

ever, 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

BY GEORGE L. CLARK AND ROBERT ROWAN

Several investigators have reported the transition yellow, orthorhombic PbO \rightarrow 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 Tyler² 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 cor-

relate 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

(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).

the "corners" which remained. These are shown in actual size along with the turning mechanism, in Fig. 1.

Apparatus for the Determination of Catalytic Activity.—

The method employed by Clark and Tyler, measurement of evolved oxygen upon catalytic decomposition of hydrogen peroxide, was used in the determination of the catalytic activities of distorted samples obtained by grinding. The procedure they described was followed in detail so that comparisons could be made between products prepared by decomposition methods and those obtained in the present work.

Attention might be called to an improvement which was made on the apparatus used by Clark and Tyler. One of the main difficulties in the technique of such measurements is that the decomposition occurs so rapidly that one operator has not time to do everything essential. He must keep the leveling bulb level with the top of the liquid in the buret, read the level of the liquid, and at the same time read and record the time. Consequently a device was designed which would read and record the time automatically so that the operator's eyes could be kept on the buret throughout the measurement. This consisted of a moving tape which was unrolled from a motor-driven spool at a constant rate. Pressing against the tape was a pencil held with a spring clip such that the point could be deflected at right angles to the lengthwise dimension of the tape. As the pencil was deflected at intervals by a tap with the finger, a sawtooth pattern was produced in which the "teeth" corresponded to the exact time the pencil was tapped. After calibration with a stop watch, this method gave an estimated accuracy of ± 0.5 second.

Procedure for the Preparation of Active Tetragonal Lead Monoxide by Grinding Orthorhombic Lead Monoxide.—The grinding procedure was standardized and maintained the same, except for time, for all of the preparations. Exactly 2 g. of yellow PbO, prepared in one large lot by decomposition of basic lead carbonate at 650° , was weighed and placed in the ball mill. The sample, balls, and ball mill were then dried in an oven for one hour at 115° . For all grinds the mill contained sixteen one-fourth inch and nineteen one-half inch steel balls and three of the short rods previously described. The turning time was two revolutions per second.

Samples of active material were prepared by grinding for arbitrarily selected lengths of time: namely, $\frac{1}{2}$, 1, 3, 10, 30, and 60 hours.

Results.—X-Ray examination of active samples prepared by grinding showed the characteristic broadening of certain lines and the fading of high order reflections observed for distorted lead monoxides prepared by other methods. It was found that, with the grinding method used, all of the yellow PbO was not converted entirely in less than about three hours. Patterns of the material ground one-half and one hour contained yellow PbO lines.

Duplicate activity runs on the same sample usually checked within 10%. Considering the difficulty of the method and the number of vari-

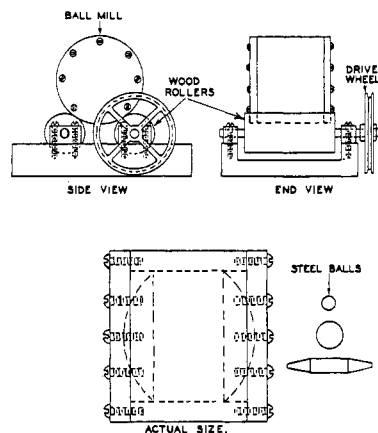


Fig. 1.—Grinding apparatus.

able factors, this is satisfactory. Reaction rate constants taking the hydrogen peroxide decomposition to be a first-order reaction and the ultimate total yield of oxygen (about 32 cc.) as the initial concentration, were found to be extremely constant. The criterion for activity used by Clark and Tyler, however, was cc. of oxygen evolved per second, obtained from the almost straight initial portion of the curve.

Although the activity data were not as consistent as was hoped, it can be said, in general, that an increase in grinding time up to ten hours gives an increase in catalytic activity. This was not marked for very long grinding times, since there was no significant difference between the thirty and sixty hour grinds. If results are calculated on the same basis, the more active samples prepared by grinding were about on a par (1.5–2 cc. O₂/sec.) with the more active samples prepared by Clark and Tyler by other methods, although none of the former were as active as two or three of their most active ones.

In Table I are presented average activity data from a number of runs, for samples ground for varying lengths of time.

TABLE I
SUMMARY OF ACTIVITY RESULTS

Grinding time	O ₂ evolved per sec., cc.	
	Av.	
$\frac{1}{2}$ hr.	1.02	
1 hr.	1.5	
3 hrs.	1.8	
10 hrs.	2.0	
30 hrs.	1.7	
60 hrs.	1.65	
Yellow PbO	0.16	

Three of these activity curves are shown in Fig. 2. Curve no. 1 represents a sample of low

activity and curve no. 2, one of high activity. Curve no. 3 was plotted from the data of Clark and Tyler on one of their more active samples prepared by the vacuum decomposition of PbCO_3 at 250° .

