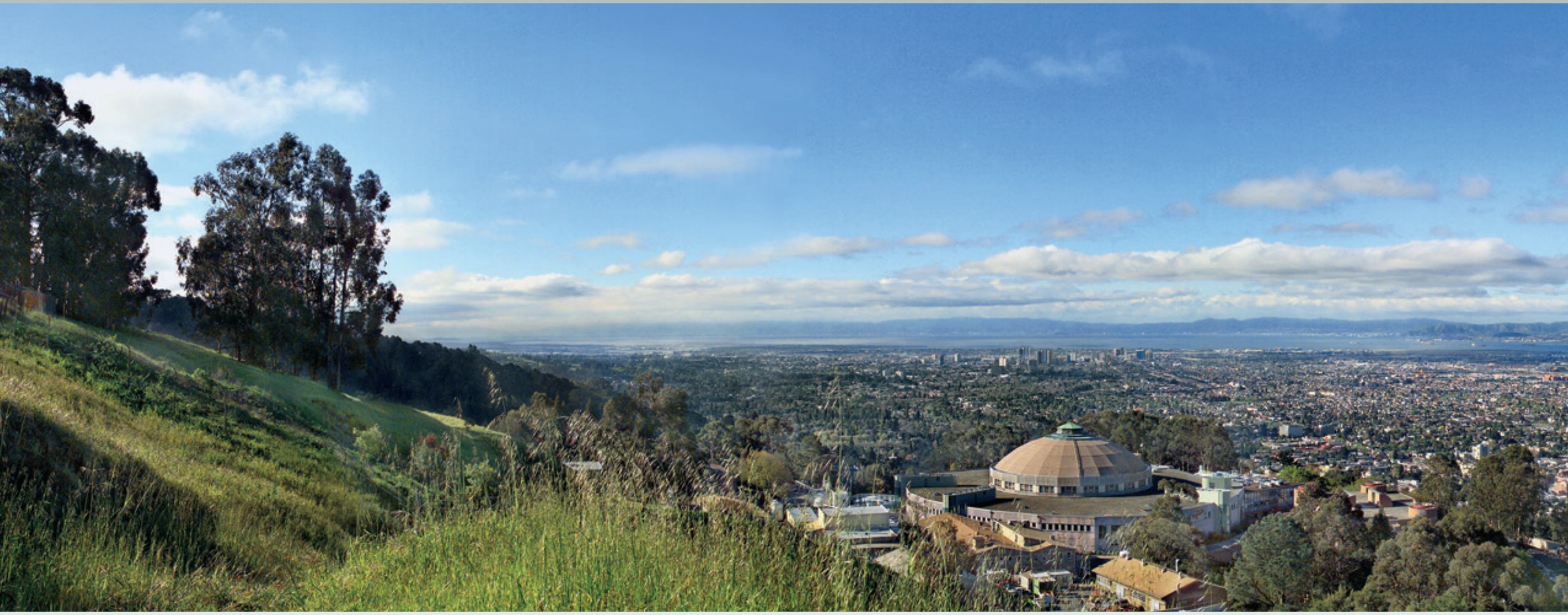
PHOTON SCIENCE FOR RENEWABLE ENERGY

at Light Source Facilities of Today and Tomorrow

Lawrence Berkeley National Laboratory
JULY 2012



TOOLS FOR JOULES

Our current fossil-fuel-based system is causing potentially catastrophic changes to our planet. The quest for renewable, nonpolluting sources of energy requires us to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels.

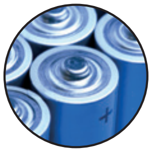
Light source facilities—the synchrotrons of today and the next-generation light sources of tomorrow—are the scientific tools of choice for exploring the electronic and atomic structure of matter. As such, these photon science facilities are uniquely positioned to jump-start a global revolution in renewable and carbon-neutral energy technologies. In these pages, we outline and illustrate through examples from our nation's light sources possible scientific directions for addressing these profound yet urgent challenges.

FUNDAMENTAL QUESTIONS

To establish the scientific foundations for the kind of transformative breakthroughs needed to build a 21st-century energy economy, we must address fundamental questions involving matter and energy. At right is a sampling of such questions that can be addressed by light source facilities:

How can we modify the behavior of electrons and holes in semiconductors to more efficiently convert **solar energy** into electricity using earth-abundant materials?

How can we harness photosynthesis and efficiently transform abundant plant material into **biofuel?** Can we produce fuel directly from sunlight by developing **artificial photosynthesis?**

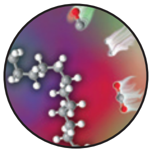


How can we increase the energy capacity and durability of lithium-ion **batteries** to maintain performance over hundreds to thousands of charge–discharge cycles?

How can we understand the electrical and chemical properties of a working **electrochemical fuel cell** to tailor its properties for the production of electricity?

How does **carbon dioxide** interact with naturally occurring materials under ambient conditions during **storage**, and what can we learn about these materials to improve their **capture** capacity?

How can we identify **combustion** products at the parts-per-million level to improve efficiency and control pollution that results from the burning of fuel?



How do we tailor the electronic properties of nanostructured **catalysts** to achieve higher activity or selectivity with inexpensive materials?

ABOUT LIGHT SOURCES: SYNCHROTRON RADIATION AND FREE-ELECTRON LASERS

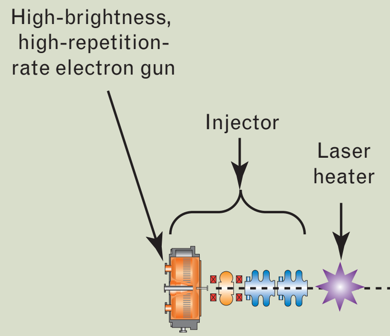
Synchrotron radiation is emitted by electrons that are accelerated to near the speed of light through bending magnets around a storage ring with a circumference ranging from few hundred meters to a kilometer. This synchrotron "light," which may be a million times more intense than that produced by x-ray tubes, covers the spectrum from infrared to ultraviolet and from soft (long-wavelength) x-rays to hard (short-wavelength) x-rays. With the use of special multipole magnetic devices known as wigglers and undulators, the brightness of the emitted radiation can be increased to achieve high resolving power for **spectroscopy/spectrometry,** high spatial resolution for **microscopy/spectromicroscopy/microtomography,** and high coherence for **diffraction/scattering**.

The radiation emitted by a synchrotron storage ring scales with the number of electrons (n) per bunch for a bending magnet, nN for a wiggler, and nN^2 for an undulator (N is the number of magnetic poles in the wiggler or undulator). Recent developments in linear accelerator technology using free-electron lasers have decreased the size of the electron bunches enough to emit coherent radiation in the soft to hard x-ray range with intensities that scale as n^2N^2, increasing brightness by ten orders of magnitude and timing resolution by five orders of magnitude.

