Bill Gates is cochair of the Bill & Melinda Gates Foundation, chairman of Microsoft, and a member of the American Energy Innovation Council.

The Energy Research Imperative

AS SOMEONE NOW WORKING FULL TIME IN GLOBAL HEALTH AND DEVELOPMENT, I SEE FIRSTHAND how the U.S. government's support for scientific research has improved people's lives. That support is vital in another area—affordable, clean energy. I believe it is imperative that the government commit to clean energy innovation at a level similar to its research investments in health and defense.

In a time of economic crisis, asking policy-makers in Washington, DC, to spend more money might not be the most popular position. But it's essential to protect America's national interests and ensure that the United States plays a leading role in the fast-growing global clean energy industry. There is really no other choice. Carbon-based fuels are prone to wild price gyrations and are causing the planet to overheat. The United States spends close to $1 billion a day on foreign oil, while countries such as China, Germany, Japan, and Korea are making huge investments in clean energy technologies. The creation of new energy products, services, and jobs is a good thing wherever it occurs, but it would be a serious miscalculation if America missed out on this singular opportunity.

The United States is uniquely positioned to lead in energy innovation, with great universities and national laboratories and an abundance of entrepreneurial talent. But the government must lend a hand. Market incentives, alone, will not create enough affordable, clean energy to get the nation to near-zero CO_2 emissions, the level of emissions that developed countries must achieve if we are going to keep Earth from getting even hotter.* Moreover, developing major new technologies, where the time frames necessary for true innovation stretch past the normal horizons of patent protection, requires up-front investments that are too large for venture capital and traditional energy companies.

History has repeatedly proven that federal investments in research return huge payoffs, with incredible associated benefits for U.S. industries and the economy. Yet over the past three decades, U.S. government investment in energy innovation has dropped by more than 75%. In 2008, the United States spent less on energy R&D as a percentage of gross domestic product than China, France, Japan, or Canada.

Last year, I joined with other business leaders in a call to increase federal investment in energy R&D from $5 billion to $16 billion a year.† (Others, including the President's Council of Advisors on Science and Technology, have also recommended substantial increases.‡) Recently, our group, the American Energy Innovation Council (AEIC), issued a second report outlining ways to ensure that government research dollars are targeted wisely to achieve optimal returns. The report also suggests ways to pay for the increased investment: reducing or eliminating current subsidies to well-established energy industries, diverting a portion of royalties from domestic energy production, collecting a small fee on electricity sales, or imposing a price on carbon. Any combination of these could provide the funds needed to increase energy innovation. Even at almost triple the current level of government investment in energy innovation, the research dollars that the AEIC is advocating would represent a small fraction of the money presently spent on renewable energy subsidies and efficiency grants.

Energy transformations take generations. But if the United States begins in earnest today, the nation's energy challenges can be solved in ways that truly set America on a path of energy independence and that provide affordable energy for everyone, especially the poor. The return on this kind of investment could change—perhaps even save—the world and provide generations to come with a brighter future.

— **Bill Gates**

*www.agu.org/pubs/crossref/2008/2007GL032388.shtml. †www.americanenergyinnovation.org.
‡www.whitehouse.gov/administration/eop/ostp/pcast.
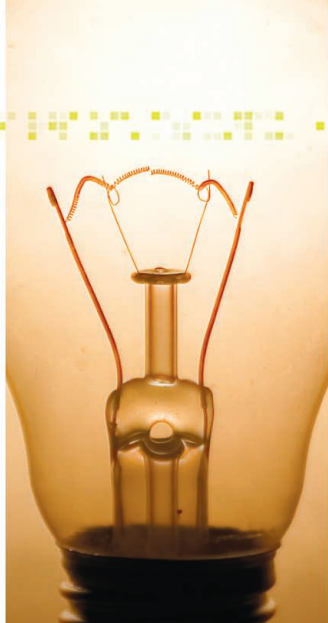
INTRODUCTION

Electricity Now and When

WHETHER IT STARTED WITH FALLING WATER OR WITH THE BURNING OR RADIOACTIVE decomposition of fuels, creating and delivering electrical power used to be a straightforward process of trying to balance generation, distribution, and demand at a reasonable cost to end users. Peak power requirements have grown, as has the size of the fluctuations between daily maximum and minimum requirements. Very little capacity exists for storing electricity, but an increased reliance on renewable sources, especially solar and wind power, will require better solutions to electricity storage to cope with their intermittent nature.

Dunn *et al.* (p. 928) review the present situation with regard to electrical energy storage, which is now dominated by sodium-sulfur (Na/S) and sodium–metal chloride (Na/MeCl$_2$) batteries that operate with high-temperature electrolytes. Redox flow and lithium batteries are emerging options, and they also discuss the "rolling storage" of electricity in battery-powered vehicles. In a related Perspective (p. 917), Gogotsi and Simon demonstrate a need for a better way to assess and compare the properties of electrochemical capacitors and lithium ion batteries, because current metrics do not necessarily reflect device performance.

If there were efficient conversion methods, electrical energy could be stored as a fuel rather than directly as stored charge. This is often discussed in terms of a hydrogen economy, but that is by no means the only fuel of interest. Solid-oxide fuel cells, which operate at high temperatures, could allow distributed electrical generation from natural gas or regenerated fuels created from excess electrical power, or allow supplementation of the grid during peak power periods. Wachsman and Lee (p. 935) discuss developments that should allow lower operating temperatures and costs for these sources, which could widen their adoption as both stationary and mobile sources.

Two News stories describe aspects of better ways to harvest solar power. Cartlidge (p. 922) describes efforts to improve thermal storage, a technology that enables solar plants to continue generating electricity after dark. Service (p. 925) discusses recent progress in artificial photosynthesis to create hydrogen and hydrocarbon fuels, which could be used either for transportation or for centralized electricity generation.

A growing population and the push toward renewable and less polluting resources are driving the construction of a wider range of methods for electricity generation and a much more complicated electricity grid. In many developed countries, a reliable supply of electrical power is taken for granted, but in many developing countries, regular and widespread outages can be the norm. The research outlined in these pieces points to some of the ideas being considered to ensure that the lights can stay on.

– MARC LAVINE, PHILLIP SZUROMI, ROBERT COONTZ

Materials for Grid Energy

CONTENTS

Science

SAVING FOR A RAINY DAY

Materials for thermal storage may make cheap solar energy available around the clock—even when the sun doesn't shine

The Andasol complex at the foot of the Sierra Nevada mountains in Granada, southern Spain, is one of the world's largest solar power stations. Its 600,000 parabolic mirrors, lined up in hundreds of rows over an area of several square kilometers, concentrate the sun's rays to provide heat that creates steam for electricity generation. The plant produces some 150 megawatts, enough to meet the needs of about half a million people. What sets Andasol apart, however, is not how much energy it delivers—it's how much it holds back. The plant is designed to store part of the solar energy it collects so that it can produce electricity after the sun sets or disappears behind a cloud.

The fickleness of sunlight, like the unsteadiness of wind, poses a major obstacle for renewable energy. Grid operators can take up the slack with fossil fuel or nuclear plants, but this need to compensate limits the contribution of wind and solar plants—

particularly those that use photovoltaic panels, which convert sunlight directly into electricity. In principle, batteries could store such renewable energy, but they remain very expensive.
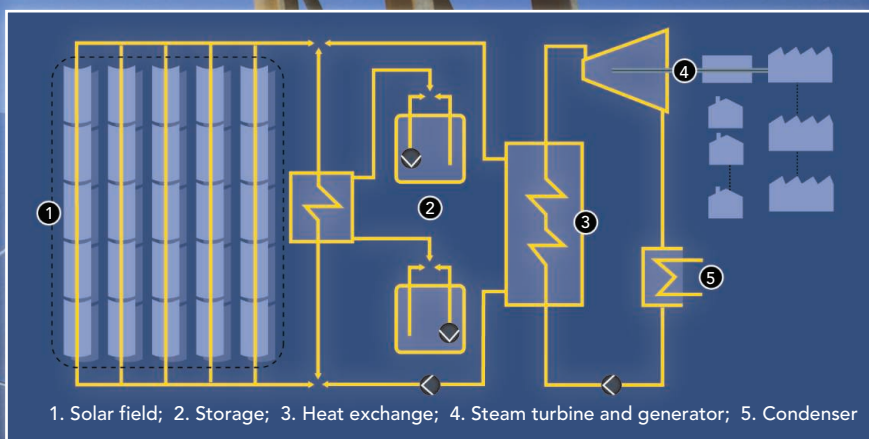
Instead, Andasol hoards its raw product: heat. Its "batteries"—three pairs of innocuous-looking metal tanks containing molten salt—hold enough energy to generate electricity for about 7.5 hours, allowing the plant to provide almost round-the-clock electricity during the summer. Indeed, Spain's national grid operator has classified Andasol as a "predictable" source of energy, allowing the percentage of locally generated electricity that is provided by renewable sources to increase.

Experts say storage systems could help concentrating solar power (CSP) clear another major hurdle: cost. Its price per kWh is currently about $0.17—slightly more expensive than that of photovoltaics ($0.16), and nearly three times the cost of natu-

ral gas (about $0.06). Increasing output by being able to generate electricity after sunset will reap economies of scale, says Yogi Goswami, a chemical engineer at the University of South Florida in Tampa. But capital costs must also be reduced. Cheaper, simpler mirrors will be essential, says Fabrizio Fabrizi of Italy's national agency for energy research, ENEA, and improved storage technology also has an important role to play. "There is a need to force down the cost of investment," Fabrizi says, estimating that improvements in storage "could reduce that cost by up to 25%."

Oil, salt, and steam

The standard storage material for plants like Andasol, a mixture of 60% sodium nitrate and 40% potassium nitrate, already does its job very well. It is stable at temperatures up to 600°C. Its high specific heat capacity and a high density enable it to store a lot of energy in very little space. Its low vis-

Canned heat. The Andasol power station in Spain uses tanks of molten salt to store solar energy so that it can continue generating electricity when the sun isn't shining.

1. Solar field; 2. Storage; 3. Heat exchange; 4. Steam turbine and generator; 5. Condenser

cosity when molten makes it easy to pump through pipes. And its ingredients are cheap and abundant. The challenge is to make better use of its virtues.

Andasol produces electricity in two stages. First, the parabolic mirrors concentrate the sun's energy along the length of a pipe fixed just above their surface. Then synthetic oil flowing through the pipe heats up and travels to a heat exchanger, where it generates steam that turns a turbine.

En route, some of the oil takes a detour through a separate heat exchanger. Molten salt being pumped from a "cold" tank at a temperature of about 290°C takes heat from the oil, flows into a "hot" tank at about 390°C, and sits until it is needed. Later, the salt is pumped back to the cold tank; as it passes back through the heat exchanger, it reheats oil returning from the steam generator, giving it enough thermal energy for another round. In this "two-tank indirect storage" system, the oil serves as a heat

transfer fluid (HTF). The salt provides the heat that keeps the electricity flowing, but it's the HTF that raises steam.

The obvious way to improve on this approach is to cut out the middleman. Instead of using one material to absorb the sun's heat and a second material to store it, why not use one material to do both? Such a "direct storage" approach would eliminate one heat exchanger. With the right material—one that remained stable at higher temperatures—it would also raise the temperature of the hot tank, making electricity production more efficient, and would increase the amount of heat stored in a given volume.

Direct storage has already supplied electricity to the grid in California. The Solar Energy Generating Systems (SEGS) I power plant in the Mojave Desert—one of nine sister plants that together make up the world's largest operating solar power station—used hot mineral oil to meet

demand on winter evenings starting in 1985, but in 1999 the storage system was damaged by a fire and was not replaced. Installing storage systems in SEGS II through IX would have been prohibitively expensive because the HTF used in those plants, a synthetic oil called Therminol, would need special pressurized tanks to keep it liquid. (Most of the plants use gas boilers as backup when the sun doesn't shine.)

Most current research projects on direct storage rely on molten salt—the same mixture used at Andasol. One is the Italian energy agency ENEA's Archimede project, which switched on in July 2010. Archimede is a 5-megawatt pilot plant incorporated into a combined-cycle gas power station close to the Sicilian city of Syracuse. The plant's hot tank is maintained at 550°C—160° higher than Andasol's. As a result, Fabrizi says, more heat is lost in transit from the mirrors to the steam generator, but higher generating efficiencies and savings on storage considerably outweigh the loss. "Using the same molten salt as Andasol, we can store the same amount of energy but using about 40% less salt," he points out. "That's a very dramatic reduction of cost."

One significant challenge for Archimede arises from the salt's melting point, 240°C. If the molten salt cools to that temperature, it will freeze solid and block the pipes—a problem that could be extremely costly and time-consuming to resolve. To keep the pipes hot, Fabrizi says, the plant continuously circulates the salt through them and turns on electric heaters if necessary. If salts with lower melting points were available, Fabrizi notes, Archimede's operators could use less energy to keep the pipes hot and—if circulation were to stop for some reason—would have more time to intervene before the fluid froze.

Researchers at Sandia National Laboratories in Albuquerque, New Mexico, are working on the melting-point problem. David Gill, a mechanical engineer at Sandia, says that he and colleagues have found several mixtures that freeze below 100°C, but reaching such low temperatures cheaply is a challenge. Two of the salt mixtures—a four-component salt that freezes below 80°C, and a five-component salt that freezes closer to 70°C—should be "economically

feasible," Gill says, although the cost is hard to gauge because both contain the economically volatile element lithium.

Towers and blocks

Gill and other researchers hope that new designs will keep direct-storage CSP plants from freezing up. Plants like the 20-megawatt Gemasolar plant in Seville, Spain, which opened in June, attack the problem by doing away with parabolic mirrors entirely. Instead, hundreds or thousands of small reflectors known as heliostats direct the sun's radiation to the top of a tall tower and onto a single receiving module through which the HTF flows. Such "power tower" designs achieve high operating temperatures and thus very high efficiencies. Like Archimede, Gemasolar uses molten salt as both HTF and storage medium. But the much shorter length of its tubing minimizes both heat losses and the chance that the salt will freeze.

Gill says the combination of high efficiency and low losses is attracting increasing investment to power towers in the United States. "Parabolic troughs have a long track record and so are generally seen as a less risky investment," he says. "But putting molten salt in is seen by some investors as putting the risk back in."

Another approach to thermal storage scraps flowing molten salt in favor of solid materials that just sit still. In a "passive" storage system developed by researchers at the German Aerospace Center (DLR) in Stuttgart, HTF from the mirror array passes through pipes embedded in concrete or castable ceramic materials. The scientists have found that the ceramics offer superior heat capacities and thermal conductivities but are too expensive and impractical. "On the one side you want good thermophysical properties, and on the other side the material has to be durable, workable, and cheap," DLR's Doerte Laing says. "Concrete represents a good compromise between the two."

Since 2008, the German group has been making detailed thermal tests of a 20-cubic-meter concrete block at a test facility at the University of Stuttgart. The tests have shown good heat transfer between the concrete and embedded pipes while at the same time

avoiding undue stress inside the material as a result of thermal expansion. The researchers say a storage system with the same energy capacity as the molten-salt tanks at the Andasol plant would require some 250 concrete blocks, each 200 cubic meters and weighing 400 tons, spread out over an area equal to about five football pitches.

Let it freeze?

In a still more radical departure, some researchers hope to achieve much higher storage capacities by harnessing the heat associated with a material's change of phase. Instead of raising the temperature of already molten salt, their scheme uses solar energy to change salt to a liquid. Hot HTF passes

Light work. Power towers may prove cheaper than parabolic mirrors.

through solid salt, melting it; later, cool HTF absorbs energy, so refreezing the storage material into a solid. Because the latent heat associated with a material's change of phase is much greater than the "sensible" heat required to raise its temperature, much less storage material would be needed than in conventional molten-salt storage.

Again, nitrate salts are likely to be the storage medium of choice. But because they are relatively poor conductors of heat, several research groups are working on designs that cause the salts to absorb or lose heat more effectively.

To increase the surface area of heat transfer, Goswami and colleagues at the University of South Florida seal the salt inside

small capsules with diameters of a few centimeters and let the HTF flow around them. The team is currently working on optimizing the size of the capsules and developing an industrial-scale method for carrying out the encapsulation process. Laing and co-workers, meanwhile, route the HTF through the salt via pipes outfitted with aluminum fins to speed heat transfer.

