NEW IDEAS ON THE LEAD–ACID BATTERY

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Summary

After a century of research and use of the lead–acid battery there are still unresolved scientific and technical problems. However, there are now two new lines of research to follow using techniques developed in recent years for the study of solid state and liquid–solid surfaces.

Recent work on the presence of a hydrogen species in the PbO_2 electrode is summarized briefly and the work which still needs to be done is highlighted.

A description of the membrane/osmosis model of the hydration of Portland cement is outlined and its relevance to the behaviour of the lead–acid battery is discussed.

Introduction

We can make a list of unsolved problems for the lead–acid battery. Some are related to product performance and others more to the science.

Product performance problems

(1) Shelf life of charged batteries.

(2) Recovery after discharged stand.

(3) Loss of capacity on cycling, especially with Ca grid alloys.

(4) Charge acceptance: electrical efficiency and low temperature problems.

(5) Faradaic efficiency.

Scientific queries [1]

(1) What is the effect of changes in PbO_2 atomic structure on softening, shedding, and electrochemical activity?

(2) What role do H_2O, H^+, and OH^- play in electrochemical activity and electrode microstructure?

(3) What is the relationship between the various crystal structures of PbO_2 and plate microstructure?

(4) How do changes in PbO_2 atomic structure affect plate microstructure and cycle life?

There is of course a connection between the two lists, but at present the problem is that we do not know what it is.

These lists look equally daunting, if only because they have been the same for most of the last century. The empirical technology has only taken us so far. I want to try to stimulate some fresh approaches.

A first approach is easy — we should stop relying on current, voltage, time (i, v, t) curves as the only way forward and take advantage of all the new methods of looking at electrodes.

Another approach is summed up by the idea 'we have had the formula for the lead dioxide electrode wrong for a century', or, in an alternative phrase, 'hunt the proton'.

A third approach is that 'making battery paste is like making concrete'.

Of course these three approaches are not mutually exclusive, and may not even be so very different, but in making this classification it helps me to express my ideas.

Only by a radical shift of viewpoint can we expect to progress. Even the pedagogical approach to electrochemistry itself has been questioned recently [2]. My ideas may not be right but by stimulating thought and experiment in proving them wrong, positive benefits may be obtained. I believe that we are at the threshold of a renaissance of the lead–acid battery, and that battery technologists have much to learn from the solid state scientists.

We have to take account, of course, of the voluminous literature on lead–acid batteries, but somehow we have to sift out only the useful information. Not knowing too much detail may be a great help when thinking of new theories. We also have to question the validity of much of the earlier work and read the experimental sections more carefully than the discussions.

One thing that strikes me is the way techniques are perpetuated over time with only minor changes, not big changes. An example will show what I mean. Many linear sweep rates, if they are not instantaneous pulses, are usually in the 0.1 - 10 mV/s range. Now the Battery Council International (BCI) cold cranking test is from a theoretical 12.0 to 7.2 V for 12 V battery in 30 s, i.e. 27 mV/s per cell. The equivalent test in the International Electrotechnical Commission (IEC) specification yields a value of 10 mV/s. Therefore what has been measured on the lead–acid electrode by the electrochemist is the phenomenon under *cranking conditions*. Can we really expect the behaviour to be the same at low rate discharge? We know the Faradaic efficiency is not the same. Again, the electrochemist takes care to carry out discharges in mA/cm^2, which have been shown to give 'clean' interpretable i, v, t curves, but do not necessarily represent real battery behaviour.

Thus, pulse/sweep voltammetry may give us a misleading view of the electrochemistry of lead–acid batteries, as will become evident in the discussion of 'proton hunting' and 'concrete making'.

Hunt the proton

One of the fundamental observations enshrined in the folklore of lead–acid batteries is that chemically prepared lead dioxide cannot be made to

work in a battery [3, 4]. There has never been a satisfactory explanation of this. Now Flinders and Harwell workers are showing that the folklore is not necessarily true [5, 6].

