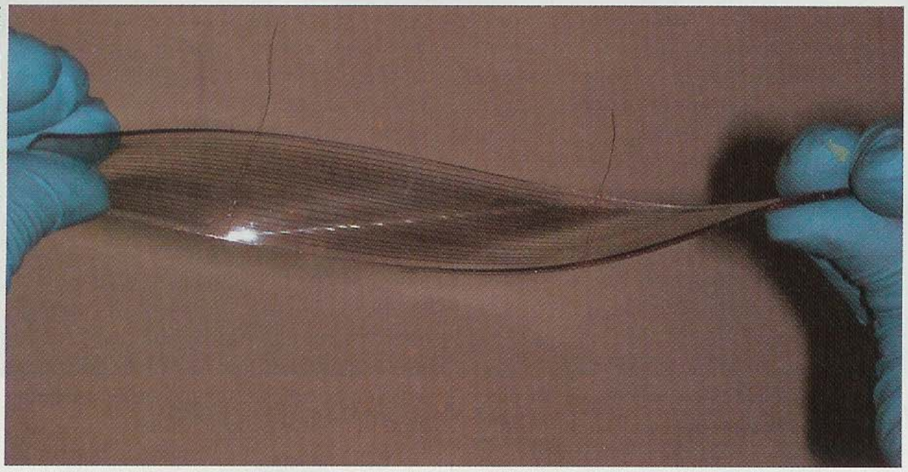
ITN ENERGY SYSTEMS PHOTO



TWISTABLE A prototype PowerComposite developed by ITN Energy Systems contains 19 PowerFibers (thin-film batteries on fiber substrates) embedded in a flexible plastic.

SOFTER, PLIABLE ELECTRONICS

Symposium highlights advances in mating electronics with textiles and plastics

RON DAGANI, C&EN WASHINGTON

LOOK AT ANY ELECTRONIC DEVICE and typically what you'll see is a hard, rigid, rectangular artifact that is mounted in or bolted to another hard, rigid, rectangular structure, observes Elana C. Ethridge, a microsystems technology program manager at the Defense Advanced Research Projects Agency (DARPA). But electronic systems, she thinks, "especially those that operate in or interact with the natural environment, should be able to conform to an environment that is characterized by irregular shapes and forms and is softer, more pliable, and flexible."

Ethridge is not alone in entertaining this vision. Many teams of chemists, physicists, materials scientists, engineers, textile scientists, and computer scientists are working to develop new electronic technologies based on conducting fibers or organic thin-film materials. These technologies include lightweight, flexible displays on paperlike sheets of plastic (C&EN, Jan. 15, 2001, page 40), thin-film batteries and solar cells that can easily be carried and used anywhere, and textiles that have electrical functions.

Remember that old electric blanket you were afraid to put through the washing machine? The one with the gnarly resistance cable running through the fabric? That's been replaced on the market with washable heating blankets in which electrically conducting metal fibers are woven into the ultrasoft fabric. If you know where to go, you can also buy a self-heating diving suit, a ski jacket with a built-in mini-disc music system, and—soon perhaps—a washable garment that can continuously record the physiological functioning of the wearer.

At last month's Materials Research Society meeting in Boston, a two-day symposium titled "Electronics on Unconventional Substrates" devoted the first day to electrotextiles and the second day to thin-film flexible circuits.

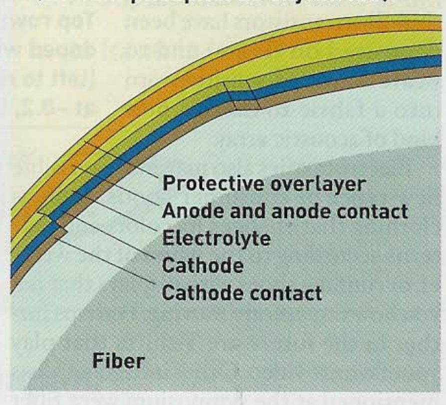
That first day was awash with discussions of ambitious development projects involving electrotextiles, with military applications being a major thrust of the work. For example, Patricia M. Wilson, a senior engineer at Foster-Miller, a technology development firm in Waltham, Mass., described how she and her colleagues are working to incorporate antennas into soldier apparel. The aim, she explained, is to make it possible for every combat soldier in the U.S. Army to carry a disguised antenna in his clothing and thus remain in radio contact with other members of his squad without attracting undue attention. Enemy combatants normally are looking to take out the "radio guy"—the soldier with the whip antenna extending a meter above his head. Making the antenna an integral part of the fabric of the soldier's uniform also helps to lighten the equipment load the soldier must carry and reduce encumbrances.