In tests carried out with the utility company Endesa at the Litoral power plant in southern Spain, the German group has shown that this phase-change-based technology could provide storage for so-called direct steam generation. This technology, which uses the water from a solar power plant as the HTF, does away with the expensive oils and the steam generator that normally feeds the turbine. It also reaches higher temperatures than oil-based HTFs do—up to 550°C with superheated steam.
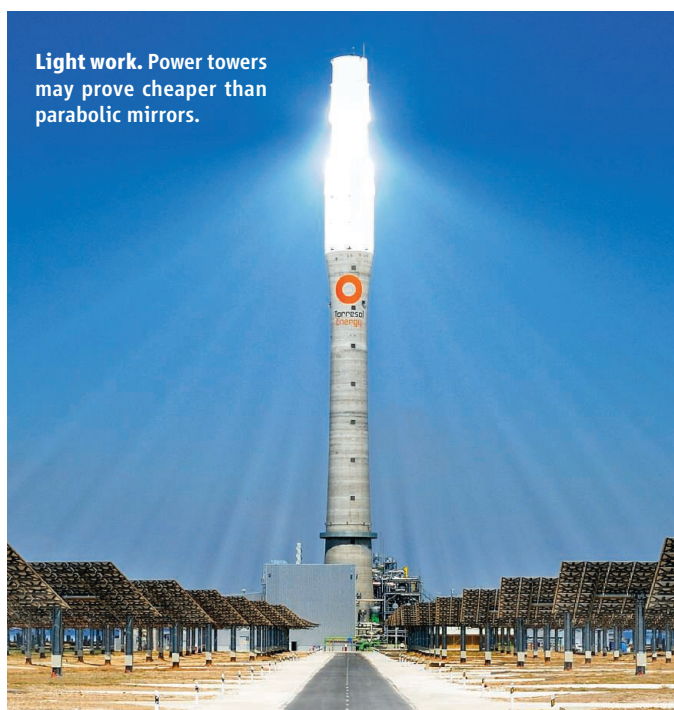
The method is potentially cheap and efficient, but it requires that heat be transferred to and from the storage medium at a near constant temperature, which would require an enormous volume of salt in the case of sensible heat storage. The phase-change approach would be far better suited, Laing says. She adds that her group has shown that the approach is technically feasible and is working to reduce costs for industrial-scale application.

Other researchers are working on approaches that include adding nanoparticles to a molten salt or an ionic liquid to increase the material's specific heat capacity, and studying ways to store both hot and cold salt in the same tank.

Whichever storage technology—or combination of technologies—eventually pans out, it will be critical to the future of CSP. The current global capacity of solar thermal power plants is minuscule: just over 1 gigawatt, about the power output of one large fossil-fuel or nuclear power station. Another 15 gigawatts are currently in development or under construction in the United States, Spain, North Africa, China, India, and elsewhere, according to the International Energy Agency. If CSP is to become a major player in the future, the ability to store some of the sun's energy and then use it to generate electricity when needed will be essential.

–EDWIN CARTLIDGE

TURNING OVER A NEW LEAF

Artificial photosynthesis researchers dream of using sunlight's energy to generate chemical fuels. Despite progress, the approach must become more efficient and cheaper to make an impact on where the world gets its fuel

The next time you groan when it's time to mow your lawn, take a second first to marvel at a blade of grass. Plants are so commonplace that it's easy to take their wizardry for granted. When they absorb sunlight, they immediately squirrel away almost all of that energy by using it to knit together a chemical fuel they use later to grow and multiply. It sounds so simple. Yet it's anything but. Modern society runs on fossil fuels precisely because researchers have never managed to duplicate the chemical mastery of a fescue. Now, with the side effects of our massive-scale use of fossil fuels piling up (climate change, acidified oceans, oil spills, and so on), researchers around the globe are struggling to play catch-up with biology in hopes of harnessing the sun's energy to synthesize gasoline or other fuels that are the bedrock of modern society.

Humans, of course, already have ways to capture solar energy. Today's photovoltaic solar cells typically trap 10% to 20% of the energy in sunlight and convert it to electricity, and PV prices continue to drop. But because electricity is difficult to store on a large scale, the effort to store sunlight's energy in chemical fuels has risen to one of the grand challenges of the 21st century. "You're talking about turning the energy world on its head. Today we turn hydrocarbon fuels into electricity. But in the future, we need to find a way to turn electricity [from sunlight] into fuels," says Daniel DuBois, a chemist at the Pacific Northwest National Laboratory in Richland, Washington.

The problem is daunting. Energy production is the world's largest enterprise. Today the world consumes power at an average rate of 17.75 trillion watts, or 17.75 terawatts, 85% of which starts out as fossil fuels, coal, oil, and natural gas. Thanks to rising populations and incomes, by 2050 the world's demand for power is expected to at least double. To keep fossil fuels from stepping in to fill that need, with potentially devastating side effects, any new solar fuels technology will have to provide power just as cheaply, and it must have the potential to work on an equally massive scale.
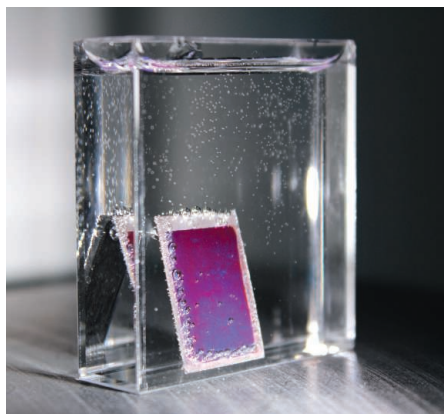
Enter artificial photosynthesis. Researchers around the globe are working to combine materials that capture sunlight with catalysts that can harness solar energy to synthesize fuels. This dream has been pursued for

The splits. An artificial leaf harnesses energy in sunlight to split water into oxygen and hydrogen.

decades. But recent strides are adding new zip to the field. "In the last 5 to 10 years, there has been amazing progress," DuBois says. Anthony Rappé, a chemist at Colorado State University, Fort Collins, agrees. However, he adds, "the bottom line is we're not there yet."

Molecular shuffle

To get there, most artificial photosynthesis researchers look to natural photosynthesis for inspiration. During photosynthesis, plants absorb sunlight, water, and CO_2. Then they use two protein complexes—called photosystem I and II—to split water and synthesize fuel. First, in photosystem II, energy in sunlight splits two water molecules into four hydrogen ions (H^+), four electrons, and a molecule of oxygen (O_2). The O_2 wafts away as waste; the protons and electrons are sent to photosystem I and used to energize the coenzyme NADP to NADPH, which in turn is used to help synthesize sugars—a key series of metabolic steps.

Of course, artificial photosynthesis researchers aim to make fuel not for plants but for planes, trains, and automobiles. So after splitting water into H^+, electrons, and oxygen molecules, most make very different use of those ingredients. Some researchers are working to combine the protons and electrons with carbon dioxide (CO_2) to make methane gas and other hydrocarbon fuels (see sidebar, p. 927). But most are working on what they believe is a simpler approach: combining the pieces they get from splitting pairs of water molecules into molecules of O_2 and hydrogen gas (H_2). That H_2 can then either be burned in

an engine or run through a fuel cell, where the water-splitting reaction runs in reverse: combining two H_2s with O_2 from the air to generate water and electricity.

Although plants split water with seeming ease, it's not a simple task, and it requires electrons to perform an intricate quantum-mechanical dance. Quantum mechanics dictates that electrons can exist only at discrete energy levels—or "bands." In semiconductors, for example, electrons can sit in either a lower energy state known as the valence band, where they are closely bound to the atom on which they sit, or a more freewheeling energized state in the conduction band. Molecules like chlorophyll in plants act like tiny semiconducting proteins. When they absorb sunlight, they kick an electron from the valence to the conduction band, leaving behind a posi-

In 1972, Japanese researchers took on the challenge by using particles of titanium dioxide to split water. The method was impractical for commercial use because TiO_2, which absorbs only ultraviolet light, could make no use of 95% of the solar spectrum. But the demonstration inspired numerous other water-splitting systems. One setup uses molecular dyes made with ruthenium and other rare metals to absorb a variety of wavelengths of light and pass the charges to metal catalysts. Another, developed by Turner's NREL team, absorbed light with semiconductor wafers made from gallium arsenide (GaAs) and gallium indium phosphide (GaInP). A platinum electrode served as the catalyst to split water and generate O_2, while the semiconductor acted as the electrode to produce H_2.

ple is the quest for H_2-forming catalysts. Natural photosynthesis carries out the reaction using enzymes called hydrogenases, which are built from the abundant elements iron and nickel. The enzymes have evolved until they can knit roughly 9000 pairs of hydrogen atoms into molecular H_2 every second. Many early water-splitting systems performed the same reaction even faster using pure platinum as the catalyst. But platinum is too rare and expensive to be broadly useful.

In recent years, researchers have synthesized numerous compounds aimed at mimicking the core complex of hydrogenases. All work more slowly (if at all), however, largely because they lack parts of the natural protein around the core that optimizes the core's activity. In 2008, Thomas Rauchfuss, a chemist at the University of Illinois, Urbana-
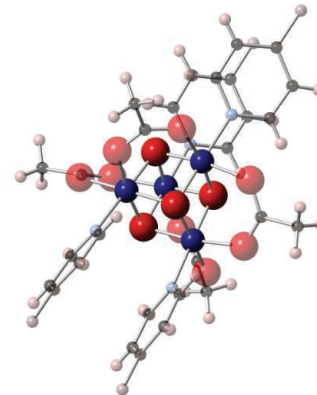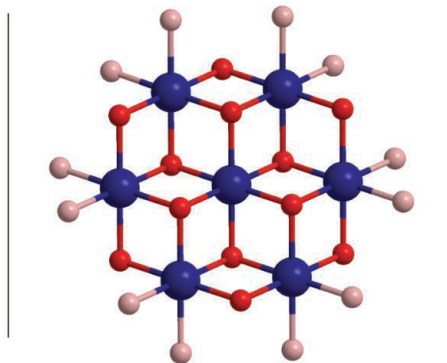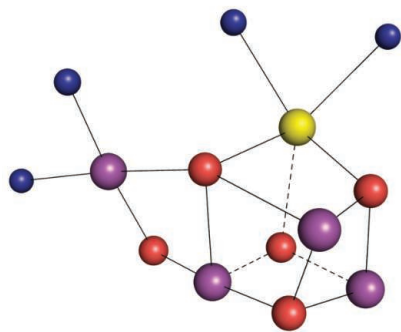
Box step. Natural photosynthesis depends on a molecular cube (*left*) made from manganese atoms (purple), oxygens (red), and a calcium atom (yellow). The catalyst splits water molecules (blue), generating molecular oxygen. Synthetic versions (*center and right*) have similar cube-shaped cores.

tively charged electron vacancy called a hole.

The holes are shuttled over to a compound called the oxygen-evolving complex, which grabs two oxygen atoms, holds them close together, and rips out an electron from each to fill the holes. The electron-deficient oxygens regain their stability by combining to form O_2. In an artificial system, the electrons and protons liberated by water splitting then must migrate to a second catalyst, which combines them into two molecules of H_2.

A successful artificial photosynthesis system must therefore meet several demands. It must absorb photons, use the energy to create energized electrons and holes, and steer those charges to two different catalysts to generate H_2 and O_2. It also has to be fast, cheap, and rugged. "This is a much more stringent set of requirements than [those for] photovoltaics," says John Turner, a water-splitting expert at the National Renewable Energy Laboratory (NREL) in Golden, Colorado.

Unfortunately, these systems, too, had drawbacks. The metals in the best light-absorbing molecular dyes are too rare to be viable as a large-scale technology. To get enough ruthenium to power the world with water splitting, "we would need to harvest 1% of the Earth's total continental crust to a depth of 1 kilometer," Rappé says. Scale-up is problematic with the semiconductor system as well. Although Turner's devices convert 12% of sunlight to hydrogen, the materials would cost as much as $50,000 per square meter, according to an estimate by Harry Gray, a chemist at the California Institute of Technology (Caltech) in Pasadena. To be viable on a large scale, "we need to build something this good for $100 per square meter," Gray says.

Wanted: the perfect catalyst
So more recently, much of the work in the water-splitting field has begun to shift to trying to make light collectors and catalysts from abundant and cheap materials. A prime exam-

Champaign, and colleagues devised catalysts with molecular arms that act like a bucket brigade to ferry protons to the catalytic core. In the 12 August 2011 issue of *Science* (p. 863), DuBois and his colleagues described how they had refined this strategy further by creating a nickel-based catalyst that stitches 106,000 H_2 molecules together every second (http://scim.ag/_DuBois).

The new H_2 makers still aren't ideal. They work only at high speed when researchers apply an electrical voltage of more than 1 volt to their system, a sizable energetic penalty. So DuBois's team is now working to tweak the catalysts to work at a lower added voltage. In a paper published online in *Science* on 29 September (http://scim.ag/Nocera), Dan Nocera, a chemist at the Massachusetts Institute of Technology in Cambridge, reported that he and his colleagues had come up with another H_2 catalyst that works with an extra voltage of only 35 thousandths of a volt (millivolts). It, too, is made from rela-

tively cheap metals: molybdenum, nickel, and zinc. But Nocera's catalyst is slower than DuBois's, so the race is on to marry the best attributes of each.

Balancing speed and extra energy input has been an even tougher problem with the catalysts needed for other reactions in water splitting, which grabs oxygen atoms from two water molecules and links them together as O_2. In 2008, Nocera and his team made headlines when they unveiled a cobalt-phosphate (Co-Pi) catalyst that works at 300 millivolts applied potential over the minimum 1.23 electron volts required to link two oxygen atoms. The group followed that up with a nickel-borate compound that does much the same thing. And in the 29 September online paper, the researchers described a triple-layer silicon wafer lined with their Co-Pi catalyst on one face and with their H_2 catalyst on the other. The silicon absorbed sunlight and passed charges to the two catalysts, which then split water. "I love the triple junction. It's pretty sexy," says Felix Castellano, a chemist at Bowling Green University in Ohio.

Turner cautions that the overall efficiency of the device—it converts just 5% of the energy in sunlight to hydrogen—is still too low, and the extra voltage input required is still too high, to be commercially useful. Nocera counters that this initial system was built using amorphous silicon wafers as the sunlight absorbers. Such wafers are only 8% efficient in converting light to electrical charges. An artificial leaf based on crystalline silicon solar cells, which are 20% efficient, could convert sunlight to chemical energy with an efficiency of 12%, he says. But Nocera's team has yet to demonstrate such a device.

Other related catalysts are also entering the picture. Charles Dismukes, a chemist at Rutgers University in Piscataway, New Jersey, and colleagues reported last year that they had made a series of O_2-forming catalysts using lithium, manganese, and oxygen. And earlier this year, Dismukes's team reported in the *Journal of the American Chemical Society* that they had created another oxygen-forming complex with cobalt and oxygen. What's unique about all these new oxygen formers is that they share almost an identical cubic molecular structure, which is also at the heart of the natural O_2-forming complex in photosystem II. "There is only one blueprint from biology that can be copied," Dismukes says.

Many other advances are also making their way out of the lab. Castellano and colleagues have recently created a family of cheap polymers capable of absorbing the energy from

Sunlight in Your Tank—Right Away

Using sunlight to split water and generate hydrogen doesn't make the most useful chemical fuel. To use hydrogen on a large scale, societies would have to develop a new infrastructure to store, transport, and distribute the energy carrier. With that limitation in mind, some researchers are looking to use artificial photosynthesis to generate hydrocarbon fuels like those we already burn.

Their goal is essentially to run combustion in reverse, starting with carbon dioxide (CO_2) and water and using the energy in sunlight to knit the chemical bonds needed to make hydrocarbons, such as gaseous methane and liquid methanol. "That's a technology that's going to come," says Harry Gray, a chemist at the California Institute of Technology in Pasadena. "But it is hard."

The difficulty is that CO_2 is a very stable molecule. In converting CO_2 to hydrocarbons, the first step is to strip off one of the oxygen atoms, leaving behind a molecule of carbon monoxide (CO), a more reactive combination of carbon and oxygen. CO can then be combined with molecular hydrogen and converted into liquid hydrocarbons using an industrial process known as Fischer-Tropsch synthesis.

That first step of converting CO_2 to CO is the energy hog. A minimum of 1.33 electron volts (eV) of energy must be applied to carry out the reaction. Over the past few decades, researchers have developed numerous catalysts that carry out the process. But virtually all of them require adding a lot of extra energy, typically another 1.5 eV. As a result, it would take far more energy to synthesize a hydrocarbon fuel than the fuel's molecules could store in their chemical bonds.

