



Gaston Planté Medal acceptance speech

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Thank you, Mr. Secretary, for your very kind words. And may I express my sincerest thanks to the Gaston Planté Medal Committee for doing me this honour.

I do regard this award as an enormous honour but I feel very strongly that it actually represents not what I have done as much as it is a recognition of the success of the Advanced Lead–Acid Battery Consortium (ALABC)—and I will return to that later.

In the few minutes available to me, I would like to say a few words about developments in the realm of lead–acid batteries relating particularly to materials; initially relating to the positive plate, and then to the negative plate.

When I first began to study the lead–acid battery it was a major concern that utilization of the active material, particularly on the positive plate, was very limited. There were several theories about

the factors that might affect the capacity of the positive: First it was clear that lead dioxide can be present in one or other of two crystalline modifications; the alpha form is orthorhombic and the beta form tetragonal. Next there was a theory that, unless the lead dioxide was prepared by an electrochemical route, it would be incapable of providing a discharge capacity. And then there was a theory that lead dioxide needed to contain some hydrogen if it was to provide capacity. I had a background in crystal structure analysis and therefore chose to look at some of these issues using diffraction and scattering techniques.

Taking the last factor first, I had previously solved the crystal and molecular structure of a complex zinc hydride [1]. In this structure a hydrogen atom is revealed bonded directly to a zinc atom. It is clear from this and other crystal structure studies that, if hydrogen atoms are present on a regular crystallographic site, that is to say they are ordered in the crystal in three dimensions, they will be clearly visible to the diffraction technique. In the case of lead dioxide, diffraction techniques provide no sign of any hydrogen atoms ordered in the structure for either the alpha or the beta form. Both forms do however yield capacity—whether they are prepared chemically or electrochemically [2].

Inelastic neutron scattering provides some insight into the problem. In some forms of lead dioxide there is hydrogen present, either in the form of water molecules, as shown here (Table 1) or as hydroxyl groups [3]. In either case it is not present as an ordered form in the crystal structure but is disordered—on the surfaces of regular crystals or in the gel form that has been described by Professor Pavlov's team. In summary, the capacity of the positive active materials is not governed by the choice of crystal form—alpha or beta and it is not essential that it contains hydrogen or that it can be prepared electrochemically. Rather, the smaller the particle size the better, and the form containing some disordered hydrogen, perhaps in a gel, certainly contributes.

When the focus of research moved on to attempts to deep-cycle valve-regulated batteries there was immediately a problem due to a phenomenon that became known as 'Premature Capacity Loss' or PCL [4]. PCL came initially in two forms, the first of which involved the formation of a high resistance layer at the interface between the active material of the positive plate and the grid surface.

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Table 1

Hydrogen content of various forms of lead dioxide as revealed by inelastic neutron scattering.

Material	x in $\text{PbO}_{2-x}(\text{H}_2\text{O})_x$
αPbO_2 chemical	0.3
αPbO_2 electrochemical	0.2
βPbO_2 chemical	0.0
βPbO_2 electrochemical	0.08

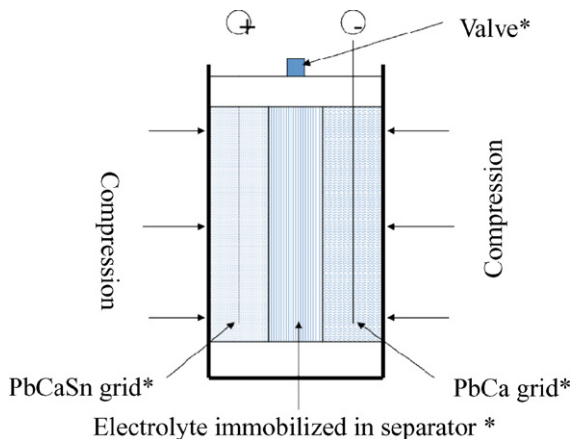


Fig. 1. Schematic of VRLA cell designed to withstand the mechanisms of PCL1 and PCL2.

