PRF#: 57882-ND10
Project Title: Investigation of Liquid-Alloy Based Growth of Alumina Aerogels
Principal Investigator: Prof. Paul A. Maggard, Department of Chemistry, North Carolina State University

RESEARCH PROGRESS REPORT – 9/1/2017 to 8/31/2018

Summary: The growth of high-surface-area alumina has been investigated with the use of a liquid Galinstan alloy (66.5% (wt. %) Ga, 20.5% In and 13.0% Sn) as an activator for aluminum metal. In this process, aluminum metal is slowly dissolved into a gallium-indium-tin alloy at ambient temperature and pressure, and which is then selectively oxidized under a humid stream of flowing CO_2 or N_2 to yield amorphous alumina. We have demonstrated that this preparative route represents a simple and low toxicity approach to obtain amorphous high-surface-area alumina with very low water content. The as-synthesized high surface area alumina aerogel is a blue-colored solid owing to the Rayleigh scattering by its dendritic fibrous nanostructure consisting of mainly alumina with small amounts of water. Upon annealing at 850 °C, the amorphous products transformed into γ-Al_2O_3, as well as θ-Al_2O_3 upon annealing at 1050 °C. Elemental analysis by energy-dispersive spectroscopy provides further evidence that the high-surface-area alumina solids are comprised of only aluminum and oxygen. The surface area of the amorphous aerogel varied from ~79 to ~140 m^2/g, depending on the initial weight percentage of aluminum used in the alloy. A correlation between the initial concentration of aluminum in alloy and the surface area of the Al_2O_3 product was elucidated from BET measurements.

Research Description: The ability for Ga-In-Sn alloys, with dissolved aluminum, to reduce water to hydrogen gas is widely known. During the direct oxidation of the aluminum, the protons of water are reduced to molecular hydrogen after it is absorbed on the activated aluminum surface. Conventionally, the aluminum is directly submerged in the water and hydrogen bubbles out the solution. In our new experiments, water vapor is passed over the activated metal to drive the production of the aerogel. After the aluminum was dissolved within the Ga-In-Sn liquid alloy, i.e., Galinstan alloy, the activated aluminum at the surface reduces the water vapor to produce hydrogen gas and the freshly oxidized alumina aerogel. Fresh aluminum diffuses to the surface of the liquid alloy to continuously react with the water vapor to grow the aerogel out from the Galinstan alloy. Within the first few seconds of flowing H_2O vapor carried by CO_2, the mixture turned dark, after which light blue solids grew out of the mixture. Varying the initial aluminum percentage produced light blue and partially transparent solids, except for the 2% aluminum mixture. Similar aerogel growth was observed using a non-recyclable 7075-aluminum alloy, indicating that this process is not limited by the low purity of aluminum in the alloy. Higher percentages of aluminum (30-60%) favored the growth of tendril-like morphologies compared to the monolithic growths of alumina observed with the 2% and 10% mixtures. At the higher dissolved concentrations of aluminum in the liquid alloy, i.e., 40% and 60%, the aluminum within small isolated droplets of the liquid alloy become oxidized and form an amorphous alumina shell. The droplet is then squeezed out of the shell whereupon further aluminum in it oxidizes again to form another alumina shell. This process repeats itself to generate worm-like tubular structures of the alumina aerogel material. The worm-like structures and internal droplets of the liquid alloy are both visible in the optical microscope images in Figure 1. This process occurs across the numerous liquid alloy droplets that then produces a bulk amount of blue-tinted worm-like tubular structures.

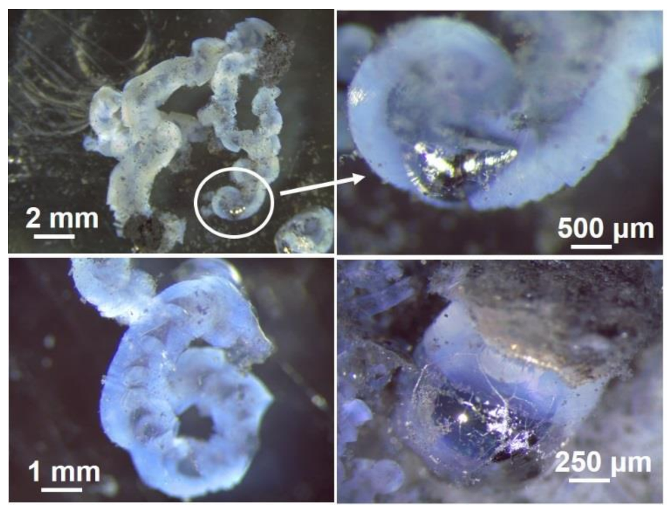

Figure 1. Optical images of the amorphous worm-like structures of alumina synthesized from an aluminum-alloy mixture. Small isolated droplets of the liquid alloy spheres (on the right) migrate and leave behind the worm-like structures of the blue-tinted alumina.

