

Less is More with Aerogels

A laboratory curiosity develops practical uses

by Eric J. Lerner

With the lowest density, highest thermal insulation, lowest refractive index, and highest surface area per unit volume of any solid, aerogels exhibit remarkable properties. But until a decade ago, the high cost of producing these extremely porous

materials (up to 99.9% empty space) prevented their widespread application. Now, aerogels have begun moving from the exotic—for example, being used to catch space dust—to more mundane applications such as ultrahigh-density capacitors. Reducing production costs further could make aerogels a multibillion-dollar industry with applications such as insulating and soundproofing homes and purifying air and water supplies.

Making solid smoke

Aerogels, first produced in 1931 from silicon dioxide (Figure 1), consist of tangled, fractal-like chains of spherical clusters of molecules each 3–4 nm in diameter (Figure 2). The chains form a structure surrounding air-filled pores that average about 30–40 nm across. Despite the extremely high porosity, the chains themselves are rigid, which gives aerogels considerable mechanical strength. In the early 1990s, researchers developed aerogels made from pure carbon, and they are now made from a variety of materials.

The combination of high porosity and extremely small pores provides aerogels with their extreme properties. Densities of aerogels can be as low as 3 mg/cm³, only a factor of 3 greater than that of air. This directly leads to indexes of refraction as low as 1.01. In addition, because the solid conducts heat only through the exceedingly narrow chains, thermal conductivity can be as low as, or lower than, that of air. Conversely, the surface area of the material is huge—as much as 1,200 m²/g.

In one process for making silicon aerogels, orthosilicic acid (Si(OH)₄) polymerizes and then breaks up into a colloidal suspension of silicon dioxide particles, linked into chains, with the pores filled with methanol and water. This produces an intermediate product, an alcogel, that is dried slowly, including for 1.5 days at 240 °C and 80 atm. “Obviously, if one wishes to produce an aerogel,

he must replace the liquid with air by some means in which the surface of the liquid is never permitted to recede within the gel [which would shrink it],” wrote inventor Samuel S. Kistler. “If a liquid is held under pressure always greater than the vapor pressure, and the temperature is raised, it will be transformed at the critical temperature into a gas without two phases having been present at any time.”

Drying removes both the methanol and water from the aerogel and fills the pores with air without allowing it to shrink. Because the resulting aerogels are hydrophilic, some water is bound into the aerogel, but chemical treatments can produce highly hydrophobic aerogels that eliminate the water.

Carbon aerogels are obtained by pyrolyzing an organic compound in an inert medium. For example, ethanol can be pyrolyzed at 1,000–1,200 °C in an argon flow. This process removes everything except the carbon and leaves behind so-called solid smoke.

Because of high production costs and weeks-long production times, aerogels remained largely a curiosity until



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Figure 1. Scanning electron micrograph of porous silica aerogel.

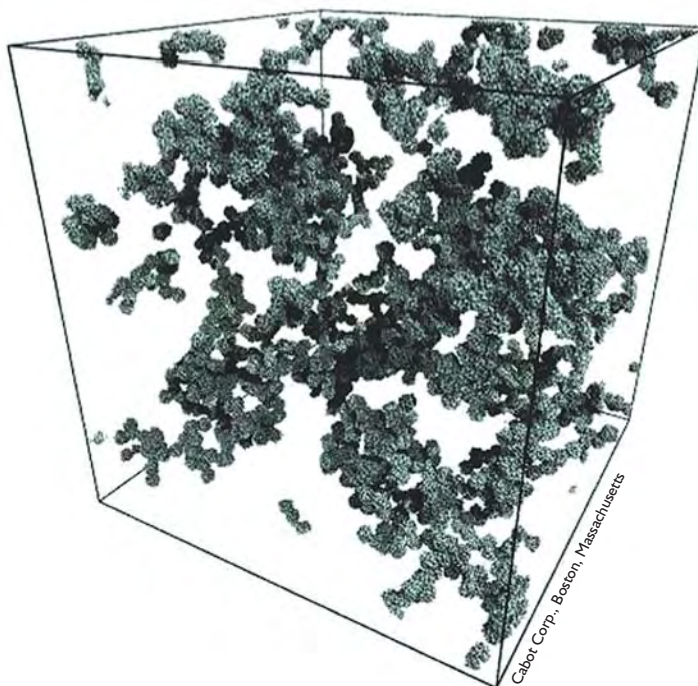
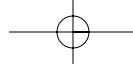


Figure 2. Computer simulation of a silica aerogel product called Nanogel, which is surface-treated to be hydrophobic and suitable for thermal and acoustic insulation.



