



Short communication

## Fabrication of porous hollow glass microspheres

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### ARTICLE INFO

#### Article history:

Received 18 May 2011

Accepted 14 July 2011

Available online 23 July 2011

#### Keywords:

Lead-acid battery

Porous hollow glass microsphere

Porous additive

### ABSTRACT

Porous hollow glass microspheres have many uses, including porosity enhancers for lead-acid batteries. A fast, facile and high yield synthetic method for fabricating porous hollow glass microspheres with diameters around 45–55  $\mu\text{m}$  is demonstrated. The process involves shaking commercially available hollow glass microspheres in dilute hydrofluoric acid for 20 min. This process yielded two pore morphologies by using different commercially available starting materials; sponge-like submicron pores etched from S38 microspheres, and straight through micron pore etched from K25. Yields were 33% and 40%, respectively. The simplicity of the reported fabrication technique has the potential to be scaled up for large scale production.

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### 1. Introduction

Interest in porous hollow microspheres has increased due to the many proposed uses for such a material. Similar in use and function of silica gel [1], porous hollow microspheres have the added benefit of lower density due to the interior void space, increased storage capacity, and highly permeable surface. Uses of porous hollow microspheres (PHMs) include drug delivery vehicles for controlled release of antibody, anticancer and antibacterial drugs [2–8]. Their interior hollow volume and porous shells offer greater storage capacity and pathways for retaining and releasing these drugs than silica gel. PHMs have also been used to improve ultrasound image contrast and quality [9]. Further, PHMs have potential applications in lead-acid batteries [10], sensor materials [11], hydrogen storage for nuclear waste disposal, fuel cells [12], solar cell [13], chromatograph column fillers [14], and as micro reactors to encapsulate Pd for catalytic hydrodechlorination of chlorophenols in water [15].

Synthetic methods for PHMs fabrication include double emulsion [16,17], templating [4], sol-gel [18], spray drying [9], and glass phase separation and selective etching [19]. All these synthetic approaches suffer drawbacks such as time consuming procedures, low yields, chemical residues, and limited internal void volume.

In order to increase the utilization of the lead-acid battery at fast discharge rates (1 h rate and faster), mass transport of sulfuric acid and/or increased storage of acid inside the active material must be achieved. Although the theoretical specific energy of the lead-acid battery is 167  $\text{Wh kg}^{-1}$ , during a typical fast discharge only around 30  $\text{Wh kg}^{-1}$  is achieved [20]. The addition of hollow glass

microspheres has been shown to increase fast discharge utilization [21]. Adding porous hollow glass microspheres would allow the interior volume of the microspheres to be used as acid reservoirs as well as displacing unreacted active material.

In this work, we present a rapid, easy, low cost, and high yield synthetic method to produce porous hollow glass microspheres (PHGMs) for use as a lead-acid battery additive by chemically etching commercially available hollow glass bubbles from 3M<sup>TM</sup>. The starting hollow glass microspheres (HGMs) have diameters around 40–55  $\mu\text{m}$  and approximately 1  $\mu\text{m}$  walls thicknesses. Yields of 33–40% were obtained by shaking the microspheres in 1% HF for 20 min. Pore size varied from several hundred nm to 1.5  $\mu\text{m}$ . Pore morphology was observed to be either straight through (Swiss cheese-like) or tortuous (sponge-like) paths based on the starting material. The size of the starting materials was chosen based on their expected use as porosity enhancers for the lead-acid battery [22–25].