On 29 September, however, researchers led by Richard Masel of Dioxide Materials in Champaign, Illinois, and Paul Kenis of the University of Illinois, Urbana-Champaign, reported online in *Science* (http://scim.ag/_Masel) that they've come up with a less energy-intensive way to convert CO_2 to CO. By adding a type of solvent called an ionic liquid to the CO_2 in their setup, they reduced the added energy needed for splitting CO_2 by 90%. Ionic liquids are liquid salts that are adept at stabilizing negatively charged compounds. Adding a negative charge is the first step required to convert CO_2 to CO; the Illinois researchers suspect the increased stability reduces the voltage needed to do the job.

The Illinois catalysts are slow, and so far the researchers have not powered them with electrical charges from a solar cell. But other labs are taking an approach that looks more like full-fledged artificial photosynthesis. At Lawrence Berkeley National Laboratory in California, for example, chemist Heinz Frei and his colleagues reported in 2005 that for the first time they had used energy from visible light to convert CO_2 to CO using a porous catalyst made from silica and impregnated with zinc and copper. Frei's team has used related catalysts to split water to generate molecular hydrogen. Now the group is working to put the two pieces together to combine light-generated CO and H_2 to make methanol, one of the simplest hydrocarbons.

It's not ExxonMobil yet. But with further developments, the technology could lead to fuels made basically from air, water, and sunlight.
–R.F.S.

low-energy green photons and reemitting it as lower numbers of higher energy blue photons. They are now working on using this upconversion process to make use of more of the solar spectrum to split water. Researchers led by Steve Cronin of the University of Southern California in Los Angeles are adding metal nanoparticles to conventional solar absorbers as another way to convert low-energy photons to electrical charges that can then be harnessed to improve the efficiency of water-splitting setups. And Gray's group at Caltech has teamed up with students at 17 other universities to create a "solar army" that has already made progress in finding new water-splitting catalysts.

These and other advances will need to continue if artificial photosynthesis ever hopes

to contend with fossil fuels. With today's low natural gas prices, companies can use a mature technology called steam reforming to convert natural gas to hydrogen at a cost of about $1 to $1.50 per kilogram of H_2 generated, which contains about the same amount of energy as a gallon of gasoline. Yet a recent analysis by Turner and his colleagues showed that, even if researchers could create an artificial photosynthesis system that cost $200 per square meter for the equipment and was 25% efficient at converting sunlight to H_2, the H_2 would still cost $2.55 per kilogram. That's not saying artificial photosynthesis isn't worth pursuing—only that fossil fuels are the leading energy source for a reason, and they won't be easy to dethrone.

–ROBERT F. SERVICE

REVIEW

Electrical Energy Storage for the Grid: A Battery of Choices

Bruce Dunn,[1] Haresh Kamath,[2] Jean-Marie Tarascon[3,4]

The increasing interest in energy storage for the grid can be attributed to multiple factors, including the capital costs of managing peak demands, the investments needed for grid reliability, and the integration of renewable energy sources. Although existing energy storage is dominated by pumped hydroelectric, there is the recognition that battery systems can offer a number of high-value opportunities, provided that lower costs can be obtained. The battery systems reviewed here include sodium-sulfur batteries that are commercially available for grid applications, redox-flow batteries that offer low cost, and lithium-ion batteries whose development for commercial electronics and electric vehicles is being applied to grid storage.

The August 2003 blackout in the Northeast and the recent September 2011 power failure that extended from Southern California to Mexico and Arizona are two of the more widely publicized examples in which power outages affected many millions of consumers. From a broader perspective, such power outage events underscore the complex set of issues associated with the generation and use of electricity: the reliability of the grid, the use of fossil fuels and related carbon emissions, the development of electric vehicles to decrease dependence on foreign oil, and the increased deployment of renewable energy resources. Underlying these considerations is the recognition that inexpensive and reliable energy is vital for economic development. Moreover, most of these issues are international in scope, with the additional caveat that worldwide demand for electricity is projected to double by 2050.

Electrical energy storage (EES) cannot possibly address all of these matters. However, energy storage does offer a well-established approach for improving grid reliability and utilization. Whereas transmission and distribution systems are responsible for moving electricity over distances to end users, the EES systems involve a time dimension, providing electricity when it is needed. A recent study identified a number of high-value applications for energy storage, ranging from the integration of renewable energy sources to power quality and reliability (1). Despite the anticipated benefits and needs, there are relatively few storage installations in operation in the United States. Only ~2.5% of the total electric power delivered in the United States uses energy storage, most of which is limited to

pumped hydroelectric storage. This is far below the energy storage levels in Europe (10%) and Japan (15%), where more favorable economics and policies are in place (2).

Energy storage technologies available for large-scale applications can be divided into four types: mechanical, electrical, chemical, and electrochemical (3). Pumped hydroelectric systems account for 99% of a worldwide storage capacity of 127,000 MW of discharge power. Compressed air storage is a distant second at 440 MW. The characteristics for several of these EES systems in terms of power rating, which identifies potential applications, and duration of discharge are illustrated in Fig. 1. Potential grid applications range from frequency regulation and load following, for which short response times are needed,

to peak shaving and load shifting, both of which can lead to improvements in grid reliability, stability, and cost (4). The electric power profile shown in fig. S1 indicates how storage can integrate renewable resources and be used to accommodate peak loads. Load shifting represents one of the more tantalizing opportunities for EES because of the benefit in storing energy when excess power is generated and releasing it at times of greater demand. The technical requirements, however, are quite rigorous.

As indicated in Fig. 1, there are several energy storage technologies that are based on batteries. In general, electrochemical energy storage possesses a number of desirable features, including pollution-free operation, high round-trip efficiency, flexible power and energy characteristics to meet different grid functions, long cycle life, and low maintenance. Batteries represent an excellent energy storage technology for the integration of renewable resources. Their compact size makes them well suited for use at distributed locations, and they can provide frequency control to reduce variations in local solar output and to mitigate output fluctuations at wind farms. Although high cost limits market penetration, the modularity and scalability of different battery systems provide the promise of a drop in costs in the coming years. Today, sodium/sulfur (Na/S) battery technology is commercially available for grid applications, with some 200 installations worldwide, accounting for 315 MW of discharge power capacity. Moreover, there are emerging opportunities for other battery systems because of potential low cost (redox-flow) and enhanced performance [lithium (Li)–ion]. In this Review,
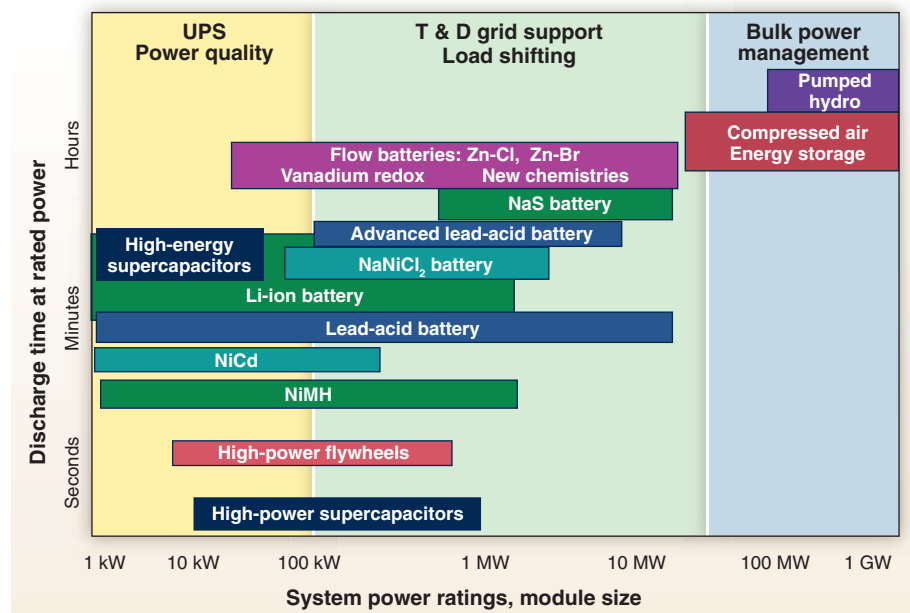
Fig. 1. Comparison of discharge time and power rating for various EES technologies. The comparisons are of a general nature because several of the technologies have broader power ratings and longer discharge times than illustrated (1). [Courtesy of EPRI]

[1]Department of Materials Science and Engineering and California NanoSystems Institute, University of California, Los Angeles, Los Angeles, CA 90095, USA. [2]Electric Power Research Institute (EPRI), Palo Alto, CA 94304, USA. [3]Université de Picardie Jules Verne, Laboratoire de Réactivité Chimie des Solides, Amiens 80039, France. [4]Collège de France, Paris 75231, France.

we present some of the overarching issues facing the integration of energy storage into the grid and assess some of the key battery technologies for energy storage, identify their challenges, and provide perspectives on future directions.

Utility Perspective on Energy Storage

EES has often been described as the "Holy Grail" of the electric utility industry. This phrase evokes the eagerness of utilities and other stakeholders to achieve cost-effective storage options, which could potentially cure many of the ills faced by the electric power enterprise. However, the phrase Holy Grail also suggests that the search for energy storage will be long, difficult, and perilous. We are unlikely to find, at least in the near term, a single technology that can repeatedly and efficiently store large quantities of electric energy at low cost. On the other hand, a portfolio approach that is based on using a combination of technologies may be the most effective means to introduce and integrate energy storage.

The usefulness of EES stems from the operational characteristics of the grid as a supply chain of a commodity, electric power. At present, the electric power infrastructure functions largely as a just-in-time inventory system in which a majority of energy is generated and then transmitted to the user as it is consumed. Without the ability to store energy, there must be sufficient generation capacity on the grid to handle peak demand requirements, despite the likelihood that much of that capacity sits idle daily as well as for large portions of the year (fig. S2). Correspondingly, the transmission and distribution system must also be sized to handle peak power transfer requirements, even if only a fraction of that power transfer capacity is used during most of the year. Operationally, electrical power generation must be continuously ramped up and down to ensure that the delicate balance between supply and demand is maintained. The up and down cycling reduces power plant efficiency, resulting in higher fuel consumption and higher emissions per kilowatt-hour (kWh) produced. This procedure also causes more wear on the equipment and reduces the lifetime of power plants (5).

By decoupling generation and load, grid energy storage would simplify the balancing act between electricity supply and demand, and on overall grid power flow. EES systems have potential applications throughout the grid, from bulk energy storage to distributed energy functions (1). The availability of energy storage would help to eliminate the distinction between

peak and baseload generation (fig. S1), allowing loads at any time to be serviced by the lowest cost energy resources (6).

Storage solutions based on the technologies we have today are so expensive that historically it has been far more cost-effective to expand generation as well as transmission and distribution to serve the peak load and provide sufficient operating margin to meet consumer demands for reliability. In those cases in which storage is used, pumped hydroelectric plants are generally involved. These plants are composed of low-cost materials (dirt, concrete, and water) that have a lifetime of over 40 years, minimal maintenance costs, and relatively high round-trip ef-

energy (7). Batteries, regardless of their chemistry—aqueous, nonaqueous, Li or Na-based—store energy within the electrode structure through charge transfer reactions. By comparison, fuel cells, which are not rechargeable, store energy in the reactants that are externally fed to the cells. Both of these differ from redox-flow cells, which store energy in the redox species that are continuously circulating through the cells. Supercapacitors offer yet a different energy storage mechanism, via a capacitive process arising from an electrochemical double layer at the electrode-electrolyte interface. Each mechanism has different strategies that can be used to improve the power and energy densities of the EES approach.

Table 1. Energy storage for utility transmission and distribution grid support. The megawatt- and kilowatt-scale energy storage systems listed here have potential impact in several areas, including transmission and distribution substation grid support, peak shaving, capital deferral, reliability, and frequency regulation (1). [Courtesy of EPRI]

Technology option	Maturity	Capacity (MWh)	Power (MW)	Duration (hours)	% Efficiency (total cycles)	Total cost ($/kW)	Cost ($/kWh)
CAES (aboveground)	Demo	250	50	5	(>10,000)	1950–2150	390–430
Advanced Pb-acid	Demo	3.2–48	1–12	3.2–4	75–90 (4500)	2000–4600	625–1150
Na/S	Commercial	7.2	1	7.2	75 (4500)	3200–4000	445–555
Zn/Br flow	Demo	5–50	1–10	5	60–65 (>10,000)	1670–2015	340–1350
V redox	Demo	4–40	1–10	4	65–70 (>10,000)	3000–3310	750–830
Fe/Cr flow	R&D	4	1	4	75 (>10000)	1200–1600	300–400
Zn/air	R&D	5.4	1	5.4	75 (4500)	1750–1900	325–350
Li-ion	Demo	4–24	1–10	2–4	90–94 (4500)	1800–4100	900–1700

that capacity sits idle daily as well as for large portions of the year (fig. S2). Correspondingly, the transmission and distribution system must also be sized to handle peak power transfer requirements, even if only a fraction of that power transfer capacity is used during most of the year. Operationally, electrical power generation must be continuously ramped up and down to ensure that the delicate balance between supply and demand is maintained. The up and down cycling reduces power plant efficiency, resulting in higher fuel consumption and higher emissions per kilowatt-hour (kWh) produced. This procedure also causes more wear on the equipment and reduces the lifetime of power plants (5).

By decoupling generation and load, grid energy storage would simplify the balancing act between electricity supply and demand, and on overall grid power flow. EES systems have potential applications throughout the grid, from bulk energy storage to distributed energy functions (1). The availability of energy storage would help to eliminate the distinction between

ficiency (between 65 and 75%). Although there are obvious limitations because of geographical considerations, pumped hydro will be the benchmark for grid-scale storage for years to come.

In the near term, utilities are aware of the rising need for EES solutions but are skeptical of the technologies that have been proposed to date. Even in cases in which technology has substantial merit, the absence of cost-effective products with a track record of safe and reliable operation has made the industry skittish about their use. Table 1 lists some of the current maturity levels for various energy storage technologies, their operational characteristics, and cost estimates. If successful, the outcomes from these projects may alleviate industry concerns of matters such as performance, cycle life, economics, and risks. Another promising development is that the industry has begun working to establish standards and targets.

Electrochemical Energy Storage

Electrochemical energy storage approaches can be distinguished by the mechanisms used to store

Although not discussed here, capacitive energy storage offers some promising opportunities for grid-scale applications (Fig. 1). Supercapacitors provide higher power and longer cycle life than that of batteries and are receiving renewed attention as researchers try to better understand fundamental interfacial processes and improve energy density (8). The technology is of interest for power quality applications, such as alleviating short-term disruptions of a few minutes until a generator, fuel cell, or battery can be placed in service. Because the lifetime costs for supercapacitors can be attractive (6), there is the prospect that this technology will be used in conjunction with batteries so as to provide future grid storage solutions.

A battery is composed of several electrochemical cells that are connected in series and/or in parallel in order to provide the required voltage and capacity, respectively. Each cell is composed of a positive and a negative electrode, which are where the redox reactions take place. The electrodes are separated by an electrolyte, usually a solution containing dissociated salts so as to

enable ion transfer between the two electrodes. Once these electrodes are connected externally, the chemical reactions proceed in tandem at both electrodes, liberating electrons and providing the current to be tapped by the user (*9*, *10*). The energy storage properties for most of the common rechargeable batteries are shown in Fig. 2, with additional details provided in table S1.

Lithium Ion Batteries

The Li-ion battery (LIB) technology commercially introduced by Sony in the early 1990s is based on the use of Li-intercalation compounds. Li ions migrate across the electrolyte located between the two host structures, which serve as the positive and negative electrodes (Fig. 3). Li-ion batteries outperform, by at least a factor of 2.5, competing technologies [nickel (Ni)–metal hydride, Ni-cadmium (Cd), and lead (Pb)–acid)] in terms of delivered energy while providing high specific power (Fig. 2). The overwhelming appeal of Li-electrochemistry lies in its low molecular weight; small ionic radius, which is beneficial for diffusion; and low redox potential [$E°(Li^+/Li) = -3.04$ V vs standard hydrogen electrode (SHE)] (*11*). The latter enables high-output voltages and therefore high-energy densities. Such attractive properties, coupled with its long cycle life and rate capability, have enabled Li-ion technology to capture the portable electronics market and make in-roads in the power tools equipment field. LIBs are also regarded as the battery of choice for powering the next generation of hybrid electric vehicles (HEVs) as well as plug-in hybrids (PHEVs), provided that improvements can be achieved in terms of performance, cost, and safety (*12*). Because long-term stability, high-energy density, safety, and low cost are common to developing batteries for both automotive and grid applications, considerable synergy should exist between the two areas, although there will be certain differences. Figures of merit for electric vehicle applications call for a reduction in the price per kilowatt-hour by a factor of 2 and a doubling of the present energy density. The realization of such goals will be beneficial for grid storage systems, although with probably more emphasis on cost and less on energy density. Other differences between the two technologies include safety, which is easier to achieve in stationary situations than in mobile ones, whereas long cycle life is a key factor for grid applications. LIBs for vehicles require versatility in their energy and power capabilities in order to meet the needs of the various types of electric vehicles and the associated performance requirements, whereas LIBs for the grid are likely to be modular.

