Alkaline Capacitors Based on Nitride Nanoparticles

One key to success is an oxygen-free, plasma-assisted nitride-synthesis process.

High-energy-density alkaline electrochemical capacitors based on electrodes made of transition-metal nitride nanoparticles are undergoing development. Transition-metal nitrides (in particular, Fe₃N and TiN) offer a desirable combination of high electrical conductivity and electrochemical stability in aqueous alkaline electrolytes like KOH. The high energy densities of these capacitors are attributable mainly to their high capacitance densities, which, in turn, are attributable mainly to the large specific surface areas of the electrode nanoparticles. Capacitors of this type could be useful as energy-storage components in such diverse equipment as digital communication systems, implanted medical devices, computers, portable consumer electronic devices, and electric vehicles.

Although the desirable properties of the transition-metal nitrides were known prior to the present development, realization of the inherent electrochemical stability of these materials and of the large specific surface areas and high electrical conductivities needed for high-energy-density capacitors was prevented by side effects of processing:

- Synthesis of these materials involved thermal conversion at temperatures so high (>600 °C) as to cause nucleation of larger particles from smaller ones, with consequent reduction of specific surface areas.
- The nature of the synthesis was such as to yield oxynitrides and oxides in addition to the desired pure nitrides. As a result, electrochemical series resistance (ESR) values were excessive.
- Unlike the nitrides, the oxynitrides and oxides are not sufficiently chemically stable in alkaline electrolytes.

The present development effort follows a multifaceted approach in addressing the aforementioned issues as well as others. In this approach, transition-metal nitride nanoparticles are synthesized at room temperature under conditions that exclude oxygen and thereby prevent the formation of oxynitrides. A synthesis according to this approach involves radio-frequency-plasma-assisted conversion of a nanoparticle precursor material (e.g., iron acetate, titanium hydride, or titanium chloride) in the presence of anhydrous ammonia gas flowing at a suitable low pressure.

Current collectors for the electrodes of the developmental capacitors are made of films of an electrically conductive composite material that consists mostly of TiN nanoparticles in an elastomeric matrix. To ensure highly electrically conductive interfaces with the electrode materials, thin (250-Å thick) coats of TiN can be sputtered onto the surfaces of the current-collector films.

Capacitors designed and fabricated according to the present approach have been characterized in a variety of tests (for example, see figure). A specific capacitance in excess of 150 Farads/gram (F/g) or 800 F/cm² has been observed. Capacitors of this type, containing both anodes and cathodes made of transition-metal nitride nanoparticles, have withstood potentials >1.75 V. Tests of single-cell and multiple-cell stacks have yielded encouraging results, and significant improvements are expected in future efforts.

This work was done by Matt Aldissi of Fractal Systems, Inc., for Glenn Research Center. For further information, access the Technical Support Package (TSP) free online at www.nasatech.com.

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Commercial Technology Office, Attn: Steve Fedor, Mail Stop 4–8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17083.

Low-EC-Content Electrolytes for Low-Temperature Li-Ion Cells

Electrolytes comprising LiPF₆ dissolved at a concentration of 1.0 M in three different mixtures of alkyl carbonates have been found well suited for use in rechargeable lithium-ion electrochemical cells at low temperatures. These and other electrolytes have been investigated in continuing research directed toward extending the lower limit of practical operating temperatures of Li-ion cells down to ~60 °C. This research at earlier stages was reported in numerous previous NASA Tech Briefs articles, the three most recent being “Ethyl Methyl Carbonate as a Cosolvent for Lithium-Ion Cells” (NPO-20605), Vol. 25,
No. 6 (June 2001), page 53; “Alkyl Pyrocarbonate Electrolyte Additives for Li-Ion Cells” (NPO-20775), Vol. 26, No. 5 (May 2002), page 37; and “Fluorinated Alkyl Carbonates as Cosolvents in Li-Ion Cells (NPO-21076), Vol. 26, No. 5 (May 2002), page 38. The present solvent mixtures, in terms of volume proportions of their ingredients, are 1 ethylene carbonate (EC) + 1 diethyl carbonate (DEC) + 1 dimethyl carbonate (DMC) + 3 ethyl methyl carbonate (EMC); 3EC + 3DMC + 14EMC; and 1EC + 1DEC + 1DMC + 4EMC. Relative to similar mixtures reported previously, the present mixtures, which contain smaller proportions of EC, have been found to afford better performance in experimental Li-ion cells at temperatures $< -20 ^\circ \text{C}$. 

This work was done by Marshall Smart, Ratnakumar Bugga, and Subbarao Surampudi of Caltech for NASA’s Jet Propulsion Laboratory. For further information, access the Technical Support Package (TSP) free on-line at www.nasatech.com. NPO-30226