

Molecule transforms metal-organic framework to become conducting

Although they have been around for just over a decade, metal-organic frameworks (MOFs) are already considered to be promising materials for gas storage, gas separation, drug delivery, and other conventional applications for porous materials. Many MOFs are inexpensive to synthesize, can be deposited under mild conditions, and are heat-tolerant and chemically stable. Alec Talin of Sandia National Laboratories at Livermore and the National Institute of Standards and Technology, Andrea Centrone of NIST and the University of Maryland, and their colleagues have taken these materials one step farther. By introducing a guest molecule within its pores, a well-studied MOF known as HKUST-1 becomes electrically conductive, opening an entirely new array of possible applications.

MOFs, as the name implies, are comprised of metal cations bonded to rigid organic “linkers,” creating a stable nanoporous structure. With record-setting surface areas (as high as 7000 square meters per gram), they are ideal for applications such as CO₂ sequestration and catalysis. While efforts to develop MOFs for these applications made major strides over the past decade, electrically conducting frameworks were much more illusory. “What motivated us were the possible applications,” said Talin, lead author of

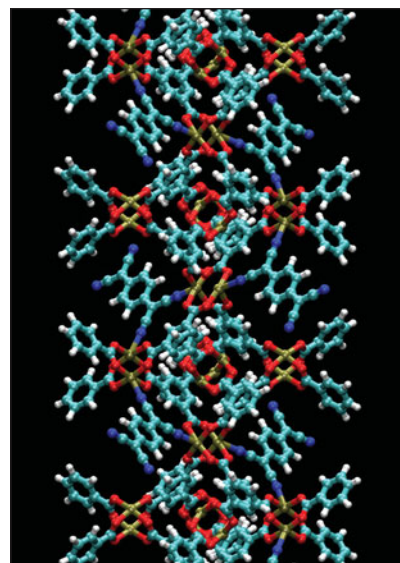
the study published in the January 3, 2014 issue of *Science* (DOI:10.1126/science.1246738; p. 66). He cites a host of promising avenues, such as novel electronic devices, photovoltaics, supercapacitors, and electrocatalysis.

But creating an electronically conductive MOF was not a simple matter. Until this innovation, virtually all known MOFs were electrically insulating, due to the primarily ionic nature of the metal-linker bonds. Rather than trying to change the framework itself, the research team took this different approach of introducing a guest molecule into the pores.

The molecule they chose, tetracyanoquinodimethane, or TCNQ, is also an insulating material. However, it has been known that in combination with other organic molecules or metal ions such as copper, TCNQ forms electron-conducting charge-transfer complexes. The researchers started with a well-known copper-containing MOF known as HKUST-1.

They soaked a thin film of HKUST-1 grown on patterned electrodes in a solution of TCNQ, causing the TCNQ molecules to infiltrate the pores. The result was startling: the MOF film became >10⁶ times more conductive than the film without TCNQ. “The framework is insulating, the guest molecule is insulating,” said Talin, “but when they come together, they make a conducting material.”

Moreover, the effect is tunable. By altering the exposure time to TCNQ, the magnitude of the conductivity could be controlled. TCNQ is the first step, said Talin; there are many other types of



The molecule tetracyanoquinodimethane (TCNQ) was added to a metal-organic framework (MOF). The chain of TCNQ molecules creates an electrically conducting path through the MOF structure. The turquoise spheres represent carbon atoms, white are hydrogen, blue are nitrogen, red are oxygen, and bronze are copper. Courtesy of Sandia National Laboratories.

guest molecules that create other electronic behaviors leading to a wide range of applications.

From here, Talin plans to investigate what happens when these MOF devices are scaled to much smaller dimensions, approaching those of molecular electronic devices that require a high level of adaptable control. Energy-storage and energy-conversion applications are also a top priority.

Meg Marquardt

Energy Focus
Inexpensive organic flow battery is metal-free

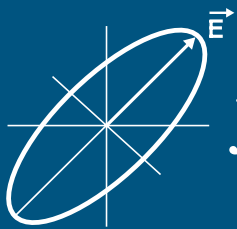
The mismatch between the availability of intermittent wind or sunshine and the variability of demand is a major obstacle to getting a large fraction of electricity from renewable sources. A growing number of engineers have focused their attention on flow battery technology, which reversibly converts chemical energy directly to electricity.

