PICTURE CREDITS
13, 15, 16, 19, 22, 25, 27, 28, 31 — Verity Smith; 14 — Roberto Osti; 17 — Materia, Inc.; 18 — Chris Snow; 20-21 — Lance Hayashida; 23 — John Takai; 27 — Shannon Boettcher; 29 — Christoph Falter; 30 — National Renewable Energy Laboratory

POWER PLAYERS

Summer is almost upon us. The mercury is going through the roof, and the air-conditioning and gasoline bills are following right behind. What to do, what to do?

At Caltech, we're thinking globally and acting locally, as someone once said. This special section includes a two-page campus map, suitable for framing, that highlights our efforts to be good stewards of our own little 129 acres. In the other 16 pages, you will meet nine people whose alternative-energy research will, we hope, help change the world. Many of these faces will be familiar to regular readers of *E&S*.

Clockwise, starting from the upper left, are aeronautical engineer John Dabiri; chemist Bob Grubbs; chemical engineer Frances Arnold; chemist Harry Gray; computer scientists Steve Low and Mani Chandy; materials scientist Sossina Haile; applied physicist Harry Atwater; and, in the center, chemist Nate Lewis. —*DS*

Fishing for Wind

By Marcus Y. Woo

One day about five years ago, John Dabiri (MS '03, PhD '05) had a fishy idea. He was studying how air flows around solid structures—not unusual for an aeronautical engineer. In particular, he was trying to make wind turbines work efficiently amid the swirling gusts near buildings and skyscrapers, providing a source of renewable energy for cities. But as he played with the equations, he realized that they looked a lot like the ones that govern the flow of water through a school of swimming fish.

The arrangement of wind turbines is crucial for their efficiency, Dabiri says. Nature is often quite the engineer, and—mathematically, at least—the fluid dynamics around swimming fish are more or less optimized for efficiency. Once he saw the connection between fish schools and wind turbines, it seemed natural to put them together. Now, what began as a curiosity has become a new approach to wind power that offers a tenfold improvement over conventional wind farms.

Because wind speeds are always changing, wind turbines produce only 25 to 30 percent of their maximum potential power output. But if every currently existing wind turbine were churning out as much power as possible, the United States would have the capacity to generate some 40 billion watts of wind power, which would account for 2 percent of the nation's electricity. The maximum potential capacity of land-based wind power in the continental United States is estimated to be about 10 trillion watts, or terawatts (TW). Building wind farms on every suitable patch of land in the world could provide 75 to 100 TW. Considering that global power consumption was about 15 TW in 2008, wind could—in principle—power the entire planet.

But one big problem with wind power is that conventional turbines—the ones that resemble huge propellers—need a lot of space. If these so-called horizontal-axis wind turbines are too close together, the wake behind the spinning blades interferes with adjacent turbines. To get the most out of each turbine, they have to be about 6 to 8 blade lengths apart and 20 blade lengths downwind of each other. With blades that can be 100 meters long, these turbines quickly occupy a lot of real estate.

Wind farms supply about 2.5 watts of power for every square meter of land. (See "Sustainable Energy—Without the Hot Air," *E&S* 2010, No. 3.) If wind were to be the world's sole source of energy, those wind farms would have to occupy a combined area equivalent to more than 60 percent of the United States. That's clearly impractical, even without considering the minor difficulties: the wind doesn't blow all the time, and some places can only muster a gentle breeze at best.

Wind power is generally considered a mature technology. In theory, wind turbines can convert 60 percent of wind energy into electricity. In practice, the best are already at 50 percent. But even though we seem to be pushing the limit, Dabiri is discovering that there's still plenty of room for improvement.

Dabiri's fish-inspired wind farms use the lesser-known vertical-axis turbine, which looks a little like an eggbeater jutting out from the ground. When fish swim, they leave a horizontal row of regularly spaced vortices in their wakes; what would happen, he wondered, if he placed his downwind turbines in those vortices, and let them spin the turbines? In the spring of 2009, he assigned two grad students, Robert Whittlesey (MS '09) and Sebastian Liska (MS '09), to run a simple simulation of this arrangement as a class project. Astonishingly, they found that the turbines pumped out 10 times more energy per square meter.

"I play around with a lot of ideas, and the majority of them go to the scrap heap," Dabiri says. "But after the students came back with such compelling results, I started to get excited that this could be a viable option."

Individually, a vertical-axis turbine is less efficient than its monolithic cousin. But taken as a group, they can be positioned to squeeze as much power as possible from a given plot of land. Horizontal-axis turbines only capture the wind that blows through the circles swept by their blades, allowing precious energy to escape through the gaps between them. Vertical-axis turbines, on the other hand, can be bunched together until they're almost touching, harnessing the energy of almost all the air that blows by.

At the beginning of 2010, Dabiri used some of his faculty start-up funds—which are provided to new faculty to build their labs—to buy a two-acre plot of land on the windy plains outside Lancaster, California. Here, at the Field Laboratory for Optimized Wind Energy

Far right: John Dabiri is a professor of aeronautics and bioengineering.

Right: When a fish swims, it leaves behind vortices in its wake. By arranging vertical-axis turbines in a pattern similar to those vortices, Dabiri is designing wind farms that are up to 10 times more efficient than conventional ones.

(FLOWE), an array of half a dozen turbines has proven that Whittlesey's and Liska's results were right—and since then, the researchers have even improved on the fish-school models. "When we say we can increase the power output by an order of magnitude," Dabiri says, "it's not just a theoretical prediction."

The key is that every turbine rotates in the opposite direction from its nearest neighbors. "That's the secret sauce," Whittlesey says. No one's exactly sure why, but it may be that the opposing spins lower the local drag on each turbine, allowing it to whirl faster and generate more power.

Vertical-axis turbines have other advantages. They're safer for birds. And instead of being 100-meter-tall structures that would send Don Quixote into a tizzy, vertical-axis turbines are around 10 meters tall. Because they're quieter and smaller, they can be distributed more widely and can be built closer to population centers. In fact, Dabiri is already working with the Los Angeles Unified School District to construct turbines at a new high school in San Pedro in 2012.

Other Caltech faculty members have gotten in on the action. Chemist Robert Grubbs is developing new materials to build stronger, lighter, and cheaper turbines (see page 16), and, by manipulating structures at the nanoscale, Julia Greer is creating other materials for more durable blades. Aeronautical engineers Beverley McKeon and Mory Gharib (PhD '83) are fine-tuning turbines to control the airflow for maximum efficiency. And mechanical engineer Tim Colonius is running complex computer models of turbine wakes.

Meanwhile, the field tests continue. In one set of experiments, postdoc Matthias Kinzel is throwing fake snow into the whirling turbines. By taking pictures and video of the swirling flakes, he can measure exactly how the air flows and compare the physics with conventional turbines.

Even if Dabiri's arrangements aren't yet optimized, they're still a vast improvement over the status quo—and more than good enough for commercial use. This summer, he's building a few dozen more turbines at the test site, bumping the total to 42. "These experiments will, for me, be the conclusive evidence that this approach works," Dabiri says. And there's nothing fishy about that.

Dabiri's wind-energy research is supported by grants from the Gordon and Betty Moore Foundation and from the National Science Foundation's Energy for Sustainability program.

For more information, see http://bioinspired.caltech.edu.

Creative Chemistry

By Kathy Svitil

Often, the Nobel Prize rewards work that seems esoteric or even impenetrable to the Average Joe and Jane. It's probably not obvious how palladium-catalyzed cross-coupling reactions (which received the 2010 Nobel Prize in Chemistry) or spontaneous symmetry breaking in subatomic physics (one-half of the 2008 Nobel in Physics) fit into a regular workaday life.

At first blush, the olefin metathesis catalytic reactions for which Robert Grubbs shared the chemistry Nobel in 2005 seem just as confounding. "Olefin metathesis" isn't exactly cocktail party chatter. But what Grubbs's catalysts have made possible is definitely something to talk about: countless new types of environmentally friendly plastics, lubricants, biofuels, herbicides, pharmaceuticals, and more.

