Tech Highlights

Direct Electrochemical Synthesis of ZrO_2 Nanotubes

Nanoscale materials such as nanowires, nanorods, nanofibers, and nanotubes have attracted great interest recently due to their importance in basic scientific research and their potential technology applications. Extended and oriented nanostructures are desirable for many applications, but direct fabrication of complex nanostructures with well-aligned morphology, orientation, and surface architectures remains a significant challenge. Smyrl and co-workers at the University of Minnesota recently reported a simple, robust method for fabrication of ZrO_2 nanotubes based on a one-step, templateless anodization process in aqueous hydrofluoric acid. Characterized by scanning electron and transmission electron microscopy, these nanotubes were observed to be straight and perpendicular to the Zr substrate, to be arranged in an open ended array of continuous, well-aligned conformation, and to have very narrow (*ca.* 10 nm) diameters. Due to the unique chemical and physical properties of ZrO_2, these nanotubes have great potential for chemical sensing, catalysis, optical emission, and nanoelectrode assembly for batteries and electrochemistry. Further work is underway in the authors' lab to elucidate the formation mechanism of the ZrO_2 nanotubes. ■

From: Electrochem. Solid-State Lett., 8 (3), B7 (2005).

Design and Testing of an Impedance-Based Sensor for Monitoring Drug Delivery

A significant challenge in the application of *in vivo* drug delivery schemes is the validation and verification of correct diffusion profiles. Especially confounding is the case where a complex or pulse-type delivery profile is required and the environment surrounding the implant changes due to encapsulation. Traditional methods for characterizing drug delivery are typically invasive with each data point requiring a new test animal and device implant. Johnson, Sadoway, Cima, and Langer of the Massachusetts Institute of Technology describe a monitoring system that promises to overcome these obstacles. Reservoirs in a MEMS-based delivery system were functionalized with gold electrodes on either side of the reservoir. A two-electrode impedance measurement was used to monitor the dissolution of a nonconductive drug (powdered mannitol in the current case) and its replacement by conductive fluid from the surrounding medium. Impedance data were collected between 103 and 106 Hz and solution resistance and interfacial capacitance were calculated as a function of time following drug release. The solution resistance decreased rapidly over the first 20 min then approached a constant value after approximately 100 min. The capacitance values showed a corresponding increase during drug delivery. Ongoing work is aimed at correlating the output from the impedance sensor and the rate of drug transport through various transport barriers. ■

From: J. Electrochem. Soc., 152 (1), H6 (2005).

Effect of Counterion Placement on Conductivity in Single-Ion Conducting Block Copolymer Electrolytes

To improve the performance of lithium rechargeable batteries, researchers at the Massachusetts Institute of Technology are developing a single-ion conducting solid polymer electrolyte wherein the lithium ion mobility is promoted by enhancing the ion dissociation. These researchers explored overcoming the problem of ion pairing interactions between the lithium ion and the tethered anion by spatially isolating the carboxylate anions in a secondary phase of a block copolymer electrolyte (BCE). Three distinct molecular architectures were synthesized by incorporating the charge carrier lithium methacrylate (LiMA) either randomly in the hydrophobic – poly(lauryl methacrylate), PLMA – or hydrophilic – poly(oxyethylene) methacrylate, POEM – block, or entirely in a separate block. The near constant unity transference number and electrochemical stability were verified for each polymer. Remarkably, the ion conductivity was greater in the two BCEs having the anion bound outside the POEM block, which conducted the lithium ion. Complexing the carboxylate anions with BF_3 to decrease its charge density resulted in no enhancement of lithium ion conductivity in these two BCEs, but improved the conductivity of the P(OEM-*r*-LiMA)-containing BCE which does not have counterion isolation. Together, these results support the conclusion that ion dissociation is effectively achieved by designing a BCE such that the tethered counterion is spatially isolated from the ion-conducting block. ■

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Improved Li-Ion Battery Performance Using Li-Mn Spinel / Li-Ni-Co-Mn Oxide as the Positive Electrode

Lithium manganese oxide ($LiMn_2O_4$) with a spinel structure has always been an attractive positive electrode material for Li-ion batteries because of its high-rate capability, low cost, and excellent tolerance to abuse. However, when the material is cycled or stored at elevated temperatures, it has been observed that Mn ions dissolve into solution, eventually leading to capacity fade. This fade has prevented spinel-based Li-ion cells from replacing Ni-metal hydride batteries in hybrid electric cars. Researchers at the Sanyo Electric Company in Japan have discovered a very surprising method to decrease the capacity fade in this cathode that involves physically mixing the material with another cathode material, $LiNi_{0.4}Co_{0.3}Mn_{0.3}O_2$. In addition, the capacity fade in the mixture cathode was observed to be smaller than either of the two materials when stored at 45°C for 30 days. Tracking the changes in the lattice constants with storage, the authors report that while changes in the spinel are suppressed by mixing, the lattice constants in the Li-Ni-Co-Mn oxide cathode show similar changes in both the single material and the mixture. While no clear explanation appears to exist for the suppression in the fade, the results offer hope for the commercialization of spinel-based cathodes in Li-ion cells. ■

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High-Performance Circuit Boards Based on Mesoporous Silica Filled PTFE Composite Materials

The evolution in performance of electronic products continues to drive research and development of improved materials. Printed circuit board (PCB) substrates with lower dielectric constants, lower dissipation factors, and coefficients of thermal expansion (CTE) that closely match those of deposited metals are required for advanced applications such as radio-frequency and microwave circuits. Researchers at Chung Yuan Christian University and the Industrial Technology Research Institute in Taiwan have reported improvements in PCB materials obtained by preparing composites from poly(tetrafluoroethylene) (PTFE, a common high-frequency PCB substrate material) and a hydrophobic porous silica material. They silylated a mesoporous silica powder (MCM-41) with hexamethyldisilazane and trimethylchlorosilane, and then thoroughly mixed this with an aqueous PTFE emulsion. The mixture was dried, formed into boards by a milling process at 120°C, and sintered at 360°C. The authors determined that the composite boards are thermally stable, have ultralow dielectric constants (1.70 to 2.05), low dissipation factors (0.0008 to 0.0049), and low CTE values (12 to 118 ppm/°C). The ultralow dielectric constants are attributed to the presence of the moisture-free, ordered mesoporous structure provided by the uniformly dispersed silica powder filler. The properties of the composites can be tailored by careful control of the filler content; in this manner, a near-exact CTE match of the composite with that of deposited metal traces can be achieved. ■

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