LAWRENCE BERKELEY NATIONAL LABORATORY

Environmental Energy Technologies Division NEWS

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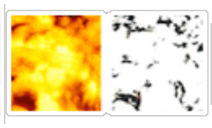
Advanced Lithium Ion Battery Research at Berkeley Lab

This issue's special focus is on advanced lithium ion batteries for hybrid electric vehicle applications. The four articles addressing this area explore the modeling of lithium ion battery chemistries; the use of advanced diagnostic methods to study the physics and chemistry of battery materials; a laboratory for advanced battery testing; and approaches for improving battery safety. EETD's research is funded by the Department of Energy's BATT (Batteries for Advanced Transportation Technologies) program, FreedomCar and Vehicle Technologies Program.

In this issue we also celebrate EETD scientists' contributions to the 2007 Nobel Peace Prize-winning Intergovernmental Panel on Climate Change.

—Allan Chen



EETD News reports on research conducted at Lawrence Berkeley National Laboratory's Environmental Energy Technologies Division, whose mission is to perform research and development leading to better energy technologies that reduce adverse energy-related environmental impacts. The Division's staff of nearly 400 carries on research on energy efficiency in buildings, indoor environmental quality, U.S. and international energy issues, and advanced energy technologies. The newsletter is published on-line once a quarter. For more information, contact Allan Chen, (510) 486-4210.

The *Center for Building Science News* was published between 1993 and 1998. It covered news of the Division's research in energy efficiency and buildings, the indoor environment, and energy analysis. You'll find all back issues, from Winter 1993 through Summer 1998 available here.

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Environmental Energy Technologies Division

NEWS

Batteries of the Future I
Modeling Lithium-ion Battery Behavior

The BATT Program (Batteries for Advanced Transportation Technologies) is a $6 million DOE program that aims to develop the next-generation batteries for use in electric, hybrid-electric, and plug-in hybrid-electric vehicles. Berkeley Lab's Environmental Energy Technologies Division (EETD) assists the U.S. Department of Energy in managing research conducted under this program, which takes place not only at Berkeley Lab, but other national labs, universities, and private companies.

The next generation of batteries in your car is coming from laboratories—and from computer models. Advanced battery development is no longer just a question of trial and error engineering; scientists increasingly use computer models to design the best possible battery.

Batteries based on lithium are considered by many experts to be the most promising, in part because of their high cell voltage—as much as 3.7 volts, as compared to 2.0 volts for a lead-acid battery or 1.2 volts for a nickel metal hydride cell. This high voltage translates directly into higher energy, which has been key to commercializing lithium ion (Li-ion) batteries for cellphone and laptop applications.

And lithium batteries, says Venkat Srinivasan, a staff scientist in Lawrence Berkeley National Laboratory's Environmental Energy Technologies Division (EETD), "will also allow for significant improvements in the presently available hybrid-electric vehicles, HEVs. In addition, it is hoped that lithium batteries will pave the way for the development of plug-in HEVs and the electric vehicles of the future."

For lithium batteries to become widespread in vehicular applications, however, their performance and life need to improve, their safety must be enhanced, and their costs need to decline. "While the HEV market will be the low-hanging fruit, with plug-in HEVs expected within the next decade, pure electric vehicles will be a major challenge," Srinivasan says. Even fuel-cell-powered vehicles will need high-performance batteries, because only batteries can provide the necessary acceleration. Fuel cells can't ramp power up and down fast enough for rapid acceleration.

"The mechanism of charge/discharge in lithium cells involves shuttling the lithium between an anode and a cathode," explains Srinivasan. "The choice of materials for the anode, cathode, and electrolyte has a major impact on the various problems facing lithium batteries today. Even after a decade of research, no magic combination of material has been found that has all the good attributes. So, research continues on three classes of cathode materials, four classes of anodes, and three classes of electrolytes, all in the hope of finding the right combination that will allow for commercialization."

Srinivasan and other researchers in EETD are studying batteries in many different ways, including synthesizing new anodes, cathodes, and electrolytes; fabricating test batteries with advanced materials and measuring their performance in the lab; understanding their behavior using advanced diagnostics, including microprobe techniques; and by creating computer models of battery behavior.

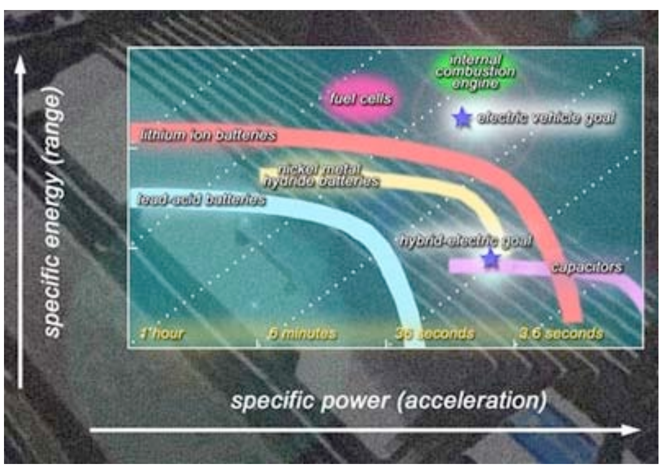
This last is the approach taken by Srinivasan, who works in EETD's Electrochemical Technologies Group. Typically the attempt to produce improved batteries involves trial and error, but Srinivasan is using a more systematic approach to help both the materials scientists who develop new materials and the engineers who are trying to optimize whole battery systems.

Srinivasan uses mathematical models of battery chemistry to evaluate the performance limitations of particular Li-ion chemistries. He simulates the performance of a particular chemistry and compares it to experiments performed in the lab to see how well his model results hold up. From the results he extracts information about what factors in a particular material are limiting the performance of the battery. Material developers and battery engineers can use the information to design a better battery that comes closer to meeting the needs of real applications.

"We get the physics from simple lab-scale experiments," Srinivasan says, "and then we use equations to describe this physics. If the model shows that the material looks promising for, say, a plug-in HEV, then we can spend the time and effort to make large amounts of this material, to make prototype batteries with it, and to see how they will perform when used in the real world." What particularly interests Srinivasan about the work "is that I can connect the materials development scientists with those who are optimizing the batteries, and I can make this connection quickly."

Acceleration and Range

In Srinivasan's presentations he uses a key image, which has become widely popular because of how clearly it summarizes where the field lies right now. It's a map depicting the current performance of batteries and other technologies, and where they have to go to be useful for electric vehicles.



A map developed by Venkat Srinivasan from product fact sheets compares the specific energy (in watt-hours per kilogram) of vehicle power sources, an indicator of their range, with their specific power (in watts per kilogram), an indicator of acceleration. Dotted lines indicate acceleration and cruise times, while blue stars show DOE's energy and power goals for electric vehicles and hybrids. Internal combustion engines still out-perform all other power sources, but battery researchers are confident that they can improve the profile of lithium-ion batteries substantially.