A number of advances have been made in the LIB field by controlling particle size in addition to composition, structure, and morphology in order to design better electrodes and electrolyte components (*13*). Decreasing electrochemically active materials to sub-micrometer and smaller
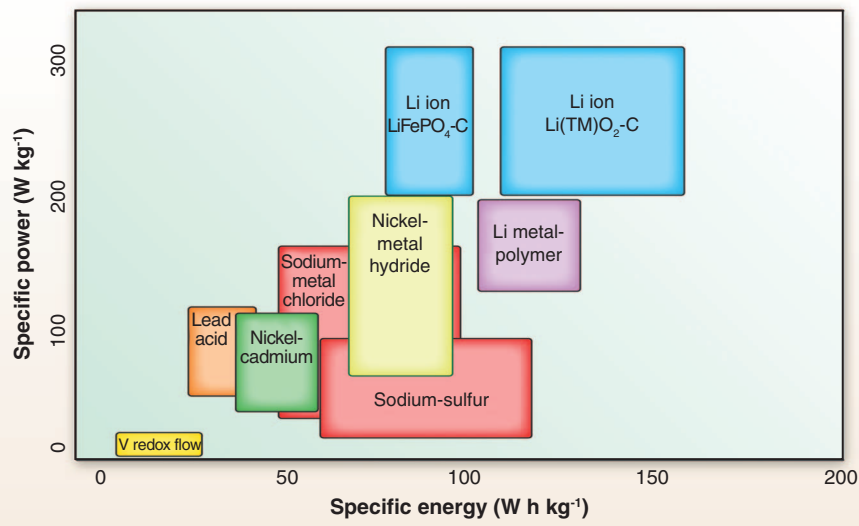
Fig. 2. Gravimetric power and energy densities for different rechargeable batteries. Most of these systems are currently being investigated for grid storage applications.
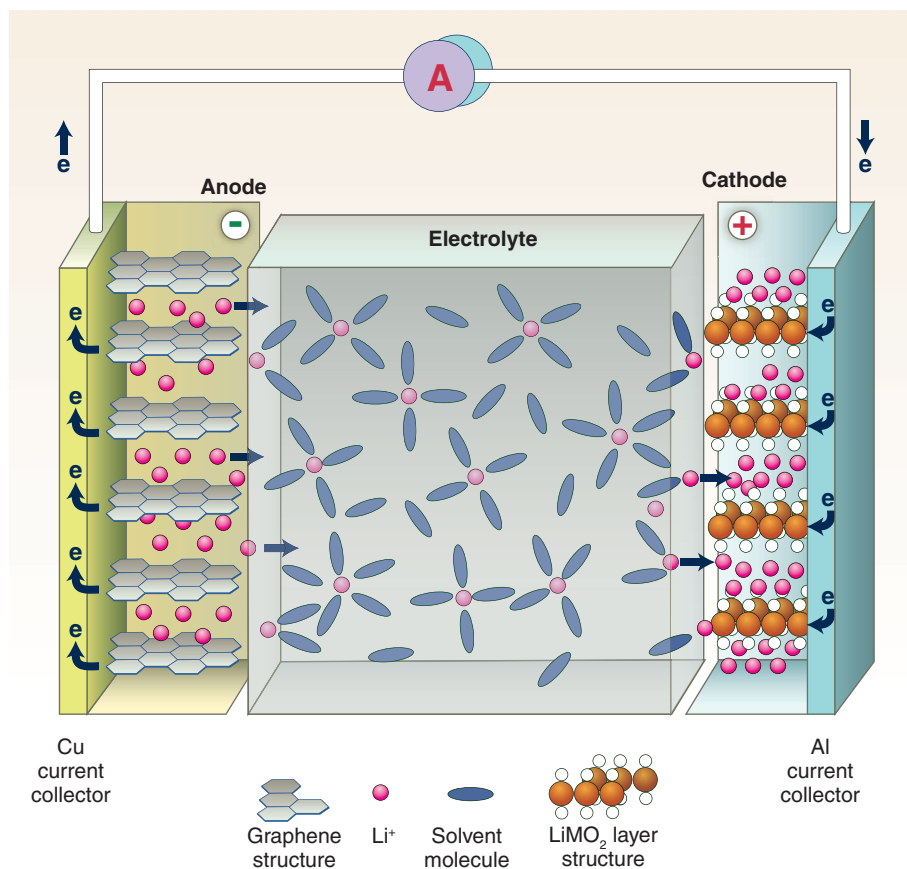
Fig. 3. Schematic of a LIB. The negative electrode is a graphitic carbon that holds Li in its layers, whereas the positive electrode is a Li-intercalation compound—usually an oxide because of its higher potential—that often is characterized by a layered structure. Both electrodes are able to reversibly insert and remove Li ions from their respective structures. On charging, Li ions are removed or deintercalated from the layered oxide compound and intercalated into the graphite layers. The process is reversed on discharge. The electrodes are separated by a nonaqueous electrolyte that transports Li ions between the electrodes. [Derived from (*4*)]

sizes combined with carbon-coating approaches to achieve core-shell morphologies has led to new directions in electrode materials (*14*). Reaction mechanisms and materials systems that were previously discarded are being reconsidered for the next generation of LIBs. Moving from bulk materials to nanosize particles has enabled (i) the ability to use new Li-reaction mechanisms, in which conversion-reaction electrodes show enormous capacity gains (*15*); (ii) the use of negative electrodes based on alloy reactions—Tin (Sn)–based LIB technologies have already reached the marketplace (such as NEXELION), and Si-based ones are emerging (*16*); (iii) the identification of poorly conducting polyanionic compounds or fluorine-based compounds that exhibit excellent electrochemical performance (*17*); and (iv) the transformation of the poorly conducting lithium iron phosphate ($LiFePO_4$) insertion electrode into perhaps the most valued electrode material for electric vehicle applications (*18*). LIBs based on $LiFePO_4$ are extremely attractive because of safety and cost. The former arises from the fact that the operating voltage of the $LiFePO_4$ system is compatible with the thermodynamic stability of the electrolyte, whereas the latter is based on the use of abundant and low-cost constituents. In addition to being an attractive LIB for the electric vehicle market, $LiFePO_4$-based batteries are being evaluated in stationary energy storage demonstration projects (*1*).

A substantial segment of the battery materials community is moving toward developing electrode materials on the basis of abundance and availability of the relevant chemicals. Materials centered on sustainable 3d metal redox elements such as manganese (Mn) [lithium-manganese oxide ($LiMn_2O_4$)], Fe ($LiFePO_4$, Li_2FeSiO_4) and titanium (Ti) (TiO_2, $Li_4Ti_5O_{12}$), and made via eco-efficient processes, are receiving increased attention (*19*). In addition, there is resurging interest in low-temperature–solution chemistry routes in which hydro(solvo)thermal, ionothermal, and bio-mineralization processes are used to prepare electrode materials at temperatures >500°C lower than traditional powder synthesis (*20*).

Life cycle costs represent another important consideration. A foreseeable strategy for battery processing will involve the use of electro-active organic electrode materials synthesized from "green chemistry" concepts through low-cost processes free of toxic solvents; this will also enlist the use of natural organic sources [carbon dioxide (CO_2)–harvesting entities] as precursors, which will be biodegradable and easily destroyed by combustion (providing CO_2) so that the battery assembly/recovery processes will have a minimal CO_2 footprint. Proof of this concept was demonstrated with the development of renewable organic electrodes belonging to the family of oxocarbons ($Li_2C_6O_6$) or carboxylates ($Li_2C_8H_4O_4$) and the assembly of the first eco-compatible LIB laboratory prototype (*21*). This work is extreme-

ly promising and suggests that the performance of organic electrodes could become comparable in gravimetric energy density, life cycle, and power rate to today's best inorganic electrodes, with the distinct advantage of providing a botanic alternative to the mineral approach currently in practice.

At the research level, there is interest in rechargeable LIB systems that have significantly higher energy densities (*22, 23*). Although the $Li-O_2$ system has been available for many years as a primary battery, the prospect of developing it into a reversible (secondary) battery has become tantalizing because of a projected three- to four-fold increase in gravimetric energy density as compared with the current Li-ion technology (*24*).

little doubt that rechargeable Li-air cells either for electric vehicles or grid storage applications still have a long research and development path.

The prospect of developing Li-ion technology for both transportation and stationary storage raises the issue of whether the demand for lithium will affect the existing world reserves. Na is an attractive alternative because its intercalation chemistry is similar to that of Li, there are ample reserves, and its cost is low. These advantages are partially offset by the gravimetric energy density penalty for using Na, which is both heavier and less electropositive than Li. The development of room-temperature Na-ion cells that are cost-effective, sustainable, and environmentally benign will require a new generation of Na-intercalation
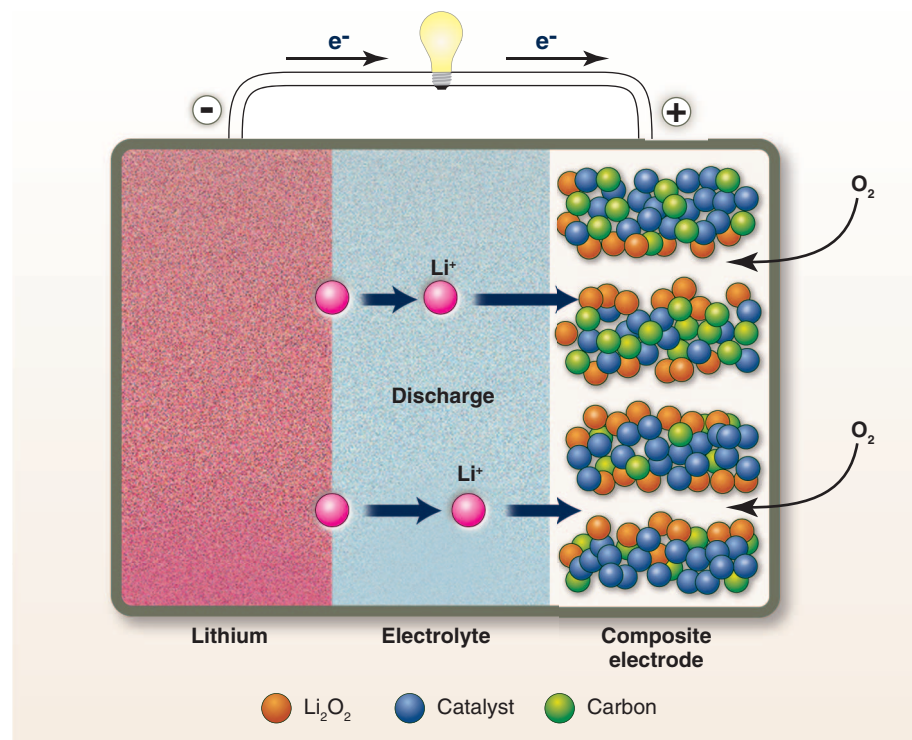
Fig. 4. The Li-air cell uses Li as the anode and a cathode consisting of a porous conductive composite, usually carbon and a catalyst, that is flooded with electrolyte. Oxygen from the atmosphere dissolves in the electrolyte and is reduced. On discharge, Li ions pass through the electrolyte and react with the reduced oxygen. The process is reversed on charging. Either aqueous or nonaqueous electrolytes can be used. For the former, a Li-ion–conducting solid electrolyte separates the metallic Li from the aqueous electrolyte.

However, the volumetric energy density may not be much greater than that of Li-ion batteries (*25*).

The renewed interest in this system can be traced to the rechargeable behavior demonstrated in a nonaqueous $Li-O_2$ system (Fig. 4) (*26*). Although there has been considerable progress in the past 5 years in the area of electrode materials and architectures (*27, 28*), a number of fundamental problems still need to be addressed, and it is difficult to anticipate which of the advanced $Li-O_2$ aqueous and/or $Li-O_2$ nonaqueous systems will be able to achieve capabilities beyond today's Li-ion batteries (*29*). Thus, there is

compounds (*30*). The knowledge gained from developing Li-ion insertion electrodes should be applicable here. Thus, the demonstration of a viable Na-ion technology for stationary energy storage should come well before that of Li-air technology because of the accumulated experience with Li-ion technology and high-temperature Na battery technologies.

Sodium-Sulfur and Sodium-Metal Halide Batteries

High-temperature Na-based battery technologies can be traced back to the 1960s, when researchers

at Ford discovered that a common ceramic re-fractory, sodium β-alumina ($NaAl_{11}O_{17}$), exhibited extremely high ionic conductivity for Na ions (*31*). At 300°C, the ionic conductivity for $NaAl_{11}O_{17}$ approaches that of the aqueous electrolyte, H_2SO_4, suggesting the possibility of using $NaAl_{11}O_{17}$ as a solid electrolyte in a high-temperature electrochemical cell. Although solids with high ionic conductivity had been known previously, none had β-alumina's combination of chemical and thermal stability and low electronic conductivity. The recognition that inorganic materials with high vacancy concentrations could exhibit "fast ion conduction"—many orders of magnitude greater than traditional alkali halides—led to the development of the field known as solid-state ionics.

The two high-temperature Na batteries, Na/S and Na-metal chloride ($Na/MeCl_2$), are based on using β-alumina as a Na^+-conducting membrane between two liquid electrodes (*32*). The batteries operate at temperatures of 270 to 350°C so as to take advantage of the increased conductivity of the β-alumina at elevated temperatures and ensure that the active electrode materials are molten. During discharge in the Na/S battery, Na is oxidized at the solid electrolyte interface, and the resulting Na^+ migrates through the electrolyte to react with S that is reduced at the positive electrode, forming Na_2S_5 (Fig. 5). Initially, a two-phase liquid is formed because Na_2S_5 is immiscible with S at these temperatures. Over half of the discharge occurs in the two-phase region, where the open-circuit voltage is 2.08 V (*33*). During charge, the Na polysulfides are oxidized, and when the Na content falls below Na_2S_5, the two phase-region of Na_2S_5 and S reappears. In this case, the formation of S must be managed appropriately, or else the S can deposit on or near the electrolyte, increasing cell resistance and limiting the amount of charging.

Early in its development in the 1980s, the $Na/MeCl_2$ battery was nicknamed the ZEBRA battery partially because of its scientific origins in South Africa, although its acronym stands for Zero-Emission Battery Research Activities. The positive electrode in this battery is a semisolid combination of an electrochemically active metal chloride such as $NiCl_2$ and a molten secondary electrolyte, $NaAlCl_4$, which conducts Na^+. During discharge, metallic Na is oxidized at the solid electrolyte interface. Na^+ ions are transported through the β-alumina electrolyte to the cathode via the molten $NaAlCl_4$. The solid metal chloride is converted into NaCl and the parent metal (Ni in the case of $NiCl_2$). The open-circuit voltage is 2.58 V (*34*). On charge, the Ni is oxidized, and the charge capacity is determined by the amount of NaCl available in the cathode.