"THE ULTIMATE in unobtrusive antennas is one that conforms to the body" and does not interfere with the normal movements of the soldier, noted Justyna Teverovsky, a materials scientist at Foster-Miller.

Teverovsky, Wilson, and their colleagues are currently trying to figure out how a fabric-based antenna can best be protected from the effects of mechanical abrasion, wetness during operation, and washing. According to Teverovsky's poster presentation in Boston, trials are leading to the conclusion that applying a waterproof

BATTERY ON A FIBER

The "lithium-free" PowerFiber is fabricated without a lithium anode. The metallic lithium that forms the anode plates out onto the anode contact (nanoengineered copper) during the initial charging. The electrolyte and overlayer are the same material: glassy Lipon (lithium phosphorus oxynitride).



Silicon technology cannot, at this point, make flexible displays possible; organic materials potentially could.

coating to the yarn before it is woven into a fabric may provide the most effective waterproofing.

Electrotextiles also are being studied as a potential matrix or scaffold for acoustic arrays. Today, soldiers set up arrays of microphones in the field to track and identify tanks or other military vehicles, detect incoming missiles, and monitor other security threats. It would be far easier to unfurl a swath of electrotextile studded with tiny microphones and deploy it on the ground or on a vehicle, for instance. Vibrations picked up by the fabric's microphones would be transmitted to a computer, which would use algorithms to determine the source of the sounds.

A group of scientists at North Carolina State University, Raleigh, has demonstrated the concept by attaching 20 button-size microphones to a 3-foot by 10-foot swath of electrotextile. The next step is to build a larger array containing 96 microphones.

A member of the NC State team—Ph.D. student Anuj Dhawan of the department of textile and apparel technology and management—told C&EN that, at present, microphones have to be manually attached to wires in the fabric after it has been woven. The eventual goal, though, is to incorporate microphones on the yarn (in much the same way as thin-film transistors have been deposited on fibers) and to weave the sound-sensitive yarn into a fabric to make a new kind of acoustic array.

Electrotextiles also may make possible new types of consumer goods, such as clothing that changes its colors and patterns according to the whim of the wearer, or running shoes with displays that tell you how fast you are moving. Perhaps further in the future are T-shirts that play your favorite video. Other intriguing ideas mentioned at the symposium were fiber networks that serve as the nervous system of a skyscraper, warning of stress and strain, and a "smart" carpet that would unobtrusively screen people treading on it for security threats such as firearms or explosives.

The opportunities seem endless, but scientists and engineers face many challenges in merging electronics with textiles and other flexible materials. One of the major challenges in electrotextiles is forming reliable interconnections between wires that cross each other, according to John F. Muth, an assistant professor of electrical and computer engineering at NC State. And you also need to be able to disconnect—or isolate from each other—two wires that cross in the fabric but are not part of the same circuit. Disconnects can be achieved by a chemical process, Dhawan noted, but there's no way yet to make interconnects and disconnects in an automated fashion.

MANY POTENTIAL applications of electrotextiles won't truly fulfill their promise without a major advance in battery technology, asserted Robert Rix, a British inventor whose company, Gorix, has commercialized products based on an electroconductive textile of the same name.

PHOTOS BY DEAN M. DELONGCHAMP

ELECTROCHROMES Thin-film polymer composites assembled layer by layer change color at different potentials. Top row: Film containing poly(hexylviologen) and PEDOT doped with sulfonated poly(styrene) at –0.9, –0.4, and 0.5 V (left to right). Bottom row: Polyaniline/Prussian blue film at –0.2, 0.2, and 0.6 V.

