

### Li<sub>4</sub>C<sub>60</sub> Fulleride Polymer Displays Superionic Conductivity

Typical solid-phase ionic conductors, called superionic conductors, are disordered or glassy materials with interstitial sites due to defects or imperfect stoichiometry, and not intrinsic to the crystalline structure. Ions diffusing within the unoccupied sites give rise to ionic conductivities comparable to those observed in the molten state. Despite the large free volume in their crystal structure, fullerides have not (and would not be expected to, except at high temperatures) displayed ionic conductivity because the interstitial sites are connected by narrow channels. Recently, however, M. Riccò and co-workers at the University of Parma, Italy; D. Quintavalle and A. Jánossy at Budapest University of Technology and Economics, Hungary; and G. Csányi of the University of Cambridge, UK, showed that Li<sub>4</sub>C<sub>60</sub> forms a two-dimensional polymer with extraordinary superionic conductivity at temperatures <400 K. The researchers previously showed that the interfullerene covalent bonds distort the structure into a mono-

clinic space group. Two Li<sup>+</sup> ions occupy the tetrahedral sites of the cubic parent structure, while the other two Li<sup>+</sup> ions doubly occupy the corresponding octahedral sites.

As reported in the April 10 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.102.145901; #145901), Riccò and co-researchers prepared Li<sub>4</sub>C<sub>60</sub> samples by thermal decomposition of Li azide. They found that above 130 K the conductivity displays Arrhenius behavior reaching a value of 0.01 S/cm at room temperature. The activation energy for Li<sup>+</sup> diffusion was calculated to be 240 meV, which the researchers said is surprisingly low for an ionic conductor. The researchers confirmed the ionic character of the conductivity with ac- and dc-conductivity measurements, <sup>7</sup>Li nuclear magnetic resonance spin-lattice relaxation measurements, and density functional theory (DFT) calculations. The Li<sup>+</sup> ions are frozen in their crystallographic positions at temperatures below 130 K. The impedance measured at three temperatures all showed a single loss peak, which the researchers attribute to

bulk Li<sup>+</sup> ion conduction through sites with well-defined barriers. In contrast to disordered ionic conductors, the loss peaks are well described by an ideal Debye process with a single relaxation time,  $\tau$ , for the imaginary part of the impedance. The activation energy calculated from the Arrhenius plot of  $\tau$  is in good agreement with the value calculated from conductivities. The DFT calculations confirm the x-ray crystal structure except for the position of the Li<sup>+</sup> ions in the octahedral site, which are displaced slightly in the DFT-optimized structure. In addition, the DFT calculations predict two unoccupied interstitial sites in addition to the two occupied sites in voids derived from the octahedral sites. Configurations with more than two Li<sup>+</sup> ions in the octahedral site have low energies that would allow Li<sup>+</sup> diffusion in the lattice even at low temperatures. The researchers said that their study "opens the possibility for a new application of fullerides, intercalated with small size ions, in batteries."

STEVEN TROHALAKI

### Ir(III) Organometallic Complexes Studied for Oxygen Sensing

Organometallic compounds are increasingly being used for applications such as sensing devices and organic light-emitting diodes (OLEDs). Due to their high emission quantum yields, cyclometalated Ir(III) complexes are particularly important among these compounds. Now C.S.K. Mak and W.K. Chan of the University of Hong Kong, China; and D. Pentlehner, M. Stich, O.S. Wolfbeis, and H. Yersin of the University of Regensburg, Germany have presented a study of two of these Ir(III) complexes: Ir(ppy)<sub>3</sub> and Ir(ppy-NPh<sub>2</sub>)<sub>3</sub>. Their study is available in a recent communication to *Chemistry of Materials* (DOI: 10.1021/cm9003678; published online on May 4, 2009).

By measuring the emission spectra of Ir(ppy)<sub>3</sub> and Ir(ppy-NPh<sub>2</sub>)<sub>3</sub> and the emission decay time of Ir(ppy-NPh<sub>2</sub>)<sub>3</sub>, the researchers compared the triplet excited state properties of both complexes and used Ir(ppy-NPh<sub>2</sub>)<sub>3</sub> to build oxygen-sensing devices.

