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SRNL UNIQUE POROUS WALL, HOLLOW GLASS MICROSPHERES (PW-HGMS) FOR HYDROGEN STORAGE, SEPARATIONS AND OTHER APPLICATIONS

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ABSTRACT

The Savannah River National Laboratory (SRNL) has developed a new medium for storage of hydrogen and other gases. This involves fabrication of thin, Porous Walled, Hollow Glass Microspheres (PW-HGMs), with diameters generally in the range of 1 to several hundred microns. What is unique about the glass microballons is that porosity has been induced and controlled within the thin, one micron thick walls, on the scale of 10 to several thousand Angstroms. This porosity results in interesting properties including the ability to use these channels to fill the microballons with special absorbents and other materials, thus providing a contained environment even for reactive species. Gases can now enter the microspheres and be retained on the absorbents, resulting in solid-state and contained storage of even reactive species. Also, the porosity can be altered and controlled in various ways, and even used to filter mixed gas streams within a system. SRNL is involved in about a half dozen different programs involving these PW-HGMs and an overview of some of these activities and results emerging are presented[1].

INTRODUCTION

The Savannah River Site (SRS) and its Laboratory (SRNL), located in Aiken, South Carolina, have had a long and successful history of working with hydrogen and its isotopes for national security, energy and waste management/ environmental remediation applications. This includes more than 40 years of experience in handling and processing tritium/ deuterium/ hydrogen and more than 30 years of experience developing, processing and implementing special ceramics, including glasses, for a variety of Department of Energy (DOE) missions. In the case of glasses, the site has been involved in both the science and engineering of vitreous or glass-based systems, especially in the waste management field. This includes developing 40-component SRS nuclear waste glass systems, with the technical ability to incorporate and immobilize high level radioactive (HLW) wastes into inert and safe products. In addition to the science involved in these programs, the engineering aspects have also been developed and demonstrated, as exemplified by one of the most unique, vitrification or glass making plants in the world, called the Defense Waste Processing Facility, or DWPF. This is a more than one billion dollar facility built at the SRS site, that is currently in production, immobilizing the 34 million gallons of radioactive SRS HLW stored on site, into complex borosilicate glass forms, producing waste glass products in canisters that are 2-ft. in diameter, and almost 10-ft. high. The DWPF began operations in 1996 and has run almost continuously since then producing more than 2000 canisters or 4,000 tons of glass immobilizing more than 10 million curies of radioactivity[2].

As a part of this glass experience and expertise, SRNL has also developed a number of niches in the glass arena, one of which is the development of porous glass systems for a variety of applications. These porous glass systems include *sol gel glasses*, which include both xerogels as well as aerogels, as well as *phase separated glass compositions*, that can be subsequently treated to produce another unique type of porosity within the glass forms. The porous glasses can increase the surface area compared to ‘normal glasses’, of 1 to 2 orders of magnitude, which can result in unique properties in areas such as hydrogen storage, gas transport, gas separations and purification, sensors, global warming applications, new drug delivery systems, etc.[3-7].

One of the most interesting porous glass products that SRNL has developed and patented is Porous Wall, Hollow Glass Microspheres (PW-HGMs), that are being studied for many different applications. Many of these new initiatives are being conducted collaboratively with industry, government and academia for a variety of applications

SRNL PW-HGHs

SRNL Hollow Glass Microspheres, and subsequent, Porous Wall, Hollow Glass microspheres are fabricated using a flame former apparatus as in Figure 1A and shown, with the microsphere team, in Figure 1B[8].

