Activating the Growth of High Surface Area Alumina Using a Liquid Galinstan Alloy

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Supporting Information

ABSTRACT: 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. In this process, the aluminum is slowly dissolved into the gallium–indium–tin alloy, which is then selectively oxidized at ambient temperature and pressure under a humid stream of flowing CO₂ or N₂ to yield amorphous alumina. 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 was 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 product transformed into γ-Al₂O₃, as well as θ-Al₂O₃ upon annealing at 1050 °C. Elemental analysis by energy-dispersive spectroscopy provides further evidence that the high surface area alumina is composed of only aluminum and oxygen. The surface area of the amorphous alumina varied from ~79 to ~140 m²/g, depending on the initial weight percentage of aluminum used in the alloy. A correlation between the initial concentration of aluminum in the alloy and the surface area of the alumina product was found to peak at ~30% Al. These results suggest a novel route to the formation of amorphous alumina aerogel-type materials.

INTRODUCTION

Aerogel materials have been the subject of a large field of research since the initial discovery by Kistler in 1931.¹ Since then, the formation of highly porous three-dimensional networks has been intensely investigated for a wide variety of compounds including organics, organic–inorganic hybrids, and inorganic oxides.² The open and airy nature of aerogels make them ideal materials for a wide array of applications including for high-temperature thermal insulation, as refractory catalyst supports, for absorption of heavy metal ions and pollution removal, and in many other applications.³–⁵ However, conventional methods for producing these highly porous aerogel materials are generally complex, involving a precise sequence of hydrolysis and condensation reactions, followed by solvent removal that can lead to cracking or up to a complete collapse of the open network.

Recent studies into the growth of aluminum-based aerogels have resulted in highly ordered and monolithic forms via a direct oxidation of aluminum by activating the surface of aluminum metal with either mercury,⁶–¹³ or gallium.¹³–¹⁵ The amalgam produced by the interaction of the different metals inhibits the formation of a passivation layer from developing on metallic aluminum, thereby achieving a continuous diffusion of aluminum through the liquid metal to react with the air and/or water vapor to produce the alumina aerogel and hydrogen gas.¹⁶ As the mercury and gallium wet the surface of aluminum, the liquid metals penetrate the aluminum grain boundaries through a process known as liquid metal embrittlement.¹⁷–²⁷ Some issues surrounding the previous production of alumina aerogels are the use of toxic mercury, a high water content in the final product that is difficult to remove, and the need for high-purity aluminum metal for the reaction to proceed to completion.

Described herein is an investigation into the conditions for the growth of high-purity alumina aerogel that can be accomplished using a gallium–indium–tin liquid metal alloy, that is, without the use of toxic liquid mercury and very low or no water content in the product. Many reports have recently demonstrated the capability of Ga–ln–Sn and similar alloys to activate the surface of aluminum for its rapid hydrogen evolution reactions with water.²⁸–⁴⁴ However, investigations have not yet focused on the potential growth of aerogels using this alloy at room temperature. A novel process has been investigated that can function to activate aluminum contained within either pure or impure aluminum alloys, such as 7075 used for aircraft parts, for its oxidation and growth, producing a...
high-purity, high surface area similar to an aerogel-like material. Thus, the ability to harness waste sources of impure aluminum in this process offers an innovative way to recycle aluminum that has been conventionally difficult to recycle previously.45,46

Results and Discussion

After the aluminum was dissolved within the Ga—In—Sn liquid alloy, that is, Galinstan alloy, the activated aluminum at the surface reacts with the water vapor to produce hydrogen gas and the freshly oxidized alumina aerogel. The reaction vessel has sources for either a wet or dry carrier gas by bubbling through water to introduce water vapor. Within the first few seconds of flowing H₂O vapor carried by CO₂, the mixture turned dark, after which light blue solids grew out of the mixture. The synthesis of the solid material continued over the course of 4 h until the gas flow was halted. By varying the initial aluminum percentage, light blue and partially transparent solids were produced, except for the 2% aluminum mixture, as shown in Figure 1. Similar aerogel growth was observed using the 7075-aluminum alloy, as shown in Figure S2 in the Supporting Information, indicating that this process is not inhibited 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, as shown in Figures 2–4. As shown in Figure 2, at the higher dissolved concentrations of aluminum in the liquid alloy, that is, 40% and 60%, the aluminum within small isolated droplets of the liquid alloy will become oxidized and form an 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 2. This process occurs across the numerous liquid alloy droplets which then produces a bulk amount of blue-tinted worm-like tubular structures.

