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Microspheres and Microworlds

SRNL'S POROUS, HOLLOW GLASS BALLS OPEN NEW OPPORTUNITIES FOR HYDROGEN STORAGE, DRUG DELIVERY AND NATIONAL DEFENSE.

G.G. Wicks, L.K. Heung and R.F. Schumacher

Editors note: What looks like a fertilized egg, flows like water, is stuffed with catalysts and exotic nanostructures and may have the potential of making the current retail gasoline infrastructure compatible with hydrogen-based vehicles of the future – not to mention also contributing to arenas such as nuclear proliferation and global warming?

Take another look again at the photo on the cover. The microscopic permeable glass balloon whose shell has been partially removed to reveal its palladium contents will give you a sense of what's in store for the future, if the SRNL researchers are right. ACerS is honored to be the first to publish information on this startling and promising discovery and the captivating, never-before-seen photos of these glass microspheres in action.

The Savannah River National Lab has developed a novel class of materials for a variety of potentially new and exciting applications. This unique material is called porous wall, hollow glass microspheres. It consists of tiny glass microballoons that are smaller than the diameter of a human hair. The distinguishing characteristic of the SRNL glass microspheres is the interconnected porosity of their thin outer walls that can be produced on a scale of 100 Å to 3,000 Å.

The porosity in these one-of-a-kind microspheres results in unique and desirable properties. For example, one can use these open channels to fill the microballons with absorbents as well as other materials, thus providing a contained environment and a new type of glass-absorbent composite. Gases can then enter the microspheres through the pores and be stored or cycled on absorbents inside, resulting in solid-state and contained storage, even of reactive species. This wall porosity also can be used to generate new nanostructures of absorbents as well as other materials of interest.

The permeability of the walls can be used for noncomposite purposes, too. For example, the porosity can be altered and controlled in various ways that allow the spheres to filter mixed gas streams within a system.

In fact, the SRNL is involved in more than a half dozen programs and collaborations involving the PW-HGMs in areas such as hydrogen storage in vehicles, gas purification and separations, and even diverse applications, including abatement of global warming effects, improving lead-acid battery performance and nuclear nonproliferation. Applications such as the development of new drug delivery systems and MRI contrast agents also are blossoming in the medical field.

The Savannah River site and its lab have worked for many years with a variety of ceramics and ceramic-based systems, with hydrogen and its isotopes, and on applications that include energy security, nuclear and hazardous waste management, and environmental remediation. SRNL has more than three decades of experience developing, processing and implementing special ceramics, including glasses, for a variety of Department of Energy missions and more than four decades of experience in handling and processing tritium, deuterium and hydrogen.

In the case of glasses, the site has been involved in the science and engineering of glass-based systems, especially for waste management. In particular, the SRS is known for its work on a 40-component nuclear waste glass system that has the technical ability to incorporate and immobilize high-level radioactive wastes into inert and safe products.

In addition to the science involved in these programs, SRS researchers also have developed and demonstrated the engineering aspects, as exemplified by one of the most unique glassmaking plants in the world, the Defense Waste Processing Facility. Built at a cost of more than $1 billion at the SRS site, the DWPF is in the process of locking up 34 million gallons of SRS' high-level wastes stored on site into complex borosilicate glass forms.

The DWPF produces waste glass products in 10 ft × 2 ft diameter cylindrical canisters. The facility began operations in 1996 and has run almost continuously since then, producing more than 2,000 glass-filled canisters. The canisters' 4,000 tons of glass immobilize more than 10 million curies of radioactivity.[2]

As a part of this glass experience and expertise, SRNL also has developed several niche abilities in the glass arena. One of these abilities is the development of porous glass systems for a variety of applications, such as sol–gel glasses including xerogels and aerogels- and phase-separated glass compositions. These can be treated later to produce another unique type of porosity within the glass forms that can increase the surface area by one or two orders of magnitude.

This unique property of porosity is what opens the door to applications for hydrogen storage, gas transport, gas separations and purification, sensor technologies, global-warming applications, new drug delivery systems, etc. These porous glass systems can be fabricated into a variety of forms, including coatings, plates, fibers, beads and hollow microspheres.

The last of these – formally called porous wall, hollow glass microspheres – is one of the most interesting porous glass products developed and patented by SRNL because of the variety of potential uses. Many of the applications currently in development involve collaborations and contributions with Alfred University, Clemson University, University of Idaho and Medical College of Georgia. Industrial partners include Toyota, MoSci Corp., Air Products and Milliken. Other DOE sites, such as NETL, also are involved.