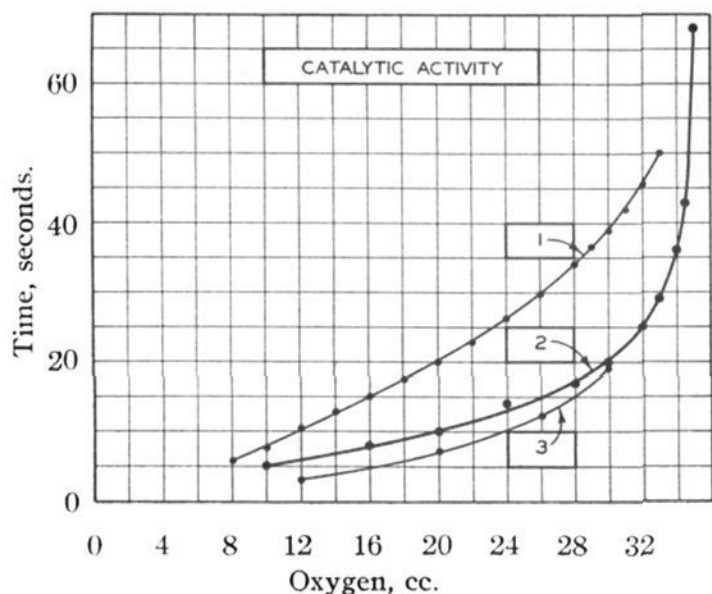


Fig. 2.

Clark and Tyler found an increase of 1-2% in heat of solution for active lead oxides prepared by decomposition methods. Since samples prepared by grinding parallel their rather closely, both as to catalytic activity and X-ray line broadening, it is reasonable to suppose that they would also show an abnormal heat of solution, so that it was not considered necessary to perform the rather laborious heat of solution measurements.

The relative increase in reactive power of these samples was also demonstrated by a semi-quantitative test for active oxygen on the residues from the catalytic activity tests. A measured volume of hydrochloric acid was placed in the flask, and the solution was boiled, the evolved chlorine being bubbled through a small amount of potassium iodide solution. In general, there was a direct correlation between the resulting color of the potassium iodide solution and the catalytic activity previously measured, the more active samples producing the darkest colors and, therefore, evidently were more reactive toward hydrogen peroxide.

The Removal of Distortion in Active PbO .—

The question of distortion in PbO is of immediate practical importance in the storage battery field because of the greatly increased reactivity.³

(3) These experiments will be presented in detail in a subsequent paper in this series; for example, the formation of Pb_3O_4 by refluxing distorted PbO and PbO_2 in water at 100° , whereas no such reaction occurs with ordinary yellow or red PbO . For greatly increased rate of reaction with oxygen see the next paper.

Thus, a method for the removal of distortion may have a practical significance, besides the light which the conditions of removal might throw upon the actual structure of the distorted state in lead monoxide.

The experiments previously described have indicated that long-time grinding, far in excess of that required to produce the distortion, did not remove it. This is contrary to what might be expected if, as the evidence of Clark and Tyler has indicated, the distortion effects are due to incompletely formed lattice areas. Another effect which might be expected on the basis of the above postulation, is that the distortion could be removed by annealing at a temperature below the Red $\text{PbO} \rightarrow$ Yellow PbO transition temperature. Consequently, samples of a distorted PbO prepared by grinding thirty hours were annealed for three and one-half hours at 500 , 400 , and 300° . X-Ray patterns taken of these annealed preparations showed complete relief from distortion for the 500 and 400° treatment and partial relief for the 300° treatment; 300° is probably the practical limit below which the relieving process takes place at a very slow rate. This is borne out by later experiments in which lead carbonate was decomposed *in vacuo* for as long as seventy-two hours at 215° to produce a very distorted PbO . One would expect complete removal of distortion in such a length of time if the process was not negligibly slow. Thus, the belief that distortion in PbO is due to a poorly oriented lattice, with perhaps atoms missing at random throughout the lattice, as a result of the fact that the shift in positions from the orthorhombic to tetragonal arrangement is still incomplete is given further support.

Attempts to remove the distortion by subjecting samples to liquid air temperatures and to supersonic waves of moderate intensity were unsuccessful. Although not much could reasonably

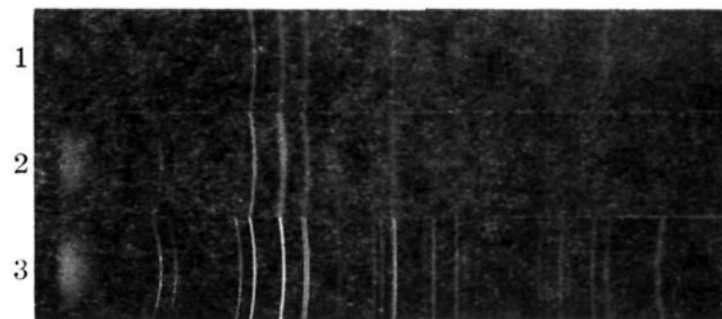


Fig. 3.—Typical diffraction patterns of normal and distorted tetragonal PbO .

be expected of the former treatment, supersonic waves might have some effect if the intensity were great enough.

