

# Supercapacitors Yield Energetic Secrets

**I**N the race for advanced energy storage systems, researchers are increasingly turning to the supercapacitor, a seemingly straightforward device made attractive by its many advantages over most batteries, including higher power density, faster charge–discharge cycling, enhanced safety, lower cost, and better endurance. Dynamic processes at the interfaces between electrodes and electrolytes are essential for supercapacitors to operate efficiently, but not enough is known about these interfaces to improve the capabilities of supercapacitors. This is where Livermore researchers are making key strides in understanding this critical energy technology.

The paucity of knowledge about supercapacitors persists because of the technical challenges involved in monitoring their electrode–electrolyte interfaces during operation. Yet this area is precisely where detailed understanding is needed to design more efficient devices for practical, widespread use. To expose the details of operating supercapacitors, a Livermore-led team developed a new experimental capability in x-ray absorption spectroscopy (XAS) and coupled the results to improved methods for quantum-mechanical modeling and simulation.

This tightly coupled experiment-and-modeling approach enabled Livermore researchers to measure, for the first time, the dynamic changes that occur in the electronic structure of graphene supercapacitor electrodes as they charge and discharge. The measurements—published as the cover article of the March 4, 2015,

An artist's rendering shows an x-ray photon entering the experimental cell (upper left) at the Advanced Light Source, illuminating a hydroxyl ion ( $\text{OH}^-$ ). The  $\text{OH}^-$  ion, disassociated from an aqueous solution of sodium chloride, has bonded to a carbon atom, forming part of a supercapacitor electrode made of sheets of graphene aerogel. The  $\text{OH}^-$  ion is colored red and is bonded to a white hydrogen atom to its immediate right. This achievement was featured as the cover story of the March 4, 2015, issue of the journal *Advanced Materials*. (Rendering by Ryan Chen.)

issue of the journal *Advanced Materials*—revealed two unexpected phenomena contributing to capacitive charge storage.

These findings bolster scientific understanding of how carbon-based electrodes store charge at the electrode–electrolyte interface. The results contradict conventional models and suggest strategies to optimize electrodes for their surprisingly complex operational state. More broadly, the results demonstrate the potential of using the new Lawrence Livermore in situ technique to study other important materials for energy storage.

The supercapacitor effort brought together Lawrence Livermore electrochemists, physical chemists, materials scientists, physicists, and theory and simulation experts, along with colleagues from Lawrence Berkeley National Laboratory. A substantial portion of the research was supported by the Laboratory Directed Research and Development Program.

Says Livermore chemist Jonathan Lee, “Our aim was to obtain an improved understanding of the physical and chemical processes involved in electrode operation.” Lee notes that a significant amount of research has been conducted on supercapacitor electrolytes, but until now only limited experimental work sought to characterize operating electrodes, even for widely used materials such as graphite. Supercapacitor electrodes were considered to be static, with charge accumulation or depletion being the only responses to polarization of the electrode–electrolyte interface. The limitations of this view of the electrode’s behavior largely reflected a previous lack of experimental and theoretical methods to characterize electrodes under operating conditions.

The Livermore-led team turned to XAS as a powerful technique to measure the changing electronic structure of operating graphene electrodes. Their XAS measurements revealed two unexpected features—covalent (that is, chemical) bonding between the negative ions and the otherwise inert carbon electrode surface, along with local stresses and strains that change electrode bonding and morphology. These two distinct phenomena were also found to have different behaviors in time—one nearly instantaneous, the other taking many minutes. In addition, both processes were largely reversible once charging stopped, explaining why they could only have been observed during operation.

### **Aerogels Bolster Supercapacitor Advantage**

The Laboratory’s findings have gained widespread attention in the energy world because of the growing hopes being pinned on supercapacitors. A capacitor stores energy by means of a static charge instead of an electrochemical reaction. Whereas a conventional capacitor is made up of positively and negatively charged conductive materials separated by an insulator, supercapacitors contain no solid insulator. Instead, two conductive, high-surface-area solids are immersed in an electrolyte solution. When a voltage is applied across the positive and negative plates, the negative electrode attracts positive ions from the solution, while the positive electrode attracts negative ions, charging the supercapacitor.

“Because of the large surface area and the atomic-scale distance between the ions and the electrode surface, carbon electrode supercapacitors can hold hundreds of times the electrical charge as standard capacitors and can therefore serve as a replacement or companion for batteries in many industrial and commercial applications,” states materials scientist Juergen Biener. Supercapacitors can also undergo frequent charge and discharge cycles at high current and short duration—an important property for meeting peak loads for electric vehicles or grid-scale demands, such as farms of wind turbines.

