Materials

Microsphere Insulation Panels

Thermal performance and lifetime exceed those of foam insulation.

John F. Kennedy Space Center, Florida

Microsphere insulation panels (MIPs) have been developed as lightweight, long-lasting replacements for the foam and vacuum-jacketed systems heretofore used for thermally insulating cryogenic vessels and transfer ducts. Whether preformed or applied in place, foam insulation deteriorates fairly rapidly: on cryogenic transfer lines, it has a life expectancy of about three years. Vacuum-jacketed insulation is expensive and heavy. For both foam and vacuum-jacketed insulation, intensive maintenance is necessary to keep performance at or near its original level. Relative to a polyurethane foam insulation panel, a comparable MIP offers greater thermal performance and longer service life at approximately the same initial cost.

The microsphere core material of a typical MIP consists of hollow glass bubbles, which have a combination of advantageous mechanical, chemical, and thermal-insulation properties heretofore available only separately in different materials. In particular, a core filling of glass microspheres has high crush strength and low density, is noncombustible, and performs well in soft vacuum. A typical MIP includes microspheres in an evacuated space between flexible vacuum-barrier layers made of a multilayer polyester-based laminate [Mylar® 250SBL300 (or equivalent)]. Included in the laminate are several non-foil layers that serve as barriers to permeation by water vapor and other atmospheric gases. The polyester-based laminate material has a projected life in excess of 20 years.

An MIP can be made in clamshell-like halves that can be fitted into a cryogenic vessel or transfer duct. In general, MIPs can be applied to transfer ducts along with jacketing materials conventionally used on foam insulation, and can be installed by use of essentially the same techniques used to install preformed foam insulation. On the basis of tests according to standards C518 and C177 of the American Society for Testing and Materials, the thermal performance of a flexible vacuum-barrier MIP is about two times better than that of a comparable polyurethane foam insulation panel.

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In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:

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Refer to KSC-12675, volume and number of this NASA Tech Briefs issue, and the page number.

Single-Wall Carbon Nanotube Anodes for Lithium Cells

Capacities are greater than those of graphite anodes.

John H. Glenn Research Center, Cleveland, Ohio

In recent experiments, highly purified batches of single-wall carbon nanotubes (SWCNTs) have shown promise as superior alternatives to the graphitic carbon-black anode materials heretofore used in rechargeable thin-film lithium power cells. The basic idea underlying the experiments is that relative to a given mass of graphitic carbon-black anode material, an equal mass of SWCNTs can be expected to have greater lithium-storage and charge/discharge capacities. The reason for this expectation is that whereas the microstructure and nanostructure of a graphitic carbon black is such as to make most of the interior of the material inaccessible for intercalation of lithium, a batch of SWCNTs can be made to have a much more open microstructure and nanostructure, such
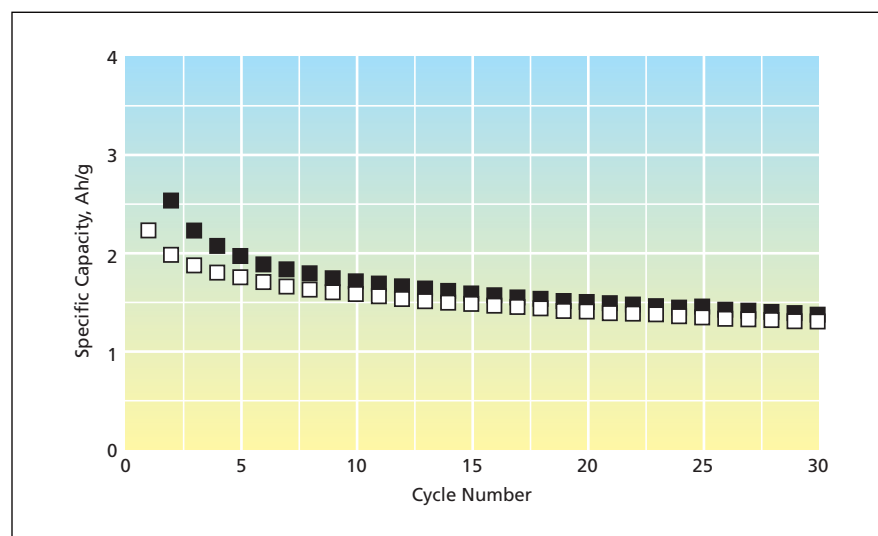
Specific Capacity of a carbon-nanotube anode material as a function of cycle number was calculated from charge and discharge times measured in galvanostatic cycling.

that most of the interior of the material is accessible for intercalation of lithium. Moreover, the greater accessibility of SWCNT structures can be expected to translate to greater mobilities for ion-exchange processes and, hence, an ability to sustain greater charge and discharge current densities.

