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The performance of Ebonex® electrodes in bipolar lead-acid batteries

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Abstract

Recent work by Atraverda on the production of an Ebonex® material that can be cheaply formulated and manufactured to form bipolar substrate plates for bipolar lead-acid batteries is described. In addition, data obtained by Atraverda from laboratory lead-acid batteries is presented indicating that weight savings of around 40% for a bipolar 36 V design (20 Ah capacity, 5 h rate, 9 kW) are potentially achievable in comparison to more conventional designs containing monopolar lead grids.

Results indicate that their use as bipolar substrate materials will provide light-weight, long-lasting lead-acid batteries suitable for automotive, standby and power tool applications.

Keywords: Lead-acid batteries; Bipolar; Inorganic separators

1. Introduction

1.1. Titanium suboxide materials

Titanium suboxide ceramic materials, typically Ti_4O_7 and Ti_5O_9, are manufactured by Atraverda Ltd. in the U.K. under the registered trade name of Ebonex®. The materials are available in a number of forms for commercial use in applications that require an electrical conductor with excellent corrosion resistance and oxidation resistance [1,2]. Since 2001, the use of Ebonex® electrodes for the cathodic protection of reinforced concrete structures and buildings has been licensed [3]. Further general information on Ebonex® ceramic may be obtained from the Atraverda website [4] or from the book by Hayfield [5].

Ebonex® ceramic is a metallic-type conductor having a conductivity (up to 300 S cm^{-1}) comparable to that of carbon but with superior oxidation resistance. Its combination of corrosion resistance, oxidation resistance and electrical conductivity may be explained by the crystal structure of the Magnéli phase titanium suboxides [6]. The parent structure is rutile titanium dioxide, which can be described as a network of TiO_6 octahedra sharing edges in a plane and edges along the axis perpendicular to that plane. The Magnéli phases (Ti_nO_{2n-1}) can be defined as a sheared rutile structure, accommodating the oxygen deficiency in the structure by the formation of crystal shear planes along the *n*th plane of octahedral. For example, Ti_4O_7 has one TiO layer for every three TiO_2 layers. The TiO plane is attached to the adjacent TiO_2 plane via shared faces instead of shared edges as in rutile titania. The result is a conductive band intimately surrounded by titania. The conductivity of Ebonex® ceramic material arises from the TiO layers and the chemical resistance from the TiO_2 layers sandwiching and protecting the TiO layer.

In the field of batteries, this combination of properties has prompted studies into the use as an additive in a wide range of power storage/conversion devices [7–11] with particular emphasis on the positive active mass (PAM) of lead-acid batteries [10,11]. Use of Ebonex® powder and particularly fibres have been shown to enhance formation and to improve the active-mass utilisation of the positive active paste. Improvements in the available capacity of 15–17% have been observed for pasted flat plate automotive type batteries containing low levels of Ebonex® fibres. The inclusion of Ebonex® ceramic is believed to enhance connectivity of the active PbO_2 material and to act as a reinforcement to the active mass thereby aiding retention of form and porosity during cycling.

A comparative study of potential positive paste additives has shown that Ebonex® ceramic is most effective at high rates of discharge [11].

This paper will concentrate upon the use of a novel form of Ebonex® material, a resin bonded composite prepared from Ebonex® ceramic filler and a resin matrix, as an electrode substrate material in lead-acid bipolar batteries.

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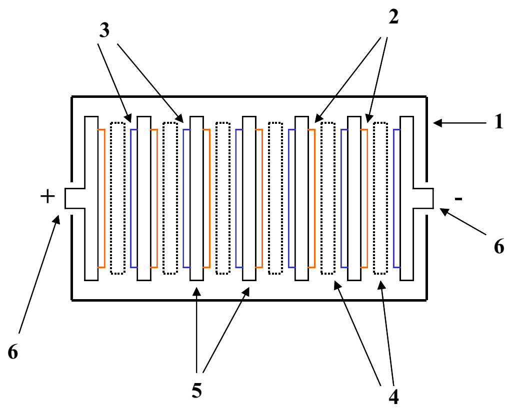

Fig. 1. A schematic cross-section of a bipolar lead-acid battery.

