Miniaturized POWER

With nanobatteries, power sources finally shrink with the rest of electronics

By Charles Q. Choi

The transistor, dating from 1947, has shrunk from a kludgy, half-inch-high contraption to a device whose components boast dimensions a few hundreds of atoms in length. Batteries, on the other hand, have improved how much power they deliver at roughly one fiftieth of that pace.

Bell Laboratories, which built the first transistor, has now become involved with the reinvention of the battery. The goal is to apply the techniques used for manufacturing transistors to mass-produce a battery that can be built in with the other circuitry on a chip. The device, called a nanobattery, shrinks features of the electrodes to the nanometer scale.

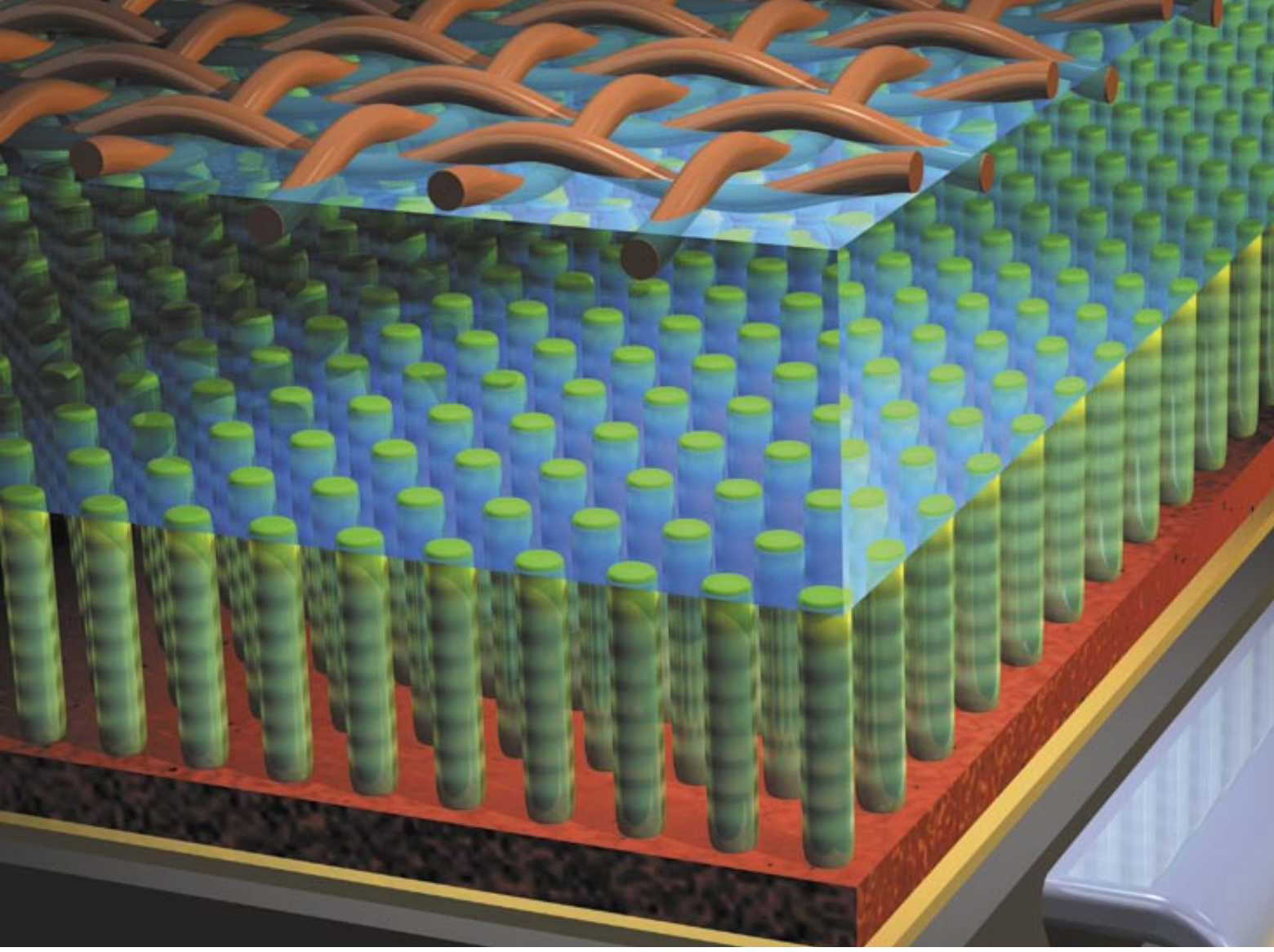
The design of the nanobattery enables it to lie dormant for at least 15 years, perhaps as a power source for a sensor that monitors radioactivity or one that tracks the buildup of toxic chemicals. It is then capable of waking up and immediately providing a burst of high energy. The concept could also lead to the first batteries that can clean up after themselves, by neutralizing the brew of toxic chemicals inside.

