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Ultracapacitors Challenge the Battery

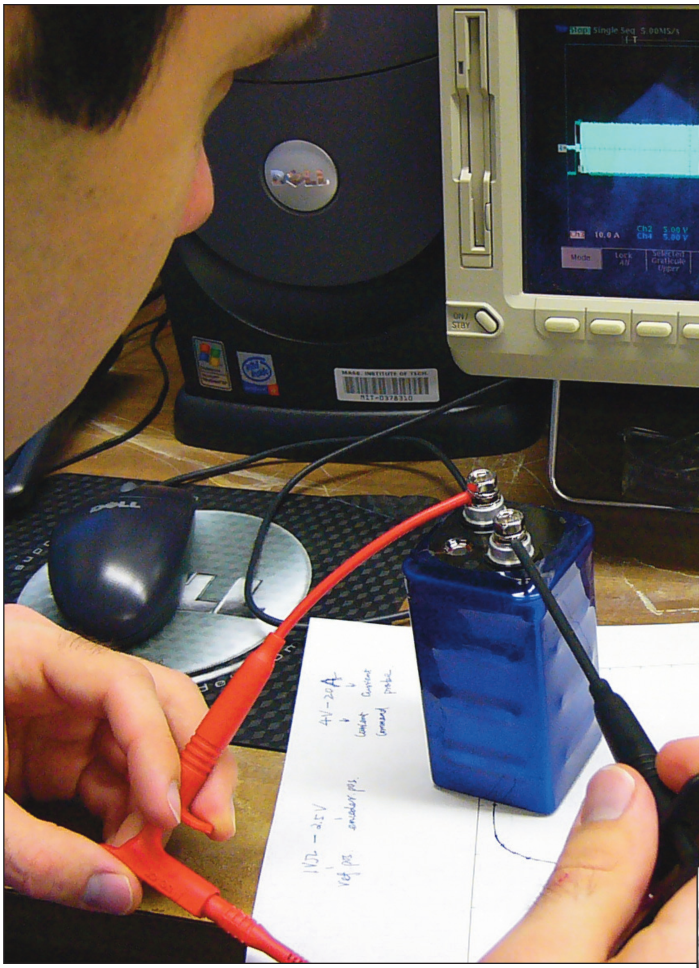
John M. Miller

Traditionally quick and powerful but energy poor, capacitors have transmuted into quick, powerful, and energy-rich storage devices whose first applications are likely to be in hybrid electric vehicles and backup power supplies.

Known for storing a short-lived jolt of electricity essential to the successful operation of electrical circuits in devices and appliances ranging from PCs to microwave ovens, cell phones, and televisions, the capacitor is in the midst of a major, ongoing upgrade of its energy storage capabilities. After nearly two centuries in which batteries have been the obvious choice for storing usable amounts of energy, high-end capacitors, known as ultracapacitors, are poised to challenge them in a growing range of applications.

"In fuel cell vehicles, ultracapacitors have demonstrated a higher recovery of energy from braking than batteries, are considerably lighter, have a longer economic life, and are more environmentally friendly in their manufacture and disposal," says Pierre Rivard, president and CEO of Hydrogenics of Mississauga, Ontario, a clean power generation company with a focus on fuel cells.

Looking beyond applications in cars, he continues, "When paired with fuel cells in stop-and-go mobility applications, such as forklifts, ultracapacitors provide burst power for lifting and acceleration and enable regenerative braking; in backup power



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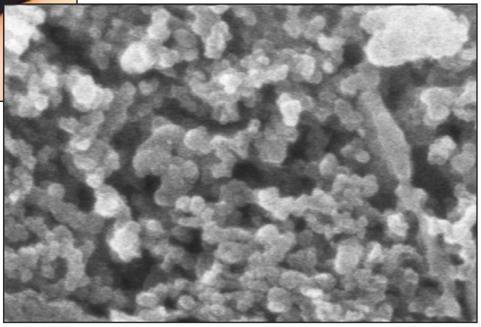


COURTESY OF RICCARDO SIGNORELLI / MIT

Above: Investigating possible automotive applications for ultracapacitors, MIT researcher Riccardo Signorelli here is setting up a test of the charge and discharge behavior of a 3,000-farad capacitor, whose stored energy is about one-eighth that of a D cell battery. **Right**: A high-resolution scanning electron micrograph of the ultracapacitor's electrode material reveals a tiny fraction of its highly involuted surface, on which charged species form a double layer.