The scanning electron microscopy images of the blue-tinted alumina revealed a densely packed fibrous structure similar to aerogels produced from mercury-based amalgams. The fibrous products were studied further with the use of TEM after the initial synthesis and after annealing the solid. The spindles of solids are approximately 10-30 nanometers across in both high-density and low-density growth areas. Energy dispersive spectroscopy of the aerogels grown from pure aluminum indicated the presence of only aluminum and oxygen. Images were also taken after approximately five minutes of water vapor exposure using 7075-aluminum alloy. A distinct interface was observed where the solid alumina aerogel broke through the high surface tension liquid metal, shown in Figure 2. The alumina growth was halted after ~30 seconds to analyze the growth front of the alumina on top of the liquid Galinstan alloy. Elemental analysis showed the aluminum and oxygen are concentrated at the upper half of the growth zone, while the gallium, indium and tin are concentrated at the lower half of the growth zone that constitutes the liquid alloy.

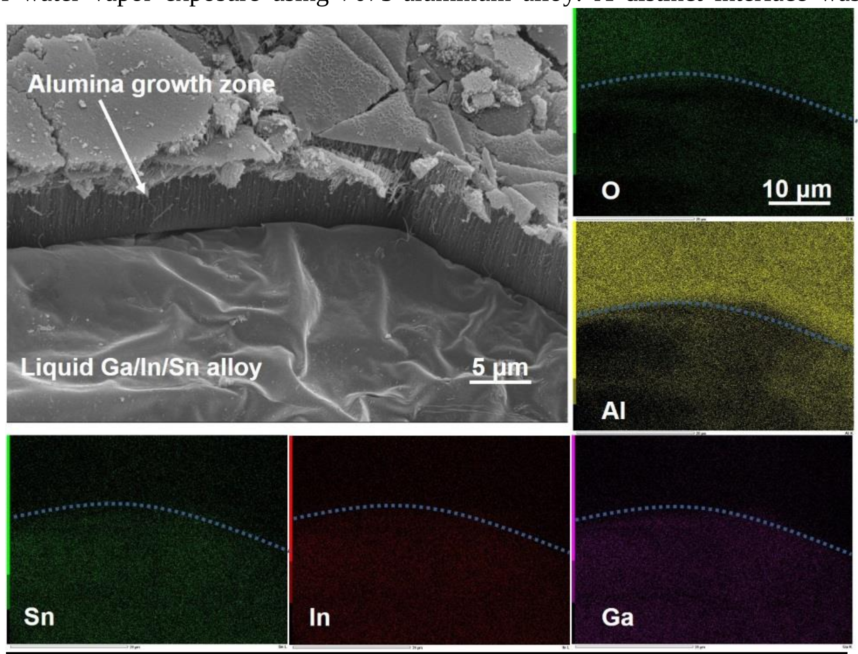

Figure 2. Image from scanning electron microscopy (upper left) and energy dispersive spectroscopy of the elemental composition for the growth interface between the alumina aerogel and the liquid Ga/In/Sn alloy composition with 40% dissolved aluminum; The growth zone is indicated by the dashed blue line in for each of the elemental compositions, with the upper part the alumina aerogel and the lower part the liquid alloy.

The alumina aerogel growth of densely packed fibers from the 7075-aluminum alloy sample matched closely to the solids formed using the high-purity aluminum the lower concentrations in the Galinstan alloy (i.e., 2% and 10%) demonstrating a similar growth mechanism, even when additional metals are present in the mixture. Elemental analysis shows the growth front confirmed that the amorphous alumina solid is devoid of the impurity metals that are initially present in 7075-aluminum alloy, including zinc, magnesium, and copper. The ability to produce a relatively pure aluminum-based oxide from alloys such as 7075 *enables a potentially wide range of recycling applications.* Powder X-ray diffraction patterns of the as-synthesized alumina aerogels, as well as after heating to high temperatures, were collected and fitted to known alumina crystalline phases. Each of the solids remained amorphous after annealing at 600 °C for 24 hours in air. New diffraction peaks corresponding to γ-Al_2O_3 were detected after annealing the materials at 850 °C for 48 hours for all samples. Further heating at 1050 °C for 48 hours lead to the growth of diffraction peaks likely corresponding to the θ-Al_2O_3 polymorphs, but which is difficult to distinguish owing to the nano-crystallinity of the product and the broad diffraction peaks. Results from the TGA shows a continuous mass loss over 800-1200 minutes as water is removed from the system before reaching a stable mass. The total amount of water loss was calculated by the decrease between the initial and final masses and found to range from ~1.2% to ~7.5% weight percent. This represents the lowest water content within any reported alumina-based aerogel grown from an amalgam.

Impact of the Research: This research has so far yielded a novel and very interesting and productive direction of research in the growth of aerogel materials, resulting in one publication (currently) as well as the preparation of larger proposals with a focus on recycling aluminum and on the growth of aerogel materials. Two federal proposals have been prepared and submitted on this topic. Students involved on this project have received training in the operation of scanning and transmission electron microscopy as well as powder X-ray diffraction analysis. One undergraduate student has been motivated to apply to graduate school in chemistry starting this next year where she would like to continue working on aerogel types of materials.