



A Neutron Powder Diffraction Study of α - and β -PbO₂ in the Positive Electrode Material of Lead-Acid Batteries

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ABSTRACT

A neutron powder diffraction study of α - and β -PbO₂, both chemically prepared and electrochemically formed in cycled battery plates, was carried out to correlate the electrochemical activity of the lead-acid battery with the atomic arrangement of the electrode constituents. Our results are consistent with the presence of hydrogen in the structure of β -PbO₂, but the departure of the occupancy factors from stoichiometric values are not large enough to unambiguously establish whether there are lead or oxygen deficiencies. If the Pb:O ratio corresponds to exact stoichiometry, any hydrogen which is present must be accompanied by a reduction of Pb⁴⁺. There is a significant increase in the lattice parameter *a* of β -PbO₂ in cycled battery electrodes relative to the value found in chemically prepared β -PbO₂. No change in the *c* parameter, however, was detected. These dimensional changes are consistent with a configuration for hydrogen similar to that observed in the rutile-type structure of SnO₂, in which there are OH⁻ ions oriented perpendicular to the *c* axis. The profile parameters obtained in this analysis show that the crystallites of β -PbO₂ in the positive plate material of a battery cycled three times (Y3) are smaller than those in the chemically prepared compound (~450 Å vs. 800 Å), while there are no significant differences between the latter and β -PbO₂ in the positive plate material of a battery cycled 36 times (Y36). The average structure of α -PbO₂ cannot be accurately determined by profile analysis, at the present time. The difficulties encountered in the refinement may be due to extensive defects, nonspherical crystallites of small size, and/or small departures of the structure from orthorhombic symmetry.

The active materials of the lead-acid battery are formed electrochemically by charging a commercial paste made from a mixture of PbO and sulfuric acid. In the charging process, the α - and β -phases of PbO₂ are formed at the positive plate and spongy lead at the negative plate. During discharge, both forms of PbO₂ transform into PbSO₄. Positive battery plates cannot be fabricated by directly pasting the grids with chemically prepared α - and β -PbO₂, for these prove to be electrochemically inactive forms, i.e., a battery made with these materials would not spontaneously generate a current when connected to an external circuit (1). The reason for this different behavior, resulting solely from the different methods of preparation of PbO₂, is not known at present.

Another phenomenon not yet understood is the loss of capacity of a battery after a number a charge-discharge cycles. Although mechanical factors may play a role in battery failures, chemical and structural changes must also be present (1). Caulder (2) has hypothesized that an inactive type of PbO₂ may form in increasing amounts during cycling. This hypothesis is consistent with differential thermal analysis (DTA), thermogravimetric analysis, high-temperature mass spectrometry, and pulsed nuclear magnetic resonance (NMR) measurements.

The origin of the electrochemical activity has also been linked with the presence of a hydrogen species

in the crystal structures of α - and β -PbO₂. NMR relaxation studies show that the active materials contain small amounts of hydrogen in two configurations, while the inactive oxides, chemically or electrochemically prepared, showed that the bulk of the hydrogen is predominantly in only one configuration (3).

It has been suggested, from results of DTA measurements, that an electrochemically active amorphous form of PbO₂ exists in the positive plate materials in addition to the α - and β -phases (2). This amorphous oxide would undergo some structural reordering during cycling (with loss of hydrogen species) and would be converted to an electrochemically inactive PbO₂ with NMR, DTA, and mass spectroscopic characteristics similar to those obtained from the chemically prepared materials.

The studies mentioned above lead us to conclude that the oxide often labeled as "PbO₂" can in fact be one of the following materials: (i) α -PbO₂ and (ii) β -PbO₂, as they are present in the active material of the positive plate; (iii) α -PbO₂ and (iv) β -PbO₂ as present in the positive plate after loss of capacity; and, finally, (v) α -PbO₂, (vi) β -PbO₂, and (vii) amorphous PbO₂ chemically prepared.

In order to understand the nature of the electrochemical activity of the lead-acid battery, it is important to determine if there are detectable structural differences between the active and the inactive forms of each phase. This, of course, implies the determination of the detailed crystal structures of the materials listed above. Studies in this direction have been carried out by powder neutron diffraction on the chemi-

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cally prepared α - and β -PbO₂ (4, 5) and, more recently, on electrochemically active β -PbO₂ (6, 7) and on the lead dioxides obtained from the positive plate of the lead-acid battery (8). The results of these studies show that, while the structure of the β -phase is well determined, that of the α -phase has not yet been understood in detail. In addition, it seems that there is considerable disagreement about the presence of an "amorphous" phase in the plate materials.

As a part of a study of lead dioxides, we have decided to refine the structures of α - and β -PbO₂ as they exist at different stages of the battery life and compare these structures with those of the chemically prepared materials. Neutron diffraction has been used throughout this analysis to take advantage of the favorable values of the scattering lengths of oxygen and lead and to avoid the problems connected with high absorption and preferred orientation which impose severe limitations on the x-ray diffraction experiments. Since none of the materials of interest can be prepared as single crystals, the powder method has been used in all the experiments.

Experimental

Samples.—The material labeled Y-36 was obtained from a commercially available 12 A-hr (c/10 rate) battery. The battery contained acid with a specific gravity of 1.260. The cycling regime consisted of a 6.0A constant current discharge to a 10.50V cutoff (1.75 V/cell). The battery was then recharged at 4.0A constant current until a crossover constant voltage of 15.00V (2.50 V/cell) was reached. Charging at constant voltage was continued until 110% of the previous discharge capacity was obtained. The initial discharge capacity of the battery was 7.47 A-hr. After 6 cycles, the capacity had leveled off to 7.20 A-hr. The average capacity of these first 6 cycles was 7.35 A-hr. The final capacity measurements prior to disassembly, after 36 cycles, was 6.30 A-hr. This value represented a 15% decrease in capacity from the average of the first 6 cycles. After disassembly, the PbO₂ electrodes were washed in distilled water and vacuum dried. The samples used in the diffraction experiments were then ground and air dried at 135°C.

The Y3 material was obtained from another battery cycled in the same manner as above, and the PbO₂ electrode was disassembled after three cycles. The average capacity of the battery at this point was 7.53 A-hr.