Some recent advances in battery technology were discussed by chemist Bernd J. Neudecker, manager for thin-film batteries at ITN Energy Systems, a company based in Littleton, Colo. ITN has developed a family of small, flexible, rechargeable solid-state batteries based on thin-film lithium technology. Sold under the LiTE*STAR name, the batteries can be recharged tens of thousands of times, meaning that "once you put that battery into your product, you never have to replace it," Neudecker told his listeners.

The batteries, which are manufactured by ITN's spin-off Infinite Power Solutions (IPS), can recharge by capturing various forms of ambient energy, such as radiofrequency energy. Recharging times are fast: from "empty" to more than 90% of capacity within two minutes and to 96% in five minutes. Furthermore, the batteries lose only 1% of their charge per year while sitting on the shelf, said Neudecker, who this month joined IPS as chief technology officer.

LiTE*STAR batteries, which were introduced to the market in 2002, lend themselves to diverse low-power applications, including implantable medical devices, smart identification cards, and body-worn electronics. Currently, they are being used in military applications.

Neudecker, senior engineer Martin H. Benson, and their colleagues at ITN are now taking thin-film battery technology to the next level. Under a DARPA contract, the firm is developing rechargeable thin-film batteries on fiber substrates. As Neudecker explained it, layers of a cathode material (such as $LiCoO_2$), solid-state electrolyte, and copper are sequentially deposited onto a fiber. During the initial charging of this battery, lithium from the cathode migrates through the electrolyte (lithium phosphorus oxynitride) and plates out on the copper layer, forming the anode.

The battery can be built around almost any structural fiber, be it carbon, ceramic, metal, or plastic. As a result, these so-called PowerFibers can perform a mechanical (load-bearing) function as well as releasing electrical energy. This dual functionality is especially attractive for space applications, Neudecker noted, because the spacecraft structure doubles as the battery.

Layers of PowerFibers can be embedded in a matrix to provide potentially much more power and energy than a flat thin-film battery of the same thickness, he pointed out. PowerFibers in a polymer composite were cycled electrochemically under ambient conditions more than 2,000 times, losing less than 0.025% capacity per cycle.

Like their flat, thin-film progenitors, the fiber batteries promise that once they are built into a device, you can forget about them, Neudecker said. And since they are fibers, it is conceivable that they could be woven into an electrotextile to provide power for the textile's electronic functions.

Electrochemical cells also are central to the research of Dean M. DeLongchamp, but his cells are designed to change color, not to provide electrical current. DeLongchamp, a graduate student in chemical engineering professor Paula T. Hammond's group at Massachusetts Institute

PHOTO BY PEDRO ARRECHEA

NEXT GENERATION MIT's DeLongchamp studies the behavior of electrochromic polymer films.

of Technology, is trying to develop better electrochromic materials and devices for applications such as windows that "darken at the touch of a button" or an electronic newspaper "that refreshes itself every day to provide you with the latest news."

DELONGCHAMP'S DEVICES are thin-film composites containing an anode, an electrolyte, and a cathode in a battery-like configuration. In this case, the electrodes are polymeric materials that change color depending on whether the electrochemical cell is fully charged or discharged.

To make these polymer films, DeLongchamp uses layer-by-layer (LBL) assembly, a technique developed more than a decade ago that has numerous advantages over traditional methods for fabricating electrochromic films. LBL assembly involves alternately dipping a charged substrate such as glass into two dilute aqueous solutions of polymers with opposite functionality—for example, a polycation solution and a polyanion solution. Each film electrode is built up from polycation/polyanion bilayers, "enabling you to build a film of whatever thickness you would like, simply by adding to the number of bilayers on the surface," DeLongchamp explained in Boston. This technique, he believes, "may be the perfect tool" to tailor electrochromic films.

DeLongchamp's first-generation electrochromic device incorporated polyaniline, poly(3,4-ethylenedioxythiophene) (PEDOT), and other ionic polymers. It worked reasonably well, cycling between two hues, he reported, but the contrast and difference between the two colors left room for improvement.