Both batteries are based on the ion transport properties of the β-alumina family of materials. The high ionic conductivity of these materials is the result of an unusual structure
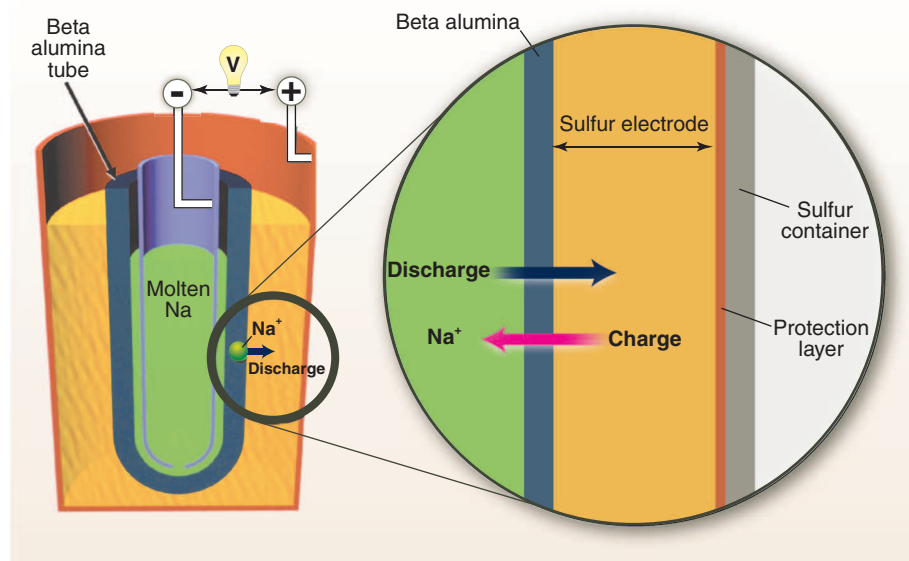
Fig. 5. Schematic of the Na/S battery. The central Na design has molten Na (negative electrode) contained within a Na β''-alumina solid electrolyte tube with molten S (positive electrode) surrounding the tube. The S electrode includes carbon in order to provide sufficient electronic conduction to carry out the electrochemical reactions. The magnified cross section of the cell shows the direction of Na^+ transport through the β''-alumina electrolyte. On discharge, Na combines with the S to form Na polysulfides. These reactions are reversed during charge, and Na returns to the interior of the tube.

in which "blocks" of closely packed Al-O are separated by "conduction planes" (*35*). The latter are loosely packed layers that contain the mobile Na^+ along with O^{2-} ions that bridge adjacent blocks. Ion motion occurs in two-dimensional honeycomb-like pathways around the bridging oxygen. The polycrystalline β''-alumina tubes used in the Na/S and $Na/MeCl_2$ batteries do not exhibit the anisotropic transport properties of single crystals because the fine-grained, randomly oriented microstructures effectively eliminate the anisotropy. Nonetheless, there are grain boundary and tortuosity effects so that the conductivity of single-crystal Na β''-alumina at 300°C, ~ 1 S cm^{-1}, is three to five times greater than the corresponding polycrystalline material (*32*). A recent study suggests that tortuosity effects can be diminished because Na β''-alumina electrolytes in a planar configuration exhibit higher ionic conductivity than that of tubular materials (*36*).

From inception, development for both systems targeted stationary energy storage and electric vehicles. As a result, the technologies share a number of common features (and challenges), even though specific designs differ somewhat. In both cases, the β''-alumina ceramic tubes are acknowledged to be the key element for determining battery operation and cost. Considerable development effort has gone into establishing large-scale manufacturing processes for automating the fabrication of high-quality ceramics with appropriate mechanical and electrical properties (*37*). Fracture of the ceramic is

a vital concern because it leads to cell failure, whereas poor control of the ceramic microstructure results in interfacial reactions with the reactants. Large-scale production of β''-alumina has been established, but production yields and costs are major concerns (*38*). Other critical battery components are seals, which must not only be hermetic in the 300 to 350°C range but also withstand the vapor and/or actual contact with the highly reactive molten electrode materials. Recent activities in this area have involved the development of glass-ceramic sealing materials whose thermal expansion coefficient matches that of α- and β-alumina components (*39*). There is also the issue of identifying a low-cost material for containing the molten positive electrode. The corrosion problem is particularly difficult for Na/S batteries because both S and polysulfides are highly corrosive. The deposition of corrosion-resistant coatings such as carbides onto inexpensive substrates has proven successful (*40*).

Na/S battery technology has been commercialized in Japan since 2002, where it is largely used in utility-based load-leveling and peak-shaving applications. Among the advantages identified for stationary storage are its relatively small footprint (a result of high energy density), high coulombic efficiency, cycling flexibility, and low maintenance requirements (*41*). The production of megawatt-size energy storage batteries has involved considerable effort on such interrelated issues as electrical networking, cell reliability, thermal management, and safety (*42*).

To provide appropriate voltages, energy, and power, cells are assembled in series-parallel configurations to form modules, and the modules themselves are connected in series-parallel arrangements to form batteries. This networking approach is designed to minimize the effect of individual cell failures. Modules are thermally insulated and equipped with auxiliary heaters in order to maintain a minimum operating temperature. Thermal management is especially challenging. The internal temperature of a module increases on discharge because of joule heating and exothermic cell reactions, whereas during charge, there is a gradual cooling largely because of the cell endothermic reaction (41).

The Na/MeCl$_2$ batteries were developed almost exclusively for electric vehicles. At the time of their development, the technology seemed to offer certain advantages over Na/S in terms of tolerance to overcharge and overdischarge, the ability to assemble cells in the discharged state, a safe low-resistance failure mode, and potentially easier solutions for corrosion and sealing (42). Only recently have these batteries been directed at potential utility applications (43).

Redox-Flow Batteries

Redox-flow batteries also have their origins in the 1960s, with the development of the zinc/chlorine (Zn/Cl) hydrate battery. As a general description, a redox-flow cell uses two circulating soluble redox couples as electroactive species that are oxidized and reduced to store or deliver energy (44). By comparison, batteries rely on internal solid electrodes to store energy.

The flow-cell assembly (Fig. 6) has an ion-selective membrane separating the positive and negative redox species, which are contained in separate storage tanks. During operation, redox-active ions undergo oxidation or reduction reactions when they are in contact or close proximity to the current collector; the membrane allows the transport of non-reaction ions (such as H$^+$ and Na$^+$) to maintain electroneutrality and electrolyte balance.

Since the 1970s, numerous types of redox flow battery systems have been investigated (45). A partial list includes iron/chromium, vanadium/bromine, bromine/polysulfide, zinc-cerium, zinc/bromine (Zn/Br), and all-vanadium. The all-vanadium (1.26 V) and Zn/Br (1.85 V) systems are the most advanced and have reached the demonstration stage for stationary energy storage. Interest in the all-vanadium system is based on having a single cationic element so that the cross-over of vanadium ions through the membrane upon long-term cycling is less deleterious than with other chemistries (46).

Redox-flow batteries possess a number of advantages (47). The simplicity of the electrode reactions contrasts with those of many conventional batteries that involve, for example, phase transformations, electrolyte degradation, or electrode morphology changes. Perhaps their most attractive feature is that power and energy are uncoupled, a characteristic that many other electrochemical energy storage approaches do not have (48, 49). This gives considerable design flexibility for stationary energy storage applications. The capacity can be increased by simply increasing either the size of the reservoirs holding the reactants or increasing the concentration of the electrolyte. In addition, the power of the system can be tuned by either (i) modifying the numbers of cells in the stacks, (ii) using bipolar electrodes, or (iii) connecting stacks in either parallel or series configurations. This provides modularity and flexible operation to the system.

Despite the apparent advantages for redox-flow batteries, application of this technology to

issues associated with the lack of appropriate membranes for controlling long-term ion cross-over effects. Designing better membranes is necessary, but whether such membranes can be of low cost is far from certain. Another important issue with redox-flow systems is that the currently used redox couples, even with enhanced solubility, are limited to concentrations of about 8 M. This feature is largely responsible for the fact that redox-flow systems do not surpass 25 Wh kg^{-1} (Fig. 2). The identification of lower-cost redox couples with high solubility would seem to be an essential development in order for this technology to succeed.

Researchers recognize that redox-flow approaches represent potentially new directions for increasing energy density. The semisolid Li battery
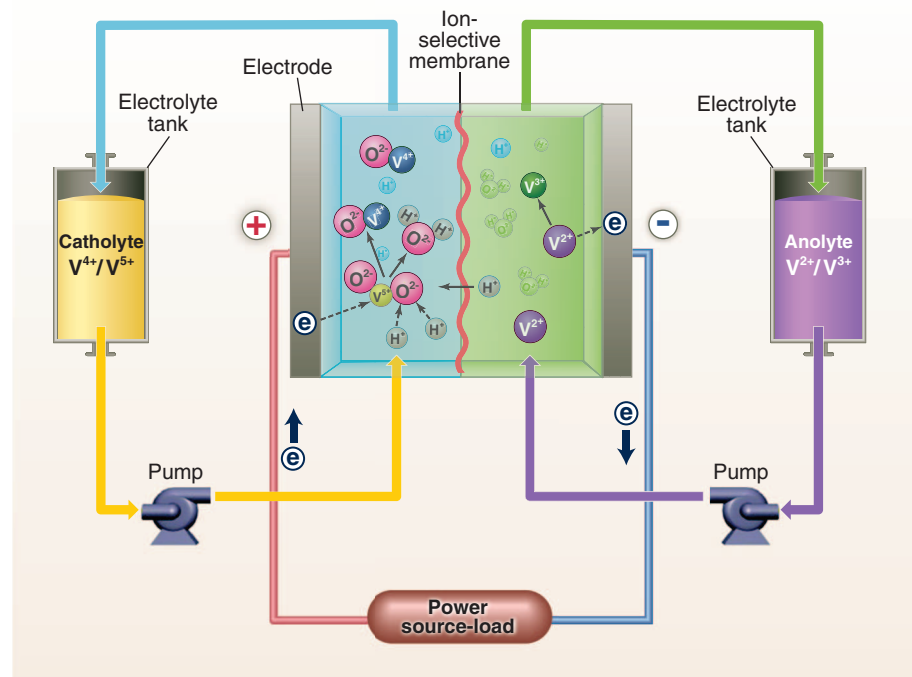
Fig. 6. Schematic of the various components for a redox-flow battery. The cell consists of two electrolyte flow compartments separated by an ion-selective membrane. The electrolyte solutions, which are pumped continuously from external tanks, contain soluble redox couples. The energy in redox-flow batteries is stored in the electrolyte, which is charged or discharged accordingly. In practice, individual cells are arranged in stacks by using bipolar electrodes. The power of the system is determined by the number of cells in the stack, whereas the energy is determined by the concentration and volume of electrolyte. In the vanadium redox-flow battery shown here, the V$^{(II)}$/V$^{(III)}$ redox couple circulates through the negative compartment (anolyte), whereas the V$^{(IV)}$/V$^{(V)}$ redox couple circulates through the positive compartment (catholyte). [Derived from (38)]

stationary energy storage is still uncertain. One principal reason is that redox-flow systems have been limited to relatively few field trials. In contrast, other battery technologies have benefited from extensive experience in the development of products for portable electronics and automotive applications. A related disadvantage of flow batteries is the system requirements of pumps, sensors, reservoirs, and flow management (48, 49). From a technical standpoint, there are reliability

demonstrated by Massachusetts Institute of Technology researchers uses electrode materials identical to those found in the LIB, but now the electrode materials are conducting inks (for example, suspensions of LiCoO$_2$ and of Li$_4$Ti$_5$O$_{12}$ powders in nonaqueous electrolyte solutions) rather than solids (50). The inks circulate separately on either side of a membrane that regulates the Li-ion transport between positive and negative electrodes. Both half cells and full cells have been demonstrated.

The novel feature here is the use of redox-active materials in suspension so as to circumvent the problem of the relatively low solubility of the metal ion redox couples in aqueous solution. The flowable inks will be in the 10 to 40 M range, which is at least 5 times higher than traditional redox flow systems. Combining the higher materials concentration with the feasibility of achieving 4-V working systems is likely to lead to considerable improvement in energy density, perhaps without substantially affecting power density.

Another Li-ion–based flow system was demonstrated recently by Goodenough and colleagues. In this design, an aqueous cathode operating in a flow-through mode was separated from a metallic Li anode by a Li-ion–conducting solid electrolyte and an organic liquid electrolyte (51). This redox-flow system used an aqueous cathode containing 0.1 M $K_3Fe(CN)_6$ and demonstrated highly efficient energy storage at 3.4 V. The design strategy presented here offers some noteworthy advances: (i) Li^+ ion transport in solution is enhanced as compared with that in a solid insertion cathode and (ii) the absence of structural changes during charge/discharge is beneficial for long-term cycling. The first laboratory prototypes were limited by low solubility of the metal-ion redox couple in the aqueous solvent and the poor mobility of Li^+ in the solid electrolyte. It is expected that the performance of the rechargeable alkali-ion cathode flow battery will improve substantially through the use of a better solid electrolyte and the possibility of using cathode inks. But perhaps the more important point illustrated in these studies is that redox-flow concepts adapt to other chemistries and hold considerable promise for improving battery performance and especially energy density.

Future Directions

There are two related questions that need to be addressed: What are the expectations for EES in the future, and what role will batteries play in this future? The first part is becoming clearer as the value of energy storage becomes increasingly evident. A recent EPRI study identified a number of high-value opportunities for energy storage, including wholesale energy services, integration of renewables, commercial and industrial power quality and reliability, transportable systems for transmission and distribution grid support and energy management (1). Moreover, some of these benefits are complementary, further improving the economics of energy storage.

The success of these applications of energy storage will depend on how well storage technologies can meet key expectations. The most important of these are low installed cost, high durability and reliability, long life, and high round-trip efficiency. The installed cost comprises the materials costs, production costs, and installation costs for the system. In the future, the preferred energy storage technologies will be composed of low-cost, easily acquired materials that are developed into

products through a relatively simple manufacturing process and installed with few special requirements. Operations and maintenance costs are also important; these costs are often tied to the durability and lifetime of the energy storage solution, for which the lifetimes of most assets are measured in decades. Last, a premium will be placed on energy-efficient systems that do not lose energy through self-discharge or parasitic losses. With so many potential financial considerations, it is not surprising that cost is given as the reason that energy storage is not widely used on the grid.

The battery systems reviewed here satisfy several, but not all, of the energy storage criteria mentioned above. Na/S is commercially viable, and if this emerging technology follows patterns similar to others, costs can be expected to decrease as more production and operational experience is gained. The technology, which is more than 30 years old, needs to integrate some of the scientific advances that have taken place in the design of materials, creating new electrode architectures and identifying new chemistries to provide safe operation. Lowering the Na/S operating temperature is one topic that will affect the technology. Moreover, these advances will benefit Na-ion technology, which is of growing interest because of its promise as a low-cost approach for grid storage applications. Redox-flow batteries possess several promising attributes for energy storage, with low cost being one of the important drivers for this technology. A number of demonstration projects, ranging in size from 5 to 50 MWh and using a variety of different chemistries, are under way (48). The outcomes from these projects over the next 2 to 4 years will have a substantial influence on the future of this technology. The recent developments involving Li-redox flow and alkali-redox flow batteries stand as great opportunities that leverage existing knowledge of Li-ion batteries with the advantages of redox-flow systems.

Energy storage systems based on Li-ion batteries are expected to take a different route than either Na/S or redox-flow batteries. The development of Li-ion batteries for commercial electronics and automotive applications enabled this technology to address reliability, cycle life, safety, and other factors that are equally as important for stationary energy storage. The research environment for developing new low-cost materials is well established, and recent efforts directed at low-temperature processing and renewable organic electrodes provide the basis for future advances in the field. However, it is the volume production anticipated for the electric vehicle market that can lead to improvements in manufacturing process and provide an economy of scale that will bring about the lower costs required to make this battery technology viable for EES. Another interesting scenario is the prospect of recovering Li-ion batteries used in automotive industries and to give them a "second life" in large-scale energy storage applications.

Note added in proof: Na/S batteries were responsible for a fire that occurred at a power plant in Joso City (Ibaraki Prefecture) on 21 September 2011 (www.ngk.co.jp/english/news/2011/1028_01.html). Although the cause of the fire is still under investigation, this event underscores the fact that safety issues for Na/S batteries have not been completely resolved.