For the electrode material, Livermore scientists turned to graphene aerogel, which Livermore researchers have pioneered for

more than 30 years. In particular, Lee and his team focused on a three-dimensional nanographene bulk electrode material consisting of ruffled sheets one to three layers of carbon atoms thick. Says chemist Ted Baumann, “Being built from single-layer graphene sheets gives graphene aerogels the highest internal surface area of any pure carbon material—nearly 3,000 square meters per gram.” (See S&TR, April/May 2015, pp. 14–18.) This is key because the higher the surface area to store ions on both sides of the graphene sheets, the higher the overall charge storage capacity. Compared to traditional carbon-based electrodes, graphene aerogels also offer greater control of density and pore-size distribution, from 1 nanometer to several micrometers in diameter. Furthermore, conductivity is increased through interconnectedness of the carbon sheets and the absence of nonconductive binder materials.

### **Seeing the Light**

Probing the processes involved in graphene electrode operation presented “huge engineering challenges,” notes materials scientist Michael Bagge-Hansen, the first author of the *Advanced Materials* paper. The biggest challenge was conducting in situ XAS experiments on the Advanced Light Source (ALS) synchrotron at Lawrence Berkeley. To provide monochromatic x rays, the ALS generates a hair-thin ( $0.20 \times 0.01$  millimeter) beam of electrons and accelerates them first in a linear accelerator and then in a booster ring to nearly the speed of light, causing the electrons to emit x-ray light 1 billion times brighter than the Sun. Directed to an experimental apparatus, the light interrogates the electronic structure of matter.

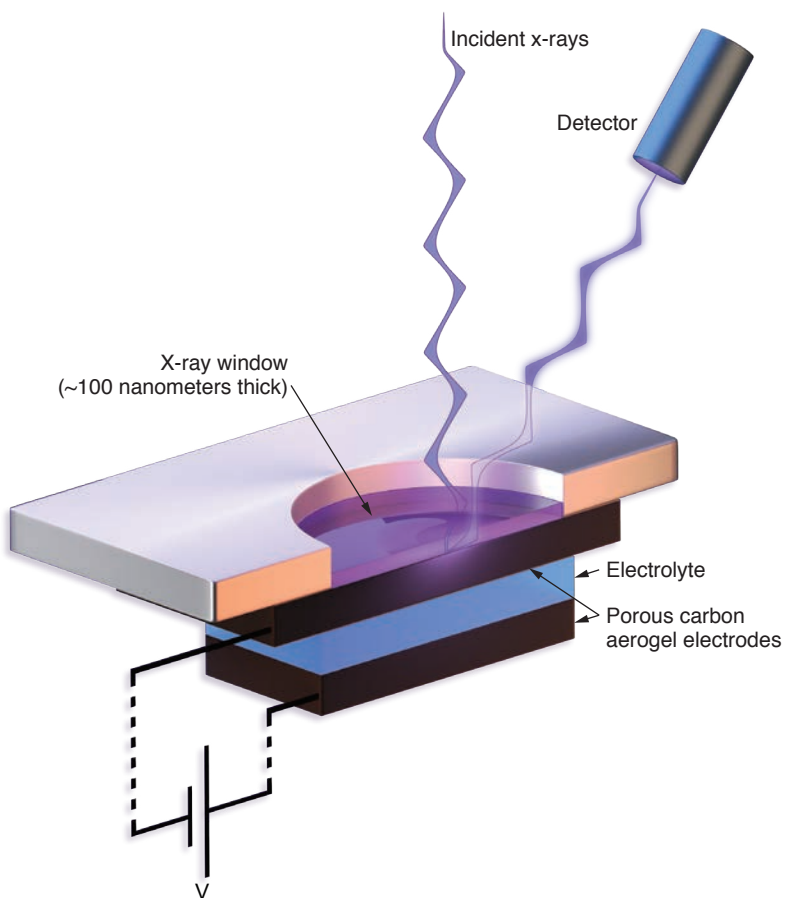
The Livermore team was already adept at XAS for studying the unoccupied electronic structure of elements in vacuum environments. XAS is extremely sensitive to changes in electron structure in ways that more traditional techniques cannot approach. Because carbon is a low-atomic-number element having only six protons, the appropriate x rays are low energy or “soft,” about 300 electronvolts. Soft x rays will not transmit through air, so experiments must be conducted under vacuum.

To measure the electrode material under in situ operating conditions, however, a fluid electrolyte was required. Lee therefore marshalled an effort to design and build a vacuum-compatible cell 2 centimeters in diameter and featuring a tiny supercapacitor measuring about 5 millimeters tall and 0.1 millimeter thick. The electrolyte was a standard 1 molar aqueous solution of sodium chloride.