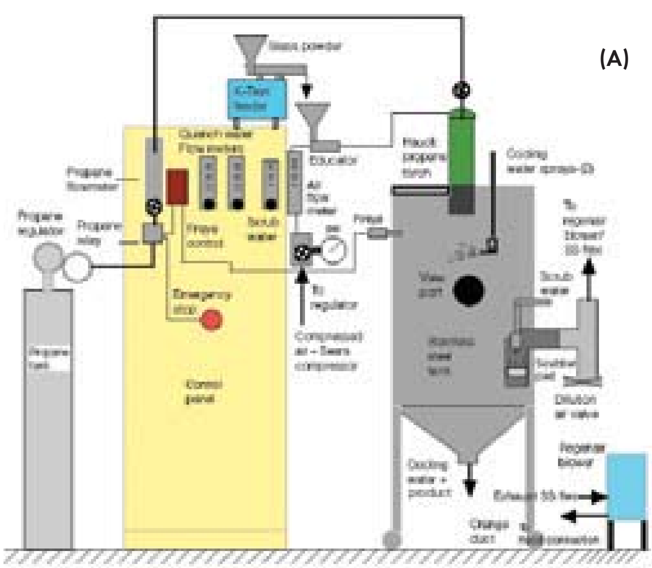

Fig. 1 (A) Schematic of SRNL microsphere system and (B) SRNL microsphere team with flame former apparatus.

Since the SRNL pioneering development work in 2005 that created tritium applications using these unique microspheres, investigators have been attempting to extend this technology into many new areas and funding opportunities. These breakthroughs began to be publicized in February 2008, when the first of a series of key papers was presented at the new ACerS-ASM joint conference on "Materials Innovations in an Emerging H-Economy."

Fabrication of PW-HGMs

SRNL's hollow glass microspheres and their porous-wall cousins are fabricated using a flame former apparatus schematically illustrated in Fig. 1(A) and 1(B). They are fabricated by heating ~20 µm to 40 µm glass powders in a hot zone formed by a controlled gas-air flame. As the glass particles pass through the zone, the flame softens the glass and forms a spherical particle. The glass contains a latent blowing agent that becomes unstable as the glass is heated and forms a gas nucleus or bubble. The bubble expands as the glass is heated and forms the HGMs.

The HGMs then are quenched with a water spray and carried with the quench water and collected by flotation. They have an average density between 0.10 g/cm^3 and 0.70 g/cm^3 depending on the HGM size and the flame temperature conditions. The important primary formation parameters include the powder feed rate, air to gas ratio, flame velocity and the length of the flame.

Some solid beads also are formed in the process, and the HGMs are separated by flotation in the collected quench water. To diminish exhaust loss of HGMs, a wet scrubber system is used. After collecting and weighing, researchers further define the HGMs by size to reduce the percentage of <30 µm, high-density HGMs.

The conversion of the HGMs into PW-HGMs occurs when the microspheres are heat-treated and acid leached with 3.0M hydrochloric acid.

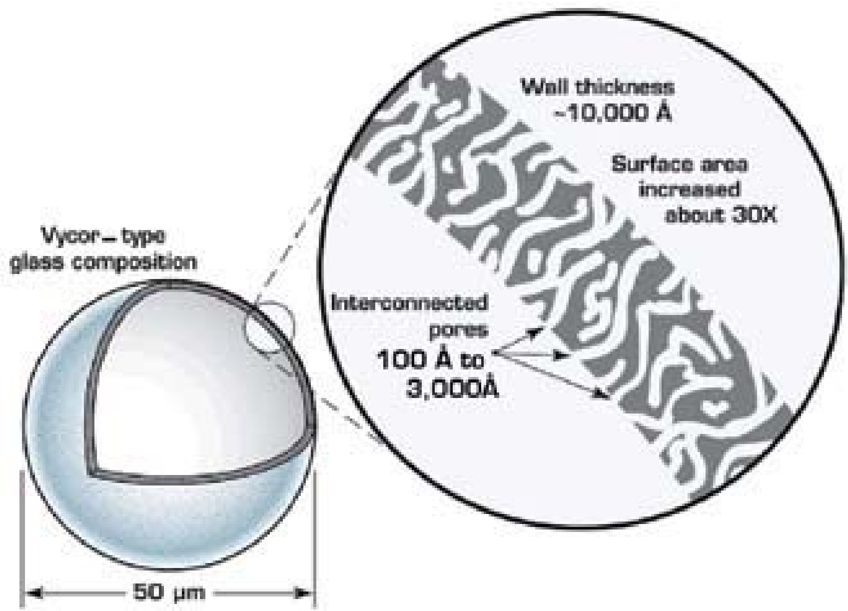

Fig. 2 Schematic representation of SRNL microsphere and wall porosity.