The map's horizontal axis is power, and represents acceleration; for acceleration comparable to internal combustion engines, electric cars need to be able to ramp up power quickly. The map's vertical axis is energy, representing the amount of energy a battery can store. It's a measure of range—the more energy the battery stores, the farther the car can travel.

Different types of batteries are represented on the map by curved lines, which show the decrease in stored energy as power increases. All batteries show a big decline in energy—that is, range—as they achieve more and more power, or acceleration.

A star on the lower right of the map represents the U.S. Department of Energy's goal for hybrid electric vehicles. Some lithium-ion batteries on the market today already meet the goal established for hybrid vehicles; these batteries provide sufficient acceleration but not much range. Nickel metal hydride batteries fall just short, and lead acid batteries, the oldest of all technologies, trail the pack.

The upper star on the map represents DOE's range and acceleration goal for future electric vehicles. Internal combustion engines sit high on the performance curve, but no battery technology currently meets the goal, although lithium-ion batteries come closest. According to some claims, fuel cells could theoretically come close to the range and acceleration needs of electric vehicles, but this technology is still unproven.

From Real Batteries to Models and Back Again

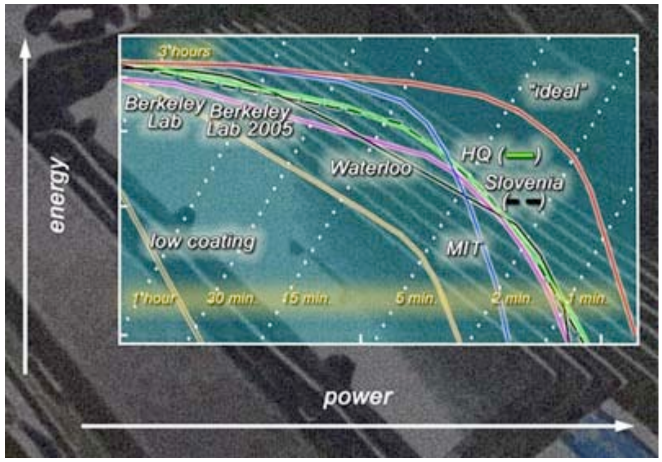
Srinivasan models lithium-ion materials sent to Berkeley Lab from many groups throughout the world who are developing these materials. A model's output for a specific material might be a plot of how its voltage and capacity changes with increasing power, for example.

Srinivasan and other Berkeley Lab researchers perform lab tests on the materials, and similar battery chemistries from different sources are compared. Srinivasan's model can tell whether differences in performance are caused by a battery's design or by something intrinsic to the material itself. Anything from electrode thickness, to porosity, to particle size, to the parameters of the battery's chemical reactions can affect the results.

The basic model that Srinivasan starts with was developed by John Newman, head of the Electrochemical Technologies Group at Berkeley Lab and a professor of chemical engineering at UC Berkeley. Newman's group has been modeling batteries since the 1970s, and their approach is widely used throughout the field. Fitting the model to the specific chemistry he's working with allows Srinivasan to get close to a battery's actual performance.

"This is what I love about batteries," he says. "Each one has its own idiosyncrasies; there's something a little different about each battery chemistry. To get the right physics, you have to keep adding more details."

Srinivasan has graphically summarized some of the materials he has modeled recently, again plotting their energy against their power. Materials come from all over the world—from Berkeley Lab's own groups, from MIT, from a researcher in Slovenia, and from the Canadian power company Hydro-Quebec, which sent a commercial prototype. So far no material has come close to the theoretical maximum performance, which Srinivasan represents by a curve labeled "ideal." The ideal battery material would have the particle size of the MIT sample and the conductivity of the Hydro-Quebec sample, so there is still a lot of room for improvement in this particular set of chemical combinations. Particularly promising are compounds of lithium iron phosphate with graphite, an electrically conductive form of carbon.



The performance of batteries developed by groups at Berkeley Lab, MIT, Hydro Quebec, and in Slovenia is compared. All batteries use similar lithium compounds but are engineered differently. The red curve, based on a model by Venkat Srinivasan, shows the theoretical maximum performance of electrodes using compounds such as lithium iron phosphate with graphite.

One important conclusion Srinivasan drew from this study was that research groups who provide the materials could identify the maximum energy density of a battery cell by varying the porosity and thickness of the electrodes.

"My hope is that five years from now, we will have a plug-and-play model for these battery materials," says Srinivasan. "Lithium ion batteries are much more complex than lead acid cells, partly because of the wide variety of materials under consideration."

Although he concedes that "We are not at that stage right now," he notes that computer models have gotten better over the years. "This is because our understanding of the physics is getting better. As better diagnostics tools are developed, researchers are beginning to understand the numerous complexities that characterize batteries."

This has happened because interest in batteries has led to increased funding and more people studying the problems. "You need a critical mass of researchers thinking about batteries every day to make progress," he says.

"And there are still other battery-related problems to solve," he adds. "For example, we don't really understand why batteries fail."

But that's another story—see the next article in this issue, "Batteries of the Future II, Building Better Batteries Through Advanced Diagnostics [http://eetd.lbl.gov/newsletter/nl27/eetd-nl27-2.html] ."

— Allan Chen

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- The Department of Energy's FreedomCAR and Vehicle Technologies Program

  [http://www1.eere.energy.gov/vehiclesandfuels/technologies/energy_storage/index.html]

This research is sponsored by the U.S. Department of Energy's BATT Program (Batteries for Advanced Transportation Technologies).

LAWRENCE BERKELEY NATIONAL LABORATORY
Environmental Energy Technologies Division
NEWS

Batteries of the Future II
Building Better Batteries Through Advanced Diagnostics

Developing the science and technology for next-generation battery systems has long been a focus of research at Lawrence Berkeley National Laboratory, dating back to the early 1980s. Lithium-ion batteries (sometimes abbreviated Li-ion) are the primary focus of current research, because their light weight and high energy-density make them ideal candidates for transportation use.

The Department of Energy's Office of FreedomCar and Vehicle Technologies is supporting researchers in the Lab's Environmental Energy Technologies Division (EETD) who are developing high-performance rechargeable batteries for use in a veritable alphabet soup of transportation: electric vehicles (EVs), hybrid-electric vehicles (HEVs), plug-in hybrid-electric vehicles (PHEVs), and fuel-cell electric vehicles (FCEVs).

Batteries and other energy storage technologies are critical to advanced, fuel-efficient transportation—so much so that they are one of DOE's Energy Strategic Goals. The automotive industry is working together with the FreedomCAR and Vehicle Technologies Program to identify technical barriers to improving energy storage technologies; DOE-funded research is aimed at toppling these barriers.