### 2. Materials and methods

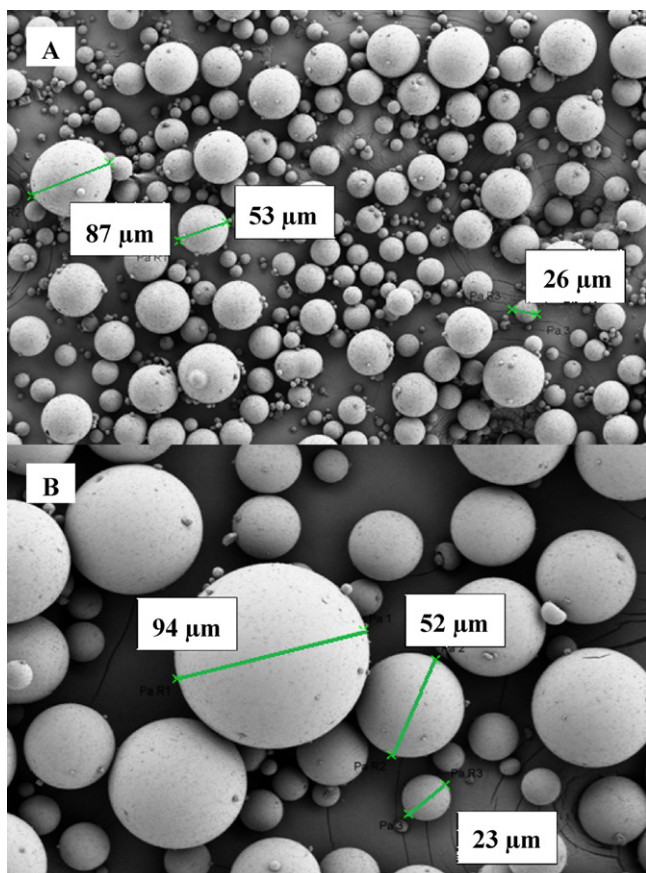
#### 2.1. Materials and apparatus

The S38 and K25 glass bubbles (HGMs) were obtained from 3M<sup>TM</sup> Co. (St. Paul, MN, USA). Table 1 lists several typical properties of these two products. Unmodified S38 and K25 as received from 3M<sup>TM</sup> are shown in Fig. 1. Hydrofluoric acid and sodium hydroxide were purchased from Fisher Scientific (Morris Plains, NJ, USA). The reciprocating shaker was obtained from Eberbach Corporation (Ann Arbor, MI, USA). All scanning electron micrographs (SEMs) were obtained with a Zeiss Supra 35 Scanning Electron Microscope (Carl Zeiss, Germany). Brunauer, Emmett, and Teller (BET) surface

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**Table 1**  
Typical properties of K25 and S38 glass bubbles from 3M™.

Product	50th% size ( $\mu\text{m}$ )	Isostatic crush strength (psi)	Density ( $\text{g cm}^{-3}$ )	Apx. wall thickness as measured ( $\mu\text{m}$ )
K25	55	750	0.25	1
S38	40	4000	0.38	1



**Fig. 1.** SEM of as received S38 glass bubbles (A), and K25 glass bubbles (B).

area was determined for as received and etched PHGM using a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA, USA).

Special precautions are needed when working with hydrofluoric acid. Calcium gluconate gel was always present during handling of HF. Waste HF was neutralized after use before disposal.

## 2.2. Porous hollow glass microspheres fabrication procedures

Porous hollow glass microspheres, PHGM S38 and PHGM K25, were fabricated by etching commercially available hollow glass microspheres (S38 and K25) with 1% hydrofluoric acid. Approx-

**Table 2**  
Multipoint BET analysis of as received 3M™ microspheres and porous etched microspheres.

Product	HGM surface area ( $\text{m}^2 \text{g}^{-1}$ )	PHGM surface area ( $\text{m}^2 \text{g}^{-1}$ )
K25	1.5548	3.0298
S38	1.0895	7.3854

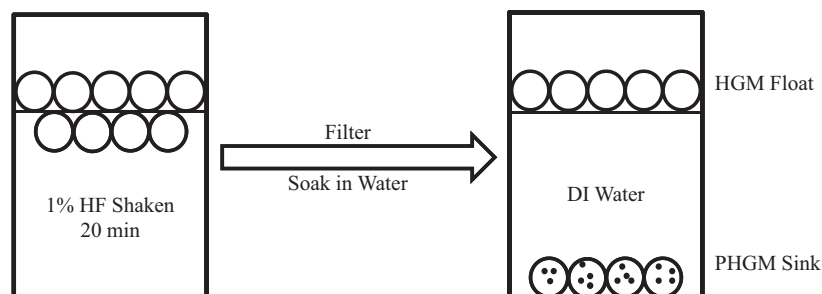
imately 3 g of HGM was mixed with 200 ml 1% HF acid in a well-sealed vial then placed in the reciprocating shaker for 20 min. After etching the spheres were vacuum filtered and rinsed with 200 ml of 2% NaOH then 500 ml of house deionized water. The collected and washed spheres were soaked in deionized water to separate the HGM (which floated on the surface) from the PHGM (which sank to the bottom) (Fig. 2). The PHGMs were then dried in an oven at 100 °C.

