Aerogels: Much Ado About 'Nothing'

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Aerogels have been called potentially the most useful substances ever created.

This curious material, composed of as much as 65 to 90 percent air, are the lightest solids ever produced. A six-foot block of it would weight less than a pound yet can support 1,500 times its own weight - enough to support a compact car.

Aerogels are the best thermal insulator ever discovered. A double-pane window filled with a one inch layer of the transparent material provides the same insulating value as 15 standard thermopanes. NASA used aerogel last summer to insulate the electronics on the intrepid Sojourner from the chisel cold of the Martian night.

Aerogels have amazing thermal properties. A flower, resting on a cracker-sized aerogel disk, is unaffected by a torch burning blue 1 cm below.

Electrical insulators fabricated with aerogels may double computer speed. Contemporary circuit boards have dielectric constants (an index of non-conductivity) between 2.5 and 4. (Air, the perfect insulator, has a dielectric of 1.) Decreasing that number can increase the speed of computers by allowing engineers to place components closer together. Researchers have already successfully created aerogel films - made mostly of air - with dielectric values ranging between 2.3 and 1.01.

Besides being the best thermal, electric and acoustic insulators known, aerogels are finding application as filters for seawater desalination, micrometeoroid collectors and subatomic particle detectors. In the future, aerogels could be used in windows, building insulation, automobile catalytic converters and high-efficiency battery electrodes.

WHAT IS THIS MIRACLE SUBSTANCE?

Aerogels are unique materials. Both their pores and their properties are smaller than the wavelength of light (less than 100 billionths of a meter). All aerogels are mostly air. Scientists at the University of California's Lawrence Livermore National Laboratory (LLNL) have produced samples made almost entirely (99.98 percent) of air. Silica (silicon dioxide or common sand) aerogels consist of bonded silicon and oxygen atoms joined into long strands and then into beads randomly linked together with pockets of air between them.

The fabrication of aerogels, in general, involves two major steps - the formation of a wet gel and the drying of the wet gel to form an aerogel. A simplified silica aerogel recipe, according to the Aerogel Research Laboratory at the University of Virginia, begins by combining a silica-based solution with 200-proof ethanol, ammonium hydroxide and water, which forms a Jello-like substance called alcogel. The alcogel is then soaked in ethanol for a length of time sufficient to extract the water from the alcogel. Once the majority of the water has been replaced by alcohol, the alcogels are ready to be supercritically dried. This process removes liquid from the microstructure of the alcogel. The alcohol in the alcogel is replaced by carbon dioxide. After nearly all of the alcohol has exited the alcogel structure, it is heated and pressurized in a supercritically drying process. When it returns to room temperature and standard pressure, the process is finished and aerogels are the final product.

Several potential applications have been identified for this emerging technology by startup companies like Ocellus, which markets small quantities of aerogels through Marketech International, San Francisco.

Other companies with a presence in the aerogel marketplace include Nanopore, Albuquerque, which focuses on lower-cost granular aerogels. This enterprise resulted from the work of C. Jeff Brinker and Douglas Smith at the University of New Mexico, who have become increasingly successful at eliminating the supercritical drying step used in aerogel production by chemically modifying the surface of the gel prior to drying.

Aspen Systems, Marlboro, MA, manufactures a variety of aerogel products, including an aerogel powder, monolithic aerogel, and clamshell preformed aerogel insulation. Their flexible aerogel blankets, one for cryogenic and room-temperature applications and the other for high-temperature uses, were developed for NASA.

Cost for the products currently run high since the demand is low. A half-inch sheet of flexible aerogel blanket not much bigger than a breadboard now costs $900, although Aspen Systems projects short-term prices to drop to $35 per square foot; long-term, the company sees the cost of the blankets falling as low as $10 per square foot once production runs exceed 600,000 square feet a year. The same is true for the aerogel powder. The same cubic foot of silica aerogel powder available now for $2,300 will fall to $60 once demand pushes production to 50,000 cubic feet a year.

Silica aerogels, composed mainly of silicon dioxide, are called "amorphous form of common sand" by researchers at LLNL. They are nonflammable, nontoxic and environmentally safe. Another type of aerogel is organic, which are made of carbon and hydrogen atoms. Organic aerogels are stiffer and stronger than silica aerogels and are measurably better insulators. Organic aerogels have extremely high thermal resistance (six times higher than fiberglass) and can be converted to pure carbon aerogels while still retaining many properties of the original aerogel - in addition to becoming electrically conductive.

A third form of aerogel, resorcinol-formaldehyde (R-F) are primarily used as a precursor for carbon aerogels, which opened up a completely new area of aerogel research. Marketech, for instance, offers standard R-F aerogel as a high density (0.6 g/cm3) material with a surface area of 600 m2/g.

