



# The external surface area of carbon additives as key to enhance the dynamic charge acceptance of lead-carbon electrodes



J. Settelein<sup>a,\*</sup>, J. Oehm<sup>a</sup>, B. Bozkaya<sup>a</sup>, H. Leicht<sup>a</sup>, M. Wiener<sup>b</sup>, G. Reichenauer<sup>b</sup>, G. Sextl<sup>a,c</sup>

<sup>a</sup> Fraunhofer Institute for Silicate Research ISC, Neunerplatz 2, 97082 Würzburg, Germany

<sup>b</sup> Bavarian Center for Applied Energy Research (ZAE Bayern), Magdalene-Schoch-Strasse 3, 97074 Würzburg, Germany

<sup>c</sup> University of Würzburg, Chair of Chemical Technology of Materials Synthesis, Röntgenring 11, 97070, Würzburg, Germany

## ARTICLE INFO

### Article history:

Received 5 September 2017

Received in revised form 18 November 2017

Accepted 18 November 2017

Available online xxx

### Keywords:

Lead-acid batteries

Carbon additives

Dynamic charge acceptance

External surface area

Double-layer capacity

Hydrogen evolution

## ABSTRACT

The dynamic charge acceptance (DCA) of modern lead-carbon batteries is one of the key parameters for their future application in micro- and mild-hybrid cars. This work elucidates the impact of the external surface area of carbon additives on the electrochemical performance of lead-carbon electrodes with respect to the DCA. Five specially synthesized amorphous hard carbon powders with different specific external surface area ranging from  $13 \text{ m}^2 \text{ g}^{-1}$  to  $192 \text{ m}^2 \text{ g}^{-1}$  were added to the negative active material of laboratory lead-carbon test cells. Results from cyclic voltammetry reveal that the specific external surface area of amorphous carbons exhibits a clear correlation to the electrochemical activity of lead-carbon electrodes. Firstly, an almost linear increase of the activity of the hydrogen evolution reaction with increasing specific external surface area of the carbon additive can be found. Secondly, the specific double-layer capacity of the negative active material is directly linked to the specific external surface area of the additive, as well. Thirdly, a clear correlation to the DCA can be established. In conclusion, a high specific external carbon surface in the negative active material seems to be a key to improve the dynamic charge acceptance of modern lead-carbon batteries.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Since the introduction of micro- and mild-hybrid powertrains into the automotive market, new requirements for lead-acid batteries have been established [1]. Due to braking energy recuperation functions and stop/start-systems, the car battery is no longer fully charged most of the time and additionally suffers from an increased amount of charge/discharge events [2–4]. The rechargeability of the car battery is essential for providing reliable stop/start functionality and a maximum of recuperation energy but strongly depends on the state-of-charge (SOC), the temperature and the short-term history of battery operation [4–6]. In order to account for the variable recharge ability of those batteries, the so called dynamic charge acceptance (DCA) was introduced [7]. With the help of a new, harmonized test protocol, the EN standard EN 50342-6 now provides a more realistic validation of the recuperation currents of lead-acid batteries [6,8].

The classical lead-acid battery was not developed for an application including a partial state of charge cycling regime at high charge and discharge rates. Therefore, an early battery failure and a disabling of the hybrid functions in the car was very often observed [4,5]. As was shown in recent years, the negative electrode is most often responsible for the low charging power of the battery due to its low specific surface area and an irreversible  $\text{PbSO}_4$  crystal growth in partial state of charge [9,10]. However, adding small amounts of carbon additives, such as carbon black or graphite, to the negative active material (NAM) seems to be a facile and low-cost way to improve the DCA [11–13]. These so-called lead-carbon electrodes exhibit a higher electrochemical activity and are able to increase the cycle-life and the charging power significantly. Several mechanisms have been proposed about the function of the carbon additives in the NAM. The most prominent are the increase of electrode surface area and double-layer capacity as well as the improved electrode microstructure due to additional nucleation sites and steric effects [12]. Yet, it is neither fully understood nor proven which of these effects actually make a difference in the electrical performance of the batteries, especially on the DCA, and how their impact can be enhanced. A direct link

\* Corresponding author.

