
Hollow Glass Microspheres as Micro Media for Complex Metal Hydrides Hydrogen Storage Compounds

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To improve the safety of handling and storing complex metal hydrides on board of automobiles, complex hydrides encapsulation in hollow glass porous microspheres was proposed and researched. Formation of intact hollow glass microspheres with an open through wall porosity following phase separation and acid leaching of the boron oxide rich phase was demonstrated. Encapsulation of sodium alanate within the prepared microspheres by diffusion through wall porosity was illustrated. The observation of unusual alanate structures in the form of needle bundles on the interior and exterior surfaces of the spheres following the encapsulation was obtained.

Introduction

Storing the hydrogen needed to power Proton Exchange Membrane Fuel Cell (PEMFC) stacks is considered the most challenging problem facing PEMFC vehicular applications. This is particularly due to the gravimetric and volumetric hydrogen density requirements in order to achieve a 300 mile cruising range. For example, the 2015 US Department of Energy revised system based targets require 5.5 wt% and 40 g/L onboard hydrogen storage density [1]. Unfortunately, due to hydrogen's very low density (i.e. 0.089 g/L at STP conditions), high pressure storage systems at 70 MPa are needed to achieve storage densities up to 4.4 wt% and 25 g/L [1]. Liquid cryostorage under 20 K (70.8 g/L) is another option for improving system based hydrogen densities to 6.5 wt% and 36 g/L [1]. However hydrogen liquefaction costs and boil off issues often make this approach impractical. Therefore, other strategies for storing hydrogen are needed in order to meet practical onboard storage requirements.

The utilization of complex metal hydrides for storing hydrogen has been an active research area due to their high hydrogen densities [2,3,4]. The interest in these materials for onboard storage was particularly catalyzed by Bogdanović's discovery in 1997 [5,6], which illustrated the possibility of using dopants such as titanium chloride in order to reverse sodium alanate (theoretical 7.4 wt% H₂); a property needed for onboard storage application. Since this discovery, complex metal hydrides have received considerable research attention which resulted in improved hydrogen release thermodynamics or kinetics [7], however, further enhancements in their hydrogen storage thermodynamic and kinetic properties are still needed if they were to become a viable alternative to the compressed hydrogen gas option for onboard storage.

An unfavorable property complex metal hydrides possess, from an application point of view, is their reactive nature when exposed to oxygen and moisture. While the extent of their

reactivity was observed to vary function of the elements forming the compound, i.e. alkaline based alanates are known to react more vigorously compared to the corresponding borohydrides, this reactivity does pose a safety concern for onboard storage. That is, even if their thermodynamics and kinetics properties reach their forecasted targets, the safety of their onboard storage could eventually hinder their utilization. While a safe onboard storage of complex metal hydrides could be achieved by engineering a suitable well protected tank (macro-level), it would be easier to handle and safer to store them if their reactive properties could be controlled on a micro-level utilizing a micro barrier against contact with the ambient. Therefore, we propose the concept of micro-level containment of reactive hydrogen compounds inside hollow glass porous microspheres. While solid and hollow glass microspheres; pioneered by Beck [8] and later expanded by Howell [9] and Marshall [10], have been made for many years for a variety of applications, the microspheres used in this work possessed two interconnected glass phases of different compositions; i.e. a silica rich and a boron oxide rich phases, within the thin microsphere walls as they were produced. This meant that leaching out the interconnected phase would result in a porous microspheres wall structure formation with the potential of porosity tunability. The presence and tunability of this porosity would allow for materials filling, pores sealing, and potentially the formation of a hydrogen selective silica based protective membrane.

Here, we will discuss the results from a study conducted to illustrate the feasibility of open through wall porous glass microspheres formation and show the possibility of complex hydrides encapsulation inside the cavity of the hollow glass microspheres.

