RESEARCH/RESEARCHERS

Low Voltage Achieves Large Strain in Electroreactive Polymer

Soft polymeric materials that can convert electrical energy into mechanical energy have become an intensive area of study recently, owing to their potential to mimic biological responses. Mohsen Shahinpoor of the Artificial Muscle Research Institute (AMRI) at the University of New Mexico and Kwang Kim from the Active Materials and Processing Laboratory (AMPL) of the University of Nevada have combined lithium-doped poly(ethylene oxide) (PEO) with the plasticizer poly(ethylene glycol) (PEG) to fabricate 320-μm-thick actuators exhibiting large strain (>1% bending strain) at a relatively low applied electric field (<10 V/mm). Actuator motion in these materials arises from the cation attraction to the anode relative to the polymer host, which creates a pressure gradient leading to deformation. This deformation is reversible with the direction of the electric field and also displays stable operation after more than 10 million cycles in air.

As reported in the May 6 issue of *Applied Physics Letters*, the actuation of ionic conductive polymers such as PEO is increased by the use of the plasticizer PEG, which decreases the crystallinity of the medium, leading to increased ion mobility. Load and force measurements indicate that the polymer solid-state actuator produces a useful force density of up to 20 *g*-force/g of PEO-PEG polymer in a cantilevered configuration, under an applied voltage of 1–3 V, while maintaining a constant frequency of 0.5 Hz. Furthermore, the researchers report that strain power-density variations for the PEO-PEG solid-state actuators indicate that the current 2% strain values can lead to power densities of over 50 J/kg, while further improvement of these actuators to enable them to generate 4% strain would lead to power densities of 200 J/kg, comparable to biological muscles.

KYLE BRINKMAN

3D Imaging of Materials Achieved with Differential-Aperture X-Ray Microscopy

X-ray diffraction provides two-dimensional (2D) information on the structure, orientation, and distortion of a crystal. However, information along the path of the incident beam is hidden within the superposition of patterns and cannot be discerned. A group of researchers from Oak Ridge National Laboratory have obtained depth-resolved three-dimensional (3D) images of crystals using a technique they call differential-aperture x-ray microscopy (DAXM).

As reported in the February 21 issue of *Nature*, B.C. Larson and colleagues incorporated an x-ray-absorbing wire as a knife-edge depth profiler. The wire is moved stepwise across the diffraction patterns, selectively blocking out diffracted x-rays from reaching the charge-coupled-device (CCD) detector. Through computer reconstruction, knowledge of the position of the wire can be used in conjunction with the intensity for each pixel located by the CCD detector to obtain the Laue diffraction pattern for that position of the wire. Depth resolution of the order of a tenth of a micrometer is possible, depending on the position of the x-ray-absorbing wire relative to the sample and detector.

This technique allows for a point-by-point detailed determination of structure and 3D mapping. It can be used for extracting detailed information including microstructure and strain from a small, localized volume of a crystal. Particularly on the mesoscopic length scale, it allows for experimental determination of microstructural evolution that was previously only amenable to multiscale modeling and numerical simulations. The researchers provided examples of studies on grain structure in polycrystalline aluminum and orientation and strain measurements in cylindrically bent silicon.

GOPAL RAO

Ordered Arrays of Aluminum Nanoclusters Grown on Silicon

Novel approaches for forming ordered structures of nanoclusters will likely play a role in using these clusters in technological devices. To address this issue, researchers from the Chinese Academy of Sciences, the National Research Council of Canada, Tohoku University, and the National Renewable Energy Laboratory have devised a way to create ordered, two-dimensional arrays of Al_6 clusters on Si(111) surfaces.

They report in the April 29 issue of *Applied Physics Letters* that they formed nanocluster arrays by evaporating Al on a Si(111) 7×7 surface. At substrate temperatures above 200°C, an ordered array of uniform Al clusters is formed. The arrays were studied with scanning tunneling microscopy, which showed that the clusters contain six Al atoms, occupying both halves of the Si(111) 7×7 unit cell, giving the nanocluster array the same geometry as the underlying 7×7 substrate. First-principles total-energy calculations find an optimized structure for the Al_6 clusters, which is in agreement with the experimental images.