Much work has been carried out and a fascinating literature on the chemical structure of PbO_2, as determined by X-rays, has grown up. Most authors have assumed a formula in which PbO_2 is oxygen deficient and where there are two important forms of PbO_2 — α and β. Batteryman's lore says that α gives cycling capability whilst β gives capacity.

It is certainly true that a rough correlation can be found for this, provided that it is accepted that the data are not very reproducible and not completely quantitative. This see-saw of characteristics is of course an explanation of the well-known 'bean-bag' problem in the lead–acid battery. If increased capacity by higher utilization is required, then cycle life has to be sacrificed — or vice versa. This can be expressed in more technical terms: only a finite quantity of coulomb movement can be got out of a positive plate, and this depends on the formulation characteristics of the paste, etc.

These statements, however useful they may be in the world of battery technology, are not really soundly based in science. We have no explanation or theory, and no scientific methods of manipulation.

Recent work has shown, however, that we have the formula for PbO_2 wrong. The structure is lead deficient, not oxygen deficient, and the electrical neutrality is preserved by the presence of a hydrogen species. (I realise that not all electrochemists and crystallographers have fully accepted the evidence, but it is a fruitful hypothesis to explore.) In brief, the evidence from work on PbO_2 is as follows.

Bagshaw *et al.* [7] showed that PbO_2 has a variable stoichiometry, and that its thermal decomposition can be by any one of four different pathways, which appear to depend on the method of preparation. Bound water is present in the lead dioxide and is only removed at the decomposition point.

Caulder *et al.* [8] suggested that electrochemically active PbO_2 has hydrogen species in two configurations, whilst inactive PbO_2 has hydrogen present only in one.

Moseley *et al.* [9] found no evidence in chemically prepared PbO_2 of the crystallographic disorder that would follow from an oxygen deficient structure. The same authors [6], through neutron diffraction studies, showed that electrochemically prepared PbO_2 contains hydrogen species and that the charge balance is through the lead species. The oxygen lattice appears to be essentially complete.

Jorgensen *et al.* [10] examined electrochemical PbO_2 from a cycled battery plate and concluded that hydrogen to the level of 0.21 atoms per PbO_2 unit was present. Deuterium experiments showed that the hydrogen species was probably incorporated into the lattice, and that the oxygen lattice was complete.

Hill [11] agrees that the oxygen lattice in electrochemical PbO_2 is complete, and that charge balance comes from hydrogen in water or hydroxyl groups.

Outside the lead-acid battery industry it is commonly accepted that rutile oxides in particular incorporate hydrogen into the lattice very readily. Recent studies on manganese dioxide and nickel hydroxide in their respective batteries now demonstrate a hydrogen species as a key component of the mechanism.

An established technique for inserting hydrogen into molybdenum and tungsten bronzes proved to be capable of being used for inserting hydrogen into PbO_2 from a battery plate (P. G. Dickens, personal communication; cf. ref. 12). We should begin to take notice of the world of solid state chemistry outside the lead-acid battery industry.

We need to be able to answer the following questions. Where is the hydrogen species? How many different hydrogen species are there? (Hydrogen atoms, protons, hydroxyl ions, and bound water have all been suggested.) What quantity of hydrogen species is present and how does it vary with plate preparation and charge — discharge cycling? Can we manipulate the hydrogen content by chemical rather than electrochemical methods? (An old trick in making battery oxide is to control the water content of the air stream to the pot or mill.)

We also need to examine how many other techniques for looking at crystal structures and surface phenomena which have been developed over the years can be used to examine lead-acid battery electrodes.

If possible we should 'hunt the proton' using *in situ* methods. Not all the modern techniques may allow this, but we must try to get away from methods which only measure i, v, and t. The latest i, v, t techniques of AC impedance are a great improvement over the older methods but they are still too limited in my view [13].

Semiconductor properties of lead oxides

The interpretation of AC impedance, for example, still rests on a model of electrode behaviour in an equivalent circuit simulation of what is thought to go on at a porous lead battery electrode. I am cautious about accepting the equivalent circuit. The i, v, t signal can probably be made to match several circuits. The one we use comes from a period when semiconductor physics was in its infancy, and when computations were difficult to carry out. It is almost tautological in that it models electrically a plausible model of the electrode derived from a study of i, v, t curves.