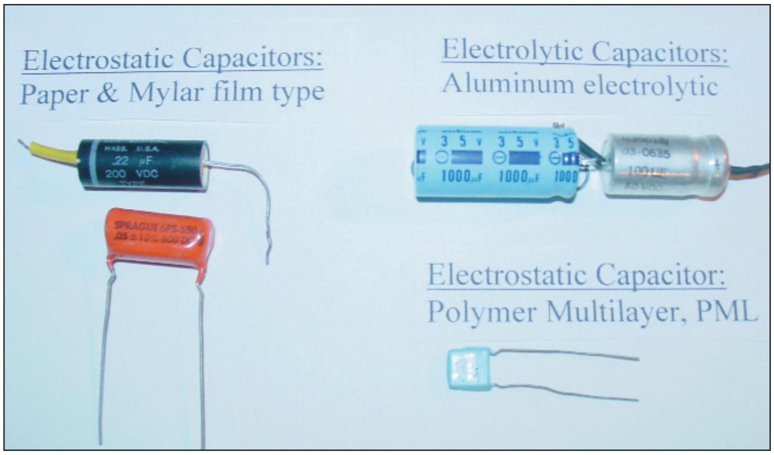
applications [ranging from hospitals to office buildings, factories, and homes], they provide instantly available short-term bridge power. In many applications they buffer power demand peaks, allowing our scalable fuel cell systems to be optimized for size and low cost."

Honda Motor Company is using ultracapacitors in its FCX hybrid fuel cell vehicle, a few test models of which are already on the road in California. According to a spokesman for Honda, "Utilizing ultracapacitors, we have gained an edge in energy efficiency and throttle responsiveness over competitors that are pursuing the hybrid battery/fuel cell model."

In February 2004, Maxwell Technologies of San Diego announced that it has contracted to provide ultracapacitors for 27 hybrid gasoline-electric buses being built for Long Beach Transit of Long Beach, California. Beyond these already superlative ultracapacitors, yet another generation with 10 times more energy-storage capacity was recently announced.

Battery's older brother

The capacitor has come a long way since it was invented in 1745 as a liquid-filled glass jar with a layer of foil wrapped around the outside. Through their generations of technological improvement, capacitors have progressed from a laboratory curiosity to an important laboratory instrument and, throughout the twentieth century, a key component of electrical circuits. The basic principle underlying the capacitor's operation is that of charge storage: Positively charged particles collect on one surface and negatively charged particles on a second nearby, but electrically separate, surface. The



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■ Capacitors of one of the three different types represented here perform essential roles in most electronic circuits. Note their relatively small capacitance rating, such as .22 microfarads (220 billionths of a farad) and 1,000 microfarads (one-thousandth of a farad).

two surfaces are called electrodes. Capacitors store electrical charges in static form for later use.

Three main factors determine how much electrical energy a capacitor can store: the electrode surface area; the electrode separation distance; and the properties of the insulating layer separating the electrodes. The history of capacitors has been written by numerous scientists, who have discovered the principles of capacitor operation and improved their storage capacity by increasing the electrode surface area, decreasing the electrode separation distance, and improving the insulating layer.

The physics of electricity evolved in tandem with improvements to the original jar accumulator, which was soon called the Leyden jar after the city where it was invented. An early and important technical improvement involved replacing the fluid electrode with a layer of foil lining the jar. Other important developments included replacing the jar's enclosing glass wall with a glass plate, which in turn was replaced by thinner and more pliable insulating materials. On a parallel path, electrode materials became thinner.

These developments opened the way for the spiral-wound capacitor invented in 1926 by Robert Sprague. To make it, Sprague simply rolled together a pair of thin conducting foils (the electrodes) separated by a paper insulating sheet, or dielectric.

During the early 1980s, ITW Paktron of Lynchburg, Virginia, and Siemens (now Epcos) of Munich developed stacked film capacitors for use in consumer electronics, automobiles, and appliances. Called polymer multilayer capacitors, such units are simply stacks of several thousand pairs of conducting plates, each separated by an insulator. Both spiral-wound and polymer multilayer capacitors are examples of electrostatic capacitors, which are based on the original concept of two physically distinct electrodes separated by a distinct insulating layer.

