

Short Communication

The use of scanning photocurrent imaging to study the distribution of lead monoxide in corrosion layers on lead/acid battery grids

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Abstract

Lead/acid batteries with lead-calcium alloy positive grids can exhibit early loss of capacity when subjected to deep-discharge cycling. This has been attributed to the development of a high-resistance layer of α -PbO that separates the grid metal from the active material. Hitherto, direct evidence for such a layer has been difficult to obtain because even minute quantities can exert a potent effect on plate performance. A novel method for studying the distribution of α -PbO via its laser-stimulated photocurrent is presented. In the type of experiment reported, the method is selective for α -PbO since other phases likely to be present in, or on, the grid alloy do not give rise to photocurrents.

Introduction

The introduction of 'maintenance-free' lead/acid batteries (pasted-plate types), which have made an enormous commercial impact in recent years, has been made possible by the use of antimony-free alloys for the fabrication of positive grids. Traditional alloys have used high contents of antimony (3 to 6 wt.%) and are prone to gassing and water loss. With these alloys, antimony leaches from the positive plate during charge/discharge cycling and migrates to the negative, where it forms a couple with the lead active material. This antimony transport results in a lowering of the hydrogen overpotential and, thereby, promotes gassing and self discharge of the negative plate. Antimony-free alloys, e.g., lead-(~0.1 wt.%)calcium, invest the grid metal with a high hydrogen overpotential and thus suppress hydrogen evolution at the negative electrode. Although maintenance-free batteries exploiting this principle have been extremely successful for standby-power applications, it has not been possible to extend their use to duties that require repeated deep discharges, e.g., motive-power applications. Under

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such service, the batteries exhibit an early and rapid walkdown in deep discharge capacity.

The premature capacity loss of lead-calcium-based batteries has been attributed [1-14] to the development of a high-resistance corrosion layer close to the grid/active-material interface (for recent reviews, see refs. 15 and 16). Evidence has been presented [17] of gross differences in the microstructure of the corrosion layers formed on lead-calcium alloys, as opposed to those produced on conventional alloys. Furthermore, many studies [3, 5, 7, 11, 13, 14] have indicated that an uninterrupted corrosion layer of tetragonal lead monoxide (α -PbO) plays an important role. Nevertheless, exact details of the distribution of this phase have been difficult to obtain either by conventional microscopy (optical or electron) or by X-ray diffraction methods, due both to the fine scale at which the α -PbO is present and to the similarity between the contrast afforded by the several phases involved in the corrosion process.

The present paper describes a new technique which is uniquely suited to the study of the formation and distribution of the α -PbO layer.

Scanning laser microscopy

The principle underlying the function of scanning laser microscopy involves the measurement of local photocurrents produced in response to a perturbation on a solid electrode phase by laser illumination. Such measurements can be made through an aqueous electrolyte. When incident photons of sufficient energy are directed on to the surface of a semiconductor, they will be absorbed and will produce an electron/hole pair in the conduction and valence bands, respectively. Under the influence of the electric field present at the surface, the carriers become separated. In the case of a p-type semiconductor, for example, the electrons move to the surface and the holes migrate into the bulk (see Fig. 1). If the electrons have sufficient energy to react with the oxidized form of a redox couple in the electrolyte phase, then an external wire connecting the bulk semiconductor to the electrolyte phase will pass a

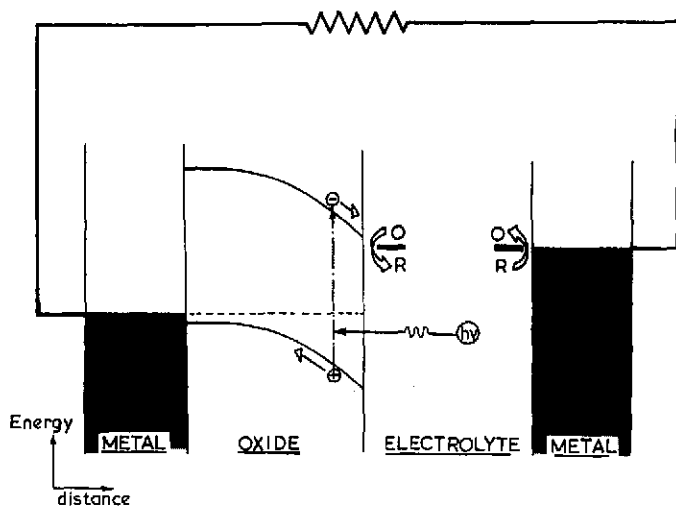


Fig. 1. Schematic of generation of photocurrent at a semiconducting-oxide/electrolyte interface.

