

Short communication

Electrochemical behaviour of barium metaplumbate as a lead carrier

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Abstract

Barium metaplumbate (BMP), known as a good electrical conductor, has been used as a matrix for the deposition of lead. This kind of electrode can be employed as a carrier and current collector in bipolar lead acid batteries.

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1. Introduction

Barium metaplumbate (BMP), BaPbO_3 , crystallises at high temperatures in regular perovskite form, with a lattice constant a_0 estimated as equal to 0.4267 ± 0.0005 nm [1]. Recently, Zhong et al. [2] have reported three parameters for rhombic type lattice: $a_0 = 0.6024$ nm, $b_0 = 0.6065$ nm and $c_0 = 0.8056$ nm. The starting materials to the synthesis of BMP are $\text{Ba}(\text{NO}_3)_2$, PbO , and Pb_3O_4 [1].

Barium metaplumbate is a good electronic-metallic type conductor. Its resistivity at 25°C is $8.3 \times 10^{-4} \Omega\text{cm}$, and the temperature coefficient of resistivity is equal to $+0.15\% \text{ }^\circ\text{C}^{-1}$ [1]. For this reason, BMP has been used, for example, as an electrode material for the production of ozone, for electrolytic synthesis of manganese dioxide [3], and also as a support to bipolar batteries [3,4]. Barium metaplumbate has also been proposed as an additive to lead acid battery pastes to improve their mechanical properties [3,5].

This work was aimed at understanding the electrochemical behaviour of BMP as a matrix for the deposition of lead and the possibility of using such a composite electrode in

lead acid batteries. It has to be noted that no other works on electrochemical behaviour of BMP material has been published.

2. Experimental

The working electrode was a BMP plate (active area: 2cm^2). BMP material was synthesised from lead nitrate $\text{Pb}(\text{NO}_3)_2$ (POCh, Gliwice, Poland) and barium hydroxide $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (POCh, Gliwice, Poland) by heating in the oven at 880°C . This procedure was described in detail in the earlier work [6].

Before each experiment the electrode was washed in acetone and thoroughly rinsed in triply distilled water. Usually, the potential of the electrode was cycled between -1.4 and $+1.7$ V. The counter electrode was a platinum black foil (ca. 4cm^2 geometric area) and the reference electrode was a $\text{Hg}, \text{Hg}_2\text{SO}_4, \text{K}_2\text{SO}_4(\text{sat})$ (0.680 V versus NHE). The lead deposit was formed on BMP using the acetate bath ($10\text{g dm}^{-3} \text{Pb}(\text{CH}_3\text{COO})_2$, $20\text{g dm}^{-3} \text{NaOH}$, $50\text{g dm}^{-3} \text{KNaC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$) and cycling polarisation in the potential range from -1.4 to 1.7 V at a scan rate of 10mV/s .

The experiments were carried out in a glass cell. Typically, the cyclic voltammograms were obtained at a sweep rate of 10mV/s . The electrolyte used was 0.5M sulphuric acid

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deaerated with argon. The experiments were carried out at room temperature (298 K).

The micrographs of the electrodes were obtained with the scanning electron microscope LEO 435 VP. The surface compositions were analysed using EDAX analyser (EDR-286) coupled with a LEO 435VP scanning electron microscope. Lead was electrodeposited at a constant potential on BMP matrix from solution containing lead acetate as a main component.

3. Results and discussion

In Fig. 1, the scanning electron micrographs (SEM) present the images of the BMP material prior to any electrochemical treatment. The “craters” seen over the whole surface are the effect of heating of the sample, required for the BMP electrode preparation procedure. No composition difference between the interior and the edges of the craters was indicated by the EDAX analysis.

Fig. 2 shows the cyclic voltammograms of BMP material (without any prior electrochemical treatment). The electrode was cycled in 0.5 M H_2SO_4 in the whole available potential range from -1.4 to $+1.6$ V with sweep rate 10 mV/s. It can be seen from Fig. 2 that the obtained voltammogram is featureless, i.e. no currents due to any faradic processes are