Silica aerogels, known for being extremely lightweight solids (down to <0.005 g/cm3), are excellent for applications requiring thermal insulation, high temperature stability, low dielectric constants and extremely high surface area. These aerogels, resembling smoke or fog (they have been called "frozen smoke), attracted international attention in the early 1990s after Livermore scientists created a silica aerogel 10 times less dense than the previous lightest version. <P>Carbon, the newest form of aerogel material, is also the first electrically conductive aerogels developed. This unique class of material with high surface area, controllable pore size and high purity, is responsible for the revolutionary developments in supercapacitors with power densities to 4,000 W/kg. Marketed in monolith (blanket), thin film or powder forms, some carbon aerogel powders have been produced with surface areas approaching an astonishing 2,500 m2/g.

"Carbon aerogels are the ones we feel that really have the potential for electrolytic capacitors," says Jerry Spieckerman, president of Marketech International, a 10 year old high tech distribution company. "Carbon aerogels have the ability to store and discharge a large amount of energy very quickly, which is different than a battery. Also, the don't break down like rechargeable batteries. Except for a few, small areas [like NASA], silica aerogel, because of its high cost, is really a solution looking for a problem. The main market thrust is going to be in the carbon aerogel areas because those really have applications that are down-to-earth." Some are not so down-to-earth. Spieckerman sent one buyer home empty-handed who wanted them to build a lightweight sail board.

Carbon aerogels have been used as electrodes in energy storage devices known as double layer capacitors. Such devices are able to deliver power faster than conventional batteries and thus have potential application in electric vehicles, "pure power" stations, load leveling devices, telecommunications and microelectronics.

Potential applications for carbon aerogels seem limitless: aerogels can be used on composite structures, as reinforcing agents for organic rubbers, in pigments for ink-jet printers, as insulators for electro-chemical storage devices, in media for gas separation or storage, for high temperature insulation, as carriers for controlled release agents, on electrodes for fuel cells and metal catalyst supports. They could also serve as an environmentally friendly replacement for harmful CFC-blown polyurethane foam for refrigerators.

One of the applications uses aerogels as catalysts to reduce nitrous oxide emissions from automobile exhaust. Some scientists expect aerogels will be used as catalysts within a few years because of their high surface area (an aerogel the size of a grape has approximately the same surface area as two basketball courts) and because metallic atoms can be placed in aerogels to cause reactions.

Capacitive deionization is another application of carbon aerogel electrodes. In this purpose, ions are absorbed at the surface of a carbon aerogel electrode under an applied electric field for removal of heavy ions from waste streams or water purification systems. The open lattice structure and interconnected pore structure of carbon aerogels allow for more efficient devices to be built.

AEROGEL HISTORY

It may seem surprising, given their remarkable properties, that aerogels have been around since the Great Depression. They were first discovered in 1931 by physicist Steven S. Kistler of the College of the Pacific, Stockton, CA, who wanted to prove that a "gel", once dried, contained a continuous solid network the same size and shape as the wet gel. This process of discovery proved to be quite time consuming and dangerous. As recently as 1984, an explosion in a small aerogel manufacturing plant in Sweden blew the roof off the plant and injured several employees.

Although Monsanto Corp. took an interest in Kistler and his aerogels in the 1930s and 1940s, for a time using the substance as an additive in cosmetics and toothpaste, interest dwindled and little other activity ensued. For the most part aerogel research was generally abandoned for the next 50 years.

Then, in the 1980s, newer, safer production processes to create aerogels were developed under the leadership of Arlon Hunt, at the Lawrence Berkeley Laboratory, leading to the identification of applications for aerogels as insulators for rocket fuel storage and later as cosmic dust collectors on two shuttle missions.

"Partnerships between companies and the national laboratories and universities to commercialize aerogels are starting to appear," says LLNL polymer chemist Rick Pekala. "The basic research is continuing, but now it is at least partially focused on issues important to industry, like 'How can we better process the material?'"

An example is the work being done at the University of Virginia. One of Hunt's post-doctoral students, Pam Norris, now has an aerogel laboratory of her own, where she is leading three separate research projects investigating the near miraculous properties of aerogels. She has a National Science Foundation grant to build on her study of heat transfer properties of aerogels, which she began under Hunt, to help scientists custom-tailor aerogel thermal properties for specific applications.

Norris is also working with IBM to explore the uses of aerogel film as an insulator for printed circuit boards, helping to reduce the dielectric constant lower and lower, allowing electrical engineers to increase computer speed by reducing the distance between components on a chip.

Her third research effort is exploring the use of the highly porous aerogel material as environmental sensors and detectors of airborne warfare agents. This work could one day find its way onto hospital wards as a screening agent to detect harmful virus and bacteria, or onto factory floors to detect toxic chemicals in manufacturing plants.