## 3. Results

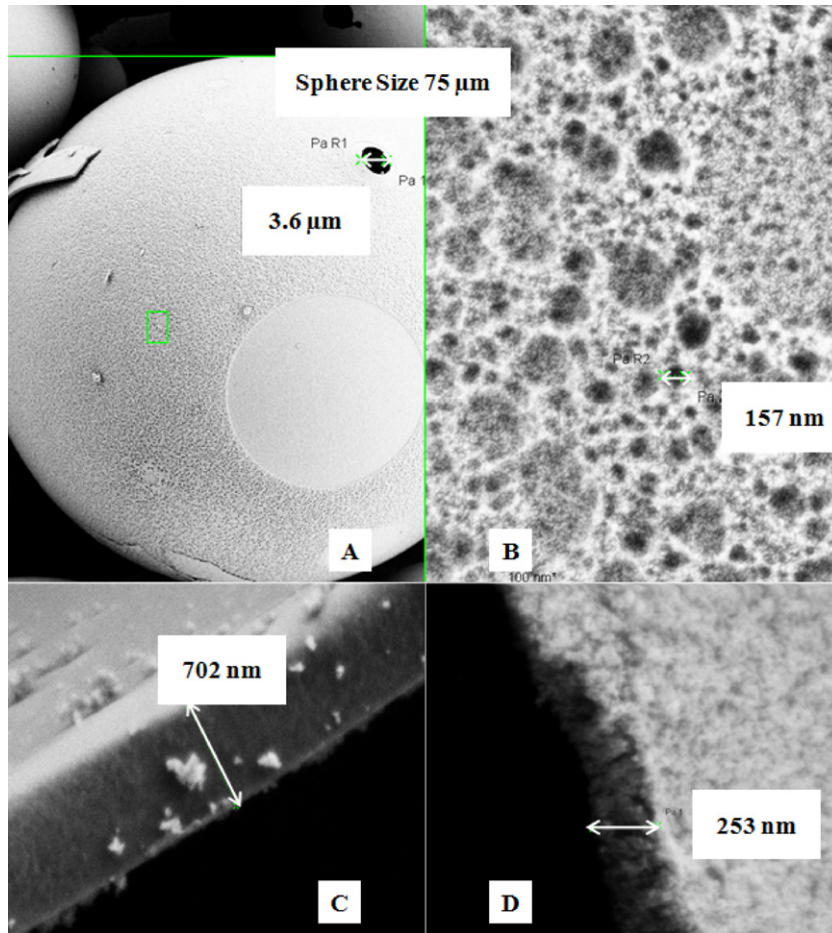
Fig. 3 shows the PHGMs produced after etching S38 glass microspheres with HF. Regular formation of pores smaller than 500 nm, with occasional formation of micron size pores (Fig. 3A and B). A comparison of the wall structure of the unmodified S38 and the porous S38 are shown in Fig. 3C/D. The wall structure changes significantly, going from a solid to a spongy porous one. Pores penetrate through the PHGM walls in a tortuous path pattern, as evidenced in the cross sectional SEM (Fig. 3D) and that they sink when added to water.

The pore structure of the etched K25 is markedly different than those of the porous S38. The circular pores had inconsistent diameters of between 0.2 and 2  $\mu\text{m}$  (average 0.86  $\mu\text{m}$ ) with an irregular number of pores per sphere developing (4–78 pores). Unlike tortuous path pores of the etched S38s the etched K25s had straight through or “Swiss cheese” pattern. Fig. 4 shows the pore formation of etched K25 with no sign of wall sponginess. The decrease in thickness was observed to be 60% (Fig. 4). Surface area measurements for both the PHGM K25 and PHGM S38 are listed in Table 2.