The cell incorporated an x-ray window of silicon nitride only 100 nanometers thick (or a hundredth of the thickness of a human hair). The window separates the ultrahigh vacuum of the analysis chamber from the fluid electrolyte environment of the supercapacitor while allowing x rays to pass in and out of the sealed experimental cell, for detection of both x-ray absorption

and emission. The ultrahigh vacuum environment, with a pressure of  $10^{-9}$  torr (approaching that found in deep space), ensured that the soft x rays did not interact with air.

Probing the graphene aerogel with XAS, the researchers consistently saw two peaks corresponding to two events occurring on the positive graphene electrode. (No peaks were evident during the charging or discharging of the negative electrode.) Incoming x rays temporarily promote some of the carbon atoms' electrons to higher unoccupied electron states, leaving behind a hole. These



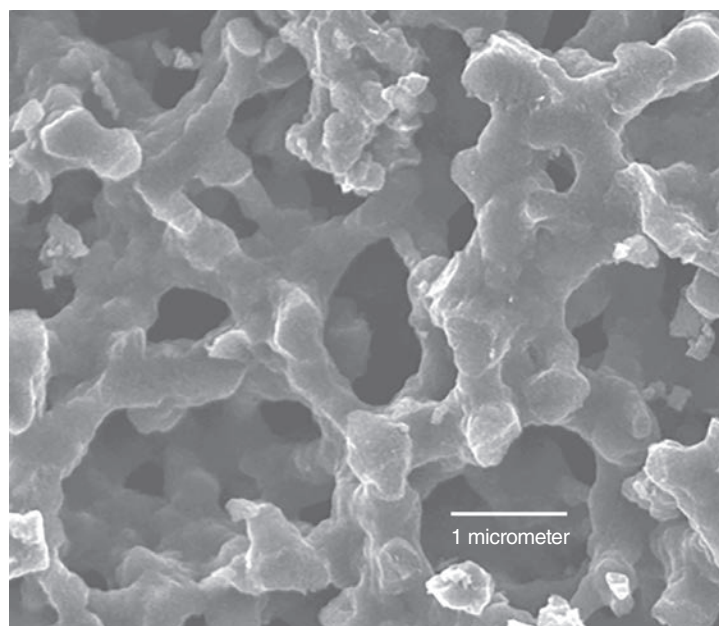
To enable measurements of supercapacitor electrodes while they operate, Livermore researchers built a vacuum-compatible cell that measured 2 centimeters in diameter and contained a tiny supercapacitor (5 millimeters tall and 0.1 millimeter thick) placed in an aqueous solution of sodium chloride, the electrolyte. The cell incorporated a window of silicon nitride 100 nanometers thick that lets x rays pass through the cell to permit detection of both x-ray absorption and emission. Although appearing solid in this illustration, the electrode is extremely porous to permit the buildup of large amounts of electrical charge at the electrode–electrolyte interface.

excited carbon atoms can return to a lower or ground state as electrons from filled states drop into the holes. When this happens, photons of particular wavelengths are emitted and can be detected as a function of incident x-ray energy, revealing the carbon's electronic structure. In short, the recorded peaks in photon intensity provide information about specific, significant physiochemical phenomena in the electrode.

## Two Surprises

To elucidate the mechanisms behind the two XAS signatures, Lee and his team brought in Livermore experts in advanced modeling and simulation, led by materials scientists Brandon Wood and Tadashi Ogitsu. One recorded peak was consistent with adsorption of a specific anion—a negatively charged ion—on the positive electrode surface. Wood and Ogitsu showed that this peak represented the nearly instantaneous adsorption of hydroxyl ions ( $\text{OH}^-$ ) from water molecules to the carbon atoms.

The sudden binding of  $\text{OH}^-$  from the dissociation of water molecules, rather than chloride ions, was a surprise to the team. The reaction is reversible—the ions return to solution upon removal of the applied voltage. The reversible adsorption of  $\text{OH}^-$  upon charging corresponded to a different means of storing charge



This scanning electron microscope image shows the extremely complex structure of a nanographene aerogel making up the Lawrence Livermore supercapacitor electrode. The gaps represent large pores, while crossing branches called ligaments possess much smaller pores. The interconnectedness of the carbon sheets increases electrical conductivity.

called pseudocapacitance, in which a direct chemical bond forms on the electrode surface and adds to the supercapacitor's total stored charge. "The observation of pseudocapacitive interactions, particularly the identification of the specific anion involved, was beyond our initial expectations," Lee emphasizes.

The second—and larger—peak at higher energies reflected a process unfolding on a much longer timescale—20 to 30 minutes. Lee explains that the electrodes of extremely thin sheets of graphene are not straight, instead resembling wrinkled or rippled pieces of paper combining to form larger intersecting structural features called ligaments. The resulting structures have pores with diameters ranging from the nanometer to micrometer scales.

