pb-Sb-Ag alloys is promoted by a high current density, a high acid concentration, lower temperatures of anodization, and lower amounts of alloying agents.

Although many opinions have been expressed concerning the significance and beneficial action of the presence of αPbO_2 in a positive plate, only Dodson's report (42) contains test results specifically directed to answering the question. He indicated that plates containing relatively large amounts of αPbO_2 showed a low initial capacity which gradually increased to normal values on cycling. In a standard cycle-type test, production plates and plates containing large amounts of αPbO_2 showed about the same life. On the other hand, the plates containing large amounts of αPbO_2 outperformed the production plates in an overcharge test.

Obviously there is a need for further investigation of the cause of the appearance of αPbO_2 in the charged positive plates and for the definition of its function, if any.

The Reversible Electrodes

The emf of the electrode reaction of Eq. (1) relative to the standard hydrogen electrode is expressed by the Nernst relationship. For βPbO_2 (43)

$$E_\beta = 1.6871 - 0.1182\ pH + 0.0295 \log a_{SO_4^{-2}}, \tag{2}$$

and for αPbO (44)

$$E_\alpha = 1.6971 - 0.1182\ pH + 0.0295 \log a_{SO_4^{-2}}. \tag{3}$$

The difference in the standard potentials indicates a difference of -0.40 kcal/mole in the standard free energy of formation of βPbO_2 from αPbO_2 at 25°C. Thus, the β phase is the more stable under standard conditions. Angstadt, et al. (45), demonstrated that in acid solutions up to a pH of about 4, both αPbO_2 and βPbO_2 behaved according to the equilibria in Eqs. (2) and (3), and they determined the temperature coefficients as

$$(dE_\beta/dT)_p = -0.20\ mv/°C,\ 4.62M\ H_2SO_4$$

and

$$(dE_\alpha/dT)_p = -0.36\ mv/°C,\ 4.62M\ H_2SO_4\ .$$

The stability of the open-circuit potentials of αPbO_2 electrodes in H_2SO_4 has been accepted as the criterion of the reversibility of the reaction, and the higher temperature coefficient indicates that in 4.62M H_2SO_4 at 50°C and above, the α phase becomes the more stable phase. Ness (46) has recently presented an excellent summary of the thermodynamic data available for both αPbO_2 and βPbO_2.

Aguf (47) has put forth the concept that in addition to the above Nernst relations, Eqs. (2) and (3), the observed open-circuit voltages depend on the stoichiometry of the PbO_2. The stoichiometry, in turn, varies with the concentration of the acid. This approach was, of course, delineated by Vetter (48) for nonstoichiometric oxide electrodes, and this is probably the first application of it to the PbO_2 electrode, although such a possibility has been discussed many times. The calculated stoichiometries are unusual in that in concentrated H_2SO_4 PbO_2 would contain a significant amount of excess O_2. The material is usually deficient in O_2, and Aguf admits that the experimental verification of his calculations is difficult, because of the limitations of presently available analytical methods.

Cycling PbO_2 Electrodes

The relative amounts of αPbO_2 and βPbO_2 change on cycling a battery plate containing both polymorphs (14,24,30,39). αPbO_2 discharges to normal $PbSO_4$, which, in turn, is converted to βPbO_2 on recharge (49-52). This may give rise to a coating over of the crystals of αPbO_2 with a layer of βPbO_2. This coating-over process acts to protect the underlying αPbO_2 in subsequent discharges. After the initial decrease in the amount of αPbO_2, the plate content of this phase remains substantially constant.

The rate and extent of the discharge of the two polymorphs in H_2SO_4 has been examined in a number of investigations (42,51-54). It is now generally accepted that in a mixture of the two polymorphs, such as the battery plate, βPbO_2 contributes by far the greater share of the electrochemical capacity. This conclusion leads to complications in the analysis of the relative action of the two polymorphs; however, it appears that, intrinsically, the α form discharges at a higher rate than the β form per unit surface area, but its physical distribution and morphology, its tendency to passivate, and the extent of plate porosity limit its performance in actual practice.

MECHANISM OF THE POSITIVE PLATE REACTION

The plate reaction expressed by Eq. (1) has been established beyond all reasonable doubt and is straightforward enough, but the steps and charge exchange mechanism are not known, because they seem to be complex. These complexities arise from the fact that two electrons take part in the overall reaction, whereas fundamental concepts of electrode mechanisms are restricted to single-electron transfer steps. In addition, two solid phases are involved in the reaction. It is difficult to formulate a mechanistically satisfactory picture of the dynamic equilibrium between the PbO_2 solid and the Pb^{+2} ion in solution, because the Pb^{+3} ion is unknown and the Pb^{+4} ion is not detected in solution.

Beck, Lind, and Wynne-Jones (55) have very succintly described the restrictions of the reversible reaction. The mechanism may not include any spontaneous nonelectrochemical step in which equilibrium is impossible, since reversibility demands that the total free energy change be exactly equivalent to the electrochemical work of the cell reaction. A spontaneous nonelectrochemical step is one involving a free energy change which contributes nothing to the work of the cell. Such intermediate steps have commonly been included in proposed reaction mechanisms, steps such as:

$$H_2O \rightarrow (OH) + H^+ + e \qquad \text{(electrochemical)}$$

followed by

$$PbSO_4 + 2(OH) \rightarrow PbO_2 + H_2SO_4 \qquad \text{(nonelectrochemical),}$$

or

$$PbO_2 + 2e \rightarrow PbO + O^{-2} \qquad \text{(electrochemical)}$$

followed by

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O \qquad \text{(nonelectrochemical).}$$

These are unacceptable, because the nonelectrochemical reactions are not reversible, and therefore free energy changes associated with them may not be included in the total free energy change of the reversible electrode reaction.

