

nated by intergranular fracture, while in AJM it was in a manner resembling ductile behavior. Improved surface finishing by AJM resulted in a 15% improvement in flexural strength, compared with both ground and ground-plus-lapped samples. The researchers concluded that a higher compressive residual stress observed on the AJM-processed surface, combined with the smoother surface and a reduction in machining flaws, is responsible for the enhancement of the flexural strength.

SHIMING WU

### Ceramic-Based Anode for Solid-Oxide Fuel Cell Utilizes Higher-Weight Hydrocarbon Fuels without Coking

Solid-oxide fuel cells (SOFCs) based upon hydrocarbon fuels are susceptible to loss of performance due to the deposition of carbon, a process known as coking. The standard anodes in many SOFCs contain high levels of Ni, which is known to promote coking. However, recent studies performed on a ceramic-based anode have led to a method that minimizes the amount of nickel required for SOFCs, so that electrochemical reactions are catalyzed while minimizing the amount of carbon deposited. In the June issue of *Electrochemical and Solid-State Letters*, Zhiqiang Ji of Applied Thin Films Inc. in Evanston, Ill., and Juang Liu, Brian D. Maddison, and Scott A. Barnett of Northwestern University report that by altering the composition of an electronic conductor,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$  (LSCM), by mixing it with an ionic conductor,  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (GDC), the three-phase boundaries increase and thus enable hydrocarbon oxidation without coking.

Multilayer fuel-cell pellets were manufactured by pressing GDC powder into pellet form and sintering the pellets at 1500°C for 6 h. The anode was made by mixing metal oxides of lanthanum, strontium, chromium, and manganese in water prior to ballmilling for 24 h, followed by calcining at 1100°C for 2 h. After drying and grinding, the powder was mixed with 50 wt% GDC, 5 wt% NiO, water, and polyvinyl alcohol, ground and then painted on one side of the GDC pellet and sintered at 1100°C for 3 h. The NiO had a 16-nm average particle size, while the average particle size of the GDC was 50 nm. An anode with 50 wt% Ni and 50 wt% GDC was also fabricated in a similar fashion for comparison. The cathode consisted of 50 wt%  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) and 50 wt% GDC synthesized in the method described and sintered at 900°C for 3 h. Both the anode and the cathode were ~20 μm thick, with an area of 0.3–0.6 cm<sup>2</sup>.

In tests, both the LSCM-GDC-Ni and Ni-GDC anodes performed about the same in hydrogen; however, when tested with propane, the power density was larger for the LSCM-GDC-Ni anode. No obvious carbon deposits were seen on the LSCM-GDC-Ni anode, but the GDC-Ni anode was heavily covered. As expected for SOFCs, power density increased as temperature increased, with a proportional decrease in cell resistance. Final results show that LSCM, although a poor catalyst for hydrocarbon oxidation, acts as the electronic conductor and the mechanical support, while the nickel acts as the oxidation catalyst.

DONALD CARTER

### Polymeric Additive Provides Morphological Control of Calcium Oxalate Dihydrate Crystals

Control of crystal morphology and size are well-known approaches to solving many problems in various areas of materials, including catalysis, medicines, electronics, ceramics, pigments, and cosmetics. Researchers from the College of Chemistry at Peking University in Beijing have discovered a method for morphology-controlled synthesis of calcium oxalate dihydrate (COD). As reported in the June 17 issue of *Chemistry of Materials*, Dongbai Zhang and co-workers at Peking have described a technique for the preparation of tetragonal rodlike prisms using a double-hydrophilic block copolymer.

The researchers performed the crystallization of calcium oxalate in aqueous solutions of a double-hydrophilic block copolymer of poly(ethylene glycol)-*block*-poly(methacrylic acid) (PEG-*b*-PMAA) at different PEG-*b*-PMAA and Ca<sup>2+</sup> concentrations, as well as at different  $[\text{Ca}^{2+}]/[\text{C}_2\text{O}_4^{2-}]$  ratios. The morphology of COD crystals was characterized by x-ray diffraction and scanning electron microscopy. The researchers observed that the increase of polymer concentration changes the morphology of resulting COD crystals from tetragonal bipyramids dominated by the {101} faces to rodlike tetragonal prisms dominated by the {100} faces, which is a morphology adopted by some plant COD crystals but not obtained *in vitro* previously. The COD square prisms obtained in different experiments ranged in size from side lengths of 0.6–2.3 μm and side widths of 0.2–1.4 μm, resulting in the maximal aspect ratio of ~3.5.

