# **TECH HIGHLIGHTS** •

## Characteristics of Gadolinium Oxide Nanocrystal Memory with Optimized Rapid Thermal Annealing

The implementation of nanocrystalline materials into real-world device applications has taken a step forward with the recent discoveries of enhanced nonvolatile memory (NVM) characteristics of gadolinium oxide (Gd<sub>2</sub>O<sub>3</sub>) nanocrystals embedded within an amorphous Gd<sub>2</sub>O<sub>3</sub> environment. Because of its large dielectric constant, Gd<sub>2</sub>O<sub>3</sub> has been proposed to replace silicon dioxide in a variety of semiconductor devices applications. However, its use in NVM may show the most promise since amorphous Gd<sub>2</sub>O<sub>3</sub> possesses a larger bandgap than its corresponding crystalline form. Thus, a Gd<sub>2</sub>O<sub>3</sub> nanocrystal embedded within an amorphous  $Gd_2O_3$  matrix can behave as a node for the storage of charge carriers within an NVM architecture. By exploring the annealing temperature that creates nanocrystals within amorphous environments, scientists from Chang-Gung University, National Cheng-Kung University, and Chung-Shan Institute of Science and Technology in Taiwan were able to optimize both the nanocrystal density and the capacitance-voltage (C-V) hysteresis window while minimizing the charge loss within the NVM. The observed nanocrystal densities, program/erase cycling tolerances, and extended memory window help inform the future progress of nanostructured Gd<sub>2</sub>O<sub>3</sub> composites in memory device applications.

## From: Electrochem. Solid-State Lett., 12, H202 (2009).

### High-Capacity, Microporous Cu<sub>6</sub>Sn<sub>5</sub>-Sn Anodes for Li-Ion Batteries

The drive for higher volumetric and gravimetric energy densities for lithium ion batteries requires an alternative anode. The challenge with alternative anodes as a replacement for graphitic carbon is the large volume change upon charging and discharging, resulting in cell failure. Researchers at Argonne National Laboratory have developed a porous electrode structure, akin to the nickel current collector for the Na/NiCl<sub>2</sub> ("zebra") cells, to manage this volume change. The electrode fabrication consists of two separate electrochemical depositions. The first deposition produces the copper foam, which serves as the current collector. and the second deposition forms the active material. There is a sintering step between depositions and the final product is annealed to form the Cu<sub>6</sub>Sn<sub>5</sub>-Sn active material. Electrochemical testing with a lithium counter electrode shows a reversible capacity greater than 600 mAh/g for 30 cycles, followed by an onset of declining capacity. The authors identified possible causes for this capacity fade, including passive film formation, physical separation of active

material from current collector, and formation of inactive phases. This unoptimized electrode which incorporates a mechanically robust porous current collector is a promising alternative to a graphite anode on copper foil for lithium ion batteries.

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# High-Performance Flexible Miniature Fuel Cell

Miniaturized fuel cells are the subject of research and development for possible applications in a variety of portable electronic devices. There are a number of approaches to miniaturization of polymer electrolyte fuel cells including several developed by researchers at the University of Minnesota's Corrosion Research Center. Here, Smyrl et al. have reported in past years on miniaturized fuel cells fabricated from silicon as well as others based on the use of anodized aluminum as a support material. In this publication, the Smyrl group describes design and fabrication of a flexible fuel cell manufactured with low-cost, readily available materials. They used a Nafion® catalyst membrane, Toray® carbon paper, gold-plated copper mesh, Parafilm®, and overhead transparency sheets to fabricate a small (approximately 3 cm x 3 cm) fuel cell with a total material cost of about 7 U.S. dollars. The performance of the fuel cell was quite reproducible and very good, with maximum power densities as high as 57 mW/cm<sup>2</sup> at 0.35 V observed. The researchers conclude that this simple, flexible fuel cell can serve as an excellent laboratory vehicle to rapidly and effectively evaluate membranes, electrode catalysts, and other fuel cell components.

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#### Effect of LiCoO<sub>2</sub> Cathode Nanoparticle Size on High-Rate Performance for Li-Ion Batteries

Because of its high energy density, LiCoO<sub>2</sub> has been used extensively as a cathode material in commercial Li-ion batteries; however, these batteries traditionally have demonstrated a low power density due to extensive polarization at high currents. NanostructuredLiCoO<sub>2</sub>electrodesexhibit both high power density and high energy density, primarily because the reduced dimension of LiCoO<sub>2</sub> nanoparticles results in shorter lithium-ion diffusion lengths and times. In an effort to quantify the relationship between nanoparticle size and high-rate performance, researchers in Korea studied 50 nm, 100 nm, 300 nm, and 1 µm LiCoO<sub>2</sub> nanoparticles, produced by annealing hydrothermallyprepared, oleylamine-capped 50 nm  $LiCoO_2$  particles at 500°C, 700°C, and 900°C, respectively. While the smaller nanoparticles have shortened intraparticle lithium-ion diffusion lengths, TEM images show that lithium ions must diffuse through a thicker solid electrolyte interphase (SEI) as the relative surface area of the particle is increased. LiCoO<sub>2</sub> particles of each size were assembled into separate electrodes and cycled at 2C, 4C, and 7C discharge rates. The authors report that the cathode utilizing 300 nm LiCoO<sub>2</sub> nanoparticles possessed the greatest high-rate discharge capacity and capacity retention—indicating that the 300 nm LiCoO<sub>2</sub> nanoparticle size was the most favorable compromise between particle size and SEI thickness.

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#### Relation Between the Semiconducting Properties of a Passive Film and Reduction Reaction Rates

The passive films formed on a commercial Ni-Cr-Mo-W engineering alloy, Alloy C22, and pure chromium were compared using a variety of electrochemical techniques in order to investigate relationships between the semiconducting properties of the oxide and the cathodic reaction rates, which could be supported as a function of applied potential. Mott-Schottky analyses of measured electrochemical impedance spectra were used to probe the semiconducting nature of the oxide films on both metals. The oxide layers for both alloy C22 and pure chromium were found to be n-type semiconductors, and consequently, polarization of the materials to potentials more positive than each oxide's flatband potential resulted in the measurement of a negligible cathodic current density. Once polarized below the flatband potential, the measured cathodic current density increased sharply. At a given potential, larger currents were observed for alloy C22 than for pure chromium, attributed to the more negative flatband potential of the pure metal. The flatband potentials measured via cathodic polarization were compared to a series of literature-based calculations, and found to agree most closely with those of Brug (1984). Based upon these results, it was concluded that for materials with an n-type semiconducting passive film, cathodic polarization represents a reliable method to corroborate the carrier identity and assess the accuracy of the calculated flatband potential.

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