Physically, the mechanism of discharge has been shown to be a passivation or covering over of the available PbO_2 with a deposit of $PbSO_4$ (56). Recharge is the reverse of this process, and a healthy positive plate (one which is not too near the start nor end of life) is remarkably efficient in behavior. It may be partially discharged and recharged over and over again with little energy loss. If care is taken to eliminate harmful elements from the cells, they operate with close to 100% efficiency in such installations as telephone float service and similar standby power stations.

Most attempts to analyze the reactions of charge and discharge from a kinetic standpoint have been made on electrodes formed by anodic treatment of Pb metal or electrodeposited PbO_2. Such an electrode is not, of course, an equilibrium mixture of the two solid phases and cannot be expected to behave in the reversible manner. To polarize a monophasic electrode so that its potential crosses into a range of thermodynamic metastability is much the same as cooling a liquid below its freezing point in the absence of nuclei. The resulting supercooling has nothing to do with the bypassed equilibrium condition. Equilibrium is not established until both phases are present in sufficient quantity and in suitable physical juxtaposition. It is thus more likely that the kinetics of the reversible plate reaction will be solved when a suitable electrode is designed. A kinetic study of the massive porous battery plate is impractical, because the reactions are diffusion limited and the constantly changing porosity renders a stabilized surface impossible to maintain for kinetic evaluation of the reversible plate reaction itself.

Fleischmann and Thirsk (57) attempted to analyze the mechanism of the oxidation of $PbSO_4$ to PbO_2 using constant-voltage techniques. Polarization of 0.1 v at 45°C and 0.15 v at 15°C did not result in oxidation of the $PbSO_4$ layers; higher overvoltages were required. At the elevated overvoltages, it was conceived that at selected points the voltage gradient across the $PbSO_4$ layer was approximately 5×10^4 v/cm. At local centers of imperfections in the sulfate crystals, electrons were ejected, and the centers reached the set stabilized potential. At these local regions of high potential on the surface, the oxidation reaction was initiated, and they acted as nucleation centers for PbO_2.

These authors have determined two rate constants: one a rate of formation of nuclei of PbO_2 in the $PbSO_4$ layer and the other a constant related to the rate of growth from a center, the square of the age of the nucleus, and the total possible number of nuclei.

A peak in the polarization curve at the beginning of the reaction was regarded as "nucleation overvoltage." Having once formed this physical picture, the two rate

constants were shown to be related to the sequential processes of nucleation of growth centers, spherical growth, and overlap of growing PbO_2 crystals in the volume of the $PbSO_4$ layer. Initiation of the growth began at the crystal/electrolyte interface, and one center per sulfate crystal was assumed for some deposits of $PbSO_4$, several centers in others.

Detailed analysis of the rates showed that the system was much too complex to obtain a mechanism definition, and it was suggested that there is a continuing change in the surface-layer free energy of the PbO_2, related to the overvoltage. This is, of course, a possibility and not too far removed from the suggestion of Aguf (47). However, the electrode mechanism has a large activation energy, and this is inconsistent with its reversibility.

The analysis of Fleischmann and Thirsk for the conversion of $PbSO_4$ to PbO_2 may also be applied to analyzing the discharge characteristics of the two forms of PbO_2 observed by Mark (52) and others. On constant current discharge of a βPbO_2 electrode, a cusp appears in the voltage-time plot. The initial low potential would correspond to the nucleation overvoltage of $PbSO_4$ in the PbO_2, followed by a recovery in potential on growth of these centers and establishment of the discharge overvoltage of the reversible reaction. Fleischmann and Thirsk indicated that once the nucleation process had passed a peak, the rate of formation of additional nuclei was not significant. In a series of interrupted current studies, Mark showed that once the initial discharge had occurred, subsequent partial discharges of βPbO_2 electrodes showed very insignificant cusps, indicating that creation of new nuclei was not a significant process. Once the nucleation of $PbSO_4$ had occurred, Mark and Vosburgh (58) observed that the overvoltage of the discharge reaction was linear with current density and did not deviate from this relation until the electrode became passivated.

Discharge of αPbO_2 was observed to take place by what appeared to be a different mechanism. If Fleischmann and Thirsk's analysis may be applied to this case, there was no nucleation at centers; rather, deposition of the $PbSO_4$ took the form of sheets. The αPbO_2 electrode does not rapidly recover to a constant open-circuit voltage on current interruption (52,58,59). Crystallization of the $PbSO_4$ on the electrode surface in sheets would introduce resistance components into the measurements, and slow dissolution rates and recrystallization processes would explain the delayed recovery to the characteristic open-circuit voltage.

It is obvious that nothing is known about the electrochemical mechanism of the charge and discharge reactions of the positive plate of the lead-acid cell other than that it is a reversible electrode. All attempts to analyze the electrode kinetically have resulted in a physical picturization involving nucleation and growth from these nuclei on the surface or in the volume of the electrode mass. These are phenomena related more to the physical morphology of the electrode materials than to charge exchange mechanisms. It is, however, interesting that the investigations of charge and discharge of sheet Pb electrodes when examined by electron microscopy are in essential agreement with the conclusions arrived at by the attempts at kinetic analysis. The electron micrographs of Feitknecht (60), for example, show the nucleation and growth of PbO_2 in a $PbSO_4$ coating on metallic Pb and show the discharge of the PbO_2 layer by nucleation and growth of $PbSO_4$ crystals.

Several investigators have examined the polarization and discharge behavior of electrodes fabricated from mixtures of αPbO_2 and βPbO_2 (51,52). The results are in some conflict, and discussion of the varying conclusions here would only add unnecessary confusion to the picture. Further definitive experimentation is called for in this area.

