

Bipolar batteries based on Ebonex® technology

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Abstract

Continuing work by Atraverda on the production of a composite-laminate form of the Ebonex® material, that can be cheaply formulated and manufactured to form substrate plates for bipolar lead–acid batteries, is described. Ebonex® is the registered trade name of a range of titanium suboxide ceramic materials, typically Ti_4O_7 and Ti_5O_9 , which combine electrical conductivity with high corrosion and oxidation resistance.

Details of the structure of the composite, battery construction techniques and methods for filling and forming of batteries are discussed. In addition, lifetime and performance data obtained by Atraverda from laboratory bipolar lead–acid batteries and cells are presented.

Battery production techniques for both conventional monopolar and bipolar batteries are reviewed. The findings indicate that substantial time and cost savings may be realised in the manufacture of bipolar batteries in comparison to conventional designs. This is due to the fewer processing steps required and more efficient formation.

The results indicate that the use of Ebonex® composite material as a bipolar substrate will provide lightweight and durable high-voltage lead–acid batteries suitable for a wide range of applications including advanced automotive, stationary power and portable equipment.

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1. Introduction

Initial performance data involving bipolar batteries containing Ebonex® ceramic based bipolar plates has been recently presented [1].

The advantages of bipolar operation for batteries in general and lead–acid batteries in particular have been well documented and are generally widely understood and appreciated. However, one major barrier to progress in the lead–acid field has been the identification of a bipolar substrate material that is stable to the acidic and oxidising conditions that are present at the positive active mass of the battery. This report describes further research conducted to ascertain the lifetime and durability of lead–acid batteries containing the novel Ebonex® substrate material. The

report also contains a brief review of lead–acid battery manufacturing procedures and a process scheme for the production of the equivalent bipolar product is presented.

Ebonex® ceramic is a metallic-type conductor having a conductivity that is comparable to that of carbon but with superior oxidation resistance. Further details regarding the structure and properties of Ebonex® ceramic are available elsewhere [1,2].

The main requirements for a substrate material for a bipolar battery are electrical conductivity, corrosion resistance, electrochemically inert under conditions of use, impermeability to acid, good adhesion to active pastes and sufficient mechanical handling strength.

Aspects regarding electrical conductivity, corrosion resistance and inertness under conditions of use of the Ebonex® substrate have been previously discussed [1]. This paper will provide further information on specific testing of the substrate and bipolar batteries under cycle life and overcharge conditions.

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2. Experimental

2.1. Ebonex[®] plate manufacture

Two types of plates are required to fabricate a bipolar battery. Each battery requires two end plates or monopole plates with provision for external connections as well as a number of intermediate bipolar plates. Both types of Ebonex[®] plates are produced by a simple hot pressing technique. The Ebonex[®] plate may be described as a laminated composite comprising Ebonex[®] particulate in a polymer matrix with an outer layer of lead alloy on each face.

The plates are prepared by mixing Ebonex[®] powder with a known quantity of matrix material and sandwiching between two thin lead alloy foils. The sandwich is then hot-pressed between two patterned mould plates for a short time to produce a plate of the type shown in plan view in Fig. 1.

The gridded pattern provides a key for the active material pastes that are subsequently applied. Fig. 3a shows a cross-sectional view through a bipole plate showing the exterior lead interfaces and Ebonex[®] ceramic particles embedded within the cured polymeric matrix. Monopole plates are gridded on one face only and have provision for external connections on their reverse face. The height of the grids may be varied to control the thickness of paste to be applied.

2.2. Bipolar battery fabrication

The pressed plates are then ready for the application of active pastes. No changes to the paste formulation from those typically used for conventional batteries are required and a wide range of paste densities ($3.5\text{--}4.6\text{ g cm}^{-3}$) have been successfully pasted onto the plates. Similarly, no special changes to curing regimes are required. All the pasted plates were

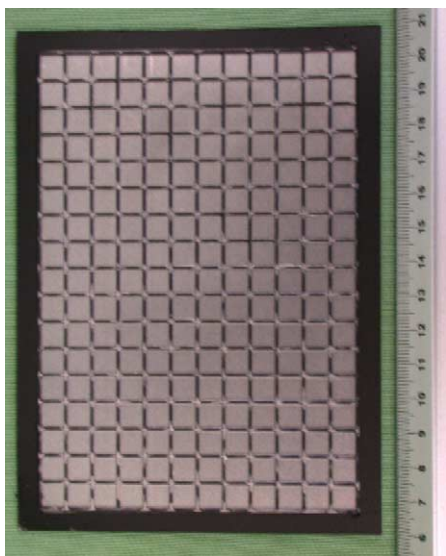


Fig. 1. Plan view of an Ebonex[®] plate for a bipolar lead-acid battery, prior to pasting with active materials.

cured using a standard regime of 24 h at 50 °C followed by drying at room temperature for a further 48 h to form tribasic lead sulphate.