According to their results, there are several reasons why Ir(ppy-NPh<sub>2</sub>)<sub>3</sub> might be a good candidate for oxygen-sensing applications: (a) the compound has good solubility in organic solvents; (b) its excited state lifetime has a wide range of values as a function of the oxygen partial pressure; (c) due to its high phosphorescence quantum yield, Ir(ppy-NPh<sub>2</sub>)<sub>3</sub> provides sensing devices with a high sensitivity; (d) Ir(ppy-NPh<sub>2</sub>)<sub>3</sub> is less sensitive to self-quenching or triplet-triplet annihilation, and its emission

light can be easily separated from its excitation light, which can be provided using low-cost LEDs; and (e) the compound has a reasonably long emission lifetime.

The oxygen sensors were prepared by dissolving Ir(ppy-NPh<sub>2</sub>)<sub>3</sub> in ethyl cellulose and then spraying this solution over a titanium dioxide-coated aluminum support. These sensors display high sensitivity to changes of oxygen partial pressure, even for air pressures as high as 1500 mbar.

According to the researchers, the potential applications of this Ir(ppy-NPh<sub>2</sub>)<sub>3</sub>-based sensing material range from uses in fiber optic sensors and microplates, to applications in aerodynamic measurements.

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### Electrothermal Reaction with Ammonia Allows Generation of *n*-Type Graphene

The *p*-type graphene has been already produced by using adsorbates and oxygen groups on edges. However, for device applications, scientists need to access the *n*-doped material as well. Previously, graphene edge-terminated by nitrogen species has been shown to exhibit *n*-type behavior in transistors. X. Wang, X. Li, L. Zhang, H. Wang, and H. Dai from

Stanford University, together with Y. Yoon and J. Guo from the University of Florida and P.K. Weber from the Lawrence Livermore National Laboratory, functionalized graphene nanoribbons (GNRs) by nitrogen species through high-power electrical joule heating in ammonia gas, leading to *n*-type electronic doping, as they reported in the May 8 issue of *Science* (DOI: 10.1126/Science.1170335; p.768).

The researchers synthesized GNRs (10–150 nm width) chemically or obtained

them by patterning lithographically pristine peel-off graphene. They dispersed the GNRs on a 300-nm SiO<sub>2</sub>/Si chip, and located and imaged them by scanning electron microscopy and atomic force microscopy. With these GNRs the researchers fabricated field-effect transistors (FETs) with palladium metal source/drain and highly doped Si backgate. The researchers observed that as-synthesized GNRs exhibited *p*-doping behavior that was reduced when they annealed the devices in high

vacuum ( $\sim 10^{-6}$  Torr) with a high power electric field. This caused electrothermal self-heating of the GNR to hundreds of degrees which removed *p*-doping sources. The researchers, then, functionalized GNRs by introducing electron-rich nitrogen species by e-annealing the GNR devices in a  $\sim 1$ -Torr  $\text{NH}_3/\text{Ar}$  environment. The GNR devices functionalized in this way showed Dirac point positions shifted by  $\sim 20$  V before and after e-annealing in  $\text{NH}_3$ , that stayed stable and constant in vacuum, signifying *n*-type electronic dop-

ing without degradation of their carrier mobility. The researchers demonstrated by x-ray photoelectron spectroscopy and nanometer-scale secondary ion mass spectroscopy that the thermal annealing with  $\text{NH}_3$  generated carbon-nitrogen species mostly at the edges of the graphene where chemical reactivity is high. Theoretical calculations performed by the researchers showed that GNRs functionalized by oxygen and nitrogen species on their edges were *p*- and *n*-doped, respectively, which agreed with the experimental

results the researchers obtained.

Using the e-annealing approach in  $\text{NH}_3$ , the researchers fabricated *n*-type sub-10 nm GNRFETs with Ti contact metals and a 5 nm Pd buffer layer that operated at room temperature with a subthreshold slope similar to that of the as-made *p*-type GNRFETs. The researchers said that the ability to control graphene chemistry through edge doping at the nanoscale is an important step toward controlled graphene electronics.