GEOMETRICAL MORPHOLOGY

The importance attached to the geometrical morphology of the positive active material cannot be overemphasized, because the strength and elasticity of porous solids are functions of their microstructures (61). This has been recognized for many years for materials such as hydraulic cements and plasters, which bear a close morphological analogy to the positive active material of the lead-acid cell. The battery plate is a porous polycrystalline aggregate which must serve while liquid electrolyte percolates throughout the mass. Not only does this in itself present a difficult and unusual demand on mechanical strength, but the electrochemical functioning of the plate constitutes a cyclic volume change between $PbSO_4$ and PbO_2 for the duration of the life of the cell. The complexity of the essential structural problem is self-evident. It has been stressed that the geometrical morphology determines the strength and service life of the active mass of the positive plate. Simon and Jones (37,62) have emphasized the significance of the optical morphology and concluded that a network of relatively large euhedral crystals, possibly consisting of αPbO_2, imparts maximum structural durability. Other reports (22,38,63,64) have stressed the importance of the morphology of the active material as seen in the electron microscope, Fig. 2. In some positive plates crystals in both size ranges have been observed to occur together.

Aside from the question of the possibility of an intrinsic crystallite-size requirement, it is apparent that the structure must be a porous mass of PbO_2 whose individual crystals or grains are firmly welded together. The porosity is a necessary adjunct of the structure so that the active material may present a high relative surface area to the electrolyte. Totally enclosed porosity is of course valueless for this purpose. The solid mass must possess sufficient strength to withstand the electrochemical working of the superficial layers throughout many cycles of charge and discharge. The porosity must serve the dual purpose of permitting access of the electrolyte to the active surface and offering free space to accommodate the enlarged volume required by the change of PbO_2 to $PbSO_4$. These requirements are forbidding, but battery plates do operate in precisely this manner for considerable periods of time.

In addition to the identification of the crystal phases present in the mass of the positive active material, the geometrical disposition of the phases throughout the plate thickness has been determined (31,32,39) and is shown schematically in Fig. 1. Although many lead-acid-battery positive plates do not contain significant amounts of αPbO_2, in those where it does form a considerable percentage of the mass, its physical distribution is of interest, especially so if it contributes durability and strength to the active material as suggested by Dodson (42) and Simon (62).

A beneficial action of αPbO_2 in the positive active material has been ascribed to its relatively larger particle size and durability under electrochemical cycling of the plate. The assessment of particle size has been made on electrode deposits of the material and, therefore, is somewhat suspect when it is formed in the active material of the lead-acid battery under rather different conditions. It does not seem likely that larger particle size can be an intrinsic characteristic of this material but, rather, may be expected to be related to the method of preparation. Different procedures for synthesis have been shown to give rise to significantly different morphologies and crystallinities of αPbO_2 (5,14).

Kordes (14) examined the positive active mass by x-ray diffraction, small-angle scattering, and neutron diffraction. He concluded that the interior of the mass was well crystallized, whereas the outer layers, or grain boundary material, were "poorly" crystallized. The small-angle scattering studies indicated that the shape factor for the PbO_2 grains was 1.2 to 1.3 (for spherical particles this factor is 0.5); however, it was not possible to determine whether the particles were rods or platelets. The average particle

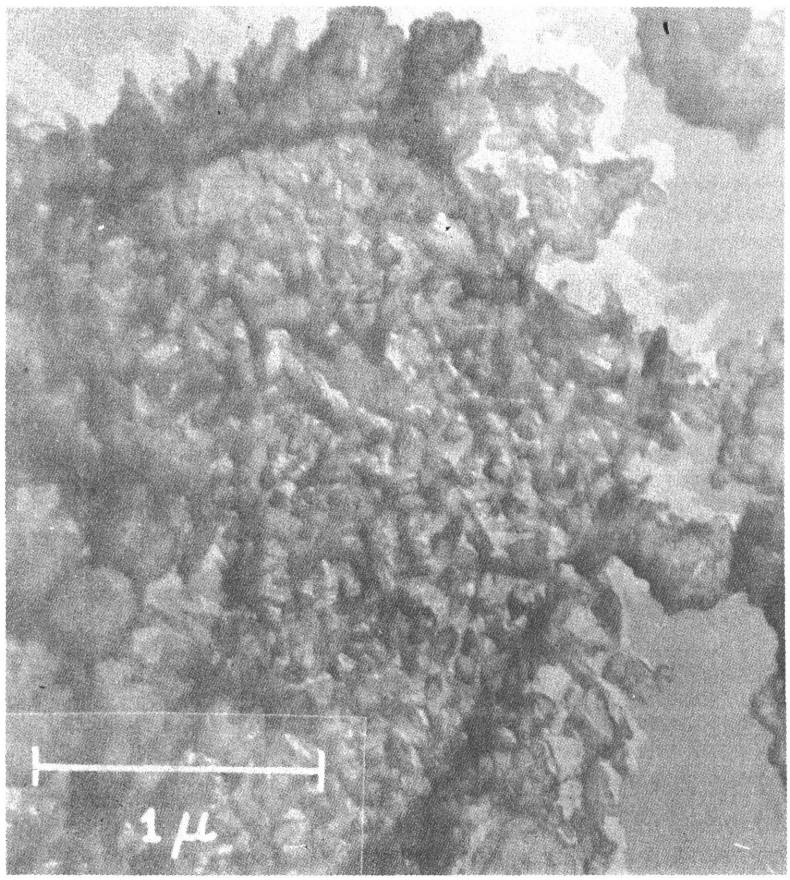

Fig. 2 - Electron micrograph of a carbon replica of PbO_2 crystals taken from a positive plate having high strength and long life. A firmly welded interlocked mass of small prismatic crystals of this type is considered to be an ideal morphological structure for a positive plate.

size was between 0.38 and 0.56 μ, giving a calculated specific surface area of between 15 and 24 m^2/g. Surface-area determinations by gas-absorption methods show lower values, in the order of 7 m^2/g (14,53). Burbank and Ritchie (65), using electron microscopy to examine the morphology of positive plates immediately after oxidation in dilute H_2SO_4, came to the conclusion that compound spikes of 0.5-μ crystals were covered with a layer of sessile crystallites which appeared to be about 0.1 μ or less in diameter; rodlike crystallites or whiskers were also present (Fig. 3). Thus, the direct morphological examination agrees with the evidence from x-ray line broadening, small-angle scattering, and neutron diffraction. Furthermore, the electron morphology did not reveal any "amorphous" material as such. The particles were well formed but small crystallites.