1.2. Bipolar batteries

A schematic diagram of a bipolar battery is shown in Fig. 1. The components are housed in a container (**1**) and current flow through the battery is provided by endplates (monopoles, **6**). The current passes orthogonally through each intermediate plate (bipole, **5**) in a uniform fashion. Each bipolar plate acts as a cell wall and has positive active mass (PAM) on one face (**2**) and negative active mass (NAM) on the other face (**3**). A microporous glass fibre separator (**4**) defines the interelectrode gap and retains sulphuric acid electrolyte.

In comparison to conventional batteries containing lead grids, the weight savings are due to the replacement of lead grids by lower density bipole and monopole plates and the elimination of cast-on lead straps and intercell connectors. The lead-acid industry has long been aware of the theoretical advantages available from bipolar batteries—particularly, bipolar lead-acid batteries. A selection of recently published papers is provided [12–16]. Kao [12] in particular predicts specific power exceeding 4 kW kg^{-1} for 30 s discharges. Arias et al. [15] demonstrated batteries which although short lived exhibited energy densities of around 50 Wh kg^{-1}. Attempts to replace lead grids with lead clad metal substrates have also suffered from problems of lifetime with cycle lives of up to 60 cycles being recorded [16].

The work of both Kao [12] and Coux [13] indicate that the key issue in such bipolar systems is the stability of the bipolar electrode substrate.

2. Physical and electrochemical properties of Ebonex® electrodes

2.1. Preparation of Ebonex® composite electrodes

The key attributes of Ebonex® electrodes as replacements for lead grids are their light weight, corrosion resistance to sulphuric acid solutions and wide operating electrochemical potential range. The composite is produced from Ebonex® particulate with a polymer binder by a conventional plastics processing procedure using moulds to produce thin plates having a grid pattern to retain active material paste and to define the thickness of paste to be applied. The procedure used is amenable to high-volume, low-cost production. A photograph of a typical Ebonex® composite bipolar plate is shown in Fig. 2. The metallic lead alloy interface has been found to improve paste adhesion and is applied directly during plate production. The resulting plates are pasted with conventional lead pastes and cured conventionally. The size of plate shown in Fig. 2 (150 mm × 110 mm) has a measured capacity of 6.5 Ah (20 h rate).

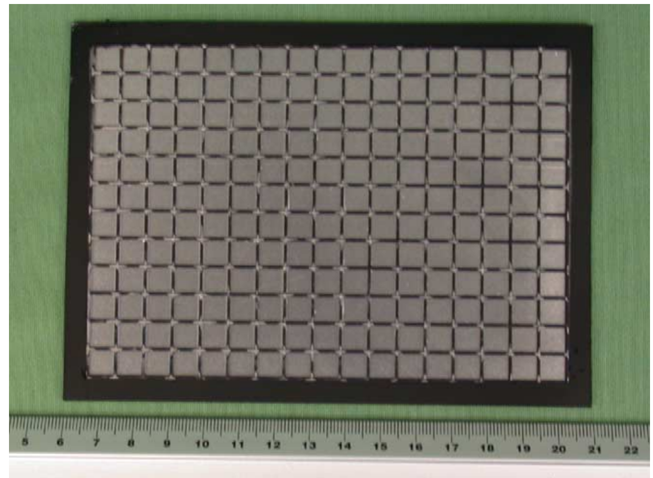

Fig. 2. An Ebonex® bipolar electrode prior to pasting with active material.

Fig. 2 shows an Ebonex® bipolar electrode prior to pasting with active material.

2.2. Physical properties of Ebonex® bipolar electrodes

Table 1 is a list of some physical properties for both lead metal and Ebonex® composite.