Experimental

Formation of porous hollow glass microspheres

The fabrication techniques started with heating of a glass powders (~20 to 40 microns), containing a sulfate blowing agent, in a heated zone formed by a controlled gas-air flame. As the glass particles were passed through the heated zone in the flame, they softened and formed a spherical particle. As the spheres were heated up, the blowing sulfate agent became unstable thus forming gas nuclei. Further heating of the glass resulted in expansion and formation of a hollow glass microsphere. The flame was quenched with a water spray and the hollow glass spheres were carried with the quenched water and collected by flotation. Following this, the microspheres were acid leached in 3 Molar hydrochloric acid solution at 580 °C for 15.5 hours to preferentially remove a boron oxide rich leachable phase thus leaving behind a silica rich phase with interconnected porosity. The collected spheres were washed in 0.5 Molar sodium hydroxide solution followed by rinsing with DI water and were left to air dry.

Filling hollow glass microspheres with complex metal hydrides

All the filling work was conducted inside an argon glove box with water and oxygen controlled down to 0.1 ppm. In this study, sodium alanate, purchased from Sigma Aldrich, was selected as a model complex hydride in order to illustrate the filling feasibility. Incipient wetness technique was used for filling the spheres by dissolving eight grams of sodium alanate in 100 ml of tetrahydrofuran (Sigma Aldrich). One gram of the glass spheres prepared was placed in a glass vial which was evacuated and then soaked in about 20 ml of the prepared sodium alanate/tetrahydrofuran solution. The spheres which sank in the solution were expected to have a through wall open porosity and therefore were separated and left to dry under vacuum for 2 hours, then left inside the glove box to dry under Ar for more than 7 days. A small amount of these sinkers was stabilized in ambient air prior to the microscopic examination. All the microscopic characterizations were made using Hitachi FESEM 4800 and HD 2000 STEM used for the examination of samples cross sections and elemental mapping. Cross sectioning was conducted by embedding the samples in EM-bed 812 and sectioning on the Reichter Ultramicrotome with a diamond knife. The cross sections obtained were placed on a copper grid for imaging.

Results

Electron scanning microscopy SEM was conducted for the hollow glass microspheres obtained prior to and following leaching with hydrochloric acid HCl and the results are shown in Figure 1.a and 1.b. HCl is expected to result in an interconnected porosity across the spheres wall by leaching of the boron oxide rich phase. As seen in Figure 1.a, spheres produced following the heat treatment appeared to be intact with more than 60% having diameters ranging between 60-80 μm . Some spheres breakage was noted as seen in Fig. 1.b following acid leaching probably due to mechanical weakening of the spheres wall. Overall, the spheres were of good quality judging from the images obtained and therefore were selected for the filling experiment with sodium alanate. Prior to the filling, confirmation of through wall open porosity presence was conducted by cross sectioning of the spheres wall

(approximately 900 °A per cross section) and the electron microscopy and elemental mapping of a selected cross section is shown in Figure 2.

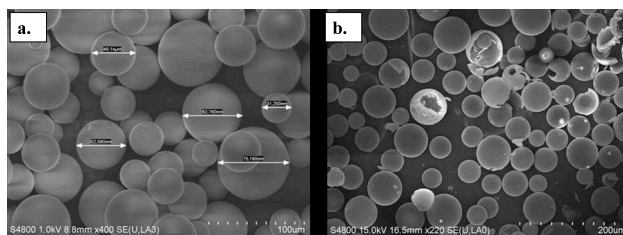


Fig. 1 Scanning Electron Microscopy of hollow glass spheres: a) Before acid leaching and b) After acid leaching

As seen in Figure 2, formation of open channels across the wall was corroborated by the absence of both silicon and oxygen (remaining silicon oxide following leaching), in the areas which seemed to indicate the presence of a porous structure in the micrograph. A final confirmation of the through wall porosity was conducted by evaluating the spheres pycnometer density before and after acid leaching. The density increase from 0.49 g/ml (before leaching) to 2.87 g/ml (following leaching) supported through wall open porosity presence.