During the course of charge and discharge cycles, Kordes further determined that the PbO_2 particles increased in size to 0.55 to 0.6 μ, while the shape factor was reduced to 0.9, indicating a gradual growth and anhedralization of the PbO_2 grains was taking place. The end of life was attributed to these changes. Earlier, Burbank (63) had suggested that active material stability was related to the particle morphology of the PbO_2

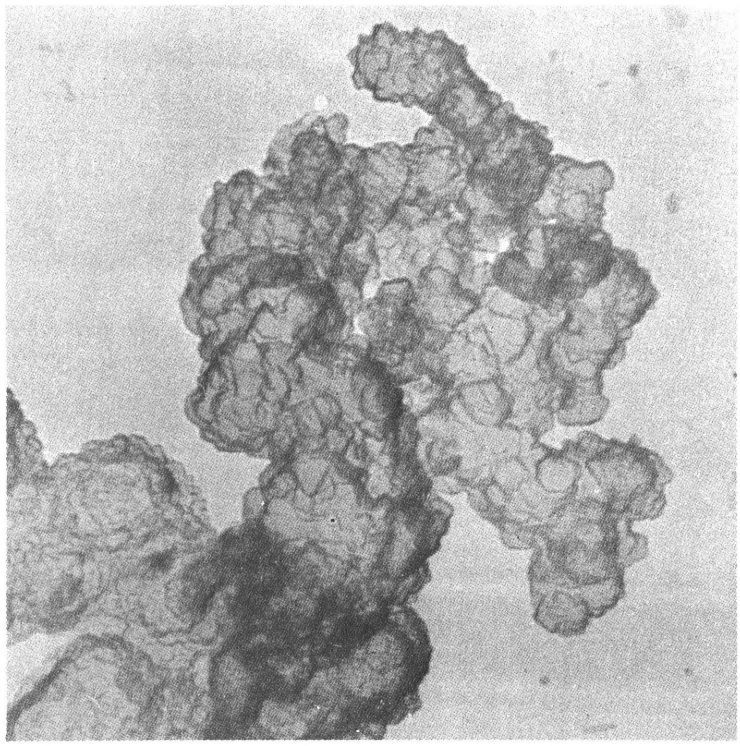

Fig. 3 - Electron micrograph of a carbon replica of freshly formed positive active material from a plate of a standard automotive battery type. No αPbO_2 was detected in this plate. The structure appears to be made up of compound spikes of larger crystals overgrown with small sessile crystallites. Small clusters of dendrites or whiskers are also present (65).

and that anhedralization of the PbO_2 grains was associated with paste deterioration by softening.

All evidence presently available indicates that further study of the factors controlling particle size and morphology in the positive active material is one of the most promising fields for research in the lead-acid battery. Because relatively little is known from a general viewpoint about the fundamentals that control crystallization processes, it is necessary to study each individual system in detail. The growth characteristics of PbO_2 are under investigation at the present time with the ultimate aim of developing a firm scientific basis for controlling the microstructure of the positive active mass. It has been concluded from a study of crystallization phenomena in general that to obtain prismatic growth of interlocked crystals from solution (a) there must be permeation by at least a capillary film of liquid ahead of the growing crystal, (b) the liquid must wet the surface of the growing crystal, and (c) the intercrystal boundaries must have a lower energy than the liquid/crystal interface, or the crystals will not weld during growth. These factors must be considered in any adequate fundamental approach to study of the morphological control of the positive active material.

ANTIMONY IN THE POSITIVE PLATE

Most lead-acid cells are fabricated with grids of Pb-Sb alloy containing as a rule from 4 to 12 wt-% Sb. The primary purpose of the Sb is to strengthen the grid metal so that it can be cast and fabricated with greater ease than pure Pb, which is very soft and easily deformed. The action of the Sb, however, is not solely metallurgical. It is leached from the grid metal and causes detrimental as well as beneficial side reactions. The most destructive effect is the increased rate of self-discharge induced at both negative and positive plates (66-68). In addition, Sb has a low hydrogen overvoltage, and if it is allowed to accumulate excessively on the surface of the negative plate, it will interfere with charging, because H_2 will be liberated in preference to the reduction of $PbSO_4$. The poisonous gas SbH_3 is formed during overcharge conditions, which becomes a health hazard when cell gases are vented into enclosed spaces.

Herrmann, Ilge, and Proepstl (69,70) recently studied the migration of Sb in the lead-acid cell by means of radioactive tracers. Of the Sb removed from the positive grid during formation (1.5% of the total Sb present), 92% remained associated with the positive plate. Even when the Sb was contained only in the negative grid metal, it migrated to the positive active material, although not in as large amount as when present in the positive grids themselves. This relatively large accumulation of Sb in the positive active material persisted from formation through cycling and overcharge testing of the cells. In other investigations (38) Sb present in the positive grid had the beneficial effect of maintaining the prismatic morphology of the PbO_2 crystals.