The circuit does not use any active component such as a diode junction. However, Beck [14] proposes a semiconductor model for the passivation of lead dioxide on discharge. Moreover, recent work using photocurrent spectroscopy shows that the lead-acid system contains semiconducting oxides which must participate in the overall reaction scheme. The photocurrent spectroscopy of semiconductor lead oxides reduced from PbO_2 gives us important new insights into the behaviour of the lead-acid system.

Fletcher and Matthews of Flinders University [15] give a good discussion of the photochemistry of the lead dioxide system and are broadly in agreement with earlier work by Peter of Southampton University [16].

PbO can exhibit both n- and p-type semiconductor behaviour and different mechanisms of formation during the oxidation and reduction steps. The degenerate behaviour of the PbO is ascribed to non-stoichiometry, but the precursor PbO_2 is thought to be oxygen deficient and not hydrogen rich. Again, interpretation should be considered in the light of evidence for hydrogen species.

Matthews also postulates the possibility of micro-crystalline (amorphous?) phases which depend on the pre-history of the electrode under cycling, and discusses the formation of micro-environments in relation to a $PbSO_4$ barrier. The importance of this I highlight later in relation to the analogy of the setting of Portland cement.

The work by Peter [16] is interesting because he postulates, in effect, a solid state mechanism for the reduction of α-PbO_2 films to some fraction of the stoichiometry available. The reduced film has an unusual stoichiometry, which is probably due to the amorphous nature of the material.
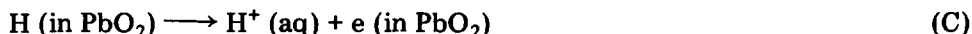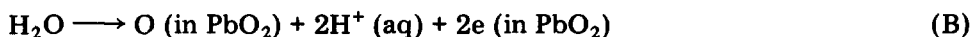
Later work by Peter (personal communication) confirms the existence of tetragonal PbO as a result of $PbSO_4$ behaving as a semipermeable membrane, and the subsequent formation of α-PbO_2 from this during oxidation. The rates of the various phenomena appear to be of the same order as the rate processes in high cranking SLI batteries. The rapid voltage drop at these rates may be due therefore to solid state reactions, and not to the problems of mass transfer of H_2SO_4 to the electrode surface.

Kinetics — i, v, t curves

This discussion has taken me from my theme of 'hunt the proton' to my proposal to 'stop relying on i, v, t curves alone'.

As well as the photocurrent spectroscopy techniques which have shown that the lead dioxide electrodes are not as simple as they might appear, there has been recent work to show that the i, v, t curves we have been measuring are very complex and probably the result of three electrode reactions, one of which involves hydrogen.

Pohl and Rickert [17] deal with the PbO_2 in the recharge, anodic direction and separate the reaction into three.

$$Pb \text{ (in } PbO_2) \longrightarrow Pb^{2+} \text{ (aq)} + 2e \text{ (in } PbO_2) \tag{A}$$

$$H_2O \longrightarrow O \text{ (in } PbO_2) + 2H^+ \text{ (aq)} + 2e \text{ (in } PbO_2) \tag{B}$$

$$H \text{ (in } PbO_2) \longrightarrow H^+ \text{ (aq)} + e \text{ (in } PbO_2) \tag{C}$$

They write the formula as $PbO_{2-s}(xH_2O)$ and, since s and x are small quantities, the overall reaction is effectively

$$Pb^{2+} (aq) + 2H_2O \longrightarrow PbO_2 + 4H^+ (aq) + 2e \text{ (in } PbO_2) \qquad \text{(D)}$$
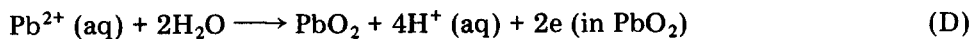
which follows from $2(B) - (A) = (D)$. (PbO_2 is described as the sum of the activities of lead and oxygen in the PbO_2 lattice.) The hydrogen reaction (C) has not previously been observed. The major piece of evidence that Pohl and Rickert adduce is the demonstration of the ready transmission of hydrogen through PbO_2 by means of a bipolar cell.

