Journal of Power Sources, *19* (1987) 1 - 6

THE APPLICATION OF PHOTOACOUSTIC SPECTROPHOTOMETRY (PAS) TO THE STUDY OF POSITIVE PLATES IN LEAD–ACID BATTERIES

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(Received April 24, 1986)

Summary

A preliminary investigation has been undertaken into the application of photoacoustic spectrophotometry (PAS) in the characterisation of materials in the lead–acid battery system. In particular, studies have been carried out on samples of lead dioxide taken from positive battery plates.

It has been shown that the photoacoustic response depends on the history of the samples. In particular, samples which have undergone many discharge–charge cycles show an overall gain in response together with a change in the spectrum. Samples which have undergone a small number of charge–discharge cycles show an increased PAS signal which correlates with the amount of PbO_2 in the samples.

Introduction

The study of the composition of positive-plate material has been of interest for many years. A wide variety of techniques has been used including wet chemical analysis, electrical measurements and, more recently, X-ray diffraction [1]. We have been interested in the use of PAS for surface analysis of different materials [2, 3] In this short note we present some results on the positive plates of lead–acid batteries.

Although PAS is a very old technique it has only been utilised as an analytical tool in the last decade A description of the technique and the theory has been given by Rosencwaig and Gersho [4].

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0378-7753/87/$3 50

In brief, the technique is as follows a sample, which can be in almost any form, *i e* , powder, liquid, solid or gell, is illuminated with chopped monochromatic light in an air-tight chamber If this light is not converted into photochemical energy or luminescence, it is degraded to heat This heat then flows to the surface of the sample where it heats the gas immediately above it As the heating following the illumination is pulsed, it gives rise to an acoustic wave which can then be monitored by a microphone inserted into the sample chamber This signal is then amplified and detected with a lock-in voltmeter A scan of the signal *versus* wavelength gives an uncorrected spectrum which will be dominated by the output of the light source (in this case a xenon arc) and the response function of the monochromator The true spectrum can be found by dividing the signal thus obtained by that obtained using carbon black, as this gives 100% light absorption

The penetration of the thermal wave into the sample is governed by the modulation frequency of the light Low modulation frequencies give deepest penetration so that it is possible to carry out depth profile studies

Experimental

The first set of measurements was made on two cell recombination batteries intended for a miner's cap lamp (MCL). These were cycled to 50% depth of discharge, samples being taken immediately after jar formation and after 50 and 400 cycles PAS spectra were obtained both on powdered samples and solid samples The main effects are that as the number of cycles increases, the photoacoustic response, *i e* , the light absorption, also increases In addition there are some changes in the spectra, see Figs 1 - 3

The second set of measurements was made on plates obtained from a deep cycling experiment based on an automotive plate design The plates were jar formed and cycled to 100% depth of discharge (1 75 V per cell) Samples were taken after formation and after 1, 3, 5, 7 and 10 cycles The samples were ground and sieved prior to the measurements All spectra were obtained at least twice and a high level of reproducibility was demonstrated With these samples the PAS signal increases with the number of cycles, see Fig. 4. This increase, however, is not strictly monotonic with cycle number, see Fig 5 When these plates were analysed for PbO_2 content using standard chemical analysis, it was found that a monotonic correlation was observed between PAS response and PbO_2 content, see Fig 6 and Table 1.

It is clear that the overall increase in photoacoustic response is related to the amount of PbO_2 in the samples, which is only an indirect measure of the number of cycles In the case of the MCL samples we believe that the changes in spectral shape which occur might relate to the relative amounts of α and β forms of PbO_2