All the batteries tested were of a sealed design containing absorptive glass mat (AGM) to retain the sulphuric acid electrolyte. Battery assembly involves stacking the required number of bipoles and intermediate AGM separators between the external monopolar endplates. For example a 4 V battery requires 2 endplates and 1 bipole, a 6 V battery requires 2 end plates and 2 bipoles, a 12 V battery requires 2 end plates and 5 bipoles, a 24 V battery requires 2 end plates and 11 bipoles, a 36 V battery requires 2 end plates and 17 bipoles and a 48 V battery requires 2 end plates and 23 bipoles. Once the stack is assembled the desired degree of compression is applied and the edges sealed.

The resulting sealed stack requires no additional external case and may be filled with acid by a simple gravity fill or vacuum fill. Sealing of the stack presented no problems. After acid filling the batteries were allowed to stand for at least 1 h before forming took place. The batteries may then be formed using conventional formation techniques. All the batteries were formed at a constant current density of 3.06 mA cm^{-2} with a charge input of 0.343 Ah g^{-1} ($1.53\times$ theoretical capacity, less than the $1.7\text{--}2.5\times$ theoretical capacity used for conventional monopolar designs [3] and indicating good efficiency for formation). One-way valves, housed in short lengths of polyethylene tubing adapted to enable connection to the fill and vent tubes were then fitted to the batteries. Two 6 V batteries constructed in this way are shown in Fig. 8.

Fig. 2a and b shows the Ebonex[®] plates that have been pasted, cured and formed and Fig. 3a–d shows the cross-sections of unpasted, pasted and cured as well as formed positive and negative plates, respectively.

2.3. Battery testing

All testing has been carried out as far as possible to international standards. Cycle life under float conditions was carried out according to BS6290, part 4. A lifetime of 50 cycles is required for compliance with this specification.

All battery testing was carried out using a commercially available 12-channel battery tester (PEC SBT 2100, PEC Electronics, Leuven, Belgium) at room temperature unless otherwise stated. Each channel is limited to 100 W discharge and consequently the battery evaluation work described here concentrated on the evaluation of 4 and 6 V batteries.

2.4. Plate porosity testing

A test was designed to evaluate the degree of through porosity in a bipolar plate. The existence of through porosity can lead to self-discharge of the two cells adjoining the permeable plate. Any through pores in the polymer binder or lack of adhesion to the Ebonex[®] particles that allows ingress

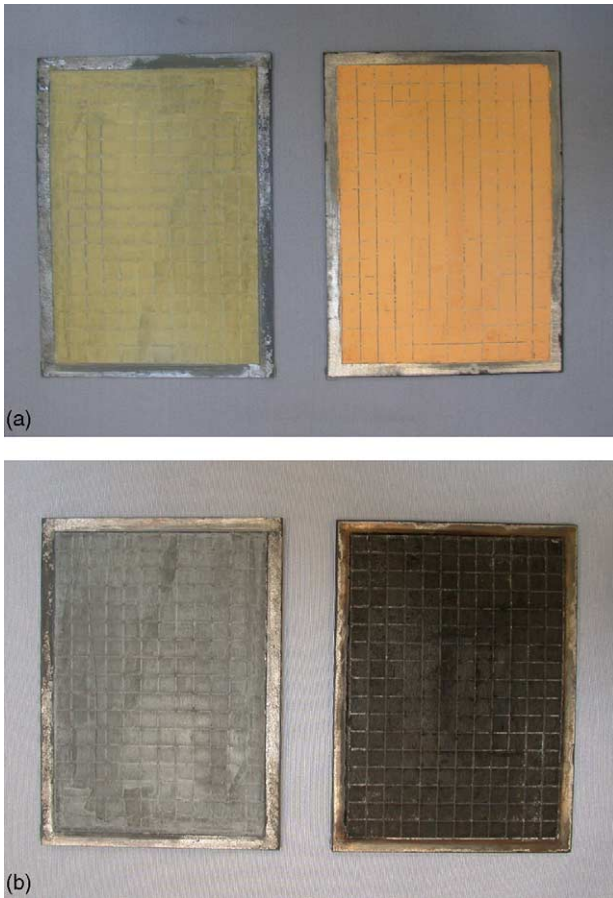


Fig. 2. (a) Pasted and cured negative (left) and positive (right) Ebonex[®] plates. (b) Negative (left) and positive (right) Ebonex[®] plates after formation.

of solution and bridging across adjoining faces will result in current flow. Long term testing of the materials enables an evaluation of the durability of the polymer matrix material. Fig. 4 shows a schematic diagram of the experimental set-up and further details of the test are available elsewhere [4].

2.5. Overcharge testing

Testing to determine the durability of the lead interface to conditions of extreme overcharging has been based on that described by Kurisawa et al. [5]. A schematic diagram of the test set-up used in this study is shown in Fig. 6 and utilises a whole bipolar plate of the type shown in Fig. 1.

2.6. Miscellaneous

Cross-sections of plates were made using a Meiji polarising microscope and digital camera (Nikon Coolpix 995). Mercury–mercury sulphate reference electrodes were obtained from Russell pH, Auchtermuchty, Scotland. Valve regulated seals having an opening pressure of 70 mbar were purchased from Frötek GmbH, Osterode am Harz, Germany.

