# Characterisation of defects observed within the positive grid corrosion layer of the valve regulated lead/acid battery

R.J. Ball[a,*], R. Evans[b], M. Deven[c], R. Stevens[a]

[a]Department of Engineering and Applied Science, University of Bath, Bath BA2 7AY, UK
[b]Invensys, Westinghouse site, Chippenham, Wiltshire SN15 1SJ, UK
[c]University of Warwick Science Park, Buehler/Krautkramer, Nillburn Hill Road, Coventry CV4 7HS, UK

## Abstract

An investigation into the failure of a series of cycled 40 Ah valve regulated lead acid batteries, identified a number of different defect types present in the corrosion layer. In this paper, a detailed description of the materialographic preparation method used to produce cross-sections of the corrosion layer is given. Each of the defect types identified is described and illustrated in an appropriate micrograph. Variations between the defect types suggest that there is more than one mechanism for defect initiation and growth. Possible mechanisms for sources of the defects and their subsequent growth are proposed. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* VRLA; Corrosion layer

## 1. Introduction

During operation of a valve regulated lead acid battery a corrosion layer forms on the surface of the positive grid [1]. This layer acts as an interface between the current collecting grid and current producing positive active material. Characteristics of the corrosion layer are important in determining battery efficiency, as electrons must flow across the layer during battery operation [2].

Corrosion layer properties such as structure and composition have an influence on the flow of electrons and, therefore, efficiency of battery operation [3]. An additional factor that can affect performance by altering the corrosion layer properties is the formation of defects within the corrosion layer. The defects observed are normally in the form of cracks and pores, which have two main effects. Firstly, they act to reduce the effective electrical conductivity of the layer, as electrons cannot flow across cracks, and secondly, to increase diffusion rates of gases, such as oxygen, and electrolyte, through the corrosion layer by provision of an easy pathway.

During examination of positive grid corrosion layers from valve regulated lead/acid batteries a number of different types of defect were observed. A summary of the defect types found is presented in this paper.

## 2. Experimental methods

### 2.1. Production of test batteries

The batteries examined in this study were all constructed using identical materials and the same design. A 40 A, 12 V monobloc unit was used. Positive electrodes were produced using a standard grey oxide positive paste. The negative paste mix was also manufactured from grey oxide. Positive and negative grids were produced from pure lead strip. Glass microfibre separators were used in the design, 70% coarse, 30% fine fibre.

### 2.2. Battery cycling

Cycling was carried out automatically using Digitron charging units. Each cycle consisted of a constant current discharge at 7.05 A to 10.2 V followed by a constant voltage recharge at 14.7 V for 16 h. This was repeated until the capacity after charging was <80% of the starting capacity. The cell that showed the greatest voltage difference between end of discharge and end of charge was examined as this cell exhibited the thickest positive grid corrosion layer.

### 2.3. Preparation of corrosion layers for microscopy

The corrosion layer structure on the positive grid bars of a battery can provide important information as to why a

* Corresponding author. Tel.: +44-1225-826826;
fax: +44-1225-826098.
*E-mail address*: r.j.ball@bath.ac.uk (R.J. Ball).

battery cell has failed. An effective way to study these features is to examine a polished cross section using optical microscopy.

Dried battery plates consist of a soft lead grid, which has very low stiffness, surrounded by friable, brittle active material. When handling plates great care must be taken to avoid unnecessary bending as this can lead to the formation of additional cracks in the active material. After removal of the plates from the battery they were washed in distilled water to remove acid and dried in a vacuum oven for approximately 24 h. In order to minimise the risk of causing further damage to the plates after drying, they were quickly stabilised by encapsulation in resin. This was achieved by laying the plates horizontally, jacked up on small plastic blocks approximately 3 mm high, within a specially made latex mould. Resin was then poured into the mould to a height of approximately 7 mm, thus, surrounding each side of the plate with several millimetres of resin.

In order to ensure consistency of results, cross-sections of the electrodes were always taken from the middle position of the plate. However, exceptions to this procedure were made if this area contained cracked active material caused by post tear down damage. Samples were normally taken by cutting a strip of electrode approximately 15 mm in width from the centre of the plate. This strip was then cut into smaller sections and remounted in smaller cylindrical moulds suitable for polishing.