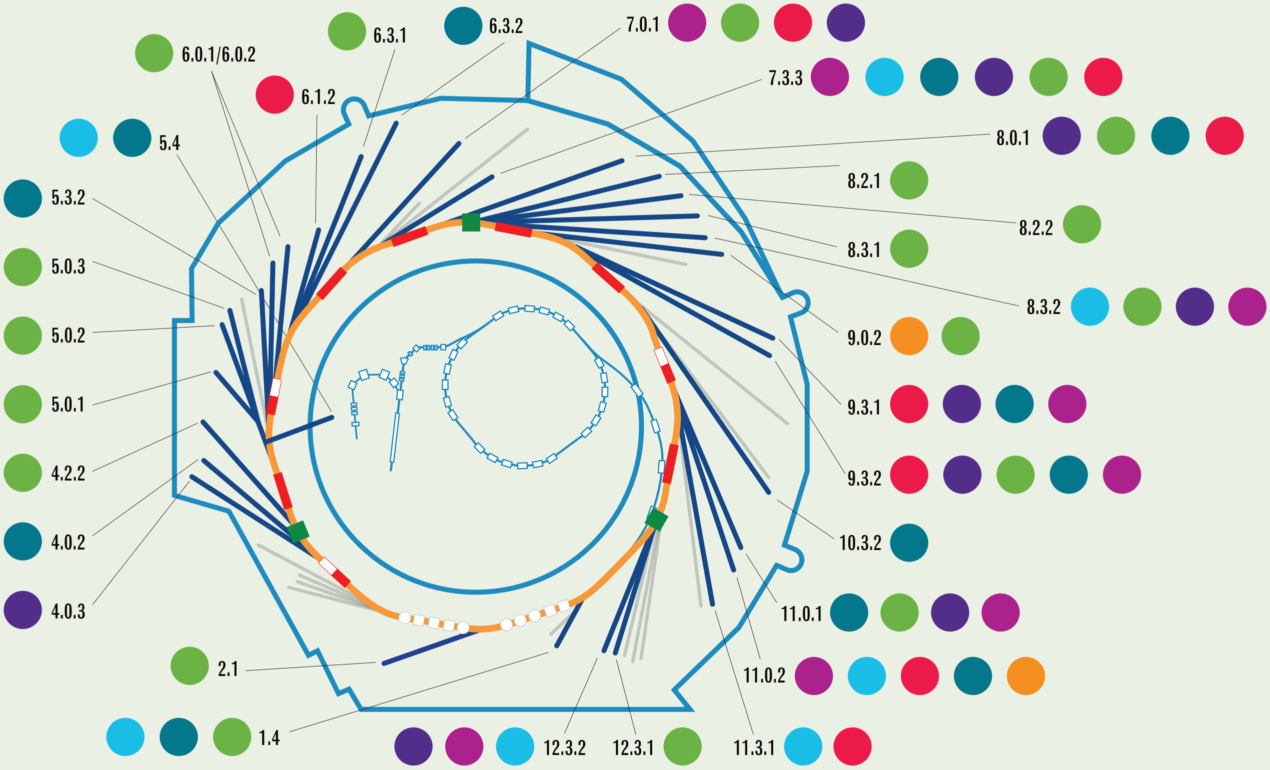
KEY

●	**Sunlight to electricity**
●	**Sunlight to fuel**
●	**Batteries**
●	**Fuel cells**
●	**CO_2 capture & sequestration**
●	**Combustion**
●	**Catalysis**

A survey of beamlines that have performed energy-related research at the Advanced Light Source (ALS) as of July 2012.



A proposed next-generation light source (NGLS) would consist of an array of soft x-ray free-electron lasers (FELs), each optimized for specific scientific needs. It would revolutionize our understanding of atoms, electrons, and the flow of energy on fundamental space and time scales. Courtesy of J. Corlett and P. Denes (Berkeley Lab).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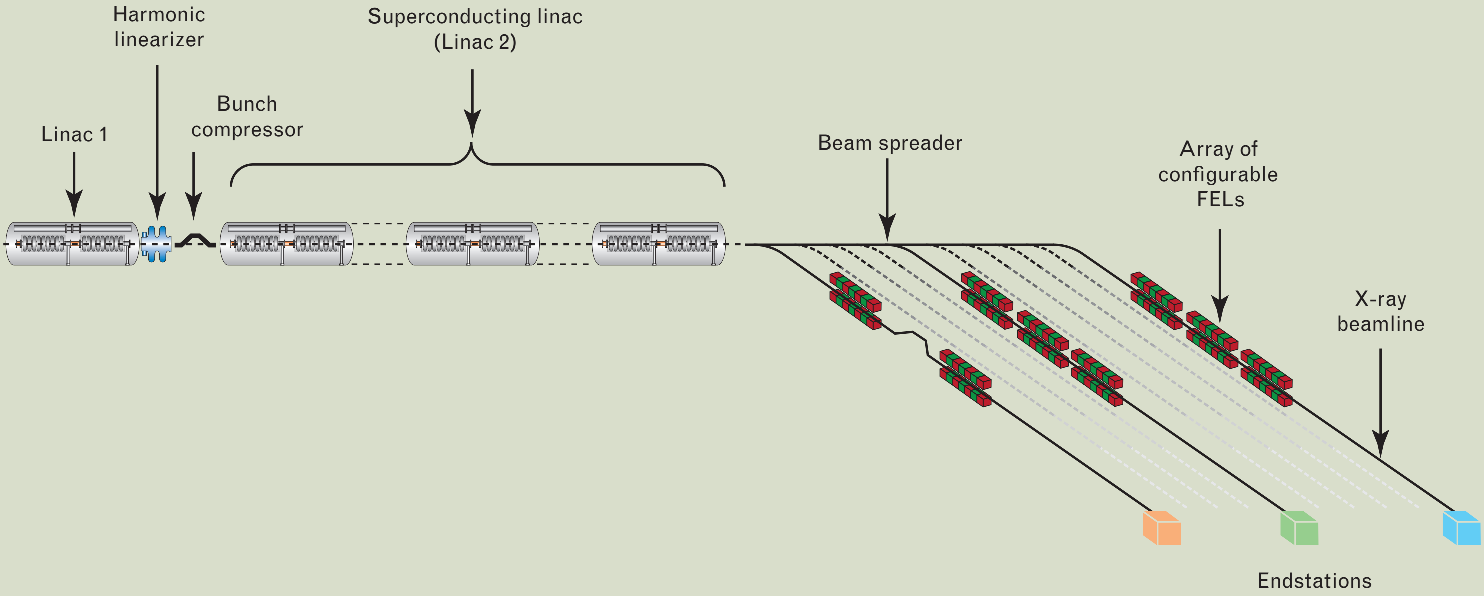
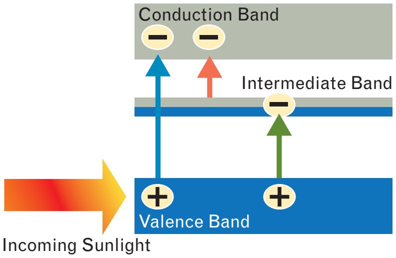

Harmonic linearizer
Superconducting linac (Linac 2)
Linac 1
Bunch compressor
Beam spreader
Array of configurable FELs
X-ray beamline
Endstations

SUNLIGHT TO ELECTRICITY

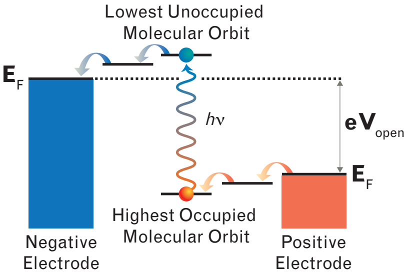
The sun delivers to earth in one hour the amount of energy consumed globally in one year. However, solar power supplies just 1.5% of the world's demand, due to its higher cost relative to fossil fuels. To become competitive, rapid advances in converting solar energy into electricity are needed in order to produce low-cost, high-yield, and high-efficiency solar cells.

Sunlight consists of a broad rainbow of colors representing a wide spectrum of different energies. However, typical solar-panel materials only utilize a fraction of the energy within that spectrum. Silicon, for example, has an electronic band gap of 1.1 eV. Energies below 1.1 eV are not absorbed, and excess energy above 1.1 eV does not contribute to producing electricity and is generally wasted as heat. Novel approaches for improving the efficiency of solar energy coversion include engineering a material with multiple energy levels, allowing the absorption of multiple photons and thus utilizing a much greater part of the solar spectrum. With x-ray absorption and emission **spectroscopy**, scientists can study these energy levels with atomic- and chemical-state specificity, tools essential to a rational, systematic approach to designing optimally performing photovoltaic materials.



