



Short communication

## Porous microspheres as additives in lead–acid batteries

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## ABSTRACT

The theoretical specific energy of the lead/acid battery is  $176 \text{ Wh kg}^{-1}$ . The specific energy actually achieved depends on the discharge rate but is typically only about 15–25% of this maximum value. The major reason for the lead acid battery's inability to obtain higher specific energies is that much of the active material in both the positive and negative electrode is not discharged. This is especially true at the higher discharge rates where the diffusion of sulfate ions into the positive plate limits the reaction. Porous, hollow, glass microspheres (PHGM) would allow for more electrolyte storage in the electrodes and enhance the high rate energy storage of lead acid batteries. In this paper, we present a method for making hollow, glass microspheres (HGMs) porous. Presently our process only produces small yields. We believe in the future that the yields with our process can be substantially increased. PHGMs could substantially improve the high rate performance of lead acid batteries and make these batteries more attractive for hybrid electric vehicle applications.

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### 1. Introduction

The lead–acid battery has a high volumetric energy density, high specific power performance, and high power density. This coupled with the low cost of materials makes it an excellent power source for use in electric and hybrid electric vehicles (HEVs). Improving the specific energy performance of these batteries would help them in these HEV applications. This is particularly true for the plug-in HEVs (PHEVs) which can be charged from the power grid and can be driven as an electric vehicle for short distances without operating on internal combustion engines. Because a typical vehicle on a daily basis is driven less than 80 km 80% of the time, a PHEV having an electric vehicle range of 80 km would satisfy most daily driving requirements. For this PHEV application, increasing the specific energy performance at the high discharge rates, 1 h or higher, is desirable. A battery that could provide a 1 h discharge for a PHEV travelling at 88 km/h would provide an electric vehicle range that would satisfy most daily driving needs. Improving the high specific energy performance of lead acid batteries is therefore important for PHEV applications.

Although the lead acid battery's overall chemical reaction has been well known for years, the system is complex and some of the physical mechanisms that limit the reaction under different scenarios are not well understood. The theoretical specific energy of the lead/acid battery is  $176 \text{ Wh kg}^{-1}$ . The specific energy actually

achieved depends on the discharge rate but is typically only about 15% of the maximum  $176 \text{ Wh kg}^{-1}$  number [1,2] at high discharge rates. The major reason for the lead acid battery's inability to obtain higher specific energies is that much of the active material in both the positive and negative electrode is not discharged.

At normal discharge rates, diffusion usually limits the reaction whereas at low rates, where diffusion is less important, the conductivity of the active material in the electrode limits the reaction. Previous researchers [3–5] found that after a sufficient amount of active material had reacted, the remaining material became electronically isolated and could not react. The amount of active material that reacts before the remaining material becomes isolated is the maximum amount of material possible for reaction. The critical volume fraction is defined as this maximum amount of material that can react divided by the total amount of material available for reaction.

Fig. 1 shows the critical volume fraction of paste having different additives plotted against the per cent of additive volume. The figure is based on the results of a two-dimensional conductivity model developed at the University of Idaho (UI) where different size additives, both conductive and non-conductive, and different amounts of additives are used in the active material [6]. The different curves represent different size additives with the higher critical volume fraction curves associated with the conductive additives and the lower curves with the non-conductive additives. In the model, the active material is represented as square nodes and the smallest additive shown in the figure (i.e.  $1 \times 1$ ) is one node. The  $2 \times 2$  additive would therefore represent four nodes in the model. From our observations, we believe that a  $1 \times 1$  particle

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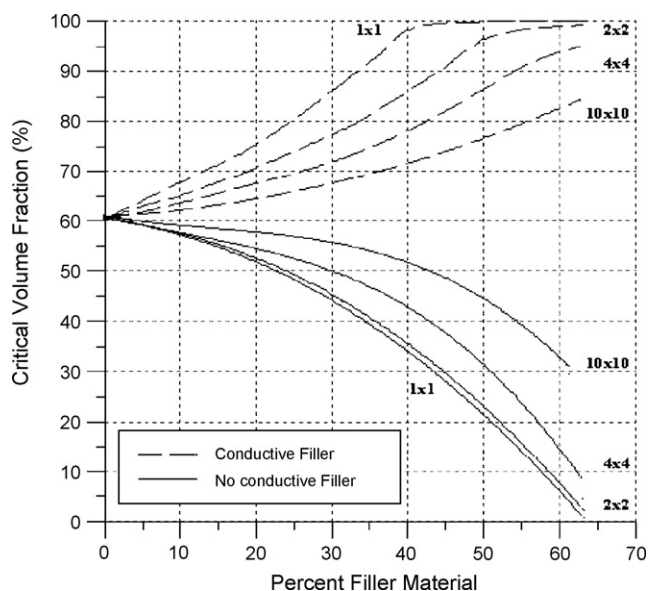


Fig. 1. Utilization curves for active material with additives [3].

in the model corresponds to approximately  $5\ \mu\text{m}$  (i.e.  $1\text{--}10\ \mu\text{m}$ ) particle in the in the active materiale (Fig. 1).