As mentioned previously, during the course of charge and discharge cycles (14), the particle size of the PbO_2 increased, and the end of life was associated with this increase as well as with the anhedralization of the grains. Freshly prepared active material had about the same electron morphology and particle-size characteristics whether formed on the pure Pb or the Pb-Sb alloy (14,65). Kordes (14) found that in active materials on pure Pb grids the increase in particle size with cycling was more rapid than on Pb-Sb grids, reaching a maximum after only eight to ten cycles. The same paste on antimonial grids increased in particle size at a markedly slower rate and reached a maximum after 20 cycles. It has been reported that the presence of Sb in the grid metal gives rise to an increased content of αPbO_2 in the formed active material (38). Furthermore, Ritchie (71) has recently found that the presence of Sb_2O_3 in an unformed paste mix inhibits the oxidation of free metallic Pb and, hence, the normal curing process of leady oxides. To some extent Sb in the grid metal may give rise to this same inhibiting reaction in the areas near the grid bars, and the physical distribution of αPbO_2 in the plate, Fig. 1, suggests that this may be a possibility.

The mechanisms of the behavior of Sb should be investigated further, because when it is fully determined how the Sb functions in the positive active material, it may be possible to designate a substitute that will have the same beneficial properties and be free of the detrimental ones.

OXYGEN OVERVOLTAGE ON THE PbO_2 ELECTRODES

The theoretical standard potential for the O_2/H_2O reaction is 1.23 v relative to the standard H^+/H_2 electrode. In acid solutions, the standard potentials of the $PbO_2/PbSO_4$ electrodes lie some 400 mv anodic to the O_2 electrode, and H_2O should be decomposed on contact with PbO_2. The fact that the $PbO_2/PbSO_4$ electrode is essentially stable in aqueous solutions shows that the O_2 liberation reaction is experimentally very slow on PbO_2 and requires a high overvoltage to proceed at significant rates.

A number of investigators have determined the O_2 overvoltage on PbO_2 and have concluded that the reaction follows a Tafel equation:

$$\eta = (2.303\ RT/\alpha F) \log i + a, \tag{4}$$

where η is the overvoltage, R the gas constant, T the absolute temperature, F the Faraday, α the transfer coefficient, i the current density, and a is a constant.

In the O_2 liberation reaction on βPbO_2 electrodes, α in Eq. (4) has a value of 0.5, the same value found for O_2 liberation on Pt in H_2SO_4 and associated with a single-electron transfer step as the rate controlling reaction.

On αPbO_2 electrodes, α in Eq. (4) has a value close to unity (72). The difference in the Tafel slopes suggests that the O_2 liberation mechanism is different for the two polymorphs; however, Ruetschi, et al. (72), consider that the higher Tafel slope on βPbO_2 may be caused by strong adsorption of SO_4^{-2} covering active sites, changing the structure of the double layer, and thus increasing the potential for a given apparent current density

Studies of the liberation of O_2 on PbO_2 electrodes are complicated in that the surfaces of the electrodes change with time. The nature of this change has not been determined, but it has been suggested that the lattice vacancies of the nonstoichiometric PbO_2 become saturated with O_2. This process should result in increased electrical resistance, as fewer free electrons should be available to the conduction band. Jones, et al. (73), ruled out this explanation, because they searched for but could not measure any change in resistance with time. Fleischmann and Thirsk (57) and others have suggested that the change in the O_2 overvoltage with time may be caused by a change in the surface-layer free energy, which increases up to the capillary maximum (74,75). The change, whatever its nature, is slow enough so that in any given experiment it does not interfere with obtaining the Tafel slope; however, it does prevent reproducing the magnitude of the overvoltage at a given apparent current density on aged electrodes or on different electrodes.

Decay of O_2 overvoltage on the two polymorphs shows the negative of each Tafel slope (72), and such O_2-charged electrodes, when discharged by reverse currents, will recover up to 100 mv on current interruption. This behavior has been attributed to the presence of some oxidized species adsorbed or absorbed in or on the surface of the electrodes.

The different Tafel slopes for the two types of PbO_2, 0.14 for βPbO_2 and 0.07 for αPbO_2, may be of importance from a practical viewpoint. Consideration of this relationship indicates that on an electrode comprising a mixture of the two polymorphs, such as may be present in some positive plates of the lead-acid battery, the current distribution on the two phases during overcharge periods will be different. At a given polarization, the amount of current going to O_2 gassing on αPbO_2 will exceed that on βPbO_2. As indicated previously, Fig. 1, the major portion of αPbO_2 is in the internal portions of the plates, and these areas may gas at a higher rate during overcharge. Such a phenomenon might be expected to cause undue disruption of the active material, perhaps abetting the physical breakdown of the plates in overcharge tests. Dodson (42) showed that plates containing large amounts of αPbO_2 gave better performance on constant current overcharge testing than plates containing average amounts, and the plate polarization was some 50 mv lower when large amounts of αPbO_2 were present. He concluded that the lower polarization reduced the grid corrosion rate and extended plate life for this reason.

As mentioned earlier, Fleischmann and Thirsk (57) determined that the overvoltage for the formation of βPbO_2 from $PbSO_4$ was approximately 0.1 to 0.15 v, depending on experimental conditions. It is possible that O_2 liberation on αPbO_2 may be kinetically

easier than oxidation of $PbSO_4$ to βPbO_2. This question has not been investigated; however, if the O_2 reaction on αPbO_2 is the easier of the two, charging current will be wasted and crystals of $PbSO_4$ will remain in the "charged" plate. These residual crystals could act as nuclei for deposition of more $PbSO_4$ during subsequent discharge. Gradually the $PbSO_4$ crystals would grow in size, producing the "hard" sulfate associated with some types of plate failure. Experimental examination of these possibilities would be of interest.

A SUMMARY LIST OF RESEARCH PROBLEMS

Perhaps the major purpose of a review of this nature is the delineation of areas where more research is needed; the following list of challenging problems may serve to stimulate the curiosity and imagination of research electrochemists:

- Can the efficiency of PbO_2 electrodes be improved without sacrificing durability?

