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Influence of electrically conductive polymers on the operating parameters of lead/acid batteries

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Abstract

An investigation has been made of the possible application of electrically conductive polymers in efforts to improve the performance of lead/acid batteries. Results show that the new class of organic compounds may be used as modifiers of the active material to suppress self-discharge and irreversible sulfation and to increase the specific capacity of the battery, especially under automotive discharge rates and at low temperature. © 1997 Elsevier Science S.A.

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1. Introduction

In spite of the fact that the lead/acid battery has been in production for more than a hundred years and has been well studied, work continues on its improvement. During the past few years, the influence of additives intended to be introduced into the active paste, grid alloy or the electrolyte have been studied. The mechanisms of their influence are different. Analysis of the data available from the literature and other sources enables a distinction to be made between three classes of such modifiers, namely, those that influence: (i) the structure of the corrosion film; (ii) the morphology of lead dioxide, and (iii) the porosity and the structure of pores within the active paste.

The additives of type (i) are intended to moderate the effects of the layer at the interface between the grid and the active material. It has been shown that the structure of the film formed on the grid surface during the anode polarization of the electrode exerts a significant effect on the capacity of the electrode. For example, the interface resistance decreases when the surface layer becomes denser.

Modifiers of type (ii) influence the morphology of the active material. As a rule, the mode of their action is via adsorption. When adsorbed on the surface of the crystals of lead dioxide, these additives lead to the formation of dispersed deposits and thus increase the active surface of the electrode and decrease the real current density.

Many studies have been dedicated to examining the action of modifiers of type (iii) in influencing the porosity and structure of the pores. These additives are normally introduced into the active material. During plate formation, the additives dissolve in the electrolyte and, thereby, cause an increase in the porosity of the active material.

It is considered worthwhile to investigate the influence of the addition of electrically conductive polymers, such as polyaniline, polypyrrol, etc., on the operating mode of the lead/acid batteries since these polymers combine almost all of the useful properties of the above additives and are relatively stable.

2. Experimental results

The usual way to introduce the conductive polymers into the battery is to add them in the form of pre-synthesized powder during the production of the electrode-active material. It is also possible to use a mixture of the monomer precursors and corresponding catalysts and perform the subsequent oxidative polymerization either during plate formation or during operation of the battery. Through

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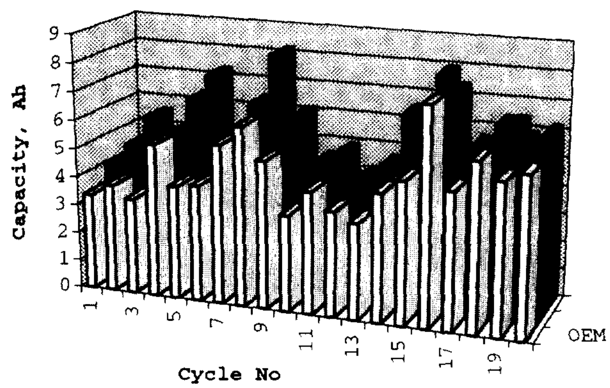

Fig. 1. Discharge curves of batteries at the 5 h rate.

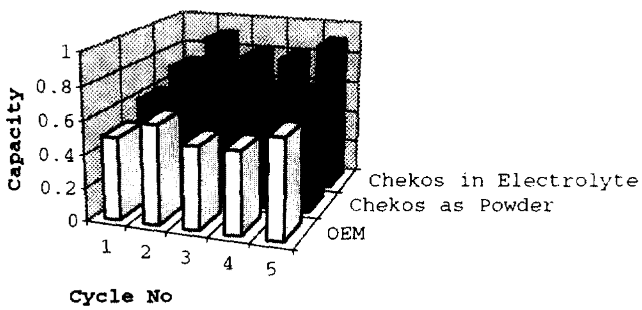

Fig. 2. Discharge to automotive batteries at − 18 °C.

application of a formulation produced in Russia under the trademark Chekos®, an increase in specific capacity of 10.20% has been achieved (Figs. 1–3).

It should be noted that the introduction of poly(paraphenylene), whose conductivity is relatively small, causes a decrease in capacity. Furthermore, the capacity decrease with increase in discharge current density, that is usually observed with lead/acid automotive batteries, is suppressed significantly by the polymer modifiers.

The optimal concentration of the additive was found to be equal to 1 wt.% when applying the pre-synthesized

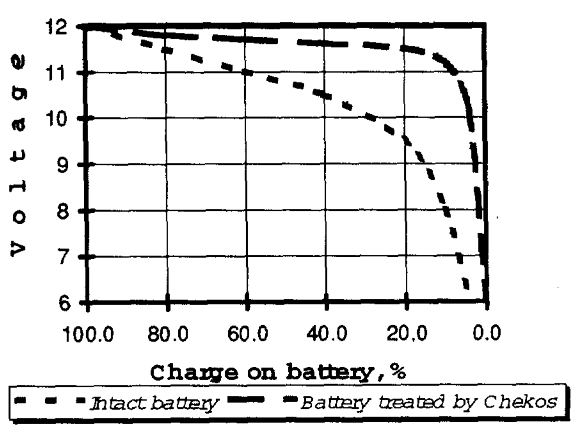

Fig. 3. Discharge curves of a normal battery and one with Chekos® modifier.

Fig. 4. Surface of the anode of a lead/acid battery treated by modifier Chekos®; specific surface area: 6 m^2 g^{-1}; magnification: ×100.

polymer powder, and to be lower by an order of magnitude when introducing the precursors together with catalyst with subsequent oxidative polymerization. An observed increase in the active-material utilization of 55.65% supports the conclusion that introduction of the polyaniline-based modifiers might be promising.

The exact mechanism of the influence of the addition of the electrically conductive polymers is now being investigated. The data show that changes in the phase composition, for instance, enrichment up to 90–95% β-PbO_2, increase the specific surface of electrodes by up to 5.6 m^2 (see Figs. 4 and 5) and cause significant suppression of self-discharge.

Work to determine the optimal concentration of the conductive polymers and investigation of the mechanism of their influence on the operating mode of the lead/acid battery are presently in progress. Even now, however, given that significant experience of the introduction of conductive polymer modifiers into the batteries of different

Fig. 5. Surface of the anode of a lead/acid battery without any additives; specific surface area: 3 m^2 g^{-1}.

types (e.g. starting, high-capacity) has been achieved, it may be concluded that modifiers based on polyaniline (the most stable and inexpensive to produce) may be highly beneficial.

3. Future work

The mechanism of the influence of the above additives is being investigated with different techniques of electrochemistry and physical chemistry. A mathematical description of the processes during the functioning of the active material (i.e. percolation, electrolyte diffusion in the pores, statistical optimization of the composition) is under development and is expected to allow the development of models of these processes and to elaborate approaches towards the improvement of electrochemical power sources.