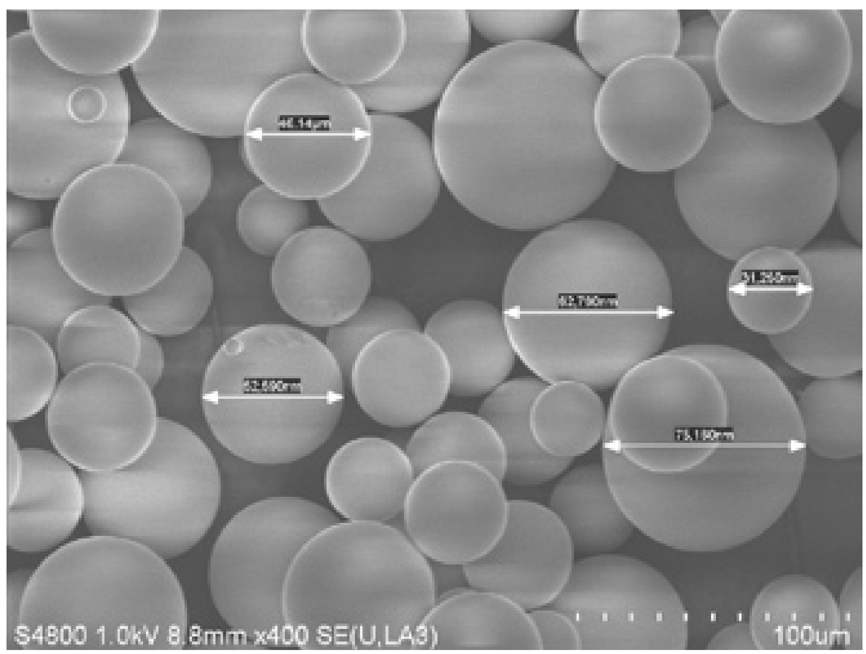

Fig. 3 Typical batch of 2 µm to 100 µm with average diameter of ~50 µm SRNL microspheres.

SRNL PW-HGMs

In order to induce this special porosity, investigators first produce phase separation in the glasses. The importance of this process is that it actually produces two different glass phases: one rich in silica and the other rich in sodium borate. The sodium borate phase is an interconnected wormlike morphology. When it is removed by a leaching process, similar to the making of commercial Vycor glass, it produces interconnected pores or channels that, in this case, extend from the outside of the microsphere shell to its inside. This is illustrated schematically in Fig. 2. These channels can later be used to fill the microspheres.

Fig.4 SRNL microsphere filled with palladium where the top of the microballon has been removed to view the inside.

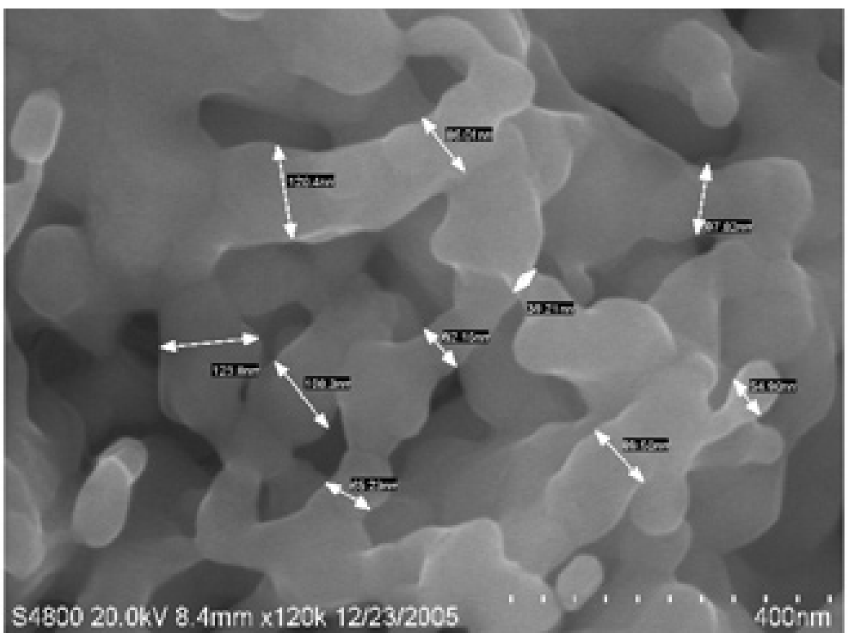

Fig. 5 Unique nanoscale wall porosity through the thin microsphere walls.