In the process of expanding his library of electrochromic films, DeLongchamp discovered that combining the electrochromes PEDOT and poly(hexylviologen) in the same LBL film electrode yielded an electrochromic device having broadband absorption and extraordinarily high contrast. In the reduced state, the device is almost black; when it is oxidized reversibly, it turns sky-blue to colorless—a change in red light transmission of over 82%. "In addition," the MIT student told his listeners, "we can get extremely fast switching speeds. So this is one of the best electrochromic materials that's ever been designed. And we did it using this cheap and relatively simple LBL technique."

One of the major challenges in electrotextiles is forming reliable interconnections between wires that cross each other.

DeLongchamp also has found an electrochromic system that features high contrast along with three distinct color states. He achieved this by combining polyaniline with an inorganic dye—iron(III) hexacyanoferrate(II), known since ancient times as Prussian blue. In the reduced state, the composite film is clear and colorless. But on partial oxidation, it turns green, and when fully oxidized, it becomes dark blue.

DeLongchamp intends to look for additional multihued composites and to use the same LBL approach to optimize the electrolyte. Finally, he hopes to use LBL assembly to combine the cathode and anode materials with the electrolyte into a complete electrochromic cell and explore its feasibility for flexible electronic paper. But even at this early stage, he believes "dual electrochromes" like the polyaniline/Prussian blue film have "strong commercial potential."

THE DEVELOPMENT of microelectronic systems based on organic thin films is driven by the promise of lightweight, flexible, large-area devices at potentially lower cost. Silicon-based electronics are relatively expensive because they require ultraclean fabrication facilities, high-temperature vacuum systems, and complex lithographic processes. Scientists have a vision that, one day, organic electronic devices will be printed "as we print newspapers today, at high speeds and in a reel-to-reel process," according to DuPont physicist Graciela B. Blanchet.

Several talks at the MRS symposium highlighted advances that may help transform this vision into reality. For example, organic chemist Beng S. Ong, who manages the Printed Organic Electronics Group at Xerox Research Centre of Canada, in Mississauga, Ontario, described the design and synthesis of new polythiophene materials that perform significantly better than current polymers.

Polythiophenes, which are organic semiconductors, have attracted interest for flexible electronics because they can be deposited via simple solution processes such as spin-coating or printing. A number of polythiophenes, when processed in an inert atmosphere, can be used to make functioning field-effect transistors (FETs), Ong pointed out. But these materials are not stable enough in air to allow them to be fabricated into transistors under ambient conditions at low cost.

With the aid of a National Institute of Standards & Technology grant, Ong and his collaborators at Xerox and other corporate labs examined known polythiophenes to gain an understanding of how their structural features limited their performance, and then devised ways to get around those limitations. Extended π-conjugation in the semiconductor polymer structure is important for achieving a high charge-carrier mobility in the FET, Ong said. But if conjugation becomes too extensive, the ionization potential of the electron-rich polymer is lowered, and the polymer becomes prone to being oxidized in air, which leads to degraded properties.

Ong and his coworkers sought a compromise position. They used several chemical tricks to reduce the conjugation length to make the polymer less sensitive to oxidation while maintaining its desirable electronic properties. The resulting polythiophene, code-named XPT, is a smectic liquid crystal with a regular substitution pattern. Its exact chemical composition is being kept secret until a patent is granted on the material, Ong told C&EN.

