

Aerogel

Aerogel is a synthetic porous ultralight material derived from a gel, in which the liquid component of the gel has been replaced with a gas. The result is a solid with extremely low density and low thermal conductivity. Nicknames include *frozen smoke*, *solid smoke*, *solid air*, or *blue smoke* owing to its translucent nature and the way light scatters in the material. It feels like fragile expanded polystyrene to the touch. Aerogels can be made from a variety of chemical compounds.

Aerogel was first created by Samuel Stephens Kistler in 1931, as a result of a bet with Charles Learned over who could replace the liquid in "jellies" with gas without causing shrinkage.

Aerogels are produced by extracting the liquid component of a gel through supercritical drying. This allows the liquid to be slowly dried off without causing the solid matrix in the gel to collapse from capillary action, as would happen with conventional evaporation. The first aerogels were produced from silica gels. Kistler's later work involved aerogels based on alumina, chromia and tin dioxide. Carbon aerogels were first developed in the late 1980s

Aerogel does not have a designated material with set chemical formula but the term is used to group all the material with a certain geometric structure.



A block of aerogel in a person's hand

Properties

Despite their name, aerogels are solid, rigid, and dry materials that do not resemble a gel in their physical properties: The name comes from the fact that they are made from gels. Pressing softly on an aerogel typically does not leave even a minor mark; pressing more firmly will leave a permanent depression. Pressing extremely firmly will cause a catastrophic breakdown in the sparse structure, causing it to shatter like glass – a property known as *friability*; although more modern variations do not suffer from this. Despite the fact that it is prone to shattering, it is very strong structurally. Its impressive load bearing abilities are due to the dendritic microstructure, in which spherical particles of average size (2–5 nm) are fused together into clusters. These clusters form a three-dimensional highly porous structure of almost fractal chains, with pores just under 100 nm. The average size and density of the pores can be controlled during the manufacturing process.

Aerogel is a material that is 98.2% air. Aerogel has a porous solid network that contains air pockets, with the air pockets taking up majority of space within the material. The lack of solid material allows aerogel to be almost weightless.

Aerogels are good thermal insulators because they almost nullify two of the three methods of heat transfer (convection, conduction, and radiation). They are good conductive insulators because they are composed almost entirely of gas, which are very poor heat conductors. (Silica aerogel is an especially good insulator because silica is also a poor conductor of heat; a metallic or carbon aerogel, on the other hand, would be less effective.) They are good convective inhibitors because air cannot circulate through the lattice. Aerogels are poor radiative insulators because infrared radiation (which transfers heat) passes through them.

Owing to its hygroscopic nature, aerogel feels dry and acts as a strong desiccant. People handling aerogel for extended periods should wear gloves to prevent the appearance of dry brittle spots on their skin.



A flower is on a piece of aerogel which is suspended over a flame from a Bunsen burner. Aerogel has excellent insulating properties, and the flower is protected from the flame.

The slight color it does have is due to Rayleigh scattering of the shorter wavelengths of visible light by the nano-sized dendritic structure. This causes it to appear smoky blue against dark backgrounds and yellowish against bright backgrounds.

Aerogels by themselves are hydrophilic, but chemical treatment can make them hydrophobic. If they absorb moisture they usually suffer a structural change, such as contraction, and deteriorate, but degradation can be prevented by making them hydrophobic. Aerogels with hydrophobic interiors are less susceptible to degradation than aerogels with only an outer hydrophobic layer, even if a crack penetrates the surface. Hydrophobic treatment facilitates processing because it allows the use of a water jet cutter.

Knudsen effect

Aerogels may have a thermal conductivity smaller than that of the gas they contain. This is caused by the Knudsen effect, a reduction of thermal conductivity in gases when the size of the cavity encompassing the gas becomes comparable to the mean free path. Effectively, the cavity restricts the movement of the gas particles, decreasing the thermal conductivity in addition to eliminating convection. For example, thermal conductivity of air is about 25 mW/m·K at STP and in a large container, but decreases to about 5 mW/m·K in a pore 30 nanometers in diameter.

Structure

Aerogel structure is the result from a sol-gel polymerization, which is when monomers (simple molecules) reacts with other monomers to form a sol or a substance that consists of bonded, cross-linked macromolecules with deposits of liquid solution between them. When the material is critically heated the liquid is evaporated out and the bonded, cross-linked macromolecule frame is left behind. The result of the polymerization and critical heating is the creation of a material that has a porous strong structure classified as aerogel. Variations in synthesis can alter the surface area and pore size of the aerogel. The smaller the pore size the more susceptible the aerogel is to fracture.