As mentioned previously, interconnected porosity is the key. The team at SRNL has used this porosity to fill the microballons with special gas absorbents. There are a number of remarkable advantages to producing new classes of absorbent-glass microsphere systems such as these.

For example, by incorporating or growing absorbents inside the microspheres, investigators can produce a protective environment or cocoon. This could be especially important for reactive or flammable absorbents or stored materials, including solids, liquids or gases, and has the potential of improving subsequent safety for handling, storing or transporting materials of this type.

The porosity also offers unique filtering abilities. By controlling the size of the pores, researchers can offer the possibility of filtering and purifying mixed gases.

Furthermore, because the microspheres are already relatively strong and can be made even stronger, these properties make them good candidates for reuse or recycling. This can be coupled with another fascinating observation about the treated glass microspheres: Their mechanical properties can be altered so they can be made to flow like a liquid. This suggests that an existing infrastructure that currently transports, stores and distributes liquids – e.g., the existing gasoline distribution and retail network – may still be employed for these types of materials.

The PW-HGMs, at present, are one-of-a-kind materials, and their porosity is responsible for many of their unique properties and potential for a wide variety of interesting and strategic applications.

Figure 3 shows a typical batch of as-fabricated microspheres, and Fig. 4 is a PW-HGM after it has been successfully filled with palladium, an important material used by SRNL to handle radioactive forms of hydrogen. The wall porosity was used to insert the palladium. Fig. 5 illustrates the unique nanoscale porosity within the microballon walls.

This isotope-storage ability of these tiny balls may even have an important impact on national security and world peace. The microballoons' hydrogen talents also are set to make a major contribution to energy innovation. As part of a program with Toyota, SRNL is investigating filling these microspheres with other special hydrogen absorbents to develop safe hydrogen-gas storage systems for vehicles of the future.

Investigators also are exploring techniques for containing and releasing internal gases and other materials by affecting the wall porosity through chemical and mechanical means. Collaborations led by Alfred University and MoSci Corp. are examining containment and release mechanisms, such as photo-induced diffusion.

As a byproduct of the Toyota col-

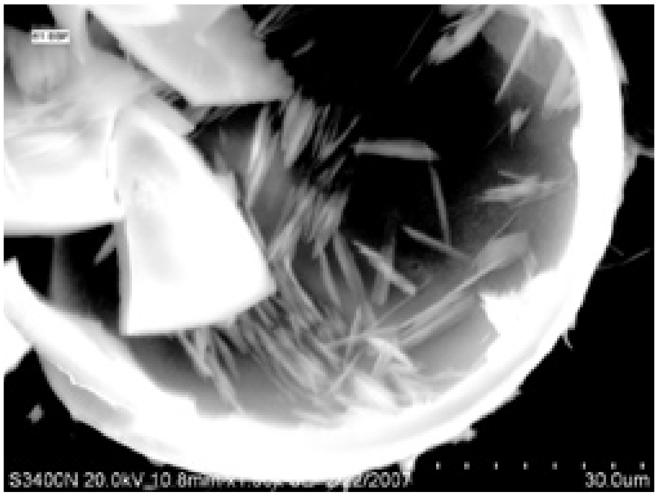

Fig. 6 Nanostructure absorbent grown inside PW-HGMs.

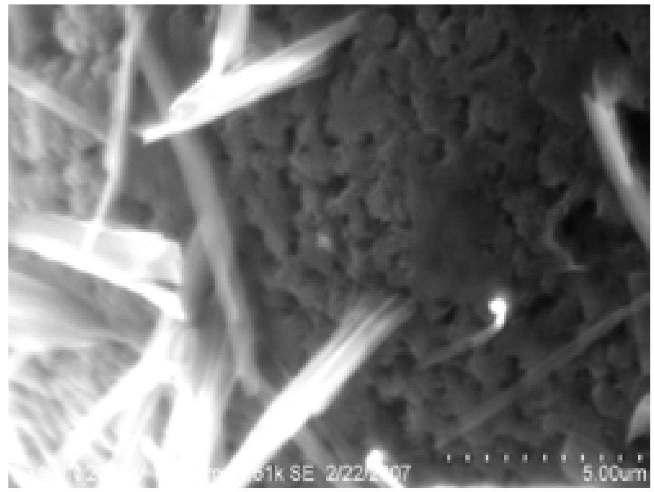

Fig. 7 Nanostructure absorbent grown outside PW-HGMs.

laboration, researchers discovered that effective and reactive absorbents could be incorporated inside the PW-HGMs and, interestingly, these absorbant materials assembled themselves into unfamiliar nanostructures. Figure 6 shows one of these novel nanosized absorbent structures with bundles of the nanosized filaments produced inside.