An "olefin" is a hydrocarbon with at least one carbon-to-carbon double or triple bond, and "metathesis," from the Greek word for transposition, is a chemical change of partners. (See "The Metathesis Waltz," *E&S* 2005, No. 4.) In the reaction, two carbon atoms (let's call them Fred and Ginger) connected by a double (or sometimes triple) bond hook up with two other carbon atoms (say, Ken and Barbie) also connected by a multiple bond. When the dance ends, Ken has embraced Ginger and Fred has gone off with Barbie. But since whatever accessories each dancer was wearing (in the form of chemical side chains) stay with their original carbon atom, the result is new chemical compounds with different properties. In nature, unassisted by chemists, these sorts of transformations just aren't possible; Bob Grubbs created chemical catalysts that don't just make them happen, but make them happen quickly, efficiently, and *greenly*.

Green because, compared to many other chemical reactions used in industry, Grubbs's catalysts

can chug along in water instead of having to be bathed in toxic solvents like benzene. The reactions require fewer reagents, which are the other chemicals needed to make the process work, and churn out higher quantities of the desired end-products—often without any annoying *by*-products.

One focus of the Pasadena-based company named Materia, which Grubbs cofounded in 1998 to manufacture and sell the catalysts, is creating tougher, lighter materials to be used for the gracefully swooping blades of wind turbines. Wind energy presented a good commercial opportunity, Grubbs says, because it's a rapidly growing field and the qualification process for new composites for turbine blades is far shorter than that for, say, airplane wings. The venture now has the interest of several major turbine producers worldwide.

These turbine blades and other parts used to be made of metal; by using fiber-reinforced composites, new designs can be tested quickly until just the right combination of aerodynamic shape, strength, and lightness is found. The process begins with an inexpensive substance called dicyclopentadiene, which is a small molecule created as a by-product of oil refining. These molecules are called monomers—the building blocks from which a polymer is made. The blades are formed from glass- and carbon-fiber mats pressed into a mold and then filled with a mixture of the monomer, the catalyst, and other ingredients. The catalyst links the monomers together into a solid polymer and, depending on what else was mixed in, the resulting materials will have a variety of different properties; more of one additive might make the blades lighter, while more of a different one might add stiffness.

Materia is helping to develop turbine blades up to 70 meters long—nearly 15 meters longer than the biggest ones out there now—for use on gigantic offshore platforms. "To get to those sizes, you need a newer generation of materials that are lighter and tougher," Grubbs says.

Closer to home, Materia is crafting blades for John Dabiri's vertical-axis wind turbines (see page 14). Meanwhile, Materia and the agribusiness conglomerate Cargill have joined forces in a start-up, Elevance, that is turning things like chicken fat and soybean oil into a host of environmentally friendly versions of consumer goods normally based on petroleum products. In addition to biodiesel and jet fuel, Elevance's smorgasbord of merchandise includes soaps, vegetable- and soy-wax candles, and ingredients used in lipsticks and skin-care products.

Grubbs continues to be surprised at the diversity of applications for his chemical progeny. "When we developed the first catalyst, we had no idea what it would be good for," he says. (See "Polymer's Progress," *E&S* 1988, No. 4.) "We're just trying to make better catalysts and understand their reactions. Every new catalyst opens up new opportunities, and then someone stumbles upon the uses." E&S

"We're just trying to make better catalysts and understand their reactions. Every new catalyst opens up new opportunities, and then someone stumbles upon the uses."

The wind-energy-technology work is funded by the Gordon and Betty Moore Foundation and the National Science Foundation.

Left: Robert Grubbs is the Victor and Elizabeth Atkins Professor of Chemistry.

Above: A prototype mold for a section of a wind-turbine blade at Materia's R&D facility.

New Power Plants

By Marcus Y. Woo

Frances Arnold joined the bioengineering revolution at just the right time. The 1970s saw the first genetic-engineering experiments, in which scientists learned to manipulate proteins, cells, and simple organisms at the DNA level. When Arnold finished her PhD in chemical engineering in 1985, protein engineering was in its infancy. Researchers were modifying proteins from the bottom up, tweaking the DNA code in an effort to make the protein do something new. But that's not easy, Arnold says, given that even today, nobody understands the incredible complexity of proteins well enough to predict useful mutations. Instead, she had her own idea.

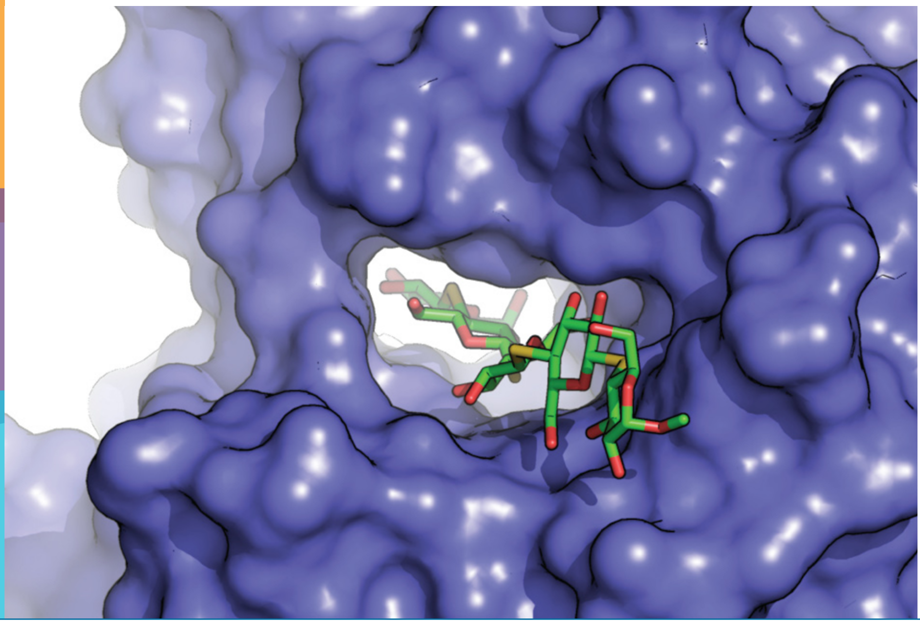
"It was obvious to me that one should use a tried-and-true process," she says. "And that's evolution." Nearly four billion years of random mutations and natural selection has led to the diverse and marvelously functional biological machinery that constitutes the life we know today, she says. Mother Nature has been the best bioengineer in history—why not harness the evolutionary process to design proteins?

Some researchers were less than enthusiastic. "People said this wasn't science, that gentlemen don't make random mutations," Arnold says. "But I'm an engineer—and a woman—so I ignored the critics."

She set off to help invent directed evolution, a technique in which you start with thousands of randomly mutated proteins, pick out those that possess a desired trait, and then breed those mutants over several generations. Her methods are now used to make products in everything from agriculture to toxicology. In the last decade, Arnold has turned directed evolution to developing better biofuels.

Biofuels, which are derived from plants, can be helpful in reducing greenhouse gases. While burning fossil fuels, such as coal or oil, pumps carbon from the ground into the atmosphere, the plants that are grown to produce biofuels absorb the carbon that burning the fuels releases.

The main biofuel in the United States is ethanol made by fermenting corn. But the process is inefficient, requiring a lot of land, energy, water, and fertilizer. Turning food crops into fuels may also cause food prices to increase. And corn-based ethanol only reduces greenhouse-gas emissions by a relatively modest amount over gasoline.



The ultimate goal is to use plant waste or dedicated energy crops—plants like switchgrass that grow easily and quickly. Biofuels from these sources generate significantly less greenhouse gases than gasoline. But breaking down cellulose—the tough molecular chain that forms a plant's cell walls—into sugars that can be fermented is complicated and costly.

Arnold and her colleagues are using directed evolution to engineer enzymes—proteins that facilitate chemical reactions—that *can* break down cellulose into glucose cheaply (see "The Race for New Biofuels," *E&S* 2008, No. 2). They've also made new enzymes for biochemical "pathways" that convert sugars into isobutanol, a more versatile chemical that in turn can be converted to aviation fuel, diesel, and plastics. And, with four carbon atoms to ethanol's two, isobutanol is a more energetic fuel.

