

In situ Fourier-transform infrared investigations of lead electrodes in sulfuric acid: formation of lead sulfate on lead and lead alloys

G. L. J. Trettenhahn, G. E. Nauer* and A. Neckel

Institut für Physikalische Chemie der Universität Wien, Währingerstraße 42, 1090 Wien (Austria)

Abstract

In order to understand the reactions on solid lead electrodes in concentrated sulfuric acid and for the further development of lead/acid batteries, it is necessary to develop methods for *in situ* studies on this system. *In situ* vibrational spectroscopic methods, e.g., FT-IR or FT-Raman reflection techniques, offer the possibility for the identification of substances occurring at definite potentials on the electrodes during the charge and discharge reactions in the lead/acid battery. In the present contribution, the external reflection absorption technique is applied to the investigation of lead electrodes during oxidation and reduction processes in 5 M H₂SO₄. By constructing a specially designed electrochemical cell with a movable working electrode and by a special selection of the experimental parameters of the applied electrochemical techniques, it is possible to characterize lead electrodes *in situ* and to determine the formation and consumption of lead sulfate quantitatively. Potentiodynamic as well as galvanostatic techniques have been used. Additionally, all commonly appearing substances in the Pb/PbO/H₂SO₄ system have been prepared and spectroscopically characterized as reference materials for the *in situ* investigations. Some recent results of experiments using cyclic treatment of the electrodes are presented.

Introduction

Knowledge of the electrochemical behaviour of lead in sulfuric acid forms a basis for understanding the mechanism of lead/acid battery and for further work in the development and improvement of modern designs of this power source. Classical electrochemical techniques assist the elucidation of the reaction mechanism [1] and, in combination with analytical techniques, the determination of different reaction products [2, 3]. For example, the different phases of lead dioxide have been detected [4, 5] and the composition of battery plates during different stages of production have been analyzed [6].

One problem has to be solved when applying common analytical techniques to the determination of products generated during an electrochemical reaction. Typical surface-sensitive methods, such as electron spectroscopy for chemical analysis (ESCA), Auger spectroscopy, secondary ion mass spectroscopy (SIMS) or scanning electron microscopy (SEM) in combination with an EDAX (energy dispersive analysis of X-rays) system, require a vacuum for the detection procedure. The process of drying that accompanies the evacuation process using so-called *ex situ* methods leads often

*Author to whom the correspondence should be addressed.

to change in the surface composition and, therefore, to problems with the interpretation of the analytical results. As a consequence, attention has been directed towards the development of *in situ* methods during recent years, especially with respect to the characterization of metal electrodes directly during the course of an electrochemical experiments [7].

In situ methods possess the advantage of obtaining analytical information of an electrode surface in contact with an electrolyte during electrochemical treatment [8]. In particular, the application of electromagnetic radiation at different wavelengths produces the generation of specific and characteristic information of substances that grow at an electrode surface [9]. Vibrational spectroscopic methods, such as infrared or Raman reflection techniques, offer the possibility for the identification of substances that occur at definite potentials at metal electrodes during oxidation and reduction processes [10–13]. The possibility of quantification of reaction products during the course of electro-organic reduction processes using infrared radiation has also been demonstrated [14]. Early *in situ* investigations on lead electrodes were performed by Thibeau *et al.* [15] using *in situ* Raman spectroscopy. Infrared reflection spectroscopy was employed in further experiments [16]. One main limiting factor encountered with *in situ* experiments using such radiation arises from the absorption of the infrared light by the aqueous electrolyte. This can be overcome by applying thin-layer arrangements of by using attenuated total reflection techniques [17, 18].

According to some experimental improvements during recent years [19], it is possible to investigate metal-electrode surfaces *in situ* by using infrared radiation in an external reflection absorption arrangement. This technique has also been applied for some preliminary investigations of lead electrodes in sulfuric acid [20]. During this work, it is necessary to obtain an accurate characterization of the substances produced on lead electrodes under definite electrochemical conditions, e.g. basic lead sulfates. All of the substances that are considered in the formulation of the Pourbaix diagram [21, 22], except for lead dioxide, have been investigated using infrared and Raman spectroscopy [23]. In addition, the thermal behaviour of these compounds has been characterized by thermoanalytical and infrared techniques [24].