E-mail address: [jochen.settelein@isc.fraunhofer.de](mailto:jochen.settelein@isc.fraunhofer.de) (J. Settelein).

between carbon parameters, electrode properties and dynamic charge acceptance would allow tailoring the synthesis of carbon additives for high-DCA-batteries and could result in a significant improvement of advanced lead-acid batteries, thus, providing a more cost-efficient hybridization of the car market.

In this work, we try to establish a correlation between the external surface area of carbon additives, the electrochemical activity of lead-carbon electrodes and the dynamic charge acceptance (DCA). For this, we synthesized amorphous carbon powders that have a significant difference in their mean primary particle size but exhibit a similar microporosity [14]. Thus, we are able to investigate the effect of the specific external surface area of carbon additives on the electrochemical performance of lead-carbon electrodes systematically. The comparison to a non-microporous commercial lamp black is used to validate the results and to discuss the impact of microporosity as well.

## 2. Experimental

### 2.1. Preparation of amorphous carbon powders

The amorphous carbon particles used as carbon additives within the framework of this study were prepared according to the procedure given in detail in reference [15]. Briefly, organic aqueous suspensions of resorcinol-formaldehyde particles were synthesized in a sol formation process in an aqueous solution at very low concentration of the reactants resorcinol (R) and formaldehyde (F) ( $(\text{mass (R + F)})/(\text{total mass of solution}) < 20$ ) thus suppressing the formation of a gel network. Largely different particle sizes were initiated by changing the molar ratio of resorcinol to catalyst (0.1 n  $\text{Na}_2\text{CO}_3$ ) in the aqueous starting solution from 700 to 3000. After aging of the solution for 24 h at 85 °C, the particles were extracted from the suspension by convective drying at ambient temperature for several days. Eventually, the organic powder was pyrolyzed at 800 °C under Argon.

### 2.2. Structural characterization

The structural characteristics of the synthetic carbon particles were derived by scanning electron microscopy and nitrogen adsorption analysis.

Scanning electron micrographs were taken with a ZEISS SUPRA™ SEM using the secondary electron detector at an electron-energy of 6 keV and a working distance of 6 mm.

$\text{N}_2$ -adsorption measurements at  $-196$  °C were performed for all samples with a commercial volumetric adsorption instrument (ASAP2020, Micromeritics). Prior to analysis, the samples were degassed at 300 °C for at least 12 h at pressures below  $10^{-3}$  mbar. The resulting adsorption isotherms were analyzed by BET theory [16] for the specific surface area  $S_{\text{BET}}$  according to the recommendations for microporous materials given in the respective ISO standard [17]. Furthermore, the t-plot method was applied [18]; hereby, the reference isotherm of Magee was used [19]. This approach yields the specific external surface area  $S_{\text{ext}}$ , i.e. the envelope surface area of the microporous carbon particles, and the specific micropore volume  $V_{\text{mic}}$ . Combining the results obtained

from the t-plot method with the density of the nonporous carbon phase  $\rho_c = 2.06 \text{ g cm}^{-3}$  [20], the average particle diameter was calculated with the following relationship assuming spherical particle geometry:

$$d_{\text{part}} = 6/S_{\text{ext}} \cdot (V_{\text{mic}} + 1/\rho_c). \quad (1)$$