Growing Nanograss

THE GENESIS of the nanobattery springs from an earlier Bell Labs foray into nanotechnology. In the fall of 2002 Lucent Technologies, Bell Labs' corporate parent, was preparing to launch the New Jersey Nanotechnology Consortium with the state government and the New Jersey Institute of Technology. The idea was to make the company's research, development and prototyping services accessible to industry, academic and government nanotechnologists. David Bishop, vice president of nanotechnology research at Bell Labs, had begun seminars for company scientists to share ideas on how their research might find novel applications for consortium members to develop further.

One Bell Labs presenter, Tom Krupenkin, had worked on liquid microlenses, the kind now often found in camera phones. These lenses consist of droplets that can alter their focal properties by changing shape in response to a voltage applied to a surface with which they are in contact. In response to the voltage, these so-called electrowetting surfaces can turn from superhydrophobic to hydrophilic.

Superhydrophobicity is the property that helps rain roll off duck feathers and lotus leaves. Surface tension makes drops of liquid want to bead up, but the solid they rest on can exert attractive forces that cause them to spread. On hydrophilic substances such as glass, water stretches out. But on superhydrophobic materials, droplets ball up completely,



NANOGRASS consists of 300 nanometer-wide pillars, which resemble grass blades. A radically new battery concept incorporated these structures, which kept a liquid electrolyte on top of the nanograss until the power source was ready to be activated.

essentially not interacting with those surfaces at all.

Given that droplet behavior on a superhydrophobic surface, Krupenkin reasoned, electrowetting could help control a chemical reaction. He sketched out a concept that involved rows of superhydrophobic nanometer-wide pillars that can exhibit electrowetting. Under a microscope, these resemble a field of evenly cut "nanograss." Such nanograss can be made with standard microchip industry techniques developed over the decades to work on silicon. Applying a voltage to the liquid, scientists could create a reaction that causes the pillars to become hydrophilic and draw the droplets down to penetrate the interstices among the nanopillars. The liquid could then react with any compound that rests at the bottom. It struck Krupenkin that the liquid could be used to create power in a nanobattery.

Batteries are essentially chemical reactors. A disposable battery consists of two electrodes, an anode and a cathode, bathed in an electrolyte solution. The compounds that make up both electrodes react with each other via the electrolyte to generate electrons. The problem, however, is that these electrochemical reactions happen even when batteries are not connected to devices. The average battery loses as much as 7 to 10 percent of its power a year when not in use.

So-called reserve batteries employ physical barriers to keep the electrolyte separate from the electrodes until the batteries are activated; the especially aggressive electrochemical reactions that result provide bursts of high energy. The mechanical challenge of keeping the electrolyte away from the electrodes translates into large and clunky batteries. Consequently, they mainly find use in emergency situations, such as in hospital intensive care units or operating rooms, and in military applications, such as night-vision goggles or laser illumination.

The advent of nanograss offered the possibility of making reserve batteries far easier to miniaturize. Moreover, instead of reacting all the chemicals at once, researchers can design their battery to activate only fractions of the field of nanograss at one time, Krupenkin explains.

Bell Labs started to shop the nanograss concept around. "Lucent is not a battery company but would like to revolutionize batteries," Bishop says. At a seminar in late 2003, a company called mPhase heard a presentation from Lucent about a nanotechnology-based bat-

