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Optimization studies of carbon additives to negative active material for the purpose of extending the life of VRLA batteries in high-rate partial-state-of-charge operation

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ABSTRACT

The negative plates of lead-acid batteries subjected to partial-state-of-charge (PSOC) operation fail because of the development of an electrically inert film of lead sulfate on their surfaces. It has been found that carbon additives to the negative active material can significantly increase their cycle life in this type of operation. In this paper we show that various types of carbon, including graphite, carbon black eliminate the surface development of lead sulfate and that, in their presence, the lead sulfate becomes homogeneously distributed throughout the active material. Examination of active material by energy dispersive spectroscopy after extensive cycling shows that lead formed during charge of lead sulfate preferentially deposits on the carbon particles that have been embedded in the active material. Electrochemical studies have been carried out on a number of types of carbon additives having a wide range of properties. These included flake, expanded and synthetic graphite, isotropically graphitized carbon, carbon black and activated carbon. We have investigated their effect on the resistivity and surface areas of the negative active material and also on such electrochemical properties as active material utilization and cycle life. Most of the carbon additives increase the utilization of the active material and impressive increases in cycle life have been obtained with over 6000 capacity turnovers having been achieved. However, at this time, we have not been able to correlate either the type or the properties of the carbon with capacity or cycle life. Further work is needed in this area. The increases that have been achieved in cycle life provide evidence that the lead-acid battery is a viable low cost option for hybrid-electric vehicle use.

1. Introduction

When VRLA batteries are used in a partial-state-of-charge (PSOC) mode, as in hybrid electric vehicles, an electrochemically passive film of lead sulfate is formed on the surface of the negative plates [1]. This becomes thicker with further cycling and causes a progressive reduction of capacity leading to premature failure. Furthermore, this film cannot be reduced to lead by conventional recovery cycling. Interestingly, this finding is one of the few instances where lead-acid battery life is limited by the negative electrode. This phenomenon does not occur in the positive plate nor does it appear to be a function of oxygen reduction since it also occurs in flooded batteries [2].

Recent work, primarily supported by the Advanced Lead-Acid Battery Consortium (ALABC) [3] has shown that this problem can be eliminated by addition of higher than usual levels of carbon to the negative active material. Different types of carbon have been found to be effective such as carbon black and graphite. This work has been confirmed by battery manufacturers in full-sized, commercially built batteries [4] where cycle lives of up to 300,000 PSOC cycles have been achieved. Without the carbon additives the life is reduced to only 25,000 cycles.

The reasons why carbon is so effective are not understood. This may be because there has been no organized, systematic study of how the various chemical and physical properties of carbons affect PSOC cycle life. This is understandable since the beneficial effects have only recently been discovered and there are many forms of carbon (carbon black, activated carbon, graphite, etc.) whose properties span a wide range of physical differences, making it a lengthy task to investigate all of them. Additionally, within each class of carbon there are wide ranges of properties. For example different types of carbon black show wide ranges of:

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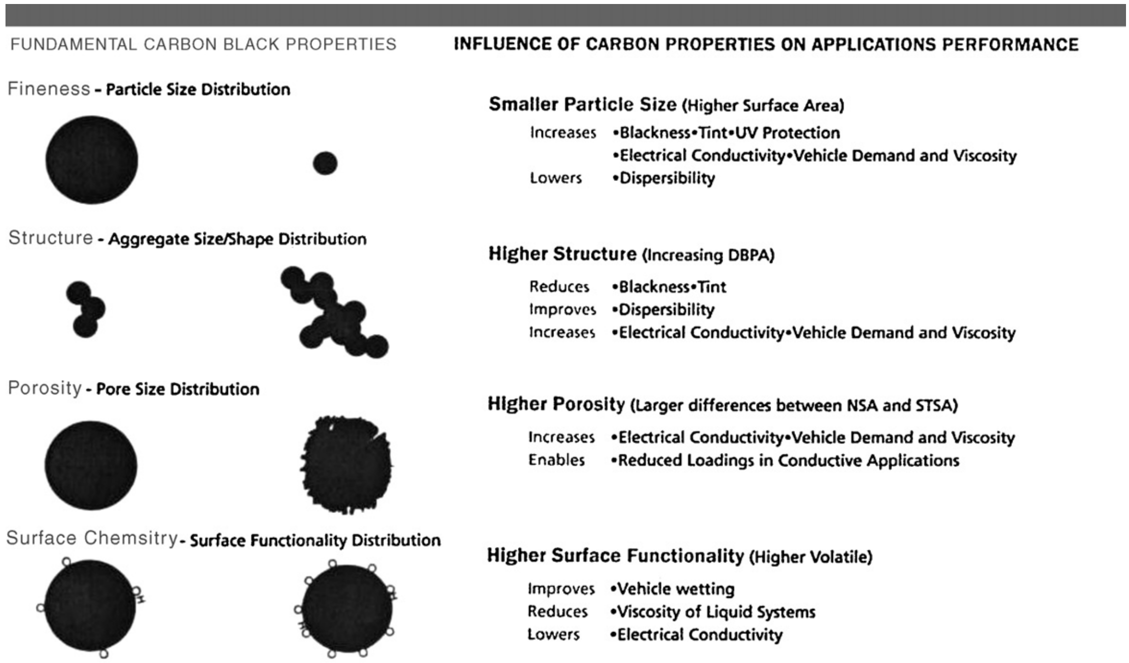