3. Results and discussion

3.1. Plate structure

Fig. 3a shows the structure of the composite battery plates with the conductive Ebonex[®] particles embedded within a resin matrix and laminated with the lead alloy interfaces. The purpose of the thin lead-based interfaces is to improve adhesion of the active masses to the surface, particularly on the positive side. The importance of a so-called corrosion layer on the surface of conventional lead grids to allow good contact with the positive active mass (PAM) has been well documented in the literature (see, e.g. [6,7]). The inertness of titanium suboxide materials to the oxidising and acid conditions present within a lead–acid battery has been previously demonstrated [1] and so the lead interface is not required to protect the underlying bipolar substrate material as in earlier published designs of bipolar lead–acid batteries (see, e.g. [8]).

Fig. 3a and b (20 \times magnification) show a bipole plate with and without paste. The bipole plates have positive paste on one side and negative paste on the other. Both active masses have been pasted to a nominal thickness of 1 mm on each face, but this may be readily adjusted to ensure that excess negative paste is not used. Fig. 3c and d shows the magnified images (200 \times) of the positive and negative interfaces, respectively, after formation and indicate good adhesion of the formed active masses to the interface. Careful measurement of the remaining thickness of the foils after formation indicates that the foil on the positive side has been reduced in thickness by 5–7 μm while that on the negative side is unaffected.

The bipolar structure is therefore made up of three materials—Ebonex[®] powder, resin matrix material and lead alloy interface. It is important that each of the materials is resistant to both acid and oxidising conditions within the PAM material. A number of tests were devised to investigate the durability of each of the components to the conditions likely to be found in a lead–acid battery. Operating data from actual lead–acid batteries containing Ebonex[®] bipolar plates have also backed up these tests and the corresponding results are presented and discussed below.

3.2. Plate porosity testing

The bipolar plate acts as an impermeable membrane and so any current observed may be attributed to through porosity allowing ionic conductivity. The plates used for this test have no lead interface and the surface has been roughened by grit blasting. Fig. 5 shows the results for the two types of resin matrix material. The first (green trace) is data for a resin investigated early in the programme. This resin is shown to have poor acid resistance due to a rapid increase in current after a few weeks. In contrast the red trace is for a more acid resistant material that has a far greater lifetime (over 19,000 h to date). In addition the ability to seal onto the surface of the plate can be evaluated in this test. The third trace (blue) is

for a plate of acid-resistant resin that has had a large hole (2.5 cm diameter) drilled into it and sealed using the neat resin material. The low current observed is indicative of the good seal and durable bond that is possible to achieve directly to the resin surface of the bipolar plate.

3.3. Overcharge testing

This test was carried out using the apparatus shown in Fig. 6 and involves passing a constant anodic current (5 mA cm^{-2}) for the duration of the test and monitoring the potential of the test sample with respect to a reference electrode ($\text{Hg/Hg}_2\text{SO}_4$). This level of current is comparable

to severe overcharging and may be compared to the expected level of float charging of 0.009 mA cm^{-2} for this size of plate at room temperature [9]. Changes to the value of the working potential are indicative of changes occurring at the interface of the plate and the PAM. The results obtained for a series of interface types is shown in Fig. 7. One major advantage of the technique over other methods of determining positive grid life such as accelerated float life testing is its rapidity and ability to provide a rapid screening method. The originators of the test (5) state that a lifetime of 600 h (25 days) is indicative of “an outstanding effect for suppressing corrosion”. The test provides good discrimination between interface types as shown in Fig. 7.