The chemically prepared β -PbO₂ used in this study was Baker reagent grade (lot no. 4604) dried in air at 130°C. Chemically prepared α -PbO₂ was obtained by oxidizing ammoniacal lead acetate with ammonium persulfate, and the compound was dried in air at 130°C.

Neutron diffraction measurements.—The neutron diffraction intensities were measured at room temperature with the high-resolution five-detector diffractometer at the National Bureau of Standards Reactor (9), using the experimental conditions indicated in Table I. The data were analyzed with the Rietveld method (10), modified by Prince (11) to simultaneously process the intensities collected by the five counters of the diffractometer.

Refinements and Results

From the first stages of the structural analysis, it was apparent that the peaks of all samples examined had tails too broad to conform to a Gaussian distribution. This can be seen in Fig. 1a which shows a Gaussian least-squares fit of the reflection 002 of chemically prepared β -PbO₂. The discrepancy between observed and calculated intensities, especially evident in the tails and at the peak of the reflection, can be significantly reduced by using, for the fitting, the Pearson type VII function (12), as shown in Fig. 1b. A comparison of the two figures shows that the value of the

Table I. Experimental conditions used to collect the neutron powder intensity data for PbO₂

Monochromatic beam:	reflection 220 of a Cu monochromator
Wavelength:	1.5416(3) Å
Horizontal divergences:	(a) in-pile collimator: 10 min. arc; (b) monochromatic beam collimator: 20 min. arc; (c) diffracted beam collimator: 10 min. arc
Monochromator mosaic spread:	~ 15 min. arc
Sample container:	vanadium can ~ 10 mm diam
Angular ranges scanned by each detector:	10-40, 30-60, 50-80, 70-100, 90-120
Angular step:	0.05°

goodness of fit χ , the background, and the full width at half maximum are higher for the Gaussian approximation than for the Pearson function. The differences in the background level and in the full width at half maximum, caused by the improper description of the peak shape, may result in an erroneous evaluation of the occupancy and temperature factors of the atoms in the structure and in underestimated values of the sizes of the crystallites in the sample. Because of these results, it was necessary to use the Pearson function in all refinements rather than the usual Gaussian distribution. At this stage, it was thought necessary to repeat the refinement of chemically prepared β -PbO₂ which had been previously analyzed (4) assuming that the profiles were Gaussian.

The initial values of lattice, profile, and structural parameters were those obtained previously for β -PbO₂ (4), and the initial positional parameters of α -PbO₂ were those reported by Moseley *et al.* (5). The scattering amplitudes were $b(\text{Pb}) = 0.94$, $b(\text{O}) = 0.58 \times 10^{-12}$ cm (13).

The sample of chemically prepared β -PbO₂ was free from diffraction effects due to impurities, and therefore, the entire powder pattern was used in the refinement of the structure. The samples Y36 and Y3, however, contain both α - and β -PbO₂. The study of the β -phase in these samples could only be carried out by excluding, from the calculations, the angular regions containing the diffraction peaks of the α -phase and vice-versa.

In all cases, the background was assumed to be a straight line of finite slope and was refined for each of the five channels of the diffractometer, together with the profile and the structural parameters.

The value of the parameter m appearing in the Pearson equation (12) can be determined either by fitting isolated peaks or by carrying out a series of refinements with different values of the parameter m and selecting the refinement which gives the lowest R-factor and the most reasonable temperature parameters. Obviously, the first method is preferable, but it can only be used if the peaks selected for the determination of m are well isolated and permit an accurate evaluation of the background. This can be seen in Fig. 1c, which illustrates the Gaussian least-squares fit to the same 002 reflection of β -PbO₂, performed over an angular range too small for an accurate estimate of the background. The fit, which would be considered satisfactory without prior knowledge of the peak shape, would yield not only the wrong value of m but would also result in a background level so unreasonably high that it might affect even the atomic positional parameters calculated in the refinements. To avoid errors of this type, we have followed the second procedure, and the R-values *vs.* m obtained for β -PbO₂ are shown in Table II.

β -PbO₂.—The results of the refinements of β -PbO₂ in all the samples analyzed are given in Table III, where they are compared, where applicable, with those reported by previous authors. The calculated and observed profiles, with residuals, are shown in Fig. 2.

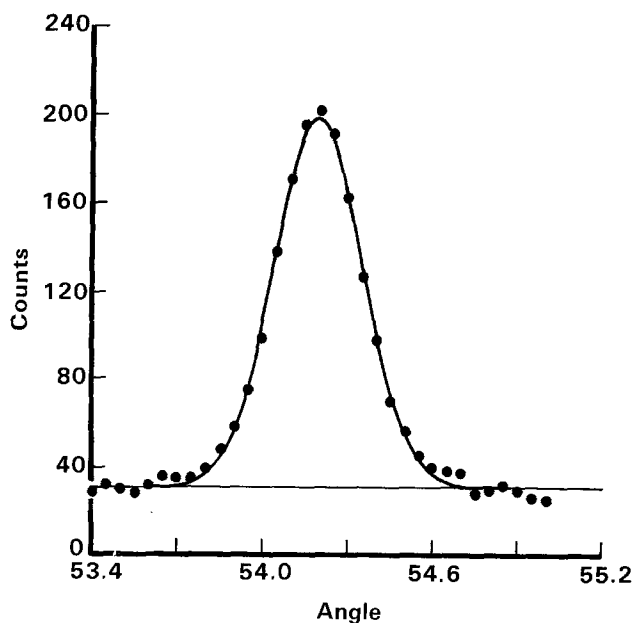
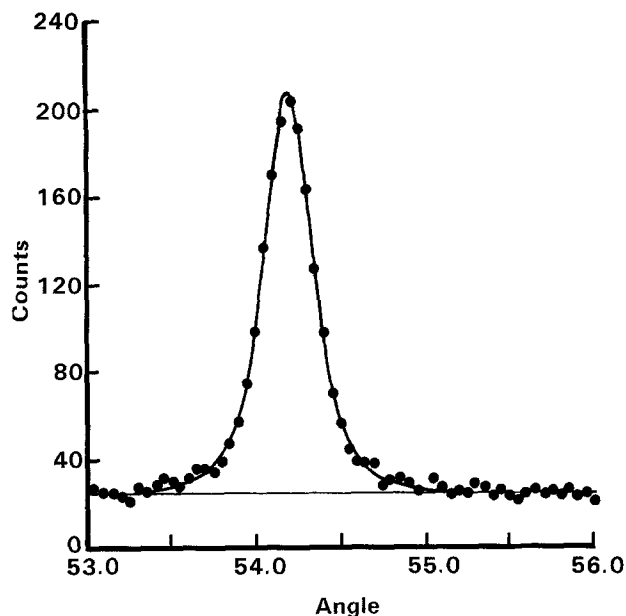
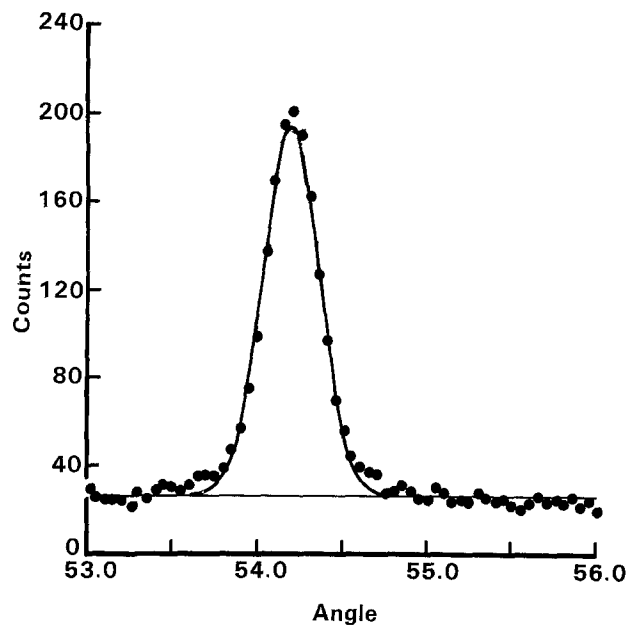