- By what mechanism does the positive plate active material soften and fail?

- Do the inhomogeneities present in the positives immediately after formation determine the suitability of the plates for "dry-charge" use? Can formation methods be developed that will eliminate these variations?

- Why not perfect the analytical methods for PbO_2 so that the stoichiometry may be established precisely, and why not determine whether the O_2 deficiency varies with the H_2SO_4 concentration in the cell?

- Is there a third form of PbO_2 and what is its polymorphic relation to the two known crystal forms?

- Why does the x-ray diffraction pattern of αPbO_2 show abnormally low intensity in standard mixtures of the two polymorphs? What is the source of αPbO_2 in modern battery plates? What function, if any, does αPbO_2 serve in determining the operational characteristics of the positive plate? Can the apparent anomalies for formation of αPbO_2 as a corrosion product on grid alloys and in the active material be resolved?

- What are the kinetic mechanism and charge exchange reaction of the reversible $PbO_2/PbSO_4$ electrode? What characterizes the behavior of electrodes of αPbO_2, βPbO_2, and mixtures of the two polymorphs?

- What factors control the geometrical morphology of PbO_2 crystals in the positive plate? Is there an intrinsic crystallite size and shape associated with plate durability?

- Can internal plate porosity be controlled by fabrication processes?

- By what mechanism does Sb in the grid alloy delay the onset of positive plate failure? Is there a suitable substitute for Sb that does not have its detrimental side effects?

- Can the nature of the surface change of PbO_2 electrodes with time be determined? Is this related to crystal structure, stoichiometry, or physical morphology of the electrodes?

- Is O_2 liberation on αPbO_2 kinetically easier than oxidation of $PbSO_4$ to βPbO_2? Does this have a bearing on the charge acceptance rate at the positive plates? Does this control the appearance and growth of "hard sulfate"?

- And one final question, a problem of utmost practical importance, but an area so difficult to investigate experimentally in a satisfying manner that it has been the subject of little published data: Why does the active material paste stay in the metal grid? What is the nature of the bond between the two?

All these questions and more remain to be answered for a complete understanding of the operation of the positive plate to permit exploitation of its potentialities to the fullest extent. Despite the emphasis on the positive plate of the lead-acid cell, answers to many of these questions are of a fundamental nature that would lend insight into problems associated with other types of battery plates.

REFERENCES

1. Bode, H., and Euler, J., Electrochim. Acta 11:1211 (1966)
2. Bode, H., and Euler, J., Electrochim. Acta 11:1221 (1966)
3. Bode, H., Euler, J., Rieder, E., and Schmitt, H., Electrochim. Acta 11:1231 (1966)
4. Barrett, C.S., Ind. Eng. Chem. 25:297 (1933)
5. Bagshaw, N.E., Clarke, R.L., and Halliwell, B., J. Appl. Chem. 16:180 (1966)
6. Bystrom, A., Arkiv Kemi, Mineral. Geol. 20A (No. 11) (1945)
7. Katz, T., Ann. Chim. (Paris) 12th ser. 5:5 (1950)
8. Butler, G., and Copp, J.L., J. Chem. Soc. 1956:727 (1956)
9. Anderson, J.S., and Sterns, M., J. Inorg. Nucl. Chem. 11:272 (1959)
10. Golovanov, I.M., Zap. Vses. Mineralogi. Obshchestva 8:333 (1959)
11. Zaslavskii, A.I., Kondrashov, Y.D., and Tolkachev, S.S., Doklady Akad. Nauk SSSR 75:559 (1950)
12. Zaslavskii, A.I., and Tolkachev, S.S., Russ. J. Phys. Chem. 26:743 (1952)
13. Ruetschi, P., Sklarchuk, J., and Angstadt, R.T., Electrochim. Acta 8:333 (1963)
14. Kordes, D., Chem. Ing. Tech. 38:638 (1966)
15. White, W.B., Dachille, F., and Roy, R., J. Am. Ceram. Soc. 44:170 (1961)
16. Sasvári, K., Acta Phys. Acad. Sci. Hung. 11:333 (1960)
17. Sasvári, K., Acta Phys. Acad. Sci. Hung. 11:345 (1960)
18. Goldschmidt, H.J., Metallurgia 62:211, 241 (1960)
19. McQueen, R.G., Jamieson, J.C., and Marsh, S.P., Sci. 155:1401 (1967)
20. Kirkinskii, V.A., Zh. Neorgan. Khim. SSSR 10:1966 (1965)
21. Ritchie, E.J., "The Transition of the Polymeric Forms of Lead Monoxide," Eagle-Picher Research Laboratories Fourth Quarterly Report on contract NONR-512(00), July 1952
22. Burbank, J., in "Power Sources 1966," D. H. Collins, editor, New York:Pergamon, p. 147, 1967

23. Burbank, J., "The Plate Materials of the Lead-Acid Cell, Part 3 - Anodic Oxidation of Tetragonal PbO," NRL Report 6613, Dec. 29, 1967

24. Dodson, V.H., J. Electrochem. Soc. 108:401 (1961)

25. Fedorova, N.N., Aguf, I.A., Levinson, L.M., and Dasoyan, M.A., Ind. Lab. (USSR) 30:914 (1964)

26. Fedorova, N.N., Aguf, I.A., Levinson, L.M., and Dasoyan, M.A., Sb. Rab. Khim. Istochnikam Toka 1966:252 (1966)

27. Thomas, U.B., Trans. Electrochem. Soc. 94:42 (1948)

28. Frey, D.A., and Weaver, H.E., J. Electrochem. Soc. 107:930 (1960)

29. Aguf, A., Rusin, A.I., and Dasoyan, M.A., Zashchitn. Metal. i Oksidnye Pokrytiya, Korroziya Metal. i Issled. v Obl. Elektrokhim., Akad. Nauk S.S.S.R., Otd. Obshch. i Tekhn. Khim., Sb. Statei 1965:328 (1965)

