H_2-Fuel from Metal Hydrides Powers Transit Bus

A coalition of academic, government, and private industry partners has built a prototype hydrogen-fueled, electric-powered transit bus that produces near-zero emissions. The H_2-fuel bus uses hydrogen fuel stored in metal hydrides. It was delivered to the Augusta-Richmond County Public Transit in late April where it will be used as part of regular operations for one year.

The technology of the H_2-fuel bus includes the metal hydride storage system, which fuels a standard internal combustion engine, which in turn drives a 70-kW electrical generator that keeps the bus's batteries charged. Metal hydrides are intermetallic alloys that, when cooled, absorb hydrogen gas into a solid form. The H_2-fuel bus uses a metallic nickel powder distributed in an aluminum foam material called Duocel®. When the hydrides are heated by energy from the bus's generator, they slowly release the hydrogen as a gas to power the bus's engine.

The bus currently carries 5,000 cubic feet of hydrogen and can travel over 100 miles before refueling. The electrical system is powered by 56 12-volt Electro-Source deep-discharge, lead-acid batteries, which charge continually while the hydrogen engine is operating.

Hydrogen-fueled vehicles are being developed, most with more costly hydrogen fuel cells than the bus uses. The internal combustion engine technology developed for the H_2-fuel bus offers a near-term, cost-effective alternative for cities trying to achieve near-zero emission levels, said Earl J. Claire, executive director of the Southeastern Technology Center.

Currently, widespread use of hydrogen is hindered by public perception about its safety and a lack of infrastructure for large-scale production and distribution. But according to the researchers, metal hydrides allow hydrogen to be converted from a highly reactive gas to a safe solid form. Researchers said that if this project goes well, it could be a major step toward widespread acceptance of hydrogen as an alternative transportation fuel.

"We have met the challenge of making hydrogen a safe fuel for public transportation," said Mario Fiori, operations manager of the Department of Energy's Savannah River Site. "Now the challenge is to make these buses more economical."

"The actual transit experience over the next year will provide critical data for the commercialization of hydrogen vehicles," said William A. Summers of the Westinghouse Savannah River Co., another project partner. "Operating data will provide a measurement of the performance, reliability and maintainability of the various system components, primarily the hydrogen engine and the metal hydride storage system."

X-Ray Imaging Allows Measurement of Properties of Diamond-Anvil Cells at Ultrahigh Pressures

Researchers from Carnegie's Geophysical Laboratory, the Laboratoire de la Terre, Ecole Normale Superieure du

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Lyon, and the European Synchrotron Radiation Facility in Grenoble have developed techniques to image directly the deformation of strong materials such as diamond under ultrahigh pressures (200–300 GPa). The measurements, reported in the May 1997 issue of *Science*, show that diamond can be bent at high pressures without failing. The results suggest ways of improving high-pressure techniques to attain still higher pressures in the laboratory.

The ability to confine and study materials at ultrahigh pressures is the result of continued refinement in the diamond-anvil cell. In this apparatus, a sample under study is contained between two facing diamonds mechanically forced together. The transparency of the diamonds allows x-ray, infrared, and other radiation to penetrate inside. While many advancements in the diamond-anvil cell have occurred over the past 25 years, scientists have been unable to determine the three-dimensional distribution of stresses and strains in the diamond itself and other materials at ultrahigh pressures. Consequently, they have had to rely on indirect measurements and extrapolations from lower pressures, which are typically unreliable.

Using intense x-ray beams from a synchrotron source, this research team was able to image and measure the stress-strain distribution in the load-bearing components of the diamond-anvil cell, including the diamond anvils and the gaskets that hold the samples being measured. Because most gaskets absorb x-rays, the researchers developed a gasket made out of beryllium, allowing the x-ray beams to pass through from the side as well as through the diamond. This allowed a "three-dimensional" view of the strain of the sample.

By directly imaging the topography of the diamond-anvil surface *in situ* to pressures of about 300 GPa, the researchers found that diamond can accommodate large strains localized over small areas in the anvil tip. Although the diamonds bent as much as 16° over a distance of 300 μm, they did not fail. Performing complementary experiments using the three-dimensional diffraction geometries, the research team found similar results.

The researchers also studied the ultimate strength of materials under pressure. Using the beryllium gasket, the group measured stresses and strains in samples of iron and tungsten subjected to pressures in the 200–300 GPa range. The researchers found that the strength of these materials is enhanced at ultrahigh pressures by up to two orders of magnitude, demonstrating that applied pressure makes these already strong materials much, much stronger.