From chemical analyses of these structures, they do not appear to be any of the anticipated phases. This suggests that along with new nanostructures produced by the porosity of the microsphere walls, new phases also may result. Further work is needed to clarify and characterize in more detail these interesting findings.

The breakthroughs are not confined to the interior of micropspheres. As noted in Fig. 7, the nanostructures also can be produced outside. Although relevant to the absorbtion of gases, these formations likely will have important medical applications. For example, a collaboration between SRNL and the Medical College of Georgia is investigating these surfaces. This partnership is using proteins and fluorescent indicators to explore the possible use of microspheres in drug delivery systems to create new types of MRI contrast agents.

Using glass microballoons less than the size of a human hair, SRNL has just begun to crack open a new world of potential applications. Fluidlike, recycleable and made from readily available resources, PW-HGMs may be the ideal solution to hydrogen storage, gas purification and targeted drug delivery.

Other new collaborations by academia, industry and government teams also are underway that already suggest that the PW-HGMs will continue to enjoy an expanding and exciting array of potential uses, from improving the performance of lead–acid batteries to the abatement of global warming effects. These tiny crystal balls have revealed a heretofore unknown and unexpected landscape that, as the research evolves, may predict much of the future of the world.

This collaboration has produced new nanostructures of complex and reactive absorbents. Also, some interesting work is currently in progress with MCG involving using the glass microspheres for a variety of medical uses, such as development of new drug delivery concepts as well as new MRI contrast agents.

This results in phase-separated glass shells in which the boron-rich phase is leached away to produce the interconnected, phase-separated porosity in the 100 Å to 3,000 Å range. The glass microspheres have diameters in the range of 2 μm to 100 μm, with wall thicknesses on the order of 1 μm to 2 μm. ■

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References

[1]Savannah River National Lab, "Science at Work …. Storing Hydrogen for the Vehicle of the Future," *Porous-Walled, Hollow Glass Microspheres*, **1** [1] 9–11 (2007).

[2]G.G. Wicks, "Nuclear Waste Glasses"; pp 218–68 in *Corrosion of Glass, Ceramics and Ceramic Superconductors*. Edited by D.E. Clark and B.K. Zoitos. 1992.

[3]L.K. Heung and G.G. Wicks, "Hydrogen Storage Composition and Method", U.S. Pat. No. 6 528 441, 2003.

[4]L.K. Heung, G.G. Wicks and M.W. Lee, "Composition for Absorbing Hydrogen from Gas Mixtures," U.S. Pat. No. 5 965 482, 1999.

[5]L.K. Heung and G.G. Wicks, "Silica Embedded Metal Hydrides," *J. Alloys Compd.*, **293–295**, 446–51 (1999).

[6]L.K. Heung, G.G. Wicks and G.L. Enz, "Composition for Absorbing Hydrogen," U.S. Pat. No. 5 411 928, 1995.

[7]L.K. Heung, R.F. Schumacher and G.G. Wicks, "Hollow Porous Wall Glass Microspheres," U.S. Pat. filed 10/21/05, PCT filed 10/17/06.

[8]R.F. Schumacher, "Apparatus to Enhance the Uniform Formation of Hollow Glass Microspheres," PCT filed 12/4/06.

[9]G. Wicks, L. Heung and R. Schumacher, "Unique Porous Wall Hollow Glass Microspheres"; presented at Materials Innovations in an Emerging Hydrogen Economy (Feb. 24–17, 2008, Cocoa Beach, Fla.), to be published in proceedings, 2008.

[10]R. Mohtadi, K. Tange, G. Wicks, L. Heung and R. Schumacher, "New Concept for Storing Reactive Complex Hydrides On-board of Automobiles"; see Ref. 9.

[11]L. Heung, G. Wicks and R. Schumacher, "Encapsulation of Palladium in Porous Wall Hollow Glass Microspheres" ; see Ref. 9.

[12]F. Raszewski, E. Hansen, D. Peeler, R. Schumacher, S. Gaylord, N. Carlie, L. Petit and K. Richardson, "Impact of Composition and Heat Treatment on Pore Size in Borosilicate Glass Microspheres"; see Ref. 9.

[13]D. Newell, D.B. Edwards and S.N. Patankar, "Using Porous Microspheres as Additives in Lead Acid Batteries"; see Ref. 9.

[14]W. Dynan, S. Li, J.-X. She, T. Hu, G. Wicks and S. Serkiz, "Porous Wall Hollow Glass Microspheres for Biomedical Applications," in draft.