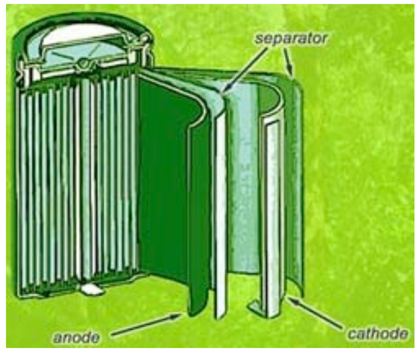
The BATT Program, Batteries for Advanced Transportation Technologies, is a $6 million program being carried out at Berkeley Lab and other institutions to research fundamental problems, those chemical and mechanical instabilities which have impeded the development of EV, HEV, PHEV, and FCEV batteries with acceptable costs, performance, lifetimes, and safety. The aim is to better understand battery cell performance and the factors that limit battery lifetime.

Microscale and Nanoscale Probes

The third lightest element on the periodic table, following hydrogen and helium, is lithium—a rising star in battery chemistry. Lithium-ion batteries are considered the state of the art, the future of battery technology. Energy is stored in these batteries through the movement of lithium ions between the cathode, or positive terminal, and the anode, or negative terminal, electrodes which effectively "house" the ions. (Ions are charged particles, in this case atoms with net positive charge.)

For transportation purposes, lithium's very light weight can provide a substantial savings compared to batteries made of heavier metals. Another big advantage of Li-ion chemistry is that compared to aqueous batteries such as lead acid, nickel metal hydride, or nickel cadmium, it yields high open-circuit voltage —

the higher the voltage, the higher the power and the better the acceleration.



One technology with great promise for future electric vehicles is the light-weight, high-voltage lithium-ion battery widely used in today's electronic devices.

Lithium ion batteries are already among the most popular for portable electronics, having a superior energy-to-weight ratio and a slow loss of charge when not in use. To be commercially viable for transportation, however, Li-ion batteries will need to last 10 to 15 years; their cost will have to be significantly reduced and their safety improved.

"Unfortunately, Li-ion batteries are thermodynamically unstable," says EETD researcher Robert Kostecki. "Sooner or later, they are destined to fail."

Basic physical law in effect determines that you can't keep recharging a battery indefinitely without gradual loss of charge capacity and power capability. The active materials in the electrodes tend to react chemically with the electrolyte. The reaction products form protective surface films on electrode surfaces, which stop or slow down these surface reactions.

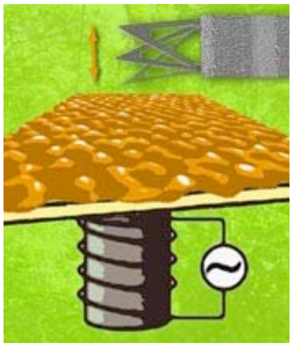
Over the long term, during charge/discharge cycling and storage, the instability of these surface films, the intrinsic behavior of battery components, and variations in engineering quality contribute to both power fade and capacity loss in conventional lithium-ion-cell chemistries.

"We need to detect and describe these processes to understand their mechanism and kinetics before we can find ways to slow them down," says Kostecki. "Interfacial phenomena often manifest themselves at nano- or microscales and can be detected and characterized only by surface-sensitive techniques."

Materials diagnostics is thus a major part of the effort to develop the next generation of Li-ion batteries for transportation. Kostecki and his colleagues are among the first to use a set of unique microscale and nanoscale techniques to study the degradation processes, and their work is leading to better materials and manufacturing techniques for advanced batteries.

Correlations Between Microscopic Phenomena and Macroscopic Behavior

"Researchers routinely use a number of standard techniques to study battery chemistry," Kostecki explains. Electrochemical techniques can monitor changes of battery charge/discharge characteristics, for example, and x-ray spectroscopy can detect chemical and structural changes in an electrode's active materials.



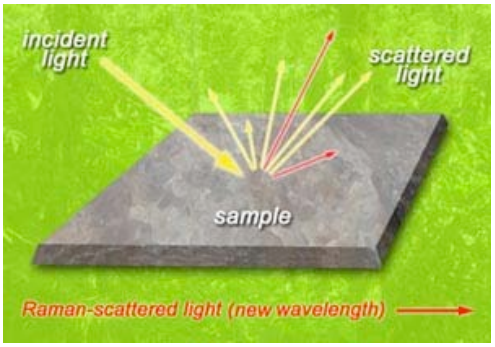
Current-sensing atomic force microscopy is used to measure both the conductance and the surface topography of electrode materials, with resolution at micrometer and nanometer scales.

But these methods usually cannot sense local phenomena in the electrodes, which take place at the microscale (measured in millionths of a meter) or even the nanoscale (billionths of a meter). Kostecki and his Berkeley Lab colleague Frank McLarnon were among the first to apply instrumental methods allowing them to monitor the composition and structural changes of battery electrodes at nanoscale or microscale resolution.

Using current-sensing atomic force microscopy (CSAFM), Kostecki and McLarnon studied the surface and electric conductance of composite electrodes used in various lithium-ion batteries. A single scan of the conductive AFM tip over the cathode surface produces two images simultaneously, a topographic image and a conductance image.

The tip of the current-sensing atomic force microscope is in physical contact with the oxide. The magnitude of the current is determined by the local electronic properties of the electrode and the tip, the voltage difference between tip and sample, and the geometries of the CSAFM tip and the local electrode surface.

The researchers also used Raman microscopy to carry out a microanalysis of the electrode surface. Raman microscopy, a spectroscopic technique used in physics and chemistry, measures laser light scattered from the sample to provide information about its chemical composition and structure. By collecting thousands of Raman spectra from small sections of electrode surfaces, they were able to produce and compare unique color-coded surface composition maps of electrodes from Li-ion cells.



Microscopy using Raman spectroscopy techniques can be used to create maps that yield high-resolution information about the chemical composition and structure of electrode materials.

"Our diagnostic evaluations of composite electrodes revealed changes in electrode surface composition, structure, electronic conductivity, and local state of charge, which accompany cell cycling and aging," says

Kostecki. "Our hypothesis is that the phenomena that cause degradation in batteries occur at micro- and nanometer scale and can only be detected with appropriate microscopic techniques. To detect them, we have developed and applied techniques and methodologies never used before in this field. We were the first to use high-resolution Raman microscopy mapping, which revealed the nonuniform distribution of the electrode state of charge at a micrometer scale. The data allowed us to identify the local processes that contribute to significant loss of electronic conductivity within the electrode and consequently to the capacity loss."

A Dopant Effect Is Not What It Seems

Kostecki applied these local-probe techniques to investigate lithium iron phosphate, $LiFePO_4$, considered one of the most promising cathode materials for the next generation of Li-ion batteries.