The lower conductivity of Ebonex® composite in comparison to lead metal is not a problem in bipolar battery designs where current flow through the battery only occurs orthogonal to the plane of the plate, e.g. for a 36/42 V design (see below) the resistance of the bipolar plate is less than 40 μΩ and that of all 19 plates combined is less than 1 mΩ.

Table 1
Physical properties of lead metal and Ebonex® composite electrodes

Property	Lead metal	Ebonex® composite
Density (g cm^{-3})	11.35	2.27
Conductivity (S cm^{-1})	48,544	2
Potential range (V vs $Pb/PbSO_4$)	−1.8 to +2.2	−1.5 to +3.2
Potential range of negative and positive plates in a lead-acid battery	−0.5 to +2.3 V	

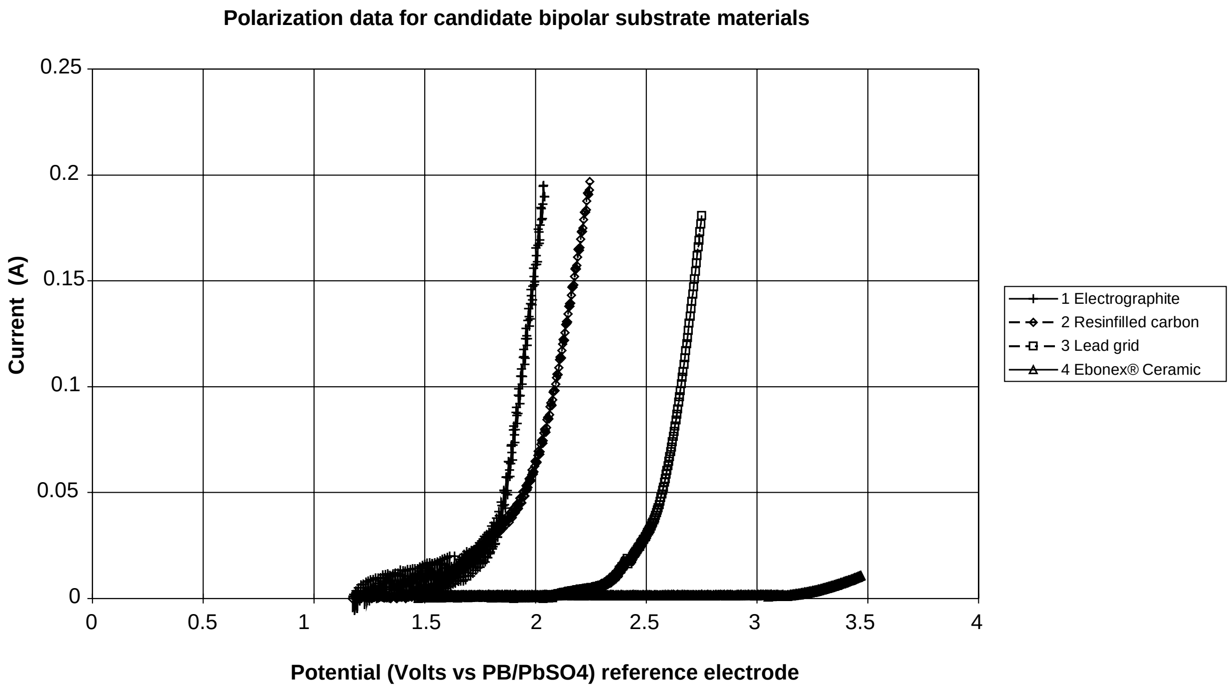

Fig. 3. Electrochemical operating range for carbon, graphite and Ebonex® composite electrodes in comparison to lead metal. The lower oxidation potentials of the carbonaceous materials indicate their unsuitability as bipolar substrate materials for long term operation.