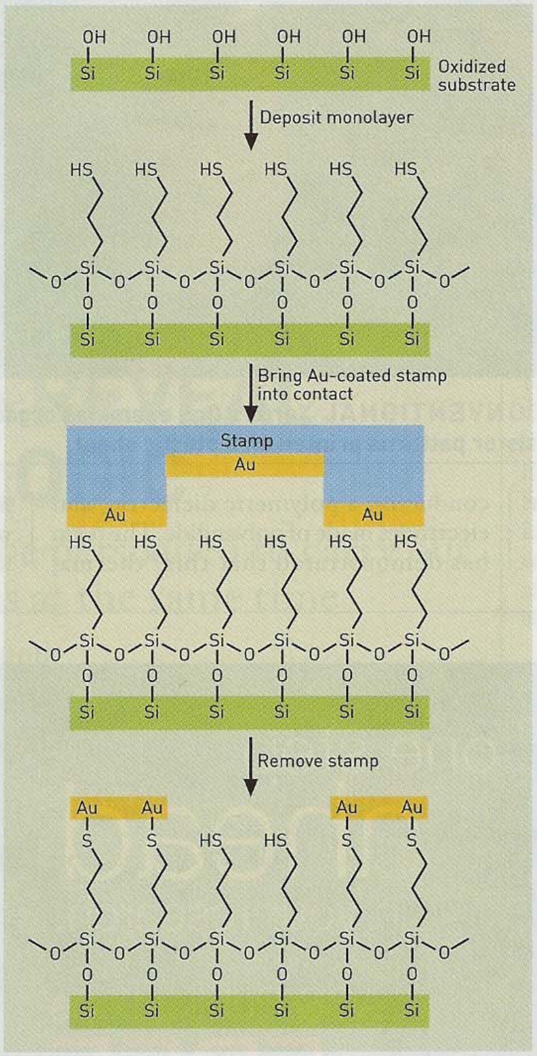
WHEN INCORPORATED into thin-film transistors under ambient conditions, XPT has excellent properties, according to Ong. For example, its carrier mobility in a FET is as high as 0.12 cm^2 per V-second. That's up to an order of magnitude greater than that measured for other polymers under ambient conditions in the same device architecture. And the ratio between the "on" and "off" current is in the excellent range of 10^6 to 10^7. The team's "breakthrough," according to Xerox, was to obtain these and other outstanding thin-film transistor properties for the first time in a material that is processible in air.

Ong said his team has produced stable dispersions of XPT nanoparticles that provide more consistent results in printing or solution coating than when a solution of the polymer is used.

Xerox (including its subsidiary, the Palo Alto Research Center in California) and its collaborators at Motorola Labs are putting XPT through its paces in a variety of printed electronics applications. One goal is to develop a roll-to-roll process for printing circuit patterns of the polymer on large sheets of plastic using ink-jet or other printing technologies. Such a process eventually could lead to flexible electronic driver circuits for portable, posterlike television screens and other large-area displays that would be prohibitively expensive to produce using today's silicon technology.

"There's no way that an organic material can compete with silicon in terms of performance for the foreseeable future," Ong told C&EN. But, he added, silicon technology cannot, at this point, make flexible displays possible; organic materials potentially could.

In their development of a plastic electronics technology, researchers are moving beyond the layer-by-layer patterning and deposition methods used in the microelectronics industry. Today, circuits are created by depositing materials, patterning them, and then selectively etching away parts of the pattern. This methodology runs into problems, however, when the goal is to fabricate circuits involving organic materials, which are sensitive to etchants and other chemicals.



NANOTRANSFER PRINTING **In a Bell Labs method, a thiol-decorated monolayer is assembled on a substrate, and a gold-coated patterned stamp is brought into contact with the monolayer. Since the Au-S bonding is stronger than the Au-stamp adhesion, the gold pattern is transferred to the substrate.**

In Boston, Yueh-Lin (Lynn) Loo described two new device fabrication techniques that are "purely additive"—that is, they involve only adding material, not removing it. Loo, an assistant professor of chemical engineering at the University of Texas, Austin, did the work while she was a postdoctoral fellow in John A. Rogers' group at Lucent Technologies' Bell Laboratories in Murray Hill, N.J.

Loo and coworkers developed a way to use a stamp to print metal patterns with nanometer features over large areas. The method, called nanotransfer printing (nTP), is a versatile means of patterning metal electrodes on plastic and other substrates using either rigid or flexible stamps.

In a typical example, the substrate surface is first functionalized with a self-assembled monolayer of mercaptan molecules so that the thiol groups are on the upper, exposed face of the monolayer. By conventional techniques, a rubber stamp is prepared that contains the desired high-resolution relief pattern, which has raised and recessed regions. A thin layer of gold (20 nm) is then evaporated onto the relief pattern, but the gold adheres very weakly to the stamp. When the stamp is brought into contact with the thiol-coated substrate, strong gold-sulfur bonds form on the raised regions of the stamp. Thus, when the stamp is peeled off, the gold pattern on the raised regions stays on the monolayer, not on the stamp.