This explicit involvement of the hydrogen species is apparently in accord with X-ray and other evidence referred to above. However, the hydrogen found in those experiments in the electrochemically formed condition, and Pohl and Rickert's mechanism requires that the hydrogen enters the lattice on discharge. On discharge the hydrogen rapidly diffuses into the PbO_2 lattice (the cranking current?) and the dissolution or reaction of PbO_2 to form $PbSO_4$ takes place more slowly. On the face of it the hydrogen seems to be in the wrong place at the wrong time — much more work needs to be done in this whole area of hydrogen in the PbO_2 lattice.

The postulate does have attractions in explaining some aspects of the practical behaviour of the lead–acid battery. Most notably it gives an explanation of the high rate capability (hydrogen species are very mobile) and the low capacity at high rate (the quantity of hydrogen in the lattice is low).

It could also explain the behaviour of the PbO_2 electrode under pulse charging reported by Caulder *et al.* and CSIRO workers [18, 19]. Workers at Varta [20] have also shown the benefits of a relaxation time in cycling PbO_2 electrodes, and discussed the behaviour in the light of Pohl and Rickert's ideas. These reactions may also be involved in self-discharge losses.

I certainly hope that all this work on hydrogen in PbO_2 will give rise to new experiments and therefore a better understanding of the complex kinetics. A full synthesis of the literature on hydrogen species in the PbO_2 lattice, the semiconductor behaviour of lead oxides and the kinetic ideas of Pohl and Rickert has not yet been attempted. We may, for example, find the Pourbaix diagram wrong, or irrelevant.

For the time being I caution anyone reading a paper on electrode reactions in lead–acid batteries which does not mention hydrogen to remember that hydrogen is a very mobile species in defect oxides. The authors of such papers now have to explain why they believe hydrogen is not participating in a reaction, not just ignore it.

'Making battery paste is like making concrete'

Somewhat at random I will list the comparisons:

(1) The setting of cement is a time dependent hydration reaction with an exotherm; so is the preparation of paste with lead oxides (hydroset).

(2) The setting of cement paste is influenced by the presence of $CaSO_4$; the behaviour of battery paste is influenced by $BaSO_4$.

(3) Lignosulphonates are common additives to cement pastes to control rheology and set — an excess can prevent setting altogether; lignosulphonates control the rheology and electrical capacity of battery electrodes — an excess gives an over-expanded useless plate.

(4) There is controversy concerning the actual mechanism of cement hydration and set, paralleled by the controversy concerning the mechanism of the lead—acid battery. Both involve solid state phenomena and crystal structures.

(5) Both structures, cement and battery electrodes, are porous.

It may be said that the above comparisons are as useful as comparisons between battery making and horticulture, but I will outline a new theory of cement hydration which I believe is very relevant to that of the lead—acid battery.

I shall follow, by exact quotation, parts of an excellent exposition on the membrane/osmosis model for cement hydration by Birchall et al. [21]. At appropriate points I will try to show the parallels and features I regard as important for study of the lead—acid electrodes.

The relevance to the lead—acid battery is not easy to demonstrate at first. However, there is a paper by Ruetschi [22] which describes the preparation of a semipermeable $PbSO_4$ membrane and discusses its relevance to the Pb negative electrode. Ruetschi precipitates his membrane inside a cellophane film and shows its perm-selective properties. I submit this is sufficient evidence to make the Birchall cement model important and relevant, both to the negative Pb electrode and the positive PbO_2 electrode.

> "Two groups [23, 24]* have pointed to a striking similarity between the generation of hydrate morphology in Portland cement hydration and the formation of 'silicate gardens'. In this process there is first formed a thin membrane-like sheath round the crystal, the result of interaction between solvent in proximity to the crystal and rich in metal ions, and the bulk solution. This membrane engorges osmotically and ruptures to give rise to the outgrowths characteristic of the 'garden'. A similar effect is produced when the 'garden' is reversed, that is when a crystal of say sodium orthosilicate is immersed in a calcium salt solution. This, it has been suggested, is more akin to events in Portland cement in which silicate is in the solid phase and the external solution is a saturated solution of calcium hydroxide. What is suggested by the proponents of a membrane/osmosis model for Portland cement hydration is that there are sufficient similarities between cement hydration and the 'garden' effect that an examination of the physical chemistry of the latter may throw light on various ill-understood features of the former."