Fig. 1. Influence of carbon black properties on function. DBPA: dibutyl phthalate absorption; NSA: nitrogen surface area (BET); STSA: statistical thickness surface area.

- particle size distribution;
- aggregate size and shape (structure);
- surface area;
- electrical conductivity;
- porosity;
- surface functionality.

Each of these properties, either separately or in combination, may have an influence on the electrochemical behavior of the negative plate. Some of these influences are shown in Fig. 1.

There are also several types of graphite, some of which have already been evaluated [5]. These include natural flake, synthetic and expanded varieties. Differences in cycle life have been reported from these materials [6].

Activated carbons, although not presently used in lead-acid batteries, have also been considered as candidate materials since they possess properties that promote reactions on their surfaces. An example of this is their use in catalytic converters in automobiles. Recent unpublished work, carried out in our laboratories, has shown that they also have the capacity to improve cycle life in PSOC operation.

Before a specification for carbon can be defined, there must be improved understanding of how the different types, and variations within those types, influence the behavior of negative electrodes in PSOC operation. Fortunately, previous work has yielded important clues, particularly that certain forms of graphite and carbon black are very effective in improving PSOC cycle life. We now need to define the critical characteristics of these materials so that the optimum choice can be made for the VRLA battery in hybrid electric vehicles.

Scholz et al. [7,8] have suggested that direct electrochemical reduction of lead compounds in hydrochloric acid can take place in the solid state on graphite paste electrodes and that the reduction takes place through epitactic solid state conversion without any dissolved intermediates. A similar mechanism may occur during reduction of lead sulfate in sulfuric acid. More recently Pavlov et al. [9] have proposed that electrochemical reduction of lead ions to lead in sulfuric acid takes place preferentially on the surface of electrochemically active carbon. The beneficial properties of carbon make it worthwhile to carry out further work to optimize its properties and to elucidate the mechanism by which it increases PSOC cycle life.

This paper describes a program of work to evaluate several types of carbon, including graphite, activated carbon and carbon black in the negative electrodes of VRLA batteries undergoing PSOC cycling to determine which properties are the most important in achieving long service life. It involves determining the effects of these materials on the conductivity of lead sulfate and NAM, electrochemical testing and studying the effects of the materials on the morphology of the active material before, during and after cycling.

2. Experimental approach

Two separate studies have been carried out. In the first of these (Task 1), only two types of carbon were studied, carbon black and purified natural flake graphite. The carbon materials that were selected are shown in Table 1 with some of their physical properties.

The carbon black was chosen because of its relatively high specific surface area, long chain length and small particle size while

Table 1
Selected physical properties of carbon additives used in Task 1 studies.

Additive	Surface area ($m^2\,g^{-1}$)	Mean particle size	Conductivity ($\Omega^{-1}\,cm^{-1}$)	Supplier
Carbon black Grade: N134	143	18 nm	100	S. D. Richardson Company, 3560 W. Market Street, Suite 420, Akron, OH 44333, USA
Purified Flake Graphite Grade: 2939APH	9	28 μm	100	Superior Graphite Co., 4201 W. 36th Street, Chicago, IL 60632, USA