

Influence of crystal and gel zones on the capacity of the lead dioxide active mass (extended abstract)

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The lead dioxide positive active mass (PAM) exhibits some oddities in its behaviour. When prepared from chemically-obtained PbO_2 , its capacity is low. When, however, it is produced by electrochemical oxidation of lead oxides and/or basic sulfates, the capacity of PAM is high. Despite numerous attempts, no reliable PAM quantitative method based on X-ray diffraction has been devised so far. This comes to indicate that the amount of PbO_2 in PAM is not equivalent to its crystal phase only.

Up to now PAM has been treated as a crystal system comprised of PbO_2 . Its behaviour has been interpreted in terms of the concepts and laws of solid-state physics. Lead dioxide is a degenerated semiconductor with electron conductivity [1–4] and α - or β -crystal and amorphous modifications.

Some experimental data have been reported recently indicating that PbO_2 particles and agglomerates are built up of crystal and amorphous zones [5–10], and that amorphous zones are hydrated and exchange ions with the solution [10].

These experimental findings gave grounds for a new concept of PAM to be forwarded [11]. According to this new approach, the particles and agglomerates of PAM represent gel systems ($\text{PbO}(\text{OH})_2$) which are partially dehydrated, forming crystal zones (PbO_2 with α - or β -structure) [11]. This structure of PAM can be clearly seen on the transmission electron micrograph taken at high resolution and presented in Fig. 1 at two magnifications. There are zones (d) in which the layers of the crystal lattice are distinctly seen at high magnifications, and other lighter zones (c). They are hydrated and, as evidenced by the micro-micro electron diffraction, they have an amorphous constitution.

Since PAM particles and agglomerates contain gel zones, then an ion-exchange process is possible between the gel zones and the solution. It has been established that PAM does exchange ions with the solution, whereby the equilibrium between the crystal and amorphous zones is affected [10]. Besides, gel zones in PAM can hold water tightly and remain chemically and thermally stable [12]. PAM has a much weaker crystal structure than chemically-obtained PbO_2 [10, 11]. All these features are typical of proton conductors [13, 14]. PAM seems to be a good proton conductor owing to the presence of gel zones in its structure. This conjecture is confirmed experimentally by the discharge behaviour of positive battery plates. The reaction of discharge involves hydrogen ions and if PAM were not a good proton conductor, the polarization of the positive plates would be high.

Gel zones allow the reaction of PbO_2 reduction to proceed in the bulk of the particles and agglomerates, probably at the interface between the crystal and hydrated zones. This results in a low-current density of discharge (electrochemical reduction). This is the second reason for the low polarization of the positive plates during battery discharge.

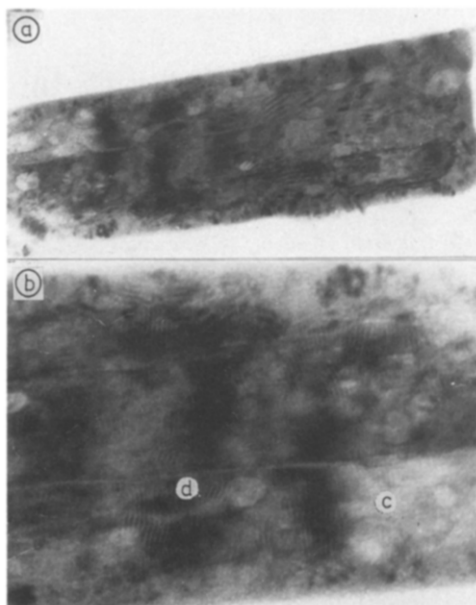


Fig. 1. Transmission electron micrographs of a PAM particle. (a) at magnification $400\,000\times$. Light regions reflect hydrated amorphous zones. Crystal planes are distinguished in some of the darker (crystal) zones. (b) a sector of the particle at magnification $1\,000\,000\times$ (photographic). Crystal planes are distinctly seen in the crystal zones (d). The lighter zone (c) features individual dark lines (linear polymer chains).

As established earlier [15], the process of PAM discharge proceeds in two stages. The first stage includes the electrochemical reaction:



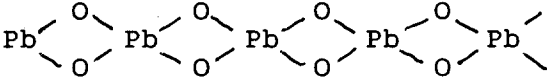
It proceeds in the bulk of PAM particles and agglomerates. During the second stage, a reaction proceeds between the particles and H_2SO_4 :



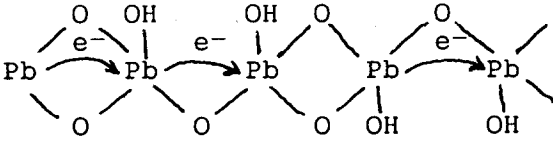
For reaction (1) to proceed, two flows should enter simultaneously one and the same particle or agglomerate: of H^+ (protons) and of electrons (e^-). This is the so-called double-injection process or proton-electron mechanism. To reach a given agglomerate in the bulk of PAM, hydrogen ions have to diffuse into the solution in PAM pores and get into the gel zones of the agglomerates and particles. Their movement in these zones is realized by the proton-conductivity mechanism. Electrons have to pass from the plate grid, through the corrosion layer and the agglomerates of PAM, to the agglomerate that is being reduced. On their way they will pass through both crystal and gel zones. It can be assumed that the electrochemical reaction itself proceeds at a high rate. Then, the rate-limiting stages in the discharge process will be the transfer of electrons and of protons to the site of the reaction.