30. Bode, H., and Voss, E., Z. Elektrochem. 60:1053 (1956)

31. Dugdale, I., in "Power Sources 1966," D.H. Collins, editor, New York:Pergamon, p. 142, Discussion following paper by R.G. Acton, p. 133, 1967

32. Carey, W.C.M., "X-ray Diffraction as a Technique for Studying Lead-Acid Battery Plates," British Railways Research Department Report C.R. 21, July 1965

33. Mazza, L., Atti Reale Accad. Lincei 4:215 (1926)

34. Mazza, L., Atti Reale Accad. Lincei 5:117 (1927)

35. Ruetschi, P., and Cahan, B.D., J. Electrochem. Soc. 105:369 (1958)

36. Baker, R.A., J. Electrochem. Soc. 109:337 (1962)

37. Simon, A.C., and Jones, E.L., J. Electrochem. Soc. 109:760 (1962)

38. Burbank, J., J. Electrochem. Soc. 111:1112 (1964)

39. Ikari, S., Yoshizawa, S., and Okada, S., Denki-Kagaku 27:487 (1959) (in Japanese). A brief extract of this paper is available in English in J. Electrochem. Soc. Japan, Overseas Ed. 27:E-186 (1959); however, this contains a misprint: line 21, p. E-187, where "tetragonal PbO" should read "tetragonal PbO_2."

40. Greenburg, R.H., Finan, F.B., and Agruss, B., J. Electrochem. Soc. 98:474 (1951)

41. Levinson, L.M., Aguf, I.A., and Dasoyan, M.A., J. Appl. Chem. (USSR) 39:525 (1966)

42. Dodson, V.H., J. Electrochem. Soc. 108:406 (1961)

43. Beck, W.H., Singh, K.P., and Wynne-Jones, W.F.K., Trans. Faraday Soc. 55:331 (1959)

44. Bone, S.J., Singh, K.P., and Wynne-Jones, W.F.K., Electrochim. Acta, 4:288 (1961)

45. Angstadt, R.T., Venuto, C.J., and Ruetschi, P., J. Electrochem. Soc. 109:177 (1962)

46. Ness, P., Electrochim. Acta 12:161 (1967)

47. Aguf, I.A., Russ. J. Phys. Chem. 39:598 (1965)

48. Vetter, K.J., Z. Elektrochim. 66:577 (1962)

49. Ruetschi, P., and Cahan, B.D., J. Electrochem. Soc. 104:406 (1957)

50. Burbank, J., J. Electrochem. Soc. 104:693 (1957)

51. Ikari, S., Yoshizawa, S., and Okada, S., Denki-Kagaku 27:552 (1959) (In Japanese). A brief extract of this paper is available in English in J. Electrochem. Soc. Japan, Overseas Ed. 27:E-223 (1959)

52. Mark, H.B., Jr., J. Electrochem. Soc. 109:634 (1962)

53. Voss, E., and Freundlich, J., in "Batteries," D.H. Collins, editor, New York: Pergamon, p. 73, 1963

54. Ruetschi, P., Sklarchuk, J., and Angstadt, R.T., in "Batteries," D.H. Collins, editor, New York:Pergamon, p. 89, 1963

55. Beck, W.H., Lind, R., and Wynne-Jones, W.F.K., Trans. Faraday Soc. 50:147 (1954)

56. Kabanov, B.N., Leikis, D.I., and Krepakova, E.I., Doklady Akad. Nauk S.S.S.R. 98: 989 (1954)

57. Fleischmann, M., and Thirsk, H.R., Trans. Faraday Soc. 51:71 (1955)

58. Mark, H.B., Jr., and Vosburgh, W.C., J. Electrochem. Soc. 108:615 (1961)

59. Drotschmann, C., Batteries 17:472 (1963)

60. Feitknecht, W., Z. Elektrochem. 62:795 (1958)

61. Van Vlack, L.H., in "Microstructure of Ceramic Materials," National Bureau of Standards Misc. Pub. 257, p. 1, Apr. 6, 1964

62. Simon, A.C., in "Batteries 2," D.H. Collins, editor, New York:Pergamon, p. 63, 1965

63. Burbank, J., in "Batteries," D.H. Collins, editor, New York:Pergamon, p. 43, 1963

64. Burbank, J., J. Electrochem. Soc. 111:765 (1964)

65. Burbank, J., and Ritchie, E.J., J. Electrochem. Soc. 116:125 (1969)

66. Zachlin, A.C., Trans. Electrochem. Soc. 82:365 (1942)

67. Zachlin, A.C., Trans. Electrochem. Soc. 92:259 (1947)

68. Lander, J.J., J. Electrochem. Soc. 99:339 (1952)

69. Herrmann, W., and Proepstl, G., Z. Elektrochem. 61:1154 (1957)

70. Herrmann, W., Ilge, W., and Proepstl, G.H., in "Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy," Geneva: United Nations vol. 19, p. 272, 1958

71. Ritchie, E.J., "Pastes and Grids for the Lead-Acid Battery," Eagle-Picher Industries, Inc., Progress Report 2 on combined ILZRO research contracts LE-82 and LE-84, Dec. 1967

72. Ruetschi, P., Angstadt, R.T., and Cahan, B.D., J. Electrochem. Soc. 106:547 (1959)

73. Jones, P., Lind, R., and Wynne-Jones, W.F.K., Trans. Faraday Soc. 50:972 (1954)

74. Kabanov, B.N., Kiseleva, I.G., and Leikis, D.I., Doklady Akad. Nauk SSSR 99:805 (1954)

75. Leikis, D.I., and Venstrem, E.K., Doklady Akad. Nauk SSSR 112:97 (1957)

Appendix

ESSENTIAL CHARACTERISTICS OF THE LEAD-ACID CELL

The lead-acid cell is over 100 years old, and in the review of recent research on the positive plate, covered in the main body of this report, a familiarity with the system has been assumed. For convenience, however, a brief background is presented in this Appendix which is a small part of the information readily available in texts.*

The lead-acid cell is fabricated from Pb, PbO_2, H_2SO_4, and H_2O, encased in a jar of acid-resistant material, such as hard rubber, glass, or plastic. The top of the cell has two sturdy terminals (one positive and one negative) for making external electrical contacts and an opening for adding water, when necessary, and for withdrawing the electrolyte to measure its specific gravity. The opening is normally closed with a vented cap or porous ceramic dome which acts as a flash arrester.

