

Letter to the Editors

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

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This paper describes a series of very interesting and innovative experiments designed to determine:

(a) the physical nature and abundance of the water in the so-called "microstructure" and "macrostructure" regions of the positive active mass (PAM) of lead/acid battery plates;

(b) the influence of water chemically bound to the surfaces of PbO_2 crystals on the capacity of the PAM.

For part (a) of the study, the H_2O and O_2 partial pressures were measured during decomposition of PAM taken from hand-pasted flat plates. The PAM was ground and, for some experiments, heated for 6 h at 260°C prior to the decomposition in order to discriminate between (i) physically bound water, (ii) chemically bound water, and (iii) hydrogen incorporated into the crystal lattice. The pore volume and surface area of the samples were also measured before and after heating. For part (b) of the study, the ground (and heated) samples were packed into specially designed tubular powder electrodes for the measurement of discharge capacity. The conclusions reached from the studies are that water driven from the PAM in the temperature range $250 - 450^\circ\text{C}$ corresponds to hydroxyl ions formerly bonded to the PbO_2 crystal surfaces and that the removal of these species dramatically reduces the PAM capacity.

There is no argument with the above conclusions. After all, the electrolyte in a lead/acid battery is an aqueous solution of sulphuric acid, and PbO_2 surfaces in contact with this solution would be expected to become hydrated. Furthermore, surfaces that do not come into contact with the electrolyte (for one reason or another) cannot participate in the charge/discharge reaction directly, so that empty pores cannot be anything but electrochemically inactive.

However, issue is taken with the notion, implied several times in the paper, that the water/hydroxyl species on and near the PAM crystal sur-

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faces have a role above and beyond their normal one of serving as a diffusion medium and wetting agent. It could be suggested that the reported experiments only confirm the fact that the capacity of the PAM is a very sensitive function of its physical properties. If this delicate situation is disturbed (*e.g.*, by the described procedures of grinding, heating to 260 °C, and repacking in a foreign environment) and, as a result, large areas of the PAM are no longer in contact with the electrolyte, then an observed decline in capacity is not surprising.

The following points are advanced in support of this view:

(i) The paper provides no details of the changes (if any) in either the crystallite size, strain, order/disorder, phase composition (*e.g.*, change in the ratio of the PbO_2 polymorphs, decomposition of residual basic lead sulphates, etc.) or amount of amorphous material accompanying the heat treatment and repacking of the PAM. Changes in any one of these characteristics would be expected to alter the capacity of the PAM independently of the removal of water. In fact, the volume and surface area of the micropores do increase after heating, but these changes (Fig. 3 of the paper) are dismissed as insignificant (see point (ii) below).

(ii) Porosimetry measurements are incapable of determining the surface area or volume of the trapped and/or the smallest pores in a sample. Thus, the measured values of pore volume and area will not only underestimate the true values, but they are unlikely to provide a true estimate of the physical effect of heating. For the same reason, the area measurements should not be used (as done in the paper) to estimate the extent of hydration of the PbO_2 surfaces; this is the very point made by Hill and Houchin [1].

(iii) The claimed link between the much lower water content of chemically prepared PbO_2 and its much lower capacity is interesting. However, it is difficult to attach unequivocal significance to this statement without complementary information about the physical properties of chemical material relative to its electrochemical counterpart. The same could also be said for the results of the decomposition experiments; the reader is given no idea of the reproducibility of the measurements, yet is asked to accept the significance of the relatively small differences between the thermograms for the two heated samples in Fig. 4 of the paper.

(iv) Recent measurements of bulk hydrogen content (*i.e.*, the amount of water/hydroxyl present in all of the pores and on all of the surfaces) obtained [2, 3] from neutron attenuation experiments on large numbers of battery and chemical samples of PbO_2 that have been subjected to a wide range of battery service and preparative histories, failed to reveal a relationship between the amount of hydrogen in the sample and its electrochemical activity. Similar conclusions have been obtained from proton magnetic resonance studies [4] of a similar series of battery and chemical samples. In other words, although all of the samples contained some water/hydroxyl species, presumably as a function of surface hydration and pore trapping during crystal/grain growth, the amount present could not be related to their prior electrochemical activity.

References

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