

## Discussions on the Lead/Acid Battery. No. 2

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### Hydrogen and Order-Disorder in PbO<sub>2</sub> in Lead/Acid Positive Plates

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#### Summary

The effect of crystal-structural hydrogen atoms and disorder on the electrochemical activity of lead dioxide in the positive plate of the lead/acid battery has long been the subject of conjecture and controversy. In this discussion, the evidence for the 'hydrogen-loss' model of battery failure is examined using results from a wide range of experimental techniques, and is found wanting.

#### Introduction

The performance of lead/acid batteries operated under deep-discharge conditions at temperatures in the range 25 °C - 50 °C is usually determined by the physicochemical properties of the positive plate [1 - 3]. Most of the evidence suggests that the decline in positive-plate capacity with battery service arises from progressive electrical isolation, surface-area reduction, and shedding of the plate material.

In addition to these 'traditional' explanations for the loss of positive-plate capacity, it has been suggested that the intrinsic electrochemical activity of the PbO<sub>2</sub> itself can change with charge/discharge service [4 - 9]. In this model, it is proposed that the activity is related to the abundance and nature of structural hydrogen atoms (henceforth denoted H), as well as to the amount of disorder in the crystal structure of PbO<sub>2</sub>. Specifically, the model argues that:

- (i) electrochemically prepared PbO<sub>2</sub> contains more H than the chemically-prepared (inactive) variety;
- (ii) electrochemically active samples have H present in at least two different configurations, one of which does not correspond to the H present in water molecules;

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(iii) the amount of the non-water H in the electrochemically active  $\text{PbO}_2$  decreases as the number of charge-discharge cycles increases;

(iv) electrochemically active  $\text{PbO}_2$  contains an amorphous/disordered component that undergoes structural re-ordering (associated with the H loss) as it is cycled.

This 'hydrogen-loss' (HL) model was very appealing because it was able to draw analogies between the low H-content and the well-ordered crystal structure of  $\text{PbO}_2$  samples from failed batteries, and the corresponding properties observed in chemically prepared  $\text{PbO}_2$ , which was claimed to be electrochemically inactive. Furthermore, it was consistent with the so-called 'stoichiometry-changing current' (SCC) model for the  $\text{PbO}_2$  electrode [10 - 12] in suggesting that the non-water H was a catalyst for, or an essential intermediate chemical species in, the reduction process.

The SCC model assumes that interstitial protons and quasi-free electrons are the dominant disorder centres in  $\text{PbO}_2$ . The application of a potential to the electrode leads, in the first few seconds, to a movement of H into, or out of, the  $\text{PbO}_2$  crystal structure and, hence, to a change in stoichiometry, before a stationary state involving the usual deposition or dissolution of  $\text{PbO}_2$  begins [11]. Since the transfer of protons across the phase boundary between the  $\text{PbO}_2$  and the electrolyte is largely unhindered, with kinetics determined mainly by the diffusion-controlled reactions of  $\text{PbO}_2$  dissolution and/or the anodic oxidation of gaseous oxygen, it has been claimed [13] that the effects of the SCC model are likely to be witnessed best during discharge at high (*i.e.*, cranking) rates. Indeed, the model provides an explanation for the high-rate capability (very mobile protons) and low capacity at high rate (small number of protons) of the lead/acid battery [13].

That H is involved at some point in the discharge process of  $\text{PbO}_2$  to  $\text{PbSO}_4$  is in little doubt. The surfaces of the  $\text{PbO}_2$  particles in an aqueous solution of  $\text{H}_2\text{SO}_4$  are essentially completely hydrolysed, and the  $\text{Pb}^{4+}$  and  $\text{SO}_4^{2-}$  ions in the electrolyte will have co-ordination spheres of  $(\text{OH})^-$  and  $\text{H}^+$  ions, and water molecules.

Thus, the point at issue in the HL model for battery failure is not whether H is involved in the discharge reaction. Instead, the question is whether the electrochemical activity of the  $\text{PbO}_2$  is dependent on the prior existence of H atoms contained within its (disordered) crystal structure, or whether it is sufficient for the H atoms participating in the charge/discharge reactions to be supplied from the hydrolysis layers of the particles and/or from the electrolyte itself, as required. It is this latter issue that is at the focus of the HL model and of the present discussion.