current. This is the photocurrent. The value of the photocurrent, and its dependence on parameters such as wavelength and bias potential, reflect the intrinsic features of the semiconductor/electrolyte interface. It has already been shown [18–20] that, under an appropriate bias potential, a photocurrent can be obtained from α -PbO.

The corrosion layers formed on lead alloys are particularly favourable for study by scanning laser microscopy since only the α -PbO phase produces an appreciable photocurrent under normal experimental conditions. The light source can be focused on a small surface area of the solid surface and rastered across the specimen to produce an image of the distribution of the phase by a mechanism similar to the function of a scanning electron microscope. Images can be recorded through a layer of sulfuric acid electrolyte under any chosen regime of applied potential.

Experimental procedure and results

Lead-calcium grids were recovered from lead/acid cells after cycling to the point of large-scale loss in capacity. Specimens of grid were cast in epoxy resin and polished to reveal a cross section through the alloy and the accompanying corrosion layer. Scanning electron microscopy showed that, as expected, the grid had undergone extensive attack and that the resulting corrosion layer was extensively defective.

Photocurrent images were obtained by direct scanning. This is a real time method in which the total signal (dark current and photocurrent) is measured directly into the image processor to provide the image. The dark current is treated as a constant background signal. Scanning can be achieved at rates upto 5 ms per line; this provides an image of 500 lines every couple of seconds, or so. Any time-variant effects that are comparable with the line scan-rate appear as streaking across the image and are aligned with the direction of the scan. This phenomenon provides extra information.

The sample was immersed in 1 M H_2SO_4 and scanned twice between -1.1 and $+0.8$ V versus Hg/Hg₂SO₄, 1 M H_2SO_4 at 20 mV s⁻¹. Note, all potentials are reported with respect to this reference electrode. A typical voltammogram is shown in Fig. 2; the characteristics of the curve are similar to those observed for lead in sulfuric acid [6, 21, 22]. The sample was held at a potential of $+0.4$ V, under which conditions a layer of lead sulfate will be present on the alloy surface. Illumination with a scanning red laser ($\lambda = 632.8$ nm) yielded a spatial variation of photocurrent. The latter is reproduced as a grey-scale image in Fig. 3. The scale corresponds to a photocurrent range from 0 nA (black) through to 50 nA (white). The illumination intensity was measured with a calibrated photodiode. The theoretical photocurrent, assuming one electron generated per incident photon, is 780 μA for full-beam illumination. The photocurrent conversion efficiency is therefore small, i.e., 0 to 6×10^{-5} over the contrast range. This implies that either the photoactive layer is extremely thin (and, therefore, it absorbs only a small fraction of the incident light) or there is considerable recombination of the electron/hole pairs.

Similar images were obtained using the blue laser line ($\lambda = 442$ nm) at 0.433 V. In all cases, the distribution of photocurrent across the specimen was far from uniform but significant levels appeared in the centre of the specimen, i.e., directly on the grid alloy. This indicates that α -PbO, which is photoactive, has deposited on the exposed metal at the potentials used in the various experiments. It should be noted that the lead sulfate, which overlies the α -PbO, is not photoactive and is transparent at the wavelength of the illumination used in these experiments.