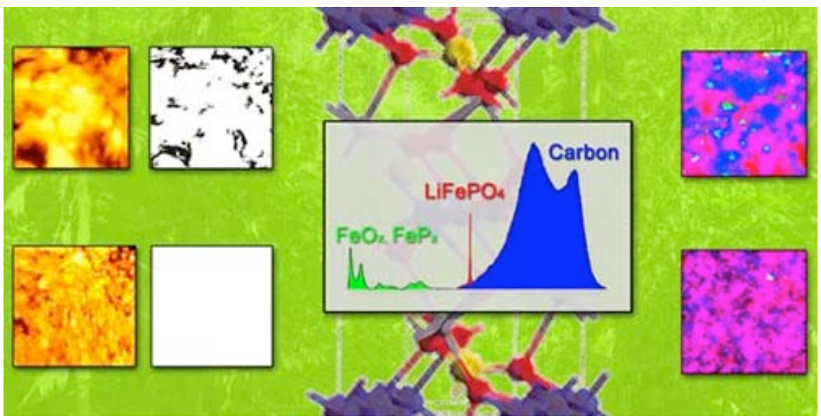
However, says Kostecki, "The poor electronic conductivity of $LiFePO_4$ compared to transition-metal oxide cathodes is a serious limitation on its use in high-power Li-ion systems. Controversial reports in the literature suggested different pathways to improving its electrochemical performance. The lack of understanding of the $LiFePO_4$ operating mechanism has delayed introducing this material into a new generation of Li-ion batteries."

Kostecki and his colleagues performed CSAFM and Raman microscopy on two samples of lithium iron phosphate powder, one pure and one that had been one-percent doped with niobium by a team of MIT scientists, replacing some lithium atoms with niobium atoms in an attempt to improve the compound's electronic conductivity.

In the CSAFM images, the researchers detected no electronic conductance in pristine lithium iron phosphate at any location; the conductance image was pure white. The niobium-doped sample, on the other hand, had better electronic conductivity, at first suggesting that the niobium was indeed responsible for adding conductivity.

A closer look at the niobium-doped sample raised questions, however. In the conductance image, black splotches revealed numerous small sites with good conductance, scattered across the surface—but curiously, on the corresponding morphology image, the researchers identified grains of active electrode material that had become completely insulating. Indeed, conductivity was very nonuniform, localized mainly in deep crevices and pockets between agglomerates.

Typical Raman spectra of lithium iron phosphate powder showed that the material consisted not just of lithium iron phosphate but of iron oxides, phosphides, and elemental carbon impurities as well. The Raman microscopy images of the same powders, niobium-doped and pure, revealed that the carbon content in the niobium-doped sample was much higher than in the pristine lithium iron phosphate.



Panels at left are CSAFM measurements of the surface topography and conductance of lithium iron phosphate, a sample doped with niobium shown at top and a sample of the pure state at bottom. The doped sample has a different topography, and it conducts electricity better but unevenly (black regions indicate high conductance). In the center panel, a Raman spectrum of a sample reveals iron oxides, phosphides, and elemental carbon impurities in addition to the lithium iron phosphate compound. Raman microscopy images, right, reveal that the niobium-doped sample at top, which is the better conductor, contains much more carbon (blue areas) than the pristine lithium iron phosphate sample at bottom.

An organic, niobium-containing precursor used in the doping process was the source of the extra carbon. The researchers observed that the carbon distribution in the niobium-doped sample corresponded exactly to the pattern of conductivity observed in the CSAFM images. They concluded that it was actually the carbon additive, not the niobium, which was responsible for the doped material's conductivity increase and better electrochemical performance.

"We would not have been able to reach this conclusion without the unique combination of nanoprobe techniques and innovative methodologies that we applied to study this system," says Kostecki. "We determined that the key to increasing the conductivity of the material and making it a more effective cathode material was to incorporate more conductive carbon—and to improve the distribution of carbon deposits. This shifted the focus away from materials science toward better engineering."

Improving Battery Longevity

Kostecki applied the same set of instrumental methods to study the mechanism of Li-battery degradation over time. First, using Raman and CSAFM imaging, he and his colleagues characterized the surface chemical composition, structure, morphology, and electronic conductivity of a fresh Li-ion electrode. The imaging allowed them to identify the original distribution of the electrode components—the active material and carbon additives at the surface of the electrode. They reexamined the electrode with the same tools after prolonged charge/discharge cycling and storage, looking for changes that might be linked to detrimental surface phenomena responsible for the loss of electrochemical performance.

The Raman images showed a marked change in the material's structure as well as its surface composition and distribution. While some areas of the sample remained relatively unchanged, elsewhere there were large changes in both surface structure and composition—the more active material was exposed and less carbon additive was present.

"Loss of surface electronic conductivity accompanied the observed changes in the surface chemistry," Kostecki explained. As a result, some particles of the electrode active material became partially or fully electronically disconnected from the rest of the electrode and become inactive. "These highly localized phenomena had severe impacts on the overall electrochemical performance of the electrode and the whole Li-ion battery. Its charge capacity was diminished and impedance significantly increased."

Kostecki says, "The nano- and microprobe analytical tools allowed us to demonstrate that the localized deactivation processes that occur on a microscopic scale can be directly linked with the macroscopic behavior. It was the first time these techniques were applied in such an efficient and concerted way to study battery surface phenomena. The results of these studies have given us a better understanding of both the nature of the process, and some ideas about how to prevent them or slow them down."

It has also motivated materials scientists and battery engineers to work together more closely, so that the dream of cheaper, longer lasting, and safer lithium batteries for advanced electric vehicles becomes a reality sooner.

— Allan Chen

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- The BATT Program [http://batt.lbl.gov]
- The Department of Energy's FreedomCAR and Vehicle Technologies Program [http://www1.eere.energy.gov/vehiclesandfuels/technologies/energy_storage/index.html]

This research is sponsored by the U.S. Department of Energy's BATT Program (Batteries for Advanced Transportation Technologies).

Lawrence Berkeley National Laboratory
Environmental Energy Technologies Division
NEWS

The BATT FabLab: Road to a Better Battery

The better transportation battery—a battery for hybrid-electric and plug-in hybrid vehicles—needs to be lighter than today's battery, store more charge, and last through more charge-discharge cycles. Also, it needs to be safe, affordable, and compact enough to fit under the hood.

BATT FABLAB

That's a tall order. Developing a better battery for vehicles requires a multipronged approach to research and development, that of the Department of Energy's BATT program: Batteries for Advanced Transportation Technologies. Lawrence Berkeley National Laboratory's Environmental Energy Technologies Division (EETD) assists DOE in managing BATT research, which takes place here and at other national labs, universities, and private companies.

At Berkeley Lab and the University of California, Berkeley, BATT research includes using nanoprobe diagnostics to study advanced battery materials and computer modeling to improve lithium-ion (Li-ion) battery chemistry. Li-ion batteries are of considerable interest because they are lightweight and store more charge per unit weight than those currently used in hybrid electric vehicles.