What is the mechanism of electron transfer through the gel zones? Gel zones should not only be proton- but also electron-conductive.

It has been known for over a century now [16, 17] that high-valent lead oxides form polymer chains of the type:



It can be assumed that gel zones are built of similar polymer chains that are hydrated, however:



These chains keep the distances between the lead ions small enough for electrons to jump easily from one lead ion to the other along the chains. Hence, electrons have to overcome low-potential barriers on their way from one crystal zone to the other, i.e., the gel structure has high-electron conductivity.

Consequently, the mechanism of the electron conductivity in the gel-crystal systems is as follows. Crystal zones are 'islands' in which electrons move freely within the whole volume (conductivity band of degenerated n-type semiconductors). These 'islands' are interconnected by gel polymer chains forming 'bridges' along which electrons move between the crystal zones (Fig. 2). The gel polymer chains contain a certain amount of free electrons which are electroneutralized by free protons in the gel chains.

The 'island-bridge' conductivity of the gel-crystal system depends on the ratio between the gel and crystal zones (and this, in its turn, on the initial product and the method of PAM preparation or on the charging mode of the plate), on the number of parallel polymer chains that interconnect the crystal zones in the gel (and these on the density of PAM), on the additives (dopants) to PAM or to the grid alloy. These may impede or facilitate the electron transport along the polymer chains.

A critical PAM density is found to exist at which the number of parallel polymer chains becomes so small that the electron transfer is hampered [18]. Though PAM seems to be in good condition, the plate capacity is low because PAM density in the gel zones is reduced below the critical value.

On charging of the positive plates, when a 60 to 70% state-of-charge is reached, evolution of oxygen starts. This reaction proceeds probably also in the bulk of the agglomerates and particles. The released oxygen tears down or sets apart the polymer chains in the gel, thus increasing the potential barriers that electrons have to overcome and hence the polarization of the plate [15]. Besides, the evolved oxygen and OH⁻ radicals destroy partially the lattice of the crystal zones and thus increase the volume of the gel zones. Polarization grows. On opening of the circuit, evolution of oxygen

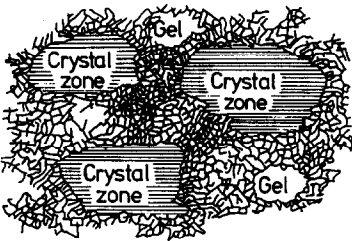


Fig. 2. A model of the structure of the gel-crystal system characterized by an 'island-bridge' conductivity mechanism of the electron movement in the agglomerates and particles of PAM.

stops, the latter diffuses out of the particles, the crystallinity of PAM grows and the electrode potential is decreased [15].

It has also been established that additions of arsenic and antimony to the grid alloy improve significantly the contact between the hydrated zones of adjacent PAM agglomerates [18]. These dopants probably take part in the polymer chains and facilitate the electron transport through the gel zones.

Faber [19] has found that PbO_2 rich in water has lower picnometric density than nonwater-containing oxide, and is electrochemically active. The crystallized $\beta\text{-PbO}_2$ has higher electron conductivity, but is electrochemically inactive. The electrochemical activity of PbO_2 is measured with the time of current generation on discharge of 1 g of PAM. The electron conductivity is related to the crystal PbO_2 zones and the polymer chains in the gel zones. The proton conductivity depends only on the gel zones. The concurrent existence of crystal and gel zones determines the electrochemical activity of PAM.

If PAM is composed only of crystal PbO_2 , its electron conductivity is high [19], while the proton conductivity is low. Reaction (1) proceeds at the crystal surface only. During discharge, the cross sections of the intercrystal contacts decrease more quickly than the volume of the crystals, forming PbSO_4 which weakens the bonds between the PbO_2 crystals or interrupts them altogether. PAM capacity is low. This is the case with PAM prepared from chemically-obtained PbO_2 .

If PAM consists of hydrogel particles only, its proton conductivity is high. The electron conductivity depends on the gel density. The electrochemical reaction proceeds in the bulk of the gel zones, i.e., in the regions with higher gel concentration. When this concentration falls below the critical value in a given zone, this zone or particle is excluded from the discharge process. PAM capacity is low.

If the active mass is a gel-crystal system, it has both high-electron and proton conductivities. As the crystal and gel zones are in equilibrium [10], a relatively high concentration of the gel is maintained on the whole. The electrochemical reaction proceeds in the bulk of the agglomerates. The plate capacity is high. Such is the case with PAM produced after the current technology of battery production.

As can be seen from the above, the dependence of PAM capacity versus its crystallinity passes through a maximum. An optimum capacity of PAM can be obtained at an optimum ratio between the crystal and gel zones, and optimum electron and proton conductivities. To determine these optimum ratios and maintain them throughout the battery service life is one of the major tasks of the technology and design of lead/acid batteries.

Remark

The present paper is an extended abstract of the lecture presented at the ILZRO Battery Seminar and can be found in greater detail in the *J. Electrochem. Soc.*, 1992 (ref. 11).

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