As shown in Figures 4 and 5, scanning electron microscopy (SEM) images of the blue-tinted alumina revealed a densely packed fibrous structure similar to aerogels produced from mercury-based amalgams.14 The fibrous products were studied further with the use of transmission electron microscopy (TEM) after the initial synthesis and after annealing the solid at 600 °C for 24 h, as shown in Figure 4. The spindles of growth are approximately 10–30 nm across in both high- and low-density growth areas. The energy-dispersive spectroscopy image of the aerogels grown from pure aluminum indicated the presence of only aluminum and oxygen with the relative weight percentages listed in Table 1. The calculated molar ratios between aluminum and oxygen for each reaction mixture indicate that the composition of the aerogel matches roughly with that calculated for Al₂O₃. Images were also taken after approximately 5 min of water vapor exposure using the 7075-aluminum alloy, as shown in Figure S3 in the Supporting Information. A distinct interface was observed where the solid alumina aerogel broke through the high-surface-tension liquid metal, shown in Figure 5. The alumina growth was halted after ~30 s to analyze the growth front of the alumina on top of the liquid Galinstan alloy. Elemental analysis shows that the aluminum and oxygen are concentrated at the upper half of the growth zone, whereas the gallium, indium, and tin are concentrated at the lower half of the growth zone that constitutes the liquid alloy. Some dissolved aluminum is also detected in the liquid alloy on the lower half, as the growth has not yet consumed all of the aluminum in the 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 at 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 that the growth front confirmed that the amorphous alumina solid is devoid of the impurity metals that are initially present in the 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 (PXRD) patterns of the as-synthesized alumina aerogels, as well as after heating to high temperatures, were collected and fitted to known alumina crystalline phases, shown in Figure 6 and given in the Supporting Information in Figure S4. The initial diffraction
shows no distinguishable peaks indicating the formation of an amorphous material or particles too small to diffract. This is consistent with other reported products of aerogels grown from the direct oxidation of aluminum in a liquid metal amalgam. Next, the amorphous alumina was heated separately at 600, 850, and 1050 °C to crystallize the alumina. Each alumina sample transformed similarly under the different heating temperatures, with the samples changing color from light blue to white. Each of the solids remained amorphous after annealing at 600 °C for 24 h in air. New diffraction peaks corresponding to γ-Al₂O₃ were detected after annealing the materials at 850 °C for 48 h for all samples. Further heating at 1050 °C for 48 h leads to the growth of diffraction peaks likely corresponding to the θ-Al₂O₃ polymorph, but which is difficult to distinguish owing to the nanocrystallinity of the product and the broad diffraction peaks. These data provide additional

Table 1. Elemental Analysis of the Compositions and the Surface Areas of Each Alumina Samplea

|     | 2%   |     | 10%  |     | 20%  |     | 30%  |     | 40%  |     | 60%  |     |
|-----|------|-----|------|-----|------|-----|------|-----|------|-----|------|-----|
| Al (wt %) | 45.27 | 43.54 | 56.12 | 49.59 | 54.38 | 55.55 |
| O    | 29.3  | 24.37 | 43.88 | 46.25 | 35.74 | 33.80 |
| mol(O)/mol(Al) | 1.545 | 1.787 | 1.279 | 1.072 | 1.522 | 1.643 |
| surface area (m²/g) | 79 | 83 | 110 | 140 | 120 | 110 |

aThe molar ratios of oxygen to aluminum are listed on the bottom row.
evidence that the as-synthesized and annealed products likely are of the same composition with no other metal impurities arising from the Galinstan alloy.

One major obstacle faced with the previously synthesized alumina aerogels has been their high water content. Infrared spectroscopy for each sample was conducted to determine if water was a major component of the aerogel, shown in Figure 7. Relatively small peaks were detected at $\sim$1595 and $\sim$3350 cm$^{-1}$ corresponding to O–H stretches and bending from water in each of the synthesized aerogel materials.$^{37,38}$ However, these peaks are greatly diminished or disappear entirely after heating the solids in air at 600, 850, and then 1050 °C. The peaks related to Al–O stretches at $\sim$526 and $\sim$842 cm$^{-1}$ remain unchanged during the heating process.