Besides understanding Li-ion chemistry, other crucial needs are learning the best ways to engineer and fabricate advanced Li-ion batteries and how to test them for performance. Berkeley Lab's cell analysis and testing lab, recently renamed the BATT FabLab (Fab for Fabrication), has been testing the performance of new materials in experimental batteries for several years.

Evolution of a FabLab

The FabLab tests new materials from BATT programs at Berkeley Lab and elsewhere; in the process researchers learn more about the fundamentals of battery performance. They are well versed in making new battery cells by combining experimental electrode materials designed for hybrid-electric vehicles, sealing the materials in water-tight packages, and measuring their performance. "We want to understand the science and engineering of what it takes to make a high performance electrode," says EETD's Vince Battaglia, program manager in charge of the FabLab. "We also provide a reliable evaluation of new materials developed within the BATT program, using our optimized electrode designs."

BATT FabLab researcher Gao Liu prepares a battery for testing. Inside a glove box, which controls water infiltration, he compresses the electrodes for higher energy density and better electronic contact (left). The test cells are finished in watch-sized, commercial form in the Klein machine (right).

With the lab's old equipment, researchers made test-cell pouches containing variations of the same experimental materials proposed for a given battery. They ran these pouches through a large number of charge-discharge cycles to see how well they kept their maximum charge, measured how long a battery would function before its capacity began to fade, and did other tests.

Now, with assistance and feedback from researchers who model new materials on computers, the BATT FabLab has supercharged itself with new equipment. One result is a sharper focus on improving electrode engineering. The recent equipment upgrade includes new glove boxes and new equipment for manufacturing small experimental test cells.

"All battery assembly work now takes place inside of glove boxes to keep out water, which is a real killer in lithium-ion batteries," says Battaglia. Water is limited to less than one part per million in the boxes' inert atmosphere; by contrast, the dry rooms in many battery manufacturing facilities limit water in air to 50 parts per million.

The lab also has a hydraulic Klein cell machine, an automated device that combines the battery's electrodes and generates sealed battery cells reproducibly. Many battery labs manufacture cells using hand-cranked devices, resulting in cells that are inconsistent in size and composition. The Klein cell machine leads to more representative aging analysis because it accurately replicates water-tight cells.

Challenges of the Lithium-Ion Battery

Before lithium-ion batteries can be manufactured economically and meet performance requirements for hybrid vehicles, battery engineers have to learn to control the performance of the electrodes in Li-ion batteries. Measures of performance include a battery's lifetime, the number of charge-discharge cycles it can run through before degrading too much to operate, the total amount of charge it can store—which translates directly into vehicle range—and how much charge it can discharge per second—which translates into vehicle acceleration.

"Batteries are like small, self-contained chemical reactors," says Battaglia. "The entire system needs to be optimized to get the best performance from the battery."

How the electrode is constructed—including physical characteristics such as thickness and porosity, the size and volume of components, and their degree of mixing—all affect battery performance. The manufacturing process is also a factor. Electrodes are fabricated from a slurry of materials and are cast into a cohesive film using a polymer binder. One active compound currently under study is lithium iron phosphate ($LiFePO_4$) with trace components including carbon. The viscosity of the slurry is important—a less than optimal distribution of conductive particles produces a less than optimal battery. Other factors that can degrade performance include contamination by water or carbon dioxide and chemical interactions within the battery system.

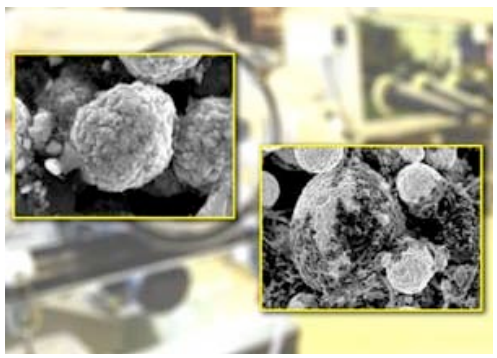
The battery lab, in partnership with researchers producing chemical models of advanced batteries, looks for solutions to all of these problems—and others too. Volume constraints are a key barrier to the introduction of high-energy batteries; reducing the amount of nonactive material increases energy density and helps reduce waste and manufacturing costs. So another concern of the battery lab, Battaglia says, is to see how much extraneous material can be removed from a battery without affecting optimal performance.

Benchmarking for Better Batteries

Researchers in the battery lab benchmark experimental materials by measuring, among other things, their surface area, particle size, and particle-size distribution. Knowing these characteristics allows the researcher to fine-tune composition. For example, carbon particles increase conductivity.

"When you get a sense of the size of particles in the electrode material, you can estimate what size of carbon particles to add to improve the material's electrochemical characteristics," Battaglia says.

The active material in the cathode (positive electrode) needs to be coated uniformly with carbon particles, then held together with a polymer binder. Poor carbon distribution can affect the battery's performance.



Better processing leads to better batteries. At left, broken particles of oxide in a lithium-iron-phosphate-based electrode show incomplete coating of carbon on their surfaces, which decreases electrode performance. At right, improved mixing of materials generates whole particles, better coated with conductive carbon.

The battery lab also does thermal measurements of experimental cells. To its differential-thermal-analysis and accelerated-rate- calorimetry facilities it will soon add differential scanning calorimetry. By studying thermal properties researchers can find ways to prevent overheating, which can lead to battery fires.

The FabLab conducts electrochemical characterization of battery materials according to testing procedures like those established by the FreedomCAR program. A current problem for lithium-ion electrodes is their tendency to dissolve. Some researchers hypothesize that positive ions (cations) from the cathodes in these chemical systems cause protective layers on the anodes to lose their protective capabilities. The dissolution of the protective layer leads to lithium depletion and eventual failure.

"We are trying to measure the rates of dissolution of the cathode materials outside the battery and correlate this to life estimates," says Battaglia.

Battery engineers try to avoid protective-layer dissolution by doping the cathode or coating it with stable Li-ion conductive films. New binders for the anodes may also limit the effect of the crossover of cations to the anode, protecting the anode and reducing passive film dissolution.

Lithium deposition on the anode during charging is another possible failure mode, especially during cold-temperature charging. Battery designers try to avoid this by using anodes with more capacity than the cathodes, but the anode's larger capacity can result in the battery having less overall cycling capacity, the ability to recharge over and over again after discharging, which reduces its lifetime. So engineers need to optimize the battery system as a whole to provide maximum protection to the anode without degrading battery lifetime.

Staying Dry

Keeping water out of the battery system is a significant problem for battery engineers. Water can react to form positively charged protons, which rapidly degrade battery performance. Water in a lithium-ion battery reacts with a lithium salt to form an acid, which is thought to attack the cathode, causing its dissolution.

"We need to know how much water can get into the system before the performance begins to degrade," says Battaglia.