I can only remark that nobody so far has elaborated the membrane/osmosis model in the lead—acid system. Ruetschi's paper did not produce any major change in thinking.

> "When a soluble di- or tri-valent metal salt crystal is immersed in a dilute solution of sodium silicate, there is an initial dissolution of the crystal and hence there is formed, at least transiently, an interface.

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*Reference and Figure numbers have been amended, where necessary, for this paper.

When one solution is viscous, or because of the geometric scale of the interface, there will be little or no bulk mixing [25]. Under such circumstances, the instantaneous supersaturation ratio at the interface with respect to the insoluble product

$$\frac{(A)(B)}{\text{solubility } (AB)}$$

can attain high values — 10^2 to 10^4 — and be greatly in excess of the critical ratio for homogeneous nucleation [26]. The critical nucleus size can, under such conditions, be smaller than the unit cell dimension so that the growth of the solid occurs without definite configuration and no long range order [27]. Hence a gelatinous precipitate results, capable of forming a continuous membrane. Even solids that are usually observed to be crystalline can be precipitated in an amorphous condition at high supersaturation. In the case of the 'silicate garden', precipitation is the result of altered pH conditions across the liquid/liquid interface."

Again I can only suggest that examination of the silicate garden will throw light on the behaviour of the lead–acid battery electrodes. The relevant species are sulphuric acid and lead ions, and the solubility of PbSO$_4$ has the necessary characteristics to form amorphous membranes, as demonstrated by Ruetschi.

"The pH will change steeply at the boundary (Fig. 1). At 'B' the pH is such that the metal hydroxide is precipitated (ca. pH 10 for Ca(OH)$_2$) and at 'A' hydrated silica is precipitated from sodium silicate solution. The result is a narrow zone within which there is heterocoagulation between calcium hydroxide and polysilicic acid and hence a combined precipitate."
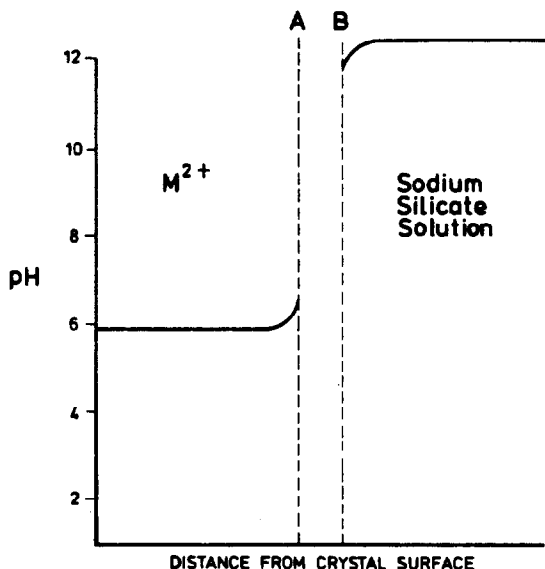

Fig. 1. pH gradient across a liquid–liquid interface. Adapted from Fig. 1 of ref. 21.

This gradient of pH will of course be different in sulphuric acid solution and at Pb or PbO_2 electrodes, and the heterocoagulation will give rise to a solid phase which has elements of several Pb species underlying a $PbSO_4$ coating. This characteristic is a common observation in studies of the morphology of battery plates (Fig. 2).

Professor Birchall has pointed out that studies on the hydration of cement over many years have attempted to give structural and compositional names to the components which arise in the first stages of hydration. He believes that the studies, usually by X-rays, are misplaced as the first products are amorphous and of mixed composition. The attempt to see crystallographic order is fundamentally unsound, and the reported structures are artefacts of a particular experimental circumstance.