References and Notes

1. "Electrical energy storage technology options" (Report 1020676, Electric Power Research Institute, Palo Alto, CA, December 2010).
2. *EPRI-DOE Handbook of Energy Storage for Transmission and Distribution Applications* (*1001834*, EPRI, Palo Alto, CA, and the U.S. Department of Energy, Washington, DC, 2003).
3. G. L. Soloveichik, *Annu. Rev. Chem. Biomol. Eng.* **2**, 503 (2011).
4. "Basic research needs for electrical energy storage" (Office of Basic Energy Sciences, U.S. Department of Energy, Washington, DC, July 2007).
5. "Power Generation from Coal: Measuring and Reporting Efficiency Performance and CO_2 Emissions" (International Energy Agency, October 2010).
6. "Energy Storage for the Electricity Grid: Benefits and Market Potential Assessment" (*Report SAND 2010-0815*, Sandia National Laboratories, Albuquerque, NM, February 2010).
7. M. Winter, R. J. Brodd, *Chem. Rev.* **104**, 4245 (2004).
8. P. Simon, Y. Gogotsi, *Nat. Mater.* **7**, 845 (2008).
9. J. B. Goodenough, Y. Kim, *Chem. Mater.* **22**, 587 (2010).
10. J. M. Tarascon, M. Armand, *Nature* **414**, 359 (2001).
11. V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **4**, 3243 (2011).
12. M. Armand, J. M. Tarascon, *Nature* **451**, 652 (2008).
13. A. S. Aricò, P. Bruce, B. Scrosati, J. M. Tarascon, W. van Schalkwijk, *Nat. Mater.* **4**, 366 (2005).
14. H. Li, Z. X. Wang, L. Q. Chen, X. J. Huang, *Adv. Mater. (Deerfield Beach Fla.)* **21**, 4593 (2009).
15. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, *Nature* **407**, 496 (2000).
16. M. N. Obrovac, L. Christensen, *Electrochem. Solid-State Lett.* **7**, A93 (2004).
17. P. Barpanda *et al.*, *Inorg. Chem.* **49**, 7401 (2010).
18. A. Yamada, S. C. Chung, K. Hinokuma, *J. Electrochem. Soc.* **148**, A224 (2001).
19. J. M. Tarascon, *Philos. Trans. R. Soc. A* **368**, 3227 (2010).
20. J. M. Tarascon *et al.*, *Chem. Mater.* **22**, 724 (2010).
21. H. Chen *et al.*, *J. Am. Chem. Soc.* **131**, 8984 (2009).
22. G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* **1**, 2193 (2010).
23. K. T. Lee *et al.*, *Adv. Energy Mater.* **1**, 34 (2011).
24. K. M. Abraham, Z. Jiang, *J. Electrochem. Soc.* **143**, 1 (1996).
25. J. P. Zheng, R. Y. Liang, M. Hendrickson, E. J. Plichta, *J. Electrochem. Soc.* **155**, A432 (2008).
26. T. Ogasawara, A. Débart, M. Holzapfel, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **128**, 1390 (2006).
27. A. Débart, A. J. Paterson, J. Bao, P. G. Bruce, *Angew. Chem. Int. Ed.* **47**, 4521 (2008).
28. Y. C. Lu *et al.*, *J. Am. Chem. Soc.* **132**, 12170 (2010).
29. G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* **1**, 2193 (2010).
30. J. F. Whitacre, A. Tevar, S. Sharma, *Electrochem. Commun.* **12**, 463 (2010).
31. Y. F. Y. Yao, J. T. Kummer, *J. Inorg. Nucl. Chem.* **29**, 2453 (1967).
32. X. C. Lu, G. G. Xia, J. P. Lemmon, Z. G. Yang, *J. Power Sources* **195**, 2431 (2010).
33. J. L. Sudworth, A. R. Tilley, *The Sodium Sulfur Battery* (Chapman & Hall, London, 1985).
34. C. H. Dustmann, *J. Power Sources* **127**, 85 (2004).
35. G. C. Farrington, J. L. Briant, *Science* **204**, 1371 (1979).
36. D. La Rosa *et al.*, *ChemSusChem* **3**, 1390 (2010).
37. J. L. Sudworth *et al.*, *MRS Bull.* **25**, 22 (2000).
38. Z. Yang *et al.*, *Chem. Rev.* **111**, 3577 (2011).
39. S. F. Song *et al.*, *J. Solid State Electrochem.* **14**, 1735 (2010).
40. B. Dunn, M. W. Breiter, D. S. Park, *J. Appl. Electrochem.* **11**, 103 (1981).

41. A. Bito, "Overview of the sodium-sulfur battery for the IEEE Stationary Battery Committee," paper presented at the IEEE Power Engineering Society General Meeting, San Francisco, CA, 12 to 16 June 2005.
42. J. W. Braithwaite, W. L. Auxer, in *Handbook of Batteries*, D. Linden, T. B. Reddy, Eds. (McGraw-Hill, 2004), chap. 40.
43. www.geenergystorage.com/
44. C. P. de Leon *et al.*, *J. Power Sources* **160**, 716 (2006).
45. M. Bartolozzi, *J. Power Sources* **27**, 219 (1989).
46. M. Skyllas-Kazacos, M. Rychcik, R. G. Robins, A. G. Fane, M. A. Green, *J. Electrochem. Soc.* **133**, 1057 (1986).
47. M . Skyllas-Kazacos *et al.*, *J. Electrochem. Soc.* **158**, R55 (2011).
48. D. H. Doughty, P. C. Butler, A. A. Akhil, N. H. Clark, J. D. Boyes, *Electrochem. Soc. Interface* **19**, 49 (2010).
49. T. Nguyen, R. F. Savinell, *Electrochem. Soc. Interface* **19**, 54 (2010).
50. M. Duduta *et al.*, *Adv. Energy Mater.* **1**, 511 (2011).
51. Y. H. Lu, J. B. Goodenough, *J. Mater. Chem.* **21**, 10113 (2011).

REVIEW

Lowering the Temperature of Solid Oxide Fuel Cells

Eric D. Wachsman* and Kang Taek Lee

Fuel cells are uniquely capable of overcoming combustion efficiency limitations (e.g., the Carnot cycle). However, the linking of fuel cells (an energy conversion device) and hydrogen (an energy carrier) has emphasized investment in proton-exchange membrane fuel cells as part of a larger hydrogen economy and thus relegated fuel cells to a future technology. In contrast, solid oxide fuel cells are capable of operating on conventional fuels (as well as hydrogen) today. The main issue for solid oxide fuel cells is high operating temperature (about 800°C) and the resulting materials and cost limitations and operating complexities (e.g., thermal cycling). Recent solid oxide fuel cells results have demonstrated extremely high power densities of about 2 watts per square centimeter at 650°C along with flexible fueling, thus enabling higher efficiency within the current fuel infrastructure. Newly developed, high-conductivity electrolytes and nanostructured electrode designs provide a path for further performance improvement at much lower temperatures, down to ~350°C, thus providing opportunity to transform the way we convert and store energy.

Fuel cells are the most efficient means to directly convert stored chemical energy to usable electrical energy (an electrochemical reaction). Although the more common proton-exchange membrane fuel cells (PEMFCs) require hydrogen fueling, because they are based on proton conducting electrolytes, solid oxide fuel cells (SOFCs) can oxidize essentially any fuel, from hydrogen to hydrocarbons to even carbon, because the electrolyte transports an oxygen ion.

An SOFC consists of three major components: two porous electrodes (cathode and anode) separated by a solid oxygen ion (O^{2-}) conducting electrolyte (Fig. 1A). At the cathode, O_2 (from air) is reduced and the resulting O^{2-} ions are transported through the electrolyte lattice to the anode where they react with gaseous fuel, yielding heat, H_2O, and (in the case of hydrocarbon fuels) CO_2, and releasing e^- to the external circuit.

Multiple cells are combined in series via interconnects that provide both electrical contacts and gas channels between individual cells. The resulting "stacks" are then arranged in series and parallel configurations to provide desired voltage and power outputs from portable power and transportation applications, to distributed generation and large-scale power generation, in both civilian and military sectors (Fig. 1B).

Among the technologies available to convert hydrocarbon-based resources (which include not only fossil fuels but also, potentially, biomass and municipal solid waste) to electricity, SOFCs are unique in their potential efficiency. For stand-alone applications, SOFC chemical to electrical efficiency is 45 to 65%, based on the lower heating value (LHV) of the fuel (*1*), which is twice that of an internal combustion (IC) engine's ability to convert chemical energy to mechanical work (*2*). In a combined cycle, there are numerous combined heat and power (CHP) applications using SOFC systems, which have the potential to achieve efficiencies of >85% LHV (*3*).

Unfortunately, government policy, the popular press, and many scientific publications have focused on fuel cells as part of a broader hydrogen economy, thereby relegating fuel cells to a "future energy" solution due to the need for a required overhaul of our current hydrocarbon-fueling infrastructure. Although this may be true for PEMFCs, SOFCs have the advantage of fuel flexibility that allows them to be used on our existing hydrocarbon fuel infrastructure (*4*) while simultaneously providing efficiency gains (and corresponding CO_2 emission reductions).

Why Reduce SOFC Operating Temperature?

The key technical issue that has limited the development and deployment of this transformative technology is its high operating temperature, resulting in higher systems costs and performance degradation rates, as well as slow start-up and shutdown cycles, the latter dramatically limiting applicability in portable power and transportation markets. Over the past decade, considerable progress has been achieved in bringing the temperature down to an intermediate temperature (IT) range of 650 to 800°C so that metallic interconnects could be used to reduce cost.

Low-temperature (LT) SOFCs (≤650°C) can further reduce system cost due to wider material choices for interconnects and compressive nonglass/ceramic seals, as well as reduced balance of plant (BOP) costs. Moreover, below 600°C, both radiative heat transfer (Stefan-Boltzmann) and sintering rates exponentially drop off, thus reducing insulation costs and primary performance degradation mechanisms, respectively.

At even lower temperatures (≤350°C), cheap stamped stainless steel interconnects, elastomeric/polymeric seals (e.g., Kapton), and off-the-shelf BOP are possible. In addition, rapid start-up and repeated thermal cycling, from ambient to operating temperature, becomes possible. These are critical parameters for portable power and transportation applications, and it was because of PEMFCs' lower operating temperature (~100°C) that they were chosen for these applications over SOFCs, even though PEMFCs require hydrogen fueling.

Another reason to reduce operating temperature is maximum theoretical efficiency. In contrast to the Carnot cycle temperature dependence of IC engines, theoretical fuel cell efficiency increases with decreasing temperature [fig. S1 and supporting online material text (SOM text)]. For example, the maximum theoretical efficiency of an SOFC using CO as a fuel increases from 63% at 900°C to 81% at 350°C.

At first glance, this would imply that PEMFCs are more efficient than SOFCs because of their lower operating temperature. However, this ignores two important contributors to overall system efficiency. The first is that the vast majority of all H_2 produced today comes from hydrocarbon resources (typically CH_4), thus requiring additional external processes [e.g., steam reforming or catalytic partial oxidation (CPOX), water

University of Maryland Energy Research Center, College Park, MD 20742, USA.

*To whom correspondence should be addressed. E-mail: ewach@umd.edu

41. A. Bito, "Overview of the sodium-sulfur battery for the IEEE Stationary Battery Committee," paper presented at the IEEE Power Engineering Society General Meeting, San Francisco, CA, 12 to 16 June 2005.
42. J. W. Braithwaite, W. L. Auxer, in *Handbook of Batteries*, D. Linden, T. B. Reddy, Eds. (McGraw-Hill, 2004), chap. 40.
43. www.geenergystorage.com/
44. C. P. de Leon *et al.*, *J. Power Sources* **160**, 716 (2006).
45. M. Bartolozzi, *J. Power Sources* **27**, 219 (1989).
46. M. Skyllas-Kazacos, M. Rychcik, R. G. Robins, A. G. Fane, M. A. Green, *J. Electrochem. Soc.* **133**, 1057 (1986).
47. M . Skyllas-Kazacos *et al.*, *J. Electrochem. Soc.* **158**, R55 (2011).
48. D. H. Doughty, P. C. Butler, A. A. Akhil, N. H. Clark, J. D. Boyes, *Electrochem. Soc. Interface* **19**, 49 (2010).
49. T. Nguyen, R. F. Savinell, *Electrochem. Soc. Interface* **19**, 54 (2010).
50. M. Duduta *et al.*, *Adv. Energy Mater.* **1**, 511 (2011).
51. Y. H. Lu, J. B. Goodenough, *J. Mater. Chem.* **21**, 10113 (2011).

REVIEW

Lowering the Temperature of Solid Oxide Fuel Cells

Eric D. Wachsman* and Kang Taek Lee

Fuel cells are uniquely capable of overcoming combustion efficiency limitations (e.g., the Carnot cycle). However, the linking of fuel cells (an energy conversion device) and hydrogen (an energy carrier) has emphasized investment in proton-exchange membrane fuel cells as part of a larger hydrogen economy and thus relegated fuel cells to a future technology. In contrast, solid oxide fuel cells are capable of operating on conventional fuels (as well as hydrogen) today. The main issue for solid oxide fuel cells is high operating temperature (about 800°C) and the resulting materials and cost limitations and operating complexities (e.g., thermal cycling). Recent solid oxide fuel cells results have demonstrated extremely high power densities of about 2 watts per square centimeter at 650°C along with flexible fueling, thus enabling higher efficiency within the current fuel infrastructure. Newly developed, high-conductivity electrolytes and nanostructured electrode designs provide a path for further performance improvement at much lower temperatures, down to ~350°C, thus providing opportunity to transform the way we convert and store energy.

Fuel cells are the most efficient means to directly convert stored chemical energy to usable electrical energy (an electrochemical reaction). Although the more common proton-exchange membrane fuel cells (PEMFCs) require hydrogen fueling, because they are based on proton conducting electrolytes, solid oxide fuel cells (SOFCs) can oxidize essentially any fuel, from hydrogen to hydrocarbons to even carbon, because the electrolyte transports an oxygen ion.

An SOFC consists of three major components: two porous electrodes (cathode and anode) separated by a solid oxygen ion (O^{2-}) conducting electrolyte (Fig. 1A). At the cathode, O_2 (from air) is reduced and the resulting O^{2-} ions are transported through the electrolyte lattice to the anode where they react with gaseous fuel, yielding heat, H_2O, and (in the case of hydrocarbon fuels) CO_2, and releasing e^- to the external circuit.

Multiple cells are combined in series via interconnects that provide both electrical contacts and gas channels between individual cells. The resulting "stacks" are then arranged in series and parallel configurations to provide desired voltage and power outputs from portable power and transportation applications, to distributed generation and large-scale power generation, in both civilian and military sectors (Fig. 1B).

Among the technologies available to convert hydrocarbon-based resources (which include not only fossil fuels but also, potentially, biomass and municipal solid waste) to electricity, SOFCs are unique in their potential efficiency. For stand-alone applications, SOFC chemical to electrical efficiency is 45 to 65%, based on the lower heating value (LHV) of the fuel (*1*), which is twice that of an internal combustion (IC) engine's ability to convert chemical energy to mechanical work (*2*). In a combined cycle, there are numerous combined heat and power (CHP) applications using SOFC systems, which have the potential to achieve efficiencies of >85% LHV (*3*).

Unfortunately, government policy, the popular press, and many scientific publications have focused on fuel cells as part of a broader hydrogen economy, thereby relegating fuel cells to a "future energy" solution due to the need for a required overhaul of our current hydrocarbon-fueling infrastructure. Although this may be true for PEMFCs, SOFCs have the advantage of fuel flexibility that allows them to be used on our existing hydrocarbon fuel infrastructure (*4*) while simultaneously providing efficiency gains (and corresponding CO_2 emission reductions).

Why Reduce SOFC Operating Temperature?

The key technical issue that has limited the development and deployment of this transformative technology is its high operating temperature, resulting in higher systems costs and performance degradation rates, as well as slow start-up and shutdown cycles, the latter dramatically limiting applicability in portable power and transportation markets. Over the past decade, considerable progress has been achieved in bringing the temperature down to an intermediate temperature (IT) range of 650 to 800°C so that metallic interconnects could be used to reduce cost.

Low-temperature (LT) SOFCs (≤650°C) can further reduce system cost due to wider material choices for interconnects and compressive nonglass/ceramic seals, as well as reduced balance of plant (BOP) costs. Moreover, below 600°C, both radiative heat transfer (Stefan-Boltzmann) and sintering rates exponentially drop off, thus reducing insulation costs and primary performance degradation mechanisms, respectively.

At even lower temperatures (≤350°C), cheap stamped stainless steel interconnects, elastomeric/polymeric seals (e.g., Kapton), and off-the-shelf BOP are possible. In addition, rapid start-up and repeated thermal cycling, from ambient to operating temperature, becomes possible. These are critical parameters for portable power and transportation applications, and it was because of PEMFCs' lower operating temperature (~100°C) that they were chosen for these applications over SOFCs, even though PEMFCs require hydrogen fueling.

Another reason to reduce operating temperature is maximum theoretical efficiency. In contrast to the Carnot cycle temperature dependence of IC engines, theoretical fuel cell efficiency increases with decreasing temperature [fig. S1 and supporting online material text (SOM text)]. For example, the maximum theoretical efficiency of an SOFC using CO as a fuel increases from 63% at 900°C to 81% at 350°C.

At first glance, this would imply that PEMFCs are more efficient than SOFCs because of their lower operating temperature. However, this ignores two important contributors to overall system efficiency. The first is that the vast majority of all H_2 produced today comes from hydrocarbon resources (typically CH_4), thus requiring additional external processes [e.g., steam reforming or catalytic partial oxidation (CPOX), water

University of Maryland Energy Research Center, College Park, MD 20742, USA.