For the experiments, soot containing carbon nanotubes was produced by laser vaporization of a graphite target containing 1.2 atomic percent Ni/Co in an argon atmosphere at a pressure of 500 torr (≈ 67 kPa) at a temperature of 1,200 °C. The soot was purified by refluxing in nitric acid at a temperature of 125 °C followed by annealing in oxygen at 550 °C for 30 minutes. By means of scanning electron microscopy, transmission electron microscopy, ultraviolet-visible spectrophotometry, and thermogravimetric analysis, 99 weight percent of the purified soot was found to consist of SWCNTs. The specific surface area of the pu-

rified material, as measured by use of the Brunauer, Emmett, and Teller (BET) technique based on adsorption of nitrogen, was found to be 1,200 m^2/g — much greater than the specific surface areas of several other carbonaceous anode materials that were also subjected to the BET test.

Anodes were fabricated by casting, onto copper foils, thin films of the purified SWCNT material dispersed at a concentration of 5 weight percent in poly(vinylidene fluoride). The anodes were incorporated into standard three-electrode test cells along with lithium-foil counter and reference electrodes and an electrolyte comprising 1.0 M $LiPF_6$ in a solution of ethylene carbonate (2 parts by volume) and dimethyl carbonate (1 part by volume). Over-potentials for interaction of the anodes with lithium and lithium capacities of the anodes were measured by use of cyclic voltammetry and galvanostatic cycling, respectively.

The figure shows representative charge and discharge capacities determined from the measurements. The plotted values show a high degree of reversibility after the initial cycle. The specific capacity after 30 cycles was found to be about 1.33 Ah/g — almost 3 times the generally accepted value (0.45 Ah/g) for graphite.

This work was done by Aloysius F. Hepp of **Glenn Research Center***; Ryne Raffaelle and Tom Gennett of Rochester Institute of Technology; Prashant Kumta and Jeff Maranchi of Carnegie-Mellon University; and Mike Heben of National Renewable Energy Laboratory. Further information is contained in a TSP (see page 1).*

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-17356-1

Tantalum-Based Ceramics for Refractory Composites

Compositions can be graded from porous substrates to impervious outer layers.
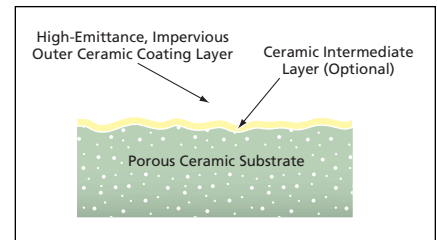
Ames Research Center, Moffett Field, California

A family of tantalum-based ceramics has been invented as ingredients of high-temperature composite insulating tiles. These materials are suitable for coating and/or permeating the outer layers of rigid porous (foamlike or fibrous) ceramic substrates to (1) render the resulting composite ceramic tiles impervious to hot gases and (2) enable the tiles to survive high heat fluxes at temperatures that can exceed 3,000 °F (≈1,600 °C). Originally intended for use on the future space exploration vehicles, insulating tiles made with these materials may also be useful in terrestrial applications (e.g., some industrial processes) in which there are requirements to protect against flows of hot, oxidizing gases.

The starting ingredients of a ceramic of this invention are the following:
- Tantalum disilicide ($TaSi_2$), which can act as either an emittance agent or a matrix material, depending upon the overall composition;
- Molybdenum disilicide ($MoSi_2$), which, depending on the overall composition, acts as a secondary emittance agent or as an oxygen getter (to inhibit the oxidation of tantalum within the finished composite);

- A borosilicate glass ($B_2O_3 \cdot SiO_2$), which acts as a source of boron and may, depending on the overall composition, act as an alternative matrix; and
- Silicon hexaboride (SiB_6), which acts as a processing aid by facilitating sintering of the aforementioned ingredients.

These ingredients are milled together in ethanol, and the resulting slurry is sprayed or painted onto a porous ceramic substrate. The underlying layers (sub-layers) of different compositions are used to integrate the outer layer (coating) with a wide variety of porous substrate materials. For this purpose, infiltration of these compositions into the substrate results in a functional gradient system that accounts for the difference in the coefficient of thermal expansion (CTE) between coating and substrate. The preferred composition for such underlying layers are in the approximate range of 20 to 60 weight percent of $MoSi_2$, 0 to 60 weight percent of $TaSi_2$, 40 to 80 weight percent of borosilicate glass, and 1 to 5 percent of SiB_6. The ingredients are then sintered by heating the treated substrate at atmospheric pressure at either a temperature of 2,225 °F (≈1,218 °C) for 90 minutes or a temperature of 2,400 °F (≈1,316 °C) for 10 min-

High-Emittance, Impervious Outer Ceramic Coating Layer

Ceramic Intermediate Layer (Optional)

Porous Ceramic Substrate

A **Porous Ceramic Substrate Is Coated** with one or more ceramic layers to render it impervious to hot gas and increase its ability to withstand high heat flux.

utes. The milling, coating, and sintering process conditions are chosen to minimize the undesired oxidation of tantalum compounds.

For an outer coating layer, the preferred composition is between 20 and 45 weight percent of borosilicate glass, between 10 and 65 weight percent of $TaSi_2$, between 5 and 30 weight percent of $MoSi_2$, and between 1 and 5 weight percent of SiB_6. An underlying layer or sublayer of different composition can be used to integrate the outer layer with the substrate and, for this purpose, may be allowed to infiltrate to some small depth below the surface of the substrate. The preferred composition for such an underlying layer lies in the approximate range of 20 to 60 weight percent of