2.3. Electrochemical properties of Ebonex® bipolar electrodes

The wide operating potential range of Ebonex® ceramic indicated in Table 1 means that the Ebonex® material operates as an inert conductive substrate and does not interfere with electrochemical reactions at the negative or positive active masses in a lead-acid battery. In comparison carbon based composite bipolar substrate materials have a narrower operating range, see Fig. 3, and will interfere with reactions occurring at the positive plate leading to enhanced oxygen evolution and carbon oxidation ultimately leading to failure of the plate if wetted by sulphuric acid. In comparison to carbonaceous materials Ebonex® ceramic is intrinsically inert in the operating environment of a lead-acid battery and does not require a protective layer of lead to prevent corrosion but an interlayer of thin lead foil between the active paste and the Ebonex® substrate has been found to be advantageous in providing good paste adhesion.

Exhaustive tests have also been carried out on a wide range of polymer binder types to identify those having excellent adhesion to the Ebonex® particles to render the bipolar plates non-porous as well as having resistance to sulphuric acid over many years.

2.4. Battery performance

The Ebonex® bipolar plates are assembled into batteries by stacking a number of bipolar plates between two end monopoles, e.g. 5, 17 and 23 bipoles are required to fabricate a 12, 36 and 48 V battery, respectively. Figs. 4 and 5 show photographs of a 4 V laboratory test cell and a valve regulated 12 V Ebonex® battery respectively.

No separate intercell connections (top lead) between the bipolar plates are required. The current flow through the battery is orthogonal and so the paste is worked uniformly across the active plate areas resulting in improved paste utilisation and efficiency. The improved utilisation efficiency of

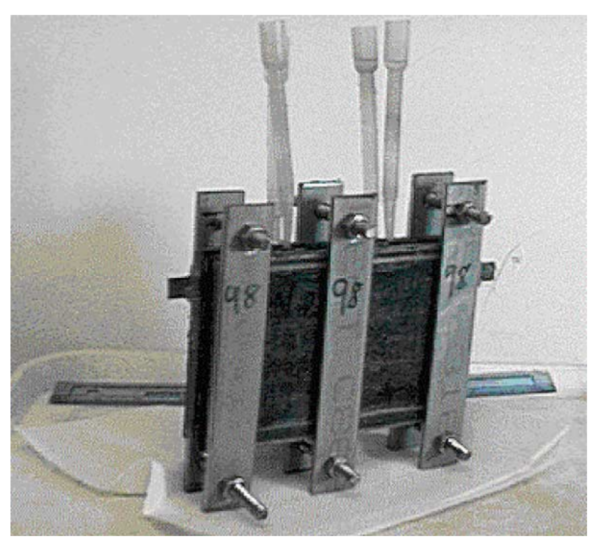

Fig. 4. A typical 4 V laboratory test battery.

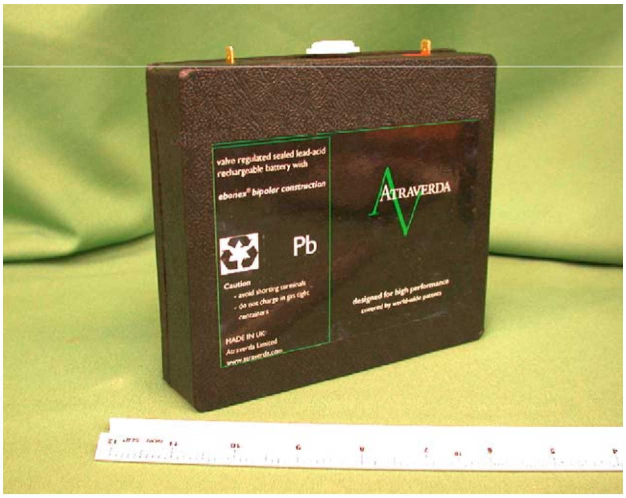

Fig. 5. A valve regulated 12 V Ebonex® bipolar lead-acid battery.

bipolar designs for the positive active mass is shown in Fig. 6 which is a graph of utilisation efficiency against discharge rate for a 4 V, 7 Ah Ebonex® bipolar lead-acid battery and a 6 V, 1.2 Ah battery of conventional monopolar design. Thus, a nearly three-fold improvement is observed for the bipolar design at the 20 h rate.

