



# Evaluating the lead affinity of graphite additives in lead-acid batteries by electrochemical deposition



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## ABSTRACT

The improvement of lead-acid batteries with respect to charge acceptance and cycle life in partial state of charge operations due to carbon additives in negative electrodes is state of the art. However, there is still a lack of knowledge about the mechanisms which generate these enhancements. Especially the influence of the physicochemical connection between the carbon additives and the surrounding lead skeleton has not been investigated in much detail yet, but seems to play an important role. Therefore, we developed a new method for characterizing the degree of interaction between lead and carbon additives with focus on graphite materials. By potentiostatic deposition of lead on graphite electrodes, we observe a correlation between the deposition overpotential and the number density of nucleation sites. Chronoamperometry is used to calculate the number density of nucleation sites on graphite electrodes which is in accordance with microscopic observations. We found that expanded graphite exhibits a significantly higher number of nucleation sites than synthetic graphite. Finally, a correlation between this number density of nucleation sites and the integration of the graphite particles in real lead electrodes is observed. Thus, the technique can be used to predict the integration of different graphite particles into the negative active material.

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## 1. Introduction

As hybridization of the car market proceeds, new requirements for the lead-acid battery are evolving. Because of stop/start systems and brake energy recuperation, especially a higher cyclability under partial state of charge conditions is needed as well as an improved dynamical charge acceptance [1–3]. Adding small amounts of carbon additives, like carbon black or graphite, into the negative active material (NAM) seems to be a facile and low-cost way to improve the battery performance [1,4–6].

The beneficial effects of carbon additives in the NAM are well known but there is still a lack of knowledge about the mechanisms behind these effects. A number of mechanisms has been proposed which include the introduction of a capacitive contribution thanks to higher surface area of the NAM, the induced higher porosity and the enhancement of the conductivity of the discharged electrode [7–9]. However, a complete understanding is still missing which hinders a tailored optimization of these additives. In literature, one finds a wide range of structural parameters of carbon additives like particle size or specific surface area, that are

investigated with respect to the electrochemical properties of the negative electrode for different weight loads [10,11]. As a rather non-obvious parameter, the connection of the carbon additives to the surrounding lead matrix, i.e. the ability of the carbon particles to integrate into the active material, is barely investigated. Nonetheless, this property is most likely playing a very important role to fully evolve the beneficial effects of the additive as was shown by Pavlov and co-workers [12]. They observed an increase of faradaic currents by adding activated carbon to a lead electrode and therefore suggested a parallel mechanism where lead is also reduced on the carbon surface [6,11]. In the same way, Boden and co-workers explained the presence of lead clusters on graphite particles in NAM by the electrochemical reduction of soluble lead ions on graphite surfaces [13]. Recently, Cericola and Spahr proposed a new way to quantify spontaneous lead deposition on different carbon additives [14].

In particular, a better connection to the active materials generates an improved electrical contact between carbon additive and lead skeleton which enhances the charge mechanism. To date, it is still not clear which carbon properties can guarantee a good incorporation into the lead skeleton of the NAM.

In order to obtain a good connection between the carbon additive and the surrounding lead matrix, the carbon particles

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must exhibit a high number of reactive sites. These active sites are usually found along the edge planes of the graphitic layers. Here, the electrochemical activity is much higher than at the basal planes of the graphite grains [15]. Surface groups of activated carbons may also provide additional spots for a nucleation of lead ions. Unfortunately, the determination of these active sites is not easy. So far, a suitable technique for the evaluation of the active nucleation sites of different carbon additives has not been established yet, but is needed to understand and predict their interaction with the NAM.

For this purpose, we created a model system to characterize carbon additives with respect to their ability of being integrated into the negative active material. In this paper, we present the characterization of two different graphite materials by electrochemical deposition of lead from aqueous solution. By using chronoamperometric measurements together with a 3D nucleation model from Scharifker and Hills [16] we were able to determine the number of active nucleation sites on graphite electrodes and correlate these finding with the integration of the corresponding particles into the NAM. Finally, a relationship between lead affinity and graphite properties is discussed.