At the Harwell Lab. we devised a scanning laser method for following the distribution of alpha PbO in the corrosion layer by imaging photocurrent [5]. The photocurrent image clearly highlighted the distribution of the alpha PbO in the corrosion layer.

In due course the ALABC mounted a major study of PCL1 and the effect was largely overcome by a judicious choice of alloy for the positive grid. For example, the rate of corrosion decreases sharply as the tin content in the alloy increases. The tin also renders the corrosion layer less resistive.

The second form of PCL involved the expansion of the positive active material due to repeated swelling and collapse that arose from the volume change of the solid phases as the battery was deep-cycled. This led progressively to the loss of electrical contact with some of the material. The solution to this problem consisted of making sure that the positive active mass remained compressed, and thus retained its integrity, throughout its useful life.

Fig. 1 sums up the situation of a VRLA cell equipped to deal with PCL1 and PCL2; a pressure release valve at the top, grids of appropriate alloys, and compression maintained on the plates. The automobile manufacturers always asked that the battery should just be a black box that behaved like the rest of their components. I think that it is more realistic to say that it behaves like a black box with an animal inside it; it breathes, it likes to be squeezed, and sometimes it burps!

When ALABC turned to working with hybrid electric vehicles (HEVs) it was clear that the battery had to work in a very different way; based at an intermediate state-of-charge it had to perform very many small cycles at very high rates and we were quickly confronted with 'PCL3'. This phenomenon involved the rapid accumulation of lead sulfate on the negative plate, and failure as a result.

However, as has become clear, the incorporation of extra carbon in the negative plate overcomes PCL3 very effectively [6].

The most successful example of this solution so far, has been the Ultra battery [7] which incorporates the extra carbon in an extension of the negative, adding a capacitive function. The rest of the battery is conventional and from outside the battery appears quite normal.

In use it is far from normal, however, operating for over 10,000 capacity turn-overs in simulated HEV duty in the laboratory. And in a hybrid automobile, in place of the usual nickel metal hydride unit, it ran faultlessly for over one hundred thousand miles without any conditioning or equalization. Perhaps the most important result of this work, though, is that the twelve modules in the 144 V battery, which were closely matched at the beginning of the test, were actually CLOSER matched at the end of the test. This suggests that it is an inherent characteristic of this form of lead-acid battery (with the capacitive element at the negative plate) that modules remain in balance with one another and require no conditioning.

It is not yet clear whether it is necessary for the extra carbon at the negative plate to be physically separated from the rest of the negative active material. It may be more convenient in manufacture if the carbon can be included in the mix for pasting in a single operation.

We have already seen that modest amounts of extra carbon included in this way bring significant benefit in simulated HEV cycling in the laboratory, and now a battery with the same modest amount of extra carbon is being tested in a Honda Civic hybrid.

Thus it seems likely that, in the future, automobile manufacturers will have a choice to make between three different battery chemistries involving three different metals: lead, nickel and lithium. This reminds me of the choice that the character Bassanio had to make in Shakespeare's 'Merchant of Venice'. Bassanio had to make a choice between three caskets, one of gold, one of silver and one of lead. Only one of the three contained a portrait of his beloved Portia. Bassanio correctly chose lead and thus was allowed to marry Portia. Let us hope that the automobile manufacturers will have the wisdom to follow Bassanio's example.

“ but thou, thou meagre lead,

thy plainness moves me more than eloquence,

and here I choose”

Bassanio in “The Merchant of Venice”, Act 3 Scene 2

I said at the beginning that I view this award as being very much an acknowledgement of all that has been achieved by the ALABC, and with that in mind I would like to add my thanks to my colleagues in the ALABC team—David Prengaman, Allan Cooper, Rob Putnam, Mark Stevenson and Anita Wright and indeed to all the contractors and the members of the Consortium who have worked so well together. And finally, but most importantly I wish to express my thanks to my wife, Heather, who has patiently put up with me traveling around the world during the course of the ALABC program.

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