Waterproofing

Aerogel contains particles that are 2–5 nm in diameter. After the process of creating aerogel, it will contain a large amount of hydroxyl groups on the surface. The hydroxyl groups can cause a strong reaction when placing it in water. The aerogel will catastrophically dissolve in the water. One way to waterproof the hydrophilic aerogel is by soaking the aerogel with some chemical base that will replace hydroxyl groups with non-polar groups on the surface, the non-polar groups (-OR) is most effective when R is an aliphatic group.

Porosity of aerogel

There are several ways to determine the porosity of aerogel; the three main methods are gas adsorption, Mercury Porosimetry, and Scattering Method. In gas adsorption, nitrogen at its boiling point is adsorbed into the aerogel sample. The gas being adsorbed is dependent on the size of the pores within the sample and on the partial pressure of the gas relative to its saturation pressure. The volume of the gas adsorbed is measured by using the Brunauer, Emmet and, Teller formula (BET) gives the specific surface area of the sample. At high partial pressure in the adsorption/desorption the Kelvin equation gives the pore size distribution of the sample. In Mercury Porosimetry, the mercury is forced into the aerogel porous system to determine the pores size, but this method is highly inefficient since the solid frame of aerogel will collapse from the high compressive force. The Scattering Methods involves the angle dependent deflection of radiation within the aerogel sample. The sample can be solid particles or pores. The radiation goes into the material and determines the fractal geometry of the aerogel pore network. The best radiation wavelengths to use are X-rays and neutrons. Aerogel is also an open porous network, the difference between an open porous network and a closed porous network is that in the open network, gasses can enter and leave the substance without any limitation. While a closed porous network traps the gases within the material forcing it to stay within the pores. The high porosity and surface area of silica aerogels allow for it to be used in a variety of environmental filtration applications.

Materials

Silica

Silica aerogel is the most common type of aerogel, and the most extensively studied and used. It is silica-based, derived from silica gel. The lowest-density silica nanofoam weighs $1,000 \text{ g/m}^3$, which is the evacuated version of the record-aerogel of $1,900 \text{ g/m}^3$. The density of air is $1,200 \text{ g/m}^3$ (at $20 \text{ }^\circ\text{C}$ and 1 atm). As of 2013, aerographene had a lower density at 160 g/m^3 , or 13% the density of air at room temperature.

The silica solidifies into three-dimensional, intertwined clusters that comprise only 3% of the volume. Conduction through the solid is therefore very low. The remaining 97% of the volume is composed of air in extremely small nanopores. The air has little room to move, inhibiting both convection and gas-phase conduction.

Silica aerogels also have a high optical transmission of $\sim 99\%$ and a low refractive index of ~ 1.05 .

It has remarkable thermal insulative properties, having an extremely low thermal conductivity: from $0.03 \text{ W/m}\cdot\text{K}$ in atmospheric pressure down to $0.004 \text{ W/m}\cdot\text{K}$ in modest vacuum, which correspond to R-values of 14 to 105 (US customary) or 3.0 to 22.2 (metric) for 3.5 in (89 mm) thickness. For comparison, typical wall insulation is 13 (US customary) or 2.7 (metric) for the same thickness. Its melting point is $1,473 \text{ K}$ ($1,200 \text{ }^\circ\text{C}$; $2,192 \text{ }^\circ\text{F}$).

Until 2011, silica aerogel held 15 entries in *Guinness World Records* for material properties, including best insulator and lowest-density solid, though it was ousted from the latter title by the even lighter materials aerographite in 2012 and then aerographene in 2013.

Carbon

Carbon aerogels are composed of particles with sizes in the nanometer range, covalently bonded together. They have very high porosity (over 50%, with pore diameter under 100 nm) and surface areas ranging between $400\text{--}1,000 \text{ m}^2/\text{g}$. They are often manufactured as composite paper: non-woven paper made of carbon fibers, impregnated with resorcinol–formaldehyde aerogel, and pyrolyzed. Depending on the density, carbon aerogels may be electrically conductive, making composite aerogel paper useful for electrodes in capacitors or deionization electrodes. Due to their extremely high surface area, carbon aerogels are used to create supercapacitors, with values ranging up to thousands of farads based on a capacitance density of 104 F/g and 77 F/cm^3 . Carbon aerogels are also extremely "black" in the infrared spectrum, reflecting only 0.3% of radiation between 250 nm and $14.3 \text{ }\mu\text{m}$, making them efficient for solar energy collectors.

The term "aerogel" to describe airy masses of carbon nanotubes produced through certain chemical vapor deposition techniques is incorrect. Such materials can be spun into fibers with strength greater than Kevlar, and unique electrical properties. These materials are not aerogels, however, since they do not have a monolithic internal structure and do not have the regular pore structure characteristic of aerogels.