Isobutanol was first made by James Liao's group at UCLA, which cobbled together existing enzymes from various yeasts and bacteria to catalyze the various steps along the pathway. Those enzymes were stuck into a host microorganism, which Arnold's laboratory is fine-tuning with directed evolution. "We use evolution to edit the whole thing and make it beautiful," Arnold says. The cellulase enzymes and isobutanol pathway will someday be packaged neatly inside a single organism—a superbug that turns plants to fuel.

In 2005, along with Peter Meinhold (PhD '05) and former postdoc Matthew Peters, Arnold cofounded a company called Gevo, which just went public in February. Gevo is now retooling old ethanol facilities to make isobutanol. The company has a facility in Minnesota that will churn out 18 million gallons of isobutanol per year starting in 2012. Gevo's process will use corn-based sugars to start, but will eventually switch to plant waste and other cellulosic materials.

Meanwhile, Arnold's research remains focused on more fundamental problems, such as streamlining directed-evolution techniques and seeing what other useful biological catalysts can be made.

In particular, Arnold's lab is looking for more efficient ways to make mutations. Instead of swapping out individual letters of DNA, which can prevent the protein from folding properly and thus deactivate it when too many changes are made at once, the researchers are trying recombination, also known as "molecular sex." In this method, the researchers join sequences of DNA strands from different parent organisms into one strand. Recombination generates many mutations simultaneously, yet each sequence has the basic information needed to preserve the original protein's ability to fold and function—albeit in different combinations. But there's a caveat: because the basic information in the offspring is already in the parent DNA, it's not yet clear how different—or how useful—the progeny proteins will be. The researchers, however, are trying to find out.

Recently, Arnold—along with former postdoc Pete Heinzelman, who's now at the University of Oklahoma, and graduate students Russell Komor and Indira Wu—created cellulose-digesting enzymes, or cellulases, that work at a toasty 70°C to 80°C, compared to a tepid 40°C to 50°C for regular enzymes. These high-temperature enzymes last longer and break down cellulose a lot faster. "They're better suited for industrial processes," Arnold says.

Right now, biofuels account for only about 3 percent of the nation's energy usage. But if the country maximized their potential by planting fields of dedicated fuel crops—without disrupting the food supply—biofuels could replace more than half of the nation's oil imports. So we won't be able to turn to plants exclusively, but they could take a big chunk out of our reliance on oil—especially imported oil, which, Arnold points out, constitutes a national-security risk.

"We need to get rid of that addiction to Middle East oil," she says. "It's an expensive and unreliable source of critical liquid fuel and chemicals." The current unrest in that volatile region has pushed oil prices above $100 a barrel, the highest levels since the 2008 financial crisis. And, of course, there's the issue of climate change.

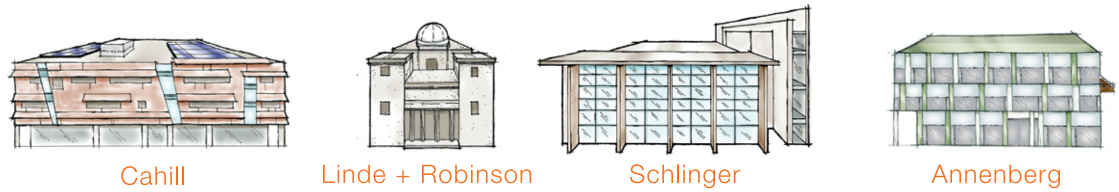
But revolutionary science and technology notwithstanding, nothing can replace a little prudence. "In the end we have to use less," Arnold says. "There's not enough biomass to feed everyone's desire for cheap fuel. Oil is a precious resource that we must stop wasting." E&S

Arnold's research is funded by the U.S. Army, the Department of Energy, the National Science Foundation, DARPA, and the Caltech Innovation Institute.

Right: Frances Arnold is the Dickinson Professor of Chemical Engineering, Bioengineering, and Biochemistry.

Left: A cellulose polymer (green) threads its way through an enzyme called cellobiohydrolase II (blue), which breaks it down.

Greening Caltech



LEED Buildings

Three Caltech building
Besides using daylight
energy-efficient fume h
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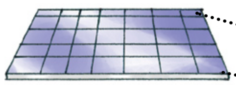
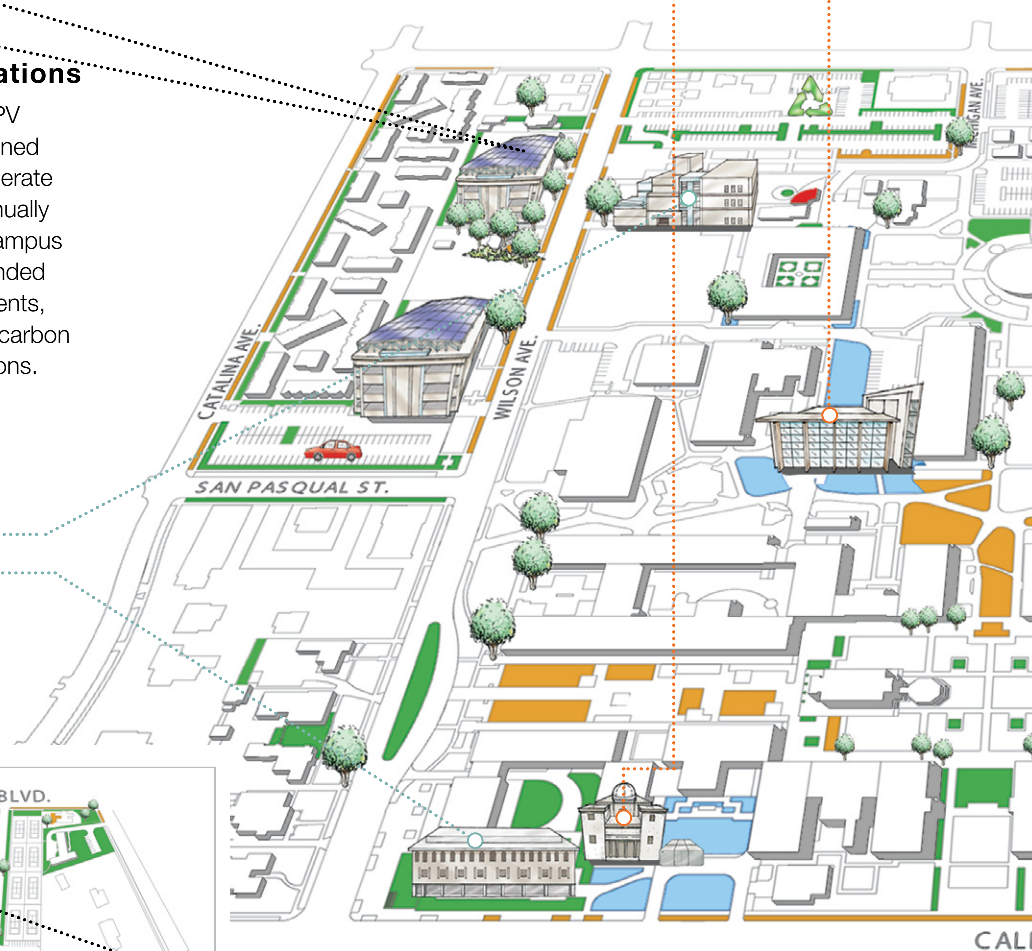


Photovoltaic Installations

Eight separate buildings fly PV arrays that produce a combined capacity of 1.3 MW and generate 1,925 MWh of electricity annually (roughly 2 percent of total campus load). These installations, funded by power-purchase agreements, reduce the Institute's yearly carbon emissions by 1,600 metric tons.

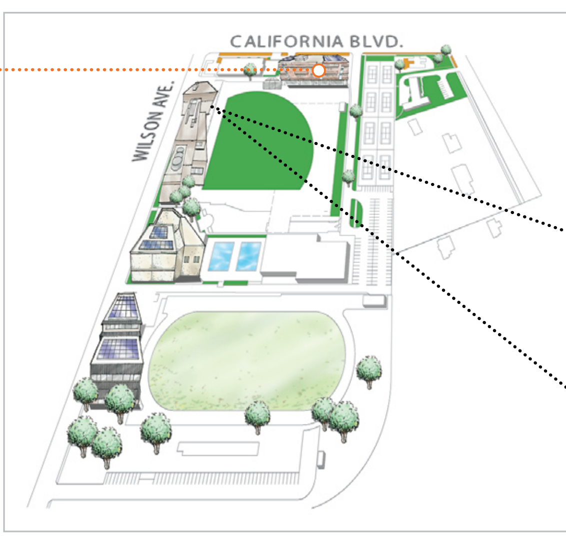


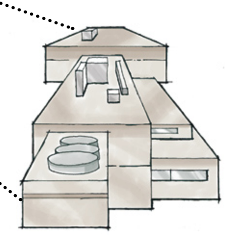
Map not to scale.