Electrostatic capacitors are widely used today in virtually every electronic item, from consumer appliances and toys to electronic boards in computers for PCs and spacecraft. In most of these applications, capacitors are tiny ceramic bricks attached directly to the electronic circuit boards. The ability to store small amounts of electricity and release them quickly makes capacitors essential components, along with transistors and resistors, of most electrical circuits.

Capacitors' Achilles' heel

The Leyden jar's property of releasing all of its stored electrical energy in a sudden spurt no doubt inspired scientists to seek a technology that could release a sustained current. This technology, the battery, was invented in 1800 by Alessandro Volta, an Italian physicist.

As Volta and numerous other scientists improved its performance, the battery quickly supplanted the Leyden jar's descendants. It has reigned as the

Electrostatic capacitors are widely used in virtually every electronic item, from consumer appliances to electronic boards in computers.

preferred technology for storing electricity for nearly 200 years. The battery doesn't store separated charged particles; instead, it stores charge through chemical changes at the electrodes. Thanks to the chemical changes, the battery can save large amounts of electrical energy and release them as a sustained current. On the downside, just as the battery is slow to take on its full charge, it is also slow to release the charge.

Ongoing improvements

The electrolytic capacitor was developed in the 1930s by the Cornell-Dubilier Electric Corporation in New Jersey. Thinking out of the box, the company's scientists and engineers introduced a new way of designing capacitors featuring three major enhancements:

- Expanded surface area: The surface of one aluminum electrode was etched with acid, leaving it roughened and pockmarked and offering more surface area on which to accumulate charge.
- Shrunken insulator thickness: After the electrode surface was etched, it was oxidized to cover it with an insulating layer of aluminum oxide that separates two layers of charges.
- A liquid (actually paste-like) electrolyte electrode: The roughened and oxidized surface of the aluminum electrode was immersed in an electrolyte, a solution whose dissolved molecules are readily ionized. The electrolyte in effect becomes an extension of the second electrode, the enclosing wall of the capacitor.

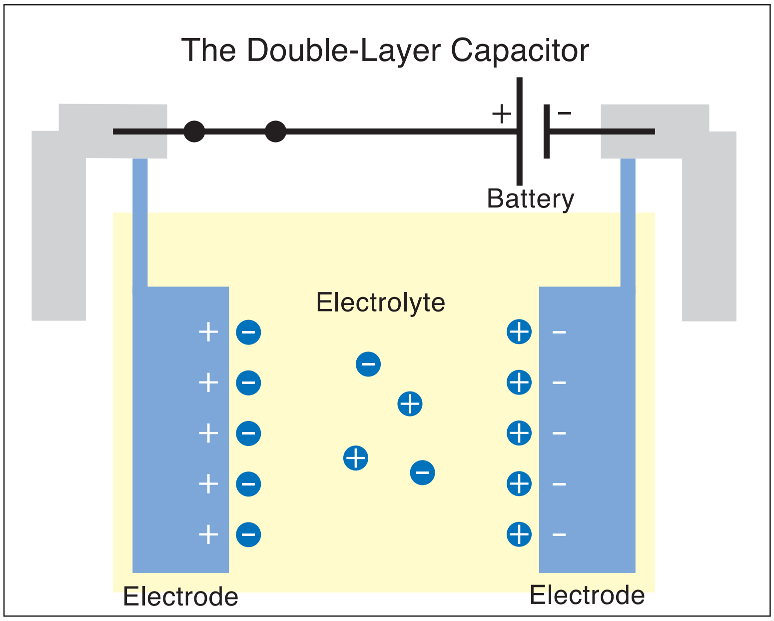
Although an electrolytic capacitor looks different than an electrostatic capacitor, it nonetheless exhibits all the characteristics of an electrostatic device: it has one conductive electrode separated from a second conductive electrode by a thin dielectric. Here, the operative word is thin. In an electrostatic capacitor, for comparison, the insulator may be a thin plate of glass or ceramic, a sheet of wax paper, or a piece of mica. As these materials are made thinner, however, they soon reach a limit—about one-tenth of a millimeter (10^{-3} meters)—based on their inherent brittleness and limited ability to withstand a voltage.

In comparison, electrolytic capacitor designs reduce the insulating layer's thickness dramatically by growing a thin film of alumina (Al_2O_3) over all the microterrain of the etched aluminum foil. This resulting insulating layer is only a few micrometers (10^{-6} meters) thick, so that charged species on opposite sides of it are separated by no more than a micron (10^{-6} meters). For electrolytic capacitors, the etched and oxidized metal foil is both an electrode and the insulating layer.