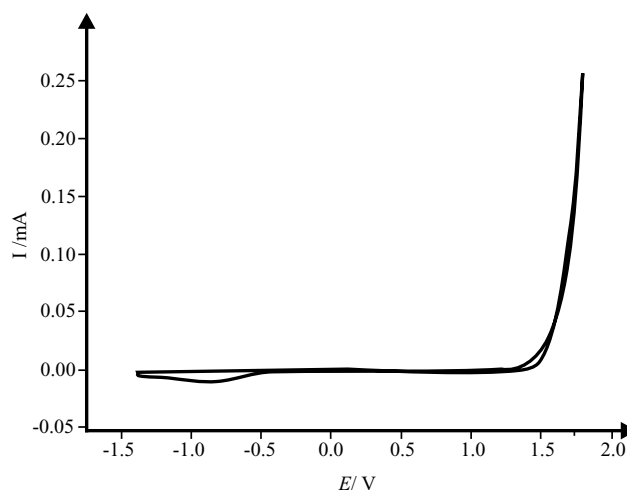


Fig. 2. Voltammogram at 10 mV/s of barium metaplumbate electrode in 0.5 M H_2SO_4 .

observed. The increase of current above $+1.6$ V is due to oxygen evolution.

Fig. 3 shows the scanning electron micrographs of BMP with electrodeposited lead, after 10 cycles of deposition. One can observe characteristic lead deposits in some “craters” of the BMP surface. In other “craters”, small crystal nuclei

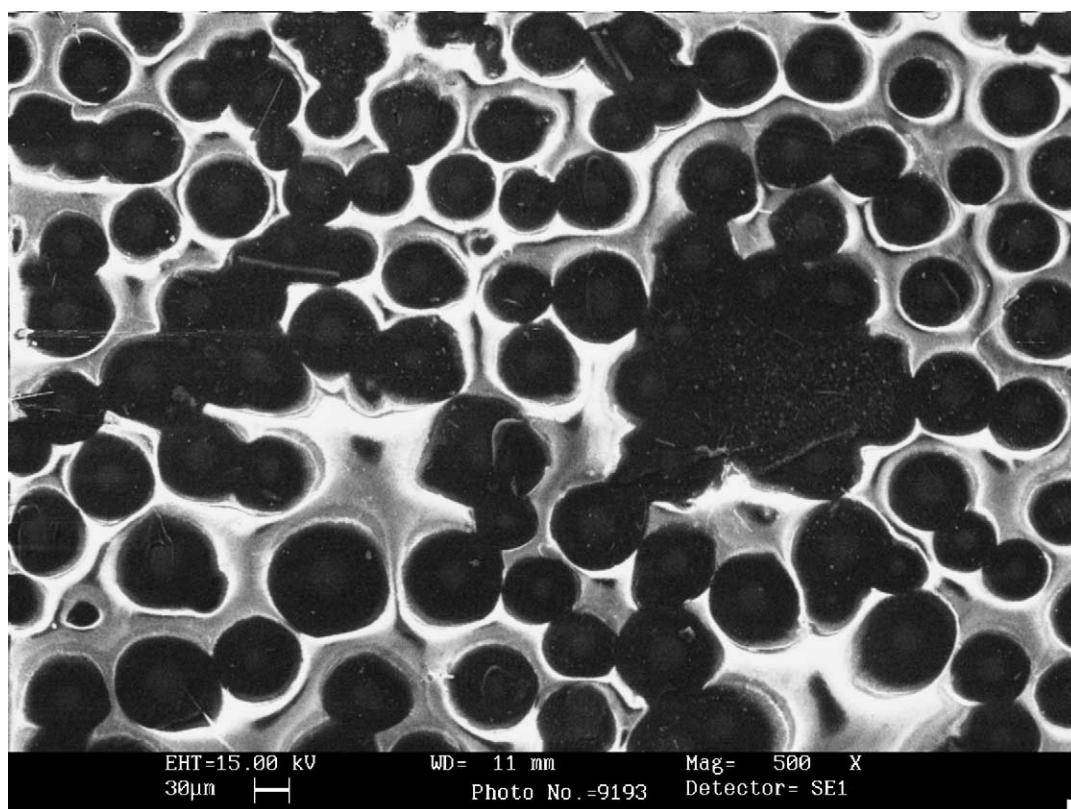


Fig. 1. Scanning electron micrographs of barium metaplumbate electrode before electrochemical treatment.