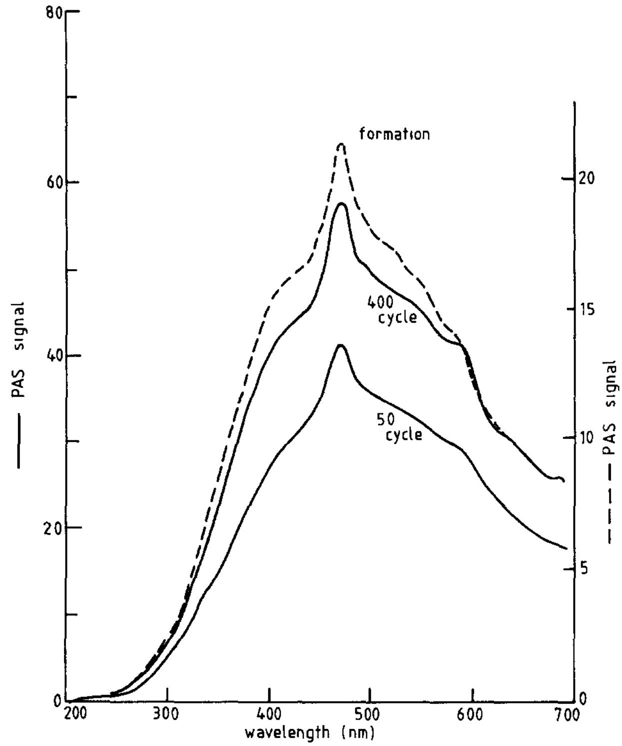

Fig. 1 PAS spectra of MCL batteries positive plate material. (a) Formation, (b) 50 cycles, (c) 400 cycles These are uncorrected spectra of solid material

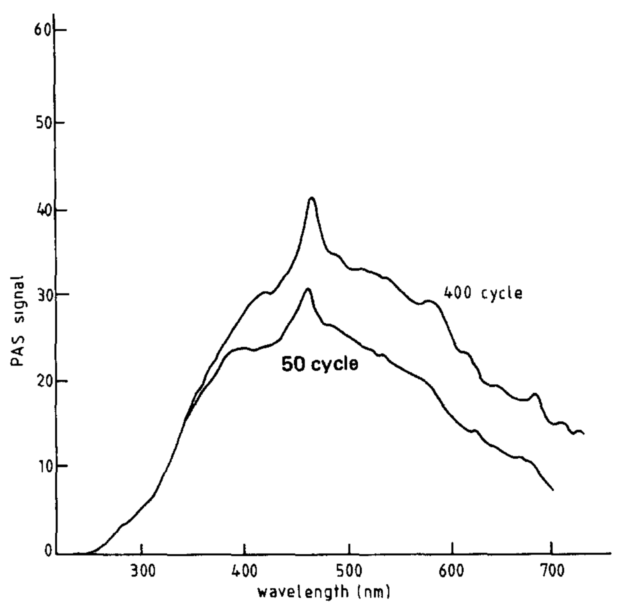

Fig 2 PAS spectra of MCL batteries positive plate material (a) 50 cycles, (b) 400 cyles Powdered sample Uncorrected spectra

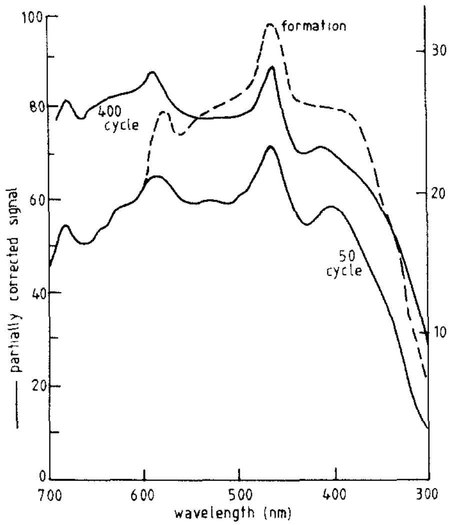

Fig 3 Partially corrected PAS spectrum of MCL batteries positive plate material in solid form