JOAN J. CARVAJAL

### Light-Assisted Writing of Bits Achieved on Low-Doped (Ga,Mn)As Ferromagnetic Semiconductors

Energy-assisted switching mechanisms for magnetic bits will be needed in future magnetic recording technology. These mechanisms use a second source of energy to reduce the material's coercivity, the applied magnetic field needed to reverse the orientation of the magnetization of a ferromagnet. Mechanisms under consideration include heating a magnetic material with a laser or stimulating it with a transverse microwave field. Ideally, such a method should be local and reversible: It should reduce the coercivity of a bit only where it is applied and only for so long as it is applied, after which it should recover fully. G.V. Astakhov and co-workers of the University of Würzburg, Germany and V.L. Korenev of the Russian Academy of Sciences have

recently found just such a mechanism in low-doped (Ga,Mn)As thin films at low temperatures using the photocoercivity effect. By removing the need for heating, this could provide a low power alternative to other energy-assisted recording technologies.

The researchers demonstrated light-assisted writing in the May 8 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.102.187401; #187401). They used low-temperature molecular beam epitaxy to deposit a 360 nm layer of  $(\text{Ga}_{1-x}\text{Mn}_x)\text{As}$  ferromagnetic semiconductors, with  $x \approx 0.005$ . These samples were measured at 2 K with the magneto-optical Kerr effect at two different laser powers, the "dark" condition at 10  $\mu\text{W}$  and the "light" condition at 1 mW. Finding the coercivity to be 525 Oe and 285 Oe, respectively, the researchers returned to 10  $\mu\text{W}$  and found the coercivity recovered to its original value—showing

that the effect is reversible. They then wrote patterns on the substrate in an intermediate field of 470 Oe, evidencing both the locality of the transition and its potential to write bits.

The mechanism the researchers propose for this behavior is the mobility of holes. The magnetic behavior of the (Ga,Mn)As is mediated by the holes, and in low-doped samples, the mobility is low. This means that the holes are not free to relocate to their most favored state when a field is applied, and therefore some extra field is required to move domain walls. In comparison, the photocoercivity effect was not seen in more highly doped samples with  $x \approx 0.05$ , in which holes move readily. This mechanism provides a clue for materials engineers on how to extend this effect to low-power light-assisted magnetic recording in consumer products.

JIM RANTSCHLER

### LaSrCoFeO Offers Alternate Cathode Material to Pt for Micro-Fuel Cells

With the proliferation of portable electronic devices, there is a critical need for reliable power sources for these devices. One solution to meet this increasing demand is the use of fuel cells. In particular, solid oxide fuel cells (SOFCs) are relatively very efficient and are flexible in the type of fuel they can use. However, SOFCs typically operate above 700°C. It would be advantageous for them to operate at lower temperatures in the 200–600°C range, allowing for greater material flexibility and efficient operation as well as reduced corrosion than for current systems. SOFCs typically use yttria-stabilized zirconia (YSZ) electrolyte. Researchers have demonstrated Pt cathodes for operation of YSZ-based SOFCs at intermediate temperatures. However, the

Pt may degrade at the higher temperatures in this range, and materials such as  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (LCSF) have been proposed and tested as alternatives to Pt for intermediate temperature SOFC cathodes. In a recently reported study, A.C. Johnson, B.-K. Lai, H. Xiong, and S. Ramanathan of Harvard University describe the fabrication of micro-SOFCs using dense ultrathin-film LCSF cathodes, formed using RF-sputtering, and YSZ electrolyte films. The results of their study were published in the January issue of the *Journal of Power Sources* (DOI: 10.1016/j.jpowsour.2008.10.021; p. 252).

The thin-film SOFCs were fabricated with both Pt and mixed conducting oxide cathodes using sputtering, lithography, and etching. Each device is comprised of 75–150-nm thick YSZ electrolyte, a 40–80-nm porous Pt anode, and a cathode made of 15–150-nm dense LCSF or 130-nm porous

Pt. Several devices were fabricated to systematically investigate the electrical properties of the individual components of these fuel cells. For fuel cell measurements, five fuel cells were developed including three LCSF/YSZ/Pt cells (LCSF cathode) and two Pt/YSZ/Pt cells (Pt cathode). While the Pt-cathode cells produced the greatest power at most temperatures, the LCSF-cathode cells were not far behind. For instance, at 500°C, power densities of 90  $\text{mW cm}^{-2}$  and 60  $\text{mW cm}^{-2}$  were observed for the Pt and LCSF cathodes, respectively. The latter is comparable to previous reports using ultrathin-film oxides.

The major advantage of the present approach is that the thin-film cathode processing is compatible with current photolithography and patterning. It is relatively simple to synthesize a multicomponent, highly dense complex oxide thin film from a single target. The results suggest that the