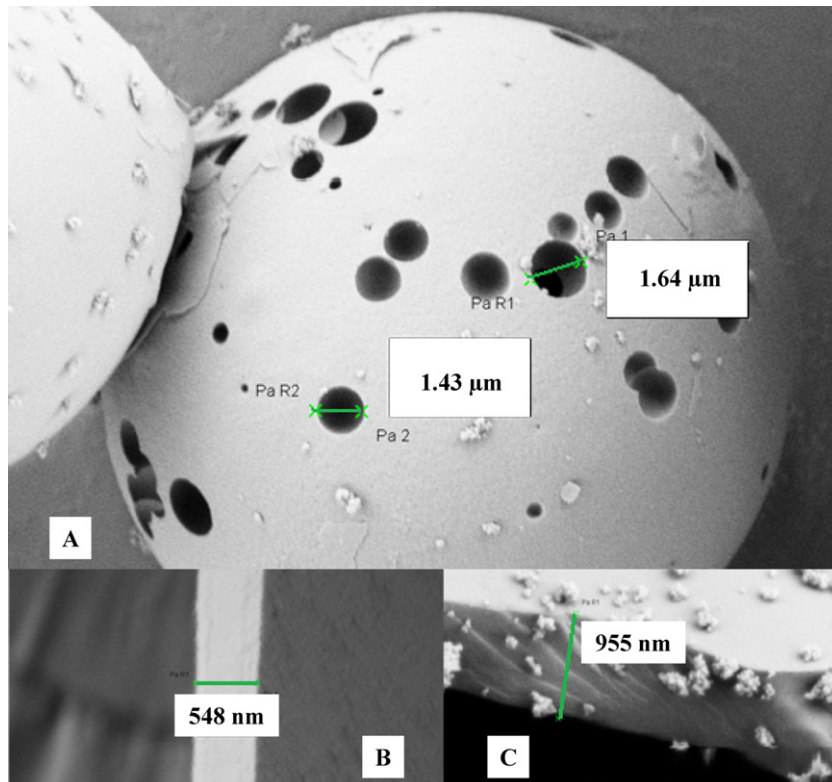
Etching parameters such as HF concentration, ratio of HF solution to spheres, etching time, and mixing technique were optimized. 200 mL of 1% HF for 20 min with 3 g of spheres on the shaker gave the highest yield of PHGM with the lowest amount of breakage. Other mixing techniques such as stirring and sonicating did not have the desired result that the reciprocating shaker did. Yields for the etching process for the PHGM S38 and PHGM K25 were approximately 33% and 40%, respectively.



**Fig. 2.** Schematic of etching HGM into PHGM.



**Fig. 3.** Porous hollow S38 after etching with HF (A), expanded view of region inside small square of A showing extensive surface porosity (B), wall thickness of unetched S38 (C), and wall thickness of etched S38 (D).



**Fig. 4.** Pore structure and size of etched K25 (A), wall thickness of etched K25 (B), and wall thickness of unetched K25 (C).

#### 4. Discussion

BET analysis of the surface area of the etched and non-etched spheres further differentiates the pore structure of the two products. The straight through pores of the PHGM K25 doubles the surface area over the HGM K25. Because of the spongy nature of the etched PHGM S38, the porosity is almost 7 times that of the HGM S38. The different pore structure of macro porous K25 and micron porous S38 hollow glass microspheres may be due to different chemical compositions of HGM K25 and HGM S38 during manufacturing. 3M™ reports that the spheres are all made of soda–lime–borosilicate glass, but the widely differing physical properties indicate differences in composition. A similar synthetic method has been reported previously [10]; however, the production yield increased significantly and control of pore size in the PHGM was obtained in this work.

#### 5. Conclusion

The simplicity of the PHGMs fabrication presented in this work has the potential of being scaled up, with yields potentially improved further with new instrumentation design. In addition to the ease of production, the pore size and structure can be controlled for with choice of easily obtained starting materials. This work offers a facile path to obtain PHGM which can be used as porosity enhancers for lead-acid batteries as well as precursor for further modification with metal oxides or other functional groups. Functionalized porous hollow spheres have been proposed for use in wide applications such as drug delivery [2–8], biosensors [26], catalysts [27], and lithium-ion batteries [28].

#### Role of the funding source

Work sponsored by the funding source was subject to final approval before submission for publication.

#### Acknowledgements

The authors are grateful to Exide Technologies for their financial support.

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