Typical data on discharge capacity as a function of discharge rate are shown on the Peukert plot in Fig. 7.

The reduction in weight due to removal of the top lead and use of a lighter substrate as well as improvements due to enhanced utilisation efficiency means that the figures of merit for Ebonex® bipolar lead-acid batteries are in excess of those for conventional monopolar designs, see Table 2.

A design study for a 36/42 V automotive battery [17] indicates that the weight and volume of a bipolar battery (20 Ah, 5 h rate, 9 kW) based on Ebonex® composite elec-

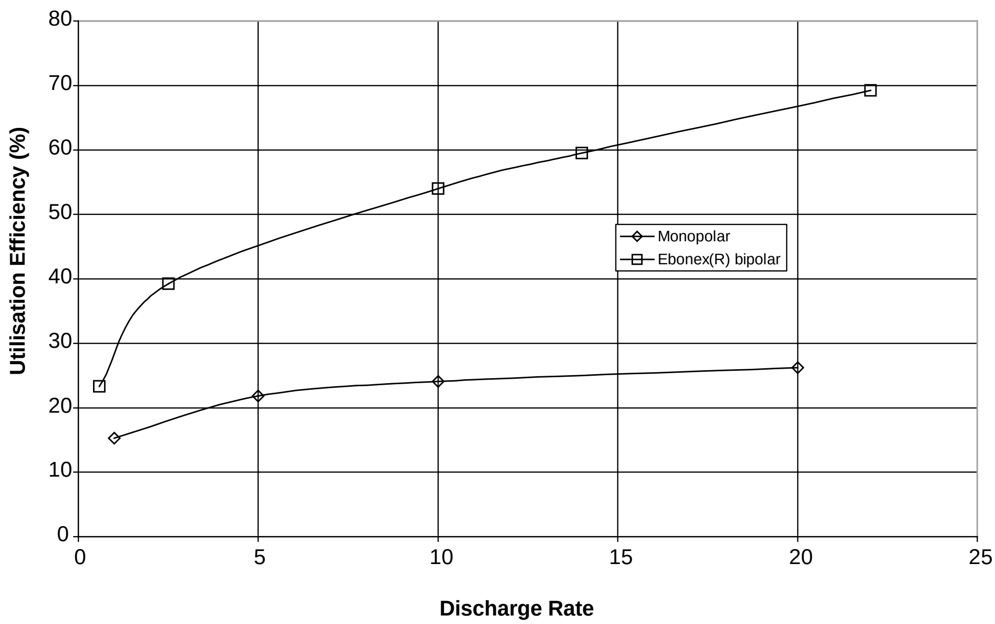

Fig. 6. The positive active mass (PAM) utilisation efficiency for Ebonex® bipolar and conventional lead-acid battery designs.

Fig. 8. Size comparison of conventional and Ebonex® bipolar 36 V lead-acid batteries.