What the figure shows is that the utilization can be improved with small, conductive additives whereas large non-conductive additives do not significantly reduce utilization until a large volume percentage is used. Note that when no additives are used, the critical volume fraction is about 60%. These additives can be used to design batteries for specific applications. For instance, because ion diffusion in the electrolyte usually limits the reaction at normal rates, not conductivity, the active material utilization is usually less than 30%. Large porous hollow glass microspheres (PHGMs) would provide structure and allow for more electrolyte storage in the electrode without a large attendant drop in the critical volume fraction. Using these additives in both electrodes would improve the utilization of the active material at high rates and could significantly increase the specific energy performance of the lead acid batteries.

Sealed, lead acid batteries having no additives can have a specific energy performance at the 1–2 h rate of about  $30\ \text{Wh kg}^{-1}$ . In previous work [7], computer simulations show that using approximately 20% by volume of porous, hollow glass microspheres (PHGMs) could improve specific energy performance to approximately  $40\ \text{Wh kg}^{-1}$  at the 1 h discharge rate. The critical volume fraction determined from the conductivity model previously discussed is used in the second model [7] to determine cell behavior. The second model uses one-dimensional finite difference equations to solve for electrolyte concentration profiles throughout the cell as a function of time during discharge and to estimate active material utilization in both plates. Although these porous, hollow glass microspheres did not exist when the computer simulations were performed [7], we eventually were able to produce these PHGMs in small quantities as we will describe in this paper.

The PHGMs that we produced can be used to provide structure and electrolyte storage in the active material of both electrodes. The pore sizes we were able to create in the microspheres were typically a few microns in diameter and, as far as we can determine, are the only PHGMs ever produced that have these large diameter pores. Researchers at Savannah River National Laboratory (SRNL) [8–10] have developed another process for fabricating PHGMs that result in very small pores that we refer to as micropores. Researchers at the University of Idaho and SRNL are presently collaborating to improve these PHGM fabrication methods so that the PHGMs can be used to develop high performance sealed lead acid batteries.

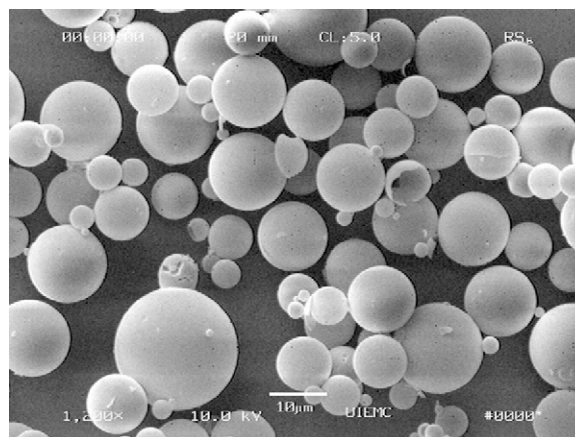


Fig. 2. Scanning electron micrograph of original borosilicate HGM.

In the remainder of the paper, we will present the experimental procedures used to fabricate our PHGMs, Section 2. In Section 3, we will give the results of our fabrication investigations and provide a discussion on these investigations. The conclusions to our work will be provided in Section 4.

## 2. Experimental procedures

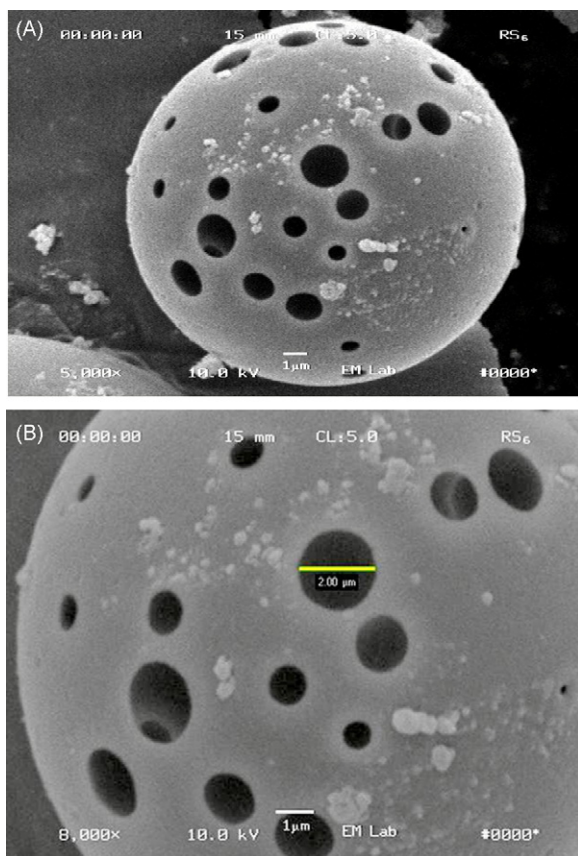
Porous hollow glass microspheres (HGM) were obtained by etching commercially available borosilicate glass hollow glass microspheres for different time intervals using hydrofluoric acid (HF) solution. Fig. 2 shows a scanning electron micrograph (SEM) of the glass microspheres which are commercially available. Concentrations of HF ranged from 2% to concentrated, and time of etching ranged from 5 min to overnight. The HF solution containing glass microspheres was constantly agitated via sonication and/or stirring with a Teflon coated magnetic stir bar. The samples were filtered, washed with purified water, and examined using scanning electron microscopy. A Hitachi S-2300 scanning electron microscope was used to examine the morphology of the etched hollow glass microspheres. The results of these investigation are discussed in the next section.