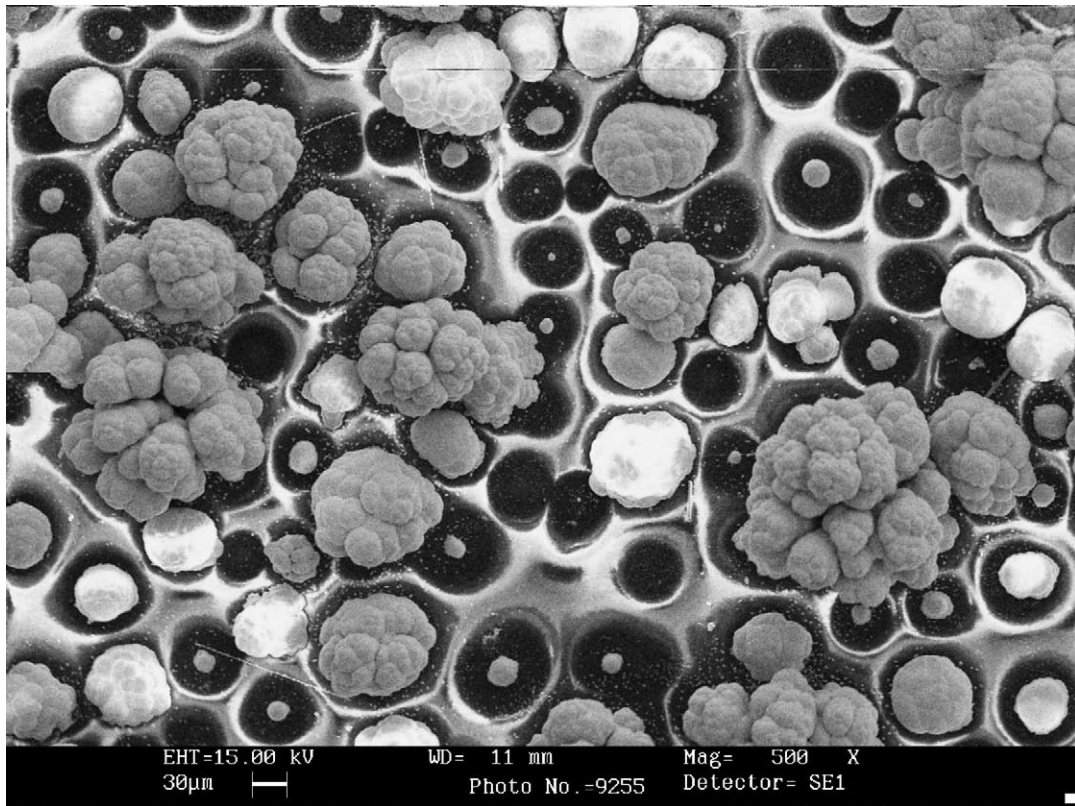


Fig. 3. The scanning electron micrographs of barium metaplumbate electrode after electrochemical lead deposition.

are visible. EDAX analyse indicated that these crystal nuclei are formed from pure lead. The amount of deposited Pb increases with the number of polarisation cycles, i.e. the time of deposition.

The presence of pure lead on BMP material is well confirmed by cyclic voltammetry. Fig. 4 shows the cyclic

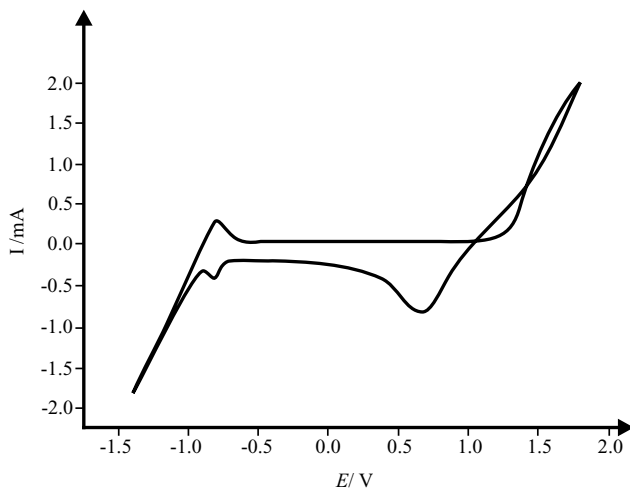


Fig. 4. Voltammogram at 10 mV/s of barium metaplumbate electrode in H_2SO_4 , after lead electrodeposition.

voltammogram of BMP material after electrochemical lead deposition (documented by SEM in Fig. 3). The electrode was cycled in 0.5 M H_2SO_4 in a potential range from -1.4 to 1.6 V at a sweep rate of 10 mV/s. This voltammogram is generally similar to voltammograms for pure lead [7]. On both voltammograms (Fig. 1 in Ref. [7] and Fig. 4), the waves typical for lead oxidation to Pb(II) and (IV) as well the waves for the reversed reduction processes can be seen. The “anodic excursion” peak, which usually appears as a result of cracking of the lead layer [8,9], is not observed here probably due to different surface morphology of Pb deposited on BMP (not homogeneous coverage with lead). The smaller ratio of the Pb redox peak currents to the charging/discharging currents of the double layer in case of lead deposited on BMP is due to the large area of non-covered BMP matrix.