Airglass AB, Staffanstorp, Sweden

Figure 3. Airglass is composed of quartz and a lot of air; is light, transparent, nonflammable, nontoxic, porous, and brittle; insulates better than mineral wool; and is more heat-resistant than aluminum.

the early 1980s, when manufacturing improvements cut drying time to days. This advance made aerogels easier to fabricate but still expensive. At that time, scientists were looking for new materials to use as Cherenkov radiation detectors for particle physics. A particle emits Cherenkov radiation when it travels faster through a medium than light, the speed of which is reduced by the medium's index of refraction. Thus, particle energies can be distinguished by whether or not they emit Cherenkov radiation in a given material. Aerogels proved ideal for this purpose because their low index of refraction filled a gap between the refraction indices of gases and liquids. In addition, aerogels' transparency and solid state made them easier to use than cryogenic liquids or compressed gases. Cherenkov counters first flew in space aboard HEAO-3, which the National Aeronautics and Space Administration (NASA) launched in 1979. Today, Cherenkov detectors have become a routine application of aerogels.

Catching stardust

After this first use, research interest in aerogels started to soar, especially after manufacturing costs began to drop again in the early 1990s. NASA scientists started to look at aerogels as a means of capturing high-velocity interplanetary and interstellar dust particles. Such particles, ranging in size from 100 nm to 10 μm and traveling between 0.5 and 10 km/s, pass easily through gases but vaporize on impact with liquids or ordinary solids. Because aerogels have greater strength than air but are far less dense than regular solids, they can slow the dust particles gradually and capture them. Aerogels also preserve the tracks made

by the particles, making it easy to isolate each particle for study after the aerogels are returned to Earth.

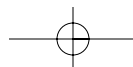
On January 2, NASA's Stardust passed close to Comet Wild 2 and collected dust particles emitted by the comet. Scientists will examine the particles after the sealed sample canister drops into Utah on January 15, 2006. The sample should provide an invaluable window into the solar system's origins because comets are believed to contain material almost unchanged from the initial cloud that collapsed to form the sun and its planets.

Capturing samples of interstellar dust passing through the solar system could be even more interesting scientifically, because such dust contributes to the formation of stars by heating the gas clouds from which stars form. However, interstellar dust can only be distinguished from the more-abundant dust within the solar system by its high velocity, which is greater than 60 km/s. Researchers at the University of California, Berkeley, NASA's Jet Propulsion Laboratory (Pasadena, CA), and Pleasanton Research Corp. (Hayward, CA) have demonstrated that alumina aerogels doped with chromium can produce fluorescent pulses that are proportional in intensity to the heating of the aerogel along the path of hypervelocity particles (Figure 6). This heating, in turn, is proportional to the particle energy, and in principle, aerogel detectors on future space missions could identify hypervelocity particles as interstellar dust.

Coming down to Earth

Low density is only one of aerogels' useful properties. Because they contain pores smaller than the wavelength of visible light, aerogels interact with light as a single, highly nonlinear substance, not as a mixture of air and solid. Research performed by an international team led by J. T. Seo of Hampton University (Hampton, VA) showed that the third-order nonlinear refraction index—a measure of how index of refraction changes with increasing light intensity—was 100,000 times that of bulk silica and comparable to that of semiconductors. This aerogel characteristic can be used, for example, to create filters that limit the total intensity of light that can pass through them, which is a valuable property for applications such as safety glasses that are worn when working with lasers.

In acoustics, aerogels can increase rather than limit intensity levels. One reason that speakers tend to high inefficiency is the mismatch in the impedance between the solid speakers and air. For short-wavelength sound, such as ultrasound, placing a quarter-wavelength thickness of aerogel between the piezoceramic generating the ultrasound and the air boosts intensity. Because aerogels have acoustic impedances intermediate between those of air and solid, they greatly reduce the impedance mismatch of each transition, which can increase the intensity of ultrasound in the air by several hundredfold. If production costs can be reduced further, one of the larger potential applications of silica aerogels lies in thermal insula-



tion, especially in houses and offices (Figures 2 and 3). Silica aerogel has a thermal conductivity at room temperature of $20 \text{ mW/m}\cdot\text{K}$, which is lower than the thermal conductivity of air, $26 \text{ mW/m}\cdot\text{K}$. The ultrashort path lengths of air molecules in the aerogel pores inhibit conduction through the air, and the tiny width of the silica filaments greatly limits conduction through the solid. These characteristics led NASA to adopt aerogels as insulation material in space suits.