"The formation of uniform Al and other metal cluster arrays provides new practical approaches for doping Si with ultrahigh uniformity and atomic precision," said Qi Kun Xue, the lead researcher on the project. "Precision doping also opens the door for fabricating *p-n* junctions across the two halves of each of the Si(111) 7×7 unit cells for diode applications. This would probably be among the highest density of integrated solid-state devices that may, one day, reach the commercial market. We are now working in collaboration with the Rowland Institute at Harvard University on proving this very exciting idea," Xue said.

The Al clusters are the most stable metal clusters that the research team has grown. The fact that the Al cluster arrays can sustain temperatures of up to 500°C is an important factor for practical applications, they said. The researchers also believe the Al_6-decorated Si(111) surface could serve as a template for the growth of other types of nanocluster arrays.

CHRISTOPHER MATRANGA

High-Efficiency Solar-Blind GaN Photocathodes Produced for Low-Level UV Detection

Researchers Bruce Wessels, Melville Ulmer, and colleagues at Northwestern University have fabricated a solar-blind UV detector based on a Cs-treated *p*-GaN photocathode. The device achieved a relatively high quantum efficiency (QE) of 30% for detecting radiation in the deep UV (λ = 200 nm), and a UV-visible light-rejection ratio of about 4 orders of magnitude.

Solar blindness is a necessity in several UV detector applications, for example, in UV astronomy, where objects studied are usually 4–8 orders of magnitude brighter in the visible than in the UV range. One of the approaches to making such UV-sensitive photodetectors is by using III–nitride materials as photocathodes by taking advantage of their negative electron affinity (NEA). NEA is obtained when the minimum of the semiconductor conduction band is above the vacuum level. In that case, thermalized electrons can escape the surface of the bulk material. To attain the NEA, the surface of the semiconductor must be treated with impurities.

As reported in the April issue of the *IEEE Journal of Quantum Electronics*, the researchers grew GaN layers 1 µm thick on sapphire substrates by metalorganic chemical vapor deposition. Magnesium was used as the *p*-type dopant, and films were treated with cesium to achieve NEA. In the as-grown materials, carrier concentrations were in the range of 5×10^{16} cm^{-3} to 1×10^{17} cm^{-3} and mobilities were in the range of 3–11.5 cm^2/V s. Subsequently, the films were processed into photocathode tubes.

In the sample with the best material quality, the researchers obtained a QE as high as 30% at 200 nm with a rejection ratio of about 4 orders of magnitude between the UV (200 nm) and visible (500 nm) ranges. They also found that the QE increases with an increase in conductivity. Based on the findings, the researchers anticipate that a further improvement in the photocathode quantum efficiency can be achieved with higher conductivity of the material. Although a 30% QE is still lower than QEs reported in the literature for the deep-UV (near 280 nm and below), the promise of achieving higher responsivity in a photocathode-type detector exists. Also, the photocathode tubes showed high stability over time.

The researchers are now working to improve the conductivity of this material to increase its efficiency as well as to improve the solar blindness of the resulting detectors.

"By adding electrically active impurities to gallium nitride, we have improved the optical properties of the material, making it very sensitive to ultraviolet light, but we know we can do even better," said Wessels. "Our goal is to make the device with greater than 50% quantum efficiency, which means it will be 10 times better than the detectors used in the Hubble Space Telescope." Quantum efficiencies as high as 90% are theoretically possible, according to the research team.

SHIMING WU

Polymeric Material Self-Repairs Without Addition of Chemicals

While many plastic materials are strong and resistant to breaking, once fractured, the broken pieces are cracked irreversibly. Although progress has been made in the development of self-healing polymers with the use of polymer catalysts or glues, further questions still remain concerning the long-term stability of the catalyst and the ability of the material to self-heal multiple times. Fred Wudl, professor of organic chemistry at the University of California—Los Angeles and director of UCLA's Exotic Materials Institute, led a research group of chemists and engineers who developed a transparent plastic that, when fractured, mends itself with heating.