(sidebar) AEROGEL BITES THE DUST

On January 1, 2004, NASA will give aerogel technology a chance to show its star quality.

On that day, five years and 173 million miles from earth, the Stardust unmanned spacecraft will extend its ethereal scoop and swoop within 150 km of comet Wild 2 at a speed of 6.2 km/sec (13,680 mph), collecting comet dust for the first time, which is to be returned to earth for analysis. En route to the comet, Stardust will also collect samples of interstellar dust, including the recently discovered dust streaming into the solar system from the direction of Sagittarius.

The dust capture mechanism will use an exciting new silica aerogel material attached to the scoop-panel reaching like tennis racket from the earth-return pod on the spacecraft to soft-catch and preserve the dust particles. The objective is to recover more than one thousand particles larger than 15 microns in diameter, as well as other volatile molecules on the same aerogel capture medium.

Aerogel has sometimes been compared to foam, but other than its light weight it's not like conventional foams at all. Rather, it's a special porous material that has extreme microporosity at the micron scale. Aerogel is composed of individual features only a few nanometers (billionths of a meter) in size, linked to a highly porous dendritic (tree-like crystal) structure.

When hypervelocity particles are captured in aerogel they produce narrow cone-shaped tracks and can easily be seen in the highly transparent aerogel by using a stereo microscope. The cone is largest at the point of entry, and the particle is collected intact at the point of the cone. This provides a directionality detector and is the basis for the mission design approach of using a single waffle of aerogel to collect both cometary and interstellar dust. Side A of the collector is exposed to the direction of comet dust impact; Side B is positioned toward the interstellar dust stream. After the encounter with Wild 2, the aerogel collector will be retracted into the Sample Return Capsule and returned to earth.

Although aerogel was discovered in the 1930s, no practical use for the chemically unique material was identified until recently. They're the lowest density solid material in the world; one inch of aerogel can insulate a home five times better than six inches of fiberglass. Their constituent pores and particles are both smaller than the wavelength of visible light. Silica (silicon dioxide) aerogels consist of bonded silicon and oxygen atoms joined into long strands and then into beads randomly linked together with pockets of air between them. They can be fabricated to be less dense than air, and have extraordinary sound, heat and electrical insulation properties.

Aerogel is also aboard another NASA spacecraft; aerogel accompanied the Mars Pathfinder onto the surface of the Red Planet last summer, providing a lightweight, highly insulating environment to protect the Pathfinder Sojourner's electronics from the harsh, cold climate of Mars.

Over the past several years the Jet Propulsion Laboratory in Pasadena, CA, has produced and flight qualified aerogel. JPL aerogel capture experiments have flown and been recovered on the Spacehab II and Eureca Shuttle flights.

The comet samples are made up of pre-solar interstellar grains and nebular condensates that were incorporated into comets at the birth of the solar system. Their analysis is expected to yield important clues about the evolution of the sun and planets, and possibly into the origin of life itself.

STARDUST is scheduled for launch in February, 1999.

sibebar2: DOUBLING COMPUTER SPEEDS

One of the most practical applications for aerogel may be found at Rensselaer Polytechnic Institute. Researchers there think computer speeds may double as the result of their having fabricated insulators for computer chips out of aerogel that are so thin and porous they are more air than matter. Some of the Rensselaer chips are 65 to 90 percent air.

The Rensselaer aerogels have low dielectric constants, making them excellent insulators, permitting electrical engineers to place lines closer together without disrupting or slowing the electrical signal.

Air, the perfect insulator, has a dielectric of 1. Chips can't be held together with air, but the research teams are learning how to solve the problem with aerogels. Aerogels, discovered in the 1930s, are unique in chemistry. Their constituent pores and particles are both smaller than the wavelength of visible light.

"We have a process to make aerogel films under ambient temperature and pressure conditions that enables us to integrate the deposition of aerogels into semiconductor processing," says Joel Plawsky, Rensselaer associate professor of chemical engineering. "This is important because the next generation of devices will have to use dielectric materials with much lower dielectric constants than the thermally grown silica-dioxide currently used to avoid propagation delays and excessive crosstalk."

The Rensselaer aerogels were announced and display last November when members of the Center for Advanced Interconnect Science and Technology (CAIST) gathered on campus to hear reports. An interdisciplinary university consortium, CAIST was established by industry to improve interconnects, the minuscule system of wires and insulation that carries messages on a chip. The team of Plawsky and colleagues Peter Wayner and William Gill from Rensselaer's Isermann Chemical Engineering Department showed it can control porosity and thickness of their aerogel. Their new films apparently do not create problems by absorbing water during processing. They also stand up well to high temperature.