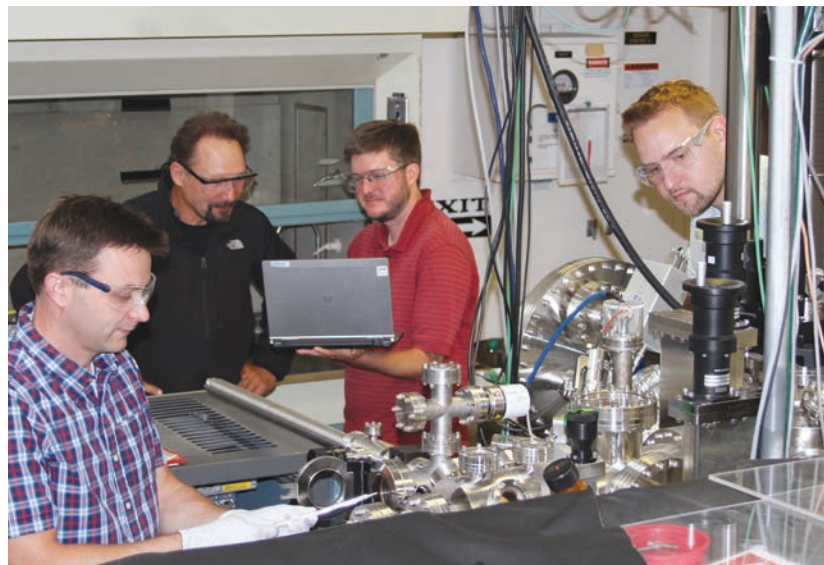
Charging occurs preferentially along the surfaces of larger pores because they offer the least resistance to diffusion. A thin layer of ions accumulates at the electrolyte–electrode interface, which serves as the primary source of charge storage in the system, as expected for a supercapacitor. However, the small, nanometer-scale pores provide much higher resistance to flow of ions in the electrolyte, and the pores' electrode–electrolyte interface takes longer to come into equilibrium.

Wood and Ogitsu's models indicate that different rates of ion flow and charge storage are locally experienced as tensile stress between neighboring pores, which initiates local planarization (flattening) of the graphene sheets. In effect, the electrode becomes stretched, removing some wrinkles and flattening the thin sheets of graphene. The phenomenon is indicated by the second spectral peak. Upon full charging, this stress gradient is partially neutralized. "We think that stress builds up initially, then dissipates slowly," explains Wood. Small areas of the sheets transition between rippled and stretched as the associated strain works its way throughout the electrode over approximately 30 minutes.

"Livermore's novel theoretical approach much more closely represents what is actually being measured and can serve as a direct interpretation of experiments," Wood comments. He explains that typically, scientists attempt to match experimental results with more conventional theoretical computations of electronic structure and make educated guesses. Instead, the Livermore method directly simulated the ALS experiments, including the applied voltage and the interaction of x rays with the graphene electrodes.

### Profound Changes

"A lot of intellectual effort across various scientific disciplines was required to figure out what was going on," notes Bagge-Hansen. "Our research findings were more complicated than we anticipated." The results, he says, were both "unexpected and not obvious." He also says that because both effects are transient and reversible, and are related to the specific interaction between the electrodes and the liquid electrolyte, "we would never have seen these two effects without monitoring operating electrodes."



(left to right) Livermore researchers Jonathan Lee, Juergen Biener, Brandon Wood, and Michael Bagge-Hansen test cell components for ultrahigh vacuum capability at Livermore in preparation for x-ray spectroscopy measurements of supercapacitor electrode behavior at Lawrence Berkeley's Advanced Light Source (ALS). The intense x-ray light at ALS—1 billion times brighter than the Sun—enabled the team to uncover previously unknown behavior.

Overturing the once generally held theory that graphene-based supercapacitor electrodes are electrochemically inert, the team demonstrated that they undergo profound changes during operation. Their research shows how capacitance and charge storage are not solely determined by the isolated properties of the electrode and electrolyte but rather are strongly influenced by electrode modifications that occur during charging and discharging.

Energy experts at Livermore declare that this more complete understanding of how operating supercapacitor electrodes function could lead to new and better strategies for improving the capacity and efficiency of supercapacitors and hasten their adoption in real-world energy storage applications everywhere, to the benefit of energy consumers the world over.

—Arnie Heller

**Key Words:** Advanced Light Source (ALS), battery, electrode, graphene aerogel, Laboratory Directed Research and Development (LDRD) Program, Lawrence Berkeley National Laboratory (LBNL), supercapacitor, x-ray absorption spectroscopy (XAS).

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