The researchers suggested a lattice-matching model (based on the similarity of COD unit-cell parameters and distances between two terminal groups in a PMAA chain) to explain the specific morphological influence of PEG-*b*-PMAA on COD

crystals. Such a model was extensively used to explain the interaction between crystal faces of inorganic compounds and organic templates/additives. The researchers tested the proposed model on the crystallization of strontium oxalate in the presence of PEG-*b*-PMAA under similar conditions, and found that the suggested model works as expected in this case.

The researchers said that the observed morphological control of COD crystals by the polymeric additive provides insights into the specific function of biomacromolecules in the morphological control of plant COD crystals and could be applied to other synthetic systems of interest.

ANDREI A. ELISEEV

### Addition of Fumed Silica Nanoparticles Enhances the Permeability of a Polymer Reverse-Selective Membrane

Recently developed, reverse-selective membranes offer improved industrial refinement of natural gas, polyolefin, and hydrogen through their counterintuitive property of preferentially permeating large organic molecules over smaller gases. T.C. Merkel and co-workers of the Research Triangle Institute in North Carolina fabricated membranes with increased permeability and selectivity by adding nanometer-scale, nonporous, fumed silica particles to a glassy, low-density polyacetylene—such as poly(4-methyl-2-pentyne) (PMP)—matrix, as reported in the April 19 issue of *Science*.

The permeability of a membrane is defined as the product of the penetrant solubility and diffusivity, while the selectivity of gas A over gas B is represented by the ratio of their respective permeabilities. Higher-molecular-weight hydrocarbon gases exhibit greater solubility than lighter gases because they are more readily condensed into liquids for transport through the membrane. However, the larger hydrocarbon chains generally diffuse much more slowly than the smaller, lighter materials. The diffusivity effect usually dominates, and conventional membranes permeate smaller molecules, such as hydrogen, more effectively than larger ones, such as methane. However, this size-sieving diffusion contribution is minimized for membranes with high free volumes because they contain diffusive pathways that transport large molecules nearly as efficiently as smaller ones. Such membranes exhibit the reverse-selective behavior that purifies natural gas by permitting the efficient removal of higher hydrocarbons from methane.

Previous attempts to improve membrane selectivity focused on the addition of

porous, size-selective, zeolite particles to polymer matrices. However, the reliability of such membranes was compromised by poor polymer/zeolite adhesion and inadequate particle dispersion. In this research study, nonporous, fumed silica particles were added to disrupt the molecular bonding in a rigid glassy polymer. Fine silica particles subtly increased the size of the free-volume voids in the polymer matrix, as revealed by positron annihilation lifetime spectroscopy (PALS). Since it is through a network of these larger voids that the penetrants are assumed to diffuse, slightly increasing their size enhanced the membrane's reverse-selectivity by further weakening the size-sieving character of the PMP and improved its permeability by enabling faster diffusion.

Critical to this method, said the researchers, was the addition of particles comparable in size to the polymer molecule; adding an equivalent volume of particles larger than 50 nm in diameter did not improve permeability since it did not uniformly alter the polymer chain packing. Transmission electron microscopy imaging of the membranes revealed well-distributed, discrete silica particles and silica aggregates within the PMP matrix, consistent with the proposed mode of enhanced transport and selectivity by molecular-scale alteration of the polymer structure.

JULIE NUCCI

### Metallo-Supramolecular Cylinders Induce Intramolecular DNA Coiling

Proteins regulate the structure and function of life encoded in DNA with their ability to recognize the genetic code in a sequence-selective manner and induce structural changes in DNA. The ability to turn processing of the genetic code on or off requires a variety of molecular tools. Advancing toward this goal, researchers from the University of Warwick in Coventry, England; Universitat de Barcelona, Spain; and the University of Bergen, Norway have employed synthetic supramolecular assemblies to selectively bind to the major groove of DNA, causing the DNA to coil significantly. (DNA's surface is not a smooth cylinder but has two differently sized grooves.)

Enantiomers are molecules that are nonsuperimposable mirror images of each other. In enantio-selective binding, one enantiomer binds but not the other. As reported in the April 16 issue of the *Proceedings of the National Academy of Sciences*, teams led by University of Warwick researchers A. Rodger and M.J. Hannon employed a variety of experimental techniques to explore the

enantio-selectivity of the binding of  $[\text{Fe}_2(\text{C}_{25}\text{H}_{20}\text{N}_4)_3]\text{Cl}_4$ —a cylindrical tetra cationic dimetallo triple helicate—to DNA. Rodger and Hannon previously showed that a racemic mixture (i.e., contains equal amounts of both enantiomers) of  $[\text{Fe}_2\text{L}_3]\text{Cl}_4$  induced a dramatic intramolecular bending, but the resulting DNA coils contained only the M enantiomer.