The work presented here discusses results obtained from an *in situ* investigation of pure and alloyed lead electrodes in 5 M sulfuric acid during oxidation and reduction reactions using external reflection absorption infrared spectroscopy.

Experimental

The principles of the infrared reflection absorption technique used in this investigation have been described previously [19, 20]. The spectroelectrochemical cell is shown in Fig. 1. The working electrode E consisted of either pure lead (99.9995%, Johnson Matthey) or a lead alloy with an antimony content up to 10 wt.% and an area of 1 cm². Prior to each *in situ* experiment, an electrode surface that was reproducible and free of oxides was generated by employing the following procedure. The electrode was ground with 1000 mesh SiC paper, cleaned with triple-distilled water, and cathodically polarized for 5 min at a potential of -1900 mV versus a saturated mercurous sulfate electrode. The working electrode was surrounded by a platinum wire that acted as the counter electrode. A Hg/Hg₂SO₄ electrode with saturated K₂SO₄ solution as an electrolyte was used as a reference electrode. All potential values are reported with respect to this electrode. A Haber-Luggin capillary enabled a short distance to be achieved between the reference electrode and the surface of the working electrode. All experiments were conducted at 25 °C in 5 M H₂SO₄ that was purged with argon.

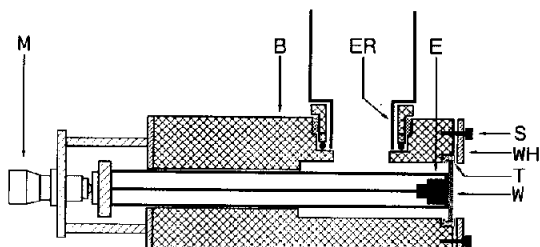


Fig. 1. Schematic diagram of a spectroelectrochemical cell. B: body of the cell; E: working electrode; ER: reservoir of the electrolyte; M: micrometer screw; S: screw; T: Teflon ring; W: infrared transparent window; WH: window holder.

The distance between the surface of the working electrode and the infrared transparent window W (a ZnSe disc with a diameter of 25 mm and a thickness of 2 mm) could be adjusted by using the micrometre screw M within a range of $\pm 0.5 \mu\text{m}$. The spectroelectrochemical cell was mounted on an adjustable probe stage in an optical equipment designed by the Harrick Scientific Corporation (Ossining, USA) for external reflection geometry.

An IMP-83 potentiostat (Jaissle, Neustadt/Waiblingen, Germany) and a Prodis 1/14 TI function generator (Dölling, Clausthal/Zellerfeld, Germany) were used to perform galvanostatic and potentiodynamic measurements. The data were recorded and evaluated using software packages developed by the authors' research group [25].

Current densities between 50 and $300 \mu\text{A cm}^{-2}$ were used for *in situ* galvanostatic experiments on pure lead electrodes, and a current density of $200 \mu\text{A cm}^{-2}$ was used for *in situ* investigations of lead alloys. Galvanostatic treatment of the electrodes was performed at a distance beyond $200 \mu\text{m}$ from the ZnSe window. The potentiostat was switched from the galvanostatic to the potentiostatic mode and the electrode was moved to within 1 and $3 \mu\text{m}$ of the ZnSe window while measurements were taken of the infrared spectra of the electrode surface. Potentiodynamic experiments were carried out under a typical thin-layer arrangement (distance between the ZnSe window and the surface of the working electrode was between 1 and $5 \mu\text{m}$) and at used sweep rates of 0.1 to 2 mV s^{-1} . The potential ranged between -1.4 and 0.0 V . During these experiments, 140 interferograms were collected and transformed to an infrared spectrum. A resolution of 20 mV was achieved on the potential scale by applying a sweep rate of 0.5 mV s^{-1} .

Infrared spectra were recorded with a resolution of 4 cm^{-1} in the middle infrared range by using a 60 SX FT-IR spectrometer (Nicolet, Madison, USA). A mercury-cadmium-telluride (MCT) detector, cooled with liquid nitrogen, together with a KRS-5 polarizer (Specac, UK) were used. For each spectrum, 500 interferograms were collected and subsequently FT-transformed. The necessary reference spectra were recorded just after prereduction of the electrodes in the spectroelectrochemical cell. For potentiodynamic experiments, the reference spectra were sampled at the beginning of each anodic sweep at the cathodic potential limit of -1400 mV .