The electrolytic capacitor's second electrode is its container wall and the organic electrolyte that is in contact with the wall. The electrolyte permeates a separator material (between the container wall and the foil electrode) and wets the coiled-up and etched metal foil. Such conductive electrolytes consist of a paste made when boric acid dissolves in and reacts with glycol, the thick liquid commonly used in antifreeze. The high ratio of surface area (on the etched foil surface) to small charge-separation distance (across the aluminum oxide layer) accounts for the electrolytic capacitors' ability to store much more electricity than comparably sized electrostatic capacitors.

Going ultra

Ultracapacitors embody another round of innovations beyond the electrolytic capacitors. The charge-separation distance in ultracapacitors (more technically known as electrochemical double-layer capacitors) has been reduced to literally the



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■ Connected to a voltage source, a double-layer capacitor (an ultracapacitor) forms a double layer of charged species at the surface of each electrode. At the negative electrode, positive ions from the electrolyte pair up with electrons trapped below the electrode surface. The opposite pairing occurs at the positive electrode, where the positive charges below the surface are holes vacated by the electrons that have accumulated at the negative electrode.

dimensions of the ions themselves within the electrolyte. Here, charges are not separated by millimeters or micrometers (microns) but by a few nanometers. In our three examples, ranging from electrostatic capacitors to electrolytic capacitors to ultracapacitors, the charge-separation distance has in each instance dropped by three orders of magnitude, from millimeters (10^{-3} meters) to microns (10^{-6} meters) to nanometers (10^{-9} meters).

Coupling the ultrasmall separation distance with a relatively vast surface area, in ultracapacitors the ratio of available surface area to charge-separation distance has grown to an amazing 10 raised to the twelfth power. It is this ratio, in fact, that makes capacitors “ultra.” The ability to hold opposite electrical charges in static equilibrium across molecular spacing is the key feature. [For more details about how ultracapacitors achieve molecular-scale charge separation, see “Making a Capacitor Ultra” on page 133.]

The developmental path leading to today’s ultracapacitors originated in the work of Standard Oil of Ohio Research Center (SOHIO) in the early 1960s. SOHIO researchers discovered that two pieces of activated carbon immersed in an aqueous electrolyte solution and connected across the terminals of a battery acted as a capacitor. Later, SOHIO’s scientists explored the use of organic electrolytes, but at the time (early 1970s) there was really no market for such devices and little understanding of what was happening in them. Nonetheless, this new type of capacitor worked very well.

SOHIO licensed its double-layer capacitor technology, as it came to be known, to NEC in 1971. During the 1980s Matsushita Electric Company patented a method of manufacturing ultracapacitors having improved electrodes. As designers became more familiar with the technology, applications proliferated, especially for the coin cell types of ultracapacitors such as those manufactured in Japan by Nippon Electric Company, Elna/Asahi Glass, and Matsushita. (Coin cell capacitors are similar in appearance to the small batteries common to watches, cameras, and portable electronics.)

In early coin, or “button,” cells, one electrode was the shallow aluminum can forming the base of the cell. The second electrode was the combined unit of the disk-shaped aluminum lid plus an attached porous carbon pellet formed by pressing together activated carbon powder and dilute sulfuric acid. In these cells, the carbon pellet and aluminum can are electrically isolated from each other by an ion-permeable separator. Contact between the can and lid is blocked by a rubber gasket.

Throughout the 1980s and ’90s, manufacturing of ultracapacitors was primarily an art.

Up, down, and everywhere

Giving numbers to trends in capacitor performance and costs requires some capacitor language: capacitance and farad. Capacitance refers to the capacitor’s unique ability to store electrostatic energy (which is different than the electrochemical energy stored by the battery). A farad is the unit measure of capacitance. Today’s ultracapacitors achieve capacitances ranging up to 2700 farads, while the whole family of capacitors offers capacitances ranging down to microfarads (10^{-6} farads), nanofarads (10^{-9} farads), and even picofarads (10^{-12} farads).

Recently, automated assembly techniques have replaced the labor-intensive aspects of ultracapacitor manufacturing and costs have decreased substantially. For instance, in mid-1980 a 2.3-volt ultracapacitor rated at 470 farads and manufactured by Panasonic (Matsushita Electric) cost roughly $2 per farad. Today, that same ultracapacitor would cost one-twentieth as much at 10 cents per farad, and costs continue to decrease rapidly as ongoing automation replaces hand assembly. According to informed sources, when ultracapacitor costs decrease by another factor of 20 to below 0.5 cents per farad, these components will be affordable in mass-market automotive applications.