The parallel with lead–acid is obvious. Behind a semipermeable membrane with unknown and uncontrolled pH and electrode potential almost any lead species found in a Pourbaix diagram could be formed. (Refer to my earlier comment on the role of hydrogen species and the Pourbaix diagram.)

Furthermore, it may well explain the variable nature, and change with cycling, of the visible morphology and topology of the PbO_2 electrode. For example, Simon et al. [28] report a coralloid structure in cycled plates, which we have rarely observed in our laboratories. What is seen may be no more reproducible than a silicate garden, and for the same reason.

"Membrane formation can thence be said to occur at a 'precipitation front' and, once a membrane has been established, the conditions are set up for osmosis. The
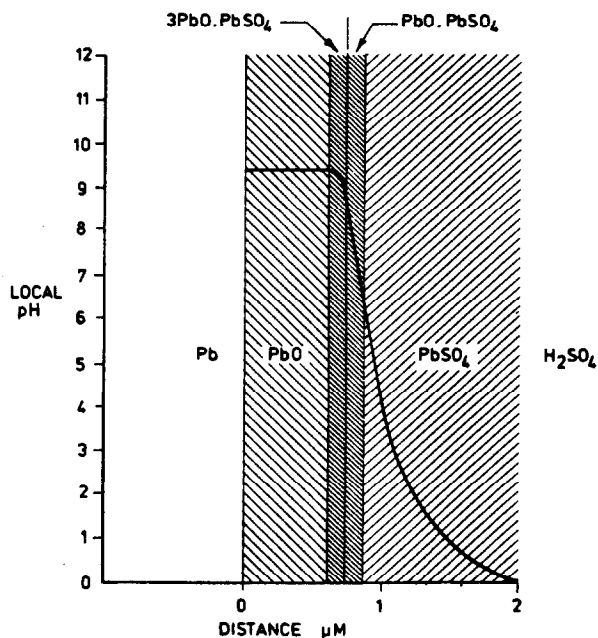

Fig. 2. Multiphase corrosion layer on lead. Adapted from Fig. 1 of ref. 22.

question is: in what way can such a process aid understanding of Portland cement hydration?"

Or, in what way can such a process aid understanding of the charge–discharge reactions of the lead–acid battery?

"Here 'A' (Fig. 3) is anhydrous C_3S and 'B' is a front of active hydrolysis moving into the anhydrous grain with time; 'C' is the intra-membrane zone — much exaggerated in thickness in the diagram — and 'D' is the initial membrane at the precipitation front. 'E' is the external solution. 'A' is the source of dissolved species in the system (which diffuse outwards from 'B' at a rate related to diffusion coefficient and concentration gradient) so that, for example, a calcium ion profile would appear as in Fig. 3."

"Whilst the exact profile within the membrane is conjectural, that outside is definable and the osmotic driving force for the transport of water across the membrane is the difference in concentration at either side of the membrane and, since the intra-membrane zone will be thin, this may be taken to approximate to the concentration difference between 'B' (at which the concentration will approach that in the anhydrous solid) and 'E' (lower by three orders of magnitude). Of course, all dissolved species need to be taken into account but calcium ion is taken here in illustration."

We can take 'A' as PbO_2 and 'B' as a front of active sulphuric acid moving under the action of the discharge reaction into PbO_2 with time. 'C' is the intra-membrane zone and 'D' is the initial membrane at the precipitation front. 'E' is the external solution. 'A' is the source of Pb ions in the system (which diffuse outwards from 'B' at a rate related to the electrochemical
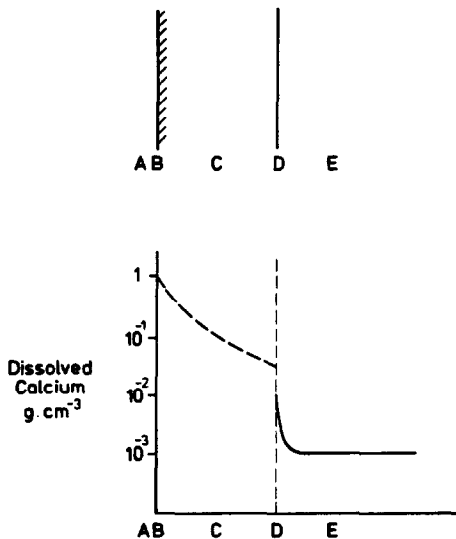

Fig. 3. Calcium ion profile at the C_3S interface with solution. Adapted from Figs. 2 and 3 of ref. 22.

discharge reaction, the diffusion coefficient and concentration gradient) so that, for example, the Pb ion profile would appear as in the Figure, with different absolute values relating to lead.