The amount of lead sulfate was determined by using the integrated band area in the interval between 610 and 645 cm^{-1} of the absorption band at 630 cm^{-1} . This absorption band does not overlap with absorption bands that originate from the sulfuric acid that was used as the electrolyte in these experiments.

Results and discussion

In situ investigations were performed on pure lead and lead alloys during galvanostatic and potentiodynamic treatments in 5 M sulfuric acid. Results received during galvanostatic and some potentiodynamic experiments with pure lead have been presented and discussed elsewhere [19]. In the work reported here, the experimental findings on lead–antimony alloys are described and the results are compared with those obtained on pure lead electrodes.

An *in situ* infrared spectrum of a Pb–10wt.%Sb electrode surface, generated during a galvanostatic experiment is presented in Fig. 2. The electrode was treated with a current density of $200 \mu\text{A cm}^{-2}$ and the potential was monitored during the course of the experiment. Spectra were recorded at short-time intervals (approximately 130 to 200 s) so the spectral information covers the whole region of the potential development. Measurements are therefore representative of the passive and the transpassive states of the electrode surface. The vibration bands at 1176 and 1022 cm^{-1} can be attributed to the ν_3 antisymmetric stretching vibration of the SO_4^{2-} anion in a solid compound such as PbSO_4 . The vibration band at 966 cm^{-1} is assigned to the symmetric stretching vibrations ν_1 [23]. The vibration bands at 633 cm^{-1} and 594 cm^{-1} are due to the antisymmetric bending vibration ν_4 . In principle, the intensity and location of the bands measured during the oxidation of lead–antimony alloys are comparable with the values obtained on pure-lead electrodes.

Nevertheless, in contrast to the experimental findings on pure lead electrodes, the antisymmetric vibrations bands (ν_3 and ν_4) exhibit a small shift to higher wave numbers for the lead–antimony alloy electrodes, while a shoulder at approximately 600 cm^{-1} is more evident. The relation of the intensities at the ν_3 vibration bands shows also a difference. The reason for this behaviour, which is more pronounced at measurements of electrode surfaces without contact to an electrolyte (Fig. 3), can be based on the different surface conditions of the lead sulfate generated by simultaneously growing the antimony compounds. Some work is in progress to identify the compounds that are formed on the electrode surface. The symmetric stretching vibration band ν_1

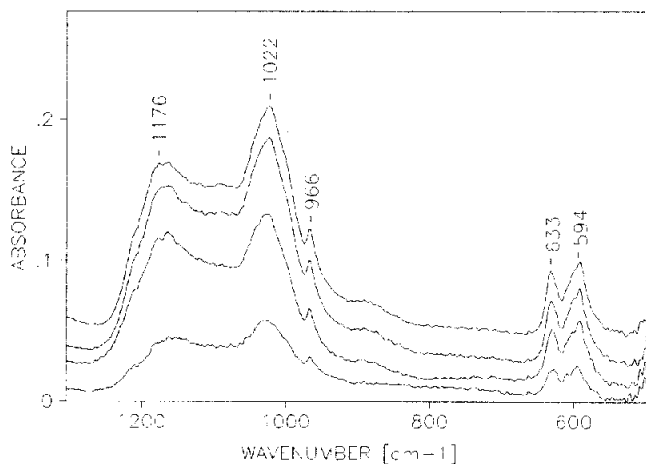


Fig. 2. Infrared spectra of a lead–antimony electrode galvanostatically oxidized with a current density of $200 \mu\text{A cm}^{-2}$. Increase in the bands is correlated with growing of a passive lead sulfate layer.

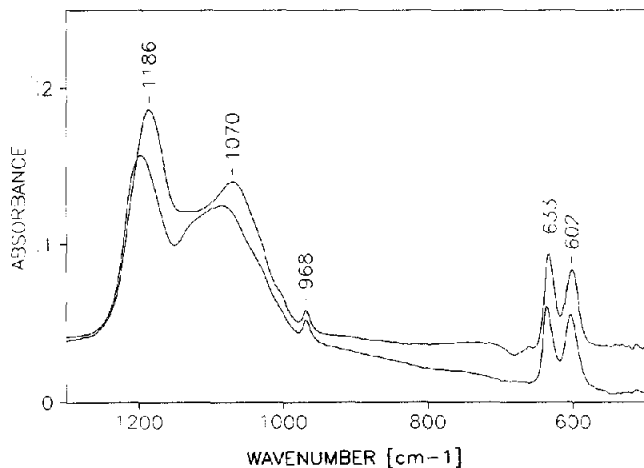


Fig. 3. Infrared spectra of galvanostatically-treated electrodes after reaching the passive state, washed with water and dried. The upper spectrum is obtained for a pure-lead electrode, the lower for a Pb-10wt.%Sb electrode.

could be found at $966 \pm 2 \text{ cm}^{-1}$ during all *in situ* experiments and also for electrode surfaces investigated without an electrolyte. This vibration band seems to be not influenced by the different composition of the lead electrode surface.