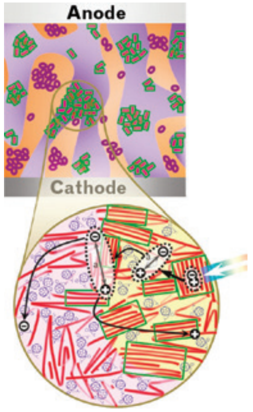
Intermediate energy levels, engineered into the electronic structure of a photovoltaic material, can act as stepping stones in the absorbtion of sunlight, utilizing a broader range of solar energies. [Walukiewicz et al., *Phys. Rev. Lett.* **106**, 028701 (2011).]

Scientists are interested in organic solar cells because these cells can be manufactured cost effectively by printing or painting organic molecules onto a variety of common surfaces such as glass or flexible plastic. In particular, dye-sensitized organic solar cells present a golden opportunity to engineer energy levels for optimized performance. Dye molecules are noted for their ability to strongly absorb certain wavelengths of sunlight, and biomimetic dye molecules mimic the structure of biomolecules such as hemoglobin (the molecule that gives blood its red color). **Spectroscopy** studies of biomimetic dye molecules in solar cells allow scientists to systematically measure the energy levels resulting from a wide variety of chemical modifications and material combinations, a key to tailoring the molecules' properties and unlocking their great potential for increasing photovoltaic efficiency. With organic molecules, an enormous repertoire of possible chemical variations can be used to optimize performance.



In a dye molecule, a photon from sunlight (wavy arrow) excites an electron (blue circle) to a higher available energy level, leaving behind a "hole" (red circle). The electron is pulled toward a negative electrode (upper blue arrows), while the hole is filled by an electron from a positive electrode (lower red arrows), creating a usable charge separation (voltage). [Cook et al., *J. Chem. Phys.* **131**, 194701 (2009).]

Researchers have also begun experimenting with organic solar cells made from a mixture of polymers and fullerenes. These require simple and inexpensive processing steps, resulting in an economically competitive and environmentally friendly energy source. The active layers were initially thought to consist of an interpenetrating network of pure polymer domains and pure fullerene domains, separated by discrete interfaces. However, resonant soft x-ray **scattering**, which provides morphology information with chemical specificity, has shown that the picture is more complex, with nanometer-sized crystallites of one type mixed within domains—hundreds of nanometers in scale—of the other type. This hierarchical morphology significantly enhances the likelihood that an electron–hole pair will fully dissociate, one of the key factors determining the performance of organic photovoltaic devices.



In organic photovoltaic devices, polymer crystallites (green rectangles) can be found in fullerene-rich domains, and fullerene crystallites (purple ovals) can be found in polymer-rich domains. This hierarchical morphology makes it more likely that an electron–hole pair will fully dissociate and migrate far enough to create a usable voltage. [Chen et al., *Nano Lett.* **11**, 3707 (2011).]

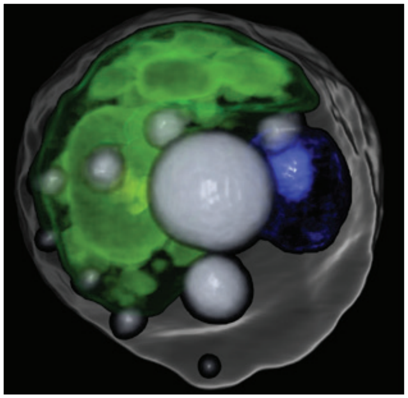
SUNLIGHT TO FUEL

Nature has devised a remarkably diverse set of pathways to convert solar photons into chemical fuels. We hope to find ways to harness those processes, whether by using plant matter as the raw material for transportation biofuels, by coaxing higher yields of fuel precursors from plant enzymes and algae cells, or by mimicking the process of photosynthesis itself in man-made devices.

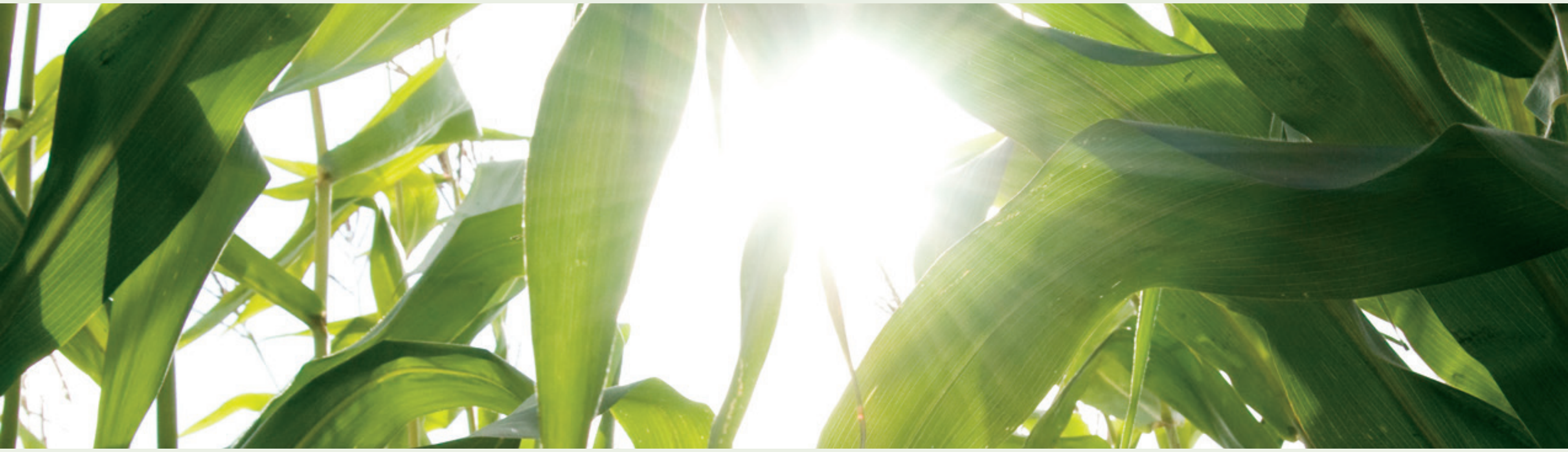
Biofuels can be produced efficiently from crops with high sugar content (the sugar is converted into ethanol by yeast). Although cellulose, a key component of plant cell walls, can be broken down into sugar components, it exists in the cell walls as a complex mixture with hemicellulose and lignin, which are naturally resistant to breakdown. Ionic liquids have emerged as promising new solvents for disrupting the crystalline structure of the cellulose. X-ray **diffraction**, **scattering**, and **spectroscopy** studies provide useful information about how to improve pretreatment of lignocellulosic biomass and thereby deliver cheaper biofuel.

Macromolecular crystallography is an important x-ray **diffraction** tool that helps biofuels researchers understand how enzymes can be used to synthesize fuels. For example, researchers have used x-ray crystallography to determine the structure of α-bisabolene synthase, an enzyme that synthesizes a precursor to bisabolane, an advanced biofuel with properties similar to D2 diesel. Detailed knowledge about the molecular mechanisms at work in bisabolene synthase can help scientists to increase yields enough to make bisabolane a viable alternative to diesel fuel.