The importance of aerogels as a possible solution to lowering the dielectric constant can be seen in the research race underway. At the December meeting of the IEEE International electron Devices Meeting in Washington, DC, Texas Instruments reported that it has demonstrated the successful combination of copper wiring with a similar aerogel substance it calls xerogel. Illustrating the importance of this new type of insulator, TI estimated that within a decade combining xerogel with copper wires and new designs could result in devices that are several times faster than today's best chips.

"TI's process for making aerogels is proprietary, but I do not believe they can make films as thick or as porous as ours," Plawsky says.

The researchers say aerogels will probably be used once device dimensions shrink much below 0.25 microns. (Gate lengths using 0.18 micron technology have been announced by several manufacturers.) "At that point they will be married with copper conductors to achieve speed increases perhaps a factor of 10 higher than current microprocessors," Plawsky says.

These aerogel materials are not limited to dielectrics. "We can make 'active' devices from them by growing semiconductor nanoparticles inside," Plawsky explains. "We generally modify the surface of our materials with organic functionality to make the material resistant to water. Such modification can also be used to make sensors, nanoreactors and other items."

There are many problems remaining for the researchers. "As chemical engineers our primary interest is how chemistry and processing combine to produce a material with a given set of properties," Plawsky says. "Our research focuses on how to control the material properties and how we can develop mathematical models that incorporate the details of the chemistry and the processing in order to predict the performance of the material."

The next step in the research is to determine how the aerogel materials interact with metallization layers such as copper. Plawsky said in particular they are interested in whether copper diffuses into the aerogel and how to control it. "We are also interested in whether copper adheres to the aerogel and how to control the surface properties of the aerogel and copper to enhance the adhesion, he said."

sidebar3: AEROGEL ULTRACAPACITORS AND THE NEXT GENERATION OF VEHICLE

They can put a man on the moon but can they build a 40 percent lighter car that gets 80 miles per gallon while increasing engine efficiency by 50 percent and energy storage by 90 percent?

Researchers for the Partnership for a New Generation of Vehicles (PNGV), a domestic auto industry and federal government initiative, have identified several technologies to help achieve these goals. Ultra lightweight materials, including aerogels, are expected to play a critical role in PNGV designs.

Carbon aerogel, one of the world's lightest materials, offers high surface area for optimum power delivery from a compact size - a primary need for the development of ultracapacitor technology. Ultracapacitors made of carbon aerogel - called

aerocapacitors - like those being developed at Lawrence Livermore National Laboratory (LLNL), Livermore, CA, for PNGV, offer one alternative for addressing energy storage needs in hybrid electric vehicles. >P>Ultracapacitors, which are capable of several times the specific power (power per unit of weight) of conventional battery systems, are the next generation of capacitor electrical energy storage. Found in most of today's electronic devices, capacitors store electrical energy by allowing a charge to build up between two conductive plates. Ultracapacitors have the potential to store a hundred times or more energy than conventional capacitors. Energy is retained by distributing it across a large surface area. Energy is stored in an ultracapacitor by charge separation within the micro pores of high surface area materials, such as those found in aerogels. These materials typically do not undergo chemical change as in traditional battery systems. This storage mechanism is a primary reason these devices are capable of extremely high (greater than 100,000) cycle life.

LLNL began working on aerogels in 1984 in relation to a laser program's need for low density, high pore volume materials. Since the discovery of carbon aerogels, numerous applications like the aerocapacitor have surfaced.

Aerocapacitors are inexpensive and show potential to be easy to produce. Because of the enormous surface area brought by the use of carbon aerogels (a chunk of aerogel the size of a grape has an internal surface area as large as 2 basketball courts), aerocapacitors can deliver 50 times more power in a given space than conventional batteries. In addition, aerocapacitors' conductivity is higher than that of capacitors made from other forms of carbon or carbon powders due to the 'honeycomb' structure of carbon aerogel.

Applications for aerocapacitors and carbon aerogels include electric and hybrid vehicles, power supplies, load leveling, memory backup, preheaters for catalytic converters, sensors, lenses, lightweight mirrors, window and skylight insulation, water heater and pipe insulation, refrigeration, cameras, speakers and ultrasound devices. Ultracapacitors are already being developed for a wide range of commercial markets, including communications, consumer electronics and medical applications as well as military and aerospace uses.

The LLNL aerocapacitors have shown capacities of up to 40 Farads (the unit of electrostatic capacitance) per cubic centimeter and excellent performance in temperatures as low as -30 degrees Centigrade. Power densities have been shown to be more than 7 kW/kg, while unpackaged energy densities with aqueous electrolytes have been reported at 4 Wh/kg. These aerocapacitors do not lose stored energy for weeks at a time.

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