Fig. 1. Least-squares fits (continuous line) of the observed profile intensities (circles) for the reflection 002 of chemically prepared β -PbO₂: (a, top left) Gaussian fit (background = 268, peak height = 1675, $2\theta = 54.20$, $m = 100$, and $\chi = 2.11$). (b, top right) Pearson fit (background = 247, peak height = 1834, $2\theta = 54.20$, $m = 1.83$, and $\chi = 1.36$). (c, bottom) Gaussian fit over a limited angular range (background = 309, peak height = 1672, $2\theta = 54.20$, $m = 100$, and $\chi = 1.63$). (The parameter m is the Pearson parameter and determines the profile shape, and χ is the goodness of fit.)

As shown in the table, the lattice parameter a of β -PbO₂ in Y3 and Y36 is significantly higher than that of chemically prepared β -PbO₂, with a shift/pooled error, Δ/Σ , of 30 and 24 for Y3 and Y36, respectively, [pooled error = $(\sigma_1^2 + \sigma_2^2)^{1/2}$]. On the other hand, the value of c does not vary significantly from sample to sample (maximum $\Delta/\Sigma = 7.6$).

The positional parameter x of the oxygen atoms seems to decrease in the sequence β -PbO₂, Y36, Y3. The differences observed could indicate a trend, but they are too small to be considered significant (maximum $\Delta/\Sigma = 5.0$). The interatomic distances and angles calculated for the samples analyzed are reported in Table IV, in which the labeling of the atoms is the same as that indicated in Fig. 3. As a result of the observed changes in the a and x parameters, the distance O(3)-O(4) increases and the distance Pb-O(1) decreases in the sequence β -PbO₂, Y36, Y3. The O(3)-O(5) distance, which is equal to the parameter c of the unit cell, remains unchanged, as does the distance O(2)-O(5). This situation corresponds to a stretching of the octahedral basal plane O(3)-O(4)-O(5)-O(6) along the direction [110] and to a compression of the octahedron along the direction [110]. The parameter x_m reported in Table III is given by

$$x_m = (1/6) [(c^2/a^2) + 2]$$

and represents the particular value of x for which all the Pb-O distances are equal. In all the samples studied, x_m is significantly larger than x , i.e., the axial distances Pb-O (1, 2) are smaller than the equatorial distances Pb-O (3, 4, 5, 6). This result is of theoretical importance in the study of rutile-type AB₂ oxides (14), and it is in agreement with the conclusions of a previous analysis of chemically prepared β -PbO₂ (4).² The occupancy factor, n , of the lead atom differs from the theoretical value by 5% or less.

The parameters U , V , and W shown in Table III appear in the equation

$$H^2 = U \tan^2 \theta + V \tan \theta + W \quad [1]$$

in which H is the full width at half maximum ($fwhm$) of the instrumental profile at the diffraction angle θ . In

² In the first study of chemically prepared β -PbO₂, a Gaussian peak shape was adopted, and subsequently it was found that the Pearson function should have been used instead. In spite of the use of the Gaussian approximation, the agreement between the results of the two determinations is very close for all structural parameters, and this may be partly due to the fact that in the first analysis the tails of the diffraction lines were excluded from the refinement.

Table II. R-factors vs. the Pearson parameter m obtained for β -PbO₂

β -PbO ₂ , chemically prepared				
m	R_N	R_P	R_W	R_E
∞	6.61	8.55	10.86	4.66
4	5.62	7.44	9.36	4.66
3	5.25	7.14	9.02	4.66
2	5.00	6.83	8.77	4.66
1	5.78	9.23	12.07	4.66
β -PbO ₂ in Y3				
m	R_N	R_P	R_W	R_E
∞	8.43	4.90	6.23	3.51
2	4.48	4.18	5.29	3.51
β -PbO ₂ in Y36				
m	R_N	R_P	R_W	R_E
∞	6.09	6.62	8.38	6.22
3	5.62	6.10	7.70	6.22
2.5	5.48	6.07	7.66	6.22
2	5.37	6.08	7.67	6.22

The R-factors are defined in the following way

$$R_N = 100 \times \left\{ \frac{\sum |I(\text{obs}) - I(\text{calc})|}{\sum I(\text{obs})} \right\}$$

$$R_W = 100 \times \left\{ \frac{\sum w[y(\text{obs}) - y(\text{calc})]^2}{\sum w[y(\text{obs})]^2} \right\}^{1/2}$$

$$R_P = 100 \times \left\{ \frac{\sum |y(\text{obs}) - y(\text{calc})|}{\sum y(\text{obs})} \right\}$$

$$R_E = 100 \times \left\{ \frac{N - P + C}{\sum w[y(\text{obs})]^2} \right\}^{1/2}$$

In the above formulas N is the number of statistically independent observations, P the number of parameters refined, C the number of constraints, I the integrated intensities, and y the profile intensities of weight w .