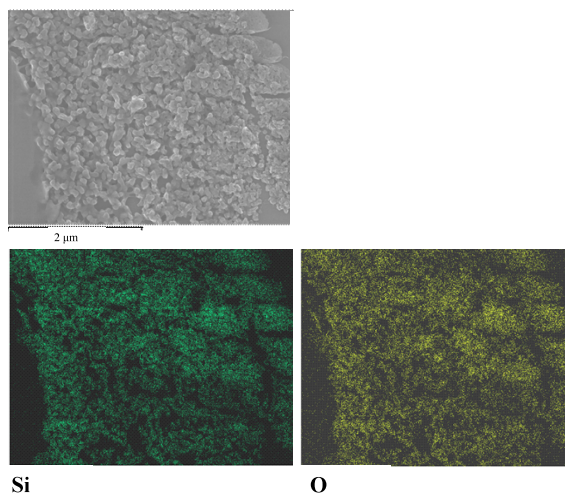


Fig. 2 900 °A sphere wall cross section following acid leaching

Following confirming the presence of intact spheres with open wall porosity, the filling experiments were conducted and Figure 3.a shows SEM for the microspheres following the filling experiments. As expected, the presence of precipitation residues was observed on the outer walls of the spheres, however, magnification of these residues revealed the presence of a needle like structures on the exterior wall of the spheres as seen in Figure 3.b. In order to determine whether sodium alanate diffused through the walls of the spheres and was lodging inside the microspheres cavities, the spheres were cracked open by applying a slight pressure and the interior of a cracked sphere was investigated as seen in Figure 4. Within the spheres, the presence of a needle type bundled structures; less than 10 μm in length and less than 1 μm in thickness, pointing towards the centers of the spheres was noted (Figure 4). In addition to this, a foamy type precipitation on the interior walls was observed and Figures 5.a and 5.b show a magnification of the both the needle and foamy structures

observed on the interior walls of the hollow glass spheres surfaces.

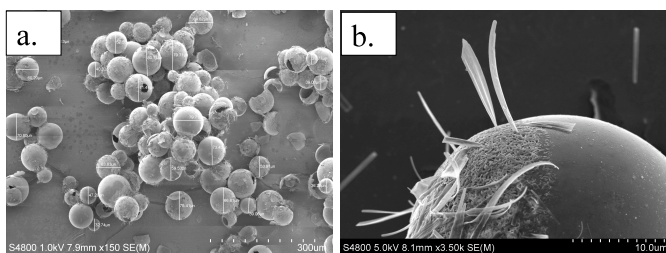


Fig. 3: Scanning Electron Micrograph obtained (a) following filling the porous hollow glass microspheres with sodium alanate and (b) illustrating the presence of needle like bundles on the exterior walls of the spheres

To confirm that these structures corresponded to sodium alanate, elemental mapping of the structures was conducted. As can be seen in Figure 6, the observation of sodium and aluminum presence on the needle structures and surface bumps confirmed the success in spheres filling with sodium alanate. While the needle structures were not reported before for sodium alanate, it is speculated that the porous silica could have provided a nucleation surface for these unusual structures growth. Nevertheless, since the samples were exposed to ambient air prior to the characterization, further studies are needed in order to eliminate the effects of any morphological changes which could have resulted from interactions with oxygen and water.

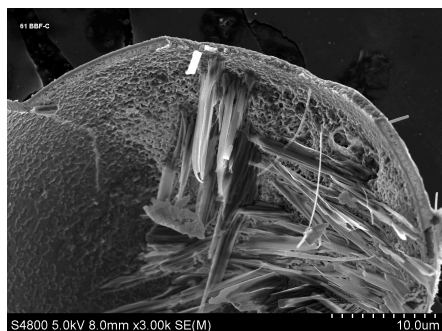


Fig. 4 Scanning Electron Micrograph showing the interior of a cracked hollow glass sphere. Presence of bumpy structures and needle shaped bundled structures was observed.