Energy Efficiency

Broad
South Mudd

Extensive upgrades have saved more than 8 million kWh and $1.3 million in the last two years.





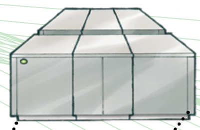
Cogeneration Plant

This on-site, 12.5-MW natural-gas power plant cogenerates heat and steam to meet approximately 60 percent of the total campus energy load. In 2004 (the year of installation), the plant won an EPA Energy Star award.

TURF REDUCTION:
Possible turf replacement (583,000 sq. ft.)

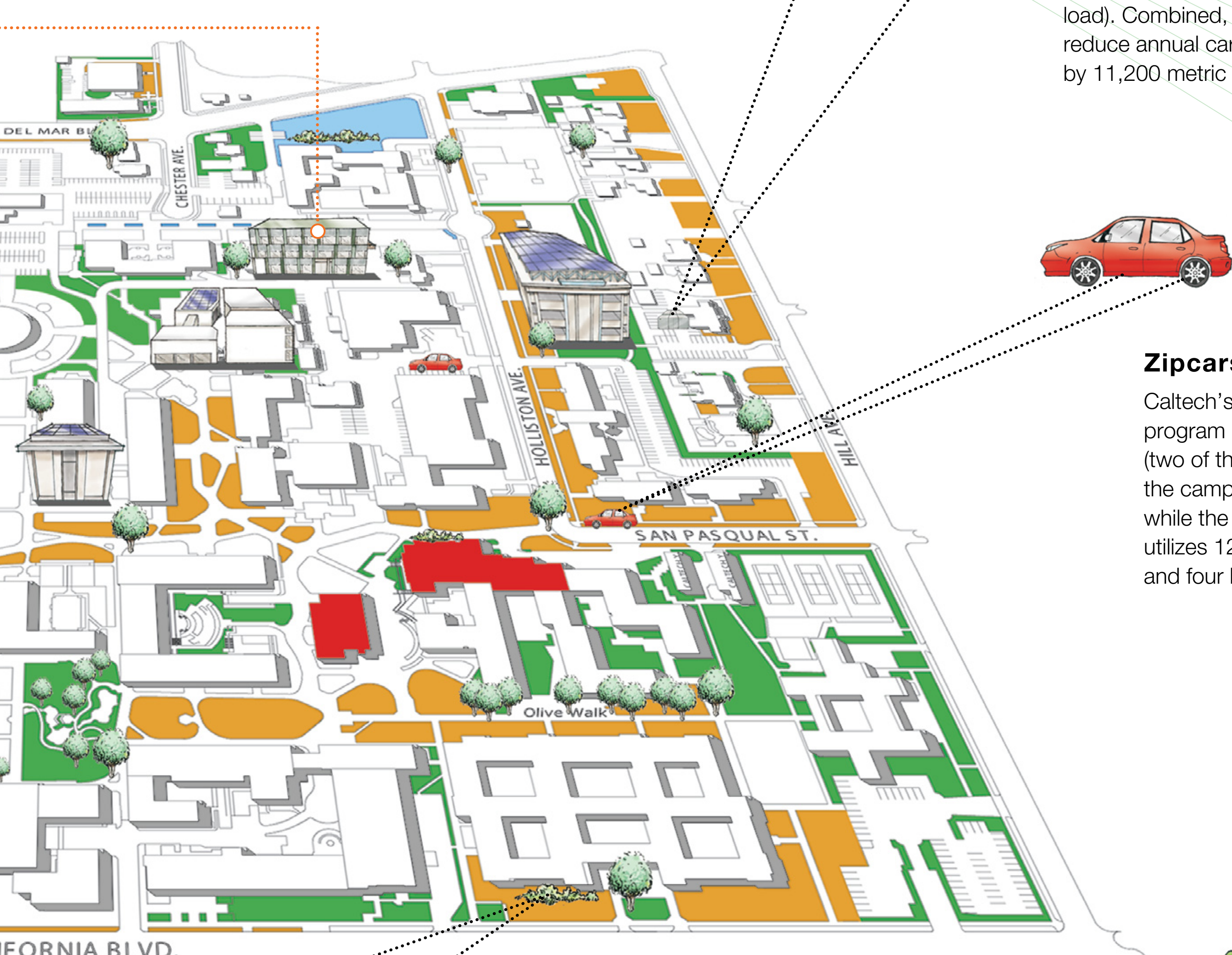
IRRIGATION SYSTEMS:
Existing high efficiency / drip systems (38,000 sq.ft.)

gs have been certified LEED Gold by the U.S. Green Building Council.
t to illuminate 75 to 90 percent of all occupied spaces, Schlinger features
hoods with auto-closing sashes; Cahill supports a 40-kW solar photo-
enberg's chilled beams lessen the need for air conditioning. And Linde
become the first renovated lab in the country to achieve LEED Platinum
vater as well as sunlight.



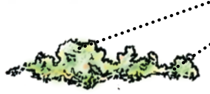
Fuel Cells

Installed with capital from the Bloom Electrons Service, Caltech's 20 units offer 2 MW of total capacity, providing 17,000 MWh of electricity annually (roughly 15 percent of campus load). Combined, these units reduce annual carbon emissions by 11,200 metric tons.



Zipcars & Hybrids

Caltech's car-sharing program offers four cars (two of them hybrids) to the campus community, while the Institute's fleet utilizes 125 electric carts and four hybrid vehicles.



Gardens

These xeriscaped open spaces feature native and climate-adapted plant species that require less water while mitigating the urban heat-island effect. All landscaped areas are now watered by a computerized irrigation system that detects and adapts to real-time climate conditions.

Campuswide Recycling

Caltech's recycling program diverts approximately 40 percent of the Institute's waste (roughly 1,000 tons) from landfills each year. Nonrecyclable materials are sent to a waste-to-energy facility in Long Beach, while hazardous and electronic waste is recycled or safely disposed of locally by licensed third-party vendors.

RAIN GARDENS:
Vegetation lets rain soak in (850,000 sq. ft.)

FOOD COMPOSTING:
Chander Dining Hall, Red Door Café, Broad Café

Going All In

By Katie Neith

Chemist Nate Lewis (BS, MS '77) is trying to beat nature at its own game, and the federal government has placed a $122 million bet that he and his team can make it happen. By replicating photosynthesis in manmade devices, he hopes to produce fuel from the sun at a rate that is 10 times more efficient than in typical crops and at a price that makes it affordable.

"We're smarter than a leaf—they have no brains!" exclaims Lewis. "We can figure this out."

As director of the Joint Center for Artificial Photosynthesis (JCAP), a new research hub funded by the U.S. Department of Energy (DOE), Lewis is charged with harnessing both the expertise of nearly 200 scientists and the energy of the sun to turn carbon dioxide and water into storable fuel.

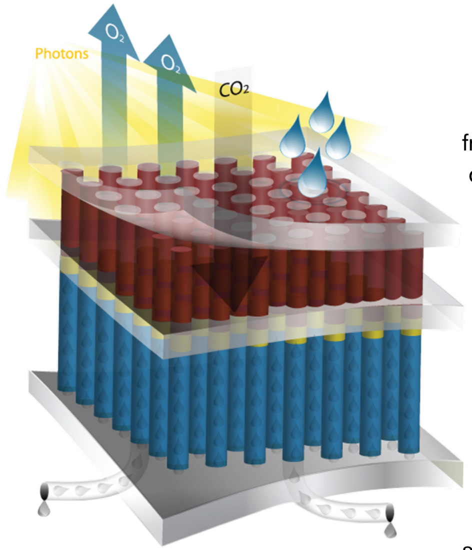
The project, which Caltech leads in partnership with the DOE's Lawrence Berkeley National Laboratory (LBL), will be housed in Jorgensen Lab, a former computer science building on the Caltech campus. However, only about 90 of JCAP's scientists will be housed there. The rest, at LBL and elsewhere, will be connected via telepresence—the latest, most technically advanced videoconferencing technology—so that the entire organization will operate under one virtual roof.