### The hydrogen-loss model of battery failure

Despite considerable research effort over a number of years [14 - 17, and references therein], the relevance of the HL model to battery capacity decline has yet to be satisfactorily resolved since much of the experimental

evidence is either ambiguous or contradictory. The two key issues in the model, namely, the influence of H on the one hand, and structural order/disorder on the other, on the electrochemical activity of  $\text{PbO}_2$ , will be treated in turn.

### *Influence of hydrogen*

Hydrogen atoms can be incorporated into the  $\text{PbO}_2$  crystal structure by a variety of mechanisms [14 - 16]: (i) coupled substitution of  $(\text{OH})^-$  for  $\text{O}^{2-}$ , and  $\text{Pb}^{2+}$  for  $\text{Pb}^{4+}$ ; (ii) direct substitution of  $4\text{H}^+$  for  $\text{Pb}^{4+}$ ; (iii) as interstitial protons, with mobile electrons.

Significant quantities of H (up to 0.6 H atoms per  $\text{PbO}_2$  unit) have been detected in samples of positive-plate material taken from both healthy and failed batteries [16, 18 - 22]. However, neutron and X-ray diffraction (XRD) studies of  $\text{PbO}_2$  have been unable to locate the H atoms in the crystal structure directly [14, 18, 20, 23 - 25]. Measured variations in the Pb:O ratio in  $\beta\text{-PbO}_2$  from exactly 1:2 have been of marginal significance (although large numbers of Pb atom vacancies have been observed in the generally minority polymorph  $\alpha\text{-PbO}_2$ ). Furthermore, no significant change has been detected in the crystal structure of  $\beta\text{-PbO}_2$  with either the method of preparation or the history of service in the battery [14, 20]. In fact, high-resolution XRD measurements of changes in  $\beta\text{-PbO}_2$  unit-cell dimensions with both battery service and amount of H in the bulk sample have shown no correlation of electrochemical activity with H content [14, 20], and have placed an upper limit of 0.01 H atoms per  $\text{PbO}_2$  unit on the amount of H that is incorporated into the  $\text{PbO}_2$  structure via the coupled-substitution mechanism [14].

Neutron inelastic and quasi-elastic studies of  $\text{PbO}_2$  have also provided conflicting results: some experiments have suggested that H is located within the octahedral chains of the structure [26, 27], while others have provided no evidence of any characteristic vibrations associated with hydroxyl or (bound) water molecules [19].

Recent nuclear magnetic resonance studies [16, 28] have corroborated the original work of Caulder *et al.* [4] in showing the presence of two kinds of H atoms in electrochemical  $\text{PbO}_2$  samples, and a reduced number in chemical material. One of these species is associated with mobile and/or isolated, adsorbed hydroxyl groups and/or water molecules that can be removed by outgassing [28]. The other proton species is more strongly bound and interacts with its proton neighbours; it most likely corresponds to water molecules and/or closely-spaced hydroxyl groups trapped on internal crystal surfaces. The relative abundance of the different forms is, however, strongly dependent on the method of sample pre-treatment. No evidence was found for a decrease in H content with longer battery service or decreased electrochemical activity, as required by the HL model for capacity decline.

High-temperature mass-spectroscopic studies of the dehydration and decomposition of  $\text{PbO}_2$  samples [16] have also confirmed the presence of

two kinds of H atoms, documented in earlier work [5]. In the recent studies, one H has been associated with physisorbed water evolved around 80 °C, and the other with particle decrepitation and cracking prior to structural decomposition of the  $\text{PbO}_2$  to  $\text{PbO}_x$  at 350 - 550 °C. This latter water probably corresponds to  $\text{H}_2\text{O}$  or  $(\text{OH})^-$  groups trapped on internal crystal surfaces and in micropores [16]. As found with nuclear magnetic resonance investigations, the relative masses of water evolved during these two stages vary from sample to sample and are dependent on preparation history and drying procedures; no correlation with battery activity has been discovered.

