

### 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.

LEANDRO LIBORIO

### 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