"JCAP's goal is to try to take what has made some progress in labs around the world, and to do in five years what would otherwise have taken maybe 55 as we waited for the individual pieces to come together. It's a bold experiment in innovation," Lewis asserts.

As Lewis points out, the problem is complex. Researchers know how to make electricity from the sun and how to make it efficiently with conventional solar panels, but they cost a lot of money. They also know how to make solar fuel efficiently, but it's not cheap—more-affordable solar panels would have to cover 10 rooftops just to power one home, says Lewis. In addition, the technology needs to be durable. For example, real leaves are cheap, but their photosynthetic complexes only last for about 30 minutes before breaking down.

"A successful commercial product has to be cheap, efficient, and long-lasting," explains Lewis. "Currently, we can give you two of those, but not all three at the same time. The goal of JCAP is to get all three."

So JCAP is upping the stakes of the solar-fuel game and going all in. Lewis says that researchers at Caltech have drawn many of the cards needed. We have light-absorbing nanowires to capture energy from the sun (see page 26). We also have



catalysts that can react with water to make hydrogen fuel (see page 24). However, we don't yet hold a winning hand—an integrated system that does everything at one time and under a single set of conditions.

"Our goal is not simply making another generation of an existing technology, or lowering the cost of doing what we already know how to do. We're aiming to develop a totally new function and that's why the prize is so great," he says.

Lewis and his team plan to accelerate the rate of discovery of cheap, durable, readily available metal oxides to see which ones can capture and convert the energy of sunlight into chemical fuels at moderate temperatures and remain functional for extended periods of time. His game plan borrows from the divide-and-conquer approach developed for the Human Genome Project, in which robotic DNA sequencers each worked on reading their own little bit of the genetic code. "We claim we're going to make, screen, and measure a million compounds every single day," says Lewis. "We're going set up a team of people with automation and robotics so that any good idea—and all its variants—can be pursued automatically, that very same day."

Other JCAP members will attack the problems inherent in melding nanoscale components into fully functional macroscale devices. These devices will then be built into ever-larger systems until a practical real-world scale is achieved.

"Individual research groups couldn't possibly do what we are trying to do," says Lewis. "Only a hub can work on all the technology gaps all at once, and, at the same time, draw on a national laboratory and on the academic infrastructure that a major research university can provide." He compares the work to another, slightly smaller team that also took a concept from nature and applied it to technology. "We're the Wright Brothers," he says. "They figured out how to make something fly like a bird, but without feathers. We're making a 'leaf,' but it won't look like a leaf."

In fact, he says his artificial leaf is more likely to look like bubble wrap and will be designed to function like a multilayer, high-performance fabric. It will absorb sunlight, CO_2, and water vapor, allowing oxygen to escape. Molecules in the inner layer will catalyze the reactions that produce the fuel, which will be wicked out by the bottom layer—the way microfiber athletic wear wicks sweat from the body. He predicts that the first fully functional prototype will be available in a few years.

"The only way to get off the ground on the sixth try is to build the first five prototypes, learn from your mistakes, and be bold enough to say 'We are willing to fail' again, if that's what it takes," says Lewis. He points out that if we can find a way to make fuel from the sun, then it doesn't matter what specific molecule it is we make; we can turn one fuel into another. "It just matters that we make *a* fuel from the biggest energy source we have," he says. "We would think about our energy problem so differently if we can get this card on the table." E&S

"JCAP's goal is to try to do in five years what would otherwise have taken maybe 55."

Besides Caltech and LBL, JCAP partners include the SLAC National Accelerator Laboratory, UC Berkeley, UC Santa Barbara, UC Irvine, and UC San Diego.

Other Caltech members of the leadership team include: Bruce Brunschwig, member of the Beckman Institute and director of the Molecular Materials Resource Center; Harry Atwater; Harry Gray; Jonas Peters, the Bren Professor of Chemistry; and Michael Hoffman, the Irvine Professor of Environmental Science.

More information on JCAP can be found at http://solarfuelshub.org.

Left: Nathan S. Lewis is the Argyros Professor and professor of chemistry.

Above: In an "artificial leaf" prototype, the upper half absorbs light, CO_2, and water and allows oxygen to escape. Customized molecules embedded in an inner layer catalyze the reactions that produce the desired fuel, which is wicked away by the base layer.

The Sunshine General

By Lori Oliwenstein

Harry Gray, a five-star general in the Solar Army, is very busy. Busy recruiting the hundreds of student volunteers needed to comb through the periodic table, looking for just the right metal-oxide mixtures to help turn sunlight and water into hydrogen fuel. Busy trying to find just the right way to determine which of these catalysts will be the munition of choice. Busy integrating the chosen catalysts into solar weapons that will work under battlefield conditions—out in the open, exposed to the elements.

In short, Harry Gray is busy trying to power the planet. Naturally.

But he can't do it alone. Which is why, on the door of his office in Caltech's Beckman Institute—of which Gray is the founding director—is taped a recruiting poster. Gray's broadly grinning face has replaced Uncle Sam's sterner visage, but that well-known finger points out with just as much urgency. "I WANT YOU," the poster reads, "FOR SOLAR ARMY."

Should you heed this call, your task would be nothing less than helping Gray and his Center for Chemical Innovation (CCI Solar) colleagues in their quest to mimic photosynthesis in the laboratory, creating a storable fuel from sunlight.

The emphasis, Gray notes, is on *storable*: Solar cells convert sunlight into electricity, but when the sun goes down, the power goes off. Fuel cells similarly convert hydrogen, methanol, or some other chemical into electricity. A solar-driven fuel cell would split water by day, producing hydrogen that could be squirreled away. At night, it would act as a standard fuel cell, producing water and electricity.

First, however, we need that elusive catalyst. "Nature's version is the oxygen-evolving complex of Photosystem II," says Gray. "That's the catalyst that makes oxygen from water here on Earth." But recreating the oxygen-evolving complex in a nonliving fuel cell is impossible; too many moving parts. And so the hunt is on for a simplified version, a combo of metal oxides that can do the trick with something close to the skill of nature itself.

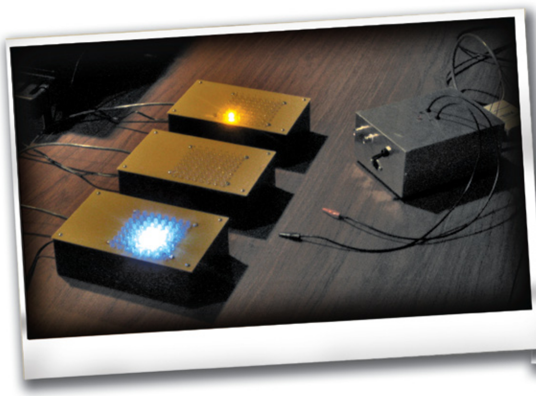
You might think the easiest way to go would be to find a single, powerful water-splitting metal oxide—and you'd be right, but naive. "The ones that are really great are so rare that we can't scale them up worldwide," says Gray. "And the ones that are abundant just don't work well enough."

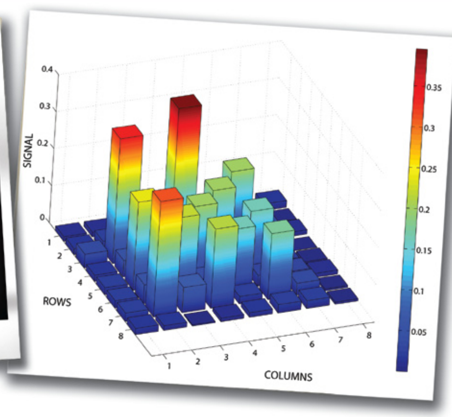
Which is why the Solar Army is focusing its search on the parts of the periodic table where the cheap, plentiful stuff lives—sodium and iron and titanium and their ilk—but looking at them in oxidized, mix-and-match amalgamations. After all, the wider a variety of metal oxides you can cram into a single catalyst, the broader the spectrum of sunlight you'll be able to gather, since each material will have certain colors of light with which it is best able to interact.