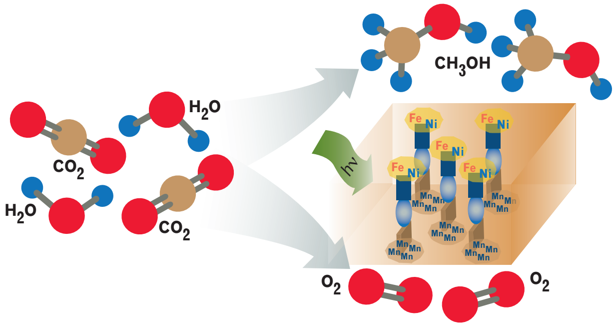
Certain types of algae also show promise as a source of biofuel because they are easy to grow and rich in lipids that can be converted into a form of biodiesel. Three-dimensional soft x-ray nano-**tomography** studies can provide valuable information about which growing conditions result in the greatest volume of lipids, allowing researchers to optimize them for fuel production [work performed by S. Singh and B. Simmons (Sandia National Laboratories) at the National Center for X-Ray Tomography at the ALS, supported by the U.S. Department of Energy, Office of Biological and Environmental Research].



Three-dimensional x-ray images of algae cells can provide accurate information about lipid volumes (gray spheres) not readily extracted from two-dimensional images. Courtesy of D. Parkinson (ALS).



Scientists are also exploring ways to use sunlight to convert carbon dioxide and water into fuel molecules (hydrogen, methane gas, or simple alcohols) in a single, integrated device made from earth-abundant inorganic materials (artificial photosynthesis). The electronic structures of these materials are determined in part by using synchrotron-based near-edge and extended x-ray absorption **spectroscopy**. Recent soft x-ray developments involving high-efficiency emission spectrographs, ambient-pressure photoemission spectroscopy, and in situ measurement techniques provide a better indication of the oxidation state, symmetry, electronic structure, and charge-transfer processes in the complexes involved.



The solar splitting of water via artificial photosynthesis. Nanotubes made up of earth-abundant materials (e.g. Fe, Ni, and Mn) are embedded within a membrane that acts like a green leaf. Incident solar radiation splits water molecules (H_2O), freeing up electrons, protons (hydrogen ions), and oxygen (O_2) that then react with carbon dioxide (CO_2) to produce a liquid fuel (e.g., CH_3OH) that can be used for vehicles. The result is a renewable green energy source that also helps scrub the atmosphere of excessive carbon dioxide from the burning of fossil fuels. Courtesy of the Joint Center for Artifical Photosynthesis.

The development of light sources based on free-electron lasers is also providing new opportunities for time-resolved x-ray experiments that would make it possible to create movies of the breaking and formation of bonds as well as of charge-transfer processes as they happen in time frames that range from picoseconds to femtoseconds to perhaps attoseconds. Such experiments would isolate the processes involved and reveal their evolution over time by combining the chemical and atomic specificity of x-rays with the use of stroboscopic pump–probe techniques.

ENERGY STORAGE: BATTERIES

Batteries give us the ability to store energy, which is important for portability (e.g., electric cars) as well as for the steady delivery of electricity to consumers where and when it is needed using a smart grid from green but intermittent energy sources (e.g., sun and wind farms). These goals require a new generation of batteries that store more energy, recharge faster, and survive more duty cycles without degradation.

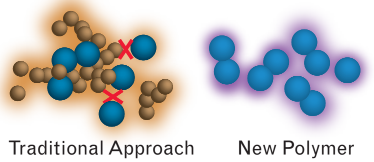
To develop better batteries, researchers must assess what is happening inside the battery materials as the batteries charge and discharge. For example, in lithium-ion batteries (used in everything from cell phones to electric vehicles), researchers would like to observe how the charge carriers (lithium ions and electrons) interact with the batteries' cathodes and anodes. In the case of polymer-based batteries, researchers want to watch the block copolymers of the electrolyte change pattern or even heal themselves through annealing during heating and cooling. Problem areas also need to be addressed, such as the swelling of materials and growth of lithium dendrites.

X-ray beamlines provide several tools and techniques necessary to keep up with the growth of the world's energy demands through rational design of new materials with real-world payoffs, such as car batteries with higher capacities and more duty cycles. Photo © General Motors.

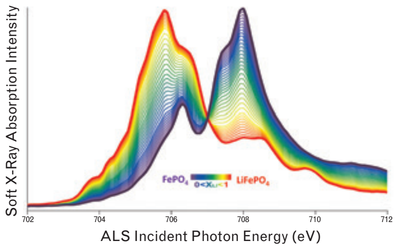
Fast small- and wide-angle x-ray **scattering** provides the metric needed to make nanoscale measurements of the structure of a rapidly changing battery system. Researchers have recently conducted an almost ideal experiment: entire lithium-ion batteries have been placed into the x-ray beam and charged and discharged in situ while small-angle x-ray scattering measurements were made. This allowed them to quantify the nanoscale changes that occur in electrode morphology during charging and discharging. This kind of information will be invaluable in developing the next generation of battery technology.

New conductive polymers have been designed and synthesized that, by providing structural stability and electrical conductivity to silicon nanoparticles, greatly improve the energy density of lithium-ion batteries. The polymers, when made into anodes (negative electrodes) with commercial silicon nanoparticles, provide both intimate contact with the nanoparticle surfaces for electrical conductivity and structural flexibility to accommodate large-volume changes during lithium-ion insertion and removal. Soft x-ray absorption **spectroscopy** provides direct information for a rational

optimization of these materials. Synthesis of the polymers is fully compatible with current large-scale lithium-ion manufacturing processes, and x-ray spectroscopy was performed directly on real-world samples without any surface treatment. Lithium battery anodes based on such polymers and silicon nanoparticles have so far shown the best cycling behavior, with an energy capacity almost an order of magnitude higher than that of the widely used carbon-based anodes on today's market.



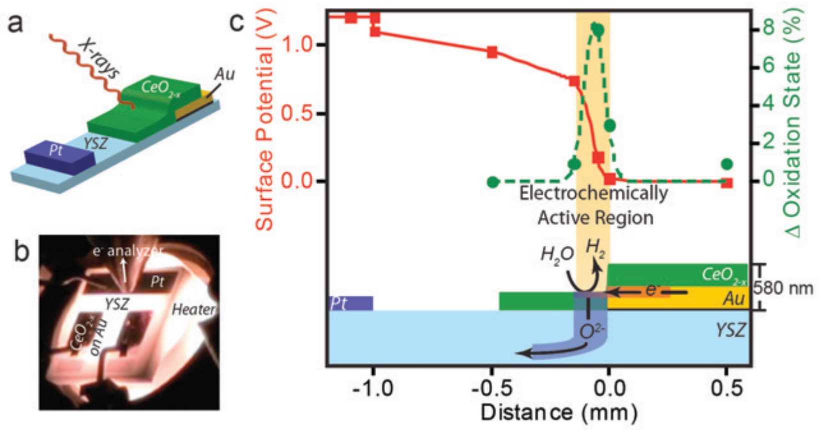
The traditional approach to composite anodes for high energy capacity involves a mixture of silicon (blue spheres), carbon for conducting electricity (dark brown spheres), and a polymer binder (light brown shading). The silicon swells and shrinks upon acquiring and releasing lithium ions. Repeated swelling and shrinking eventually break contacts among the conducting carbon particles. A new polymer binder (purple shading), discovered with the aid of x-ray **spectroscopy**, is itself conductive and continues to bind tightly to the silicon particles despite repeated swelling and shrinking. [Liu et al., *Adv. Mater.* **23**, 4679 (2011).]