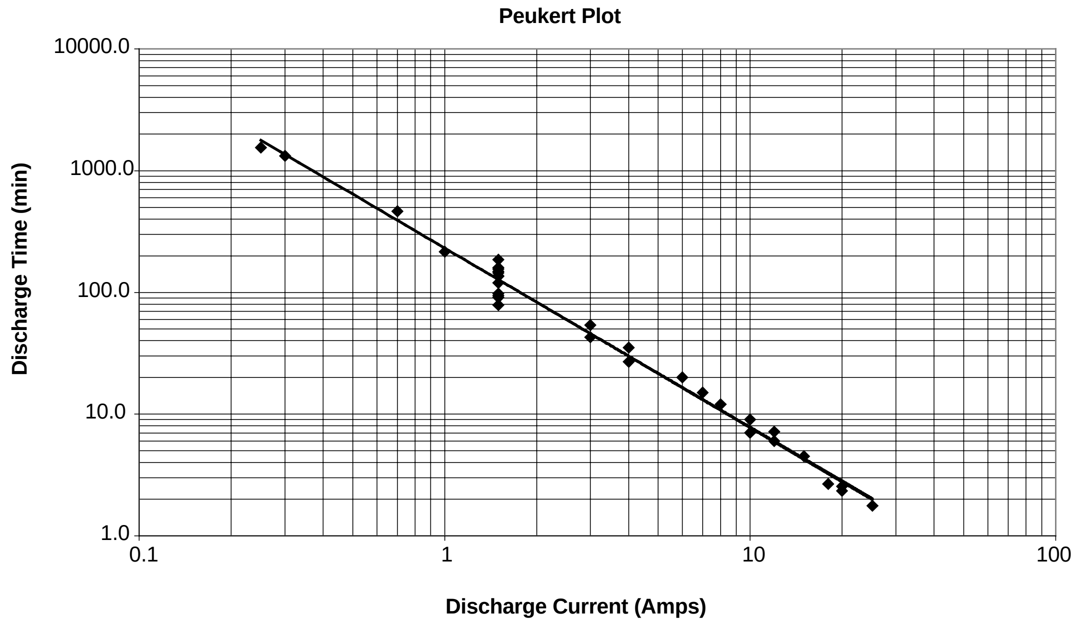

Fig. 7. Peukert plot–graph of discharge duration against discharge current for 0.25–25 A for a 7 Ah Ebonex® composite bipolar battery.

Table 2
Operating data for lead-acid monopolar and bipolar designs

Measure	Conventional monopolar	Ebonex® bipolar
$Wh\,kg^{-1}$	25–35	40–60
$Wh\,dm^{-3}$	50–60	100–120
$W\,kg^{-1}$	80–150	250–320
$W\,dm^{-3}$	300–400	700–1000

trodes would weigh 14 kg and occupy a volume of less than 7 dm^3. In comparison conventional 36/42 V lead-acid designs are known to weigh 24–28 kg and have a volume of 9–11 dm^3 [18]. The form of the Ebonex® bipolar battery is different to a conventional battery as shown in Fig. 8 which shows views of mock-ups of 36 V versions of the Ebonex® battery and a conventional design containing lead grids based on data from Nelson [18]. The flatter shape and lighter weight of the bipolar battery makes it more amenable to inclusion within passenger compartments, luggage spaces, in the recess under the spare wheel, etc. in motor vehicles. The shape is amenable to drop in/pull-out attaché case designs.

A range of durability tests including deep discharge cycle life, accelerated overcharge simulation trials and porosity tests have been carried out on Ebonex® substrates and batteries. Cycle life testing (2 h, 100% discharge to 1.75 V) is on-going and is currently in excess of 300 cycles. 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 [19]. Durability tests on the Ebonex® ceramic bipolar are on-going and show no sign of degradation leading to porosity and self-discharge after over 15,000 h.

3. Summary

The advantages of bipolar batteries over conventional monopolar designs have been discussed. The use of Ebonex® bipolar substrates has been demonstrated to fulfil the advantages of bipolar lead-acid batteries in terms of specific energy and power. The combination of weight savings (by substitution and reduction in the quantities of lead required) and increased active-mass utilisation efficiency (due to the more uniform current flow possible in a bipolar design) indicate that for a 36 V automotive design, weight and volume savings of around 40% and over 30%, respectively, are expected. In addition, the intrinsic inertness and resistance to oxidation demonstrated by the Ebonex® composite material allow for designs having lifetimes of at least equal to those of conventional batteries containing lead grids.

The inertness and durability demonstrated by Ebonex® composite electrodes indicate that their use as bipolar substrate materials will provide light-weight, long-lasting lead-acid batteries suitable for use in automotive, standby and power tool applications.

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