This makes the Solar Army's reconnaissance mission—to find the best mixture of three, four, maybe even five metal oxides—rather daunting: "There are millions of possible combinations of just two to three metals," says Gray. "If you're looking at combinations of four to five, you're talking about billions."

Gray's army has mustered brigades at more than a dozen other universities, including the University of Wyoming, Penn State, and Texas A&M, and corporations like Dow and 3M. Most recently, Gray says, the U.S. Navy has asked to hear more about the project. "The Navy has a lot of interest in our army," Gray laughs.

But the real foot soldiers in this war against energy inefficiency are the more than 400 high-school and college student-volunteers across the United States and in Germany. They are the ones who—armed with the Solar Army's best weapon to date, the Solar Hydrogen Activity Research





Right: Harry Gray is the Beckman Professor of Chemistry and founding director of the Beckman Institute.

Above left: These LED pulsers, built at Caltech, can quickly scan a glass plate of metal oxides to find the ones that make the most electricity.

Above right: In this instance, the tallest bars are the samples containing iron oxide.

Kit (SHArK)—are testing metal-oxide combinations that they prepare in their classrooms and laboratories.

It's a work in progress. Previous versions of the kit used an inkjet printer to deposit metal salts on a glass plate, which was then scanned by a LEGO Mindstorms gadget that included a laser pointer. (See "The Solar Army is Recruiting," *E&S* 2010, No. 1.) "It was this method that found our first big hit—zinc-yttrium-iron," says Gray.

Recently, however, Gray's colleagues Jay Winkler (PhD '84) and Bruce Brunschwig have developed the next generation of SHArKs, in which the LEGOs and lasers have been replaced by legions of LEDs. "The advantage of our new screening system is speed," Winkler explains. "The laser-scanning system would take four to six hours to scan a single sample plate. The LED scanners can scan a plate in one to two minutes."

The system is not only fast, but effective: To date, says Gray, the SHArKs have identified a half-dozen "really good-looking" catalysts, though the search is by no means over. "We want to find as many as we can," he says, "because the solar fuel cell isn't finished yet, and we won't know if the catalysts we find are compatible with the fuel cell until then."

And so, while the younger members of the army march toward a better catalyst, Gray and Nate Lewis (see page 22) are working to perfect that fuel cell.

In particular, Gray's group is looking for the best material for the cell's anode, where sunlight is absorbed and its energy funneled to the surface, which will be coated with the Solar Army's water-splitting catalyst. "The big challenge for the anode," says Gray, "is to get a stable material that can absorb as much light as possible."

Tungsten oxide is the best bet at the moment, but it needs a little extra help to reduce its band gap—the range of the solar spectrum it can't absorb. Enter postdoc Qixi Mi, who has doped the tungsten oxide with nitrogen and dropped the band gap from 2.6 to 1.8 electron volts (eV)—creeping ever closer to the team's ultimate goal of no more than 1.7 eV.

"It's a very promising material," says Gray. "Now, hopefully, the Solar Army will come up with a great catalyst to put on Qixi's great tungsten-oxide anode. That would be a very big win."

It's coming, Gray insists. But it's not time to stand down the troops quite yet. "The Solar Army still has a lot of work to do," he says. "And they're doing it." E&S

CCI Solar is a program of the National Science Foundation. Other parts of the program have been funded by Stanford's Global Climate and Energy Project, BP, Chevron Phillips, the Arnold and Mabel Beckman Foundation, and the Gordon and Betty Moore Foundation.

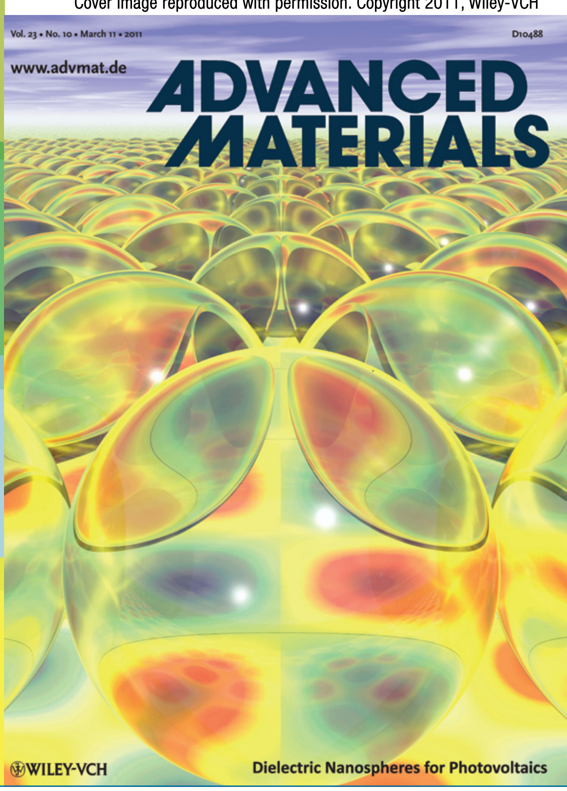
To learn more about CCI Solar, visit: http://www.ccisolar.caltech.edu/index.php.

Solar Sculptures

By Lori Oliwenstein

Harry Atwater's solar cells look like no other you've seen before. They're spiky, hairy, bendable. They resemble uninflated mylar balloons. Or they're covered in tiny glass beads, looking more like microscopic Martian colonies than devices meant to convert sunlight into energy.

These solar cells are also well on their way to being better than any other. One of them—a gallium-arsenide thin-film cell produced by Alta Devices, a Caltech startup cofounded by Atwater—recently converted a previously unheard-of 27.6 percent of the light aimed at it into electricity. Such record-breaking efficiencies, Atwater says, come from "sculpting and molding the flow of light through materials" to wring as much energy from it as possible.



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And one of the ways to do that is to trap the light, keep it contained. After all, the longer you can hold onto light, the more likely you are to absorb its energy. "We concentrate light the way a lens does, but in thin, flat films," Atwater says.

Emphasis on *thin*. Thin is most definitely in, says Atwater, because thin solar cells use less material, making them less expensive to produce, and because they can bend without breaking. You can even roll them up like bolts of fabric, which opens up a world of possibilities. Solar clothing, anyone?

Atwater's group has already made centimeter-sized thin films capable of absorbing up to 96 percent of a single wavelength of sunlight or 85 percent of the total sunlight collectible up on your roof. These films are actually arrays of silicon nanowires, each about a hundred millionth of a meter long, all reaching for the sun like stalks of corn.

Today, the team is growing "cornfields" hundreds of square centimeters in size. And "growing" is the operative word—the wires are cultivated by deposition on a crystalline template and harvested by pouring a polymer over the entire array. Peeling this thin film off exposes the bare earth, as it were, ready for another crop. Now being developed by a start-up called Caelux—founded by Atwater, Nate Lewis (see page 22), Michael Kelzenberg (MS '06, PhD '10), and Morgan Putnam (MS '08, PhD '10)—the arrays keep getting better and better. "We've made cells that are 8 percent efficient, and we have good reason to believe we will double that," says Atwater.

Meanwhile, Atwater—uninterested in resting on his wiry laurels—is pursuing even more unusual ways of milking sunlight for every watt it's worth.

The latest, developed by postdoc Jonathan Grandidier, grad student Dennis Callahan, postdoc Jeremy Munday, and Atwater, arranges tiny glass beads on a thin layer of amorphous silicon. When light shines on the beads, it becomes trapped inside and begins circulating around and around; and with each circuit, a bit of it leaks into the silicon below. This trapping method is called a "whispering gallery," because it's based on the same wave-focusing physics that allow a whispered remark on one side of the domed Statuary Hall in the U.S. Capitol to be heard clear across the rotunda.

In their quest to devise the hardest-working solar cells around, Atwater and his crew have found themselves questioning longstanding theoretical assumptions. "We're challenging what we thought were hard-and-fast efficiency limits on how much light can be absorbed by a material," Atwater says. "We know now that we can significantly exceed those limits. It turns out that, at submicron and nanometer scales, the rules are fundamentally different. It's a very different way of thinking."