## 2.4. Polishing procedure

The procedure used for polishing the sections consisted of a number of different stages. Although some polishing was done automatically, it was found that the best results were achieved by hand. A common problem encountered when polishing a multi-phase material, such as a battery plate, is the risk of a particle of a hard phase such as the oxide, becoming dislodged and consequently, damaging the softer lead phase. Little can be done to prevent this. However, damage can be minimised in two ways. Firstly, by having a small sample of electrode and secondly, by holding the sample so that its length is in the same orientation as that of the polishing wheel. Due to the variation in properties, no two samples behaved in the same way when being polished. For this reason, it was necessary to periodically check the sample at the end of each stage of preparation using light microscopy to ensure the next stage could be started without having induced extrinsic damage.

### 2.4.1. Planar grinding stage

Samples were initially ground using silicon carbide paper. However, a problem with this approach occurs when small particles of carbide break off or become dislodged. If this occurs, particles often become embedded in the soft lead grid. This proved to be unavoidable. However, the severity and quantity of embedded carbide could be reduced in two ways. Firstly, a bar of steel was rubbed against each fresh sheet of silicon carbide paper, with a generous amount of water flowing, for a few seconds before the sample was ground. The purpose of this was to remove any loose carbide particles and to break off and remove any sharp spikes of carbide that were likely to become attached to and break inside the lead. Secondly, a layer of candle wax was applied to the paper. This acted, as a soft medium to which any loose particle would become attached, rather than become embedded in the lead. A series of different grades of silicon carbide material were used ranging from 300 to 1200 grit and a platen speed of 150 rpm was used. Water was used as a lubricant and only a light pressure was applied when grinding the sample. The papers were replaced after 30 s to 1 min of grinding.

### 2.4.2. Polishing stage

The polishing stages of preparation were conducted using a Texmet polishing cloth loaded with alumina suspension. A platen speed of 100 rpm was used and normally a good sample finish was achieved after polishing with 5 and 0.3 μm alumina. Polishing was again conducted by hand and periodic checks of the surface using light microscopy were required to identify the point at which the next stage of the sample preparation route could be initiated.

### 2.4.3. Finishing stage

The finishing stage was conducted using a Buehler Vibromet 2. Buehler Masterpolish was used as a polishing media on a Texmet cloth. A polishing time of 30 min was found to produce the best results.

## 2.5. Light microscopy

Samples were examined using a ZEISS ICM405 optical microscope. When examining the polished samples care must be taken in the interpretation of the image, especially at the interface between the lead and positive active material. Even after vibratory polishing slight differences in height between the lead and corrosion layer were noticeable. However, at higher magnifications, this effect is less obvious and a shadowing effect is often observed, which could easily be mistaken as an interface or feature of the sample. Another phenomenon was reaction of polishing media with the lead grid. The most misleading effect was a reaction of the polishing media with the lead grid adjacent to the corrosion layer. On certain samples this reaction layer looked convincingly like an additional phase of the grid corrosion layer and to avoid confusion is labelled accordingly in all figures.

## 3. Results and discussion

In general, the corrosion layers in batteries that survived >90 cycles to failure were found to exhibit features which did not appear as frequently in batteries that had failed earlier, i.e. <90 cycles. The most prominent of these were
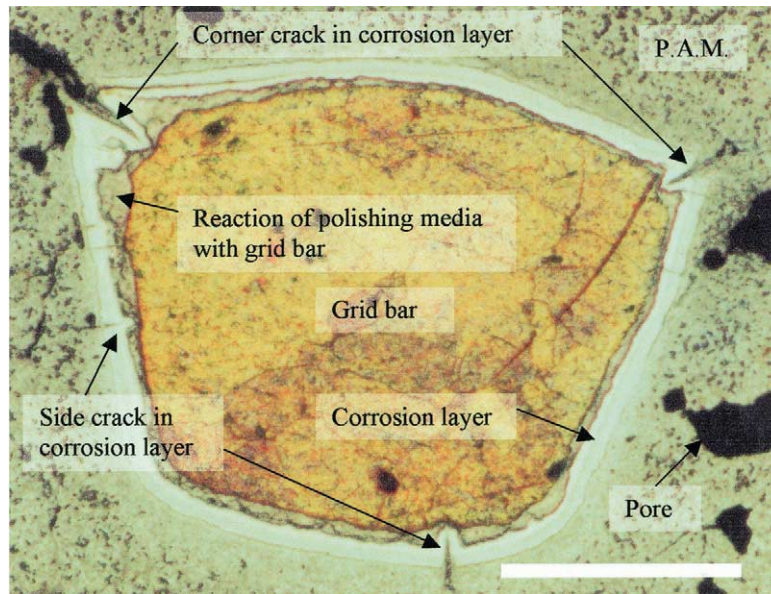
Fig. 1. Positive grid bar showing corrosion layer and cracks (scale bar: 500 μm).