A similar series of decomposition studies conducted on tubular plates containing various forms of pre-treated  $\text{PbO}_2$  battery material produced the claim [29] that H bonded to the surface of the  $\text{PbO}_2$  particles is an essential component of active  $\text{PbO}_2$ , and that if this H is removed (say, by heating), then the capacity of the dioxide is dramatically reduced. The general veracity of this result is evident, but the extension of the conclusion to require the H to be an intrinsic part of the  $\text{PbO}_2$  crystal structure (ex-electrolyte) has been disputed [29].

Rather than being present as part of the bulk crystalline structure of  $\text{PbO}_2$ , it has been suggested that H may be present as surface-adsorbed water or hydroxyl species [14, 18, 20]. Support for this possibility has been provided by X-ray photoelectron spectroscopy [30] and neutron attenuation and inelastic measurements [16, 18 - 22]. Moreover, X-ray line-broadening measurements [14], as well as direct observation of the particles by transmission electron microscopy [19, 31, 32], have indicated that  $\text{PbO}_2$  samples frequently consist of very small crystallites with diameters in the range 100 - 1000 Å. Calculations of the H content that would result from hydrolysis of the total 'internal' surface area of these samples suggest [15] that much, if not all, of the H content observed in  $\text{PbO}_2$  samples may be present in this form.

This latter method of H atom incorporation into  $\text{PbO}_2$  provides an explanation, not only for the apparent inconsistency between measurements of surface area and the bulk H content obtained from neutron attenuation studies [18], but also for the failure of neutron diffraction to locate (or indeed, to find firm evidence for the presence of) H atoms in the ordered crystalline material. Furthermore,  $\text{PbO}_2$  prepared by non-aqueous routes (*i.e.*, some chemical forms) would be expected, as observed [19, 22, 32], to contain much less H.

The assumption in the HL model, now entrenched in the literature, that chemically-prepared  $\text{PbO}_2$  is electrochemically inactive has also been disputed. Recent studies [31, 33, 34] have corroborated earlier and largely ignored work [35] in suggesting that the poor activity displayed by chemical material is related only to reduced inter-particle contact resulting from its being formed *ex situ*, *i.e.*, not on the battery plate. Indeed, significant electrochemical activity can be observed in chemical material if particle contact is provided by the use of suitable binders and cycles of condition-charging [31, 34], or by the application of pressure [33, 35, 36].

### *Structural order–disorder*

The second key issue in the HL model for capacity decline, namely, the influence of crystal-structural order/disorder on the electrochemical activity of  $\text{PbO}_2$ , has not been studied as extensively as the H question. This is in spite of the fact that chemical analyses of  $\text{PbO}_2$  always show the samples to be non-stoichiometric [27, 37 - 43], often with substantial quantities of H [16, 18 - 22], and many of the samples contain significant levels of non-crystalline, amorphous material [24, 44 - 47]. Furthermore, the XRD peaks from samples of  $\text{PbO}_2$  are often significantly broadened, suggesting that the crystals are either very small in size, or that they contain non-uniform lattice strain [48]. In addition, ellipsometric and reflectance spectroscopy measurements have shown [49] that the degree of non-stoichiometry depends on the surface-to-bulk ratio in the sample, and that it can reach the limiting composition of  $\text{PbO}$  in some cases. As a result, it has been suggested that changes in the chemical, physical, and electrochemical properties of battery positive-plate material may relate more particularly to the amorphous and near-surface or grain-boundary disordered components of the samples than to the nature of the bulk crystalline  $\text{PbO}_2$  [24].

Analyses of the XRD peak width of samples of  $\beta\text{-PbO}_2$  have shown that there is a marked decrease in peak width during the early stages of battery service [8, 14, 20]. This decrease in peak width may be caused by an increase in crystal size, or by a decrease in the amount of strain in the sample, with the latter often being associated with crystal disorder [48, 50]. Since measurements of XRD and neutron diffraction peak intensities indicate [20] that there is no change in the degree of stoichiometry and ordering of  $\beta\text{-PbO}_2$ , it was concluded that the observed change in XRD peak width reflected only an increase in crystal size. Furthermore, since the crystal size reached a stable value after only a relatively short period of cycling [14], the size change itself could not be associated with capacity decline, except as this relates to a reduction in surface area.