To determine whether the water detected through IR was a result of water being absorbed on the surface, or water content contained within the bulk of the alumina aerogel, thermogravimetric analysis was conducted for each material. The aerogel was heated at 600 °C for 24 h under flowing nitrogen to record the mass change over time. As seen from initial PXRD, the alumina remains amorphous when heated at this temperature. The results from the thermal gravimetric analysis (TGA) show a continuous mass loss for over 800–1200 min as water is removed from the material before reaching a stable mass, as shown in Figure 8 with the 10% aluminum mixture as the representative case. Thermogravimetric data from the other alumina compositions are given in the Supporting Information in Figure S5. The total amount of water loss was calculated by the decrease between the initial and final masses, listed in Table 2. The mole percentages of the water lost from the amorphous alumina aerogel were calculated for each composition and found to be in the range from $\sim$1.2 to $\sim$7.5 weight percent. This apparently represents the lowest water content within any reported alumina-based aerogel grown from an amalgam. Data from TGA and electron microscopy, in conjunction with the IR spectroscopy, support the claim that water is not a major component of the aerogel structure.

The specific surface areas of each as-synthesized high surface area alumina aerogel, measured by Brunauer–Emmett–Teller surface area measurements, are shown in Figure 9 and listed in Table 1. As the weight percentage of aluminum in the alloy mixture increases from 0 to 30%, the surface area of the product increases from $\sim$79 to $\sim$140 m$^2$/g, and then decreases with higher percentages of aluminum. Changes in the surface area are likely because of a combination of factors, including the concentration of aluminum within the mixture and the viscosity of the mixture. Increasing the aluminum weight percentage in the alloy changed the overall consistency of the liquid metal. The alloy behaved as a free-flowing liquid at low concentrations (2–10%), but manifested characteristics of a paste at the higher weight percentages of aluminum. Thus, the slower diffusion of aluminum to the surface of the alloy impacted the density of the grown aerogel with the more optimal weight percentage of 30% aluminum. As the concentration of aluminum increased, the mixture became more viscous, and thus more difficult for aluminum to diffuse to the surface, resulting in loosely packed solid fibers, and thus increasing the total surface areas. However, when the concentration of the aluminum was increased to $\sim$40–60%, the high concentration of aluminum likely overcomes the slow diffusion and creates more densely packed fibers, decreasing the surface area. Variations of the surface tension for each of the aluminum–alloy mixtures are key factors that play a role in the density of growth. The highest surface tension was observed for the 2 and 10% aluminum–alloy mixtures which lead to the beading of the liquid metal, producing densely packed fibers and thus lower surface areas.

The ability for Ga–In–Sn alloys, with dissolved aluminum, to reduce water into hydrogen gas is widely known as previously cited. During the direct oxidation of 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 of the solution. In these experiments, water vapor was passed over the activated metal to drive the production of the aerogel. Gas chromatography of the headspace during and after the aerogel growth confirms that hydrogen is also produced with this method, shown in the Supporting Information Figure S7. One advantage of this method is that during the production of hydrogen gas, atomic hydrogen is attached to the metal surface. The atomic hydrogen could then potentially be used for additional reductive reactions through a process of hydrogen spillover.$^{49}$

![Figure 8. Mass loss during thermogravimetric analysis of the 10% alumina aerogel sample as it is heated at 600 °C for 24 h under flowing nitrogen. The remaining TGA plots for all samples are in the Supporting Information Figure S5.](image-url)
Table 2. Initial and Final Weights of the TGA Samples and the Calculated Ratio of Water to Alumina in Each Sample According to the Mass Losses

| Al (wt %) | 2% | 10% | 20% | 30% | 40% | 60% |
|---------|----|-----|-----|-----|-----|-----|
| initial weight (mg) | 1.0854 | 1.5000 | 1.0664 | 1.8823 | 1.4281 | 2.0136 |
| final weight (mg) | 1.0712 | 1.4951 | 1.0582 | 1.8783 | 1.4100 | 2.0088 |
| n(H2O)/n(Al2O3) | 7.51 | 1.85 | 4.40 | 1.21 | 7.27 | 1.35 |

Figure 9. Surface areas of high surface area alumina aerogel synthesized with aluminum alloy mixtures of different weight percentages of aluminum according to the data given in Table 1.