Soft x-ray absorption **spectroscopy** can provide a "fingerprint" of various candidate materials for lithium-ion battery components. This graph depicts the changes in the electronic structure of a candidate cathode material ($LiFePO_4$) as lithium is extracted (red to purple). It provides abundant information on phase transformation (crossing point at center), the evolution of electronic states, and a quantitative definition of the energy levels of the Fe 3d states, which is important for understanding the puzzling charge-discharge behavior of this cathode material. Courtesy of W. Yang (ALS).

ELECTROCHEMICAL FUEL CELLS

When hydrogen and air are pumped into a fuel cell, electricity is generated and air and water vapor leaves. A hydrogen fuel cell can thus be classed as an energy conversion system with zero emissions, provided that the hydrogen is not generated via carbon-based fuels. In situ synchrotron-based techniques and nanofabrication are providing new insight into the operation of these electrochemical devices.



Electrochemical activity over 100 μm of a ceria anode. (a) Schematic of solid oxide cell showing Pt counter electrode, Au current collector on top of a thin alumina film (black), and ceria working electrode patterned onto a YSZ single-crystal substrate. This geometry exposes the entire cell to the x-ray beam. (b) The view through the sample chamber window during cell operation at about 700 °C. (c) A ceria anode converts H_2O into H_2 and O^{2-} in a narrow region at 1.2-V cell potential. In situ APXPS reveals gradients in surface potential (red) and the shift of Ce oxidation state out of equilibrium (green) in this region. [Zhang et al., *Nat. Mater.* **9**, 762 (2010).]

Whereas batteries store energy, fuel cells require a constant fuel supply—hydrogen, for example. The hydrogen's electrons and protons are catalytically separated, and an electrolytic membrane allows the protons to travel from the cell's anode to its cathode, while forcing the electrons through an external circuit, creating an electric current.

Fuel cells that employ solid oxide membranes typically require high operating temperatures (above 650 °C), limiting material choices. Yttria-stabilized zirconia (YSZ) membranes and cerium oxide (ceria) electrodes have received significant attention due to properties that can, in theory, expand the electrochemically active region. However, there is little direct knowledge of local overpotential and length scales of the electrochemically active regions of such materials in

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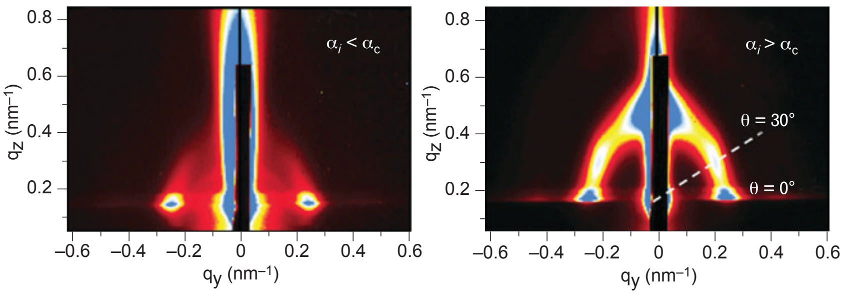


GISAXS patterns for PEMs composed of block copolymers supported by a silicon substrate. Data were obtained at two incident angles: below the critical angle (left) and above the critical angle (right). Courtesy of N.P. Balsara (UC Berkeley). [Park et al., *Adv. Mater.* **21**, 203 (2009).]

operational solid-state fuel cells. Measuring the overpotentials is quite challenging due to the high temperatures and the need to connect the components in series. The use of an ambient-pressure x-ray photoelectron **spectroscopy** (APXPS) instrument allowed, for the first time, direct, in situ study of an operating solid-state fuel cell to determine the overpotential across each component interface as well as its chemical composition. Such measurements will allow further optimizing and tailoring of the performance of solid-state fuel cells.

Another type of fuel cell employs polymer electrolyte membranes (PEMs), with hydrophilic, proton-conducting channels embedded in a hydrophobic matrix. Grazing-incidence small-angle x-ray **scattering** (GISAXS) data provided information about the orientations of the channels near the air interface and through the interior of 180-nm-thick PEMs before and after exposure to humid air. Scattering at incident angles below the critical angle (and thus dominated by contributions from the PEM/air surface) contained well-defined spots, indicating the presence of hydrophilic channels oriented perpendicular to the surface. Scattering at incident angles above the critical angle (and thus containing contributions from the entire film), exhibited a scattering ring, indicating the presence of hydrophilic channels parallel to the plane of the film.

CO_2 CAPTURE AND SEQUESTRATION

Capturing carbon dioxide (CO_2) gas from stationary sources such as power stations and then pumping it underground for storage in permeable rock is a potential way to avoid or mitigate "greenhouse gas" effects on climate. What materials are best at efficiently capturing the CO_2? What happens to the CO_2 when underground?

Metal organic frameworks (MOFs) are nanoporous materials whose pore sizes and internal surface chemistry can be tailored to selectively trap the CO_2 molecules found in flue gases. Subsequently, the MOFs can then be treated to release the CO_2 for storage elsewhere, and the MOFs can then be reused. One approach to developing such materials is to perform single-crystal hard x-ray **diffraction** in a gas cell, with the goal of precisely locating the gas species trapped inside MOFs. Another approach is to develop a gas cell for soft x-ray absorption **spectroscopy**, with the goal of measuring the traces of weak chemical reactions thought to occur as CO_2 molecules are trapped inside certain MOFs. The approaches are complementary. Both the spectroscopic and crystal structure information will provide theorists with critical data needed to validate models aimed at describing and predicting the performance of MOFs in CO_2 capture scenarios. To facilitate the development of new materials for separating CO_2 from other gases, the U.S. Department of Energy has established an Energy Frontier Research Center (EFRC) for gas separations relevant to clean energy technologies. Located in Berkeley, the EFRC uses the Advanced Light Source to gain fundamental insight into gas interactions with MOFs.

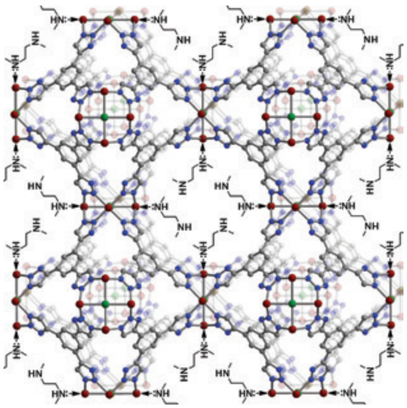
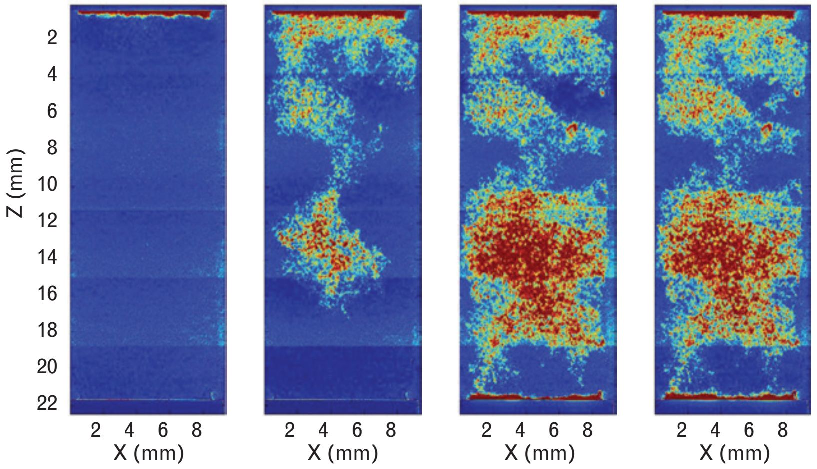


Illustration of a metal–organic framework (MOF). Metal compounds are connected via organic-molecule bridges into a lightweight scaffolding with large pores that can accommodate gas molecules such as CO_2. In this example, the pores incorporate amine functional groups that can separate CO_2 from flue gas with a significantly lower energy penalty than methods currently in use. [McDonald et al., *Chem. Sci.* **2**, 2022 (2011).]