Clearly, in order to monitor the distribution of α -PbO formed on a grid during operation within a battery it is necessary to select an appropriate potential range to

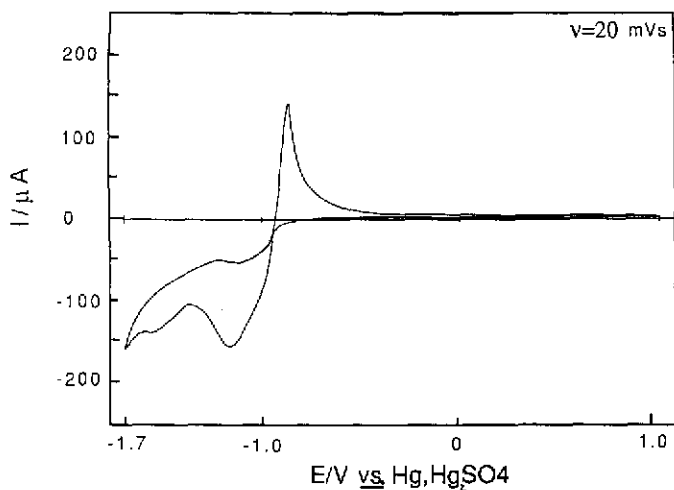


Fig. 2. Cyclic voltammogram for lead-calcium sample in 1 M H_2SO_4 . Electrode area $\sim 2.1 \times 10^{-3} \text{ cm}^2$; scan rate 20 mV s^{-1} .

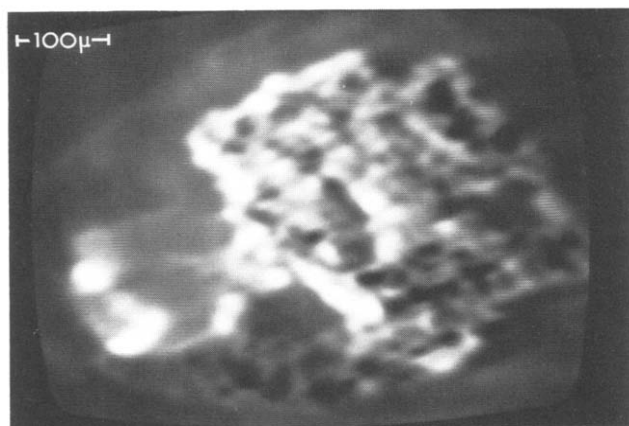


Fig. 3. Photocurrent image for lead-calcium grid polarized at $+0.4 \text{ V}$. Illumination provided by He/Ne source ($\lambda = 632.8 \text{ nm}$) at 1 mW intensity. Images obtained at 22.5 ms per line: raster direction left to right across image. Black contrast represents zero photocurrent, while contrast represents anodic photocurrent; scale range spans 50 nA . The black zone at centre-left represents a void within the alloy.

prevent the further growth of $\alpha\text{-PbO}$ during scanning-laser studies. Nevertheless, the above results indicate that it is possible to study, in real time, the formation of $\alpha\text{-PbO}$ on the metal surface.

Conclusions

In summary, scanning photocurrent imaging can be used for the specific mapping of $\alpha\text{-PbO}$ in two modes:

(1) *retrospective*—after α -PbO has been generated on a grid in normal battery service, the phase can be viewed by preparing a transverse section of the corroded specimen;

(ii) *real time*—by direct imaging of the development of α -PbO on battery grid materials.

Further improvements in image quality may be achievable through the use of a 'lock-in' method instead of the 'direct scanned' mode used here. The 'lock-in' method uses chopped illumination (usually at ~ 2 kHz) in conjunction with a slow-line scan of the order of 2 s. The signal that is imaged is an average representing only photocurrent contributions and all transient information is lost. An image is collected every 20 min, or so.

The 'direct scanned' mode tends to smear the data due to the superimposition of the transient effect arising from what can be effectively viewed as a pulse of illumination moving across the surface. A sharp rise in photocurrent, as expected from a thin film of photoactive material between the corrosion layer and the lead grid, may be better resolved by using the steady-state 'lock in' approach.

The unique capability of the scanning laser to determine the distribution of α -PbO in battery grids promises valuable new information on the mechanism of capacity loss with lead-calcium alloys, and may even promote the development of methods to overcome this serious, performance-limiting effect.

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