Fig. 4, the values of H are plotted against θ for the three samples analyzed.

α -PbO₂.—The orthorhombic phase of PbO₂ is always present in the active material of the positive plate in varying quantities. In general, its proportion with respect to β -PbO₂ decreases as the number of battery cycles increases. It has been pointed out (5) that α -PbO₂ refines poorly, and it has been suggested that this behavior may be related to the defect structure of the compound.

The results of the structural and lattice parameter refinements obtained in this study are given in Table V, where they are compared with some of the results obtained by other authors. The calculated and observed profiles are shown in Fig. 5. It is evident from the table that the agreement between the various results is poor and that the determinations of both lattice and structural parameters are associated in all cases with unusually high standard deviations. Anneal-

Table IV. Interatomic distances (Å) and angles (deg) of β -PbO₂ in the samples analyzed

	Chemically prepared β -PbO ₂	Y36	Y3
Pb-O (3, 4, 5, 6)	2.1679(3)	2.1712(6)	2.1758(9)
Pb-O (1, 2)	2.1501(5)	2.1475(10)	2.142(2)
O (3)-O (4)	2.708(1)	2.721(2)	2.734(3)
O (5)-O (6)			
O (1)-O (3, 4, 5, 6)	3.0532(2)	3.0538(4)	3.0531(5)
O (2)-O (3, 4, 5, 6)			
O (4)-O (6)	3.3861(1)	3.3844(2)	3.3856(2)
O (3)-O (5)			
O (3)-Pb-O (4)	77.30(2)	77.59(4)	77.84(6)
O (5)-Pb-O (6)			

ing the samples at 160°, 180°, and 200°C for 120 hr did not improve the quality of the powder patterns and the agreement between observed and calculated values of the parameters. Refinements of the lattice constants were also attempted by using the 2θ values reported in the literature (15, 16). In all cases, there were differences between observed and calculated values of 2θ , which cannot be attributed to experimental errors. Also the results given by Hill (8) on this phase of PbO₂ (Table V) show that the values of the lattice and structural parameters depend on the method of preparation of the compound. In addition, the large values of the standard deviation reported for the various samples are an indication that these parameters could not be determined as precisely as those of β -PbO₂.

The uncertainties in the peak positions and peak intensities make it impossible to subtract the contribution of α -PbO₂ from any pattern containing both the α - and β -phases, and this is the reason why the refinements of β -PbO₂ in Y36 and Y3 had to be done by excluding, from the calculations, quite large angular intervals.

Discussion

Stoichiometry.—Previous authors (18) have pointed out that both α - and β -PbO₂ are nonstoichiometric. At first, it was thought that these oxides had oxygen deficiency and that their electric conductivity could be, in some way, associated with the excess lead present in the structure. Subsequent neutron diffraction measurements by Jorgensen *et al.* (6, 7) showed that no oxygen vacancies were present in electrically active β -PbO₂ and that, instead, the structure seems to be lead deficient. These authors found that the refined occupation numbers of lead were 0.97(2) for β -PbO₂ cycled in H₂SO₄ and 0.95(1) for β -PbO₂ cycled in D₂SO₄. The values do agree with those obtained by Hill (8) for β -PbO₂ present in the positive plate materials. If, therefore, we assume that β -PbO₂ is lead-

Table III. Results of the refinements of the structure of β -PbO₂ in the samples analyzed. Space group: $P4/mnm$; $Z = 2$. The figures in parentheses are the standard deviations on the last decimal figure.

Parameter	Chemically prepared β -PbO ₂	Y36	Y3	Jorgensen (7)		Naidu (14)	Chemically prepared	Hill (8) Fresh battery	Failed battery
				β -PbO ₂ :D	β -PbO ₂ :H				
$x(\text{O})$	0.3068(1)	0.3061(2)	0.3052(3)	0.3070(2)	0.3070(2)		0.3066(2)	0.3054(5)	0.3072(2)
$n(\text{Pb})$	0.493(2)	0.490(4)	0.477(4)	0.475(5)	0.485(10)		0.493(5)	0.475(8)	0.479(4)
a	4.9554(1)	4.9608(2)	4.9621(2)	4.9526(1)	4.9500(1)	4.9568(5)	4.9556(1)	4.9642(4)	4.9558(1)
c	3.3861(1)	3.3844(2)	3.3856(2)	3.3789(1)	3.3771(1)	3.3866(2)	3.3867(1)	3.3867(3)	3.3820(1)
x_m	0.3084	0.3082	0.3082	0.3082	0.3082	0.3083			
oxygen B				0.90(9)					
$\beta_{11} = \beta_{22}^*$	87(3)	91(70)		103(9)	96(8)		113(6)	145(17)	127(5)
β_{33}	90(9)	103(20)		110(18)	86(17)		115(14)	207(66)	168(13)
β_{12}	-56(4)	-84(8)		-50(4)	-68(6)		-70(6)	-52(18)	-60(6)
Lead B				0.51(5)					
$\beta_{11} = \beta_{22}$	54(3)	70(6)		44(6)	53(7)		78(4)	99(16)	83(4)
β_{33}	32(7)	73(14)		38(14)	33(15)		44(11)	103(51)	74(10)
β_{12}	-2(3)	-32(7)		-7(3)	7(5)		-9(5)	-6(19)	-5(5)
U	3858(150)	4461(280)	3534(450)						
V	1979(55)	1579(105)	2079(190)						
W	1291(15)	1266(30)	1770(40)						

* The anisotropic temperature factors are $\beta_{11} \times 10^4$, $\beta_{22} = \beta_{33} = 0$ for Pb and O atoms.

