

### Polyhedral Oligomeric Silsesquioxane-Reinforced Photopolymers Demonstrate High Sensitivity for Holographic Data Storage

Holographic data storage is a promising new method for recording digital information. This is because holography allows pages of data to be written at once, while storing multiple pages of data in a given volume. Photopolymers are attractive materials for use as holographic recording media due to their high sensitivity and low cost. However, a critical drawback of photopolymers is the volume shrinkage which occurs during polymerization. Now J.-K. Park and co-workers from Korea Advanced Institute of Science and Technology (KAIST) have shown that incorporating multifunctional molecular silicate "cages" into the polymer matrix of the holographic photopolymer reduces volume shrinkage while maintaining high photosensitivity.

As reported recently in *Optics Letters*, to minimize volume shrinkage, the researchers created an organic-inorganic hybrid material using methacrylate-functionalized polyhedral oligomeric silsesquioxane (POSS) as a co-monomer. The polymer matrix consisted of PMMA with dibutylphthalate plasticizer, *n*-vinylcarbazole as a second co-monomer, and Irgacure 784 as the photoinitiator. Three compositions were tested with varying amounts of POSS: 0, 1, and 2 wt%.

The researchers showed higher diffraction efficiency with systems that contained POSS. A maximum diffraction efficiency of 80% was achieved using 1 wt% POSS, compared to ~30% without POSS. Additionally, the diffraction efficiency increased more rapidly with higher concentrations of POSS. As a result, the photosensitivity more than doubled when 1 wt% POSS was added to the system. The researchers attribute the rapid growth in diffraction

efficiency to the multiple vinyl groups provided by each POSS molecule. By increasing the polymerization rate, a larger concentration gradient is created for the *n*-vinylcarbazole monomer. This drives the diffusion of the monomer into the illuminated region and increases the diffraction efficiency. The dimensional stability of the photopolymer system was determined using Bragg angle detuning. From this experiment, the volume shrinkage was calculated to be 2.0% for systems containing 1 wt% POSS, compared to 3.0% for systems without POSS. The researchers conclude that using the multifunctional POSS molecule as a co-monomer strengthens the polymer matrix of the holographic photopolymer and reduces volume shrinkage while maintaining high diffraction efficiency and photosensitivity.

SCOTT COOPER

### Metal Organic Frameworks Achieve CO<sub>2</sub>-Specific Adsorption at Low Pressures

Metal-organic frameworks (MOFs) have emerged as an important class of materials due to their porous nature and relative ease of design. Their low density (0.20–1.00 g/cm<sup>3</sup>) and high surface area (500–4500 m<sup>2</sup>/g) have brought MOFs into the forefront of gas storage and separation research. To date, a significant portion of relevant publications has focused on large-pore MOFs due to their ability to store higher volumes of gas. However, high pressures are usually needed in order for large-pore MOFs to adsorb extreme amounts of gases. Additionally, gas selectivity would be expected to decrease with increasing pore size. In general, gas sorption can be controlled by the MOF pore structures and the functionality

present within the pores.

As recently reported in *Chemical Communications* (Issue 35, DOI: 10.1039/b911481e; p. 5230), R. Vaidhyanathan, S.S. Iremonger, K.W. Dawson, and G.K.H. Shimizu of the University of Calgary have achieved specific CO<sub>2</sub> adsorption at low pressure. Starting with commercially available materials—zinc carbonate, oxalic acid, 3-amino-1,2,4-triazole—highly crystalline MOFs with small pores (3.5 Å × 4.0 Å and 3.9 Å × 2.1 Å) were synthesized. By incorporating amine-containing molecules, the pores of the final product are functionalized with free amines, which are purported to interact with CO<sub>2</sub>. After activating the MOFs to remove all solvent, the adsorption of several gases was studied at various temperatures. Particularly of note, CO<sub>2</sub> sorption was as high as 4.35 mmol/g at 273 K

with partial pressures as low as 1.2 bar. The experimental adsorption and desorption were completely reversible for the eight trials that were repeated. The adsorption of N<sub>2</sub>, H<sub>2</sub>, and Ar were also studied, with only minimal uptake of these gases observed. The selectivity of the designed MOF is attributed to a combination of the small pores and the extensive host-guest interactions due to the presence of the free amines.

Vaidhyanathan and collaborators said this MOF may potentially be useful for removing trace amounts of CO<sub>2</sub> from recyclable gases due to its selectivity at low partial pressures. Future research aims to characterize related materials as well as the physical nature of the adsorbed CO<sub>2</sub> molecules.

DEVIN G. BARRETT

### Sulfur- and Coking-Tolerant Material Could Expand Applications for SOFCs

Solid-oxide fuel cells (SOFCs) use an electrochemical process to produce electricity by oxidizing a fuel. The ceramic electrolyte they use is yttria-stabilized zirconia (YSZ). The main drawbacks to SOFCs are their susceptibility to contamination from sulfur, deactivation from carbon build-up, and limited conductivity at low temperatures. Now M. Liu and colleagues at the Georgia Institute of Technology have developed a mixed ion conductor,

BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2-x</sub>Yb<sub>x</sub>O<sub>3-δ</sub> (BZCYYb) that may address these problems.