That's not the only place where Atwater is thinking differently. "It will take an 800-gigawatt generating capacity to meet U.S. energy needs, which will require tens of thousands of square miles of solar cells," Atwater notes. "We make concrete on that scale, but sand and gravel are abundant. On the other hand, many of the best materials for thin-film solar cells—tellurium, for instance—come from rare ores."

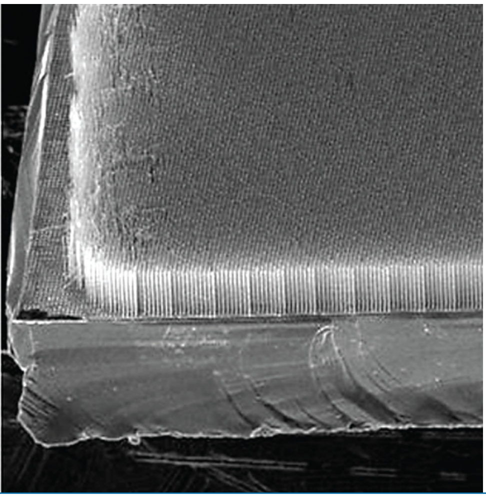
Which is why Atwater, along with Lewis, is looking to Earth-abundant materials. Many previously overlooked materials may well have solar potential, says Atwater—but only if we put in the time and effort to figure out how to exploit them.

"Zinc phosphide, copper oxide, or zinc sulfide could rival the efficiencies of the most expensive and rare materials," says Atwater. "But we haven't done the basic chemistry and physics necessary to develop them properly. We need to bring our understanding of these Earth-abundant materials up to that of our best solar materials, like gallium arsenide."

In addition, Atwater's team is searching for materials to pair up with the already well-studied elements like silicon. "If we could make tandems of solar cells with different light-absorbing properties and different band gaps—combine silicon with, say, copper oxide—we would end up with cells that are much more efficient," Atwater says.

Such down-in-the-trenches efforts are aimed at expanding "the materials genome"—creating a portfolio of new materials from Earth-abundant building blocks, and measuring their fundamental properties. The team will be making new materials, then making them better and trying to understand them more completely. These are, says Atwater, the efforts that will make the difference in the end; the efforts that will help us harness the sun.

"Beyond the basics, there are also a lot of little details that transcend fundamental discovery; they're what I call cycles of learning," he says. "That's where the science meets real engineering. And that's what makes this work so satisfying." e&s



Much of the solar-cell research is done by the "Light-Material Interactions in Energy Conversion" Energy Frontier Research Center, funded by the Department of Energy. The silicon-wire research is funded by BP, and the work on Earth-abundant materials is funded by the Dow Chemical Company.

Above: Harry Atwater is Hughes Professor and professor of applied physics and materials science, and director of Caltech's Resnick Institute.

Far left: Atwater's solar cells based on glass nanospheres were described in the March 11, 2011, issue of *Advanced Materials*.

Left: Silicon-wire solar arrays use just one-fiftieth the silicon of a conventional solar cell but still absorb 85 percent of total sunlight.

Focus on Chemical Fuels

By Katie Neith

In the spring of 2008, Sossina Haile participated in a National Research Council study on renewable electricity that discussed solar energy and how to store it. "It struck me that as a nation, and as a planet, we weren't making much progress," she says. "There was a lot of talk about the sun being our leading resource, but the majority of approaches to take advantage of it were not working." She returned to her lab armed with a list of failed ideas and the determination to cook up a new recipe for turning sunlight into fuel using ingredients from research she was already doing.

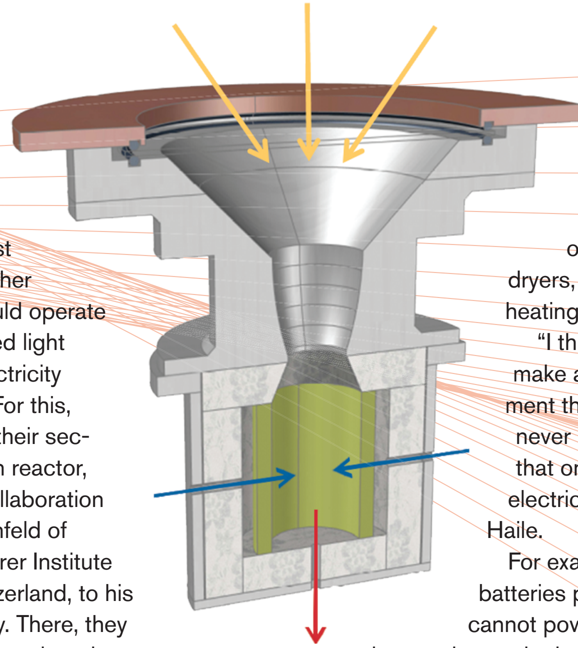
"I decided that maybe we could take advantage of our knowledge of fuel-cell materials to forge a different path," says Haile. A fuel cell is a "clean" technology that converts chemical energy to electricity. Basically, this amounts to a chemical reaction in which a fuel, let's say hydrogen, is split into electrons and protons. The electrons generate an electrical current through a wire, while the protons pass through a conductive medium called an electrolyte. They meet back up in the cathode, where they react with oxygen to form water vapor.

We usually think of electrolytes in terms of sports drinks, but Haile's electrolytes are solids; in fact, some are ceramics. One of them—cerium oxide, or ceria for short—looked like it might be the key ingredient for turning concentrated solar heat into fuel. Cerium oxide is commonly used in catalytic converters and self-cleaning ovens—both of which use heat to break down unused chemical-fuel molecules, be they unreacted hydrocarbons or rib-roast grease. And cerium is nearly as abundant as copper, an important consideration for a technology intended to be adopted globally. (See "Put Some Sunlight in Your Tank," *E&S* 2009, No. 2.)

"From working on fuel cells, we knew

Left: Sossina Haile is a professor of materials science and chemical engineering.

Above right: Concentrated sunlight enters the solar reactor, striking the ceria (green). The reacting gases (blue arrows) enter from the sides and flow through the porous ceria, and the fuel gases (red arrow) exit out the bottom.



that ceria had the ability to uptake and release oxygen, good catalytic properties, and great thermal stability," says Haile. "It appeared to have exactly the characteristics you'd like in a thermochemical catalyst, so we gave it a try."

By "gave it a try," Haile means that she and her colleagues designed and built prototype reactors that can cycle ceria through the conditions required for fuel production. A first design used electric heating, and a second, more realistic design used a parabolic mirror to focus the sun's rays into an insulated, stainless steel chamber small enough to fit on a desktop. Haile compares the solar concentration process to using a magnifying glass to start a fire.

To test their idea, the team supplied a stream of inert argon gas through the reactor while cranking up the temperature to about 1,600°C. At these temperatures, ceria pushes oxygen atoms out of its crystal lattice. The researchers then added some carbon dioxide, water, or both to the gas flow and allowed the reactor to cool to a relatively balmy 800°C. As the ceria cooled, it stripped oxygen atoms from the gas mixture and pulled them back into its crystal structure, producing carbon monoxide and/or hydrogen gas. Once the ceria was re-oxygenated to full capacity, it was heated back up and the cycle began again.

Hydrogen gas is a storable fuel on its own. But the carbon monoxide–hydrogen combo could be even more useful in the long run. Called "syngas" (short for "synthesis gas"), this mixture of two simple molecules is the raw material for making gasoline, jet fuel, diesel oil, or any other hydrocarbon your heart desires.

Experiments with the electrically powered prototype reactor showed that the material produced exactly the amount of fuel predicted by thermodynamic calculations. But the real test would be whether the reactor could operate on concentrated light rather than electricity from the grid. For this, the team took their second-generation reactor, designed in collaboration with Aldo Steinfeld of the Paul Scherrer Institute in Zurich, Switzerland, to his solar laboratory. There, they could pour energy into the reactor from a wall of high-powered spotlights that produces heat equivalent to 1,500 suns.