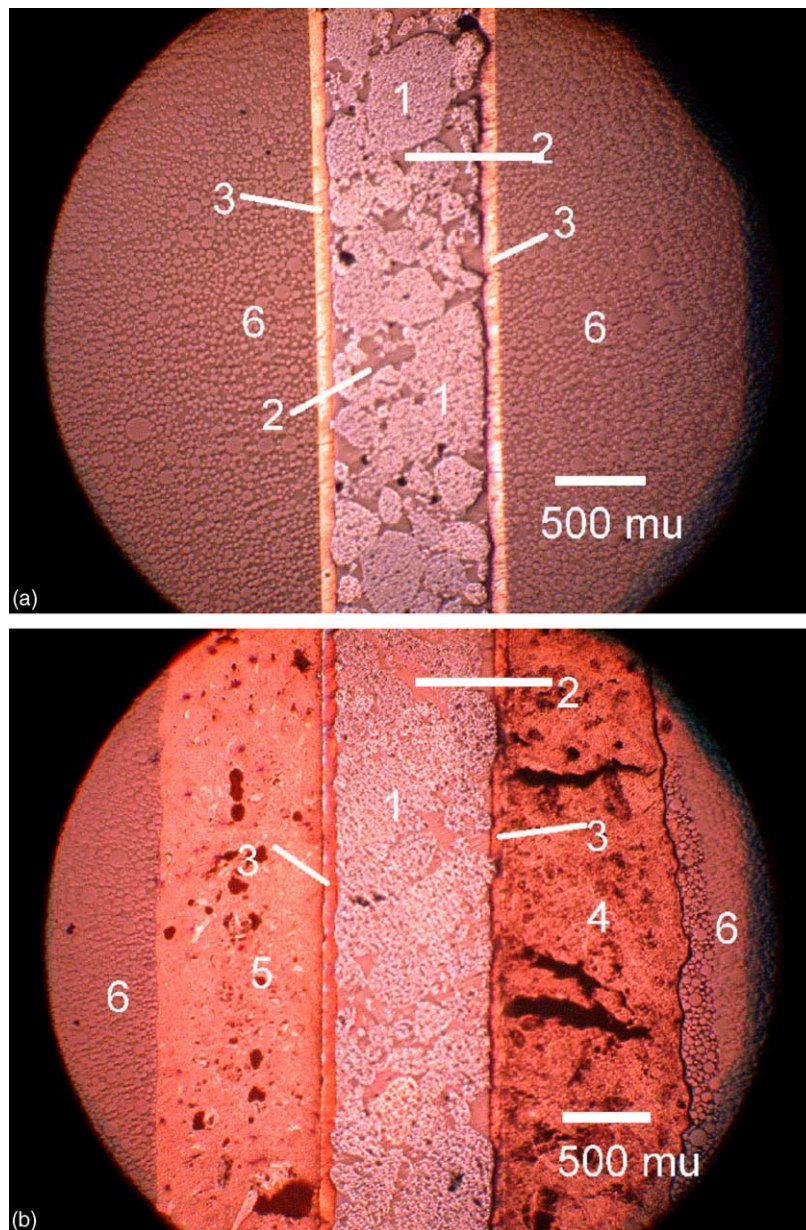


Fig. 3. (a–d) Cross-sectional views of plate interfaces for pasted, cured and formed plates. 1: Ebonex® particle; 2: polymer binder; 3: interface lead alloy foil; 4: negative active mass; 5: positive active mass; 6: potting resin for microscope sample.

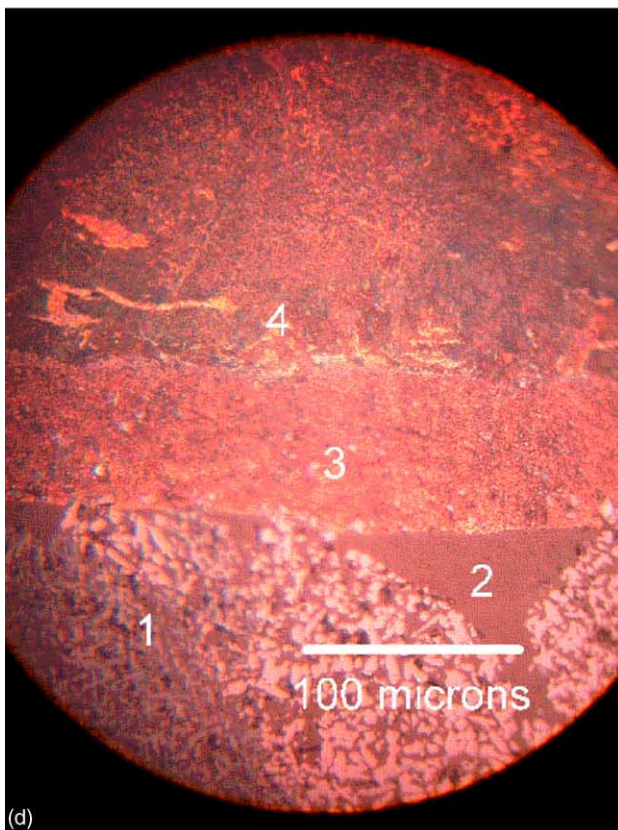
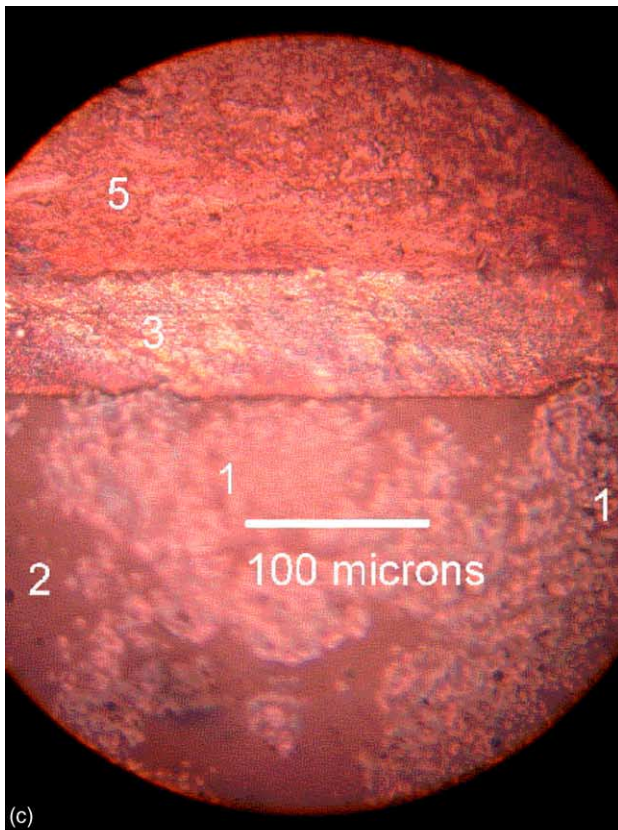


Fig. 3. (Continued).