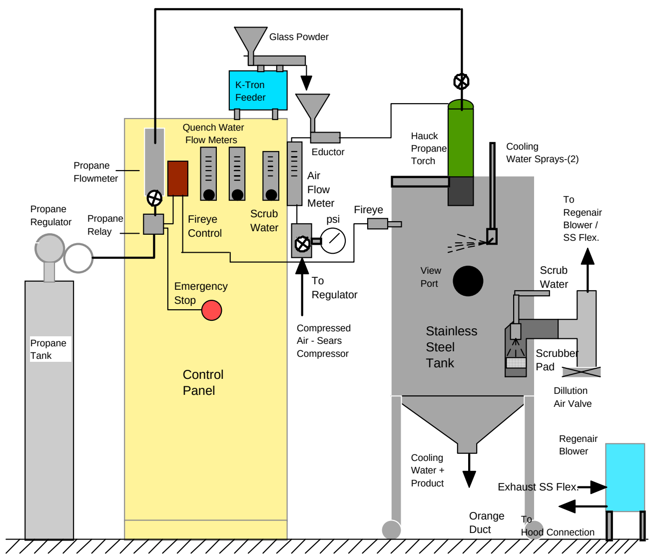

Figure 1A. Schematic of SRNL Microsphere System

The microspheres produced are generally in the range of 2 to 100 microns, with wall thickenesses on the order of 1 to 2 microns. *What distinguishes the SRNL microspheres from all others produced, is that the team has found a way to induce and control porosity through the thin walls on a scale of 100 to 3000 Å.* This is what makes these materials one-of-a-kind, and also is responsible for many of their unique properties and potential for various applications, including those in tritium storage, gas separations, H-storage for vehicles, and even a variety of new medical applications in areas of drug delivery and MRI contrast agents. These potential uses are being pursued with various industrial partners and academia. The microspheres have also been aerosolized for other uses. To date, they have not been considered for addressing Global Warming concerns, but as a result of discussions with NETL, their potential is now being examined.

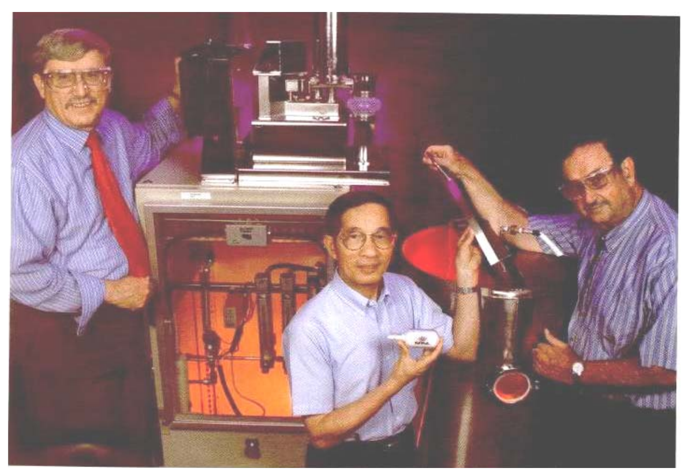

Figure 1B. Original SRNL Microsphere Team with Flame Former Apparatus

In order to induce this special porosity, phase separation in the glasses is produced which will be discussed in more detail in a later section. 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 worm-like morphology so when it is removed by a leaching process, it produces interconnect pores or channels that extend from the outside of the shell to the inside. This is illustrated schematically in Figure 2.

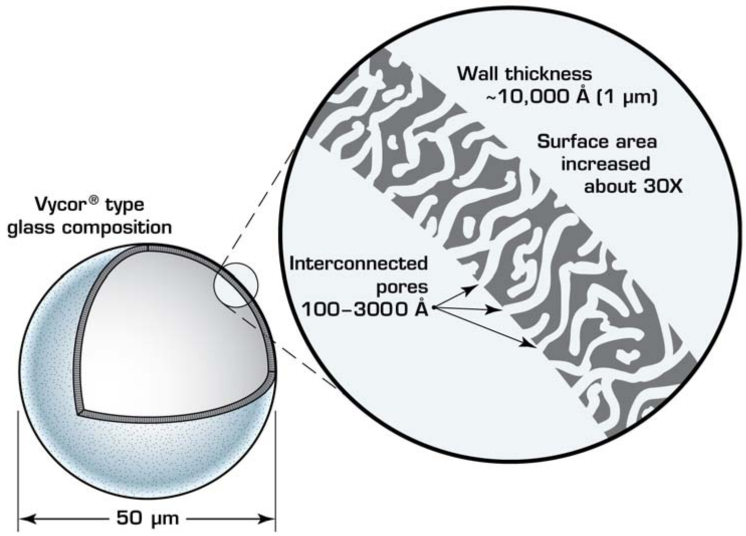

Figure 2. Schematic Representation of a SRNL Microsphere and Wall Porosity

As mentioned previously, porosity is key, and the team at SRNL have used this porosity to fill the microballons with special gas absorbents. In Figure 3, is shown a typical batch of as-fabricated microspheres, and in Figure 4, is a recently released micrograph of one of these microspheres after being successfully filled with Palladium metal, used in storage of radioactive forms of hydrogen[10]. The wall porosity was used to make the fill. In Figure 5, this nano-scale unique porosity is clearly shown within the microballon walls.