Unlike other self-healing plastics developed previously, this material, called automend, repairs itself without the addition of a catalyst or other chemicals. As reported in the March 1 issue of *Science*, automend is an extremely hard and fully transparent polymer material prepared by the Diels–Alder cycloaddition of a multi-diene and a multi-dienophile. Its density is 1.37 g/cm^3 with an index of refraction of 1.56 at 24°C, its Young's modulus is 4.72 GPa, and its Poisson ratio is 0.349. Its mechanical properties are similar to commercial epoxy resins.

Automend can be fractured and healed multiple times through heating at 120°C, due to reversible cross-linking covalent bonds formed between the polymer chains and branches. While being heated, these bonds between the polymer chains are broken; but during cooling, the polymer will be remanufactured by reforming those broken bonds. Solid-state nuclear magnetic resonance spectroscopy showed that when the temperature is above 120°C, ~30% of intermonomer linkages disconnect and then reconnect upon cooling. After healing, the original fracture is invisible, according to scanning electron microscope images, and the polymer can retain ~60% of its original fracture strength from the fracture tests.

Although this new polymeric structural-engineering material has potential use in large lenses and housings for radar or communications equipment, the researchers addressed some future studies for improvement such as the maleimide monomer's high melting temperature, curing time of the material, and service temperature range.

YUE HU

Transport Properties Measured by Hybrid Molecular-Assembly Approach

Progress in the development of nanoscale molecular electronics requires the rapid screening of molecular systems for their electronic-transport properties. An essential element of this process involves the connection of electrodes to the molecules of interest. A team of researchers led by Raymond K. Tsui in the Physical Sciences Research Laboratories at Motorola Laboratories in Tempe, Ariz., has devised a hybrid molecular-assembly technique to facilitate the rapid screening of candidate molecules: first, forming a self-assembled monolayer (SAM) on a pair of prepatterned electrodes, then using metallic nanoparticles for gap-bridging under an ac field as an alternative fabrication approach to provide a solution for transport measurements of molecules.

As reported in the April 15 issue of *Applied Physics Letters*, the researchers fabricated gold nanoparticle electrodes using a combination of photolithography and electron-beam lithography on an oxidized Si substrate. With the lift-off technique, fine features of the electrodes were patterned by a poly(methyl methyacrylate) (PMMA) resist process. After the substrate was cleaned to remove oxidized Au, the researchers assembled nanoparticles by applying an ac bias (0.5–2.5 V, peak-to-peak) ranging from 1 MHz to 10 MHz for 5–20 s. By applying an ac field, a dielectrophoretic force was created that pulled the nanoparticles in the direction of maximum field strength between the gap. The researchers measured various sizes of Au nanoparticles, ranging from 40 nm to 100 nm, trapped between the gap with a yield of almost 100%. They also discovered that as soon as the gold particle bridged the gap, the electric field in the gap was reduced, which tended to prevent additional accumulation. Additionally, since the resistance of the Au electrode–particle assembly varied from 100 kΩ to a few tens of megaohms, a larger number of nanoparticles could be clustered in the gap region if the nanoparticle size was smaller than the gap.

The researchers selected 2,5-diphenylethynyl-4′,4″-dithioacetyl-nitrobenzene (1′) as a test molecule. The SAM tested consisted of a Au-1′-Au-1″-Au structure and showed qualitative current–voltage (*I-V*) measurements with two negative differential resistance peaks similar to those observed in semiconductor heterostructures.

"Our approach is relatively simple and... can potentially allow a quick and easy way to characterize a large number of electronic molecules," said Islamshah Amlani, a senior engineer at Motorola Labs.