It can be seen how easily Professor Birchall's description can be made to fit the lead–acid battery, the major difference being that the reaction is not a simple hydration but an electrochemical reduction induced by the discharge of the battery. However, the natural self-discharge on stand may be a solubility, or thermodynamic, instability which follows this mechanism. In other words, we may not have to invoke secondary cells from impurities to explain self-discharge.

Recrystallization phenomena have been invoked to explain the formation of a non-rechargeable $PbSO_4$ layer in a lead–acid battery after discharged stand, or after many cycles [29]. The situation may be more complex than previously thought. We should now consider the osmotic and permeable behaviour of $PbSO_4$ films as well as the crystallization phenomena.

"Membrane formation initiates the dormant period during which water passes into the membrane to continue the attack on the anhydrous grain. The dormant period terminates when the intra-membrane pressure causes membrane rupture so releasing the hydrosilicate within the membrane into the external solution. Again precipitation occurs at the interface between the two solutions to give fragile forms of CSH at the grain surface. Support for such an explanation has been provided recently in experiments [30] in which Portland cement was hydrated for a short time and then placed in distilled water when the growth of unusually long and evidently hollow fibrous projections was noted: enhanced growth on exposure to a dilute environment is difficult to explain other than by an osmotic mode."

Do we have here a model for the difference in plates formed in low gravity acid in a tank and high gravity acid *in situ* in the battery?

A recent study by Bialacki *et al.* [31] of the behaviour of $PbSO_4$ films in concentrated sulphuric acid (10 M) shows that there is a change in the behaviour of the film; it becomes much tighter and more mechanically sound [32].

Bearing in mind the remarks on irreproducibility of morphology it can only be noted as anecdotal evidence that Bialacki *et al.* [33] found a different morphology of PbO_2 on grid alloys containing Sb from those containing Ca and Sn.

"Perhaps the most important point in a membrane/osmosis model is that, in cement hydration, the reactions occur at the surface of particles some tens of micrometres in diameter separated by units of micrometres of free liquid space, a scale at which there will be little or no turbulent mixing at the particle/liquid interface. It therefore seems valid to consider the reactions as occurring at a static interface between two solutions, conditions under which supersaturation levels will be very high so that solids having no long-range order result. Such amorphous materials may, of course, subsequently crystallise but early morphology will depend on the fluid dynamics within the free liquid space into which growth occurs."

"In a system such as that represented in Figure 3 there will be diffusion of species across the membrane at rates related to the diffusion coefficient and the concentration gradient. Of course, species that react with components of the external solution will not appear in any significant quantity in the bulk solution and, indeed, the membrane is defined as a 'precipitation front' and is generated in the first place by such precipitation. It is this rather than considerations of selective permeability of the membrane that determines what species appear in the external solution."

Perhaps some of the experimental observations of the concentration of Pb ions in solution by ring-disc electrode studies can be explained in this way. Certainly the electrocrystallization phenomena and explanations of the nucleation of $PbSO_4$ on electrode surfaces must now be looked at in relation to this model.

"The intra-membrane space presents an unusual physical condition, for once a membrane is formed there is created a small isolated volume of enclosed fluid (order 10^{-9} cm^3 for 10% penetration into a 30 μm diameter grain) and it is well-established [34, 35] that the probability of nucleation decreases sharply as the (isolated) volume of the phase involved falls. Hence, in a very small volume, the critical supersaturation for nucleation is considerably increased over the level appropriate in the bulk. Within the small volume of the intra-membrane space, high levels of pH will be tolerated without precipitation."

