WDS

High Spectral Resolution Analysis of Lead-Acid Batteries

Application Note # WDS-02

Introduction

Lead-acid batteries (accumulators) are rechargeable devices for storing electric energy generated by electrochemical processes. The batteries consist of electrodes made of lead (Pb) and lead dioxide (PbO_2) and dilute sulfuric acid (37% H_2SO_4) as electrolyte. Lead-acid batteries account for 90% of the global battery market with wide application in transportation, communications, power, and railway industries. Probably the best-known usage is for starters in motorized vehicles as a reliable and relatively inexpensive energy source.

During discharge of lead-acid batteries, finely dispersed lead sulfate ($PbSO_4$) forms on electrodes in a process that is reversed by recharging. However, sulfation, a permanent alteration process characterized by the formation of coarse crystalline lead sulfate deposits may lead to progressive inhibition and power loss of the battery until complete failure upon short-circuit. The nature, kinetics and spatial distribution of these crystalline deposits is thus of major research interest for battery manufacturers as well as for developers of technologies preventing sulfation. X-ray element maps are ideal for investigating the nature and spatial distribution of sulfation deposits.

This application note presents the results of WDS analyses of lead-acid batteries. The superior spectral resolution of Bruker's QUANTAX WDS system allows the user to map and precisely determine the different lead and sulfur phases on lead-acid battery electrodes.

Method

The samples investigated in the present study are from the cathode of a used lead storage battery. WDS and EDS acquisitions were performed simultaneously using XSense, Bruker's wavelength dispersive spectrometer and an XFlash® 6 | 30 EDS detector with 123 eV resolution for Mn Kα.

The analyses were carried out on a FEG-SEM at 20 kV accelerating voltage. Mapping times of only 15 minutes were sufficient to capture more than 4×10^8 total pulses for the EDS silicon drift detector and 1.3×10^5 counts for S Kα_1 (2306.7 eV) with the WDS using a PET analyzer crystal.

Results

Lead sulfate ($PbSO_4$), which is precipitated on the electrodes of the lead accumulator, is a compound of lead (68.3 wt.%), sulfur (10.6 wt.%) and oxygen (21.1 wt.%). In EDS, the Pb M X-ray peaks strongly overlap with the S K peaks of the compound, resulting in a single broad peak (Figure 1). In contrast X-ray peaks of sulfur (S Kα) and lead (Pb Ma and Pb Mb) are clearly separated in the WDS spectrum of $PbSO_4$ despite their small energy difference of only 38 eV.

The superior energy resolution of WDS can be utilized to identify areas on the PbO_2 cathode surface where localized $PbSO_4$ precipitation occurred. To this end, a combined EDS/WDS element distribution map is acquired where the lead distribution is mapped with EDS, while sulfur is mapped simultaneously with WDS (Figure 2). In the sulfur distribution map, the ability of the WD spectrometer to distinguish S Ka from Pb Ma clearly differentiates between lead phases with ($PbSO_4$ precipitate) and without sulfur (PbO_2 cathode surface). The results also indicate that with XSense, qualitative WDS mapping is possible on rough sample surfaces.

The line profile in Figure 3 was extracted from the combined EDS/WDS map and displays the X-ray intensity (and thus concentration) variations in a section across the investigated sample. The sulfur concentrations are highest within the central region of the sample where relative lead concentrations slightly decrease.

Conclusion

The example of a lead-acid battery cathode shows that WDS is a powerful analytical tool where high spectral resolution is required to determine the nature and spatial distribution of chemical phases. WDS can thus complement EDS in research and industrial quality control applications where resolution of Pb and S or similar X-ray overlaps play a key role.

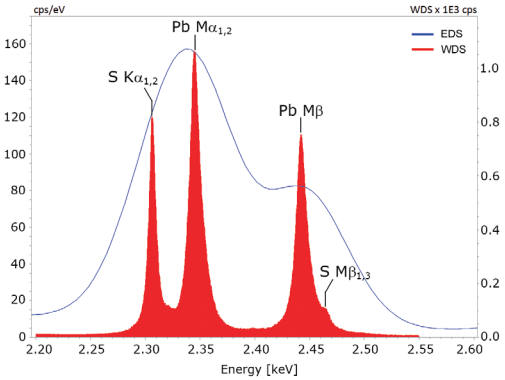

Figure 1
Highly resolved WDS spectrum of lead sulfate ($PbSO_4$) in comparison with the corresponding broad EDS spectrum.

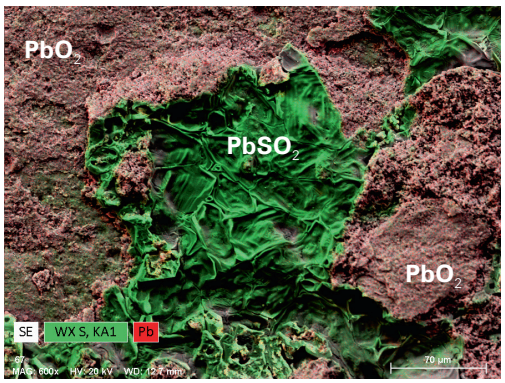

Figure 2
Element distribution map of Pb Mα (by EDS) and S Kα (by WDS).
Map size: 900 x 670 pixels (366 x 270 µm), acquisition time: 15 min.

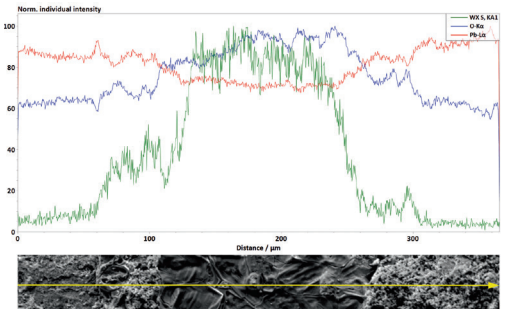

Figure 3
Linescan set horizontally across the sample area shown in Figure 2.

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