In the lab's glove boxes, Battaglia's research team manufactures test cells in an extremely low-humidity environment, then introduces water in higher and higher amounts. The researchers measure decrease in battery performance for different kinds of cells. Battery manufacturers, who need cost-effective ways to make batteries without letting in water, are extremely interested in this work. Process is half the cost of battery manufacture.

The BATT FabLab's research is multifaceted, but its goal is easy to summarize. Says Battaglia, "We are trying to understand why one battery material works better than another."

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- The BATT Program [http://batt.lbl.gov]
- The Department of Energy's FreedomCAR and Vehicle Technologies Program [http://www1.eere.energy.gov/vehiclesandfuels/technologies/energy_storage/index.html]

This research is sponsored by the U.S. Department of Energy's BATT Program (Batteries for Advanced Transportation Technologies).

Making Lithium-Ion Batteries Safer

In recent years battery failures in laptops and cell phones—many overheating, some bursting into flame—have drawn attention to one of the biggest problems posed by lithium-ion (Li-ion) batteries: overcharging can lead to battery failure and chemical leakages from the battery pack, and sometimes fire and personal injury.

Recent years have seen highly publicized incidents of PCs and other electronic devices bursting into flame because of overheating batteries, resulting in massive recalls.

"Electrolyte material in these batteries is highly flammable," says Guoying Chen, of Lawrence Berkeley National Laboratory's Environmental Energy Technologies Division (EETD). "It consists of lithium salts dissolved in organic solvents. Often, overcharging these batteries is what causes the problem. As the battery heats up it swells, and it can burst into flame."

A lithium-ion battery consists of a cathode layer, an anode layer, and a separator between. When the battery is charging, positively charged lithium ions move through a liquid electrolyte from the cathode to the anode, and in the opposite direction when the battery is discharging. The electrolyte is a lithium salt, dissolved in organic solvents. When the batteries are overcharged, the cathodes tend to release oxygen gas. Oxygen plus the flammable solvent and heat can cause battery fires.

At present, improving Li-ion batteries for plug-in hybrid vehicles (PHEVs) is the electrochemistry research frontier. Batteries based on lithium-ion chemistry hold great promise for PHEVs. They are lighter than current batteries based on nickel metal hydride and lead acid. And because their energy density is higher, they can boost both the range and power of PHEVs.

Batteries that meet the Department of Energy's program goals could make PHEVs sufficiently economical to succeed in the marketplace. But before this can happen, researchers need to develop technologies to improve safety.

"The current industry solution is to use an electronic circuit to monitor the battery's voltage and shut it off when it reaches its proper charge," says Chen. "The problem with this approach is that in a plug-in vehicle, 30 to 40 batteries would be connected in a series. Monitoring each battery with an electronic device raises the cost and weight of the battery pack substantially. And a single failure of any of the monitoring devices could cause one battery to leak or catch fire, rendering the entire battery pack unusable."

A Shorting Agent Caps the Charge

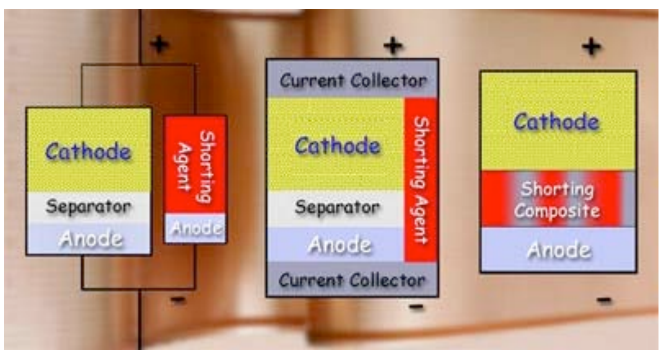
With a reliable, inexpensive method of protecting Li-ion batteries from overcharging as their goal, Chen and EETD's Thomas Richardson have studied several promising approaches. In one, they found materials that could serve as "shorting agents." Added to the battery as an additional component, the shorting agent redirects the flow of electrical current inside the battery when it becomes fully charged.

A shorting agent prevents overcharging by acting as a cap on how high the battery voltage can rise. As the battery approaches full charge the agent, which is resistive during normal operation, becomes conductive. When the agent becomes sufficiently conductive it carries the charging current (thus "shorting" the circuit), and no net charge goes to the battery.

The shorting agent has to be reversible—as the battery discharges, it has to become resistive again—and this back-and-forth reaction must take place with no degradation for as long as the battery lasts.

"We started looking at different classes of electroactive polymers," says Chen. "These are long-chained materials that are insulating when neutrally charged. When you oxidize or reduce them, they become conducting almost like a metal."

They found that a polymer called poly 3-butylthiophene, P3BT, was a shorting agent with the ability to prevent the battery cell from overcharging. The material could be placed in a number of different configurations: within the layer that separates the anode from the cathode, as a distinct internal component of the battery, or as a completely external component to the battery. The latter approach proved to be inexpensive and lightweight, and did not interfere with the battery chemistry.



Polymer "shorting agents" can redirect the flow of current when a battery is fully charged. Reversible shorting agents can be used outside the cell (left), as an extra internal component of the cell (middle), or as a composite in the separator between anode and cathode (right).

Electroactive polymers comprise a large family of compounds with various backbone structures that can be oxidized or reduced at a wide range of potentials. With the right choice of polymer and configuration, the approach could provide overcharge protection at any voltage, giving battery engineers the option of designing batteries at different voltages for diverse applications—they can choose the battery chemistry and system configuration that they need.

Electroactive polymers also have the advantage of providing safety of Li-ion batteries in cold climates. These batteries don't function well in the cold because the electrolyte, already low in viscosity, solidifies, and the lithium charges can't move around as freely as they do at room temperature. Chen and Richardson found polymers that continue to provide overcharge protection in spite of the cold. The Department of Energy is now working with a battery manufacturer to commercialize the electroactive polymer technology.

Inherently Safer Materials

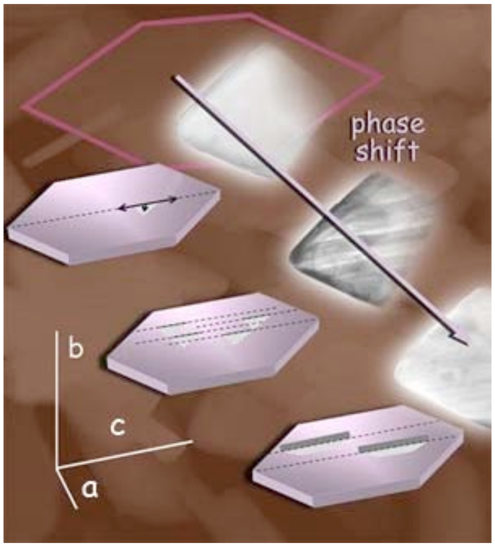
The research team is also pursuing another approach to overcharge protection: making electrodes out of materials that are inherently safer because they are less prone to overcharge. Currently they are studying lithium iron phosphate, $LiFePO_4$, for use as the cathode material. This material differs from current experimental lithium battery chemistries at Berkeley Lab, which are mostly compounds of lithium, manganese, nickel, and cobalt.

