Influence of phosphate containing additive in the formation electrolyte on the structure and cycling performance of lead battery positive active mass

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Lead batteries are one of the most popular energy sources that have applications in micro and mild electric hybrid vehicles, stationary energy storage systems and smart utility grid units. Their low cost and high reliability generally make lead batteries an appealing choice. The lead battery capacity decline over time as the battery is repeatedly charged and discharged. This effect is especially noticed at partial state-of-charge (PSoC) cycling conditions. In many cases, this is due to the processes taking place on the positive electrode of the battery. The major factors contributing to the decline in capacity of the positive plates during operation are progressive decrease of the electrical contact between the PbO_2 particles of the positive active mass (PAM) and the grid, and formation of a layer of $PbSO_4$ crystals on the electrode surface that isolates a fraction of the active mass thus reducing its utilization. During charge of a lead battery, the positive grid is oxidized, and a boundary layer forms between the grid and the active mass.

The focus of our investigation is to study the effects of phosphate containing substance as formation electrolyte additive on the structure of PAM at 17.5 % depth-of-discharge (DoD) employing PSoC protocol for automotive applications. The electrolyte additive selected for this study is similar to the one of the substances recently reported by our team [1, 2]. The investigated amounts of phosphate substance added to cell electrolyte (0.1, 0.3, 0.6 and 1.2 wt.%) were dissolved in 1.25 g/cm^3 H_2SO_4 solutions. Flooded type laboratory test cells with 2 positive plates and 3 negative plates with rated capacity of 4.0 Ah at 20 h rate of discharge and 50 % utilization of PAM were used to evaluate the influence of the selected electrolyte additive. Blank cell without the additive in the electrolyte was also tested. After formation the cells are subjected to the following electrical tests: C_{20} capacities and 17.5 % DoD test. The phase composition, morphology and microstructure, specific surface, and pore structure of freshly formed and cycled PAM samples was determined by X-ray diffraction, scanning electron microscopy, BET method and Hg porosimetry.

On grounds of the obtained results of the present study, it can be concluded that in the presence of studied additive in the formation electrolyte the specific surface area of PAM enlarged. The cycle life of the cell doped with 0.3 wt.% phosphate containing substance is 2100 cycles, which is a remarkable ~2× improvement *vs.* the blank cell. After cycling test with 17.5 % DoD XRD data confirm that addition of phosphate containing substance in the electrolyte suppresses formation of β-PbO_2 structure with high degree of crystallinity whereas preserves higher content of the α-PbO_2 phase. After cycling for the PAM of Blank sample the volume of pores with radii below 0.2 μm considerably decrease. In contrast, for the PAM of sample formed and cycled in the presence of 0.3 % A, the volume of pores with radii below 0.2 μm increases.

These results demonstrate that selected substance is promising additive for lead batteries that operate under partial-state-of-charge conditions.

References

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