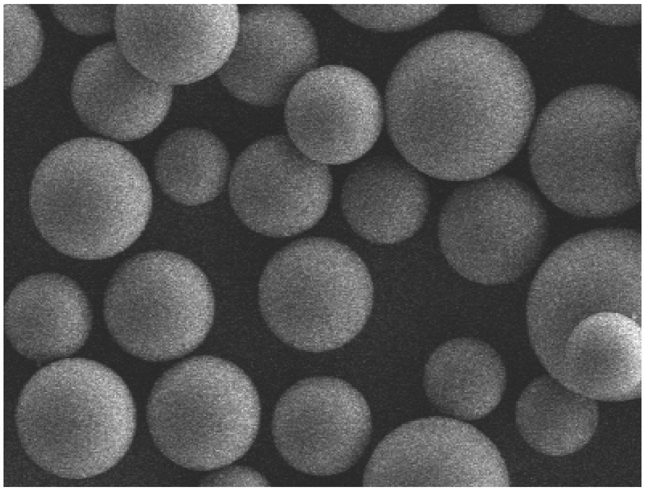

Figure 3. Typical Batch of SRNL Microspherers (Sizes 2-100μ, with avg. dia. of ~50μ)

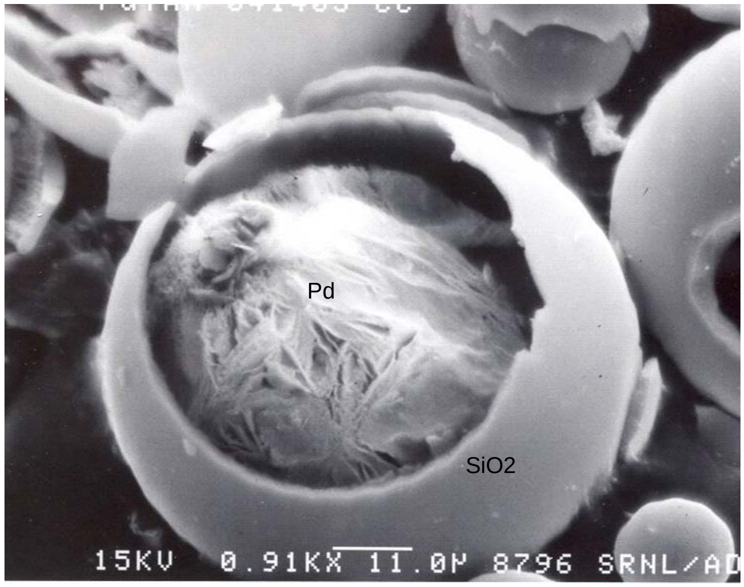

Figure 4. SRNL Microsphere Filled with Palladium (top of microballon removed to view inside)

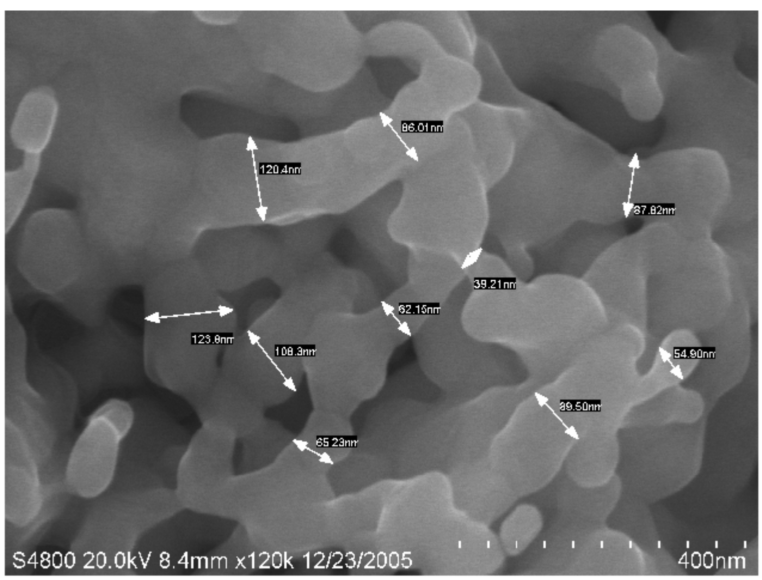

Figure 5. Unique Nano-scale Wall Porosity within the Microsphere Walls

As part of a program with Toyota, SRNL is also investigating filling these microspheres with other special hydrogen absorbents[11]. During this joint collaboration, it was discovered that very effective, but reactive absorbents could be filled and subsequently protected within the microballons or cocoons. In Figure 6, one of these nano-absorbent structures is shown for the first time, and as noted, bundles of the nano-filaments can be produced inside, as well. From chemical analyses of these structures, they do not appear to be any of the predicted phases known so not only can new nanostructures be produced by the porosity of the microsphere walls, but there is also the possibility that new phases can result. Further work is needed to clarify this interesting finding. As noted in Figure 7, the nanostructures can also be produced outside the microballons. This type of information is not only relevant to absorbents of gases, but is also being investigated with the Medical College of GA, using proteins and fluorescent indicators, for possible use in drug delivery systems and as new types of MRI contrast agents.

Figure 6. Nano-Structure Absorbent Grown Inside PW-HGMs

Figure 7. Nano-Structure Absorbent Grown Outside PW-HGMs

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