KINSON C. KAM

Field-Emission Current Induces High Stable Temperature in Multiwalled Carbon Nanotubes

S.T. Purcell and colleagues at the Université Claude Bernard Lyon 1 have induced stable temperatures of up to 2000 K in multiwalled carbon nanotubes (MWNTs) by field-emission current. As reported in the March 11 issue of *Physical Review Letters*, the researchers determined the temperature and resistance of individual MWNTs with field-emission electron spectroscopy. Both the high temperature and the light emission seen during field emission come from Joule heating of the MWNTs. The researchers propose that field emission can be used to improve the structure by heat treating. They also determined that the resistance of the MWNTs decreases with temperature.

The MWNTs were grown by chemical vapor deposition onto Ni tips. Scanning electron microscopy showed that the MWNTs were straight, ~30 nm in diameter, and ~40 μm long. Transmission electron microscopy confirmed that they were multiwalled.

Field-emission experiments were conducted in ultrahigh vacuum of ~7×10^{-11} Torr. The total-energy distributions (TEDs) of the emitted electrons were measured with a hemispherical electron-energy analyzer. Although many MWNTs grew on each Ni tip, the field-emission measurements were specific to individual nanotubes for two reasons. First, the emission current (I_{FE}) is an exponential function of field, so only a few MWNTs are able to emit. Second, the geometry of field emission allows the contributions of each MWNT to the field-emission pattern to be easily distinguished.

The researchers determined the temperature and resistance from TEDs obtained for various I_{FE}. As I_{FE} increased, the TEDs became broader and shifted to lower energy. The broadening is partly explained by the rise in the temperature due to Joule heating along the MWNTs. The shift to lower energy results from an IR drop along the tube.

ELIZABETH SHACK

Carbon Nanotube Bandgaps Manipulated with Metallofullerenes

A team of researchers from Seoul National University, Soongsil University, and Nagoya University has detected localized bandgap-energy changes in single-walled carbon nanotubes (SWNTs) that contain fullerene (C_{82}) encapsulated gadolinium ions (GdMF). As reported in the February 28 issue of *Nature*, research led by Young Kuk from Seoul National University demonstrated that bandgap energies of single SWNTs were tailored with ~3-nm accuracy using GdMF insertion to induce changes in nanotube structure and electronic environment and divide the nanotube into multiple quantum dots. Scanning tunneling microscopy (STM) was employed to monitor changes in tunneling conductivity to probe for breaks in symmetry imposed on the SWNTs. The major motivation is the development of nanoscale electronic devices as alternatives to Si-based devices.

The metallofullerene insertion into SWNTs was accomplished by heating the two in a glass ampoule at 500°C for three days. The diameters of the GdMF inserted were slightly larger than the SWNTs and could be spaced in a systematic fashion (every 1.1 nm) or quasi-periodically (every 1–3 nm), depending upon either a sonication or annealing method. The GdMF and SWNTs were both fabricated by a dc arc-discharge method, with the GdMF purified through high-performance liquid chromatography, and SWNTs purified by treatment with acid.

Using STM operated at ~5 K, dI/dV spectra were obtained from the images to estimate the bandgap at 512 points along a 10-nm section of a single SWNT. In areas that did not contain GdMF density, the SWNTs had a bandgap of 0.43 eV, while in the areas of GdMF insertion, the bandgap decreased to 0.17 eV. The evidence for such changes in tunneling conductivity along single SWNTs could be easily seen in the STM images, with bright "spots" appearing in a periodic fashion. Such bright spots are likely to be from both bandgap change and also topography change. The researchers believe insertion of GdMF into SWNTs has two effects along this line. First, the electron transfer from both the Au(111) substrate and the GdMF cluster may lead to charge transfers, resulting in the bandgap change. Second, the insertion of a GdMF with a greater diameter than the SWNTs introduces an elastic strain of the SWNTs, contributing to additional bandgap change.

The researchers believe that this ability to transform a SWNT into a one-dimensional multiple-quantum-dot system may contribute to the fields of nanoelectronics, nano-optoelectronics, and perhaps even a quantum cascade laser or quantum computer.

