

## Letter to the Editors

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### Reply to Comments on "Effect of Chemisorbed Water on the Electrical Capacity of the Lead-Acid Battery Positive Plate"

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Hill's comments on our paper [1] concern two main questions: the first refers to the participation of water/hydroxyl groups chemically bound to the surface of  $\text{PbO}_2$  crystals in the electrochemical reaction of  $\text{PbO}_2$  reduction, and the second treats the problem of the capacity-limiting elementary process. These are basic problems with lead/acid batteries. The main aim of the discussed paper [1] was to find answers to these questions through experimental studies. Since the above problems are large in scope, it cannot be expected that they could be solved within one, or even several, papers.

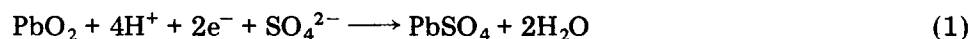
#### *Participation of water/hydroxyl groups*

On the first question: during thermal decomposition of the  $\text{PbO}_2$  active mass in the temperature range 250 - 450 °C, a maximum is observed in the hydrothermogram. The basic part of this maximum is assigned to the chemical process of water evolution from the hydrated surfaces of the  $\text{PbO}_2$  crystals in the agglomerate micropores. The assumption of the  $\text{PbO}_2$  crystals being hydrated is based on the work of Hill [2 - 4] who has shown that hydrogen is concentrated on the hydrated surface layer of the  $\text{PbO}_2$  crystals. In our paper, we raised the question: 'what is the role of this hydrate layer in the mechanism of the electrochemical reaction?' In answer to this question, we see two main roles:

(i) The contact and interaction between the  $\text{PbO}_2$  crystals and the solution occurs through the hydrate layer. This is achieved by the dissociation of the hydroxyl groups from the hydrated surface. Hill does not object to this statement.

(ii) On the basis of the model of the proton-electron mechanism [5, 6], it was assumed that hydrogen from the hydroxyl groups of the hydrated surface participates directly in the mechanism of the electrochemical reaction. Hill disagrees with this assumption.

Let us turn to the electrochemical equation of  $\text{PbO}_2$  reduction, *viz.*,



In this reaction, hydrogen ions are one of the *reacting components*. Hydrogen ions participate directly in the mechanism of the  $\text{PbO}_2$  reduction process at the crystal/solution interface. Unfortunately, their role is underestimated in the literature. The hydrate layer contains hydroxyl groups at the crystal/solution interface. These groups cannot remain indifferent to the transfer of  $\text{H}^+$  ions from the solution to the  $\text{PbO}_2$  crystal lattice.

A model for the  $\text{H}^+$ -ion participation in the electrochemical reaction and the role of the hydrate layer is provided by the proton-electron mechanism [5, 6] which is applied in the discussed paper. According to this model, the hydrate layer facilitates the transfer of  $\text{H}^+$  ions from the solution to the  $\text{PbO}_2$  crystal lattice. This is because, on the one hand,  $\text{OH}^-$  groups of the hydrate layer are easily dissociated and thereby release  $\text{H}^+$  ions that pass into the solution and, on the other hand,  $\text{H}^+$  ions are the smallest ions and move easily within the  $\text{PbO}_2$  crystal lattice. When there are negatively charged crystal-lattice defects in the latter,  $\text{H}^+$  ions from the hydroxyl groups can neutralize most readily the negative charges of these defects by passing from the hydrate layer into the  $\text{PbO}_2$  crystal lattice.

Other models for the mechanism of the electrochemical reaction could be presented. But whatever the model, it has to take into account in the reaction mechanism the role of both hydrogen ions and the hydrate layer at the crystal/solution interface. These were the basic considerations that gave us grounds to suppose that the hydrate layer plays a role greater than that of merely serving as "a medium for ionic diffusion and a wetting agent".

#### *Capacity-limiting process*

Let us now turn to the second question. In order to determine the effect of the hydrate layer on the capacity, a specially designed tubular powder electrode was used in the work under discussion [1]. With the help of this electrode, the capacities of the hydrated and dehydrated surfaces of the active masses were determined. The dehydration was carried out by heating the active mass at  $260^\circ\text{C}$  for 6 h. The oxythermograms of the heated active mass show that during this thermal treatment no oxygen is evolved from  $\text{PbO}_2$ , *i.e.*, the oxide stoichiometric coefficient does not change. Hydrothermograms imply that the active mass surface has been dehydrated during the preheating. Hill's question is whether, or not, there are other changes in the crystals' physical parameters (crystallite size, phase composition, order/disorder, crystallinity, etc.) in addition to the surface dehydration. "Changes in any one of these characteristics would be expected to alter the capacity of the PAM independently of the removal of water", claims Hill.

All the experiments, with or without thermal treatment, were carried out with the same active mass powder. Thus, the influence of grinding was eliminated. SEM observations of preheated, and not preheated, samples of this powder did not show noticeable changes in crystal morphology and grain structure. In addition, after the above thermal treatment, the X-ray peak ratio of  $\alpha\text{-PbO}_2$  and  $\beta\text{-PbO}_2$  did not change.