When injected into underground rock structures, the flow properties of CO_2 are dominated by the interaction of the CO_2 with native brines in a network of microscopic pores—the empty space between grains in sedimentary rocks. This process is governed by the geometry of the pores and the connectivity of the pore network as well as the surface properties of mineral grains. Understanding these interactions is



A sequence of x-ray micro-radiographs shows how supercritical CO_2 displaces brine inside the microscopic pores of a reservoir sandstone sample. Frames are 30 seconds apart. Courtesy of J. Ajo-Franklin (Berkeley Lab) et al.

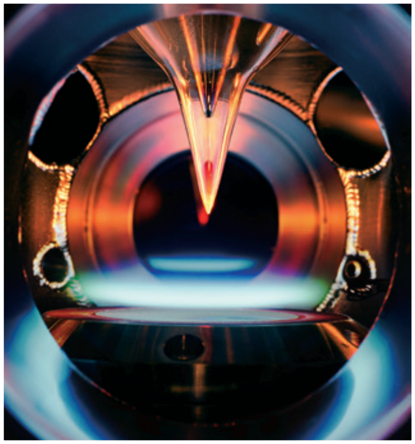
the key to predicting the behavior of underground CO_2 reservoirs. Using synchrotron light, we are able to look inside rocks with three-dimensional x-ray **microtomography** to see how fluids flow through permeable rock, displacing existing liquids. These experiments yield the data that will confirm the theoretical models being developed that will in turn be used to predict the properties of large CO_2 underground reservoirs.

The interaction of CO_2 with rocks, soil, ice, sea water, and aerosols plays an important part in the CO_2 chemistry of earth's atmosphere. In particular, chemical processes at the interfaces between solid, liquid, and vapor determine the uptake and release of CO_2. Ambient-pressure x-ray photoelectron **spectroscopy** (APXPS) allows the investigation of these interfaces under realistic conditions of relative humidity and CO_2 partial pressure. Current projects include the investigation of the uptake of CO_2 by mineral surfaces (e.g. MgO) as a function of relative humidity, where in particular the formation and possible removal of self-passivating carbonate layers (which limit CO_2 uptake by mineral surfaces) is of interest [H. Bluhm (Berkeley Lab) et al.].

COMBUSTION

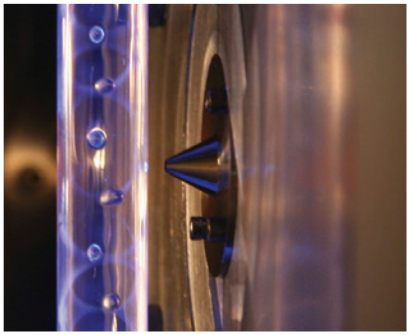
Fossil fuels, biofuels, and synthetic alcohol-based fuels all have different combustion processes. After more than 150 years of study, combustion is well understood in terms of average energy output, high-concentration intermediates, and major products. However, it is necessary to understand flame chemistry at the parts-per-million level if we are to further improve efficiency and control pollution.

As fuel burns and transforms into its final products, it goes through an intricate network of thousands of reaction pathways with hundreds of short-lived transient molecules (reaction intermediates). These often include lung-damaging particulates like soot, smog-causing nitrogen oxides, and other pollutants. Detailed mathematical models have been developed to help improve combustion efficiency and reduce pollution. However, the accuracy of these models depends on knowing all the chemical species involved and having quantitative values for the reaction constants that describe how the reactions proceed. As a result, many important rate constants have never been measured directly, nor have all the species included in mathematical flame models been directly observed.



The luminous zone of the flat flame has the typical blue-violet or blue-green color associated with chemiluminescence from electronically excited CH and C_2. The gases produced by the flame are sampled through a small aperture in a quartz cone. These gases can then be analyzed by synchrotron-photoionization mass spectrometry, which has revealed previously undetected combustion intermediates. Photo by L. Hadley (Sandia National Laboratories).

For those studying flame chemistry and the properties of combustion intermediates by means of molecular beam mass **spectrometry**, the use of tunable vacuum ultraviolet light from a synchrotron to photoionize the beam for mass spectrometry makes for a powerful technique capable of differentiating between isomers with the same molecular weight and composition. Using such a technique, researchers discovered that a class of compounds known as enols (ethenol or vinyl alcohol is the simplest of these), only recently observed as a combustion intermediate, is in fact widely present in flames burning a variety of fuels, including commercial



The chemical reactions of Criegee intermediates were studied using an apparatus at ALS Beamline 9.0.2. [Welz et al., *Science* **335**, 204 (2012).] A quartz reaction tube shows the faint blue luminescence from a 248-nm laser that creates a precursor reactant. A gas beam of the reactants and products exits the tube through a 600-μm pinhole facing the conical skimmer on the right, which collects the molecules for eventual ionization by vacuum ultraviolet photons from the ALS and detection by a mass spectrometer. Photo by D. Osborn (Sandia National Laboratories).

blends, such as gasoline. Combustion modelers will have to take this new finding to heart, as will those studying other forms of hydrocarbon oxidation, including those involving synthetic and biofuels.

In addition to chemical reactions in combustion processes, vacuum ultraviolet synchrotron light can also be used to study important tropospheric oxidation processes. In the earth's troposphere, which blankets the planet surface where we live and breathe, dust particles, gas molecules, water vapor, and sunlight provide the ingredients for a multitude of chemical reactions that can generate effects ranging from clouds and smog to acid rain and climate change. One such reaction, ozonolysis, plays a key role in the removal of unsaturated hydrocarbons (alkenes) from the troposphere.

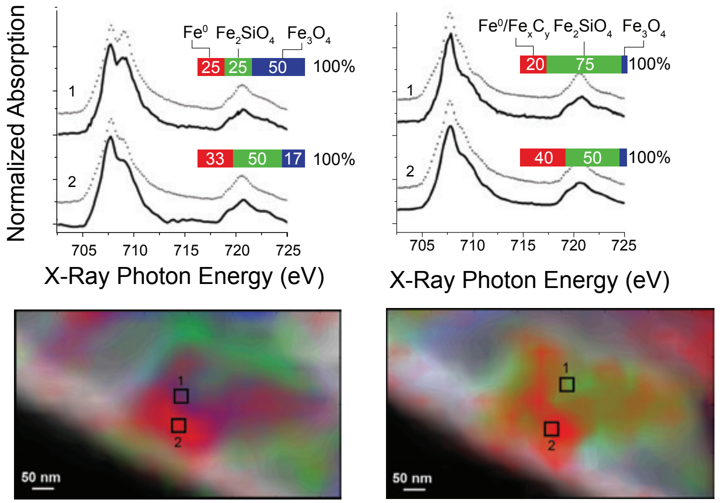
Using synchrotron radiation, scientists were able to directly measure for the first time reaction rates for so-called Criegee intermediates, elusive molecules formed at intermediate stages of ozonolysis and that also play a key role in hydrocarbon autoignition chemistry, a field critical to advanced engine design. The researchers found that the simplest Criegee intermediate reacts up to 10,000 times faster with certain atmospheric molecules than previously thought. While this doesn't change the actual chemistry occurring in earth's atmosphere, it might dramatically affect atmospheric chemistry models, portions of which we now know are incorrect.