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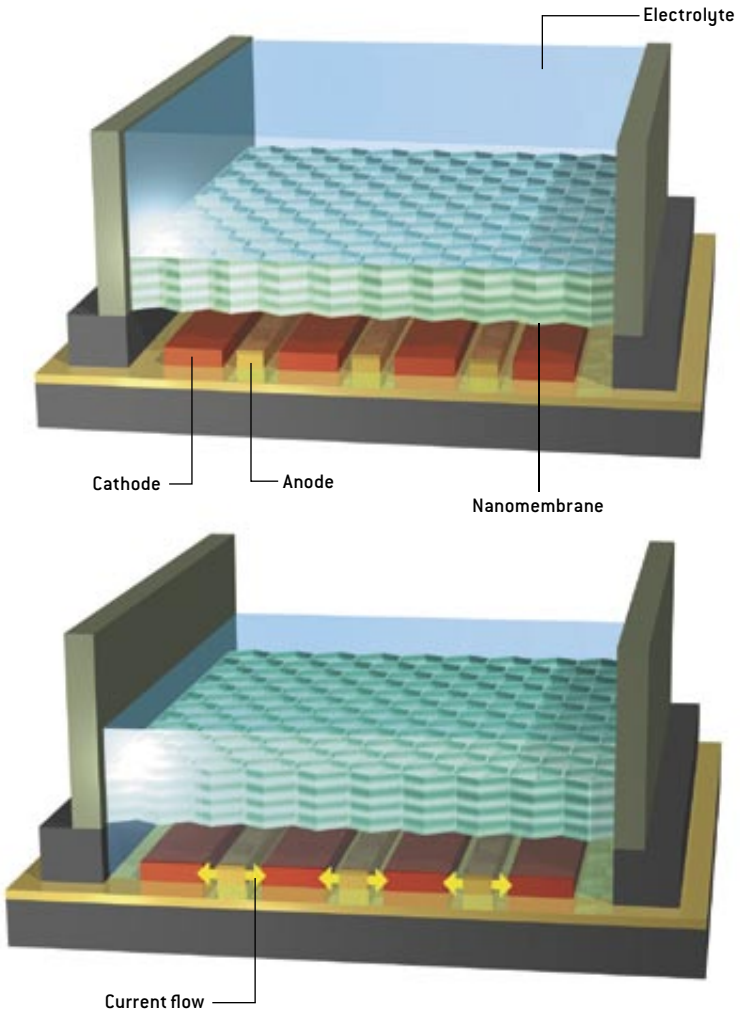
DESIGN FOR A NANOBATTERY

A battery prototype nanomembrane built by mPhase and Bell Labs keeps electrolyte separated from the negative and positive electrodes (the cathodes and the anodes), which gives the battery a longer life. In the initial, unactivated state (*top*), the zinc anodes and manganese dioxide cathodes lie in patches on the floor of the battery, physically separate from one another. Above them rests a porous honeycomb membrane, made of silicon and covered with a layer of silicon dioxide and a fluorocarbon polymer. Atop this barrier is the zinc chloride electrolyte solution.

In the activated state (*bottom*), the electrolyte has penetrated the honeycomb to immerse both the anode and cathode patches. Once the anodes and cathodes are linked by the electrolyte, they react with one another to generate electricity.



tery. "We left the room and said, 'Holy mackerel, that was spectacular,'" remembers Steve Simon, mPhase's executive vice president of engineering, research and development. At the time, mPhase was primarily a home broadband and video DSL components firm that was spun out from Norwalk, Conn.–based Microphase, a microwave electronics company for the military, aerospace and telecommunications industries.

As telecommunications hardware increasingly became a commodity market, mPhase chief executive officer Ron Durando sought to reinvent the company as a nanotechnology provider. He specifically wanted a device that would not take too long to develop, would not have medical uses that could tie it up with the red tape of clinical trials, and could serve a military market that supported the premium prices nanotechnology devices often command in early production runs. "The battery fit all three," Simon explains.

In March 2004 mPhase sealed a joint development agreement to commercialize the nanobattery. While mPhase investigates what potential customers want from the battery to create profitable devices, Lucent provides the license for the technology in return for royalties, the benefits of a $450-million clean room and access to scientists with decades of experience in silicon manufacturing.

Getting It to Work

BY SEPTEMBER 2004 the scientists had an operational model in their laboratory that could generate current. To get its prototype, the team had to create silicon pillars each roughly 300 nanometers wide and spaced about two microns apart. For power generation, the researchers employed compounds used in common alkaline batteries, with zinc as the anode material and manganese dioxide as the cathode. The silicon floor the pillars rest on is coated with zinc, whereas the pillars themselves are covered with silicon dioxide, which allows the investigators to control the voltage of the device, and the nanopillar tips are coated with a Teflon-like fluorocarbon layer, which exhibits the electrowetting behavior.

"Things that are simple conceptually are hard to get to work," Krupenkin emphasizes. Placing zinc only on the bottom involved "one huge challenge after another," he recalls. To deposit metals in specific places, scientists typically use a process known as electroplating. Electroplating does not work on oxides such as the silicon dioxide in the nanograss device, however. So a way had to be devised to make the silicon floor free of silicon dioxide, allowing the zinc to grow on it, while leaving the silicon pillars covered with the oxide. The solution was to coat both the silicon floor and pillars with the oxide but to leave the layer on the floor the thinnest. The oxide was etched away from the entire device using ionized gas, until the floor had no oxide, although the pillars still did.