BMP samples covered with electrodeposited lead were kept in air atmosphere for a few months and no changes in the morphology of the studied material was observed in SEM images. Also, the cyclic voltammograms retained the same character as in Fig. 4. The scanning electron micrographs of BMP material with electrodeposited lead taken after 3 months of air atmosphere exposure is shown in Fig. 5.

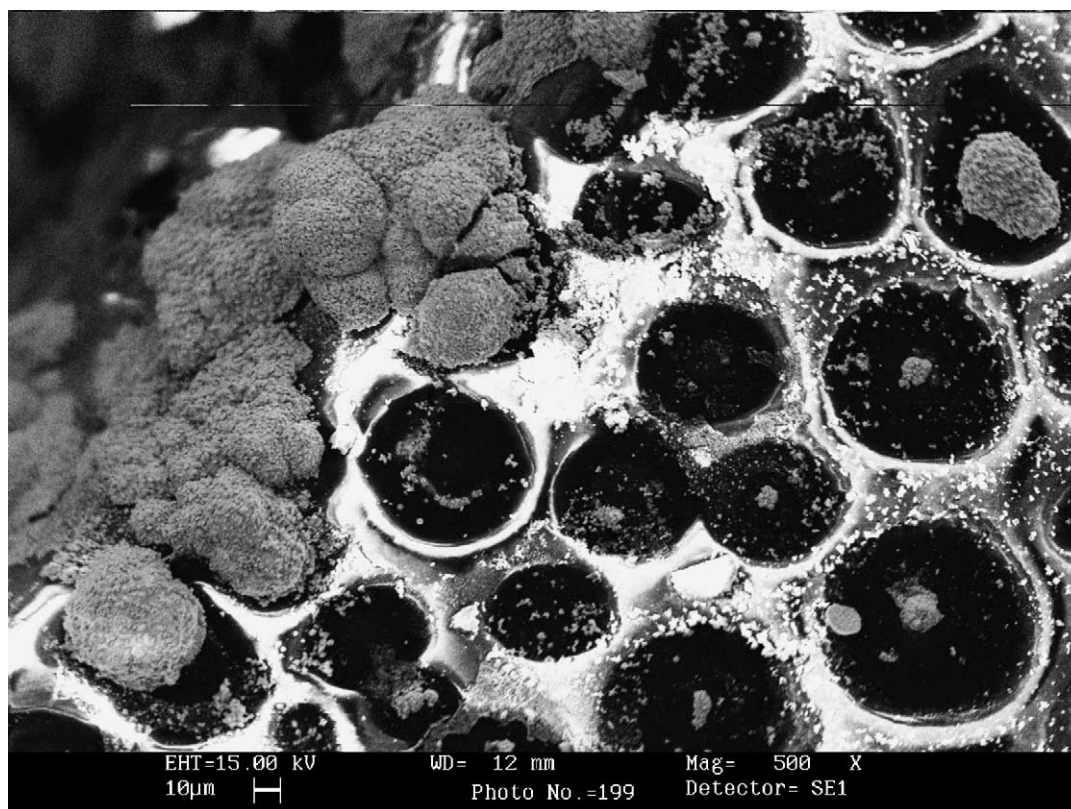


Fig. 5. Voltammogram at 10 mV/s of barium metaplumbate electrode in H_2SO_4 , after lead electrodeposition, electrochemical treatment (cyclic voltammetry) and 3 months of storage in air atmosphere.

4. Conclusions

The results of the study of the electrochemical behaviour of BMP modified with Pb lead to the following conclusions:

1. The barium metaplumbate matrix can be electroplated with lead.
2. The sizes and number of deposited nuclei increase with time of electrode polarisations (number of cycles).
3. The electrochemical behaviour of BMP modified with lead is similar to pure lead electrode.
4. The lead deposit is stable in the long term under standard experimental conditions (room temperature, air atmosphere).
5. The BMP matrix covered with Pb can be applied as a new battery material.

Acknowledgements

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