*To whom correspondence should be addressed. E-mail: ewach@umd.edu

gas shift (WGS), and membrane separation or preferential oxidation (PROX)], each step having a thermodynamic penalty that decreases overall system efficiency (5). Moreover, they cannot take advantage of the higher theoretical fuel cell efficiency of CO over H_2 at lower temperature (fig. S1) because CO is a poison for PEMFCs versus a fuel for SOFCs. The second reason that lower temperature does not necessarily result in higher system efficiency is that all of the major cell polarization losses are thermally activated. Thus, the difference between attained efficiency and theoretical efficiency increases as temperature is lowered.

What Are the Technological Issues for LT-SOFCs and Where Are We Today?

Overall efficiency depends on thermodynamics (attained voltage relative to the theoretical open circuit potential and fuel use) and kinetics (polarization losses) during operation (fig. S2 and SOM

text). Addressing the increasing polarization losses at lower temperatures (associated with electrolyte conduction and electrode reaction kinetics) is the key issue and has been the focus of many groups over the past couple of decades (4, 6).

The entire SOFC material set is predicated by the selection of the electrolyte, in terms of chemical and thermomechanical stability with the electrolyte. The vast majority of SOFCs use a zirconia-based electrolyte, typically yttria-stabilized zirconia (YSZ), because of its superior stability. Although a good oxygen-ion conductor, it is far from having the highest conductivity (Fig. 2); thus, the SOFC community has transitioned from electrolyte-supported cells to electrode-supported cells to reduce the electrolyte's ohmic polarization. These, typically anode-supported cells, allow for significantly thinner electrolytes (7) and have allowed the community to reduce operating temperatures to the IT range.

With a typical open-circuit potential (OCP) of 1 V, a targeted power density of 1 W/cm^2 requires a total cell area-specific resistance (ASR) of less than ~0.25 Ω-cm^2 (based on simple linear current-voltage behavior). Thus, assuming that 60% of the total cell ASR is attributed to the electrolyte (0.15 Ω-cm^2), an operating temperature of 950°C is necessary to achieve this targeted ASR with ~150-μm YSZ, and to operate at 500°C would require the electrolyte to have a thickness less than 1 μm (8). Therefore, a variety of deposition technologies have been employed to fabricate thin-film electrolytes (9–11). For example, the Prinz group recently reported fabrication of SOFCs with a 100-nm electrolyte (a bilayered structure of 50-nm YSZ and 50-nm gadolinia-doped ceria (GDC)), achieving a peak power density of ~400 mW/cm^2 at 400°C (12). Thus, demonstrating extremely small polarization loss at low temperatures (albeit with Pt electrodes) is possible.
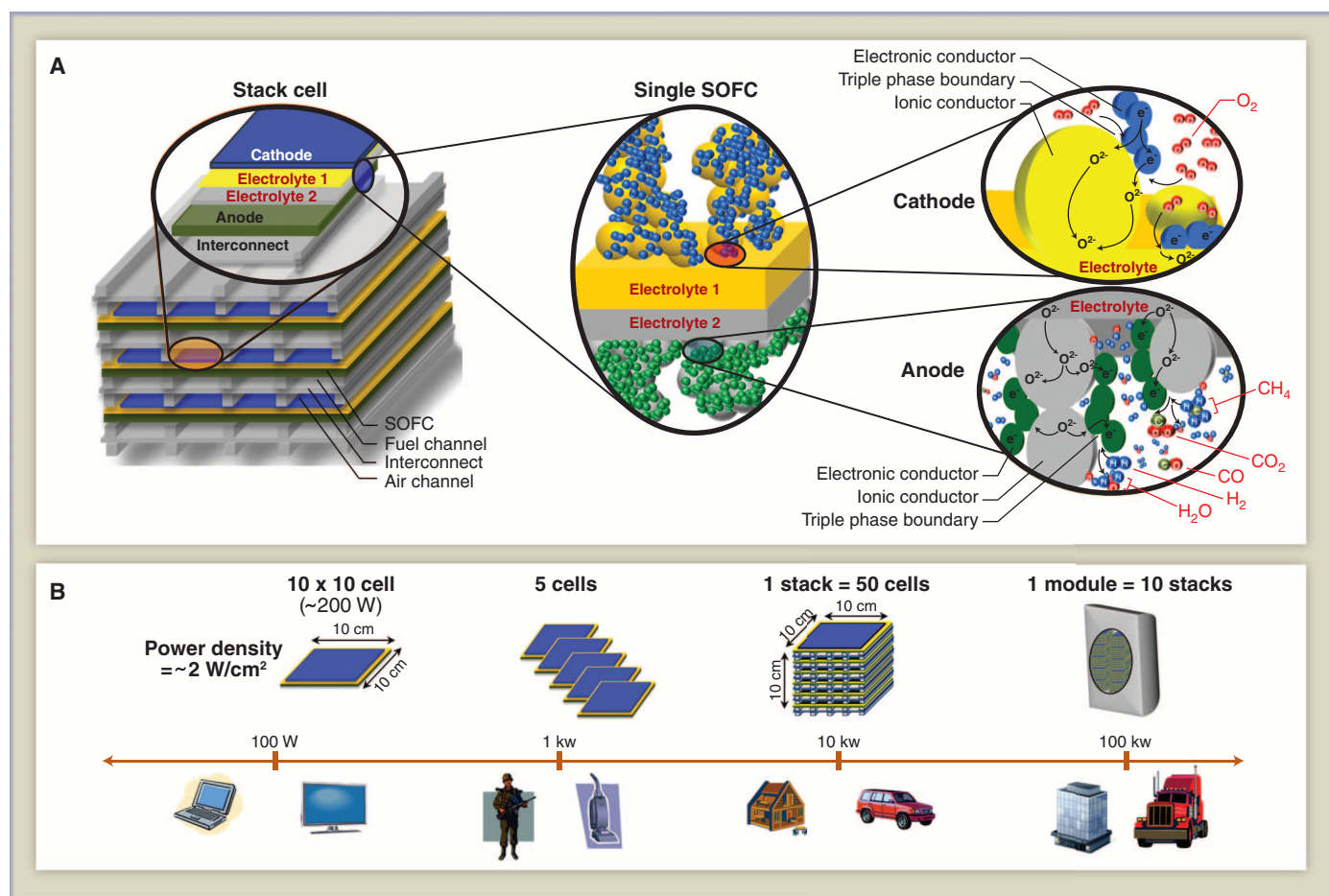
Fig. 1. LT-SOFCs across the energy conversion spectrum, from portable power and transport to stationary applications, in both civilian and military sectors. (**A**) Schematic diagrams of structure of high-performance LT-SOFCs from low magnification (stack) to high magnification (nano/micro-structured electrodes). Functionally graded bismuth oxide (Electrolyte 1) / ceria (Electrolyte 2) bilayered electrolytes effectively reduce ohmic polarization at lower temperatures. Carefully controlled nanostructured electrodes by infiltration provide highly extended reaction sites compensating exponentially reduced oxygen reaction kinetics at cathode and allow use of hydrocarbon fuels at anode at reduced temperatures. (**B**) Estimation of power output with LT-SOFCs from a single cell to a module (upper) and schematic diagram of power requirements according to various applications (lower). On the basis of demonstrated high power density (~2 W/cm^2 at 650°C) of the state-of-the-art LT-SOFC, a 10 cm by 10 cm planar cell corresponds to ~200 W power output. A stack of 50 planar cells with interconnects (10 cm by 10 cm by 10 cm) can provide 10 kW, and a module consisting of 10 stacks can provide 100 kW.
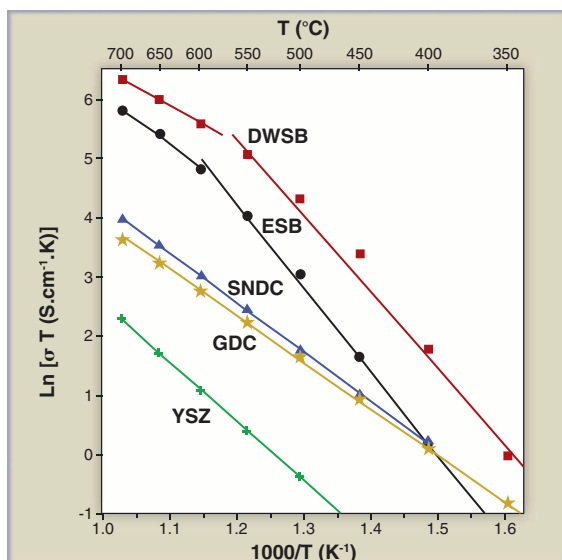
Fig. 2. Comparison of ionic conductivity of various solid oxide electrolytes. Stabilized bismuth oxides (ESB-$Er_{0.4}Bi_{1.6}O_3$ and DWSB-$Dy_{0.08}W_{0.04}Bi_{0.88}O_{1.56}$) show superior ionic conductivity compared with that of doped ceria (GDC-$Gd_{0.1}Ce_{0.9}O_{1.95}$ and SNDC-$Sm_{0.075}Nd_{0.075}Ce_{0.85}O_{2-\delta}$) and stabilized zirconia (YSZ-$Y_{0.16}Zr_{0.92}O_{2.08}$).

Fig. 3. (**A**) Schematic of ceria/bismuth oxide bilayer concept demonstrating the effect of relative thickness on interfacial oxygen partial pressure and ESB stability. (**B**) Current-voltage behavior (left y axis) and power density (right y axis) for SOFCs with GDC single-layer (solid blue line) and ESB/GDC bilayer (solid red line) electrolytes at 650°C using 90 standard cubic centimeter per minute of 3% wet H_2 (anode side)/dry air (cathode side). With ESB/GDC bilayer electrolyte, a power density of ~2 W/cm² at 650°C was achieved because of higher OCP and reduced cathodic polarization. Assuming higher OCP (~1 V) by controlling total thickness and thickness ratio of more conductive DWSB/SNDC bilayer electrolyte, the projected maximum power density (dotted red lines) is ~3.5 W/cm² under the same conditions. (**C**) Effect of total thickness and thickness ratio of bilayered electrolyte on OCP. OCP increases as total thickness and ESB/GDC thickness ratio increase and as temperature decreases, indicating the potential to achieve theoretical OCP at these temperatures (SOM text).

However, this was done with semiconductor processing (e.g., sputtering) on a Si wafer, and based on the reported active area (240 μm by 240 μm), the peak power output per individual SOFC is only ~0.23 mW. Although these methods are suitable for micro-SOFCs, it is unlikely that they are scalable and cost-effective for mass production of large-scale (kW to MW) SOFCs. Rather, from a practical standpoint for large-scale manufacturing, conventional multilayer thick-film ceramic processing (e.g., tape casting) is more appropriate. These processes imply a minimum thickness of ~10 μm, which for YSZ limits operating temperature to ≥700°C. Therefore, low-temperature (LT) SOFCs are only possible with higher conductivity electrolytes.

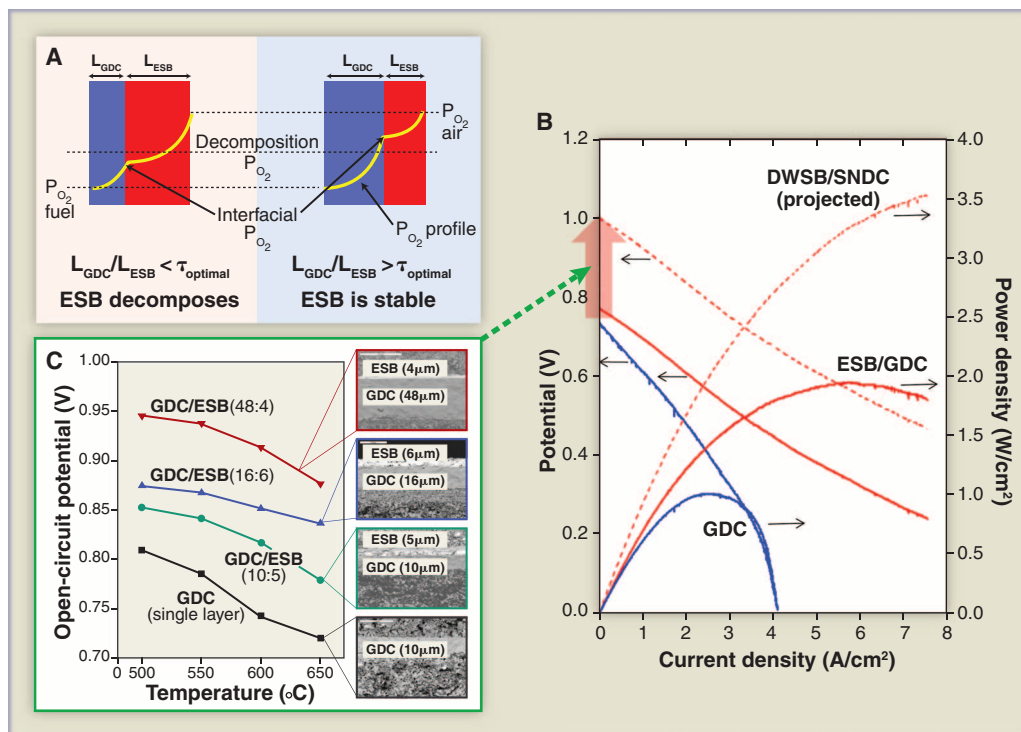Various alternative electrolytes have been investigated (13), among which aliovalent-doped ceria and isovalent-cation–stabilized bismuth oxides are particularly attractive because of their superior ionic conductivity at lower temperatures (Fig. 2). For example, at 500°C, the ASRs of 10-μm-thick YSZ, GDC, and erbia-stabilized bismuth oxide (ESB) are 1.259, 0.143, and 0.037 Ω-cm², respectively (14). Thus, at the same thickness and temperature, doped ceria and stabilized-bismuth oxide can reduce ohmic losses by 1 to 2 orders of magnitude, respectively, compared with YSZ.

Unfortunately, higher conductivity comes at the expense of lower thermodynamic stability, with CeO_2 electrolytes becoming electronically conductive and Bi_2O_3 electrolytes decomposing to metallic Bi under the reducing fuel environment (15, 16). The electronic leakage current with CeO_2 electrolytes results in a reduced OCP (4), which is a decrease in efficiency (SOM text). To overcome this issue, we proposed a functionally graded ceria/bismuth-oxide bilayered electrolyte (Fig. 3A), where the GDC layer on the anode (fuel) side protects the ESB layer from decomposing while the ESB layer on the cathode (oxidant) side blocks the leakage current through the GDC layer because of its high transference number (ratio of ionic to total conductivity). Using this synergistic structure, we demonstrated the ability to obtain near-theoretical OCP with two highly conductive electrolytes that by themselves would not have been sufficiently stable for SOFC applications (17). Moreover, the bilayer electrolyte was stable for 1400 hours of testing (17) and showed no indication of interfacial phase formation or thermal mismatch (18).

With thin highly conductive electrolytes, electrode polarization losses dominate as temperature is reduced. For example, with an anode-supported ~10-μm-thick GDC electrolyte (under wet H_2/dry air conditions) the non-ohmic electrode ASR (0.036 Ω-cm²) was only ~41% of the total cell ASR at 650°C but increased to ~73% (0.48 Ω-cm²) at 450°C (19). Moreover, the thermally activated kinetics of the oxygen reduction reaction (ORR) result in cathode polarization being the primary loss mechanism at low temperatures.

We recently integrated the concepts above into an anode-supported cell composed of a thin, dense GDC (~10 μm)/ESB(~4 μm) bilayered electrolyte with a newly developed high-performance bismuth ruthenate-bismuth oxide (BRO7-ESB) composite cathode and demonstrated an exceptionally high power density of ~2 W/cm² at 650°C (20). This is one of the highest reported power densities

for LT-SOFCs, twice that of an identical cell with a single (~10 μm) layer GDC electrolyte (Fig. 3B), and is a result of both an OCP increase and a dramatic decrease, ~40%, of the cathodic ASR. However, the electrode and electrolyte microstructures have not yet been fully optimized; thus, substantial performance improvement is envisioned, as discussed below.

How Do LT-SOFCs Compare with Competing Technologies?

For stationary applications, Bloom Energy is arguably the current commercial leader in terms of deployed SOFC units. Their zirconia-based SOFCs are reported to deliver power densities of ~0.2 W/cm^2 at ~900°C (21, 22). Our current LT-SOFC power densities (at the cell level) are higher by a factor of 10 at ~250°C lower temperature, indicating the potential for much higher energy efficiency with considerable cost reduction.