Many studies have shown that α-PbO_2, which theoretically is only stable in an alkaline environment, is present in the lead–acid battery and stable over many charge–discharge cycles. In the past, pore size geometry and diffusion rates have been used to explain this behaviour. I find the cement hydration model much more plausible.

"Following the early events in hydration (membrane formation and the generation of external excrescences), the subsequent process of hydration can be considered as proceeding by the dissolution of the anhydrous face at 'B' (Fig. 3), the transport of dissolved species across the intra-membrane space 'C' — with no nucleation because of the volume effect — but with discharge of the effective supersaturation by deposition on the internal surface of the membrane which thickens from the inside to become a shell. The process slows as the permeability of the shell falls with increasing thickness."

Does this provide some explanation for the low utilization of the active material through coating of the grain by $PbSO_4$? Does this also provide the protection of the underlying crystal structure of PbO_2 which then allows recharge reactions to reverse this process?

"The membrane/osmosis model derives from observations of the mode of formation of 'silicate gardens' (which can involve species similar to those found in cement) and the most important similarity between this process and cement hydration is in the formation of a major proportion of solids at a static interface at such local levels of supersaturation that the solid is colloidal with no long-range order and with initial morphology determined by fluid dynamics. Thereafter, morphology may change by desiccation, shrinkage, crystallisation, and the deposition of solids

"on existing surfaces, thus confusing apparent stoichiometry. Clearly, whilst much more needs to be done, the attraction of a membrane/osmosis model is that it provides the beginnings of a unity of explanation for diverse features of Portland cement hydration."

The model also provides for diverse features of Pb–acid battery electrode behaviour.

One of the most interesting features of the membrane/osmosis theory is the emphasis on the amorphous nature of the membrane and the associated precipitation phenomena. Most of the papers on the PbO_2 electrode have attempted to use standard crystallographic forms to study the behaviour. I was interested to read the recent paper by Hill of CSIRO where he explicitly draws attention to the amorphous nature of electrochemically prepared PbO_2 as opposed to chemically prepared material [11].

Perhaps now we can turn our attention to the amorphous phase and, using the membrane/osmosis model, learn how to control the morphology, cycle life and Faradaic efficiency of the PbO_2 electrode.

In this context, recent work by Matthews and his collaborators at Flinders University [5, 36] on sulphate and bisulphate ion additions to sulphuric acid in the battery should be re-evaluated. Also, the recent references in the literature to the electrochemical activity of chemically prepared PbO_2 are intriguing [5, 6]. Have these observations been possible because the method of chemical preparation has accidently produced the correct structure, including the correct amount of hydrogen? If we could manufacture PbO_2 chemically it would change the approach to the manufacture of lead–acid batteries. A recent paper by Caulder and Simon [37] showing a change in $PbSO_4$ microstructure produced by pulse discharge, and similar work by Hill *et al.* at CSIRO [19] should be re-evaluated.

My enthusiasm for regarding the battery paste as a form of cement may appear a little excessive. However, I can only repeat the suggestion that a new viewpoint, even if wrong, should stimulate productive research. We need new ideas in lead–acid research.

Professor Birchall, who is one of those responsible for the new membrane/osmotic model of cement hydration, has developed the technology to make cement as strong as aluminium. Portland cement technology is over 150 years old, so that I have expectations that the younger 100 year old technology of the lead–acid battery can be similarly improved. The task is a little more difficult than the cement case because we have to deal with an electrochemical phenomenon which is reversible.

Conclusion

At the beginning of this paper were listed scientific problems and technical problems. They are linked together as expressions of the same underlying uncertainties.

We now have two new theories to explore, which is a very unusual situation in lead–acid battery technology, where change is measured on a scale of decades, if not half centuries. We may follow the themes of 'hunt the proton' and 'battery paste is like cement'. In addition, we now have better tools to allow us to see what is going on at the electrode.

For the last twenty years or more we have examined the electrodes from the solution side inwards, and used classical wet electrochemistry. We should now look from the solid outwards and use solid state physics as well.

Acknowledgements

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