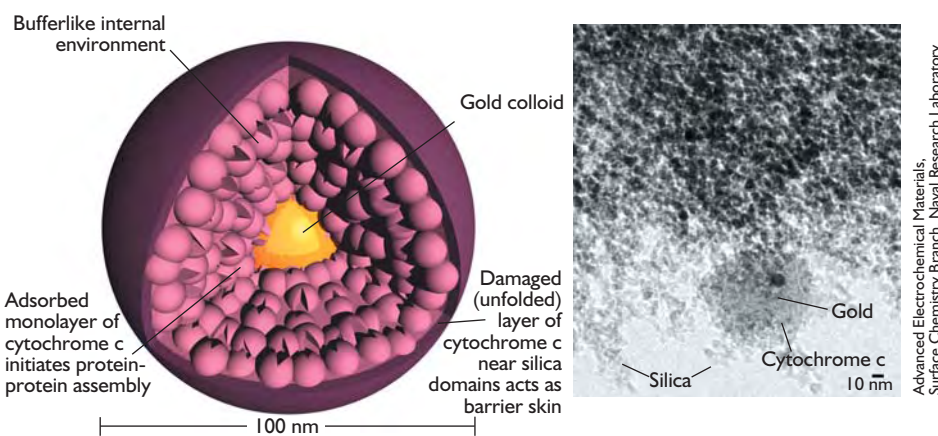
Silica aerogel also strongly absorbs most infrared (IR) radiation, but it is transparent in the visible. This makes it ideal for translucent wall materials that let in light but trap IR for solar heating. The materials have insulation values 2–3 times that of conventional triple-paned glass windows. If such insulation entered widespread use, it would provide substantial energy savings in heating.

Other potential aerogel applications include air and water purification. Activated carbon can absorb impurities from air and water, and it has long been used to do so in the form of granulated activated carbon (GAC). But silica aerogels are superior to GAC. Highly hydrophobic aerogels can exclude water from the nanopores. However, organics dissolved in or mixed with the water generally have lower surface energies and higher volatility than water, so they can enter the pores as a liquid or gas and become absorbed. Experiments performed at Lawrence Livermore National Laboratory (Livermore, CA) show that for common pollutants such as chlorobenzene or trichloroethylene, aerogels absorb 130 times the quantity of chemicals gram-for-gram than GAC.

Dark aerogels

Carbon aerogels have a shorter history than silica aerogel, but they also possess remarkable properties and promising applications. One simple property is extreme blackness, caused by internal scattering and absorption of light by the graphite molecules that make up the aerogel (Figure 5). In a broad wavelength range from 0.25 to $14.3 \mu\text{m}$, the reflection coefficient of carbon aerogels is only 0.3%. This makes the material ideal for some forms of solar-energy collectors.

More spectacularly, carbon aerogels are good electrical conductors, which allows their use in supercapacitors. Capacitance increases as the distance between conductors decreases and the surface area of the conductors increases. Because carbon aerogels have huge surface areas per unit mass or volume and tiny pores, researchers have achieved



Advanced Electrochemical Materials,
Surface Chemistry Branch, Naval Research Laboratory

capacitances as high as 104 F/g and 77 F/cm^3 . Companies such as Cooper Electronic Technologies (Boynton Beach, FL) are already producing aerogel supercapacitors. Operated at up to 2.5 V, such supercapacitors can store energy at a density of 325 kJ/kg , about 70% that of the most advanced lithium-polymer batteries, now in development but years from commercialization. Power densities are more impressive, as high as 20 kW/kg , or 700 times more than the 30 W/kg of lithium ion batteries. At present,

small aerogel supercapacitors are used in electronic equipment, but in the future, they could prove suitable for higher-voltage and higher-power applications, such as electric vehicles.