Russell J. Hemley of the Geophysical Laboratory said that such measurements allow researchers to perform "tomography" of the stresses and strains in materials at ultrahigh pressures. "Detailed modeling should further permit us to optimize the design of the apparatus. In a broader sense, the study shows us that the elasticity and strength of materials at high pressure can differ in extraordinary ways in comparison to ordinary conditions." For example, past diamond-anvil cell studies showed that diamond can flow under

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pressures approaching 200 GPa. The behavior of materials at high pressure, where they are stressed and strained in unique ways, differs considerably from their behavior at lower pressures.

Structural Anomalies Make Some Materials Flash Under Pressure

Just as wintergreen candy sparkles when crunched in a darkened room, many different crystalline materials can change shape and flash under pressure if they lack symmetry or contain structural anomalies, researchers from Towson State University and the University of Delaware (UD) report in the May 1997 issue of *Chemistry of Materials*. Triboluminescence—the phenomenon that prompts certain materials to emit light when fractured or deformed—has traditionally been associated with structures that lack a center of symmetry, according to Linda M. Sweeting, a professor of chemistry at Towson State; Arnold L. Rheingold, a professor of chemistry and biochemistry at UD; and their students.

Sweeting and her undergraduate students synthesized 12 esters—organic compounds resulting from a reaction of alcohol with 9-anthracencecarboxylic acid. They compared the triboluminescent activity of the acid and its esters with each material's crystal structure and purity, determined by Rheingold and his students. Triboluminescence was assessed objectively by measuring the wavelength of light and was judged subjectively by crushing materials in a darkened laboratory where students graded the resulting light shows.

Bombarded by a laser beam, different crystalline materials emit a characteristic x-ray diffraction pattern, Rheingold said. A computer then detects the scattered x-rays, generating a color-coded map of the molecular architecture of each sample.

Sugar and other noncentrosymmetric materials may be more likely to give off light because "breaking the crystal along a plane tends to leave one surface with a positive charge, and one surface with a negative charge," said Rheingold. By contrast, centrosymmetric materials are built like the letter X, so that charged fragments are symmetrically arranged around the center.

"Triboluminescent materials are usually noncentrosymmetric, meaning that their structure looks more like an arrow than an X," said Sweeting. "But, it seems that even X-structured or centrosymmetric substances can give off light if they contain an impurity." This may explain why wintergreen candy containing various ingredients is more intensely triboluminescent than cane sugar (sucrose), she said. While sugar emits light mainly in the ultraviolet range, she said, the presence of methyl salicylate in wintergreen candy shifts its emissions into the visible range.

Rheingold said, "The study told us a great deal about what happens when materials are mechanically deformed." Impurities appear to make centrosymmetric substances change shape; that is, some X-shaped structures can be transformed into arrows, Rheingold said. "Just prior to fracture, a plastic deformation changes the material from centrosymmetric to noncentrosymmetric."

According to Sweeting it is likely that "impurities are arranged in the crystal so as to make the X-shape into something less symmetric, by putting a cap on the X, for example."

Microwave Technique Repairs Potholes, Detects Hidden Defects

Terry White and Tim Bigelow of Oak Ridge National Laboratory are developing a technique that uses microwaves to repair potholes and cracks. The microwaves are used to heat the area to be fixed and the asphalt used to fill the hole. Repairs are seamless and much stronger than those done by compacting hot asphalt into a hole. Using microwave technology, the system can also detect cracks and flaws beneath asphalt and concrete before they surface and cause problems.

The microwave asphalt repair technique works by using high power microwaves to directly heat the asphalt area around a crack or pothole. The asphalt softens and can be compressed back to a like-new state. New material, if needed, is added to fill in the crack or pothole. The addition of heat to the old material makes a better bond to new material and the resulting joint between old and new material is seamless. The microwave technique can make seamless repairs between highway lanes that are paved individually or when utilities are installed. A 2.45 GHz, 30 kW microwave system with a waveguide applicator has been utilized to test the technology.

The flaw detection system works by probing through road surfaces using radar-like techniques to send a signal into the surface and by looking for reflected power.

"Using time delay or using swept frequency can provide depth profile data," said Bigelow of the Fusion Energy Division. "By scanning the antenna along the asphalt surface, we can look for changes that indicate underlying problems that may not be visible on the surface."

The microwave repair technique can be used with a hand-operated applicator or scaled up to a high power truck-mounted system.

Among the benefits of using microwaves is that the repairs can be made using cold material, thereby saving the expense and trouble of hauling heated asphalt to the potholes, and the repairs can be made throughout the year instead of primarily in warmer months.