In lithium iron phosphate, strong chemical bonds between the phosphorus and oxygen, known as covalent bonds, reduce the tendency of the cathode to release oxygen gas. Iron and phosphate are also cheaper than manganese and cobalt, and batteries made with this material show longer shelf-life, a larger number of charging cycles, and greater stability. And they have a high charge capacity, ideal for the plug-in hybrid application.

However, the material's electronic and ionic conductivities need to be improved before battery manufacturers can use it as an electrode material. "The work we are doing is to understand the physical mechanism of how it conducts charge, which allows us to design the material to have higher conductivity," says Chen.

Lithium iron phosphate's crystal structure changes when the lithium ion becomes mobile, leaving behind an iron phosphate matrix; the physical nature of this change is poorly understood. To make more conductive electrodes, scientists need to understand what is holding back the material's conductance.

In their lab, Chen and Richardson grew extremely pure, uniform, high-quality crystals of lithium iron phosphate. Transmission electron microscope images of these pure $LiFePO_4$ crystals revealed regular hexagonal plates. The researchers studied the physical and chemical changes of the crystal structure during phase transitions, using advanced techniques such as Raman scattering, x-ray diffraction, and Fourier transform infrared spectroscopy, carried out with the assistance of EETD scientist Robert Kostecki.



As lithium ions move out of a hexagonal lithium iron phosphate crystal, the material undergoes a phase shift to iron phosphate. Since ions flow only in the b direction, the ideal particle shape is a plate of lithium iron phosphate as thin as possible.

When lithium ions are removed from the $LiFePO_4$ crystal, the material undergoes a phase transition to $FePO_4$. Electron microscope images reveal a boundary where the phase transition is taking place. Chen and Richardson found that the phase transition progresses along the face of the flat hexagonal crystal (called the ac plane); this is the "electroactive" part of the crystal, which supplies the lithium ions for conducting the battery's electric charge. The thickness of the crystal, called its b axis, is the only direction in which the lithium ions move.

In round particles of $LiFePO_4$, only 33 percent of the area consists of the ac plane of these crystals; in the pure crystal plates Chen and Richardson grew in the lab, up to 85 percent is ac plane.

Chen and Richardson's conclusion: "The ideal particle shape is small thin plates of $LiFePO_4$, as thin as possible, to minimize the distance of Li movement. Adding a thin carbon coating to the material to create a good electrical contact on the ac plane will increase its conductivity further."

This work not only suggests a way to manufacture more conductive cathodes out of $LiFePO_4$, it also challenges current scientific thinking on the nature of phase transitions in the crystal. The existing theoretical model of the phase transition requires that the crystals display isotropy, a regular crystalline structure in all directions. But Chen and Richardson have shown that domains separated by a boundary zone form within the crystal. To explain their experimental observations they developed a model that incorporates anisotropy (crystalline structure that is different along different planes or axes) and domains within crystals of $LiFePO_4$.

Chen and Richardson are continuing to study ways of improving the safety, lifetimes, and charge capacity of battery materials. They are now applying similar observational techniques to lithium magnesium solid solutions, a candidate for use as anodes in Li-ion batteries. This material seems to suppress the formation of "dendrites" in the anode material, a surface roughness that reduces the life and number of cycles of batteries.

— Allan Chen

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- The Department of Energy's FreedomCAR and Vehicle Technologies Program [http://www1.eere.energy.gov/vehiclesandfuels/technologies/energy_storage/index.html]

This research is sponsored by the U.S. Department of Energy's BATT Program (Batteries for Advanced Transportation Technologies).

LAWRENCE BERKELEY NATIONAL LABORATORY

Environmental Energy Technologies Division

NEWS

Berkeley Lab Scientists Contribute to Climate Change Studies That Win the Nobel Peace Prize

Scientists at the Department of Energy's Lawrence Berkeley National Laboratory were important contributors to the research on global climate change that has won this year's Nobel Peace Prize.

The 2007 Peace Prize was awarded jointly to the Intergovernmental Panel on Climate Change (IPCC) and to former Vice President Al Gore, Jr., "for their efforts to build up and disseminate greater knowledge about man-made climate change, and to lay the foundations for the measures that are needed to counteract such change."

William Collins and Inez Fung of the Earth Sciences Division (ESD), and Mark Levine, Surabi Menon, Evan Mills, Lynn Price, Jayant Sathaye, and Ernst Worrell of the Environmental Energy Technologies Division (EETD) are among current members of Berkeley Lab who were leading authors of this year's IPCC working group reports.

Collins and Fung, who are also professors in the Department of Earth and Planetary Science at the University of California at Berkeley, were among the authors of the report from IPCC Working Group I, "The Physical Science Basis of Climate Change," for the IPCC's Fourth Assessment Report (AR4) in 2007. Surabi Menon, a member of the Atmospheric Sciences Department in EETD, was also an author of this report. All three authors participate in Berkeley Lab's new Climate Science Department, based in ESD and headed by Collins, which is developing a powerful Integrated Earth System Model to deliver detailed climate predictions on the regional scale more than 20 years out, and global models that can forecast worldwide changes to the end of the century.

From left to right, Stephane de la Rue du Can, Mark Levine, Jayant Sathaye, Lynn Price and Aleksandra Novikova.
Photo Credit: Roy Kaltschmidt

Levine, Price, Sathaye, and Worrell were among the authors of the AR4 report from Working Group III, "Mitigation of Climate Change." Mills was an author of AR4's Working Group II report, "Impacts, Adaptation, and Vulnerability." Levine, former director of EETD, has long studied problems of climate change and global warming with particular attention to energy use in China. He and Price, Sathaye, Worrell, and Mills are members of EETD's Energy Analysis Department, which among its other research projects develops models of energy use, assesses technological applications, and develops and evaluates policies and programs to improve energy management.

In addition to those named above, other current Berkeley Lab scientists who have contributed to the 2007 reports, or have been authors of the IPCC's Third Assessment Report issued in 2001 or other past reports, include Norm Miller, Curt Oldenburg, and Karsten Pruess of ESD, and Phil Haves, Maithili Iyer, Stephane de la Rue du Can, Hashem Akbari, John Busch, Steve Meyers, Joe Huang, Laura Van Wie McGrory and Ed Vine of EETD, and Mithra Moezzi, Willie Makundi and Lee Schipper, who are no longer at the Lab.

The Chairman of the IPCC, Dr. Rajendra Pachauri, sent a letter to the lead authors of this year's reports, remarking, "I have been stunned in a pleasant way with the news of the award of the Nobel Peace Prize for the IPCC. This makes each of you a Nobel Laureate and it is my privilege to acknowledge this honour on your behalf.... The fact that the IPCC has earned the recognition that this award embodies, is really a tribute to your knowledge, hard work and application."