Metal oxide

Metal oxide aerogels are used as catalysts in various chemical reactions/transformations or as precursors for other materials.

Aerogels made with aluminium oxide are known as alumina aerogels. These aerogels are used as catalysts, especially when "doped" with a metal other than aluminium. Nickel–alumina aerogel is the most common combination. Alumina aerogels are also being considered by NASA for capturing hypervelocity particles; a formulation doped with gadolinium and terbium could fluoresce at the particle impact site, with the amount of fluorescence dependent on impact energy.



A 2.5 kg brick is supported by a piece of aerogel with a mass of 2 g.

One of the most notable difference between silica aerogels and metal oxide aerogel is that metal oxide aerogels are often variedly colored.

Aerogel	Color
Silica, Alumina, Titania, Zirconia	Clear with Rayleigh scattering blue or white
Iron Oxide	Rust red or yellow, opaque
Chromia	Deep green or deep blue, opaque
Vanadia	Olive green, opaque
Neodymium Oxide	Purple, transparent
Samarium Oxide	Yellow, transparent
Holmium Oxide, Erbium Oxide	Pink, transparent

Other

Organic polymers can be used to create aerogels. SEAgel is made of agar. Cellulose from plants can be used to create a flexible aerogel.

Chalcogel is an aerogel made of chalcogens (the column of elements on the periodic table beginning with oxygen) such as sulfur, selenium and other elements. Metals less expensive than platinum have been used in its creation.

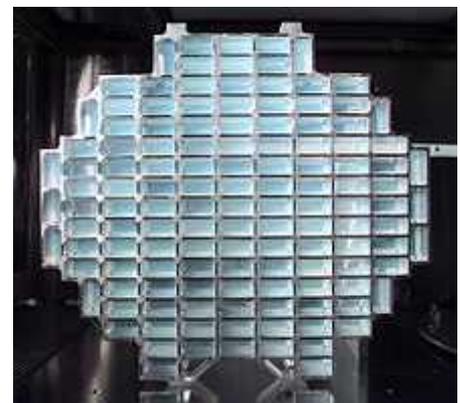
Aerogels made of cadmium selenide quantum dots in a porous 3-D network have been developed for use in the semiconductor industry.

Aerogel performance may be augmented for a specific application by the addition of dopants, reinforcing structures and hybridizing compounds. Aspen Aerogels makes products such as Spaceloft which are composites of aerogel with some kind of fibrous batting.

Applications

Aerogels are used for a variety of applications:

- In 2004 about US\$25 million of aerogel insulation product were sold, which had risen to about US\$500 million by 2013. This represents the most substantial economic impact of these materials today. The potential to replace conventional insulation by aerogel solutions in the building and construction sector as well as in industrial insulation is quite significant.
- In granular form to add insulation to skylights. Georgia Institute of Technology's 2007 Solar Decathlon House project used an aerogel as an insulator in the semi-transparent roof.
- A chemical adsorber for cleaning up spills.
- A catalyst or a catalyst carrier.
- Silica aerogels can be used in imaging devices, optics, and light guides.
- A material for filtration due to its high surface area and porosity, to be used for the removal of heavy metals
- Thickening agents in some paints and cosmetics.
- As components in energy absorbers.
- Laser targets for the National Ignition Facility.
- A material used in impedance matchers for transducers, speakers and range finders.
- Commercial manufacture of aerogel 'blankets' began around the year 2000, combining silica aerogel and fibrous reinforcement that turns the brittle aerogel into a durable, flexible material. The



The Stardust dust collector with aerogel blocks. (NASA)

mechanical and thermal properties of the product may be varied based upon the choice of reinforcing fibers, the aerogel matrix and opacification additives included in the composite.