Until now, flow batteries have relied on chemicals that are expensive or difficult to maintain, driving up the energy-storage costs. Now, a team of scientists and engineers from Harvard University has developed a metal-free flow battery that relies on the electrochemistry of naturally abundant, inexpensive, small organic (carbon-based) molecules called quinones, which are similar to molecules that store energy in plants and animals.

The active components of electrolytes in most flow batteries have been

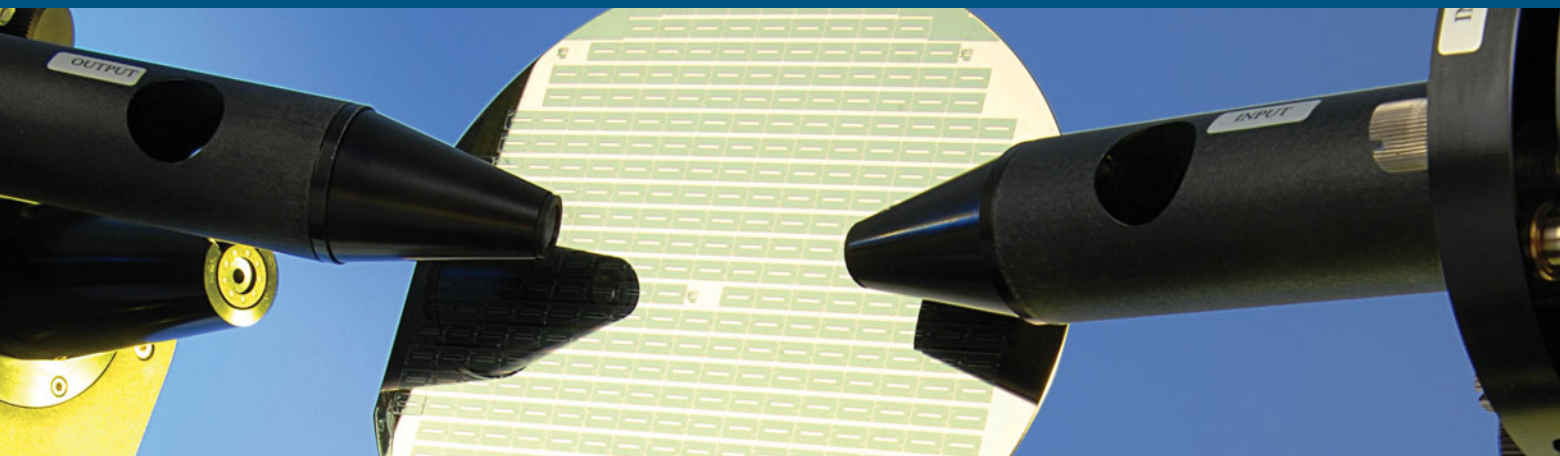
metals. Vanadium is used in the most commercially advanced flow battery technology now in development, but its cost sets a high floor on the cost per kilowatt-hour at any scale. Other flow batteries contain precious metal electrocatalysts such as the platinum.

As reported in the January 9 issue of *Nature* (DOI:10.1038/nature12909; p. 195), the flow battery developed by the Harvard team already performs as well as vanadium flow batteries, with chemicals that are significantly less



J.A. Woollam Co., Inc.

Ellipsometry Solutionssm for your Thin Film Characterization.



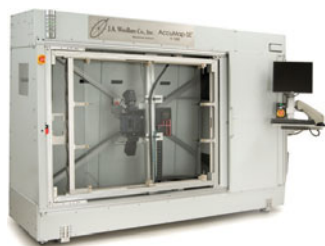
J.A. Woollam Co. has the world's widest variety of **Spectroscopic Ellipsometers** with **8** different models to non-destructively characterize thin film thickness and optical constants. After twenty-four years, over **15,000** samples characterized in our lab, and over **140** patents – we are the Ellipsometry Experts.

Ellipsometry Solutions



alpha-SE[®]

A great solution for routine measurements of thin film thickness and refractive index. Designed for ease-of-use: simply mount a sample, choose the model that matches your film, and press "Measure". Results are yours within seconds.



AccuMap-SE[®]

Characterize thin film uniformity of large panels with ease. The AccuMap-SE combines a high-speed M-2000 ellipsometer, wide spectral range, and fast mapping for large panels. Perfect for photovoltaic or flat panel display thin films.