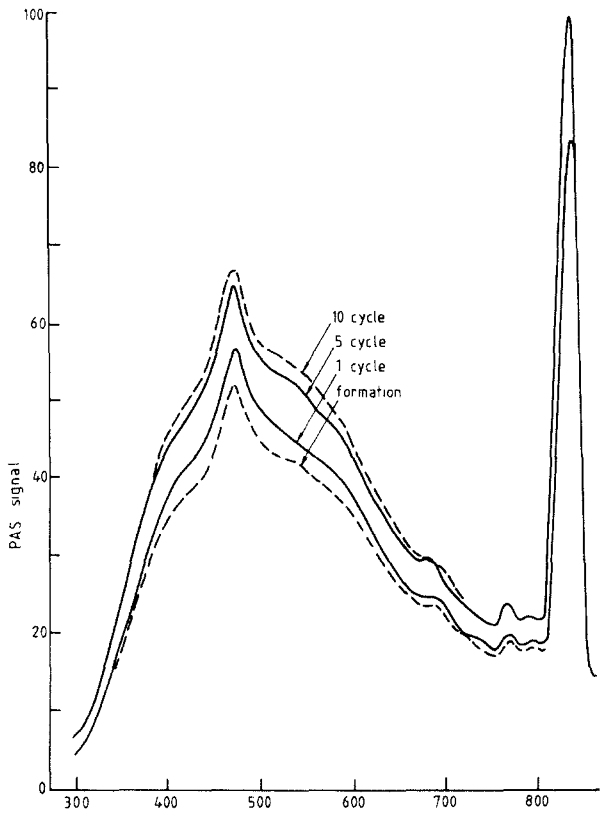

Fig 4 PAS spectra of automotive positive plate material obtained at different cycles These are uncorrected spectra

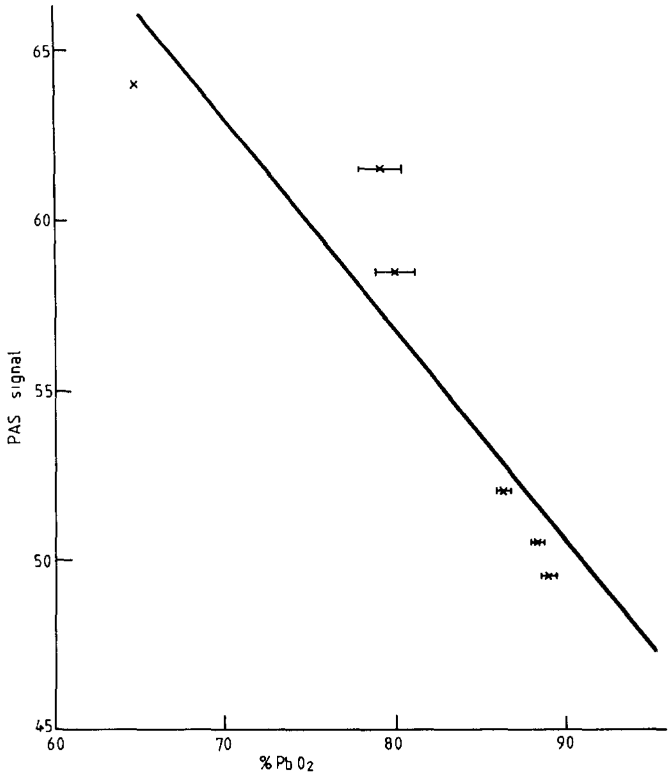

Fig 5 Plot of PAS response at 575 nm *vs* %PbO_2 Data for automotive positive plates

TABLE 1

Photoacoustic response of lead dioxide samples from positive plates of lead–acid battery

Sample	PbO_2 (%)	Photoacoustic peak heights*
Formation	79 1 (±0 6)	61 5
1 cycle	79 9 (±0 6)	58 5
3 cycles	64 7**	64 0
5 cycles	86 3 (±0 2)	52 0
7 cycles	88 4 (±0 2)	50 5
10 cycles	89 0 (±0 2)	49 5
Linear regression correlation coefficient, for % PbO_2/peak height		—0 917
Rank correlation coefficient		—1
Linear regression correlation coefficient r_2 for cycle no/peak height		—0 835
Rank correlation coefficient		—0 833

*Measured at 575 nm

**Only one determination carried out

Conclusions

The present work is a very small scale investigation into the application of PAS to battery materials. Some interesting results have been obtained and correlations established. It appears that this technique is suitable for the rapid measurement of the percentage weight of lead dioxide in positive active materials. Since this is a routine requirement for quality control in battery plant operation, it may form the basis for the introduction of an improved quality control procedure for freshly formed material, as well as providing a simple analytical technique for monitoring changes during the charge–discharge cycle

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