Berkeley Lab's contributors are among the thousands of scientists from more than 100 countries who have helped the IPCC alert the world to the reality of humanity's role in global warming through increasingly accurate scientific reports issued since the IPCC's founding by the World Meteorological Organization and the United Nations Environment Program in 1988.

— Paul Preuss

- Nobel Peace Prize 2007 press release [http://nobelprize.org/nobel_prizes/peace/laureates/2007/press.html]
- Intergovernmental Panel on Climate Change [http://www.ipcc.ch/]
- "Lab Contributes to Nobel Peace Prize and Landmark Sustainable Energy Report" [http://www.lbl.gov/Publications/Currents/archive/#1]

Lawrence Berkeley National Laboratory

Environmental Energy Technologies Division

NEWS

Research Highlights

Popular Mechanics Honors Gadgil, Galitsky for Darfur Stove

Popular Mechanics magazine has given a 2007 Breakthrough Award to Ashok Gadgil, Christina Galitsky, and the team that developed the energy efficient Darfur stove. The Environmental Energy Technologies Division researchers are among eight inventors and teams honored in the magazine's third annual awards.

Their citation for the stoves team includes a video of Gadgil and Galitsky using the stove to cook food, and describing how and why they developed it. Go here to watch a video [http://www.origin.popularmechanics.com/technology/industry/4224765.html?series=37] of the two using the stove and describing how and why they developed it.

An additional story on low-tech solutions to global problems, featuring Gadgil, is available here [http://www.popularmechanics.com/technology/industry/4225945.html] .

Presidential Leadership Award

LABS FOR THE 21ST CENTURY

The Laboratories for the 21st Century (Labs21) program has been named one of five recipients of the Presidential Awards for Leadership in Federal Energy Management. Eight individuals have been named, including three from the Environmental Energy Technologies Division: Dale Sartor, Geoffrey Bell, and Paul Mathew. The winners attended a reception in Washington D.C. at the Omni Shoreham Hotel on Wednesday night, and received their awards at a special ceremony, as well as a tour of the White House, today.

The goal of the combined DOE and EPA Labs21 program is to improve energy efficiency and environmental performance of laboratories not only in the United Sates, but around the world.

Find out more about the Laboratories for the 21st Century program [http://www.labs21century.gov/] .

A tool kit for designing energy-efficient laboratories that was developed by Berkeley Lab researchers is available here [http://www.labs21century.gov/toolkit/index.htm] .

Two Prestigious Awards for Professor John Newman

John Newman, a professor in the Department of Chemical Engineering on campus, was made an honorary member of the Electrochemical Society last week. Newman is the leader of the Batteries for Advanced Transportation Technologies Program in the Environmental Energy Technologies Division. No more than half of one percent of the active members can be an honorary member.

At the recent Electrochemical Society meeting in Washington D.C., it was also announced that Newman will receive the Vittorio de Nora Award, which is given for contributions to the field of electrochemical engineering and technology. Read more about the Newman group's research [http://www.cchem.berkeley.edu/jsngrp/] .

For more on the BATT program, see http://batt.lbl.gov [http://batt.lbl.gov]

Home Energy Saver Website Gets Its Four Millionth Visit

The Home Energy website, which was developed by researchers in the Environmental Energy Technologies Division to guide homeowners in retrofitting homes for energy efficiency, recently had its four-millionth visit to the Home Energy Saver site. It took five years to reach the first million visits, 2.5 years for the second, 1.5 for the third, and just 1 year for the 4th.

Of the 5,600 users that have answered the user survey, 91% are homeowners or renters and about a third report having taken steps to save energy in their homes based on what they learned from the website. "If this is at all representative of the entire user population, we have indeed touched a great number of homes," says EETD's Evan Mills, the Home Energy Saver team leader.

http://homeenergysaver.lbl.gov [http://homeenergysaver.lbl.gov]

San Francisco Federal Building is One of the "Best Inventions of the Year"

Time Magazine has named the San Francisco Federal Building one of its 2007 "Best Inventions of the Year [http://www.time.com/time/specials/2007/article/0,28804,1677329_1678083_1678079,00.html] " winners in the architecture category. Its citation noted that the building is "really a machine for delivering sunlight and fresh air to the people who work there. Eighty-five percent of the work space gets natural sun, and windows manned by computer let in outside air to maintain the building's temperature with a minimum of air-conditioning."

The building's energy efficiency features were modeled by scientists in Berkeley Lab's Environmental Energy Technologies Division using EnergyPlus software, led by Philip Haves, leader of the Commercial Building Systems Group.

EETD's contributions to this design may be found under Technology Tranfer's Success Stories [http://www.lbl.gov/Tech-Transfer/success_stories/articles/energy_plus.html] or the Berkeley Lab's *Today Around Berkeley Lab* [http://www.lbl.gov/today/2007/Nov/08-Thu/11-08-07.html] .

LAWRENCE BERKELEY NATIONAL LABORATORY

Environmental Energy Technologies Division

NEWS

Sources and Credits

Sources

DOE's Consumer Information Fact Sheets

These web pages [http://www.eere.energy.gov/consumer/] provide information about energy efficiency and renewable energy for your home or workplace.

DOE's Energy Information Administration (EIA)

EIA [http://www.eia.doe.gov/] offers official energy statistics from the U.S. Government in formats of your choice, by geography, by fuel, by sector, or by price; or by specific subject areas like process, environment, forecasts, or analysis.

DOE's Fuel Economy Guide

This website [http://www.fueleconomy.gov/] is an aid to consumers considering the purchase of a new vehicle.

DOE's Office of Energy Efficiency & Renewable Energy (EERE)

EERE's [http://www.eere.energy.gov/] mission is to pursue a better energy future where energy is clean, abundant, reliable, and affordable; strengthening energy security and enhancing energy choices for all Americans while protecting the environment.

U.S. DOE, Office of Science [http://www.er.doe.gov/]

U.S. EPA, Energy Star Program [http://energystar.gov/]

California Energy Commission [http://energy.ca.gov/]

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Ernest Orlando Lawrence Berkeley National Laboratory is a multiprogram national laboratory managed by the University of California for the U.S. Department of Energy. The oldest of the nine national laboratories, Berkeley Lab is located in the hills above the campus of the University of California, Berkeley.

With more than 3,800 employees, Berkeley Lab's total annual budget of nearly $500 million supports a wide range of unclassified research activities in the biological, physical, computational, materials, chemical, energy, and environmental sciences. The Laboratory's role is to serve the nation and its scientific, educational, and business communities through research performed in its unique facilities, to train future scientists and engineers, and to create productive ties to industry. As a testimony to its success, Berkeley Lab has had 11 Nobel laureates. EETD is one of 14 scientific divisions at Berkeley Lab, with a staff of 400 and a budget of $40 million.

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