

On the use of Raman microscopy for sulfation analysis in lead-acid battery research



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ABSTRACT

Enhanced flooded batteries were studied by means of spatially resolved Raman spectroscopy. Negative plate sulfation as an important failure mode in partial state of charge cycling was characterized. Raman spectroscopy turned out to be an appropriate method for sulfation analysis. The data were correlated with results from elementary analysis and EDX. A lead sulfate specific mapping along electrode cross-section was possible with a spatial resolution of $\sim 50 \mu\text{m}$.

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1. Introduction

Raman spectroscopy [1] has proved to be an analytical technique that is sensitive for many lead containing compounds. Its use for lead acid battery research was first described by Bullock in 1985 [2]. Later, Trettenhahn et al. gave a summary of the Raman spectra of many battery relevant compounds [3]. Previous studies have focused on positive plate corrosion [2,4]. Due to the use of lead-acid batteries in combination with micro-hybrid technology, certain failure mechanisms have become of higher importance [5]. Under partial state-of-charge (pSoC) cycling conditions, negative plate sulfation and corrosion of the negative lugs are described as main failure modes [6–9]. Thus, the focus of studies on battery aging has shifted from the positive towards the negative plate and the negative active mass (NAM).

A promising approach to improve the cyclability of lead-acid batteries is the use of carbon additives in the negative active mass [10–15]. In this work, spatially resolved Raman spectroscopy is used to analyze enhanced flooded batteries (EFB), i.e. flooded-type lead-acid batteries modified by adding different carbon blacks to the NAM. Two important questions can be addressed by Raman spectroscopy in these batteries:

- analysis of negative plate sulfation by detecting the lead sulfate distribution along electrode cross-sections and
- characterization of the pure carbon additives to evaluate structure-property-relationships.

Since the last item has already been addressed in a different paper [16], we focus in this work on the first one.

Sulfation means the irreversible accumulation of lead sulfate during battery cycle life due to a reduced charge efficiency [7]. Depending on cycling conditions and NAM composition, this effect can lead to different lead sulfate distributions in the negative plate. Two directions of the plate have to be distinguished: The differences in sulfation along the z-direction is mainly determined by the level of acid stratification built up during cycle life [8]. Differences in the sulfate distribution in x- and y-direction are associated with conductive graphite additives in the NAM, as Valenciano et al. have already investigated previously [14]. These examples show that both aging mechanisms and battery improvements influence the sulfate distribution. Therefore, spatially resolved techniques for the analysis of lead sulfate are demanded for battery development.

In previous studies by Valenciano et al. [14], electron microprobe analysis (EMPA) was used to acquire lead sulfate maps of electrode cross-sections. In this work, Raman microscopy is presented as an alternative technique for that purpose since EMPA is a quite demanding technique with respect to instrumentation and sample preparation – and in contrast to Raman

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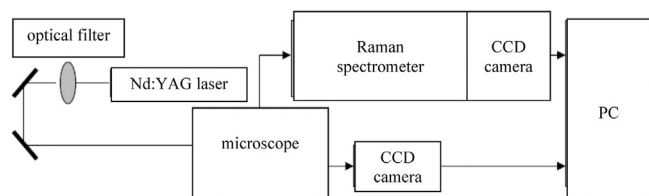


Fig. 1. Schematic overview of the experimental Raman spectroscopy setup.

spectroscopy, it cannot readily be adopted for *in situ* measurements.

The Raman spectrum of lead sulfate was reported in earlier studies [2,3]. Its most intense peak is at 977 cm^{-1} which is associated with the symmetric ν_1 stretching vibration. It appears in a range of the spectrum where no other vibrational transition of lead sulfate or other relevant lead containing compounds occur. As in general in Raman spectroscopy, peak intensities are proportional to the sample concentration, thus the idea is to use the intensity of the ν_1 peak for spatially resolved quantitative lead sulfate detection on the surface of the samples under study.

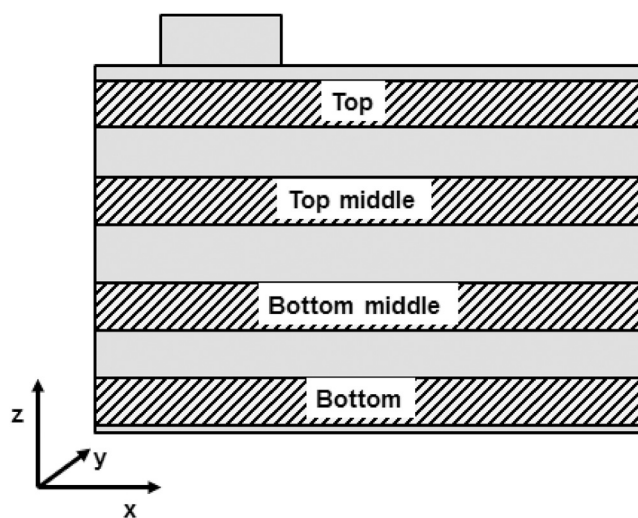


Fig. 2. Regions of negative plates under investigation.

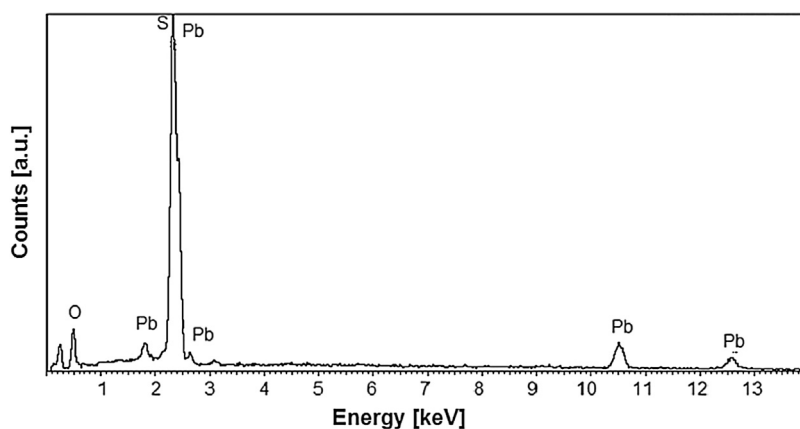


Fig. 3. Example EDX spectrum for a lead sulfate containing sample.

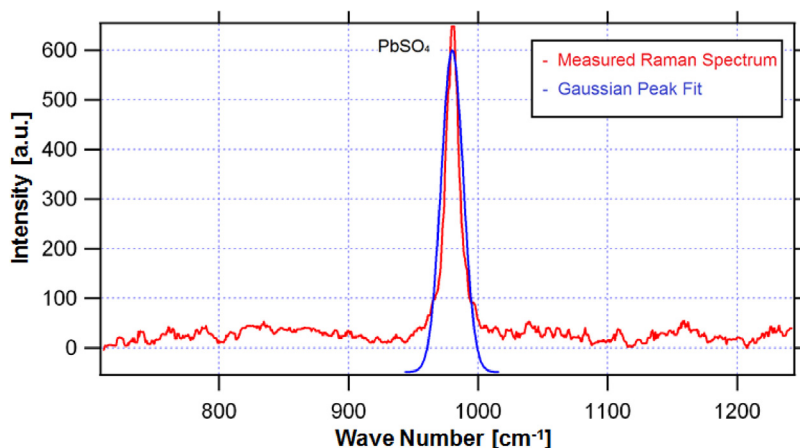


Fig. 4. Example Raman spectrum for a lead sulfate containing sample. The blue curve shows a Gaussian line shape. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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