Journal of Energy Storage 1 (2015) 15–21

Contents lists available at ScienceDirect

Journal of Energy Storage

journal homepage: www.elsevier.com/locate/est

The role of carbon in the negative plate of the lead–acid battery

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ARTICLE INFO

Article history:
Received 20 March 2015
Received in revised form 21 April 2015
Accepted 1 May 2015
Available online 15 May 2015

Keywords:
Carbon
Negative active material
Lead–acid battery
Cyclic voltammetry

ABSTRACT

Inclusion of an appropriate form of carbon as an additive in the negative active material (NAM) improves the performance of lead–acid batteries in high rate partial state of charge (HRPSoC) cycling. We have used cyclic voltammetry to evaluate the performance of different carbons – carbon black, acetylene black and graphite – in this study and found the technique to be useful in separating the capacitive and the Faradaic contributions to the total charge. It is noted that the presence of carbon at the Pb-interface substantially enhances the electrochemical activity and increases the Faradaic charge, while high surface area carbons add to the capacitive charge. The technique is further used to study combinations of carbons as physical mixtures and bilayers.

1. Introduction

Lead–acid battery technology, although over 150 years old, plays a leading role in the rechargeable battery market globally and finds wide-scale application in automotive and industrial markets. In new applications requiring high rate partial state of charge (HRPSoC) operation, such as hybrid vehicles and certain grid storage applications, the performance and life of lead–acid battery are severely limited due to negative plate sulfation. These shortcomings are overcome by the inclusion of an appropriate form of carbon as an additive in the negative plate [1–4]. This battery technology is commonly referred to as the lead–carbon battery or the carbon lead–acid battery (CLAB) and is currently the only mass produced and viable technology available for start–stop and basic micro-hybrid vehicles [5]. It is expected that the CLAB technology will play a major role in grid storage applications in the future [6,7].

Carbon additives have been experimentally observed to suppress hard sulfation on the surface of the negative plate, which has been the main failure mode of lead–acid batteries under PSoC operation [8]. Different types of carbons – carbon black, acetylene black, activated carbon and graphite – have been looked at by various research groups and have resulted in varied degrees of performance enhancement [1,2,4,7,9,10]. Much of the research literature available on these carbon additives is based primarily on empirical studies showing cycle life improvements. The reaction mechanism and the key properties (physical, chemical) of carbon which benefit the negative plate are yet not properly understood and a number of possible reasons for the improved performance of the negative plate have been put forward. Moseley [11] proposed several potential mechanisms including that carbon improves electronic conductivity of negative active material (NAM) in PSoC condition, that carbon introduces double layer capacitance which acts as a buffer to the charge and the discharge cycles of the negative plate, that carbon restricts $PbSO_4$ crystallite growth in NAM and that carbon impedes hydrogen evolution due to the presence of impurities. In addition, Pavlov et al. [12] have proposed another mechanism in which carbon promotes lead deposition electrocatalytically in NAM and improves HRPSoC performance.

Recently, Pavlov and Nikolov [13] and Xiang et al. [14] have highlighted the key processes in the capacitive behavior of the carbon additives in high rate charge and discharge conditions. They have studied the effect of carbon particle size on the porous structure of NAM and the consequent effect on HRPSoC performance and they have proposed models based on double layer capacitance arising from carbons with different particle sizes. Their studies concluded that nano-sized carbon particles result in a NAM structure with pores of less than a micron size, which severely restrict ion movement resulting in poor electrode performance. On the other hand, larger carbon particles of several tens of microns produce a highly porous structure, which results in improved HRPSoC performance. The key finding from these studies is that for the double layer capacitance of carbon to be effective as a buffer in high rate charge and discharge cycles of negative plate, a

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http://dx.doi.org/10.1016/j.est.2015.05.002

highly porous NAM structure with embedded carbon particles in the NAM's backbone is required.

In the same study, Pavlov and Nikolov [13] showed that the dominating process in the electrode reaction is the double layer capacitance (non-Faradaic process) when the charge and the discharge cycles are limited to 5 s of duration. If the charge and the discharge duration are between 30 and 50 s, then the electrochemical reactions (Faradaic processes), related to lead sulfate dissolution or lead deposition, dominate which limit the life of the battery. In order to increase the HRPSoC life of a lead–acid battery, the capacitive contribution needs to be higher such that the cycling of the Faradaic processes is kept to the minimum. The capacitance of the electrode is determined not only by the form, size and loading of the carbon but more importantly by how the carbon is incorporated into the negative plate matrix. The carbon content is limited to around 2% of the NAM, largely due to the electrode processing parameters. Given this limitation on the carbon loading, the effectiveness of the resultant capacitance is limited to high rate charge and discharge cycles of about 5 s duration as shown by Pavlov and Nikolov [13]. Thus the use of CLAB is expected to be mainly limited to start–stop and micro-hybrid applications, where the key criterion is the short duration of high rate charge and discharge cycles.

Following the CLAB approach, further increment in the capacitance of the negative plate would allow the lead–acid battery to go beyond micro-hybrid applications. The batteries then would be well suited for mild-hybrids where the battery is cycled deeper than in micro-hybrid applications. Increased capacitance without impacting the energy density has been achieved in the UltraBattery® by incorporating a supercapacitor layer over the lead negative-electrode of a CLAB [15–17].