Liposomes Tailored to React to Metals Leads to Heavy-Metal Sensors

Darryl Sasaki from Sandia National Laboratories found that when he added copper ions to a liquid solution containing liposomes, the sample's color emission under a fluorescence spectrophotometer rapidly changed from green to blue. Sasaki's research team surmised that the introduction of charged metal ions prompted the liposomes to scramble their molecular arrangements to incorporate the new ions, altering their fluorescence signal.

"When the reactive head [surface] groups accept the metal ions, they develop equally strong ionic repulsive forces, causing them to disperse across the surface of the liposome," said Sasaki. "We think the color change results from this dispersion."

The liposomes also reacted to other metals, including manganese, cobalt, calcium, and nickel. Their high sensitivities to metals suggested uses outside the protein-separation arena. "We began to see this as a candidate technology for practical sensors that could rapidly detect heavy metals in nanomolar concentrations," said Sasaki.

According to Sasaki, because the liposomes are chemically fragile, the liposome-bearing solutions had a brief shelf life. The liposomes were impractical for sensor applications when free-floating in a liquid. A solid, dry medium was needed that could physically immobilize the liposomes while stabilizing them chemically.

To solve these problems, the researchers developed a procedure to entrap the liposomes in sol-gels. The entrapped liposomes reside within cavities in the porous sol-gel matrix but are not chemically attached to the matrix. Not only did the sol-gel-entrapped liposomes react rapidly to metal ions, their sensitivities were four to 50 times greater than those observed for the liposomes in solution. Sasaki said that the negatively charged silica surface—a product of sol-gel formation—acts like an ionic sponge, increasing concentrations of positively charged metal ions near the sol-gel material's surface and the odds that a metal ion will encounter and react with a liposome.

For sensor applications, sol-gels have a number of advantages, Sasaki said. They can be applied as a thin film to a variety of surfaces or cast in bulk form into nearly any shape. They are optically clear, so liposomal color changes would be easy to read. The entrapped liposomes seem impervious to fungal or bacterial attack even after months on a laboratory shelf. They are durable—the liposomes remain intact even when the sol-gel structure is damaged. In addition, said Sasaki, the very few *in situ* heavy metal sensors currently available typically require minutes to hours to respond definitively in the parts-per-billion range. The liposomes themselves respond in less than a second. The research team is experimenting with sol-gel film thicknesses to get response times down when they are entrapped in sol-gel.

Theoretically, liposomal molecules can be created with parts-per-billion sensitivities to a variety of contaminants commonly found at environmental remediation sites. Such liposomes entrapped in sol-gels could lead to practical sensors for rapidly detecting very low levels of heavy metal or radionuclide contamination in groundwater for site characterization applications. The researchers are now working to create liposomal sensors targeted for lead, mercury, and chromium.

High Voltage Causes Large Movement in Relaxor Ferroelectrics

High voltage causes a family of crystals known as relaxor ferroelectrics to deform 10 times more than any other material currently known, according to Thomas R. Shrout, senior scientist and professor of materials at The Pennsylvania State University's (Penn State) Materials Research Laboratory.

As reported at the Piezoelectric Crystals Planning Workshop May 14–16 in Washington, DC, while trying to improve the piezoelectric performance of medical ultrasound devices by growing large single crystals, Shrout and Seung-Eek Park, postdoctoral researcher at Penn State's Materials Research Laboratory, tested crystals for high voltage properties. They found that the material deformed 1.7%. A 1-cm crystal elongates to 1.017 cm, which is 10 times more deformation than other materials. With materials that deform 10 times more, devices can either use crystals that are 10 times smaller with the same result, or not alter the size of the piezoelectric material and achieve 10 times the effect. PZT-type materials are generally limited in deformation due to voltage application to about 0.17%, making a 1-cm piece 1.0017 cm long when a voltage is applied.

To be piezoelectric, materials must be asymmetrical. The applied voltage shifts some of the atoms in the crystal lattice, elongating it. PZN-PT (lead zirconate niobate lead titanate) is an asymmetrical rhombohedral crystal, and this shape may be the key to its large movement.

"The effects of a voltage on a crystal usually occur in the diagonal 'polar' direction," said Shrout. "With PZN-PT, the direction of most movement is along the face. This is very unusual."

The researchers do not know the mechanism behind the large movement or why these crystals react differently to high voltage. They also do not know if this effect is a property of all rhombohedral materials or specific to relaxors.

Topsoil Made of Coal Ash Mixed with Industrial Byproducts Revive Land for Vegetation

Purdue University researchers have developed a process for making topsoil from coal ash, yard waste, and industrial byproducts. Jody Tishmack, ash management coordinator for Purdue Physical Facilities, said the combination of minerals from the coal ash and the nutrients in an organic-rich industrial nontoxic byproduct left over from the manufacture of antibiotics makes a very effective soil additive.