Data for five interface types are shown in Fig. 7 with lifetimes ranging from less than 100 h for an electroplated pure lead interface to around 500 h for an electroplated lead alloy interface containing 3.5% tin. Optical examination of failed interfaces comprising 100% lead show the interface to be in good condition with good adhesion to both the composite substrate and the active mass. It is postulated that the reason for the sharp increase in potential after 70 h is the formation of a poorly conductive PbO interlayer. Certainly, the inclusion of increasing quantities of tin in the interface results in an increase in the lifetime and possibly provides a more-conductive lead suboxide material by tin doping. Increasing the tin content of the interface from 0 to 1% increased lifetime from less than 100 h to around 200 h. Theories regarding the effect of tin and other alloying additives on premature electrode failure hierarchy including premature capacity loss are discussed more fully in the review by Meissner [10], among others. The interface material with the longest life to date in the test has shown a lifetime of around 1500 h, i.e., around a 30-fold improvement on pure lead interface material and is a lead alloy foil applied directly during the hot pressing procedure for fabrication of the Ebonex[®] bipolar plate substrate. Lifetimes in accelerated overcharge tests have been recorded at over 1500 h, i.e., well in excess of the 600 h deemed to be outstanding in this type of test [5].

3.4. Cycle life

One important aspect for standby batteries is their ability to cycle in addition to possessing an extended lifetime on float duty. This is thought to be becoming more important with the increase in the number of remote base stations and other facilities requiring standby power capability that are located in regions with less reliable mains power. British standard BS 6290 (part 4, 1997), which has now been superseded by IEC 896-2 as the standard for the UK, describes a test procedure to evaluate this property of lead–acid batteries. The test comprises a regime of repeated discharges at the 3 h rate to 75% depth of discharge at room temperature. After each series of cycles the batteries are recharged and subjected to a full capacity test at the 3 h rate of discharge. The end of life criterion is when the actual capacity of the battery falls below 80% of the rated capacity of the battery. The minimum specification for the standard is 50 cycles.

Two 6 V bipolar Ebonex[®] batteries of the type shown in Fig. 8 were tested according to the standard. Both batteries passed the specification and were taken off-line after 75 cycles and dismantled to evaluate the state of the lead alloy interface. Plates were cut and potted in a mounting medium to allow cross-sectioning. A typical image of part of one bipolar plate is shown in Fig. 9 and indicates that both sides of the interface are in good condition with good adhesion to the Ebonex[®] powder/resin composite substrate. This is the case for both the negative and positive interfaces and in both cases the adhesion to the corresponding active masses appears to

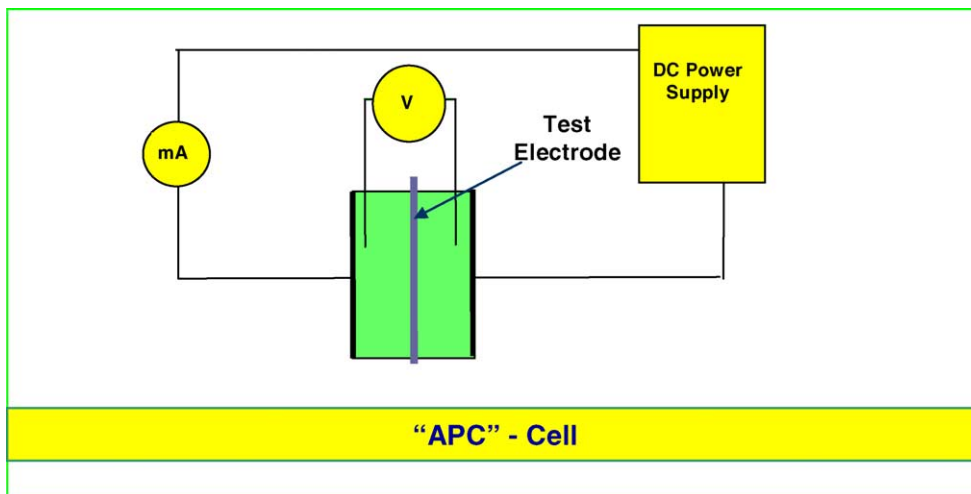


Fig. 4. Schematic diagram of the test set-up for evaluating the degree of through-porosity in an Ebonex® bipolar plate.

be excellent with no evident delamination or voids. There is evidence of a separate interphase region between the interface and the PAM material (marked as 3a in Fig. 9) and is presumably a region comprising tin doped lead suboxide (PbO_{2-x}) bridging the PbO_2 (PAM) and the metallic lead of the foil interface. This type of region has been described as the corrosion layer and active-mass collecting layer by Pavlov [6]. The thickness of the interphase region shown in Fig. 9 is 16–34 μm . Work reported by Hollenkamp et al. [7] on Pb–Ca and Pb–Sb–Sn grids has also indicated a layer structure at the interface between conventional lead grids and PAM, which contains non-stoichiometric oxides identified by electron probe microanalysis as $\text{PbO}_{1.2}$, $\text{PbO}_{1.8}$, $\text{PbO}_{1.9}$, $\text{PbO}_{2.1}$ and $\text{PbO}_{2.3}$. The layer structure at the lead grids was shown to be typically around 5–10 μm thick after formation with an increase in thickness to around 30–40 μm thick after