CONCLUSIONS

Alumina aerogels with high surface areas were synthesized by flowing water vapor over mixtures of different weight percentages of aluminum dissolved within a gallium–indium–tin alloy at ambient temperature and pressure. The high surface area alumina aerogel was a blue solid with an amorphous, fibrous structure, containing mainly alumina with small amounts of water. Upon annealing at 850 °C, the amorphous products transformed into γ-Al2O3 and likely further into θ-Al2O3 upon annealing at 1050 °C, which provides further evidence that the high surface area solids synthesized contain mainly Al2O3. The overall surface area of the aerogels was directly related to the initial weight percentage of aluminum in the alloy. This is likely an impact of a combination of the concentration of alumina, surface tension of the alloy, and the diffusivity of dissolved aluminum. The preliminary results presented in this work provide guidance to select the concentration of the aluminum–alloy mixture to maximize the surface area of the alumina. Additional investigations on the kinetics of the aerogel growth are necessary to further optimize the reaction conditions to maximize the surface areas of the alumina. Further, the synthetic method presented in this work demonstrates a nontoxic way to synthesize alumina aerogel by direct oxidation of aluminum at ambient temperature and pressure. The direct oxidation of aluminum with water vapor generates hydrogen gas, and thus the exploration of the ability of hydrogen storage and regeneration of aluminum dissolved in the Ga–In–Sn alloy will be of further interest.

EXPERIMENTAL METHODS

Materials. UHV grade aluminum foil with 99.99% purity was purchased from All Foils, Incorporated. Aluminum 7075 alloy was purchased from Alcoa. The Ga–In–Sn alloy was prepared in the lab with (wt %) 66.504% of Ga, 20.505% of In, and 12.992% of Sn. The carrier gases, CO2, and N2 of Grade 4.0 were purchased from ARCo3 Gases. The Ga–In–Sn alloy was purchased from Alcoa. The Ga–In–Sn alloy was purchased from All Foils, Incorporated. Aluminum 7075 alloy was purchased from Alcoa. The Ga–In–Sn alloy was prepared in the lab with (wt %) 66.504% of Ga, 20.505% of In, and 12.992% of Sn. The carrier gases, CO2, and N2 of Grade 4.0 were purchased from ARCo3 Gases.

Synthesis. Shredded aluminum foil was dissolved into the Ga–In–Sn alloy at weight percentages of 2, 10, 20, 30, 40, and 60% within an argon-atmosphere glovebox. Approximately, 1 g of the aluminum alloy mixture was placed into a tungsten crucible and dispersed to maximize the contact with the flowing gas. The crucible was then placed in a reaction vessel which allowed a carrier gas to pass over the metal alloy (with exclusion of oxygen), as shown in the Supporting Information, Figure S1. The carrier gas, typically carbon dioxide, was either introduced dry or was bubbled through a water-containing flask to generate a humid CO2 gas flow before entering the reaction vessel and then exiting through a beaker of mineral oil to prevent a back-flow of gas.

The blue-tinted alumina materials were separated mechanically under an optical microscope. Two heat treatments were performed consecutively for each of the aerogel products. During the first process, the sample was annealed at 850 °C for 48 h, and during the second step, the sample was further annealed at 1050 °C for 48 h. After each step, the sample was characterized by infrared spectroscopy and PXRD as described below.

Characterization. The TEM images were taken using JEOL 6010LA SEM. The working distance ranges from 10 to 12 mm, the spot size ranged from 49 to 55, and the accelerating voltage ranged from 5 to 20 kV. Energy-dispersive X-ray spectroscopy (EDXS) was used to determine elemental composition maps and spectra, using a JEOL EDXS silicon drift detector. The TEM images were recorded using JEOL 2000FX with the samples suspended on a copper grid. The structure and crystallinity of each product was measured by PXRD, which was carried out on Rigaku R-Axis Spider using Cu Kα radiation (λ = 1.54056 Å) from a sealed tube X-ray source (40 kV, 36 mA) and a curved image-plate detector. Mid-infrared (400–4000 cm⁻¹) spectra of each solid product were taken on an IRPrestige-21 Shimadzu Fourier transform infrared spectrophotometer equipped with a GladiATR accessory with 4.0 wavenumber (cm⁻¹) resolution.

TGA was performed on a TA Instruments TGA Q50 by loading 1–3 mg of each product onto a platinum pan. Under flowing N2, the pan was equilibrated and tared at room temperature, heated at the maximum heating rate to 600 °C, and held isothermally for 24 h until the weight of the sample stabilized. The water content in the sample was calculated by IR and PXRD, as described above. Specific surface areas of each product were measured on Quantochrome ChemBET Pulsar TPR/TPD. The samples were degassed by heating to 200 °C under flowing N2 for 4 h, then cooled with liquid nitrogen, and analyzed using a 30% He/N2 gas mixture.
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