"We can actually pattern a large area in 15 seconds," Loo said. The method is fast, easy, "green," and can be carried out under ambient conditions in air. Furthermore, the stamps are reusable, which helps to keep costs low.

"Flexible electronic systems represent a promising potential application for nTP," Loo and coworkers noted in their first paper on the technique [*J. Am. Chem. Soc.*, 124, 7654 (2002)]. They have used nTP to fabricate a two-transistor circuit that serves to switch voltage on and off, as well as a metal-insulator-metal capacitor. The latter was prepared by transferring a three-layer gold/silicon nitride/gold sandwich from a silicon stamp to a plastic substrate. Depositing silicon nitride directly onto the plastic would be problematic, Loo told C&EN, because the standard deposition process requires a temperature higher than the plastic's melting point.

Nanotransfer printing is only part of the transistor-fabrication process developed at Bell Labs. Loo explained that nTP is used to print, on one plastic sheet, the source and drain electrodes and the interconnections. On a second plastic sheet, the gate layer, dielectric, and organic semiconductor are deposited using other techniques. "Then we align the two sheets and laminate them together to complete the circuit," Loo said.

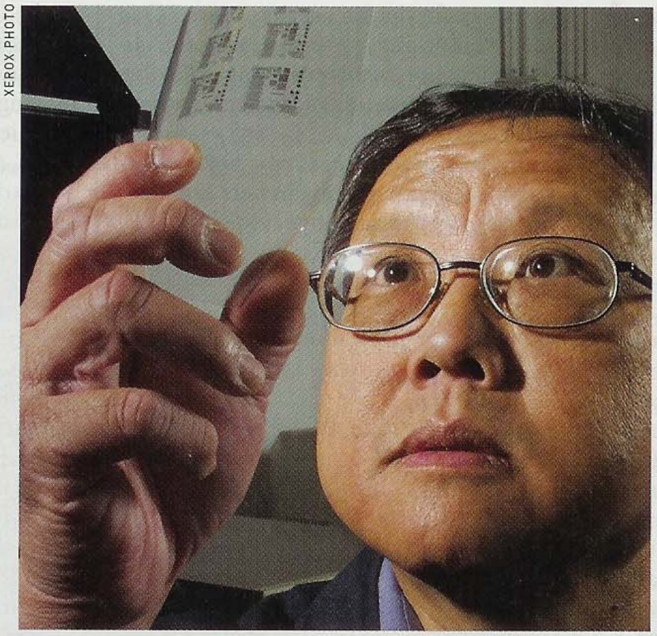
This approach offers several practical advantages. For instance, the laminated circuits are completely encapsulated and thus protected from water and other substances that could cause them to fail. In addition, they are highly resistant to fracture during bending.

Another purely additive process for fabricating organic electronic devices was presented by DuPont's Blanchet. In collaboration with Bell Labs, she and her coworkers are using a dry, laser-based method for printing circuits that contain no metal. The devices incorporate an organic semiconductor, a polymeric dielectric, and electrodes made of polyaniline. The team has demonstrated that this "thermal transfer" process can be used to fabricate a functioning 4,000-cm^2 transistor array on a flexible plastic sheet. Such an array could serve as the driver circuitry for an electronic book or a refreshable retail sign. DuPont hopes to commercialize a display product based on this technology within two years, Blanchet told C&EN.

The transistor array is flexible enough to be rolled up into a narrow cylinder. The limiting factor is going to be whether there exists a power supply that is thin enough to be incorporated into such a thin product, Blanchet said.

Although dry printing is probably the best way to get a first-generation device to market quickly, eventually you'll want to print devices continuously like you print newspapers, Blanchet told C&EN. Unfortunately, the materials and the resolution of the presses are not good enough for that right now. But wait five years, she suggested, and maybe it'll be a different story. ■

XEROX PHOTO



UNCONVENTIONAL Xerox's Ong examines organic transistor patterns printed on a plastic sheet.