three charge/discharge cycles. Study of the positive interface thickness after formation in a bipolar battery indicates a reduction in metallic interface thickness of 5–7 μm (see Section 3.1). The situation at the interfaces after 75 discharge cycles is indicated in Fig. 9 which shows a cross-section across a bipolar plate (100 \times magnification). Reference to Fig. 9 indicates that the NAM foil interface has maintained its original thickness after 75 cycles while the thickness of the remaining metallic interface foil exposed to the positive active mass has been reduced by about 10% after 75 cycles. Extrapolation of the data indicates that a cycle life of around 750 cycles is possible for the Ebonex® bipolar substrate without further optimisation if the interface is the life-limiting component. Further experimental work is being conducted on deep cycle life and accelerated float life and both sets of results will be presented in due course.

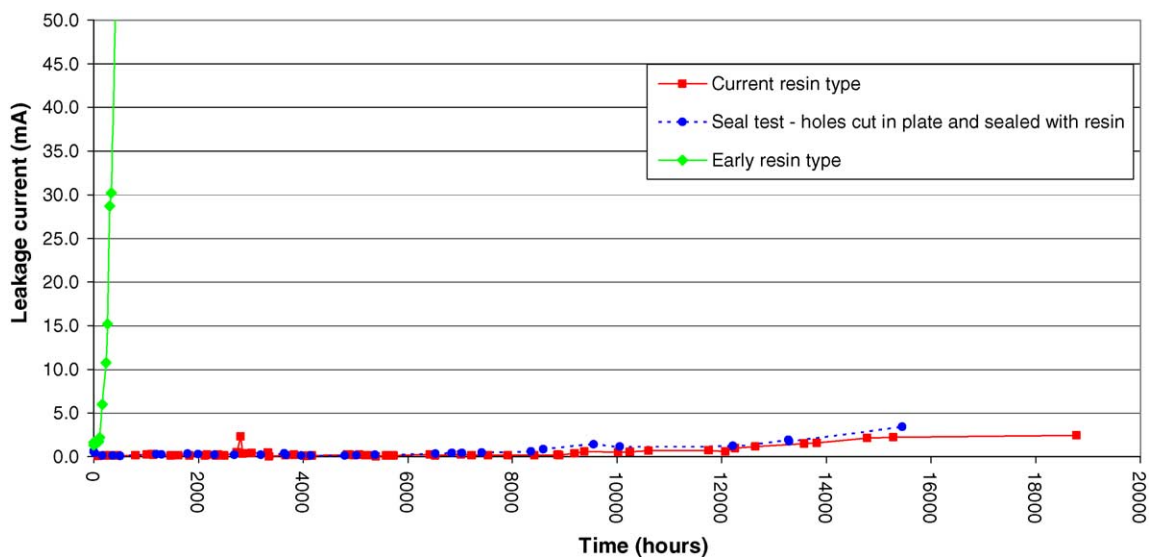


Fig. 5. Through-porosity test results on two matrix polymer types and showing the ability to effectively seal the bipolar plates.

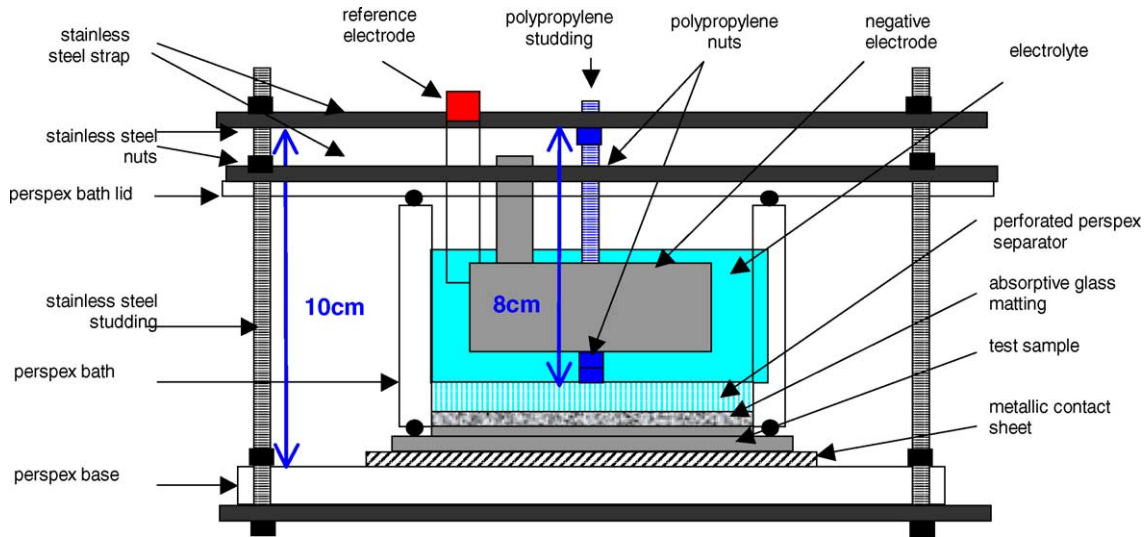


Fig. 6. Schematic cross-section of anodic overcharge test apparatus.