Making a Capacitor Ultra

Ultracapacitors resemble batteries in having two electrodes immersed in an electrically responsive liquid, the electrolyte. Applying a potential (voltage) across the ultracapacitor’s electrodes polarizes the electrolyte, with roughly half of the electrolyte molecules transferring an electron to the other half. The resulting positive and negative ions migrate via the impressed electric field to their respective electrodes. There, although they form a charged layer on the surface and the electrode is oppositely charged, no electrons are exchanged across the electrode surface due to the electrode’s electrochemical properties. Contact between the two electrodes is blocked by a porous separator.

Although the electrodes appear to be a lightweight, solid layer of carbon, examination at the nanometer scale reveals a vast labyrinth of interconnected, nearly uniformly sized caverns whose walls all become charged when a voltage is applied across the two electrodes.

The physicists’ model of conduction-band electrons in metals helps explain what happens inside the carbon when the voltage is applied. All of the involuted surface area of each electrode becomes an energy-level boundary. Just beneath the surface of the negative electrode, for example, is a conduction band occupied by a horde of roving electrons that lack the energy to escape from the surface. In a similar band at the positive electrode, “holes,” or electron vacancies, rove beneath the surface but are unable to capture electrons from outside.

When positively charged electrolyte ions form a layer on the surface of the negative electrode, electrons beneath the surface pair up with them. These two layers of separated charges, then, are a capacitor storing static charge. Similarly, at the positive electrode, holes pair up with negative ions, forming a second electronic double layer that itself is a capacitor. Electrochemists and engineers describe capacitors based on this design concept as electrochemical double-layer capacitors.

For each of the two electrochemical double layers, the negative and positive charges are separated by only half the diameter of the electrolyte ions. This molecular-scale charge-separation distance, coupled with the great surface area of the activated carbon electrodes, yields the ultracapacitor’s extreme storage capabilities.

—J.M.M.

Scientists are busy on the frontiers of ultracapacitor research, pushing up the capacitance rating and pushing down the costs. In October 2003, JEOL Ltd. in Tokyo announced an improved ultracapacitor it refers to as a nanogate or nanocarbon capacitor. This new component has an energy density of 50–75 watt-hours per kilogram, more than 10 times that of existing ultracapacitors. The device features two carbon electrodes formed of a new, patented

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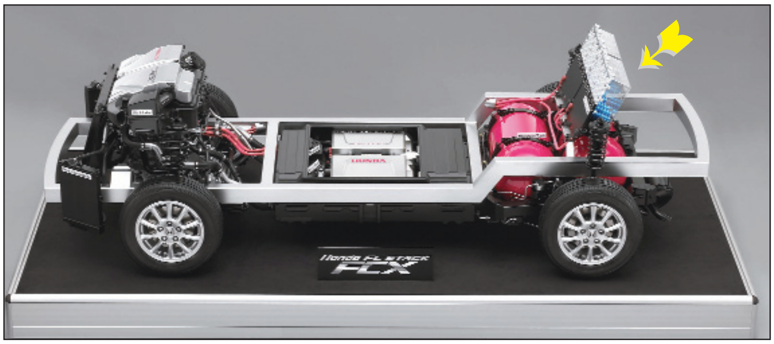

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Left: The ultracapacitor bank carried on the Honda FCX fuel cell car comprises 160 ultracapacitors, as shown in the cutaway model mounted on a demonstration base of the car. With each ultracapacitor carrying a 2.7-volt charge, the entire bank delivers electricity at more than 400 volts. The red fuel tank directly below the ultracapacitor contains compressed hydrogen, with which the car's fuel cell generates electricity for storage in the ultracapacitor or for powering the electric motor that drives the wheels. **Left below:** In the FCX, the ultracapacitor bank (yellow arrow) is positioned behind the rear seat, as shown in the FCX cut-body model.

material whose uniqueness lies in its high porosity and accessibility for storing ions. The company's goal is to start shipping samples of nanogate capacitors by the end of 2004.

Even further out on the experimental edge, researchers are exploring the possibility of using carbon nanotubes for ultracapacitor electrodes. The importance of carbon nanotubes lies in their uniform nanoscopic pores (about 0.8 nanometers in diameter), which could in theory store much more charge than the nanogate capacitors if the nanotubes could be properly assembled into macroscale units.