SLIM FILMS

Yet electroplating does not work on silicon either. So the researchers used wet-chemistry techniques to deposit nickel or titanium on the floor as a seed layer for zinc to stick to during electroplating. Growing zinc in a uniform manner so that there were not small mountains of zinc in some places and none elsewhere required laborious trial and error by fiddling with temperatures, electric current and concentrations of chemicals. "Looking back, I'm surprised it took only a year," Simon remarks.

After the scientists had a prototype working, they began to talk to potential customers. These discussions triggered a radical revamping of the battery. The initial design was a sandwich, with the cathode on top, the zinc chloride electrolyte solution in the middle, the nanograss under it and the anode on the bottom. Officials at the U.S. Army Research Laboratory in Adelphi, Md., expressed concern about how constant contact between the electrolyte and any electrode could result in unwanted chemical reactions. After the redesign, electrolyte now rests on top, the anode and cathode compounds occupy physically separated patches on the bottom, and a nanosilicon barrier is suspended in between, which, when activated, enables the electrolyte to penetrate and immerse the electrodes.

The team originally used nanopillars to separate the electrolyte from the anode because the pillar took up the least amount of space, allowing more surface area for chemical reactions between those electrodes. But the difficulty of manufacturing the nanopillar battery design prompted researchers instead to develop a nanohoneycomb membrane to isolate the electrolyte from the electrodes. Creation of the electrowetting membrane, with pores 20 microns across and thin, fragile walls 600 nanometers wide, was also a challenge. First the scientists used a plasma to etch the delicate honeycomb structure from wafers of silicon covered in silicon dioxide. Then they grew silicon dioxide on the bare silicon walls of the pores in furnaces heated to 1,000 degrees Celsius and suffused with oxygen. Finally, they coated the entire honeycomb with fluorocarbon.

The researchers developed their first redesigned samples in October 2005. One of the great advantages of the system is that it now helps the team avoid having to laboriously find the exact conditions required to grow a uniform anode layer amid a forest of nanopillars every time it wants to try out a new anode-cathode combination. Instead the scientists can simply lie the electrode patches down on otherwise featureless surfaces. At the same time, the experience they gained in electroplating should make creating the patches far easier, Simon notes. Bell Labs and mPhase are currently collaborating with Rutgers University on incorporating the kind of lithium-based battery chemistries found in digital cameras and cellular phones.

The nanobattery might also allow for a more environmentally friendly power source that includes compounds that can entomb the electrolyte. "That would keep it from leaching into the ground or, if soldiers got shot, would keep the battery from leaking all over them," Krupenkin says. Plastic nanostructures might also be used in place of employing silicon, Simon adds, potentially paving the way for flexible nanobatteries.

The scientists are not seeking to replace disposable batteries, since mass production of those "is in the fractions of cents per AA battery," Krupenkin says. Instead they are targeting more specialized applications, such as sensors dropped from military aircraft that may have to use their radio transmitters just once or twice in their lifetimes, to signal the presence of intruders, for instance, or toxins or radiation. "If the sensor sees nothing interesting, it has nothing to transmit, but if it does, it needs a lot of power," Krupenkin explains. Alternatively, devices monitoring environmental change could use that extra juice to transmit over larger distances, thereby cutting down on the number of sensors needed. Emergency reserve batteries might also be incorporated into medical implants, cell phones or radio-transmitting pet collars.

The team has considered a rechargeable version of their device. A pulse of current could run through a depleted nanobattery, causing the surface on which the electrolyte rests to heat. That could evaporate a tiny layer of the liquid, forcing the droplet to jump up back on top of the nanostructure. "In principle, it's possible. In practice, it's really far out," Krupenkin cautions. For instance, mPhase expects to get product samples to potential first adopters in two to three years. A nanobattery would demonstrate how power sources are finally beginning to keep pace with the revolution in miniaturization that has driven the rest of the electronics industry for decades. SA

A nanomembrane separated the electrolyte from the electrodes in a later battery design.

Charles Q. Choi is a frequent contributor to Scientific American.

MORE TO EXPLORE

From Rolling Ball to Complete Wetting: The Dynamic Tuning of Liquids on Nanostructured Surfaces. T. N. Krupenkin, J. A. Taylor, T. M. Schneider and S. Yang in *Langmuir,* Vol. 20, pages 3824–3827; May 11, 2004.

A film about one phase of development of the nanobattery is available at **www.mphasetech.com/video/mphase.mov**

A Novel Battery Architecture Based on Superhydrophobic Nanostructured Materials. V. A. Lifton and S. Simon. **www.mphasetech.com/nanobattery_architecture.pdf**

BELL LABS, LUCENT TECHNOLOGIES (*nanomembrane*)