3.5. Battery production

Although, as stated in Section 1, the potential performance benefits of bipolar batteries have long been recognised, and Kao [11] describes bipolar lead–acid battery designs going back to 1923, the relative simplicity and potential savings in battery manufacture are perhaps less widely appreciated.

The three main phases of lead–acid battery production are plate manufacture, battery assembly and acid filling and charging. For example, a conventional monopolar 12 V 7 Ah sealed lead–acid battery will typically have 7 monopolar plates per cell (3 positive, 4 negative) giving a battery contain-

ing 42 plates in total. The equivalent Ebonex® bipolar battery has a total of seven plates per battery (five bipoles and two monopoles) resulting in a reduction in the plate count by a factor of 6. Therefore the quantity of plates required by a bipolar battery is significantly less, but a second and even greater potential saving is in the assembly operations (see Figs. 10 and 11 which show the process schemes for the assembly of monopolar and bipolar batteries, respectively).

Comparison of Figs. 10 and 11 indicates that four fewer operations are required for the production of bipolar batteries with the cast-on strap (COS) and intercell weld operations being redundant.

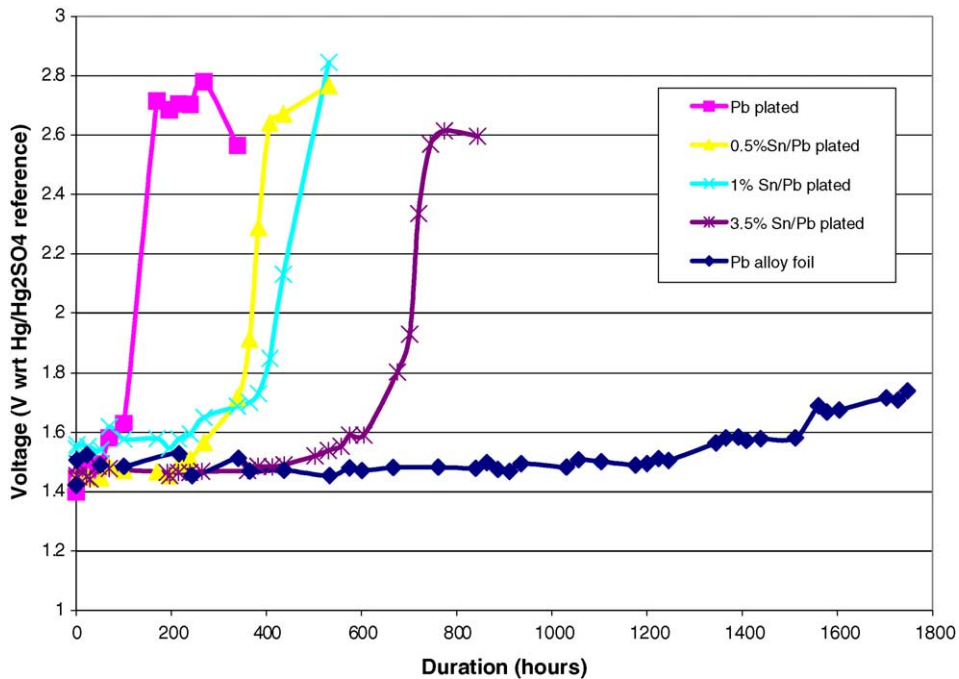


Fig. 7. Effect of tin content in electroplated interface and of a different interface type on interface life in a simulated overcharge test.



Fig. 8. Ebonex® bipolar lead-acid batteries (6 V).

The so-called COS operation fuses the same polar plates together in a conventional cell. The intercell weld machine uses extrusion fusion to join the 2 V cells together to make a 12 V battery. Both operations use high cost machines and add to the processing time. These are not necessary for production of Ebonex® bipolar batteries. Therefore it is likely that pro-

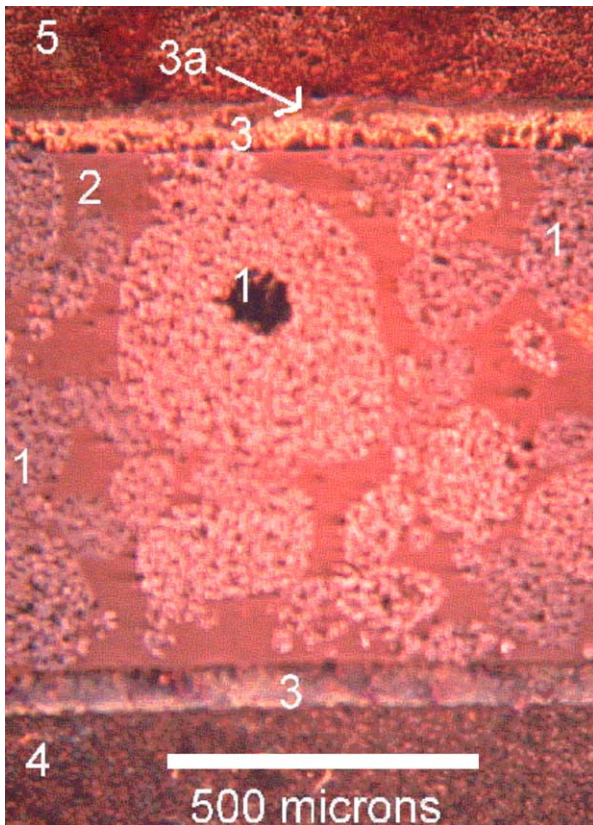


Fig. 9. Cross-sectional view through an Ebonex® composite bipolar plate after undergoing 75 cycles according to British standard BS 6290 (part 4, 1997). (1) Ebonex® particles; (2) polymer binder; (3) interface foils; (3a) PAM interphase region; (4) negative active mass; (5) positive active mass.