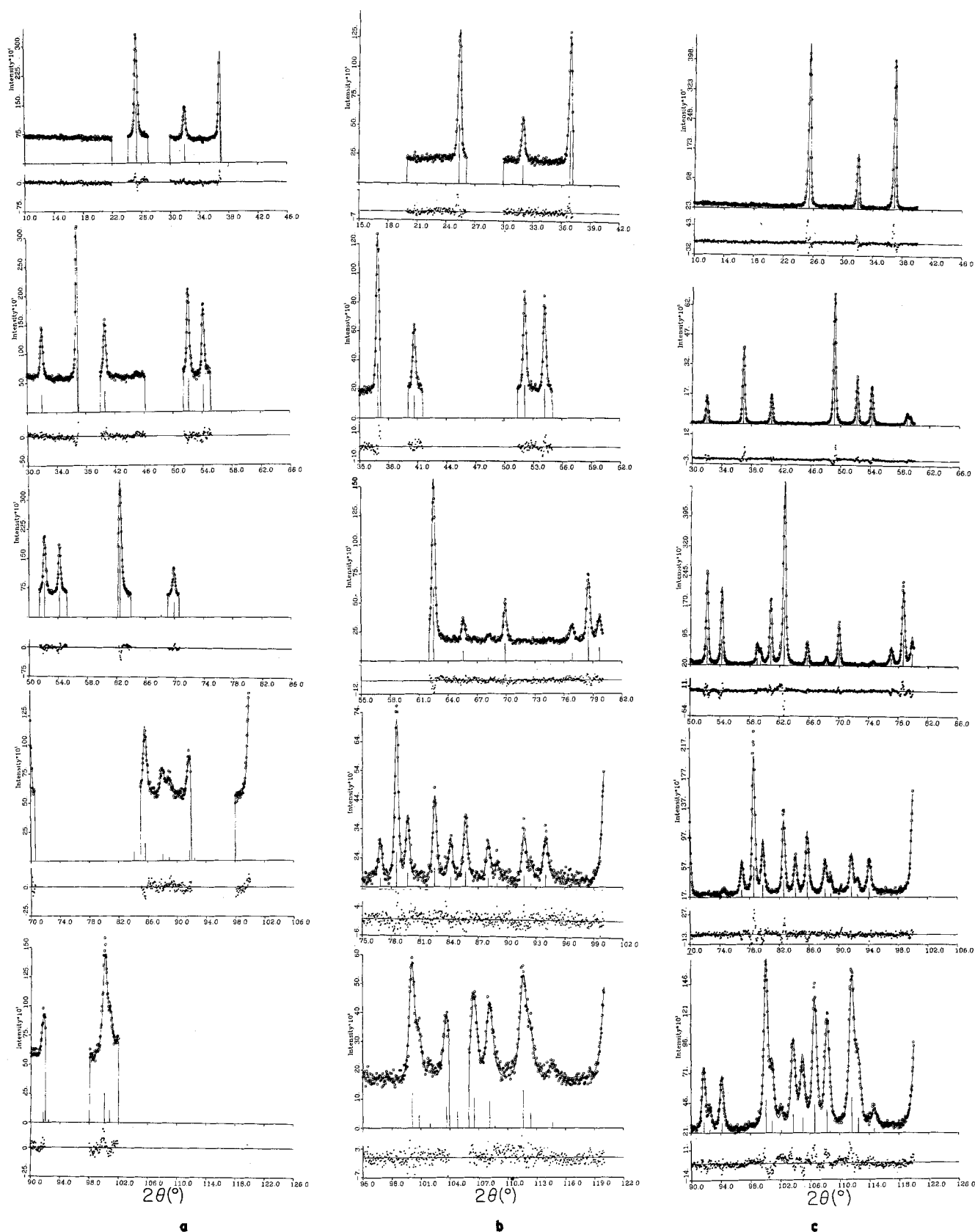
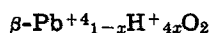


Fig. 2. Calculated (continuous line) and observed (circles) profiles, with residuals, over the five angular ranges for (a) β -PbO₂ in Y3 (b) β -PbO₂ in Y36 and (c) chemically prepared β -PbO₂.

deficient, the stoichiometry of the compound could be expressed by the formula



Our results support the view that the structure of β -PbO₂ is not oxygen deficient. In addition, the occupancy factors of lead obtained in our refinements do agree closely with those given by Jorgensen et al. (6,

7) and by Hill (8). We feel, however, that it is not possible to conclude that the structure is lead deficient. First of all, the departures from stoichiometry are only 5σ at the most, and second, the refined values of the occupation parameters may be affected by a number of factors which are difficult to account for. More specifically, an imprecise definition of the background level, especially at high values of 2θ , and/or uncer-

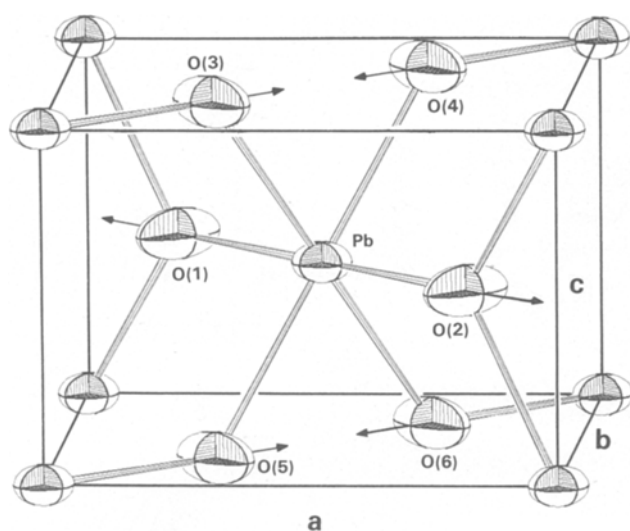


Fig. 3. Unit cell of β - PbO_2 . Atoms are represented by their thermal ellipsoids. The labeling of the atoms is the same as that in Table IV. Arrows indicate the direction of oxygen displacements accompanying cycling.

tainties in the description of peak shapes may cause departures of the type observed for β - PbO_2 . In addition, there are no chemical reasons which would require lead deficiency, not even if hydrogen must be accommodated in the structure (19). In fact, Moseley *et al.* have observed a close correlation between the quantity of hydrogen found from neutron transmission measurements and the difference between total Pb and Pb^{+4} , determined by analytical means. Consequently, they have proposed that the charge balance required by the incorporation of hydrogen in the structure is maintained by reduction of Pb^{+4} to, most probably, Pb^{+2} and have given for the compound the formula