## 3. Results and discussion

Sodium borosilicate hollow glass microspheres are strong, low density additives used in a variety of industrial applications. Commercially they are available in a wide range of densities, sizes and crush strength. The as-received sodium borosilicate HGM has a size distribution range as shown in the scanning electron micrograph, Fig. 2 a density of  $0.25\ \text{g cm}^{-3}$  and a crush strength of 5.17 MPa. The presence of the broken debris of the HGM suggests that some microspheres were damaged during manufacture.

Using the technique described earlier, it is possible to produce porous hollow glass microspheres (PHGM) as shown in Fig. 3A. Some of the pores in the PHGM are as large as  $2\ \mu\text{m}$  in size (Fig. 3B). These pores are through the wall and provide a view of the interior of the hollow glass sphere (Fig. 4). As far as we know, these are the only PHGMs ever produced that has these large diameter holes.

While few borosilicate HGMs upon etching with hydrofluoric acid developed pores with spherical morphology of varying sizes (as shown above), they were consistently produced with low HF and agitation. In retrospect, the fabrication of these PHGMs, although what we desired, was a surprise. These experiments were conducted using dilute HF as a first step in determining a method for fabricating these types of PHGMs. However, the mechanism by which these holes are produced is unclear. Generally, it would be

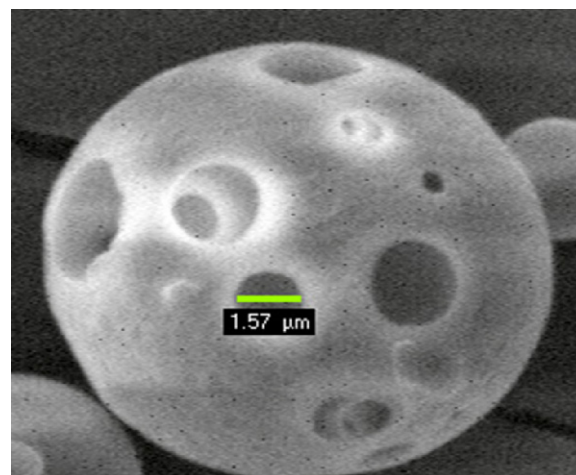


**Fig. 3.** Scanning electron micrograph of PHGM showing (A) general surface morphology and (B) size of the pores formed on the surface.

expected that the HF would uniformly etch the glass so that the shell would disappear but no large holes would be produced. However, most of the microspheres were etched on the surface as shown in Fig. 5, with only a few exhibiting the large pores that we desired. The etched HGM had uneven surfaces indicating the presence of one or more phases. It is possible the multiple phases are developed as a result of phase separation during the processing of borosilicate HGM. The uneven surface morphology on the etched borosilicate HGMs can be explained based on nucleation, growth, and spinodal decomposition mechanisms, respectively.

Phase transformation can take place via two processes [8–12]:

a. changes which are small to begin with but large spatially (Fig. 6a), and



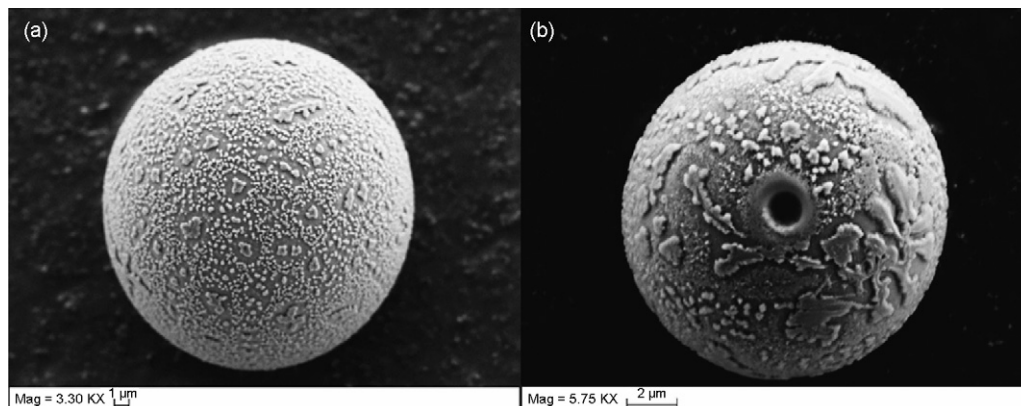
**Fig. 4.** Scanning electron micrograph of PHGM showing the pore on the rear surface.

b. changes, which are initially large in degree but small spatially (Fig. 6b).

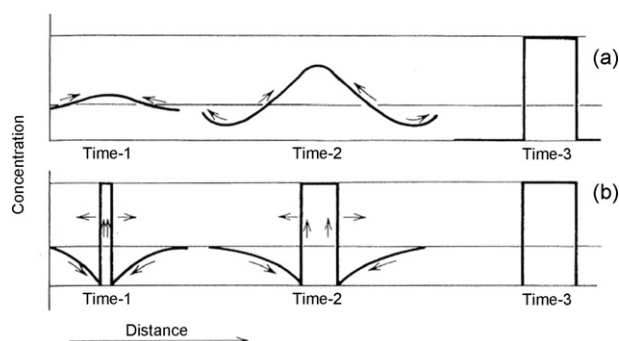
The first type of phase transformation is called spinodal decomposition; the latter is referred to as nucleation and growth. In classical nucleation and growth, the composition of the minor phase is constant throughout the transformation (Fig. 6b). During spinodal decomposition or continuous phase separation the compositions of the two phases change continuously resulting in two phase modulated structure (Fig. 6a). Note that the arrow indicates spatial distribution for the three time sequences shown in the figure.

Phase-separated glasses show two different morphologies which can be explained based on nucleation and growth and spinodal decomposition [12]. In one, individual spherical particles of one phase are imbedded in a matrix of the second phase. This is caused by nucleation and growth. In the second, the two phases are both continuous and interconnected and are caused primarily due to spinodal decomposition.

In the current study, in the absence of any heat treatment, the etching of the as-received borosilicate HGM with hydrofluoric acid resulted in different surface morphology. Some etched HGMs exhibited circular pores as large as 2 μm in diameter (Fig. 3B). These circular pores may be a result of the individual spherical particles of one phase being imbedded in a matrix of the second phase. The mechanism that governs the formation of these phases is nucleation and growth that occurs during the processing of HGM. One phase is more soluble in hydrofluoric acid than the other. The uneven surface morphology observed on borosilicate HGM could be explained



**Fig. 5.** Scanning electron micrograph of hollow glass microspheres etching using 1% HF for (a) 30 and (b) 60 min.



**Fig. 6.** Concentration profiles for (a) spinodal decomposition and (b) nucleation and growth.

based on phase separation that occurs due to spinodal decomposition (Fig. 5). These two phases show some amount of continuity and interconnectivity. It is possible that the type of large hole porosity seen in the etched HGMs is a result of droplet nucleation that occurred during the formation and cooling of the microsphere during the fabrication process.

A mechanical explanation for the large pores is also possible. The attractive PHGMs shown in Figs. 3 and 4 were produced in a dilute HF solution which was externally agitated. Unfortunately, the number of these PHGMs was not large, although we could always find some no matter where we looked with the SEM. The results were also reproducible in that every time we ran the experiment, we were able to produce a small quantity of good PHGMs. We believe that both the dilute HF solution and the agitation may be important to producing good PHGMs. Our possible explanation for these experimental results is that the dilute HF solution softens the glass but does not, at least in the short run, completely dissolve the glass. The agitation causes the microspheres to hit each other causing small craters to be formed on their soft surfaces. These craters are both thinner than the surrounding material and stressed. The HF acid dissolves these areas more quickly than the surrounding areas creating the large pores.

#### 4. Conclusions

Porous hollow glass microspheres were successfully developed by etching commercially available hollow glass microspheres using dilute HF solution. Etching of the HGM resulted in circular pores and uneven surface morphology. The study indicates that the pore size can be controlled by varying the HF concentration and duration of etching although the exact mechanism by which the large pores are created is not well understood. The uneven surface etching also shown can be attributed to either spinodal or nucleation and growth phase decompositions that result in selective etching of the microspheres. The porous hollow glass microspheres obtained can be used to store electrolyte and provide structure for both the positive and negative paste. The present research will benefit a wide range of lead acid battery designs and applications with particular importance for PHEVs.

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