To make the topsoil, the ingredients are mixed in piles on the ground. Wood chips are added to provide volume and allow air to circulate through the piles as they compost for at least three months.

"During the composting process, bacteria eat their way through these piles and digest the organic materials. The materials break down into smaller particles, combining with the minerals in the coal ash to form very nutrient-rich soil," Tishmack said.

According to Joseph Mikesell, director of utilities at Purdue University, "Different combinations of these materials can be used to produce soil for different applications. For example, we might come up with four or five types of soil or soil additives, some suitable for plants used for reclamation, and some more suitable for landscaping vegetation."

Based on greenhouse and laboratory tests at the university, the material is environmentally safe, Tishmack said, noting that coal ash is used in the construction of roads and embankments and that the industrial byproduct is used as a fertilizer on farms.

In May, over 600 tons of the soil were shipped to the Chinook Mines in Brazil, Indiana. The topsoil was spread 1.5 in. thick on three one-acre test plots, tilled into the existing soil, and seeded.

"We've incorporated this material into coal slurry ponds at the mines to determine if we can reclaim the acid-saturated land, which won't support vegetation," Mikesell said. "The goal is to show that this material will allow vegetation to take hold there."

"There are a number of sites, such as coal mines and gravel pits, where land has been depleted," Tishmack said. "To reclaim these sites quickly with vegetation requires nutrient-rich topsoil. In addition, if this process is effective on a large scale, waste management companies will have an opportunity to take waste and turn it into a 100 percent recycled commercial product."

Liquid Crystal Patterns Anchored with H- and C-Basal Compounds

A method of "anchoring" liquid crystals to make patterns that are functional as well as visually appealing has been developed by Nicholas Abbott and Vinay Gupta of the Chemical Engineering and Materials Science Department at the University of California—Davis. In the June 6 issue of *Science*, the researchers show how molecular anchors made of simple hydrogen- and carbon-based compounds can provide a stable mooring for liquid crystals in patterns, allowing researchers to exploit qualities of the liquid crystal for practical uses on both flat and curved surfaces such as diffraction gratings and curved viewing screens.

Researchers expect these anchored liquid crystals to be useful in the study of the surfaces of materials. In liquid crystal form, molecules are free to move about in space, but are ordered in such a way that the molecules, on average, point in the same direction.

In a standard application, such as a computer screen, the surface of liquid crystals is coated with a long-chain molecule, and then rubbed with cloth so that the crystals will face a preferred direction. Rubbing introduces imperfections, such as scratches, dust, and static, but it has been successful in enabling alignment of liquid crystals over a large area. Abbott and Gupta were interested in looking at an alternative way to align the crystals in different ways relative to the surface; in the past, liquid crystals generally have been aligned in a single direction.

"The challenge was how to make a surface such that the molecules will spontaneously assume a certain pattern of orientations relative to the surface," Abbott said.

Abbott and Gupta found a way to make the liquid crystals line up by building a sandwich of two glass plates, one with a uniform orientation of anchors, and the other with a maze of anchoring docks. These molecular anchors orient the liquid crystal molecules.

Metals, such as gold, have many free electrons flowing along their surfaces that cause electrically-sensitive liquid crystal molecules to orient themselves relative to the metal surface. Using a thin layer of gold, 30–50 molecules thick, adhered to a glass plate, the researchers added another single layer of alkanethiols—which sticks to gold—ranging from four to 18 carbons long. Once the layer has spontaneously formed, it directs the orientation of liquid crystals applied on top of it.

Gupta said that in order to make the more intricate patterns required of a diffraction grating used to direct the flow of light in many applications, the researchers applied the thiol with a method comparable to inking a rubber stamp. First the researchers "ink" a tiny stamp with thiol solution, then they "stamp" it on the gold-coated surface. The thiol remains in the pattern in which it was stamped. By using different thiols, the researchers created grids that caused sections of liquid crystal flowing above the thiols to orient differently from neighboring sections. Abbott said that ~30 molecules of gold on the surface, plus one molecule of thiol, directs the behavior of 100,000 molecules of liquid crystal above the surface.