Oxygen or lead deficiencies are not necessary to explain the electric conductivity of PbO_2 . In fact,

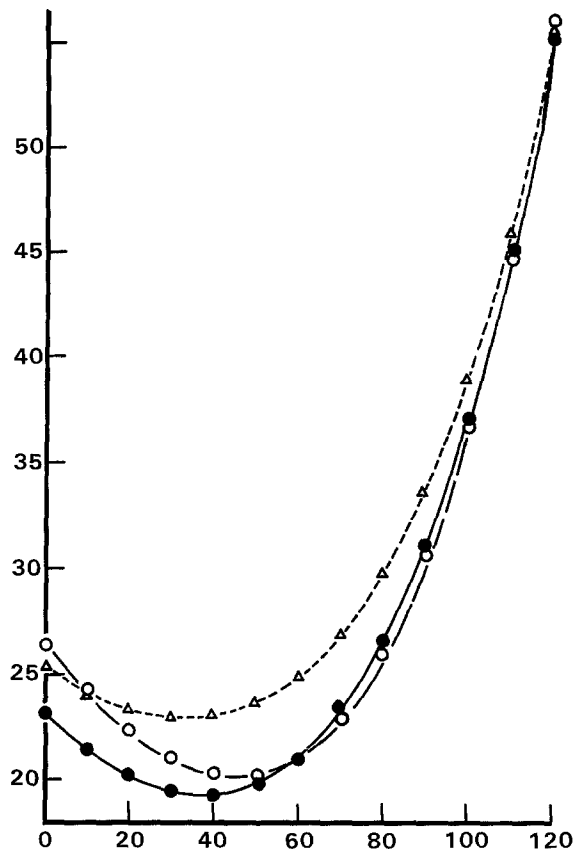


Fig. 4. The values of the full width at half maximum, H , calculated from the least-squares values of U , V , and W , using Eq. [1], are plotted vs. θ for β - PbO_2 (\bullet), Y36 (\circ), and Y3 (Δ).

Ruetschi and Cahan (20) have pointed out that free electrons may be due to OH^- groups substituting for oxygen. This model is realistic because, as mentioned in the introduction, the presence of bound hydrogen in β - PbO_2 has been established beyond doubt by a number of workers [e.g., Ref. (3)]. Inelastic neutron

Table V. Results of the structural and lattice parameters refinements α - PbO_2 $R_N = 11.65$, $R_P = 5.59$, $R_W = 7.63$, $R_E = 3.46$, $m = 1$ space group Pbcn , $Z = 4$

A) Lattice parameters

	a	b	c	
From neutron profile refinement*	4.9627 (10)	5.9588 (13)	5.4812 (8)	N
Y3 (202)**	4.980 (9)	5.964 (13)	5.473 (6)	N
Y3 (130)***	4.986 (10)	5.952 (9)	5.472 (6)	N
Annealed	4.967 (10)	5.979 (20)	5.482 (8)	N
Hill (8): chem. prepared	4.9898 (3)	5.9474 (4)	5.4656 (3)	N
Hill (8): acid electroformed	4.9947 (11)	5.9614 (15)	5.4707 (11)	N
Bagshaw <i>et al.</i> (15)	4.993 (3)	5.946 (2)	5.459 (3)	X(†)
Syono <i>et al.</i> (16)	4.998 (1)	5.958 (1)	5.465 (1)	X
Moseley <i>et al.</i> (5)	4.998 (1)	5.932 (1)	5.441 (1)	X
Zaslavskii <i>et al.</i> (17)	4.927	5.927	5.474	X

B) Structure

	Lead				
	This study	Moseley <i>et al.</i> (5)	Zaslavskii <i>et al.</i> (17)	Hill (8) Chem. prep.	Hill (8) Acid el.
x	0	0	0	0	0
y	0.1596 (8)	0.173 (7)	0.178	0.1779 (7)	0.1706 (13)
z	1/4	1/4	1/4	1/4	1/4
B	0.13 (9)	—	—	0.77 (12)	0.23 (22)
	Oxygen				
	This study	Moseley <i>et al.</i> (5)	Zaslavskii <i>et al.</i> (17)	Hill (8) Chem. prep.	Hill (8) Acid el.
x	0.2546 (12)	0.2 (2)	0.276	0.2685 (10)	0.2618 (19)
y	0.4005 (7)	0.35 (8)	0.410	0.4010 (7)	0.3977 (15)
z	0.4225 (7)	0.39 (9)	0.425	0.4248 (7)	0.4250 (14)
B	0.07 (9)	—	—	1.31 (18)	2.58 (33)

$U = 43300(4025)$, $V = 21850(1690)$, $W = 6185(230)$

* The structure was refined using the data obtained from chemically prepared α - PbO_2 .

** Peak at $2\theta = 49.48^\circ$ indexed as 202.

*** Peak at $2\theta = 49.48^\circ$ indexed as 130.

(†) X and N indicate that the corresponding measurement was made with x-rays and neutrons, respectively.

studies on chemically prepared β -PbO₂, Y3, and Y36 have indicated that the hydrogen is incorporated in the structure and is not present in pockets of pure

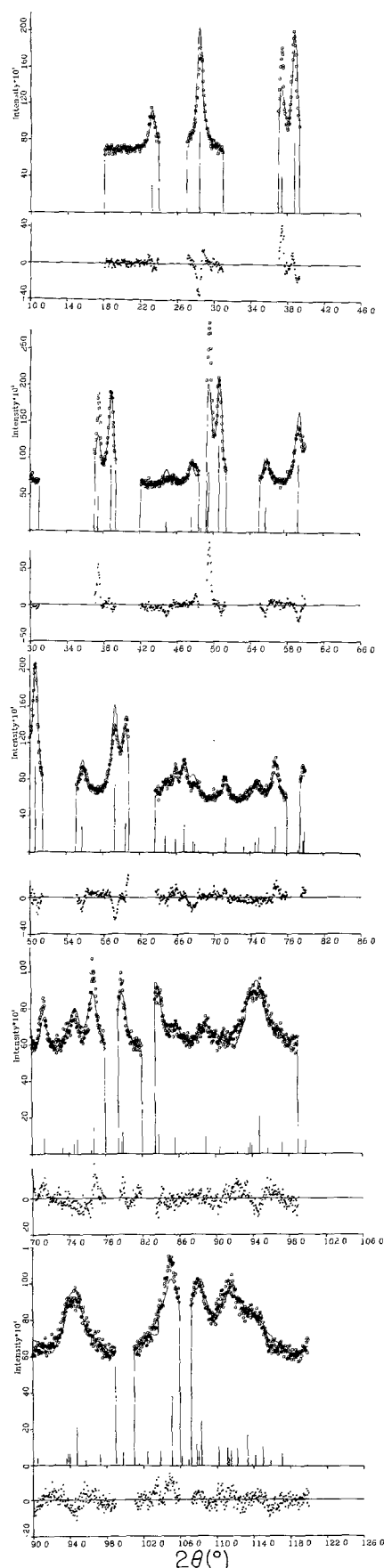


Fig. 5. Calculated (continuous line) and observed (circles) profiles, with residuals, over the five angular ranges for chemically prepared α -PbO₂.

