Evaluation of nanostructured ZnO materials on the structure and performance of $Pb/PbSO_4$ electrode

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Batteries in micro-hybrid electric vehicles operate in partial state of charge and experience short charge and discharge pulses with high currents during regenerative braking (High-Rate Partial-State-of-Charge, HRPSoC duty). Research efforts in the past few years have demonstrated the benefits of carbon materials as additives to the negative plates of lead-acid batteries (LABs) providing higher levels of charge acceptance and delaying lead sulphate accumulation on the surface of the negative plates. At the same time, however, other properties such as high rate discharge and accelerated hydrogen evolution reaction (HER) leading to increased water loss may be negatively affected by carbon addition. Several different approaches are proposed in the literature to suppress the hydrogen evolution reaction on lead and lead-carbon electrodes. One example is addition of different metal oxides, organic substances, and metal ions with high HER overvoltage to the negative active mass (NAM) formulation or to the electrolyte. The influence of seventeen residual elements in lead on hydrogen- and/or oxygen-gassing rates of LABs has been investigated [1]. Only Bi, Cd, Sn and Zn are considered as "beneficial elements" for lead-acid batteries. Addition of ZnO and ZnSO4 to NAM is proposed in order to improve the HRPSoC performance and to control the HER [2].

The goal of the present study is to evaluate the effect of crystal morphology of ZnO powder samples with different crystallite size as additives to NAM aimed to improve the HRPSoC cycling performance of LABs and suppress the HER. The studied ZnO samples are synthesized by ultrasound assisted precipitation (UAP) and by a sucrose-assisted solution combustion method (SASC). The latter method was applied to prepare ZnO samples doped with Al or Mg ions. The thus synthesized materials are evaluated by means of powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. The XRD analysis confirms that materials obtained by the different methods have similar average crystallite size of about 30 to 40 nm. The TEM images demonstrate that the samples obtained by the UAP method have spindle-like morphology, while those obtained by the SASC method comprise almost spherical particles [3].

Small-sized laboratory lead-acid cells with one negative and two positive plates per cell are assembled and set to capacity, cycle life and hydrogen evolution tests. The nominal capacity of cells is 115 mAh. The tested ZnO samples are added during negative paste mixing in concentration of 0.05 % versus the leady oxide. All negative paste formulations contain also 0.5 % PBX51 carbon black (1400 m^2/g) (Cabot Corp. product). The thus prepared paste is applied to small-sized PbCaSn grids and these are subjected to standard curing and formation processes. For comparison, reference cells without ZnO additives are tested as well.

The impact of the studied ZnO additives on the discharge capacity of the negative plates is estimated at C/20 discharge current rate. The preliminary results show that ZnO additives to NAM do not have negative impact on cell discharge capacity. The effect of addition of ZnO in the negative plate on the cycle life of lead-acid cells is evaluated under simulated high-rate partial state-of-charge (HRPSoC) cycling conditions. The negative plate potential is measured during the cycling test. The control cell (without carbon additive) completes only 600 micro-cycles. Addition of ZnO (SASC) to NAM leads to considerable improvement in cycle life, more than 3800 micro-cycles. In contrast, the reference cell with 0.5% PBX51 but no ZnO in NAM completes about 3000 micro-cycles, against about 2900 for the cell containing also ZnO (UAP) additive and about 3500 micro-cycles completed by the cells with ZnO (SASC), doped with Al+ or Mg+, in NAM. In general, addition of ZnO (SASC), comprising spherical particles of 50-60 nm average size, to NAM produce 15-25 % improvement in cell cycle life in the HRPSoC duty.

References

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