Fuels used in SOFCs, such as natural gas or propane, must be purified to remove sulfur, which increases their cost. Water in the form of steam must also be supplied to a reformer that converts hydrocarbons to hydrogen and carbon monoxide before being fed to the fuel cells, adding complexity to the overall system and reducing energy efficiency. And the high-temperature operation means the cells must be fabricated from costly exotic materials, which keeps SOFCs too expen-

sive for many applications.

As reported in the October 2 issue of *Science* (DOI: 10.1126/science.1174811; p. 126), the new material developed at Georgia Tech tolerates hydrogen sulfide in concentrations as high as 50 ppm, does not accumulate carbon, and can operate efficiently at temperatures as low as 500°C.

The material could be used in a variety of ways: as a coating on the traditional Ni-YSZ anode, as a replacement for the YSZ in the anode, and as a replacement for the entire YSZ electrolyte system. Liu believes the first two options are more viable.

So far, the new material has provided steady performance for up to 1000 hours of operation in a small laboratory-scale SOFC. To be commercially viable, however, the material will have to be proven in operation for up to five years—the expected lifespan of a commercial SOFC.

“We don’t see any problems ahead for fabrication or other issues that might prevent scale-up,” said Liu, a Regent’s professor in the School of Materials Science and Engineering at Georgia Tech. “The mate-

rial is produced using standard solid-state reactions and is straightforward.”

The researchers do not yet understand how their new material resists deactivation by sulfur and carbon, but theorize that it may provide enhanced catalytic activity for oxidizing sulfur and both cracking and reforming hydrocarbons.

Furthermore, Liu said, “Getting the temperature down to 300–400°C could allow use of much less expensive materials in the packaging, which would dramatically

reduce the cost of these systems.”

“Solid-oxide fuel cells offer high energy efficiency, the potential for direct utilization of all types of fuels including renewable biofuels, and the possibility of lower costs since they do not use any precious metals,” said Liu. “We are working to reduce the cost of solid-oxide fuel cells to make them viable in many new applications, and this new material brings us much closer to doing that.”

### Renewable Hydrogen Production Becomes Reality at Winery

The first demonstration of a renewable method for hydrogen production from wastewater using a microbial electrolysis system is underway at the Napa Wine Company in Oakville, Calif. The refrigerator-sized hydrogen generator will take winery wastewater, and using bacteria and a small amount of electrical energy, convert the organic material into hydrogen and other products, according to B.E. Logan of the Pennsylvania State University.

“This is a demonstration to prove we can continuously generate renewable hydrogen and to study the engineering factors affecting the system performance,” said Logan, Kappe professor of environmental engineering. “The hydrogen produced will be vented except for a small amount that will be used in a hydrogen fuel cell.” Eventually, Napa Wine Company would like to use the hydrogen to run vehicles and power systems.

Napa Wine Company’s wastewater comes from cleaning equipment, grape disposal, wine making, and other processes. The company already has on-site wastewater treatment and recycling and the partially treated water from the microbial electrolysis system will join other water for further treatment and use in irrigation.

“It is nice that Napa Wine Company offered up their winery and facilities to test this new approach,” said Logan. “We chose a winery because it is a natural tourist attraction. People go there all the time to experience wine making and wine, and now they can also see a demonstration of how to make clean hydrogen gas from agricultural wastes.”

The demonstration microbial electrolysis plant is a continuous flow system that will process about 1000 liters of wastewater a day. Microbial electrolysis cells consist of two electrodes immersed in liquid. Logan uses electrode pairs consisting of one carbon anode and one stainless steel cathode in his system rather than an electrode coated with a precious metal like platinum or gold. Replacing precious metals will keep down costs. The wastewater enters the cell where naturally occurring bacteria convert the organic material into ions including hydrogen ions. However, the currents produced by this process are limited because a fermentation barrier exists. The fermentation barrier can be overcome by a small applied electrical bias, on the order of 0.25 V, so that hydrogen gas is produced electrochemically on the stainless steel cathode in a much more efficient manner.

The demonstration plant is made up of 24 modules. Each module has six pairs of electrodes.

“The composition of the wastewater will change throughout the year,” said Logan. “Now it is likely to be rather sugary, but later it may shift more toward the remnants of the fermentation process.”

The bacteria that work in the electrolysis cells will consume either of these organic materials.

The project is supported by Air Products & Chemicals, Inc., The Water Environmental Research Foundation Paul L. Busch Award, and other donors. Brown & Caldwell, an environmental engineering consulting firm, was contracted to build the demonstration plant. The Napa Wine Company is donating its facilities and wastewater for the demonstration. □

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