The leading manufacturers of ultracapacitors today are Maxwell Technologies in the United States, NESS Capacitor Company in South Korea, Okamura Laboratory in Japan, and EPCOS in Europe. These companies manufacture carbon-carbon, or symmetric, ultracapacitors. That is, both electrodes have identical construction. There are some differences in the organic salts and solvents used, and this is where ultracapacitor manufacturing becomes proprietary.

According to Andrew Burke of the Institute for Transportation Studies, University of California at Davis, the carbon-carbon ultracapacitors all have relatively similar ratings. The ultracapacitors produced by the companies listed above are rated at 2.5–2.7 volts, with specific capacities clustered at 5 farads/gram (packaged product). By contrast, the new nanogate device exhibits a capacitance of 30 farads/gram.

Applications of ultracapacitors

Ultracapacitors are now finding their way into automotive and utility applications as energy storage components. Utilities have interest in ultracapacitors as replacements for battery banks that are being used to buffer short-term outages on the power grid. There are also applications of ultracapacitors in uninterruptible power sources located on the premises of critical-load utility customers such as hospitals, banking centers, airport control towers, and cell phone towers. The ultracapacitor bank would supply a continuous flow of power to such customers during the critical seconds between a utility outage and bringing a standby diesel-engine-driven generator on line.

Perhaps the most pervasive application of ultracapacitors as power components is beginning to show up in fuel cell–powered automobiles, a few of which are being manufactured by Honda Motor Company, as mentioned earlier, and also by Toyota, General Motors, and others for lease to cities in the United States and elsewhere. The performance profiles of ultracapacitors and fuel cells are highly complementary, especially for powering vehicles driving in stop-and-go traffic. Fuel cells provide the sustained energy as it is needed, but they fall short in delivering the burst energy needed for starting and accelerating. Ultracapacitors excel at providing exactly those short bursts of energy and also at receiving and storing energy bursts produced by regenerative braking.

Ready for the lithium-ion big league?

Lithium-ion batteries of the type used in cell phones, laptops, and gasoline-electric hybrid cars and fuel cell vehicles are very energetic compared to ultracapacitors. Typically, today's commercially available ultracapacitors deliver only one-tenth the energy of a comparable-weight battery, but because they deliver energy much faster than a battery does, they are gaining ground in a market already strongly courted by battery manufacturers.

The announcement of the nanogate capacitor heralds the imminent arrival of the Leyden jar's descendants into the lithium-ion big league. When nanogate capacitors enter the marketplace they will offer the rapid charge and discharge properties of ultracapacitors along with the energy storage capacity of batteries. This is amazing for a device that is simply an accumulator of electric charge.

When capacitors can store as much energy as batteries while avoiding much of the environmental threat posed by the metals (such as lead, nickel, cadmium, and mercury) required to run the battery's electrochemical process, a new era of energy for transportation will begin. Costs, of course, will need to come down, and the devices will need to be proven functional and highly reliable in daily use.

As each of these obstacles is met and overcome, the new ultracapacitors coupled with fuel cells will be a major factor in the shift toward automotive systems that are environmentally friendly and fuel efficient. Beyond automobiles, as well, the new technology seems likely to infiltrate the nooks and crannies occupied by today's batteries, ranging from flashlights to cell phones and laptop computers. In the twenty-first century, the capacitor may finally get the respect that until now has been claimed by its younger brother.■

John M. Miller, owner of J-N-J Miller Design Services, in Cedar, Michigan, holds 44 patents on various aspects of automotive power and propulsion systems. He chairs the KiloFarad International Education and Outreach working group devoted to promoting ultracapacitor technology. He retired from Ford Motor Company's Scientific Research Laboratories in 2002. The author extends his thanks to the following for helpful discussions and comments: Richard Smith Sr., Maxwell Technologies; Robert Waterhouse, Amtek Research; Joel Schindall, MIT; Tom Saunders, ITW Paktron; and Claude Letournou, KiloFarad International.

On the Internet

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MANUFACTURERS

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JAPAN: OKAMURA LABORATORY; JEOL
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RUSSIA: ESMA-CAPACITOR
www.esma-cap.com

SOUTH KOREA: NESS CAPACITOR COMPANY
www.nesscap.com/index.html

U.S.: MAXWELL TECHNOLOGIES
www.maxwell.com/ultracapacitors/index.html