CATALYSIS

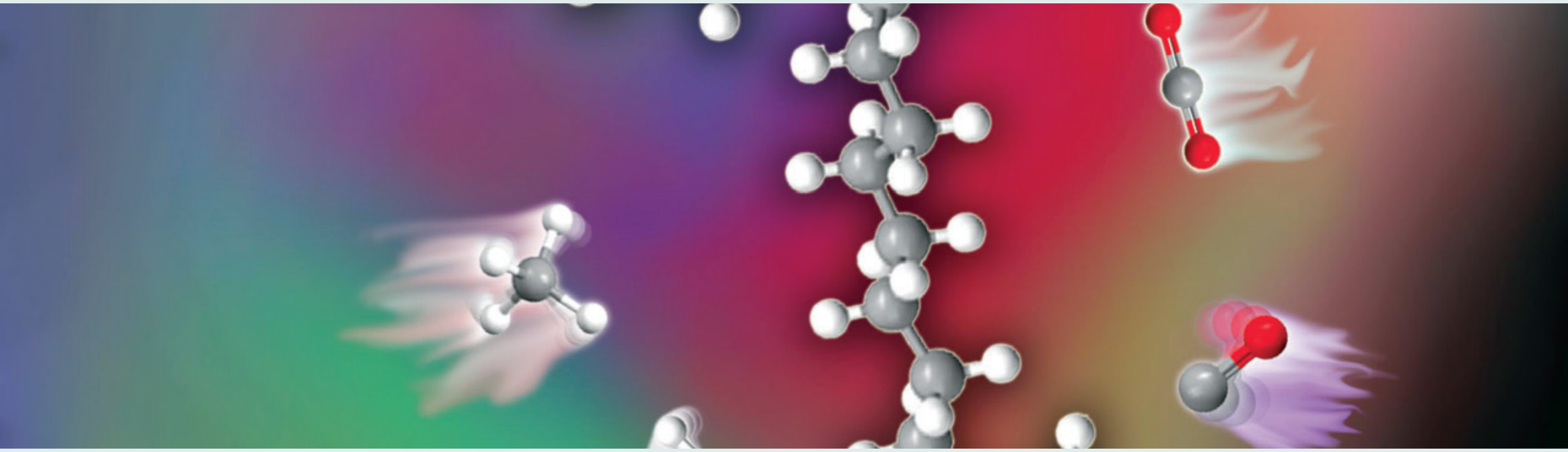
Catalysts—substances that speed up chemical reactions without being consumed—play a central role in technologies relevant to energy and the environment. Because of their importance, researchers are working to develop cheaper and smarter catalysts that are fine-tuned to accelerate reactions that, for example, drive fuel-refinement techniques, feed hydrogen fuel cells, or sweep toxins from emissions.

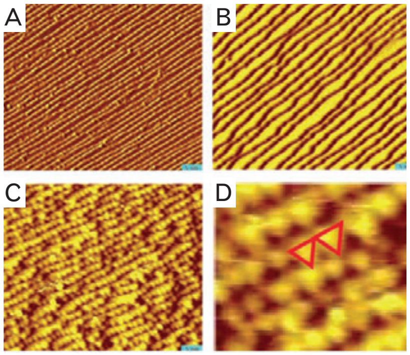
The catalysts used in chemical processes often consist of nanoscale metal or metal oxide particles dispersed on a surface. While these particles are the active elements of the catalyst, their overall performance depends not only on their size and composition but also on their interactions with the surface, reactants, products, and environment (gaseous atmospheres at high temperatures). Probing this chemical soup in real time under realistic reaction conditions is a tall order, and such catalysts could previously be observed only before and after, but not during, a reaction. In some cases even the catalytically active chemical species is not known.

By combining scanning transmission x-ray **microscopy** (STXM) with a reaction chamber adapted from electron microscopy, we can identify



Tracking changes in an iron-based catalyst. Top left: Iron spectra taken before catalysis from two regions (1 and 2) of the catalyst material. Top right: Spectra taken after catalysis. Dotted lines are calculated from reference spectra. Bar graphs show the relative contributions of different iron phases at the sampling points. Bottom: Iron species contour maps generated from the spectra taken at each pixel. The colors are keyed to the bar graphs above. Courtesy of F.M.F. de Groot (Utrecht University). [de Smit et al., *Nature* **456**, 222 (2008).]





In these scanning transmission microscope images of a platinum catalyst, (A) shows the terraced surface under ultrahigh vacuum. (B) As the CO pressure increases, the amount of adsorbed CO also increases and causes the terraces to widen. (C) When coverage is near 100% at pressures of one torr, the terraces fracture into nanoclusters. (D) Enlarged view shows the triangular shape of the nanoclusters, two of which are marked by red lines. [de Smit et al., *Science* **327**, 5967 (2010).]

the chemical species present and see their distribution on the nanoscale. Such measurements demonstrate that STXM can provide details about the morphology and composition of complex catalytic systems under realistic conditions. When developed further, this new tool may give chemists the ability to design and tailor catalysts for maximum selectivity and efficiency in a wide range of chemical processes.

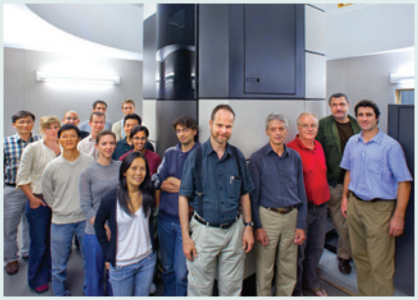
When it comes to metal catalysts, platinum is the standard. However, at about $2,000 an ounce, the high cost of the raw material presents major challenges for the future wide-scale use of platinum in fuel cells. Researchers have found that under realistic pressures—comparable to the pressures at which many industrial technologies operate—platinum surfaces can change their structure dramatically, from terrace-like to nanoclusters, in response to the presence of high-coverage reactants. Ambient-pressure scanning tunneling microscopes and ambient-pressure x-ray photoelectron **spectroscopy** (APXPS) allow researchers to bridge the gap between traditional experiments performed under vacuum and studies of the structure and composition of catalysts under more realistic conditions. These techniques could also be applied to discover the most favorable metal catalysts and reactants, as well as optimal reaction conditions for different combinations thereof. If other metal catalysts exhibit this nanoclustering effect, platinum could be replaced with less expensive alternatives, lowering the cost of the final products.

BEYOND THE LIGHT SOURCE

In addition to light sources, there are many other tools available to scientists addressing society's energy challenges. Department of Energy (DOE) national laboratories have the ability to bring together in one place an array of world-class facilities, staffed by multidisciplinary experts with complementary approaches to solving a given problem. When these experts collaborate with one another, advances occur more rapidly and with greater precision compared to trial-and-error efforts performed in isolation. These partnerships between people and facilities truly maximize the benefits of our national investment in energy research. At Lawrence Berkeley National Laboratory, the Advanced Light Source has a number of facilities from which it can draw valuable support.

National Energy Research Scientific Computing Center (NERSC). As one of the largest facilities in the world devoted to providing computational resources and expertise for basic scientific research, NERSC is a world leader in accelerating scientific discovery through computation.

Molecular Foundry. A critical part of the DOE's National Nanotechnology Initiative, the Foundry provides researchers with the instrumentation, in-house expertise, and multidisciplinary environment necessary to pursue research that can benefit from or contribute to nanoscience.