- NASA used an aerogel to trap space dust particles aboard the Stardust spacecraft. The particles vaporize on impact with solids and pass through gases, but can be trapped in aerogels. NASA also used aerogel for thermal insulation of the Mars Rover and space suits.
- The US Navy is evaluating aerogel undergarments as passive thermal protection for divers.
- In particle physics as radiators in Cherenkov effect detectors, such as the ACC system of the Belle detector, used in the Belle Experiment at KEKB. The suitability of aerogels is determined by their low index of refraction, filling the gap between gases and liquids, and their transparency and solid state, making them easier to use than cryogenic liquids or compressed gases. Their low mass is also advantageous for space missions.
- Resorcinol–formaldehyde aerogels (polymers chemically similar to phenol formaldehyde resins) are used as precursors for manufacture of carbon aerogels, or when an organic insulator with large surface is desired. They come as high-density material, with surface area about 600 m²/g.
- Metal–aerogel nanocomposites prepared by impregnating the hydrogel with solution containing ions of a transition metal and irradiating the result with gamma rays, precipitates nanoparticles of the metal. Such composites can be used as catalysts, sensors, electromagnetic shielding, and in waste disposal. A prospective use of platinum-on-carbon catalysts is in fuel cells.
- As a drug delivery system owing to its biocompatibility. Due to its high surface area and porous structure, drugs can be adsorbed from supercritical CO₂. The release rate of the drugs can be tailored by varying the properties of the aerogel.
- Carbon aerogels are used in the construction of small electrochemical double layer supercapacitors. Due to the high surface area of the aerogel, these capacitors can be 1/2000th to 1/5000th the size of similarly rated electrolytic capacitors.
- Aerogel supercapacitors can have a very low impedance compared to normal supercapacitors and can absorb or produce very high peak currents. At present, such capacitors are polarity-sensitive and need to be wired in series to achieve a working voltage of greater than about 2.75 V.
- Dunlop Sport uses aerogel in some of its racquets for tennis, squash and badminton.
- In water purification, chalcogels have shown promise in absorbing the heavy metal pollutants mercury, lead, and cadmium from water.
- Aerogel can introduce disorder into superfluid helium-3.
- In aircraft de-icing, a new proposal uses a carbon nanotube aerogel. A thin filament is spun on a winder to create a 10 micron-thick film, equivalent to an A4 sheet of paper. The amount of material needed to cover the wings of a jumbo jet weighs 80 grams (2.8 oz). Aerogel heaters could be left on continuously at low power, to prevent ice from forming.
- Thermal insulation transmission tunnel of the Chevrolet Corvette (C7).
- CamelBak uses aerogel as insulation in a thermal sport bottle.
- 45 North uses aerogel as palm insulation in its Sturmfiist 5 cycling gloves.

Production

Silica aerogels are typically synthesized by using a sol-gel process. The first step is the creation of a colloidal suspension of solid particles known as a "sol". The precursors are a liquid alcohol such as ethanol which is mixed with a silicon alkoxide, such as tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), and polyethoxydisiloxane (PEDS) (earlier work used sodium silicates). The solution of silica is mixed with a catalyst and allowed to gel during a hydrolysis reaction which forms particles of silicon dioxide. The oxide suspension begins to undergo condensation reactions which result in the creation of metal oxide bridges (either M–O–M, "oxo" bridges or M–OH–M, "ol" bridges) linking the dispersed colloidal particles. These reactions generally have moderately slow reaction rates, and as a result either acidic or basic catalysts are used to improve the processing speed. Basic catalysts tend to produce more transparent aerogels and minimize the shrinkage during the drying process and also strengthen it to prevent pore collapse during drying.



Peter Tsou with a sample of aerogel at Jet Propulsion Laboratory, California Institute of Technology

Finally, during the drying process of the aerogel, the liquid surrounding the silica network is carefully removed and replaced with air, while keeping the aerogel intact. Gels where the liquid is allowed to evaporate at a natural rate are known as xerogels. As the liquid evaporates, forces caused by surface tensions of the liquid-solid interfaces are enough to destroy the fragile gel network. As a result, xerogels cannot achieve the high porosities and instead peak at lower porosities and exhibit large amounts of shrinkage after drying.

In 1931, to develop the first aerogels, Kistler used a process known as supercritical drying which avoids a direct phase change. By increasing the temperature and pressure he forced the liquid into a supercritical fluid state where by dropping the pressure he could instantly gasify and remove the liquid inside the aerogel, avoiding damage to the delicate three-dimensional network. While this can be done with ethanol, the high temperatures and pressures lead to dangerous processing conditions. A safer, lower temperature and pressure method involves a solvent exchange. This is typically done by exchanging the initial aqueous pore liquid for a CO₂ miscible liquid such as ethanol or acetone, then onto liquid carbon dioxide and then bringing the carbon dioxide above its critical point. A variant on this process involves the direct injection of supercritical carbon dioxide into the pressure vessel containing the aerogel. The end result of either process exchanges the initial liquid from the gel with carbon dioxide, without allowing the gel structure to collapse or lose volume.

Resorcinol–formaldehyde aerogel (RF aerogel) is made in a way similar to production of silica aerogel. A carbon aerogel can then be made from this resorcinol–formaldehyde aerogel by pyrolysis in an inert gasatmosphere, leaving a matrix of carbon. It is commercially available as solid shapes, powders, or composite paper. Additives have been successful in enhancing certain properties of the aerogel for the use of specific applications. Aerogel composites have been made using a variety of continuous and discontinuous reinforcements. The high aspect ratio of fibers such as fiberglass have been used to reinforce aerogel composites with significantly improved mechanical properties.