For portable and transportation applications, volumetric and gravimetric power densities are key performance metrics. The total thickness of our LT-SOFC is 0.5 mm, and the expected interconnect thickness is 1.5 mm. Thus, based on areal power density of 2 W/cm^2, the stack volumetric power density and the gravimetric power density are ~10 W/cm^3 and ~3 kW/kg (fig. S3 and SOM text), respectively, exceeding that of an IC engine (Fig. 4 A). Moreover, with liquid hydrocarbon fueling, SOFCs and IC engines have essentially the same specific energy, that of the fuel (~1 kWh/kg) (23). Thus, because our LT-SOFC has essentially the same power and energy density as an IC engine (Fig. 4B), it could potentially transform the automotive sector as, for example, a range extender for plug-in hybrid electric vehicles (PHEVs) operating on conventional fuels. The corresponding 10-kW stack would only be a small cube of 10 cm per edge (Fig. 1B).

However, it must be noted that other groups have also achieved ~2 W/cm^2 power densities, albeit at 800°C with YSZ-based cells (7, 24), and these laboratory-scale button-cell results do not directly translate to full-scale stack performance because of numerous parasitic losses such as cell-interconnect interfacial resistances, thermal gradients, and higher fuel use. Nevertheless, this demonstrates the potential of this technology if these parasitic losses can be addressed.

### Outlook: Toward Further Performance Increase at Lower Temperatures

The high power density LT-SOFCs (~650°C) described above are already suitable for numerous stationary applications. However, significant increases in power density and reductions in temperature are readily achievable by optimizing the bilayer thicknesses to increase OCP, incorporating even greater conductivity electrolytes, and engineering infiltrated nanostructured catalytically active electrodes.

Optimize the electrolyte layers to increase OCP without increasing ASR. Although the OCP was increased with addition of the bilayer in the ~2 W/cm^2 cells (20), the full theoretical value was not achieved because neither the total nor the relative thickness was optimized. As the thickness of mixed ionic and electronic conducting (MIEC) electrolytes, such as GDC, is decreased, the electronic leakage current increases, resulting in lower OCP. As such, there is an optimum thickness in terms of tradeoff between reducing ASR with thinner electrolytes and increasing OCP with thicker electrolytes (25). For bilayer electrolytes, OCP further depends on relative thickness of the constituent layers, increasing with relative ESB thickness (26). Recently, we investigated the effect of ESB/GDC bilayer thicknesses on OCP in anode-supported cells, achieving near-theoretical OCP (~0.95 V) at 500°C by modifying total thickness and thickness ratio (Fig. 3C) (SOM text). These results show that higher OCP, and thus efficiency (SOM text), can be achieved with a thicker electrolyte and greater relative bismuth oxide thickness. However, to negate any ohmic ASR increase with thickness, we would use even more conductive electrolytes.

Based on two decades of research on the fundamentals of ion conduction (27), we developed the highest reported conductivity solid oxide electrolyte with a co-doped stabilized bismuth oxide [Dy$_{0.08}$W$_{0.04}$Bi$_{0.88}$O$_{1.56}$ (DWSB)], an increase by a factor of 4 over ESB at 500°C (14). In fact, at 350°C, the ASR of 10-μm-thick DWSB is only 0.6 Ω-cm^2, sufficiently low for SOFC operation at this temperature. Using this approach and insight from molecular dynamic simulation studies by Andersson *et al.* (28), we subsequently developed a higher conductivity co-doped ceria electrolyte [Sm$_{0.075}$Nd$_{0.075}$Ce$_{0.85}$O$_{2-\delta}$ (SNDC)] with a ~30% increase over GDC at 550°C (29). The conductivity of these newer electrolytes is compared with ESB, GDC, and YSZ in Fig. 2.

For 650°C operation, we can use the factor 1.9 higher conductivity of DWSB (versus ESB) (14) and the factor 1.4 higher conductivity of SNDC (versus GDC) (29) to increase their respective thicknesses with no impact on electrolyte ASR at that temperature. The ~2W/cm^2 SOFC (20) had a ~14-μm-thick ESB/GDC (4:10 ratio) electrolyte. Increasing this to ~21-μm-thick DWSB/SNDC (7.5:13.5 ratio) would significantly increase OCP with no change in ASR.

Moreover, considering the twelvefold higher conductivity of DWSB compared with SNDC at 650°C, increasing the DWSB thickness from 7.5 to 22.5 μm adds less than 9% to the ohmic ASR, while significantly increasing total bilayer thickness to 36 μm, relative (22.5:13.5 ratio) bismuth oxide thickness, and as a result OCP (e.g., Fig. 3C). The effect of increasing OCP to 1 V without increasing total polarization would have a significant effect on maximum power density, as
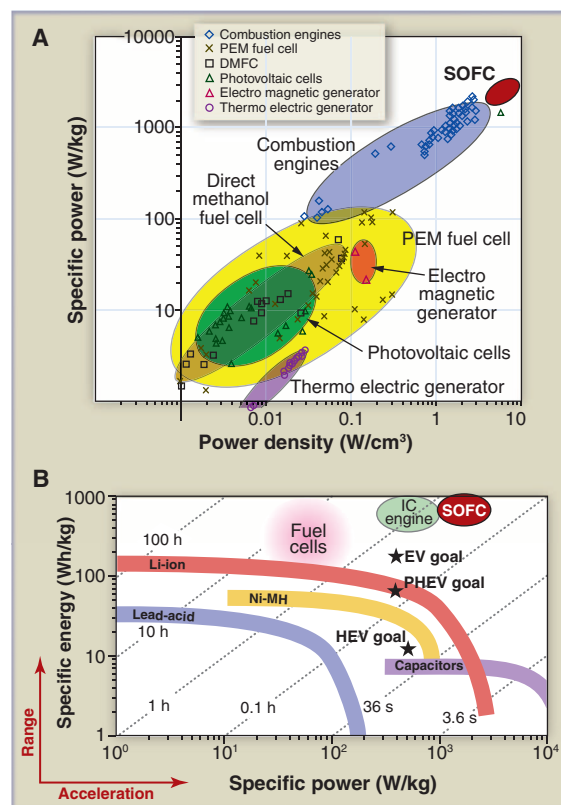
Fig. 4. (A) Comparison of specific power of the present ~2W/cm^2 SOFC at 650°C compared with various energy conversion devices as a function of power density (23). **(B)** Ragone plot (specific energy versus specific power) for various energy devices (40) compared with the present SOFC.

projected for DWSB/SNDC in Fig. 3B. However, increasing the OCP by blocking the parallel electronic current would increase the cell ASR by the small amount of electronic current that was blocked.

As temperature decreases, ceria-based electrolytes have a wider electrolytic domain (the region where ionic conductivity dominates over electronic), and bismuth oxide–based electrolytes have higher thermodynamic stability under reducing conditions. Thus, at lower temperatures, obtaining theoretical OCP using DWSB/SNDC bilayers can be achieved with both thinner total electrolyte and higher relative bismuth oxide thicknesses, further reducing ohmic resistance as temperature decreases. In fact, the Bi$_2$O$_3$ decom-

position P_{O_2} decreases from $10^{-11.9}$ atm at 650°C to $10^{-22.1}$ atm at 350°C. The latter is comparable to typical anode-fuel P_{O_2}'s and, as such, it is possible that DWSB could be used as a single layer at 350°C to take advantage of both its low ASR and unity transference number (thus obtaining theoretical OCP).

Optimize electrode microstructure to compensate for thermal activation. Exponentially decreasing area-specific electrode reaction rates (activation polarization) with decreasing temperature can be compensated by shifting the effective particle diameter of the catalytic phase from the micro (10^{-6}) to the nano (10^{-9}) regime, dramatically increasing three-dimensional triple phase boundary (TPB) density $[(10^{-6}/10^{-9})^3 = 10^9]$, and thus proportionally reducing activation polarization. Moreover, it is the reduced operating temperature that makes these nanostructured electrodes stable against coarsening, the primary performance degradation mechanism.

However, this particle size reduction must be done without negatively impacting percolation of the ionic/electronic and gas phase conduction paths that contribute to the electrode's ohmic and concentration polarizations, respectively. Therefore, nanostructured cathodes have been fabricated by infiltration of precursor solutions into porous ionic-electronic conducting scaffolds (30). For example, recent work by Zhi et al. demonstrated that infiltrated $La_{0.8}Sr_{0.2}MnO_3$ (LSM) in nano-fiber YSZ scaffolds effectively decreased cathodic polarization by 70 to ~90% compared with a conventionally mixed LSM-YSZ cathode (31). Moreover, infiltration has been demonstrated to result in low polarization and stability at temperatures below 600°C (32).

To reduce the temperature further requires a multifaceted, multidisciplinary approach to deconvolute the multiple mechanistic contributions to electrode polarization, including catalytic, solid-state, and pore transport contributions. By combining focused ion beam and scanning electron microscopy to quantify the cathode microstructure (in terms of tortuosity and porosity for gas diffusion, solid-phase surface area for gas adsorption/surface diffusion, and TPBs for the charge transfer reaction) with electrochemical impedance spectroscopy (EIS), we have been able to obtain direct logarithmic relationships between charge-transfer resistance and TPB length in typical random porous electrode structures (33). Using heterogeneous catalysis techniques (e.g., ^{18}O-exchange), we have obtained kinetic rate constants and mechanistic results to demonstrate that cathode materials like LSM have facile dissociative adsorption of O_2 and are rate limited by the lattice incorporation step, whereas $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) has rapid incorporation and is limited by oxygen surface coverage (34). These kinetic mechanistic results combined with the microstructure-polarization results provide the ability to rationally design the composition and microstructure of electrodes for LT operation.

Key for market penetration: Fuel flexibility and thermal cycling. How best to use SOFC fuel flexibility depends on desired fuel choice and operating temperature for a particular application. For stationary distributed generation applications, the ability to internally reform natural gas with conventional Ni-YSZ cermet anodes at ≥700°C has been well demonstrated. Unfortunately, at lower temperatures Ni-YSZ anodes experience performance degradation due to carbon coking and sulfur poisoning as well as Ni oxidation to NiO during thermal cycling (35). However, we use CeO_2-based anodes that have been demonstrated to increase both coking and sulfur tolerance as well as the ability to operate directly on hydrocarbon fuels [as an addition to Ni-YSZ anodes (36) and as a Cu-CeO-YSZ composite (37)].

All ceramic anodes are also being developed [e.g., $La_{0.4}Sr_{0.6}Ti_{1-x}Mn_xO_3$ (38) and $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$ (39)] because they do not undergo metal/metal-oxide phase transition (e.g., Ni/NiO) during thermal cycling. They also exhibit enhanced coking and sulfur tolerance, but to date have lower performance due to insufficient electronic conductivity and/or low electrocatalytic hydrocarbon oxidation activity.

Regardless, as temperature is reduced, the tendency toward coking can be compensated by a higher degree of external reforming. The DWSB/SNDC bilayer electrolyte makes SOFC operation down to ~350°C feasible if appropriate electrodes are developed. Although these temperatures would require a thermally integrated external fuel reformer, the overall system efficiency should still be higher than PEMFCs using hydrocarbons as the source of H_2.

Concluding Remarks

SOFCs have tremendous potential for numerous applications, from stationary to mobile power, with high system efficiencies. Depending on application requirements, such as power density, fuel choice, thermal cycling, and system costs, operating temperatures can range from 650°C down to 350°C, the latter allowing for use of simple stamped stainless steel interconnects and elastomeric sealants as well as relatively rapid start-up conditions for portable/transportation applications. It is evident that this technology has not fully matured and that major advances are still possible. Nevertheless, LT-SOFC should be a technology of choice for these applications as long as we are in a hydrocarbon-based energy infrastructure.

References and Notes

1. EG&G Technical Services, Ed., *Fuel Cell Handbook* (U.S. Department of Energy, Office of Fossil Energy, Washington, DC, ed. 7, 2004).
2. R. v. Basshuysen, F. Schafer, *Internal Combustion Engine Handbook: Basics, Components, Systems, and Perspectives* (Society of Automotive Engineers, Warrendale, PA, 2004), pp. 22–24.
3. National Renewable Energy Laboratory, *1–10 kW Stationary Combined Heat and Power Systems Status and Technical Potential* (NREL/BK-6A10-48265, 2010; www.nrel.gov/docs/fy10osti/48265.pdf).
4. B. C. H. Steele, A. Heinzel, *Nature* **414**, 345 (2001).
5. C. S. Song, *Catal. Today* **77**, 17 (2002).
6. M. Mogensen, S. Skaarup, *Solid State Ion.* **86-88**, 1151 (1996).
7. S. de Souza, S. J. Visco, L. C. DeJonghe, *Solid State Ion.* **98**, 57 (1997).
8. B. C. H. Steele, *Solid State Ion.* **75**, 157 (1995).
9. J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, L. J. Gauckler, *Solid State Ion.* **131**, 79 (2000).
10. L. G. Coccia et al., *Appl. Surf. Sci.* **96-98**, 795 (1996).
11. E. Gourba et al., *Ionics* **9**, 15 (2003).
12. H. Huang et al., *J. Electrochem. Soc.* **154**, B20 (2007).
13. J. C. Boivin, G. Mairesse, *Chem. Mater.* **10**, 2870 (1998).
14. D. W. Jung, K. L. Duncan, E. D. Wachsman, *Acta Mater.* **58**, 355 (2010).
15. K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, *Solid State Ion.* **52**, 165 (1992).
16. T. Takahashi, T. Esaka, H. Iwahara, *J. Appl. Electrochem.* **7**, 299 (1977).
17. E. D. Wachsman, P. Jayaweera, N. Jiang, D. M. Lowe, B. G. Pound, *J. Electrochem. Soc.* **144**, 233 (1997).
18. J. Y. Park, H. Yoon, E. D. Wachsman, *J. Am. Ceram. Soc.* **88**, 2402 (2005).
19. J. S. Ahn, H. Yoon, K. T. Lee, M. A. Camaratta, E. D. Wachsman, *Fuel Cells (Weinh.)* **9**, 643 (2009).
20. J. S. Ahn et al., *Electrochem. Commun.* **11**, 1504 (2009).
21. P. Wray, *Am. Ceram. Soc. Bull.* **89**, 25 (2010).
22. A. Maschietto, K. Kahler, www.mobilemag.com/2010/02/25/bloom-energy-server-unveiled-bloom-box-not-for-the-home-just-yet/ (2010).
23. S. F. J. Flipsen, *J. Power Sources* **162**, 927 (2006).
24. A. V. Virkar, J. Chen, C. W. Tanner, J. W. Kim, *Solid State Ion.* **131**, 189 (2000).
25. K. L. Duncan, K. T. Lee, E. D. Wachsman, *J. Power Sources* **196**, 2445 (2011).
26. J. Y. Park, E. D. Wachsman, *Ionics* **12**, 15 (2006).
27. E. D. Wachsman, *J. Eur. Ceram. Soc.* **24**, 1281 (2004).
28. D. A. Andersson, S. I. Simak, N. V. Skorodumova, I. A. Abrikosov, B. Johansson, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 3518 (2006).
29. S. Omar, E. D. Wachsman, J. C. Nino, *Appl. Phys. Lett.* **91**, 144106 (2007).
30. T. Z. Sholklapper, H. Kurokawa, C. P. Jacobson, S. J. Visco, L. C. De Jonghe, *Nano Lett.* **7**, 2136 (2007).
31. M. J. Zhi, N. Mariani, R. Gemmen, K. Gerdes, N. Q. Wu, *Ener. Environ. Sci.* **4**, 417 (2011).
32. J. M. Vohs, R. J. Gorte, *Adv. Mater. (Deerfield Beach Fla.)* **21**, 943 (2009).
33. J. R. Smith et al., *Solid State Ion.* **180**, 90 (2009).
34. E. N. Armstrong, K. L. Duncan, D. J. Oh, J. F. Weaver, E. D. Wachsman, *J. Electrochem. Soc.* **158**, B492 (2011).
35. C. W. Sun, U. Stimming, *J. Power Sources* **171**, 247 (2007).
36. Z. L. Zhan, S. A. Barnett, *Science* **308**, 844 (2005).
37. H. P. He, R. J. Gorte, J. M. Vohs, *Electrochem. Solid-State Lett.* **8**, A279 (2005).
38. Q. X. Fu, F. Tietz, D. Stover, *J. Electrochem. Soc.* **153**, D74 (2006).
39. Y. H. Huang, R. I. Dass, Z. L. Xing, J. B. Goodenough, *Science* **312**, 254 (2006).
40. V. Srinivasan, *Batteries for Vehicular Applications* (Lawrence Berkeley National Laboratory, Berkeley, CA, 2008); http://bestar.lbl.gov/venkat/files/batteries-for-vehicles.pdf.