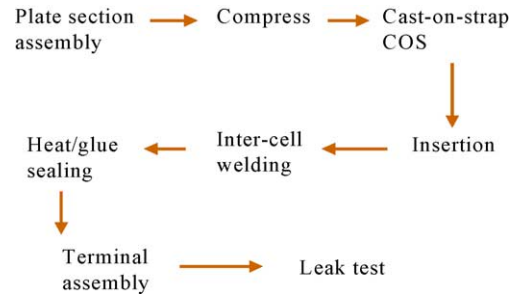


Fig. 10. Process flow scheme for the production of conventional batteries by a conventional route—eight operations (excluding pasting, curing, filling and forming).

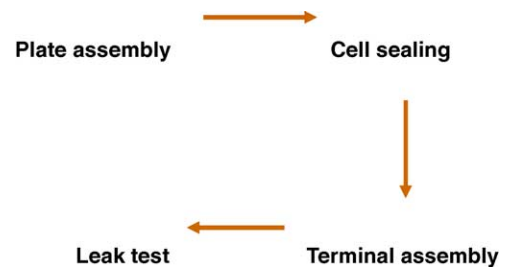


Fig. 11. Process flow scheme for the production of bipolar batteries—four operations (excluding pasting, curing, filling and forming).

cessing of bipolar plates to form batteries will be faster and require less capital equipment than conventional monopolar grids.

4. Conclusions

A range of tests carried out on Ebonex® composite bipolar substrate plates both in simulated and actual batteries has been described. Testing specifically designed to evaluate the durability of the polymeric binder has led to the identification of a class of polymeric materials that have the required degree of stability, ease of manufacture and sealability.

Although not necessary to protect the underlying Ebonex® ceramic filled composite substrate the lead interface has been shown to play an important role in extending the lifetime of batteries containing Ebonex® bipolar substrates by retarding premature capacity loss due to the formation of poorly conductive lead oxides at the plate interface. This has been confirmed by testing of 6 V batteries which have been shown to comply with the relevant British industry standard, BS6290, part 4. Further work is being conducted on deep cycle life and accelerated float life and results will be published in due course.

A review of production operations has indicated that significantly fewer operations are required for production of bipolar batteries than the equivalent conventional monopolar design resulting in potentially reduced processing time and lower capital requirements.

References

- [1] K. Ellis, A. Hill, J. Hill, A. Loyns, T. Partington, The performance of Ebonex electrodes in bipolar lead-acid batteries, in: Proceedings of the 23rd IPSS Meeting, Amsterdam, September 2003, *J. Power Sources* 136 (2004) 366–371.
- [2] <http://www.atraverda.com>.
- [3] D. Pavlov, Formation of lead-acid batteries, in: D.A.J. Rand, P.T. Moseley, J. Garche, C.D. Parker (Eds.), *Valve-regulated Lead-acid Batteries*, Elsevier, Amsterdam, 2004, p. 40.
- [4] T.J. Partington, WO 02/058174 A2 Electrode for a Battery, January 21, 2002.
- [5] I. Kurisawa, M. Shiomi, S. Ohsumi, M. Iwata, M. Tsubota, Japan Storage Battery Co. Ltd., Development of positive electrodes with an SnO₂ coating by applying a sputtering technique for lead-acid batteries, *J. Power Sources* 95 (2001) 125–129.
- [6] D. Pavlov, A theory of the grid/positive active mass (PAM) interface and possible methods to improve PAM utilization and cycle life of lead/acid batteries, *J. Power Sources* 53 (1995) 9–21.
- [7] A.F. Hollenkamp, K.K. Constantis, M.J. Koop, L. Apateanu, M. Calabek, K. Micka, Effects of grid alloy on the properties of positive-plate corrosion layers in lead/acid batteries. Implications for premature capacity loss under repetitive deep-discharge cycling service, *J. Power Sources* 48 (1994) 195–215.
- [8] W.B. Brecht, Trojan's bi-polar lead-acid batteries, *Batteries Int.* (1993) 52–53.
- [9] D. Berndt, *Maintenance-free Batteries*, 2nd ed., Wiley, 1997.
- [10] E. Meissner, How to understand the reversible capacity decay of the lead dioxide electrode, *J. Power Sources* 78 (1999) 99–114.
- [11] W.-H. Kao, Substrate materials for bipolar/lead-acid batteries, *J. Power Sources* 70 (1998) 8–14.