or loosely bound water (21). The presence of hydroxyl ions, OH⁻, has been established in other rutile-type oxides, such as SnO₂ (22) and TiO₂ (23). In SnO₂, for example, the substitution of doubly charged oxygen ions with OH⁻ ions is associated with the replacement of Sn⁺⁴ with Fe⁺³ or Cr⁺³, which have similar sizes. It has also been observed, in polarized infrared studies on single crystals of SnO₂, that OH⁻ ions are formed with oxygen atoms of type 1 and 2 (Fig. 3) and are oriented perpendicular to the *c* axis of the tetragonal cell. A similar situation seems to also be present in TiO₂ (23). The same orientation of the OH⁻ ions in β -PbO₂ is very consistent with our results. In fact, both hydrogen content and length of the *a* axis are higher in Y36 and Y3 than in the chemically prepared compound, while the *c* axis remains practically unchanged in the two groups of samples. The above considerations, therefore, lead to the conclusion that our results, as well as those of Jorgensen *et al.* (6, 7) and of Hill (8) may be interpreted by saying that the β -phase is either stoichiometric or departs from stoichiometry to such an extent that the deviations cannot be detected with certainty with diffraction measurements of the type used in the reported experiments.

It has been impossible to meaningfully refine the occupation numbers of lead in α -PbO₂ and, therefore, no conclusions regarding the stoichiometry of this compound can be reached with our results.

Crystallite size.—The non-Gaussian shape of the reflections, observed in this study and in previous analyses (24), can be explained in a number of ways. The simplest and, probably, the most reasonable explanation is that the samples do contain crystallites with a distribution of sizes. If this is the case, then the pure profile (*i.e.*, the profile due solely to the sample) is nonGaussian, and therefore, its convolution with the Gaussian instrumental profile is also nonGaussian. If we assume that this interpretation is correct, we must conclude that the distribution of crystallite sizes of β -PbO₂ does not differ very much from sample to sample since the best refinements were obtained in all cases with a value of the Pearson parameter *m* of about 2.

The parameters *U*, *V*, and *W* of Eq. [1] depend on the experimental conditions and should be identical for identical geometric configurations of the diffractometer (25). Their variation from sample to sample, indicated in Table III and in Fig. 4, may be due to a number of factors, including crystallite size effects. This can be seen in the following way. If the crystallites are sufficiently small, there will be a broadening of the reflections according to Sherrer's equation

$$h = (K\lambda)/D \cos \theta \quad [2]$$

where *h* is the *fwhm* of the pure profile, λ is the wavelength of the radiation, *D* is the linear dimension of the crystallites in the direction perpendicular to the reflecting planes, and *K* is a constant. The experimental intensity distribution is the convolution of the profiles due to the instrument and to the sample. If, for the sake of simplicity, we assume that the shape of both profiles is Gaussian, then the total *fwhm* *H*_{tot} is given by

$$H_{\text{tot}}^2 = H^2 + h^2 = [(K^2\lambda^2/D^2) + U] \tan^2 \theta + V \tan \theta + [(K^2\lambda^2/D^2) + W] \quad [3]$$

If *D* is constant, *i.e.*, if the shape of the crystallites is spherical, or approximately spherical, Eq. [1] and [3] have the same form, although the numerical values of the coefficients are different. Thus, the curves of Fig. 4 can be interpreted as due to crystallite size effects. If we adopt this interpretation, we may conclude that the crystallites of β -PbO₂ in Y3 are smaller, on the average, than those in the chemically prepared compound, while there are no significant differences between the latter

and β -PbO₂ in Y36. A rough estimate of the crystallite size in our samples indicates that the average dimension in chemically prepared β -PbO₂ is about 800Å, while in Y3 it is around 450Å. These results are in broad agreement with those of Kordes (24), who found a mean size of 600-700Å for the β -phase of the positive plate. No estimates of sizes were attempted for α -PbO₂ in this study.

Lattice parameters of β -PbO₂.—As mentioned previously, the lattice parameter a of β -PbO₂ in Y3 and Y36 is significantly greater than that of the chemically prepared compound, while the c parameter remains unchanged. These results seem to be in disagreement with those obtained by Jorgensen *et al.* (7). These authors found that both parameters are smaller in the electrochemically prepared phase than those reported for the chemically prepared compound. However, if the Jorgensen parameters for PbO₂:H are multiplied by a scale factor of 1.00248,³ the new values agree to within one standard deviation with those obtained in this study for Y3. The constant factor relating the two determinations may be the result of errors in the calibration of the diffractometers used for the measurements in the two laboratories. It is interesting to note that Hill (8) observes the same variation of the parameter a as we do. His parameter c , however, is the same for chemically prepared β -PbO₂ and for β -PbO₂ present in the plate of a "fresh battery," but it is significantly lower for β -PbO₂ obtained from a "failed battery."

Refinements on α -PbO₂.—As mentioned previously, the difficulties encountered in the refinements of α -PbO₂ have been attributed to the presence of defects in the structure. This may certainly be true, since electron microscopy studies have shown that these defects are extensive (5, 19). Other factors, however, may also play a role. For example, the large discrepancies between calculated and observed 2θ values in lattice parameter refinements may be due to small departures of the structure from orthorhombic symmetry. The nature of the discrepancies in 2θ are also clearly shown in Fig. 5 for some reflections. A second possible cause for the poor profile refinements of α -PbO₂ may be due to the fact that some diffraction peaks do not follow the behavior indicated by Eq. [1]. This is an indication that the crystallites have nonspherical shape.