MATHEW M. MAYE

Computational Technique Facilitates Modeling of Fluid Transport in Porous Media

Computational materials scientist Clint Van Siclen, from the Idaho National Engineering and Environmental Laboratory, has demonstrated a theoretical approach to modeling fluid transport in porous, variable materials such as rock. Through his approach, called the walker diffusion method (WDM), Van Siclen calculates how electricity "diffuses" through a composite material. The WDM is based on the concept of a single random walker—a theoretical construct that "walks" through the material, randomly taking a step in one direction, a step in another direction, and so on. Left alone long enough, the walker will eventually explore all the potential paths available. By tracking these paths, Van Siclen is able to map out the fluid-flow routes in a permeable material, including sharp twists and turns or the tiniest of crack lines.

As reported in the February issue of *Physical Review E*, Van Siclen maps out the movements of the walker by first digitizing the structure of the porous material. That digitized representation is thus a square or cubic array of pixels or voxels, each of which is open or closed, corresponding to pore space and impermeable rock, respectively. If a pixel is open, there is a high probability that a walker will travel through that space. If the pixel is closed, then a walker will not be able to occupy that space. In a relatively short period of time, a walker can explore the accessible space using these simple, quickly computed probabilities. The calculations go even faster if several non-interacting walkers are used. These paths reveal the overall physical structure of the material.

With the conventional approach to calculating flow paths, called the finite-difference method (FDM), researchers take the digitized sample and construct a very large set of finite-difference equations, that is, equations that define the difference between the values of a function at two discrete points. Those equations have to be solved simultaneously, a task that strains the capabilities of all but the largest computers for realistically sized systems. In contrast, the WDM can be performed on a typical PC.

Furthermore, Van Siclen reports, the WDM obtains the "correlation length" for the material under study. This parameter is the size above which a specimen is uniform (homogeneous) with respect to the transport property of interest, such as fluid permeability, and below which it is variable (heterogeneous). The existence of the correlation length, which may be tens or hundreds of meters in the case of fractured bedrock, thus fundamentally limits the extent to which results from laboratory experiments are applicable to field sites.

According to Van Siclen, the WDM enables very large, or highly resolved, materials systems to be studied. Currently, the WDM is used as a research tool to determine relationships between the geological structure of the subsurface and fluid-flow phenomena. For example, it produces the correct dynamics of the displacement of one fluid by another, such as oil by brine in an oil reservoir, and groundwater by heavier-than-water contaminants in an aquifer. WDM has also been used to predict the thermal properties of new composite materials proposed for use in nuclear reactors. Theoretical mathematical research such as Van Siclen's work aids in the development of accurate and reliable predictive models.

Switching and Memory Effects due to CDW Deformation Observed in $K_{0.3}MoO_3$

Sliding charge-density-wave (CDW) materials exhibit unique memory effects including pulse sign memory, pulse duration memory, and delayed conduction. CDW materials are composed of an elastic periodic medium under the influence of randomly distributed pinning sites. Under an external driving force, CDW materials show a dynamic phase transition from a creep phase to a slide phase. A strong nonlinear conduction, called switching, corresponds to this transition. As reported in the April 29 issue of *Applied Physics Letters*, N. Ogawa and K. Miyano of the University of Tokyo have demonstrated electro-optical switch and memory effects in $K_{0.3}MoO_3$, a CDW material. The researchers established this CDW material as an electrically writable/readable and optically erasable memory device by incorporating only two electrical leads.

The researchers demonstrated optical switching in $K_{0.3}MoO_3$ by applying an increasing voltage and light illumination to a sample at 12 K. Below the sliding voltage, V_s, the current in the sample was caused by the creeping motion of the CDW. At V_s, the current in the sample increased by about 3 orders of magnitude. According to the researchers, this observed switching at V_s corresponds to the creep-to-slide dynamic phase transition. The creep current and V_s increase with increasing light illumination, an indication of optical excitation affecting the dynamic phase transition of the CDW.