During initial experiments, the "on-sun" reactor worked on almost the first try—a huge success in the research world. Its record-shattering fuel-production rates and unprecedented stability "really set a benchmark for the solar-fuel community," Haile says. "We did it without precious-metal catalysts, and in a pre-commercial design that actually demonstrates the complete system."

The team's highest priority now is to increase the process's efficiency. Says Haile, "We were hoping for 16 to 19 percent efficiencies, but we only achieved 0.7 to 0.8 percent. This was a bit disappointing, but we could see very clearly how to change the design to make the reactor much more efficient." The catalyst needs to be improved as well, says Haile. "If we can find catalyst materials that work at lower temperatures than ceria does, we can dramatically loosen up the design constraints on the reactor."

Haile believes that the thermochemical approach to tapping sunlight will play a major role in a sustainable energy future. Besides producing hydrogen and syngas, which are useful for transportation, this approach can be used to make methane almost as easily by tuning the reaction conditions and catalyst ingredients, she says. Methane is the primary ingredient in "natural gas"—used in many homes to power appliances like ovens, clothes dryers, and central heating.

"I think one could make a good argument that we will never have a society that only runs on electricity," says Haile.

For example, batteries probably cannot power jumbo jets, and even the best electric cars still take hours to recharge. "This means we need to make chemical fuels. So here it is. This is the way you make chemical fuels," she says confidently.

Haile does, however, point out that capturing CO_2 from the atmosphere to make fuels using sunlight energy remains a challenge. "If we make methane at a power plant and immediately recycle the CO_2 that it generates, then we have a 'zero carbon emissions' scenario and all is good," she says. "But if we make liquid transportation fuels, then CO_2 is emitted by cars, trucks, and airplanes and we haven't fundamentally solved the problem of climate change. This hitch is what keeps battery and hydrogen-fuel-cell vehicles important alternatives to conventional cars."

She also points out that this project is just a small part of her group's sustainable-energy research, most of which continues to revolve around fuel cells. "If we don't solve the problem of energy, life as we know it *will* change," says Haile. So while the energy dilemma continues to magnify, it's comforting to know that a search for the solution is in full focus. E&S

***Haile's ceria reactor research was funded by the National Science Foundation, the State of Minnesota Initiative for Renewable Energy and the Environment, and the Swiss National Science Foundation. The full results of the research were published in the December 24, 2010, issue of* Science.**

Greening the Grid

By Kathy Svitil

At any given moment, the world's population tears through 15 terawatts (TW) of power—that's 15,000,000,000,000 watts' worth of burning bulbs, humming air conditioners, lurching subway cars, spinning slot-machine wheels, and more.

In the United States, a paltry 8 percent of our power comes from renewable sources like solar, wind, hydropower, and biofuels. In theory, though, *all* of our power needs could be met, with ease. Harvesting the energy of just *one-fifth* of the winds gusting across Earth's land would net at least 70 TW of power. The sunshine we bask in? A whopping 340 TW.

So do we just blanket the landscape with solar panels and wind farms to solve our energy woes? Not exactly. We'd still have to get that energy into the electric grid—and that's no small task.

Winds gust and die; clouds come and go. So how do *you rely on something that's inherently unreliable?*

The most obvious difficulty is simply connecting the dots. The best places to capture solar and wind energy are often the least accessible. "Wind is not where the population is," says computer scientist K. Mani Chandy.

If wind were a crop, the "wind belt" would stretch from Montana and North Dakota south to New Mexico and northern Texas.

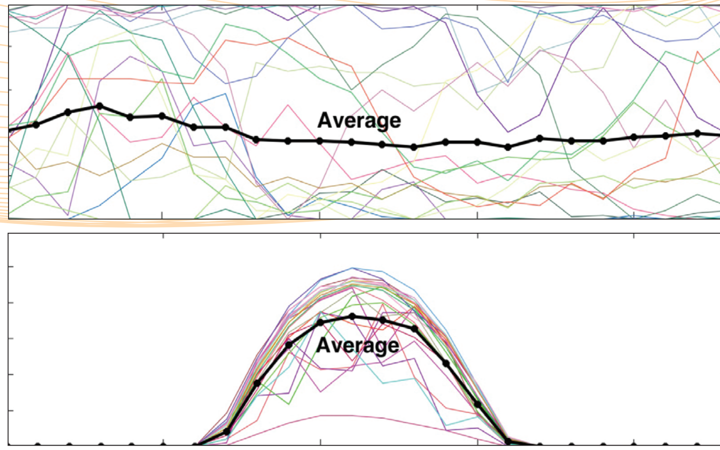
The country's population centers, in contrast, are located on the coasts. Connecting the wind belt to the power-hungry populace requires building power lines and other infrastructure, which requires a huge outlay of capital. The issue is similar for solar energy, which is more readily available in the southwest United States. The difficulties extend down to the local level, Chandy says: "The most effective places to get sunlight are where you have lots of flat roofs," such as the industrial areas of Ontario, California, "not downtown L.A., where the power is actually needed," he says.

But there's a larger problem. "Nature determines when the sun shines and when the wind blows," says Chandy, "so you have to take them when they're available. And if nature decides to make a calm and cloudy day? You don't get any energy." Winds gust and die; clouds come and go. Even on a good day, the power produced can "fluctuate widely, rapidly, and randomly," he says.

So how *do* you rely on something that's inherently unreliable? Chandy and fellow computer scientist Steven Low are working to make the electrical grid itself smarter, so that it's better able to predict routine variations—in supply *and* demand—and flexible enough to cope with unforeseen changes.

Our power grid is highly centralized, with more than 9,000 electrical generators connected through more than 300,000 miles of transmission lines. Every four minutes or so, the system evaluates power use and adjusts the supply to track fluctuations in demand. But a lot can change in four minutes, so the grid is designed with considerable excess capacity to ensure that sudden demand spikes—say, 111 million viewers simultaneously flipping on the Super Bowl—don't lead to blackouts.

Could the grid be made smaller? In an ongoing project, Chandy and Low have been simulating the power usage on Catalina Island, whose 4,000 or so permanent residents and



Right: K. Mani Chandy (left) is the Simon Ramo Professor and professor of computer science. Steven Low (right) is a professor of computer science and electrical engineering.

Above: The electricity output of a wind farm (top) and a set of solar panels (bottom) fluctuates rapidly, randomly, and by large amounts over each day. Each colored line is one day of a typical month.

a seasonal flood of tourists now import their electricity in the form of diesel generator fuel via an hour-long boat ride. The mathematical model, which included real-world weather data *and* an adjustable tolerance for the risk of occasional blackouts—determined that the entire island could get by on half a dozen wind turbines, half a dozen football fields worth of solar panels, buffered by a few tens of megawatts of battery storage.

"Right now, we tolerate no risk. We flip a light switch, and the light comes on," Chandy says. "But with other commodities, we accept not having the item if the price is too high." When gas hits five bucks a gallon, drivers might opt not to take their car to the store—or might even hop on a bus. "What if that was applied to electricity?" he asks. Would people wait to wash their sweaty summer clothes in the evening, once the air conditioners are idle? By spreading energy use over time, he says, "the system can handle greater overall load."

Alternatively, instead of each individual consumer making these individual decisions, the system could make them for you. Chandy and Low are helping design the "smart grid" envisioned by the U.S. Department of Energy, in which the cost of residential energy would fluctuate in real time with rising and falling demand. "The idea is that utilities would send pricing information to the digital meters now being installed on many homes," explains Low. The meters would relay the data to your equally intelligent thermostats, washing machines, refrigerators, and the like, and they "would make decisions about whether to run or not, based on the prices," he explains.

But, Low says, this sort of feedback system can betray itself if it's not optimized. Say you have a fleet of electric cars. With a smart grid, they will probably opt to recharge themselves on the cheap electricity—at midnight, or maybe 2:00 a.m., as power needs drop. The problem? If *all* of the cars start to charge at once, the surge in demand they create will raise prices. The result? The cars will shut back off, creating another dip in demand that will again lower prices—and flip the chargers back on. "Part of the research we're doing here is to understand that feedback," he says. "That's absolutely crucial if we're going to be able to control it properly."

The Catalina Island study is being performed under contract to Southern California Edison. Chandy's and Low's smart-grid research is funded by the National Science Foundation.