It is evident from earlier works [13,14] that an appropriate carbon should promote both the Faradaic and the capacitive processes to improve the performance of the lead–acid battery in HRPSoC operation. Understanding of the differences between the Faradaic and the capacitive processes due to the addition of carbon to the negative plate is limited to a few studies in the literature [18–20]. Pavlov et al. [18] employed cyclic voltammetry (CV) technique to demonstrate the behavior of different carbons with respect to electrocatalytic activity toward Pb^{2+} reduction and capacitive contribution. The usefulness of the same technique for screening various additives for the negative-electrode was shown by one of the authors [19]. In this study, we have employed CV to study the electrochemical properties of different carbons at the Pb interface in the negative plate of a lead–acid battery and have separated the Faradaic and the capacitive processes in the electrode reaction.

2. Materials and methods

Three types of carbon were looked at in this study – carbon black (CB-1, CB-2, CB-3), acetylene black (AB) and graphite (G). Specific surface area (SSA), apparent density and tap density of the carbons were measured using Thermo Electron Sorptomatic 1990, Scott volumeter and a home-made device, respectively. Electrical resistance of compressed carbon powders was measured in a home-made die in a 2-probe configuration and the resistance was normalized against weight.

Electrochemical properties of the carbons were studied in a test fixture, shown in Fig. 1, based on earlier works [12,19,20]. Two type of electrodes in rod shape were used – Pb and carbon. The Pb-electrode was cast from 99.999% pure metal, while the carbon-electrode was taken from a new dry AA pencil-cell. The electrode was encapsulated in a Teflon holder such that only the end ($0.2\ cm^2$ area) of the rod is exposed to electrolyte. All experiments were conducted in H_2SO_4 electrolyte with specific gravity of 1.28 g/cc.

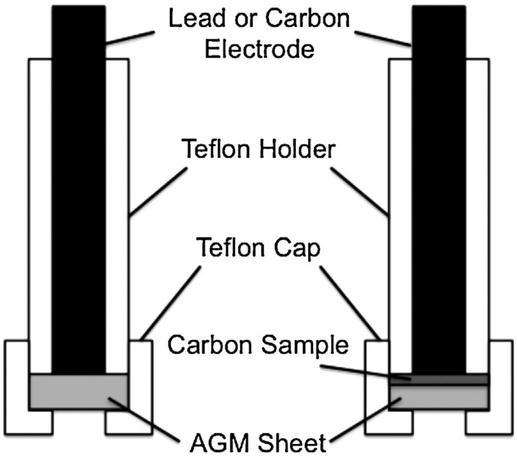

Fig. 1. Electrode assembly used in the study.

Two layers of AGM separator were soaked in the electrolyte and placed into a Teflon-cap. Carbon powder sample (5–50 mg) was poured on the AGM layer and then spread uniformly by tapping the Teflon-cap. A few drops of the electrolyte were added to wet the carbon layer and to ensure a good contact with the electrode. The Teflon-holder with electrode (Pb or C) was then finally added to complete the assembly. Cyclic voltammetry studies were conducted in a three-electrode configuration with Hg/Hg_2SO_4 (MSE) as reference-electrode and Pt-foil as counter-electrode using Metrohm μAutolab Type III Potentiostat/Galvanostat. Scans were done at 20 mV/sec between −1.3 and −0.7 V with respect to MSE; duplicate measurements were done to verify the repeatability. The charge capacity (coulomb) using the Pb-electrode was broken down into contributions from Faradaic-Pb ($Pb/PbSO_4$ reaction), capacitive (double layer adsorption/desorption) and Faradaic-H_2 (gas evolution) as illustrated in Fig. 2. Sweep direction is indicated by arrow-heads in the Fig. 2, which is the same for all CVs presented in this study. The capacitive contribution was estimated from the CV curve using the carbon-electrode, while the Faradaic-Pb contribution was estimated from the area under the peak using the Pb-electrode with base line fitting. Balance in the CV curve using the Pb-electrode gave the Faradaic-H_2 contribution.

Physical mixtures and bilayers of two different carbon types were also studied in a 50:50 weight ratio and the performance was compared to that of individual carbons. The total weight of carbon

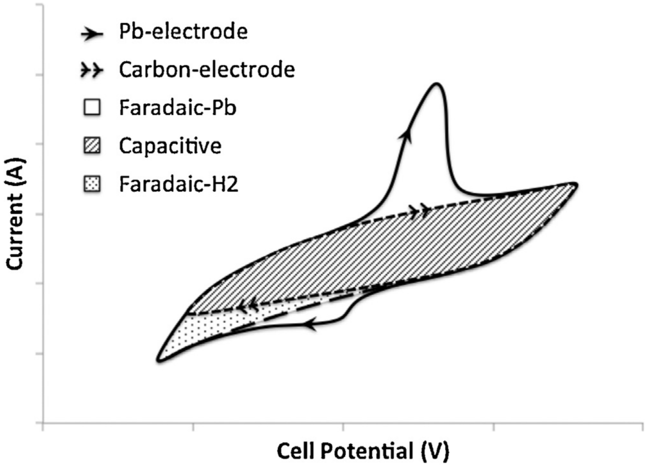

Fig. 2. Separation of Faradaic-Pb ($Pb/PbSO_4$ reaction), capacitive (double layer adsorption/desorption) and Faradaic-H_2 (gas evolution) contributions from CV curves with Pb-electrode and carbon-electrode.