New applications continually turn up for carbon aerogels, which come in a variety of forms. University of Cambridge physicists this year announced the production of a carbon aerogel made not of graphite particles but of nanotubes (see *The Industrial Physicist*, August/September 2004, pp. 13–14). The aerogel is highly elastic rather than rigid, so it can be

spun into pure nanotube fibers with unique electrical properties and a strength greater than that of Kevlar.

Cutting costs

The main problem holding up more extensive use of aerogels remains the relatively high cost of production, especially when they require supercritical drying. The alternative is to dry the sol-gel at ambient conditions and use a chemical treatment to modify the surface of the wet gels to prevent them from shrinking. This means changing the hydroxide ions on the surface to a nonreactive form. Until recently, the only way to do this required a complex chemical process that involved solvent exchange—allowing one solvent to diffuse out while another diffused into the aerogel. Because of the process's inherent slowness, it did not solve the problem

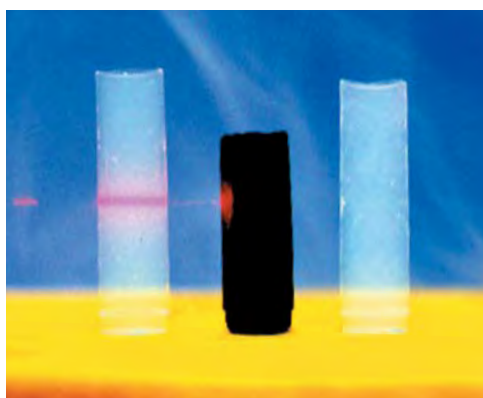
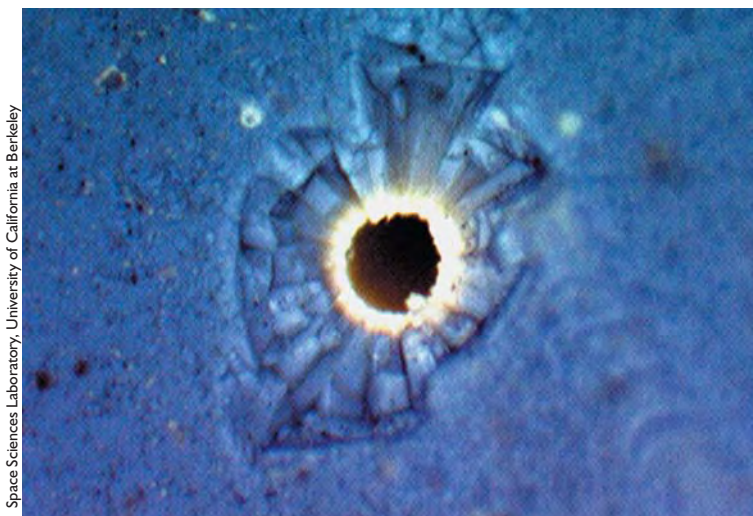


Figure 5. A helium–neon laser (from left) penetrates a silica aerogel, but no light emerges from the carbon–silica ultraporous aerogel.

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Surface Chemistry Branch, Naval Research Laboratory,
photo by Levendis/Kolison

Figure 4. Model (left) and micrograph (right) of gold colloid, which, in a silica aerogel environment, adsorbs cytochrome c to form a nanoparticle that acts as a rapid gas-phase sensor for nitric oxide.



Space Sciences Laboratory, University of California at Berkeley

Figure 6. The amount of fluorescence on the surface of this Gd:Tb-doped alumina aerogel can be used to measure the impact velocity (~5 km/s) of a captured projectile.

of speeding up drying times.

In recent years, many groups have experimented with reactions that simultaneously coat the aerogel surfaces and squeeze the water out by a phase separation mechanism. On the basis of earlier work at Hoechst (Frankfurt, Germany), Sang-Hoon Hyun and colleagues at Yonsei University (Seoul, South Korea) have developed a process involving a series of reactions that lead to the production of an extremely hydrophobic coating on the silica wet gels and the rapid expulsion of water from the gel. The group achieved porosities of up to 94%, and higher values may

be possible. The new process not only speeds and makes drying the gels less costly, it also makes use of an economical initial material, water glass ($\text{Na}_2\text{O}:\text{SiO}_2$).

If researchers can bring such new processes to commercialization, the cost of aerogels should drop substantially and turn a still somewhat exotic material into one that is in every home.

Further reading

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