Inside the lead-acid cell, submerged in aqueous H_2SO_4, is a row of flat plates, usually packed close together, with insulating porous sheets between adjacent plates. These sheets, called separators, keep the plates from shorting to each other. The insulation may be enhanced by layers of glass wool and perforated rubber known as retainers. These separator materials must be porous so that the electrolyte may wet the plates, be electronically nonconducting so that the plates will not be short circuited, and be inert to the electrolyte.

The flat plates themselves are of two kinds, packed alternately in the series negative, positive, negative. These plates are the source of the electrical energy in the cell. When the cell is ready to deliver energy ("charged"), the negative plates ("negatives") are metallic Pb and the positive plates ("positives") are PbO_2. When power is drained from the cell ("discharged"), the plate materials react with the electrolyte to form $PbSO_4$. The cell can be recharged from an external power source and used over and over again, or "cycled."

There are two types of plates, characterized by the method of fabrication. Planté plates are made by developing PbO_2 and spongy Pb from Pb metal itself by cycling in suitable electrolyte. "Pasted" plates are made on castings of Pb or Pb alloys with an intricate mesh design. Into the interstices of this mesh is forced a stiff paste of PbO basic lead sulfates, H_2SO_4, and H_2O. This paste composition, additives, particle size, density, etc., vary over a considerable range; however, the ultimate electrochemically active materials ("active materials") in the charged plates are always Pb and PbO_2. After the plates are pasted, they must be "cured" by permitting the chemical reaction of the paste materials to take place under suitable ambient conditions, followed by drying. After curing, the plates are assembled into cell elements, submerged in aqueous H_2SO_4, and given a "forming" charge. This converts the pastes into the active materials. The process is called "formation," and at the completion of the charge, the plates are said to be "formed." H_2SO_4 used for formation is usually more dilute than the electrolyte used in the working cells and is called "forming" acid.

*For example, G.W. Vinal, "Storage Batteries," 4th ed., New York:Wiley, 1955.

The castings which hold the active materials and make electrical contact with them are "grids." Their dimensions and the design of the mesh vary with the manufacturer and the intended use of the cells. The grids are cast from Pb and Pb alloyed with other metals. Pb is a soft metal and deforms easily; therefore, alloying agents are beneficial because they harden the grid, but at the same time, they must not cause deleterious side reactions in the cell nor interfere with the reactions of the active materials. The most common element used for hardening Pb grids is Sb, and in recent years Ca has been used for certain types of batteries. Neither Sb nor Ca is an "active" material in the cell; their presence is manifested only in side effects, but the corresponding cells are commonly referred to as "Pb-Sb" or "Pb-Ca," respectively. The grid in the lead-acid cell, while not considered an "active" part of the cell, is an essential part, just as the jar or connectors are. The grid is primarily intended to make electrical contact with the active material pastes, but at the positive plate it is subjected to very high anodic polarization. This results in corrosion, and many cells ultimately fail because of positive grid corrosion.

Lead-acid cells are charged by a constant current, a constant voltage, or a combination of the two, a modified constant voltage. When the charge is extended beyond the amount required to convert the $PbSO_4$ to the corresponding quantity of Pb and PbO_2 at each plate, the excess current goes to generation of O_2 at the positive plates and H_2 at the negatives. This is an explosive mixture, and appropriate precautions are necessary to prevent accidents. The portion of the charge during which the plates are gassing is referred to as "overcharge." All energy that goes to the generation of the gases is lost and not recoverable as useful discharge of the cell.

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

THE POSITIVE PLATE OF THE LEAD-ACID CELL — A CRITICAL REVIEW OF RECENT LITERATURE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Interim report; work is continuing.

5. AUTHOR(S) *(First name, middle initial, last name)*

Jeanne Burbank

6. REPORT DATE February 18, 1969	7a. TOTAL NO. OF PAGES 26	7b. NO. OF REFS 75

8a. CONTRACT OR GRANT NO. NRL Problem C05-14 b. PROJECT NO. RR 010-01-45-4755 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6859 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research), Washington, D.C. 20360

13. ABSTRACT

Recent scientific literature on the positive plate of the lead-acid cell has been critically reviewed. The principal constituent of the plate is the nonstoichiometric oxide $PbO_{1.80-1.98}(OH)_{0.11-0.26}$, which under normal conditions behaves as a semimetal, the free electrons in the conduction band imparting a conductivity of 10^3 mho/cm. Two polymorphic crystal forms are known, and the electrochemical characterization of each has been investigated. The significance of the geometrical morphology and the function of Sb in the positive plate have been shown to be related: Sb acts to preserve the small particle size of the surface crystals that give high electrochemical capacity to the plate. O_2 overvoltage is different on the two polymorphs, and it is thought that the form having the lower overvoltage serves to prolong the life of the plates in overcharge tests.

In this review particular emphasis has been placed on relating the research findings to cell behavior and to pointing out areas where further work is required.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Lead-acid cell						
PbO_2						
$PbSO_4$						
Storage batteries						
Positive plate oxides						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

Security Classification