The reflection absorption spectra for pure lead and a Pb-10wt.%Sb alloy, generated from the surface of the electrodes after galvanostatic treatment until the passive state was reached and then rinsed with distilled water and dried, are depicted in Fig. 3. Two findings are remarkable: one is connected with the significant shift of the ν_3 vibration band at 1070 cm^{-1} and the less-pronounced shift for the vibration band at 1186 cm^{-1} in comparison with the *in situ* spectra. The ν_4 vibration band at 602 cm^{-1} also shows only a small shift with respect to the location of the band measured at an electrode surface covered with an electrolyte and prepared under the same experimental conditions. The other significant observation is related to the differences in the reflection absorption spectra measured on the pure lead and the lead-antimony alloy electrodes. The spectrum from the alloy exhibits, in principle, the same shape, but with a more pronounced shift of the antisymmetric vibration bands to shorter wavelengths. The symmetric vibration band at 968 cm^{-1} and one part of the ν_4 exhibit no detectable shift, the second part of the ν_4 vibration band exhibits only a shift of approximately 10 cm^{-1} . One supposed explanation for these experimental findings takes into account the influence of some antimony compounds that are generated at the electrode surface in this cathodic potential region. During potentiodynamic experiments on lead-antimony alloys, an additional current peak, which is assigned to the formation of Sb_2O_3 , is found at more anodic potentials (around -400 mV) [26].

Additionally, some investigations using an SEM were performed to determine the thickness of the passive layers on the electrode surfaces at definite potentials in the course of an *in situ* experiment. The electrodes were washed and dried in an external vacuum chamber before starting the SEM investigations. The micrographs (an example is shown in Fig. 4) show clearly the microcrystalline structure of the sulfate layer on the surface and the homogeneous covering of the lead electrode with lead sulfate. A

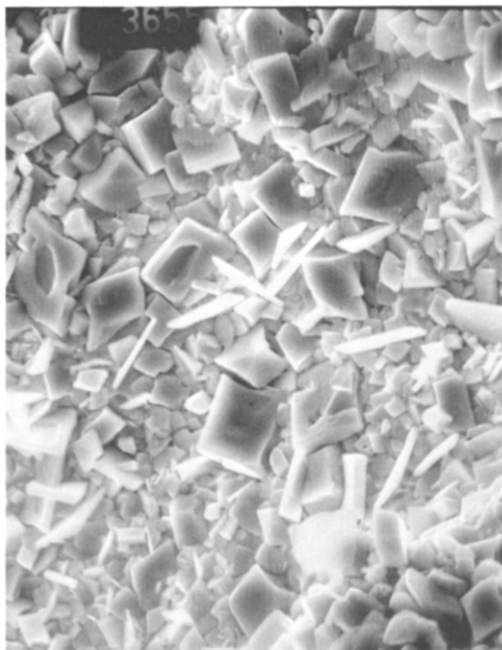


Fig. 4. Electron micrograph of a pure-lead electrode at the passive state. (Secondary electrons, $\times 2500$, reduced in reproduction 89%).

charge flow of 300 mC leads to a calculated overall thickness of about $0.8 \mu\text{m}$. The values of the film thickness, as determined by SEM, range between 0.7 and $1.0 \mu\text{m}$. This finding is in a good agreement with the calculated values. The size of the crystallites in the vicinity of the lead surface is between 0.2 and $0.6 \mu\text{m}$, some crystallites on the top of the surface have a larger size. This good agreement with the expected value suggests that an homogeneous layer of sulfate compounds grows on the electrode surface. Layers with a thickness of up to $1 \mu\text{m}$ can be penetrated by the infrared light and therefore the quantity of oxidation products on the lead electrode surface can be determined *in situ* by using infrared radiation.