cracks, most commonly occurring adjacent to grid-bar corners although a number were identified on the edge of the bar. A typical grid bar cross-section exhibiting these features is shown in Fig. 1. The corrosion layer extends around the whole perimeter of the bar. Pores are visible at a number of locations within the positive active material. There is no evidence that the presence of a pore promotes or reduces the probability of a defect occurring in the adjacent region of corrosion layer.

A higher magnification image of a crack observed in the corrosion layer on the side of a grid bar is given in Fig. 2. The layer consists of two sub-layers separated by an internal boundary. Cracking has occurred through both

layers and a short distance into the underlying lead grid. A reaction between the polishing media and lead grid adjacent to the corrosion layer produces an additional feature that should not be confused with the corrosion layer of intermediate stoichiometry produced during battery operation. Positive active material is visible on both sides of the crack walls as far as the crack tip. This is likely to have formed by the movement of small particles of lead oxide and/or lead sulphate into the crack that subsequently reacted to form a rigid, porous active material. Movement of the electrolyte during overcharging, when gases are produced, would promote the movement of particles into cracks. The crack centre contains the resin used for sample
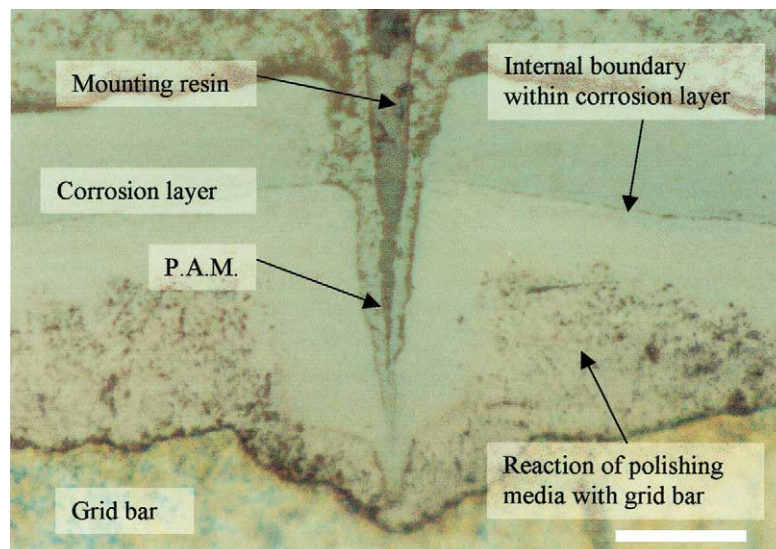


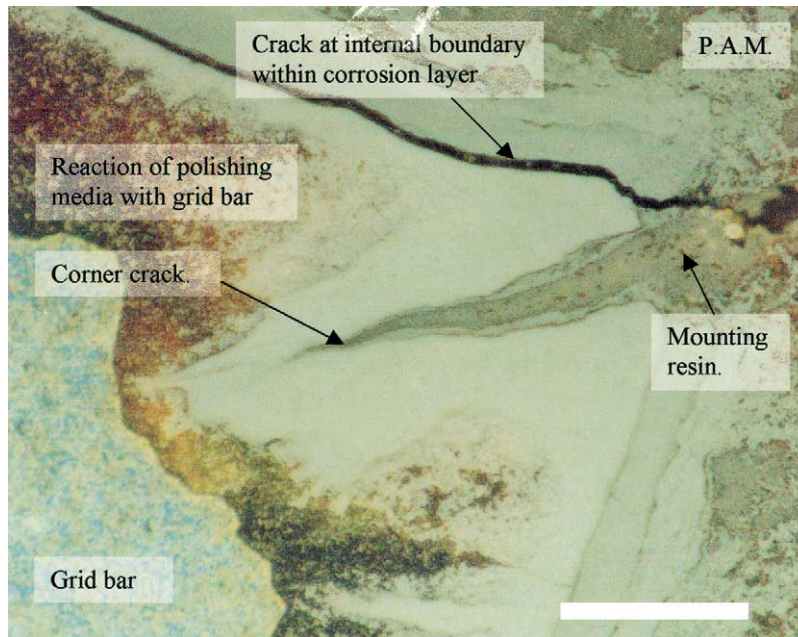Fig. 2. Typical crack observed in corrosion layer (scale bar: 50 μm).