Small synthetic molecules designed to achieve DNA sequence selectivity typi-

cally bind to the minor groove of DNA. Recognition is generally limited to 2–3 base pairs due to size limitations. Sequence recognition within the major groove may prove more fruitful because its size and shape vary much more with base sequence than does the minor groove, said the researchers. Indeed, they said, many biomolecules target the major groove. Rodger and Hannon believe that supramolecular chemistry provides an

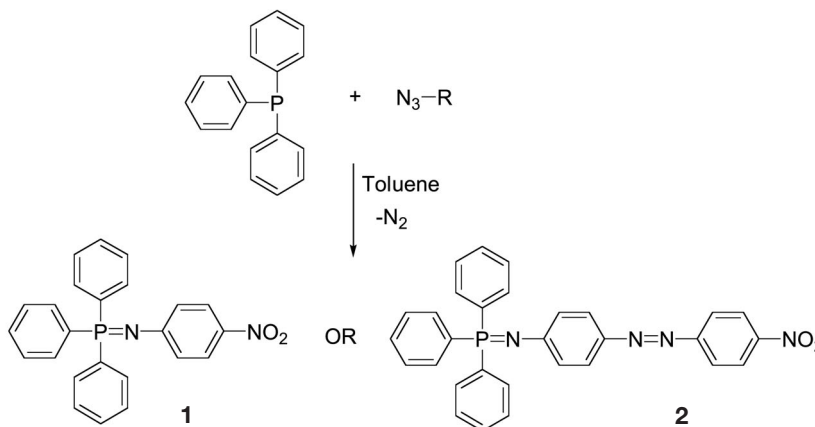
### Versatile and Efficient Nonlinear Optical Material Chromophore Developed

Researchers at the University of Missouri and the Dow Chemical Company have demonstrated that azaphosphane compounds can act as electron-donor functional groups in nonlinear optical (NLO) materials. NLO materials have found applications in optical data storage, optical information processing, and optical/electro-optical switching devices. The researchers, led by Kattesh Katti, determined that the azaphosphane chromophores exhibited good NLO activity while maintaining excellent solubility in common organic solvents. The compounds also exhibited thermal stability up to 335°C. According to Katti, "the azaphosphanes will allow the design and development of novel, thermally stable NLO materials."

As described in the June 17 issue of *Chemistry of Materials*, the researchers synthesized two azaphosphane compounds having a P=N donor group and a  $\text{NO}_2$  acceptor group that are separated by one (Compound 1) or three (Compound 2) conjugated double bonds (see Scheme). The air-stable product compounds were characterized by nuclear magnetic resonance spectroscopy and mass spectrometry. The NLO activities of the two chromophores were measured by the electric-field second-harmonic technique using 1579-nm light. This technique yields the NLO activity as a product of the dipole moments ( $\mu$ ) and the hyperpolarizability ( $\beta$ ) of the azaphosphane molecules. Compounds 1 and 2 exhibited  $\mu\beta$  values of  $3.1 \times 10^{-46}$  and  $11 \times 10^{-46}$  esu, respectively. The larger  $\mu\beta$  value corresponds to a larger change in the molecular dipole moment upon irradiation which leads to a higher NLO activity. The researchers attribute this larger NLO activity of Compound 2 to increased conjugation length, which improves donor-acceptor interactions. While these  $\mu\beta$  values are not as high as those reported for thiophene-based chromophores, Compounds 1 and 2 exhibit excellent solubility in organic solvents that decreases for molecules with large dipole moments. High solubility will allow the azaphosphanes to be used with a large number of polymer hosts in the manufacture of NLO materials.

Also important for applications in NLO materials is the thermal stability of the chromophore. The thermal stability of the azaphosphanes was studied by thermogravimetric analysis and differential scanning calorimetry. Compound 1 was stable to above 282°C, while Compound 2 was stable to 335°C, much higher than thiophene-based chromophores. The researchers attribute the high thermal stabilities to the inherent stability of P–N compounds.

GREG KHITROV



Scheme. Synthesis of azaphosphanes. Reprinted with permission from *Chem. Mater.*, June 17, 2002, 14. Copyright 2002 American Chemical Society.