Experimental results showed that preheating brought about a slight enlargement of the micropore volume. This enlargement will facilitate ion transport along the micropores and will render entrapped pores passable. These processes will lead to an increase in capacity. The experimental data showed, however, the opposite tendency — an abrupt fall in capacity is observed after thermal treatment. Porometric measurements of preheated  $\text{PbO}_2$  revealed that the pores were open, while hydrothermograms implied that no water was entering them. So it can be concluded that a dehydration of the micropores occurs and causes them to become hydrophobic. This is the reason for the dramatic decrease in capacity.

Chemically-obtained  $\beta\text{-PbO}_2$  (Merk) was used for the investigations. We have made an annoying mistake in Fig. 5. The correct way of drawing these curves is with the abscissa value increasing from right to left, *i.e.*, starting from 150 °C at the far right and reaching 500 °C at the coordinate system origin. In Fig. 5, the abscissa scale is incorrectly reversed. Chemical  $\text{PbO}_2$  is thermally decomposed at temperatures above 300 °C. Reproducibility of the hydro- and oxythermograms was within  $\pm 5\%$ .

Calculation of the quantity of hydrated water is, at best, an estimate. For this reason, we have not aimed at precise measurement of the active mass surface area by using BET data in place of porometric data. An exact calculation requires information about the surface density of the  $\text{OH}^-$  groups. Such information is unavailable in the literature. Data about  $\text{TiO}_2$  is used instead which may introduce an uncontrolled error.

We have not determined the role of the order/disorder ratio of the crystal lattice on the capacity. It could be expected that the level of order/disorder will affect to some extent the unit-cell volume. However, Hill has established [3] that there is no relation between the unit-cell volume and the long-term positive-plate capacity, *i.e.*, the capacity after extended periods of cycling. This gives us grounds to assume that the order/disorder ratio is not a capacity-limiting parameter.

In conclusion, let us consider item 4 of Hill's comments. Caulder and Simon [7, 8] advanced the idea that there were two types of  $\text{PbO}_2$  — electrochemically active and electrochemically inactive. These authors are of the opinion that hydrogen content in the crystal lattice determines the electrochemical activity of  $\text{PbO}_2$ . When hydrogen is removed from the crystal lattice  $\text{PbO}_2$  becomes electrochemically inactive, hence the PAM capacity falls. Investigating a number of active masses, Hill *et al.* "do not reveal any relationship between the amount of hydrogen in the sample and the electrochemical activity". In the paper under consideration [1], we developed a method for distinguishing surface-bound water from  $\text{H}^+$  in the  $\text{PbO}_2$  crystal interior. This experimental technique needs further development. The investigated material is porous, which suggests that the capillary forces of the micropores will be active, too. This action has to be eliminated. The method used in our paper allows us to interfere with the mechanism of the processes taking place at the oxide/solution interface. In order to explain the fall in capacity during surface dehydration, we consider the participation

of hydrogen as a reacting species in the mechanism of the electrochemical process proceeding at the oxide/solution interface. This hydrogen comes from the solution and enters the reducing  $\text{PbO}_2$  crystal. It has nothing to do with the hydrogen discussed by Caulder and Simon. Hydrogen from the  $\text{PbO}_2$  interior serves for electroneutralization of negatively charged ionic defects in the crystal lattice [1]. As to the hydrate layer on the  $\text{PbO}_2$  surface, it plays the role of a bridge for the transport of hydrogen from the solution to the crystal interior. This role of the hydrate layer maintains a low transfer polarization, resulting in a high power of current generation of the plate. By breaking the bridge of hydrogen transfer through surface dehydration, the rate of the electrochemical process at the oxide/solution interface decreases dramatically, hence, this process becomes capacity limiting for the plate.

## References

- 1 D. Pavlov, E. Bashtavelova, V. Manev and A. Nasalevska, *J. Power Sources*, 19 (1987) 15.
- 2 R. J. Hill and M. R. Houchin, *Electrochim. Acta*, 30 (1985) 559.
- 3 R. J. Hill and I. C. Madsen, *J. Electrochem. Soc.*, 131 (1984) 1486.
- 4 R. J. Hill, A. M. Jessel and I. C. Madsen, in K. R. Bullock and D. Pavlov (eds.), *Advances in Lead-Acid Batteries, Proceedings*, Vol. 84-14, Electrochemical Soc. Inc., Pennington, NJ, 1984, p. 59.
- 5 D. Pavlov, Lead-acid batteries, in B. D. McNicol and D. A. J. Rand (eds.), *Power Sources for Electric Vehicles*, Elsevier, Amsterdam, 1984.
- 6 D. Pavlov, in L. J. Pearce (ed.), *Power Sources 11*, International Power Sources Symposium Committee, Leatherhead, England, 1986, p. 165.
- 7 S. M. Caulder, J. S. Murday and A. C. Simon, *J. Electrochem. Soc.*, 120 (1973) 1515.
- 8 S. M. Caulder and A. C. Simon, *J. Electrochem. Soc.*, 121 (1974) 1546.