Fig. 3. Crack observed on corner of grid bar (scale bar: 50 µm).

mounting during polishing, suggesting that during battery operation this region could well have been filled with either electrolyte or gas.

Closer examination of the corrosion layer revealed the presence of cracks at the internal boundary within the corrosion layer, Fig. 3. Formation of a crack in this location suggests a difference in properties of these layers and indicates that the bond between them is not as strong as either of the individual layers.

Smaller fissure cracks were also observed in the lower corrosion layer, Fig. 4. They appear to be propagating in an outward direction, since cracks only grow under a tensile stress. The formation of cracks such as these could be a result of either (i) internal stress within the layer, caused by geometrical effects or (ii) stress caused by gas pressure produced during battery operation, especially during over-charging.

A number of smaller cracks and oxide fingers penetrating the grid were observed on the sides of some bars, shown in Fig. 5. Examination of the oxide finger at higher magnification, Fig. 6, revealed a small crack or fissure running down the centre. Whether this is a genuine crack, or the point at
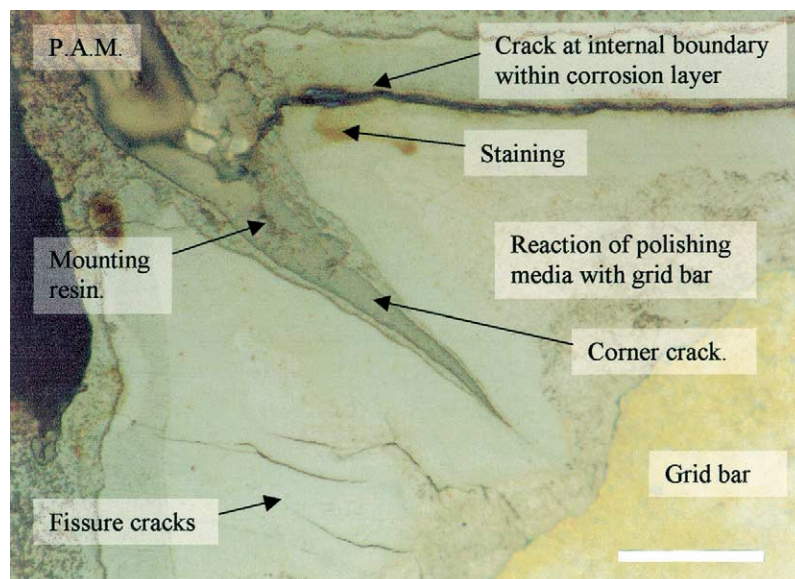


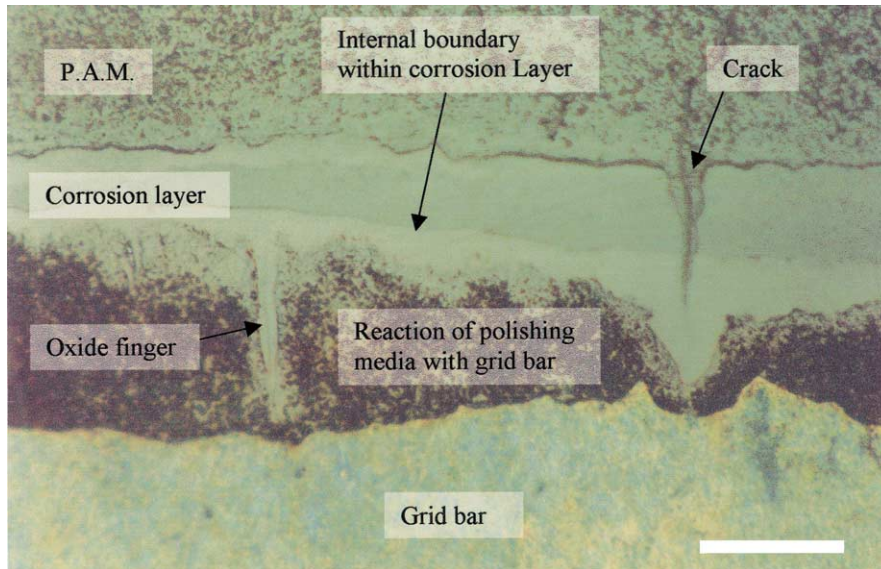Fig. 4. Fissures within corrosion layer adjacent to corner crack (scale bar: 50 µm).