M-2000[®]

The M-2000 line of ellipsometers is engineered to meet the diverse demands of thin film characterization. An advanced optical design, wide spectral range, and fast data acquisition make it extremely powerful for in situ, in-line and ex situ applications.



VASE[®]

The VASE is our most accurate and versatile research ellipsometer for all types of materials: semiconductors, dielectrics, organics, metals, multi-layers, and more. Now available with the widest spectral range from ultraviolet to infrared.

www.jawoollam.com • 402.477.7501 • 645 M Street, Lincoln, Nebraska USA



In this laboratory-scale organic molecule flow battery, energy-storing chemicals are dissolved in water and stored in containers in the background. To discharge the battery they are pumped through the energy conversion hardware in the foreground, converting chemical energy to electrical energy and becoming low-energy molecules. To recharge the battery, electrical energy is pushed into the energy-conversion hardware, converting low-energy chemicals into high-energy chemicals which are stored in these containers until electrical energy is needed again. The negative electrode is the left side of the battery and the positive electrode is the right side. In order to store more energy, the energy-conversion hardware does not need to change: only the container size and the amount of chemicals need to increase. Credit: Eliza Grinnell, Harvard School of Engineering and Applied Sciences.

expensive, and with no precious metal electrocatalysts.

“The whole world of electricity storage has been using metal ions in various charge states but there is a limited number that you can put into solution and use to store energy, and none of them can economically store massive amounts of renewable energy,” said Roy G. Gordon, Thomas Dudley Cabot Professor of Chemistry and Professor of Materials

Science at the Harvard School of Engineering and Applied Sciences (SEAS). “With organic molecules, we introduce a vast new set of possibilities. Some of them will be terrible and some will be really good. With these quinones we have the first ones that look really good.”

Quinones are abundant in crude oil as well as in green plants, and the molecule the researchers used in their first quinone-based flow battery is almost

identical to one found in rhubarb. The quinones are dissolved in water, which prevents them from catching fire.

Flow batteries store energy in chemical fluids contained in external tanks—as with fuel cells—instead of within the battery container itself. The two main components—the electrochemical conversion hardware through which the fluids are flowed (which sets the peak power capacity), and the chemical storage tanks (which set the energy capacity)—may be independently sized. Thus the amount of energy that can be stored is limited only by the size of the tanks. The design permits larger amounts of energy to be stored at a lower cost than with traditional batteries.

Team leader Michael J. Aziz, Gene and Tracy Sykes Professor of Materials and Energy Technologies at SEAS, said the next steps in the project will be to further test and optimize the system that has been demonstrated on the benchtop and bring it toward a commercial scale. “So far, we’ve seen no sign of degradation after more than 100 cycles, but commercial applications require thousands of cycles,” he said. He also expects to achieve significant improvements in the underlying chemistry of the battery system. “I think the chemistry we have right now might be the best that’s out there for stationary storage and quite possibly cheap enough to make it in the marketplace,” he said. “But we have ideas that could lead to huge improvements.”

Bio Focus

Contact lens elutes glaucoma medication sustainably for one month

Eye drops are relatively difficult to apply: one-sixth of glaucoma patients need assistance putting medicated eye drops into their eyes. Further, the eye drops can cause stinging and allergic reactions, and as glaucoma’s symptoms can be subtle, patients often feel little motivation to take their

medications. The resulting poor patient compliance can lead to irreversible blindness. While drug-eluting contact lenses were first proposed in the 1960s, poor drug release profiles have plagued prototypes.

Now, a team of Boston-based researchers led by Joseph Ciolino and Daniel Kohane of the Massachusetts Institute of Technology report, in the January issue of *Biomaterials* (DOI: 10.1016/j.biomaterials.2013.09.032; p. 432), a dual-polymer contact lens

that releases therapeutic doses of the potent glaucoma medication latanoprost *in vivo* for a month. The device starts with methafilcon (a copolymer of methyl methacrylate and hydroxyethyl methacrylate). The researchers then spin-coat a solution of latanoprost and poly(lactic-*co*-glycolic acid) (PLGA) onto the methafilcon lens blank to produce 20-, 40-, or 45- μ m-thick polymer-drug films. After solvent removal, a round aperture is incised in the center, and a topcoat of methafilcon is then