On the other hand, the structure of  $\alpha\text{-PbO}_2$  has been shown to contain high levels of non-stoichiometry and cation disorder [20, 24]. This polymorph, however, is rarely the major phase in positive plates and, in any event, is usually irreversibly converted to  $\beta\text{-PbO}_2$  during the early stages of battery cycling [1, 44, 51]. The differences in order–disorder characteristics of  $\beta\text{-}$  and  $\alpha\text{-PbO}_2$  may well explain the observed differences in the intrinsic electrochemical activity [52] and self-discharge rate [53] of the two polymorphs and, hence, may explain why battery plate capacity alters in response to changes in the as-formed  $\alpha\text{-PbO}_2$  to  $\beta\text{-PbO}_2$  weight ratio [44]. However, it is difficult to understand how the difference in order–disorder properties can continue to influence plate performance after the  $\alpha\text{:}\beta$  ratio has changed following the initial period of charge–discharge cycling [44].

Quantitative values for the crystal size and strain of both  $\alpha\text{-}$  and  $\beta\text{-PbO}_2$  have been obtained from high-resolution neutron powder diffraction data collected from fresh and cycled battery plates in both the charged and discharged condition [16, 54]. The results agree with the XRD peak width

measurements [8, 14, 20] in demonstrating that the  $\beta$ - $\text{PbO}_2$  crystals increase in size from around 250 Å to 850 Å during cycling. Furthermore, they show that the  $\beta$ - $\text{PbO}_2$  is essentially unstrained (*i.e.*, 0.015%), even in uncycled material where the size of the crystals is very small and the degree of crystal perfection may be expected to be poor. On the other hand, the observed level of strain in all  $\alpha$ - $\text{PbO}_2$  samples is an order of magnitude larger (0.14%). Both of these values remain relatively constant throughout the service-life of the batteries.

These results are not consistent with a model for capacity decline that proposes an increase in structural order of the  $\text{PbO}_2$  (*i.e.*, loss of H and lower strain) as cycling proceeds to plate failure. Furthermore, the strain and size values determined for chemically-prepared dioxides [16] are not significantly different from those obtained for electrochemical/battery material. Thus, the experimental evidence does not support the contention embodied in the HL model, that  $\text{PbO}_2$  from a failed battery more closely resembles the chemically-prepared variety than does  $\text{PbO}_2$  in uncycled (*i.e.*, "fresh") plates.

Finally, it is interesting to note that one of the early experimental indicators of the presence of amorphous/disordered (active) material in lead/acid battery plates was the appearance of an exothermic peak at around 200 °C in differential thermal analysis traces [4, 5, 34]. It was claimed that this peak was associated with the re-ordering of an amorphous component to form a less active type of  $\text{PbO}_2$ , since the peak was not observed in traces obtained either from failed battery material or from chemical  $\text{PbO}_2$ . More recent thermal analysis experiments have established [55], however, that similar exothermic peaks can appear as the result of the oxidation of very small amounts of the organic fibre binder material often added to the positive plate mass during paste mixing. Extensively cycled material may show no peak at all, or one of reduced intensity, due to the fact that most of the fibre has been shed during battery service.

## Conclusions

Experimental evidence for an active role for H and/or disorder present in the  $\text{PbO}_2$  crystal structure in determining the electrochemical properties of  $\text{PbO}_2$  in the positive plates of lead/acid batteries is not convincing. For a large number of cases examined, the evidence is either ambiguous, or is strongly dependent on the source of the samples and their treatment prior to the analysis. While the HL model may, therefore, actually have little practical validity, its proposition more than 15 years ago was a very significant benchmark in lead/acid battery research. It pointed to the importance of, and to the desperate need for, detailed studies on the crystal chemistry of  $\text{PbO}_2$  in particular, and the positive-plate material in general, before the electrochemical properties of the positive plate can be properly understood. This search is still continuing.

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