Fig. 5. Crack observed on edge of grid bar (scale bar: 50 µm).

which the layers growing out from each side of the crack join up is unknown. Formation of a finger such as this could be an initial stage in the formation of the larger cracks discussed previously. The crack featured on the right hand side of the photograph appears to be growing in an inward direction, suggesting there is more than one mechanism for crack initiation and growth.

Positive active material on the inner surfaces of a crack will affect the propagation rate. When positive active material is discharged the lead dioxide is reduced to form lead sulphate with a consequential increase in volume. This change will produce a force perpendicular to the crack direction effectively pushing the crack walls outwards and increasing the stress concentration around the crack tip, therefore, promoting propagation. It should also be noted that cracks provide effective routes for the transport of oxygen to the grid/corrosion layer interface where the brittle oxide, which is prone to cracking, can be formed.

The probability of defects initiating within the battery can be reduced by taking measures such as (i) designing grids to reduce stresses in the corrosion layer caused by geometrical factors such as sharp corners, and (ii) keeping the battery
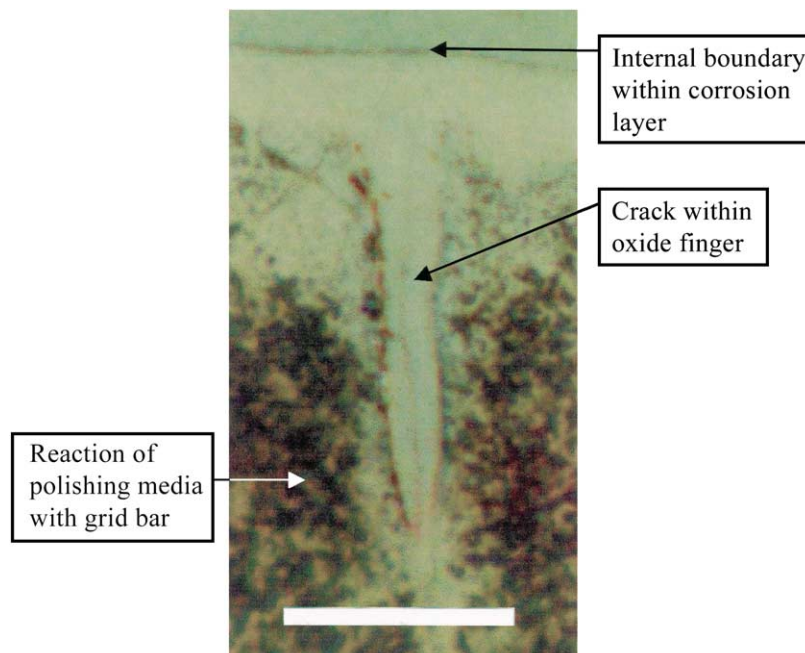


Fig. 6. High magnification of oxide finger (scale bar: 50 µm).

well ventilated to reduce heat build-up. Defects such as cracking between different phases of the corrosion layer can only be avoided by changing the nature of corrosion layer structure. This is a more difficult problem to address as structure is influenced by the reaction changes taking place in the positive active material, the composition and micro-structure of the grid alloy and the battery operating conditions.

## 4. Conclusions

Examination of the corrosion layer has allowed a number of different types of defect to be identified. Principally these were

- cracking adjacent to grid bar corners;
- internal boundary cracks within the corrosion layer;
- small fissure cracks;
- small penetrating cracks and oxide fingers.

The variation in different types of defect suggests there is more than one mechanism for defect initiation and growth.

Defects will often occur due to stresses within the corrosion layer. These can arise for the following reasons:

- thermal cycling of the oxide due to changing heat generation rates at different periods of the discharge/charge cycle;
- geometrical (volume) changes associated with the conversion of lead oxide to sulphate during cycling;
- oxygen gas evolved during overcharging pressurising and escaping through the oxide corrosion layer.

## References

[1] D.A.J. Rand, L.S. Holden, G.J. May, R.H. Newman, K. Peters, Valve-regulated lead/acid batteries, J. Power Sources 59 (1996) 191–197.
[2] 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.
[3] A.F. Hollenkamp, K.K. Constanti, 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.