As the errors associated with the parameters are large, no differences between results can be established. We must, therefore, conclude that the data on the structure of α -PbO₂ are unreliable and that it is probably more useful to examine the detailed features of the compound with techniques other than diffraction, *e.g.*, by electron microscopy.

Amorphous PbO₂.—The presence of an amorphous form of PbO₂ has been proposed as a contributing active material of the positive plate (2) and to explain the nonGaussian profiles of the diffraction lines (24). The term "amorphous," however, has been used in a rather vague way to describe the lead-acid battery materials. In one case (26), it was meant to indicate the fraction of PbO₂ having crystallite sizes equal to, or less than, about 100Å.

Amorphous materials do not possess periodicity in one, two, or three dimensions and produce diffuse diffraction patterns characterized by broad halos. The first maximum would be evident in the 10°-40° angular range of the first detector. We have found no evidence of such diffuse scattering in any of our powder patterns. This result is in agreement with the observations of Jorgensen *et al.* (7) on electrochemically prepared β -PbO₂. On the other hand, Hill (8) has found "non-crystalline" material varying between 3 and 49 weight percent in the various samples analyzed. The disagree-

ment between Hill's results and ours may be only apparent because it may depend simply on the definition of the term "amorphous" given in each case. If we define as "amorphous" a material without periodicity, as we have done previously, then we may conclude that amorphous PbO₂ is either not present in our samples or it is present in quantities nondetectable by diffraction methods of the type used in this study.

Conclusions

The results given in the previous sections can be summarized as follows: (i) The refined occupancy factor calculations indicate that the Pb:O ratio in β -PbO₂ is exactly or very near 1:2. Incorporation of hydrogen in the structure may be accompanied by reduction of Pb⁴⁺. (ii) Dimensional changes in β -PbO₂ are consistent with the presence of OH⁻ ions in the structure, oriented along the [110] direction, as has been found in SnO₂ (22). (iii) The average structure of α -PbO₂ cannot be accurately determined by profile analysis at this time. The difficulties encountered in the refinement may be due to extensive defects, nonspherical crystallites, or small departures of the structure from orthorhombic symmetry. (iv) Based on the profile parameters, we may conclude that the crystallites of β -PbO₂ in Y3 (~450Å) are smaller than those in the chemically prepared compound (~800Å), while there are no significant differences between the latter and β -PbO₂ in Y36.

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Mathematical Analysis of a Zn/NiOOH Cell

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ABSTRACT

A mathematical model has been developed to predict the time dependent behavior of a Zn/NiOOH cell. The model uses experimentally determined polarization expressions to describe the losses between the positive and the negative electrodes. The electronic losses in the plane of the electrode are simulated by a network of resistors. The potential distribution, the current distribution, the cell voltage, the power capability, and the energy of a cell can be predicted. The mathematical model provides an analytical tool to evaluate, for example, the trade-offs between power capability and current collector mass, needed to design an electric vehicle battery.

An electrode current collector carries current from the battery terminal to active sites on the electrode where electrochemical reactions take place. With a large electrode, the electronic losses in the current collector can be appreciable such that an uneven distribution of reaction current and an uneven polarization exist on the electrode surface affecting both the specific power and the specific energy. Accelerated degradation and shorting of electrodes may result due to excessive localized gassing on the electrodes.

A current collector with high conductivity will give a uniform current distribution. Most often, a high conductivity current collector is synonymous with a heavy current collector. However, one can also improve the current distribution without increasing the overall weight of the current collector by strategically orienting the members of a current collector to evenly distribute the current. A mathematical model that can predict cell performance will facilitate the design of these strategic current collectors. Eventually, a computer program can be developed that will suggest an optimized current collector design for the specific application of a battery.

Tiedemann, Newman, and Desua (1) applied the resistive network model to bare lead-acid battery grids. The potential distribution on the grid was examined by assuming a uniform current density. Various grid designs were compared based on the magnitude of the maximum potential difference between the tab and the grid node. Using the same approach, Vaaler and Brooman (2) examined the current distribution of pasted positive lead-acid battery plates relative to an equipotential surface. Electrode kinetics were not included. Tiedemann and Newman (3) then expanded their earlier model to examine the transient behavior of a lead-acid cell. Cell polarization between the positive and the negative electrodes was expressed by using an empirical equation whose coefficients were determined based on the porous electrode model developed by Tiedemann and Newman (4). Recently, Sunu and Burrows (5) used a resistive model to examine the potential distributions of the positive plate

and the negative plate of a lead-acid cell individually under uniform current density. They compared plates with different widths based on the tab-to-corner potential difference. The plate area was not kept constant in the comparison. Good agreement was shown between their mathematically predicted and experimentally measured potential distributions.

The present work describes the use of a resistive model to predict the transient behavior of a Zn/NiOOH cell with current collectors of different conductivities. The polarization characteristics of the Zn/NiOOH system was determined experimentally on small electrodes and the empirical equation obtained was used in the model to predict system behavior of cells with full size electrodes. The potential distribution, the current distribution, the cell voltage, the power capability, and the energy capability can be calculated to aid in the design of a Zn/NiOOH battery. Although the mathematical model can be applied to predict both charge and discharge behaviors, only the discharge behavior of a Zn/NiOOH cell will be discussed in this paper.

The Mathematical Model

The model simulates the electrode by a network of resistors where each model node is joined to adjacent nodes by resistors. For each node on the positive current collector, there is a node directly opposite to it on the negative current collector. Between opposite nodes, the reaction current is related to the potentials at the nodes by the empirical equation obtained experimentally on a cell with small electrodes approximately the size of the unit element (area) associated with a mathematical node. With reference to Fig. 1, the equation related to node j on an electrode was obtained by applying Kirchhoff's law

$$\frac{\phi_n - \phi_j}{R_1} + \frac{\phi_k - \phi_j}{R_2} + \frac{\phi_l - \phi_j}{R_3} + \frac{\phi_m - \phi_j}{R_4} + i_j A_j = 0 \quad [1]$$

where ϕ 's are the potentials (V), R 's are the effective resistances (Ω) between nodes on the electrode, i_j is the reaction current density (A/cm²), and A_j is the

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