# **TECH HIGHLIGHTS** •

#### Enhanced Low-Temperature Performance of Li–CF, Batteries

Subfluorinated  $CF_x$  (SFCF<sub>x</sub>), 0.3 < x < 0.66, cathode active material has previously been demonstrated as a useful Li–CF<sub>x</sub> electrochemical couple exhibiting excellent utilization under discharge rates as high as 5°C at room temperature. For this report, researchers from California and France investigated various electrolyte and SFCF<sub>x</sub> cathode compositions to optimize performance in terms of capacity at high discharge rates (C/40 to C/5) for temperatures at or below -40°C. They found the 8:2 v/v % DME/PC electrolyte performed best, recognizing that propylene carbonate (PC) has a high dielectric constant and 1,2-dimethoxyethane (DME) is a low-viscosity, good coordinating component. An anion receptor (tris(2,2,2trifluoroethyl)borate, TTFEB) was added to one electrolyte composition to solvate LiF, a discharge reactant. Various cathode thicknesses were tested for CF<sub>0.65</sub>-based cells. Increasing electrode thickness led to lower cell potential during discharge due to polarization under the C/5 rate at -40 °C. While the thicker electrodes ( $\geq$  95 µm) yielded negligible specific capacity at the C/5 rate, these same cells could deliver full capacity at lower discharge rates two to eight times slower. The addition of TTFEB to the electrolyte of a cell fabricated with a 115 µm-thick cathode maintained comparable potential and specific capacity as those containing thinner cathodes  $(\leq 57 \text{ µm})$  in cells without the additive, when discharged at the C/5 rate.

From: Electrochem. Solid-State Lett., 10, A166 (2007).

## High-Yield Synthesis of Single-Crystalline Gd2O3:Eu Nanoplates Using a Pulp Precursor

Rare-earth (RE)-doped gadolinium sesquioxide  $(Gd_2O_3:RE^{3+})$  materials have been widely employed in photoluminescence, cathodoluminescence, and laser activation applications for a number of years due to their robust, thermally stable optical properties. A portion of contemporary research in this area seeks out new nanostructured variety of these phosphors with improved quantum efficiencies, chromaticities, and other traits that take advantage of the intrinsic size dependent effects of the nanomaterials. Scientists from the Korea Research Institute of Chemical Technology and the Halla Institute of Technology have developed a high yield synthesis of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanoplates, employing a pulp precursor technique. This approach yields monoclinic nanoplates with characteristic luminescence peaks at 615 nm and 624 nm, but with red chromaticity that is preferred over the cubic-phase of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>. Further, the luminescence lifetime in these nanomaterials is markedly shorter, by approximately three orders of magnitude, than that observed in bulk forms of the compound. Such a dramatic shift in the lifetime is explained as arising from enhanced mixing of s-p electrons in the From: Electrochem Solid-State Lett., 10, J97 (2007).

#### Electron Transfer Kinetics at Oxide Films on Metallic Biomaterials

Titanium and titanium-based alloys are used in a wide variety of biomedical applications due to their inherent biocompatibility and mechanical properties. The release of potentially toxic ions from these materials into the surrounding tissue due to metal dissolution is diminished by the formation of thin, protective passive oxide films on the metal surface. As such, the electrochemical properties of these oxide films are of significant importance for the optimization of the biocompatibility of such materials as it is the oxide that is in direct contact with the biological system. Evidence from the literature suggests that for a biphasic,  $\alpha$ - $\beta$ titanium alloy, the electrical properties of the surface oxide should be a function of the underlying phase, due to compositional differences. In this paper, kinetic scanning electrochemical microscopy (SECM) studies were performed to evaluate the local electron-transfer kinetics on the oxide film of Grade 5 titanium (Ti-6Al-4V) exposed to a series of redox mediator compounds. The resolution of this technique enabled the determination of the first order rate constants for mediator regeneration at the passive film on an individual  $\alpha$  phase grain. Furthermore, the analysis allowed the flatband potential to be qualitatively mapped as a function of phase on the alloy surface, demonstrating that the flatband potentials for the  $\alpha$  and  $\beta$ phases likely do differ from one another.

From: J. Electrochem. Soc., 154, C508 (2007).

### An Electroless Plating Method to Make Conducting Microbeads Using Gold Nanoparticles

A group of researchers at the Osaka Prefecture University of Japan have developed a method to make gold nanoparticle array films on plastic substrates. The method simply involved dipping a substrate in a mixed solution of gold nanoparticles and alkanethiol binders. Recently, the authors extended this self-assembly approach to metalize microsized plastic objects. Goldnanoparticle-coated microbeads were prepared using a thiol molecule as a binder *via* a single-step coating procedure just by agitating the nanoparticle, thiol, and beads in an aqueous solution. Replating the bead with gold, nickel, silver, and copper gave metallized beads, for which conductance was close to that of the respective bulk metals. In addition to its simplicity, this technique did not use toxic chemicals such as chromic acid and cyanides as used in conventional electroless plating techniques. The gold-nanoparticle-coated films are expected to have a variety of potential applications, *e.g.*, as a conductive filler, as a lightweight electrode material, and in electronic devices.

From: J. Electrochem. Soc., 154, D462 (2007).

#### Connectivity of Manganese Dioxide and Graphite in Alkaline Electrolytes

Manganese dioxide is an important cathode material in a variety of battery systems, including alkaline Zn/MnO2, aqueous carbon-Zn, and non-aqueous Li-ion cells. Despite the prevalent use of the alkaline MnO<sub>2</sub> cathode, there are many fundamental aspects of the electrochemical discharge mechanism that are not fully understood. Arnott and Donne at the University of Newcastle in Australia have published the results of an electrochemical impedance spectroscopy (EIS) study of electrolytic manganese dioxide (EMD). They synthesized the EMD by anodic electrodeposition of  $MnO_2$  from an aqueous mixture of  $MnSO_4$  and  $H_2SO_4$ . They examined the electrochemical properties of electrodes fabricated either from large pieces (~0.5 cm diameter) of EMD or from compacted EMD/graphite powder mixtures. Their EIS results led the authors to conclude that electrode impedance is dependent on the effective establishment of the EMD-graphite-electrolyte three-phase boundary, with the proximity between proton (from the electrolyte) and electron (from the graphite) insertion determining the impedance. In addition, the relatively large charge transfer resistance observed when electron insertion into the structure is far away from proton insertion suggests a strong localization of proton-electron pairs in the MnO<sub>2</sub> structure, in contrast to other reports in the literature. Finally, the authors conclude that grain boundary impedance can contribute to conduction within the EMD, especially when the electrolyte does not completely saturate the electrode structure.

From: J. Electrochem. Soc., 154, A776 (2007).

Tech Highlights was prepared by Donald Pile; Zenghe Liu of Abbott Diabetes Care; James Dickerson of Vanderbilt University; and David Enos and Mike Kelly Sandia National Laboratories.