The potential and the band area of the ν_4 vibration at 630 cm^{-1} , integrated in the region between 611 and 650 cm^{-1} , as a function of the charge passed through the lead-antimony alloy electrode are displayed in Fig. 5. In the potential region of lead sulfate formation (around -1000 mV), there is a continuous increase in the lead sulfate concentration at the surface. The concentration rises until a charge of about 500 mC has been passed through the electrode. The potential of the electrode jumps after the passivation to high anodic values. After this rise in potential, a further increase in the amount of lead sulfate is observed.

During further galvanostatic oxidation, the lead sulfate is consumed and therefore the band area integrated for the ν_4 vibration decreases. The growing of lead dioxide on the electrode surface is not detectable, because lead dioxide shows no absorption band in the middle of the infrared region.

For a pure lead electrode, the formation of lead sulfate is terminated when the electrode reaches the passive state [19]. From comparison of some results obtained on pure lead (oxidized galvanostatically with different current densities) with those

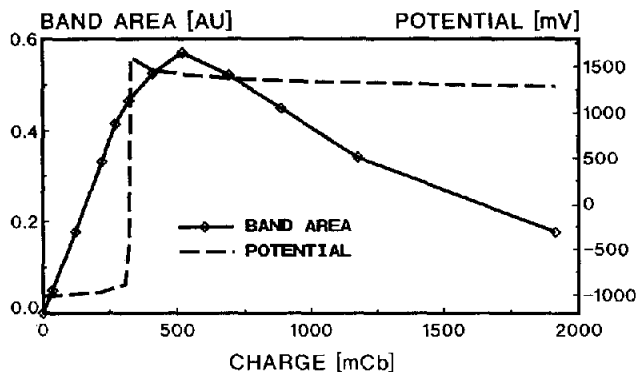


Fig. 5. Electrode potential and area of the vibration band at 630 cm^{-1} vs. time for a Pb-10wt.%Sb electrode galvanostatically treated with a current density of $200\ \mu\text{A cm}^{-2}$.

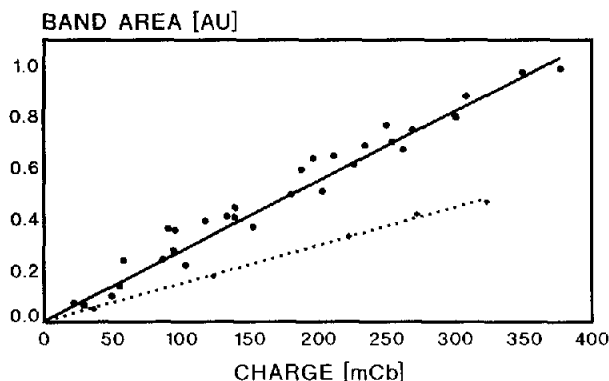


Fig. 6. Area of the absorption band at 630 cm^{-1} vs. charge for (—) lead and (· · · ·) lead-antimony electrodes oxidized at different current densities.

on lead-antimony alloys, a different slope for the integrated band area of the ν_4 vibration at 630 cm^{-1} versus the charge was obtained, see Fig. 6. The lead-antimony electrode exhibits the lower slope. This can be interpreted as a slower rate for the passivation reaction on a lead-antimony alloy surface.

Conclusions

The passivation reaction on lead and lead-antimony alloys can be investigated *in situ* through the application of external reflection absorption spectroscopy with infrared radiation. Integration of band areas of significant vibrations of the products formed the electrode surface permits the quantitative determination of the amount of lead sulfate that is present during the oxidation and reduction processes. Some spectroscopic differences in both the location and the intensity of the antisymmetric vibration bands for products formed on pure lead and lead-antimony alloys have been found. From calculation of the amount of lead sulfate, a further distinction between lead and lead alloys has been detected.

According to the above results, the method of external reflection absorption spectroscopy appears to be a powerful tool for the *in situ* investigation of electrochemical

systems and electrodes that are relevant to battery development and technology. Further work is in progress for: (i) the investigation of the oxidation behaviour of some other lead alloys; (ii) the *in situ* characterization of the formation process by investigating lead dioxide in an appropriate wavelength region, and (iii) the determination of the composition of the active mass after the mixing and curing procedure. This work will be performed in combination with thermal analysis and X-ray diffraction techniques.

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