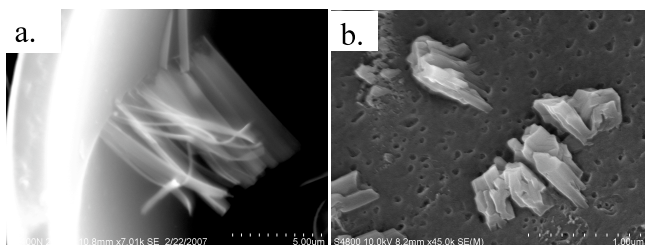


Fig. 5 The interior of a cracked hollow glass sphere illustrating the distinct presence of (a) needle bundled structure and (b) bumpy structures.

The illustration of sodium alanate presence inside the cavity of the hollow glass microspheres provided an indication of

filling success using NaAlH_4 /tetrahydrofuran solution but didn't confirm that filling occurred by solution diffusion into the spheres cavity using the in-wall porosity (i.e. diffusion could occur potentially through spheres imperfections which were not detected). To confirm this, cross sectioning of the hollow glass spheres walls following filling was made and elemental mapping was conducted. As seen in Figure 7, the presence of sodium and aluminum elements distributed across the wall was observed thus confirming material filling through the wall pores. Furthermore, these cross sections showed the impregnation of the sodium alanate along the wall of the spheres forming an alanate-silica nano composites along the wall cross section. While researching the hydrogen storage properties of the observed structures and nano-composites is beyond the scope of this article, its proposed that the porous wall morphology could provide a media for the formation of unusual structures/composites which warrants further investigation. Next steps in this work would include researching the tenability of the spheres pore size distribution such that the walls act as hydrogen selective membranes to prevent/minimize water and oxygen molecules diffusion into the spheres.

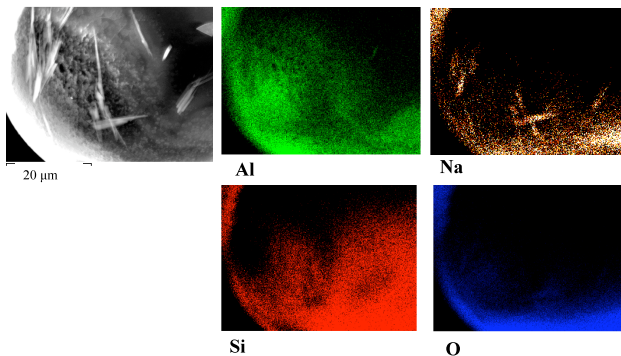


Fig. 6 Elemental mapping of the interior of a cracked hollow glass sphere following filling with sodium alanate

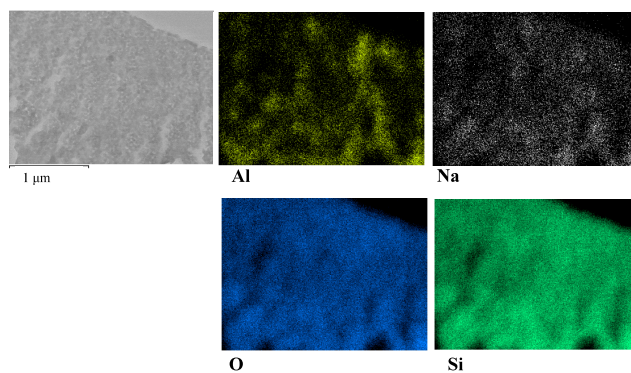


Fig. 7 A sphere wall cross section after filling with sodium alanate showing the elemental distribution of Na, Al, Si and O

Conclusions

Synthesis of porous wall hollow glass microspheres was successfully illustrated which allowed for spheres filling with sodium alanate using walls open porosity. Spheres examination following alanate's encapsulation, resulted in the

observation of unusual needle bundled structures corresponding to the alanate on the interior and exterior surfaces of the hollow glass spheres. While further work is needed to characterize these structures, it is speculated that their nucleation and growth was promoted by the spheres porous walls morphology. To provide future protection of encapsulated complex hydrides materials from the ambient, selectivity of hollow glass spheres surfaces towards hydrogen gas would need to be researched and demonstrated.

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