

of nanowires. As reported in the November 29, 2004, issue of *Applied Physics Letters* (p. 5337), the research team discovered that fragmentation of copper nanowires occurs as a function of temperature and is driven by the Rayleigh instability. The Rayleigh instability concept, introduced over a century ago to explain the instability of a liquid jet, is now being applied to describe the fragmentation of copper nanowires; it is driven by surface atomic diffusion in conjunction with any periodic variations in wire diameter. The researchers observed, by high-resolution scanning electron microscopy (HRSEM), different stages of fragmentation after annealing the nanowires at elevated temperatures and reported a clear dependence of the decay process on temperature. According to the researchers, the wires started to fragment at $\sim 400^\circ\text{C}$, form shorter segments with an increase to $\sim 500^\circ\text{C}$, and decayed into chains of nanospheres at 600°C . All of these processes occurred at temperatures far below the melting point of copper.

The nanowires employed by Toimil Molares and colleagues for the annealing experiments were fabricated by electrochemical deposition of copper into the pores of etched ion track membranes. The templates were created by irradiating thin polycarbonate foils with 2 GeV Au heavy ions. The damage zones produced by the ions along their paths were then dissolved in NaOH solution. The scientists were also able to show that these pores have a slightly biconical shape, with diameters varying between 30 nm at the center and 50 nm at the ends. These pores were subsequently filled with copper by electrochemical deposition, and the surrounding matrix was dissolved in dichloromethane for SEM investigations.

Toimil Molares said that the observed mechanism of the copper nanowire fragmentation agrees qualitatively with previous theoretical work, such as Monte Carlo calculations of fragmentation of Ge nanowires due to the Rayleigh instability. The resulting size and spacing of the nanospheres has also been linked to additional theoretical predictions.

"Our research clearly indicates that for nanoscale device applications, technological problems arising from the thermal instability of materials must be taken into account if reliable devices must be produced," said Toimil Molares. The observed phenomenon could also be used to develop new materials processing techniques, for example, to fabricate nanospheres of copper, silver, or gold.

"This new kind of nanoscopic string of spheres could also find applications in

nanophotonics, since it may be used to guide light below the diffraction limit via coherent coupling of surface plasmon polaritons," Toimil Molares said.

This increased understanding of how copper nanowires behave as a function of temperature should have an impact on both fundamental sciences and technological applications, and it could lead to substantial future studies—for instance, *ab initio* atomistic simulations of the mechanism to reveal more of the underlying atomistic details of the processes.

MARKUS J. BUEHLER

Layer-by-Layer Growth of Multilayer Thin Films Containing Microgels Allows Controlled, Tunable Release of Medications

L. Andrew Lyon and colleagues at the Georgia Institute of Technology have developed a film for drug delivery with the goal of replacing daily injections and pills with microthin, implantable films that release medication according to changes in temperature (see Figure 1).

Lyon, associate professor at the School of Chemistry and Biochemistry, said, "We loaded insulin in layers of microgel films in the lab and released bursts of insulin by applying heat to the films. They were extremely stable and could continue to release the drug for more than one month at a time."

Films assembled from microparticles allow more control over drug release than films previously made in monolithic form. As reported in the September 13, 2004, issue of *Biomacromolecules* (p. 1940), the films release their cargo at 31°C , six degrees below human body temperature. Lyon's

group is working on pushing the release point to a temperature slightly above that of the human body. Once implanted, the researchers said, the pharmaceutical-loaded films could be placed on chips with resistive heaters and designed to release drugs according to a time schedule or another trigger.

The microgels are composed of the thermoresponsive polymer poly(*N*-isopropylacrylamide) cross-linked with *N,N'*-methylenebisacrylamide. This polymer is highly water-swollen below its lower critical solution temperature of 31°C . Above that temperature, an entropically favored phase separation, or deswelling, event occurs as the hydrophobic interactions between the isopropyl groups are favored over polymer swelling.

The films were fabricated using a layer-by-layer process. Measurements demonstrated that the amount of insulin released during long-term cycling tests depended upon the number of film layers, indicating the potential for tunability of the amount of medication released.

Composite Cathode with Boroxine Ring Developed for All-Solid-Polymer Lithium Cell

The poly(ethylene oxide) (PEO)-based lithium polymer electrolyte has been regarded as the best electrolyte candidate in lithium secondary batteries since the late 1970s. However, due to the electrolyte's low conductivity, those solid-polymer lithium batteries have to be operated above a temperature of 60°C . Q. Li (Mie University, Japan), O. Yamamoto (Genesis Research Institute, Japan), and their colleagues are involved in the development of new electrolytes, especially focusing on electrical conductivity enhancement at lower temperature. In 2000, the group reported that the addition of BaTiO₃ to PEO-Li(CF₃SO₂)₂N can increase the electrical conductivity at room temperature. In 2003, they combined a composite polymer, PEO-Li(CF₃SO₂)₂N-BaTiO₃, with a hyperbranched polymer (HBP), poly[bis(ethylene glycol)benzoate] capped with the acetyl group, and found that the electrolyte's conductivity could reach 10^{-4} S/cm at room temperature and 10^{-3} S/cm at 60°C . However, there was still a rate capacity restriction by a high interface resistance at the cathode side at low temperature. To overcome it, the same group developed a novel composite cathode with the addition of a boroxine ring compound.