### 2.3. Electrochemical characterization of carbon powders

The electrochemical properties of pure carbon powders were investigated by an electrochemical three electrode setup including a rotating disc electrode (Pine Research Instrumentation) and an Autolab potentiostat (PGSTAT101, Metrohm Germany). As electrolyte, one molar sulfuric acid was used that was permanently purged by argon gas in order to prevent the presence of dissolved oxygen from the atmosphere. With help of a jacketed glass cell, a constant electrolyte temperature of  $25.0 \text{ °C} \pm 0.1 \text{ °C}$  was provided. The three electrode setup consisted of a glassy carbon working electrode, a standard platinum counter electrode (Pine Research Instrumentation) and a reversible hydrogen reference electrode (Gaskatel, Germany). An average amount of 50  $\mu\text{g}$  carbon powder was drop-casted from aqueous dispersion onto the glassy carbon electrode and dried under laminar flow in order to get a thin and homogeneous carbon layer. The dispersion was produced by ultrasonic mixing of 50 mg carbon powder with 10 ml bi-distilled water and 40  $\mu\text{l}$  Nafion<sup>®</sup> solution (5%, Sigma-Aldrich). For the cyclic voltammetry study, a scan rate of  $100 \text{ mV s}^{-1}$  was applied and the rotation speed of the working electrode was set to  $1600 \text{ min}^{-1}$ .

### 2.4. Electrode fabrication and electrical testing

The lead-carbon electrodes were prepared on laboratory level. The active material was pasted manually onto lead grids (Sn/Ca-alloy) with a geometrical area of  $10 \text{ cm}^2$  and a dimension per grid section of approx.  $5 \text{ mm} \times 10 \text{ mm}$ . After pasting, the electrodes were cured at a defined temperature of 45 °C and a humidity of 100 % and eventually dried. For the production of the active material, all paste components were mixed by a SpeedMixer™ (DAC 400, Hauschild, Germany). The total mixing time was 10 min. The paste composition comprised 80 wt.-% leady oxide (from ball mill process), 11 wt.-% distilled water, 6.5 wt.-% diluted sulfuric acid (50 wt.%), 0.6 wt.-%  $\text{BaSO}_4$  (Merck) and 0.2 wt.-% sodium-lignosulfonate (Vanisperse A, Borregaard LignoTech). The relative amount of the respective amorphous carbon powder was 1.6 wt.-%.

Three laboratory test cells for each carbon powder were assembled including one negative lead-carbon electrode surrounded by two commercial positive electrodes. A commercial polyethylene separator for enhanced flooded batteries was employed as well as a  $\text{Ag}/\text{Ag}_2\text{SO}_4$  reference electrode (0.71 V vs. RHE) [21]. The electrodes were electrochemically formed by container formation at a constant current of 0.1 C and an acid density of  $1.14 \text{ g cm}^{-3}$ . After formation, the electrolyte density was adjusted to  $1.28 \text{ g cm}^{-3}$ . The discharge capacity of the final laboratory cells was limited by the negative electrode at around 1 Ah at 20 h discharge rate.

Electrochemical performance of the lead-carbon electrodes was determined via cyclic voltammetry with a Solartron 1470 E potentiostat at 25 °C at a state of charge (SOC) of 100%. For measuring the charge acceptance of the test cells, the DCA test protocol from European standard for batteries for micro-hybrid application DIN EN 50342-6:2015 was adopted [8]. Voltages were scaled by factor 1/6 to account for the 2 V laboratory test cell. The respective currents were downscaled from an assumed 60 Ah, 12 V battery to the 1 Ah cell level. The complete test procedure can be

**Table 1**  
Structural properties of the synthesized amorphous carbon powders and the commercial lamp black.

	EAC1	EAC2	EAC3	EAC4	EAC5	LB
mean particle size $d_{\text{part}}$ [nm]	352	118	81	37	22	104
$S_{\text{BET}}$ [ $\text{m}^2 \text{ g}^{-1}$ ]	717	734	755	742	765	28
$V_{\text{mic}}$ [ $\text{cm}^3 \text{ g}^{-1}$ ]	0.271	0.267	0.275	0.245	0.229	nd
$S_{\text{ext}}$ [ $\text{m}^2 \text{ g}^{-1}$ ]	12.9	38.3	56.4	120	192	28

Download English Version:

<https://daneshyari.com/en/article/7540191>

Download Persian Version:

<https://daneshyari.com/article/7540191>

[Daneshyari.com](https://daneshyari.com)