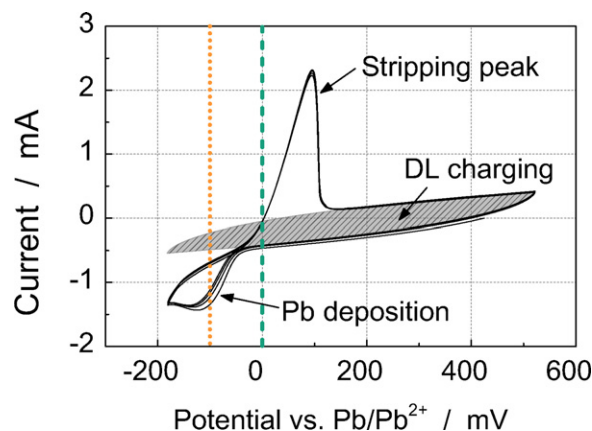
## 2. Experimental

A three electrode setup was used to perform the electrochemical deposition experiments which included a graphite working electrode, a  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$  (saturated) reference electrode (Radiometer Analytical) and high purity lead foil (99,95 %, Good-Fellow) as counter electrode. The lead foil was chosen as counter electrode in order to keep a constant lead ion concentration in the electrolyte. Hence, during deposition or reduction of  $\text{Pb}^{2+}$  ions on the working electrode, a similar amount of lead ions shall be generated at the counter electrode by oxidizing the lead foil. In order to produce the carbon working electrode, graphite powder was pressed in form of thin pellets by a pressure of  $20 \text{ kN} \cdot \text{cm}^{-2}$ . The resulting electrodes had a circular geometrical area of  $0.38 \text{ cm}^2$ . As electrolyte, an aqueous lead nitrate solution of  $20 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  with  $1 \text{ mol} \cdot \text{l}^{-1}$  potassium nitrate (analytical grade) as supporting electrolyte was used.

A commercially available expanded natural graphite (TIMCAL TIMREX<sup>®</sup> BNB90) and a synthetic graphite powder, SG, (TIMCAL TIMREX<sup>®</sup> KS5-25) were selected in order to rate the quality of the experiment and to compare the impact of the two manufacturing methods.

The potentiostatic measurements were performed at an Autolab potentiostat (Metrohm, Germany) with NOVA software. For the electrochemical deposition, a potential step experiment was conducted from open circuit potential to a fixed deposition overpotential until a defined charge was transferred. The deposition overpotential is defined as the potential difference between the equilibrium potential of the  $\text{Pb}/\text{Pb}^{2+}$  reaction in 20 mM lead nitrate solution and the applied negative potential measured vs.  $\text{Pb}/\text{Pb}^{2+}$ . The lead equilibrium potential was determined in 20 mM lead nitrate solution and is equal to  $-0.88 \text{ V}$  vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4$ . For easier understanding we refer all potentials to the  $\text{Pb}/\text{Pb}^{2+}$  equilibrium potential. By doing this, the deposition overpotential corresponds directly to the absolute value of the given potential.

For the microscopic characterization of the lead depositions each electrode was immersed in triple distilled water for 30 seconds and dried under a laminar flow of compressed air. Scanning electron micrographs were obtained via a ZEISS SUPRA<sup>™</sup> SEM using the secondary electron detector with an electron beam energy of 6 keV and a working distance of 6 mm.



**Fig. 1.** Cyclic voltammogram of expanded graphite in  $20 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  lead nitrate solution and a scan rate of  $20 \text{ mV} \cdot \text{s}^{-1}$ . The dashed line indicates the  $\text{Pb}/\text{Pb}^{2+}$  equilibrium potential, the orange, dotted line an exemplary deposition overpotential of 100 mV. The shaded area represents the capacitive background current due to double layer charging.

## 3. Results

### 3.1. Potentiostatic deposition

In Fig. 1, a cyclic voltammogram of the first five cycles of expanded graphite in 20 mM lead nitrate solution is shown (black solid line). The scan rate was set to  $20 \text{ mV} \cdot \text{s}^{-1}$ . One observes a current difference between the anodic and cathodic baseline (shaded area) that is due to double layer charging of the graphite pellet. For potentials lower than 30 mV vs.  $\text{Pb}/\text{Pb}^{2+}$ , an additional cathodic current is generated implicating the lead reduction and deposition on the working electrode. Sweeping back to potentials more positive than 0 V vs.  $\text{Pb}/\text{Pb}^{2+}$  (green, dashed line), the anodic stripping peak can be observed due to lead oxidation and dissolution. The reason for the potential difference between the two reactions is the nucleation overpotential that has to be overcome in order to deposit lead on the graphite electrode. The dotted, orange line represents an exemplary deposition overpotential of 100 mV.

In order to characterize the behavior of lead nucleation and growth on graphite a potentiostatic deposition of lead on graphite pellets was performed. The experiment was carried out at four different deposition overpotentials ranging from 100 mV to 400 mV. The transferred charge was  $100 \text{ mAs} \cdot \text{cm}^{-2}$  and  $500 \text{ mAs} \cdot \text{cm}^{-2}$ , respectively. Micrographs of the resulting electrodes are summarized in Fig. 2.

The SEM images in Fig. 2a show that at  $100 \text{ mAs} \cdot \text{cm}^{-2}$  transferred charge an increase of the deposition overpotential results in an increase of the number density of lead particles or rather of active lead nucleation sites. This is due to the fact that the activation energy for the formation of a new nucleus is lowered by applying a higher overpotential [17]. As the total charge transfer remains constant, a higher density of nuclei results in a lower particle size. As it can be seen in Fig. 2b, the density of nucleation sites at  $500 \text{ mAs} \cdot \text{cm}^{-2}$  is similar to the one observed with a transferred charge of  $100 \text{ mAs} \cdot \text{cm}^{-2}$ . The major difference, however, is in the size and shape of the particles. It is obvious that an additional charge transfer leads to almost no new nucleation sites but bigger particles and dendritic structures which results from pure lead on lead deposition. Thus, one can assume the number density of active nucleation sites being limited for each overpotential in the present electrochemical regime.

Transferred to real lead-acid batteries this behavior indicates that a higher density of active sites on graphite particles is to be

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