To prepare the solid-polymer electrolyte cell, the researchers sandwiched the composite polymer electrolyte (CPE)

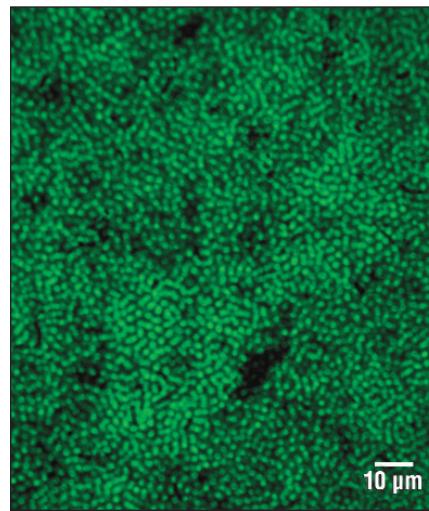


Figure 1. Fluorescently tagged insulin occupies a three-layer microgel thin film.

between the lithium metal anode and the composite cathode in a coin-shaped cell. The CPE films were cast on a flat polytetrafluoroethylene vessel from an acetonitrile slurry containing BaTiO₃ powder, lithium salt, and PEO. After solvent evaporation under a flow of nitrogen without heating, the films were dried at 60–95°C under vacuum for two days. The average film thickness obtained was ~300 μm. The composite cathode was cast on an aluminum film substrate from a (PEO-10wt%HBP)₁₀Li(CF₃SO₂)₂N-10wt%LiPF₆/10wt%BaTiO₃/acetonitrile slurry with LiNi_{0.8}Co_{0.2}O₂, acetylene black, and BP(*n*). BP(*n*) has a boroxine six-member ring with oligoether side chains attached to the 1, 3, and 5 positions, and *n* denotes the number of ethylene oxide repeat units in each of the side chains. After vacuum-drying at 100°C, the cathode materials were pressed into a 40-μm-thick film. The capacity of the lithium anode was several times higher than that of the cathode.

As the researchers reported in the December 2004 issue of *Electrochemical and Solid-State Letters* (p. A470), the boroxine ring containing BP(*n*) has been found to not only reduce the interface resistance between the lithium metal electrode and the electrolyte, but also enhance the lithium-ion transport number. In this study, BP(*n*) was added in the cathode composite, and different lengths of the oligoether side chain were tested. BP(7.2) proved to be the best at the charge-discharge cyclic performance, mainly because it worked as a Lewis acid and can improve the Li-ion transport properties.



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From three-electrode impedance analysis and charge-discharge tests, a polymer cell with the composite polymer electrolyte, (PEO-10wt%HBP)₁₀Li(CF₃SO₂)₂N-10wt%LiPF₆-10wt%BaTiO₃, the lithium metal anode, and the composite cath-

ode having LiNi_{0.8}Co_{0.2}O₂, acetylene black, and BP(*n*), showed good cycling performance at 40°C at a current density of 0.1 mA/cm². The cathode capacities were over 130 mAh/g for LiNi_{0.8}Co_{0.2}O₂.

LUCY YUE HU

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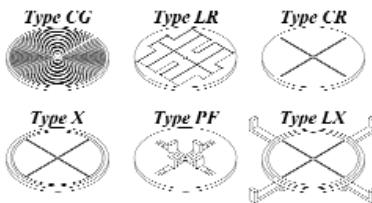
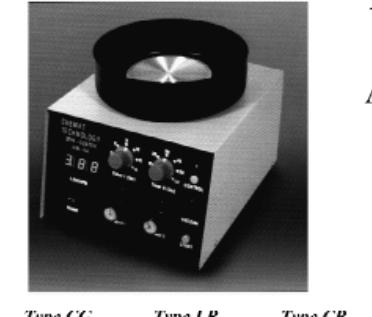
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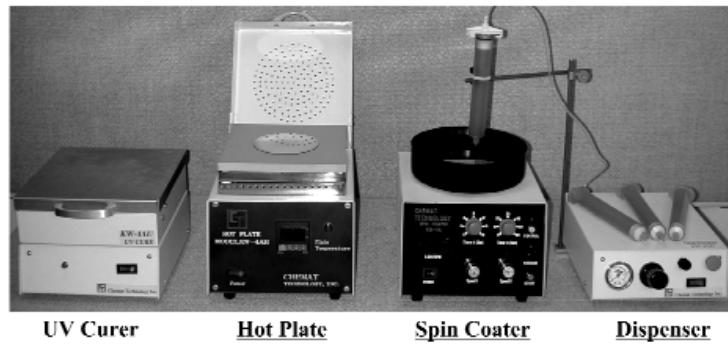
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