The X-ray diffraction patterns shown in Fig. 3 illustrate the distortion effects. Pattern no. 1 shows the product obtained upon vacuum decomposition of $2\text{Pb}(\text{OH})_2 \cdot 3\text{PbO}$ at 130° ; pattern no. 2, the distorted PbO obtained by grinding; and pattern no. 3, the normal undistorted red PbO obtained by annealing a distorted sample at 400° for three and one-half hours. A distorted PbO can be obtained also (rather unexpectedly) by crystallization from solution. This will be discussed in the next paper.

Summary

1. Subjecting metastable, yellow orthorhombic PbO to grinding converts it to a distorted red tetragonal PbO , as is evidenced by the characteristic broadening of certain lines and the decrease in intensity of high order interferences on the X-ray diffraction pattern, as well as by the increased catalytic activity of the product.

2. A quantitative study has been made to correlate extent of grinding with degree of distortion, using the rate of decomposition of hydrogen peroxide as a measure of catalytic activity. In general, increased grinding up to ten hours produces an increase in distortion. The activity of distorted samples prepared by grinding is, in general, about the same as that produced by other methods.

3. Distortion in PbO can be relieved completely by annealing. This process is rapid at 400 and 500° , slow at 300° , and apparently almost zero at 215° . Attempts to relieve distortion by subjecting samples to liquid air temperatures and to ultrasonic vibrations were unsuccessful.

4. The fact that distortion in PbO can be removed by annealing lends further support to the theory advanced by Clark and Tyler, which states that the properties observed must be due to imperfectly crystallized areas as a result of the transition from orthorhombic to tetragonal arrangement which is still in process.

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Studies on Lead Oxides.¹ V. Further Experiments on Compounds of the Type $\text{PbO}_{n(n=1 \text{ to } 2)}$

BY GEORGE L. CLARK AND ROBERT ROWAN

I. The Addition of Oxygen to PbO and its Removal from PbO_2 .—The primary purpose of this series of experiments was to determine what relation, if any, the so-called "black red lead" of LeBlanc and Eberius² bears to the compounds prepared by Clark, Schieltz and Quirke³ and to further clarify the field as much as possible. This has, of course, involved the preparation of the "black red lead" and also the crystalline Pb_5O_8 and Pb_2O_3 of Clark, Schieltz and Quirke. According to LeBlanc and Eberius, the "black red lead" can be prepared by the addition of oxygen to PbO (either red or yellow) or the subtraction of oxygen from PbO_2 . It was decided to make the preparation by both methods to see if they differed in so far as the X-ray pattern was concerned. Clark, Schieltz and Quirke give directions for the preparation of crystals of

Pb_5O_8 , Pb_2O_3 and Pb_3O_4 , using a modification of the bomb method devised by Simon.⁴

Apparatus.—The apparatus used for the vacuum decomposition of PbO_2 and for the addition of oxygen to PbO at various controlled temperatures is shown in Fig. 1. It consisted of an outer cylinder of Pyrex glass eighteen inches long and three inches in outer diameter. Inside the cylinder, the heating unit consisted of a fused quartz tube eight inches long and seven-eighths inch in diameter. The quartz tube was held in the center of the outer tube by two doughnut-shaped supports of heavy asbestos board, and the alumel wire winding was insulated with asbestos paper. Two large rubber stoppers, bored for the insertion of thermocouple, vacuum system connection, and heating current wires, were flanged to make a vacuum tight seal with the ends of the outer tube. The construction of the rest of the apparatus is evident from the diagram. The chromel-alumel thermocouple was suitably standardized according to the melting points of pure zinc, lead, and tin and the boiling point of water. The heating current was controlled by means of a lampbank and stovepipe resistances. It was found that, if the room temperature remained constant, the furnace could usually be left for hours without a

(1) For the fourth paper of this series, see Clark and Rowan, *THIS JOURNAL*, **63**, 1302 (1941).

(2) LeBlanc and Eberius, *Z. physik. Chem.*, **A160**, 69 (1932).

(3) Clark, Schieltz and Quirke, *THIS JOURNAL*, **59**, 2305 (1937).

(4) Simon, *Z. anorg. allgem. Chem.*, **185**, 280, 300 (1930).