ZBLAN Retains Glass State in Near-Zero Gravity

The glass state of ZBLAN (ZrF_4-BaF_2-LaF_3-AlF_3-NaF) has been achieved in a microgravity experiment, according to a report to be published in the September 1997 issue of the *Journal of Materials Research*. Dennis Tucker of NASA/Marshall Space Flight Center, along with co-investigators from the University of Alabama in Huntsville and Boeing, have found that ZBLAN manufactured in a nearly gravity-free environment has properties that far exceed current state-of-the-art optical fiber materials or ZBLAN made on Earth. In theory, researchers expect to be able to make a ZBLAN optical fiber cable that has the capability to carry more than 100 times the amount of data carried by current traditional silica-based optical fiber cables. In practice, however, the best achievement that has been reported has only been about 1/5 of current cables. "This is primarily because of the fact that when you make ZBLAN on the ground, it has this nasty tendency to crystallize—to come out of its glass-like state—which severely degrades its optical properties," said Tucker.

ZBLAN is a member of the heavy metal fluoride family of glasses, and has promising applications in fiber optics. It is highly transparent in the infrared region of the electromagnetic spectrum, thus opening a new energy range for optical fiber communications, sensing, and technology development.

ZBLAN was made aboard a Conquest-1 suborbital rocket flight. Tucker said, "Most of my colleagues perform experiments in space in order to make very high-quality crystals, but ZBLAN doesn't crystallize." Tucker said that more research is necessary to understand why ZBLAN retains its glassy state in microgravity.

Low-Cost Process Shows Promise for Superconducting Tape Production

A low-cost method of producing yttrium-barium-copper-oxide superconducting films has been developed by a team of University of Illinois researchers. The technique holds potential as an easily scaled, continuous process for producing superconducting tapes that could be used in a variety of applications, including power-transmission lines, magnets, and motors.

To make their films, Jennifer Lewis, a professor of materials science and engineering and researcher at the Science and Technology Center for Superconductivity at the university, and graduate students Markus Wegman and Timothy Holmstrom developed a process called magnetic field/liquid-assisted texturing. The process is based upon a traditional particulate processing technique called tape casting. Widely used in the ceramics industry, tape casting is very amenable to large-scale, low-cost fabrication of materials.

"In our apparatus, a slurry of ceramic particles suspended in a solvent is carefully cast onto a silver substrate while in the presence of a magnetic field generated by a high-field, split-coil superconducting magnet," Lewis said. "The magnetic field causes the particles to align uniaxially—like bricks in a wall—imparting the desired texture to the microstructure."

As Lewis reported at the American Ceramics Society Annual Meeting in Cincinnati on May 5, "Platinum is introduced as a second-phase additive that induces decomposition of the yttrium-barium-copper-oxide particles at a lower temperature." She said that melting will occur locally, where there is platinum. As the material densifies, she said, impurities will segregate into the resulting liquid and will be pushed away from the grain boundaries. This occurrence creates cleaner contacts and avoids weak-linked behavior. She said that the texture of the original microstructure is retained because the bulk of the material does not melt and recrystallize.

"The ability of our films to carry current is competitive with current thin-film technology," said Lewis. "But, what's most important about the types of films we are fabricating is the absence of weak-linked behavior over a broad magnetic field range."

Weak-linked behavior typically has been associated with grain boundaries, Lewis said. "Not only can misalignments between the grains cause problems, but unclean grain boundaries can create insulating junctions that impede current flow. By fabricating our films in an applied magnetic field and densifying them in the presence of a liquid, we can create a microstructure that avoids weak-linked behavior."

Lubricant-Filled, Laser-Produced Holes Reduce Friction

A laser-based process applied to interfacing metallic or ceramic surfaces has been found to reduce friction by as much as 20% of current processes. The surface-engineering process, developed by Surface Technologies (SurTech), a Technion Entrepreneurial Incubator Company in Israel, involves the creation of tiny holes or pores on the touching surfaces of metal or ceramic components. When a lubricant is applied to the pock-marked surfaces, the pores act as tiny reservoirs which continuously lubricate the moving parts as well as reduce the surface areas in contact. The system operates as a stand-alone unit or a component of a C.N.C. machine, a numerically controlled computer.

Since heat-generating friction is a significant cause of wear and parts' breakdown, the hydrodynamic engineering process significantly prolongs the life of machine parts. One of the prime applications for the process is in engine design. When an engine starts, it takes a few moments for a lubricant to be fed between the piston and cylinder wall. As a result, heat is generated and bare metal parts slide against each other causing material fatigue and eventual breakdown.

According to Izhak Etsion of the Department of Mechanical Engineering at the Technion-Israel Institute of Technology and Director of SurTech, "This process doesn't replace oils and lubricants, it complements them. However, because the process significantly reduces the direct surface-to-surface contact between moving parts, it is now possible to use less expensive materials, such as aluminum, rather than more costly materials such as ceramics in designing certain high-performance engines." □