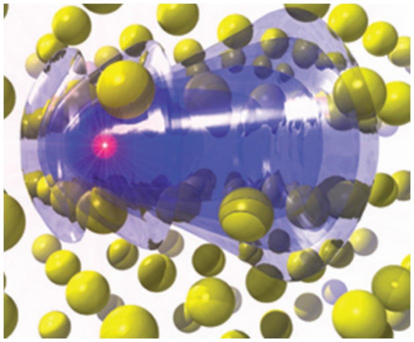
National Center for Electron Microscopy (NCEM). One of the world's foremost centers for electron microscopy and microcharacterization, NCEM provides cutting-edge instrumentation, techniques, and expertise for advanced electron-beam microcharacterization of materials at high spatial resolution.

Joint BioEnergy Institute (JBEI). One of three DOE Bioenergy Research Centers, JBEI's primary scientific mission is to advance the development of the next generation of biofuels—liquid fuels derived from the solar energy stored in plant biomass.

The Advanced Light Source also benefits from close association with the world-class faculty and superb graduate programs at the neighboring **University of California, Berkeley**. In turn, the research programs and experimental facilities at the laboratory provide exceptional opportunities for faculty and graduate students.

BRINGING IT ALL TOGETHER

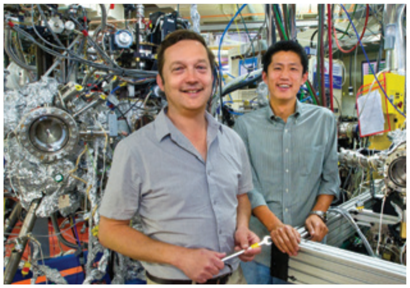
Future initiatives that promise to consolidate and leverage our existing capabilities include a formal Theory Institute for Photon Sciences (TIPS) and an Advanced Materials Beamline for Energy Research (AMBER).



Computer-rendered model of the electronic wake (blue surfaces) generated by an energetic proton (red sphere) traveling in an aluminum crystal. Improved theoretical models developed by TIPS would provide valuable insight into the real behavior of advanced materials. [Correa et al., *Phys. Rev. Lett.* **108**, 213201 (2012).]

To fully reap the rewards of our investment in advanced photon science tools, we must develop advanced theoretical methodologies and computational models. Such an effort is of crucial importance for extracting the most exciting science from the data collected and for designing effective tests of competing theoretical scenarios, so that robust, predictive models can be developed, refined, and deployed. TIPS will create a modeling environment for photon sciences that will enable researchers to move seamlessly between beamlines, facilities, and simulations, heralding a game-changing era of enhanced productivity through close collaboration between experimentalists, theorists, and modelers.

A proposed beamline at the ALS, AMBER will be dedicated to energy research, bringing together in one place the features and expertise needed to comprehensively tackle many of the questions articulated in this booklet. It will include three experiment stations fully optimized for studying energy-related materials in a real-world environment (in situ) and under operating conditions (operando). The first station will incorporate a novel, ambient-pressure, photon-in/electron-out **spectroscopy** technique pioneered by the ALS and recognized with an R&D 100 Award in 2010. The second station will be a photon-in/photon-out soft x-ray **spectroscopy** station that will allow measurement of electronic characteristics and behavior in the presence of liquids or gases (at pressures just above 1 bar) with both elemental and chemical-state sensitivity. The third station will allow scanning transmission x-ray **microscopy** of electronic and magnetic structures down to 10-nm resolution, also in the presence of liquids or gases at 1 bar and with elemental and chemical-state sensitivity.



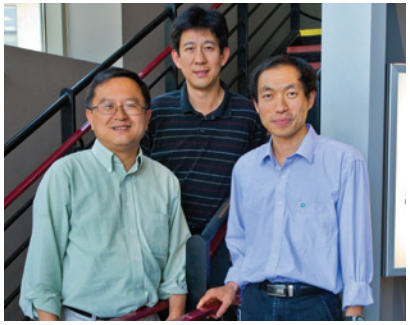
Hendrik Bluhm and Zhi Liu at one of the ALS's existing ambient-pressure spectroscopy stations. This technology, which will be incorporated into AMBER, was recognized with a 2010 R&D 100 Award as one of the top high-technology developments of that year.

Synthesis, Characterization, and Simulation

How will lowering barriers between experts, instrumentation, and infrastructure catalyze transformative discoveries? One example of a successful Berkeley Lab collaboration illustrates how combining the tools of synthesis, characterization, and simulation creates a cycle of discovery in which the ultimate goal is identified early, allowing the most promising avenues to be explored first.

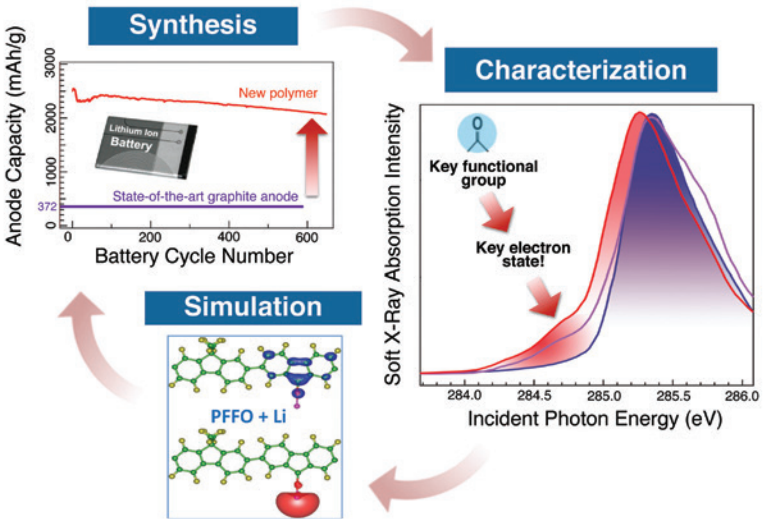
A team from the Lab's Environmental Energy Technologies Division (EETD), led by Gao Liu, designed a series of conducting polymers (synthesis).

Then, Wanli Yang of the Advanced Light Source (ALS) suggested soft x-ray absorption spectroscopy to determine the polymers' key electronic properties (characterization). To better understand these results, the team sought out Lin-Wang Wang of the Materials Sciences Division (MSD), whose theoretical calculations (simulation) conducted at the Lab's National Energy Research Scientific Computing Center (NERSC) provided insight into what was really happening in the polymer with a particular functional group of atoms. Subsequently, another functional group was added to the polymer. Scanning and transmission electron microscopy at the National Center for Electron Microscopy (NCEM) confirmed the improved performance of the modified polymer throughout numerous charge–discharge cycles. [Liu et al., *Adv. Mater.* **23**, 4679 (2011).]



Counterclockwise from far right: Wanli Yang (ALS), Gao Liu (EETD), and Lin-Wang Wang (MSD) led a highly successful collaboration between their groups, resulting in a breakthrough on battery performance.

Ultimately, through collaborative efforts like these, young scientists will be exposed to investigations of the fundamental interplay between material chemistry and physical phenomena, training the next generation of scientists and engineers to be intimately conversant with both the basic science and energy implications of photon science.



Cycle of discovery: synthesis, characterization, and simulation. A collaborative approach can lead more rapidly to material breakthroughs, showing why a particular modification works and how to further optimize the next generation of materials.

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Office of Science
www.science.doe.gov

ADVANCED LIGHT SOURCE

Roger Falcone
Division Director
RWFacone@lbl.gov

Zahid Hussain
Division Deputy for Scientific Support
ZHussain@lbl.gov

Steve Kevan
Division Deputy for Science
SDKevan@lbl.gov

Howard Padmore
Division Deputy for Experimental Systems
HAPadmore@lbl.gov

Sue Bailey
User Services Group Leader
SBailey2@lbl.gov

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