The researchers also demonstrate conduction delay of the CDW transport. Application of a voltage slightly larger than V_s and a rectangular voltage pulse causes, after a time delay, sliding motion of the CDW. By illuminating the sample before the voltage pulse, there is an increase in the time delay. The delay time depends on the amplitude of the voltage pulse and the illumination intensity. After the initial sliding effect, sliding occurs more quickly when the next voltage step is applied. This is the memory effect.

According to the researchers, these results indicate that the CDW dynamic phase transition from creep phase to slide phase can be set by an external electric field and removed by photoexcitation and that this property can be exploited to realize an electrically readable switch or memory device.

JENNIFER BURRIS

Low Humidity Content in Soil Detected Using an Indium-Doped Tin Oxide (ITO) Sensor

Agriculture is not immune to the current global trend of reducing costs to increase profitability. Automatic irrigation systems are currently available to help reach this goal. Some of these systems operate within a scheduled time frame, and others work by controlling the amount of water present in the soil, allowing watering only when it is needed and thus compensating for unexpected changes in weather. The latter can be achieved by using sensors embedded in the soil.

Sensors used to monitor the water content in the soil measure either dielectric permittivity or electrical resistance. Sensors that measure dielectric permittivity are expensive though more reliable, and are typically used for higher water content measurements. Sensors that measure electrical resistance typically measure atmospheric moisture. These are porous materials in which surface adsorption of water molecules in the internal cavities changes the conductivity; therefore, the harshness of the environment determines the capability for monitoring humidity in the soil after long periods of time.

A group of scientists from the Universitat Jaume I in Spain have attempted to develop an inexpensive sensor to provide accurate measurements at low humidity levels in the soil. Their first steps toward developing such a device from indium-doped tin oxide (ITO) are described in the April 15 issue of *Applied Physics Letters*. ITO is a wide-bandgap semiconductor with high conductivity. The cost and availability, and chemical stability in water, basic, and acidic solutions, make ITO an excellent choice for this application.

Square pieces of glass (1.5 cm × 1.5 cm) coated with an ITO film served as electrodes, with a groove 500 µm wide dividing the film in half. Silver epoxy fixed the electrical contacts on each half, and a commercial thermoplastic was thermally sealed on top of each electrode. As a first test, this sensor was used to measure the humidity in 2 kg of soil placed inside a container. The scientists placed the sensor in contact with the soil itself, and then applied a voltage of 100 mV with sinusoidal amplitude. The ac impedance response obtained had considerable reproducibility at different conditions of dryness and humidity.

At low frequencies, the results show the effect of electrode polarization. At high frequencies, the bulk response results from the combination of a resistance R_p and a capacitance C_p, in parallel. These two values, resolved by the appropriate software, varied with the water content in the soil. The resistance R_p decreased about 2 orders of magnitude with an increase in the water content from ~3 wt% to 10 wt%; the capacitance Cp increased from 1.2×10^{-10} F to 1.8×10^{-10} F from driest to water-saturated soil. Since the capacitance is negligible as compared with the values for surface polarization at the Helmholtz layer, ~5 µF/cm^2, these observations cannot be attributed to a contact effect, said the researchers.

F. Fabregat-Santiago and co-workers said the behavior of the ITO sensor in terms of the two adsorption mechanisms represents chemical adsorption, where the electrostatic field of surface ions attracts water molecules to form the first layer; and physical adsorption, where water molecules dissociate and release protons to form additional layers. In these two cases and at low-humidity levels, the released protons determine the nature of the electrical conductivity. At high humidity levels, water condenses and then electrolytic conduction also contributes to the electrical conductivity. For this reason, a plateau in the conductivity appears at humidity levels of 10% and higher, according to the researchers. This trend is consistent with measurements conducted in different conditions; in some cases, the value of the resistance increased as expected when the dielectric constant of the medium increased, but the trend remained the same.

The ITO sensor can accurately detect low levels of humidity in the soil, and it addresses the main concerns of cost and reliability of measurements at low humidity. However, the researchers said that further testing is needed under operational conditions in the field to determine the applicability of this device for triggering an automatic irrigation system during extended periods of time.

SIARI S. SOSA