



Diamond-Coated Carbon Nanotubes for Efficient Field Emission

Lyndon B. Johnson Space Center, Houston, Texas

Field-emission cathodes containing arrays of carbon nanotubes coated with diamond or diamondlike carbon (DLC) are undergoing development. Multiwalled carbon nanotubes have been shown to perform well as electron field emitters. The idea underlying the present development is that by coating carbon nanotubes with wide-band-gap materials like diamond or DLC, one could reduce effective work functions, thereby reducing threshold electric-field levels for field emission of electrons and, hence, improving cathode performance. To demonstrate feasibility, experimental cathodes were fabricated by (1) covering metal bases with carbon nanotubes

bound to the bases by an electrically conductive binder and (2) coating the nanotubes, variously, with diamond or DLC by plasma-assisted chemical vapor deposition. In tests, the threshold electric-field levels for emission of electrons were reduced by as much as 40 percent, relative to those of uncoated-nanotube cathodes. Coating with diamond or DLC could also make field emission-cathodes operate more stably by helping to prevent evaporation of carbon from nanotubes in the event of overheating of the cathodes. Cathodes of this type are expected to be useful principally as electron sources for cathode-ray tubes and flat-panel displays.

This work was done by Stevan Dimitrijevic and James C. Withers of Materials and Electrochemical Research Corp. for Johnson Space Center.

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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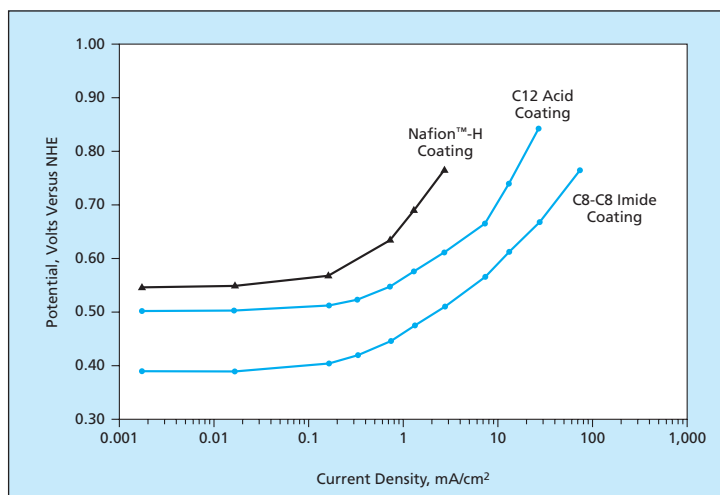
Improved Anode Coatings for Direct Methanol Fuel Cells

Two perfluoroalkanesulfonic compounds offer increased fuel-utilization rates and reduced polarization levels.

NASA's Jet Propulsion Laboratory, Pasadena, California

Two perfluoroalkanesulfonic acids and perfluoroalkanesulfonimides have shown promise as anode-coating materials for improving the performances of direct methanol fuel cells (DMFCs). Heretofore, the state-of-the-art material commonly used for coating anodes in DMFCs has been Nafion™-H — a perfluoro-sulfonic acid-based hydrophilic, proton-conducting ion-exchange polymer that exhibits relatively high thermal and electrochemical stability. Relative to Nafion™-H, the present coating materials afford greater rates of electro-oxidation of methanol, smaller polarization losses and, hence, greater energy-conversion efficiencies.

Perfluorinated solid polymer electrolytes — in particular, Nafion™-H — have been used as anode coatings in



Polarization Levels [potentials versus a normal hydrogen electrode (NHE)] of variously coated carbon-supported Pt-Sn electrodes were measured over a range of current densities in a test cell containing a solution of 1.0 M methanol in 0.50 M sulfuric acid.

DMFCs to (1) ensure contact between electrolyte membranes and electrocatalytic anode materials (typically, alloys containing Pt) and (2) help prevent catalysts from being poisoned by adsorption of anions. However, the perform-

ances of electrodes coated by perfluorinated solid polymer electrolytes have not been ideal, especially at room temperature. Consequently, there has been continued interest in developing means of reducing polarization losses and increasing rates of oxidation and efficiencies of utilization of methanol in order to improve the performances and increase the energy-conversion efficiencies of DMFCs.

In preparation for experiments, DMFC anodes made of carbon-supported Pt, Pt-Ru, and Pt-Sn were prepared and coated, variously, with Nafion™-H or six different perfluoroalkanesulfonic materials: perfluorooctanesulfonic acid (C8 acid), perfluorododecanesulfonic acid (C12 acid), perfluoroheptadecanesulfonic acid (C17 acid), bis-perfluoro-*n*-butyl sulfonyl acid

imide, bis-perfluoro-*n*-octylsulfonic acid imide (C8-C8 imide), or perfluoro-*n*-butyl-perfluoro-*n*-octylsulfonic acid imide. The experiments involved electro-oxidation of methanol on each anode installed as one of the electrodes in a three-electrode electrochemical test cells. The performances of the electrodes were characterized by galvanostatic polarization measurements and cyclic voltammetry. Of the compounds investigated, C12 acid and C8-C8 imide were found to afford the greatest increases in rates of ox-

idation of methanol and the greatest reductions in levels of polarization (see figure), relative to those of Nafion™-H.

This work was done by G. K. Surya Prakash, Qun-jie Wang, and George A. Olah of the University of Southern California and Marshall C. Smart, Sekharipuram Narayanan, and Subbarao Surampudi, of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

In accordance with Public Law 96-517, the contractor has elected to retain title to this

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Advanced Ablative Insulators and Methods of Making Them Reinforced, filled silicones and carbon phenolics are laser-milled to final shapes.

Lyndon B. Johnson Space Center, Houston, Texas

Advanced ablative (more specifically, charring) materials that provide temporary protection against high temperatures, and advanced methods of designing and manufacturing insulators based on these materials, are undergoing development. These materials and methods were conceived in an effort to replace the traditional thermal-protection systems (TPSs) of re-entry spacecraft with robust, lightweight, better-performing TPSs that can be designed and manufactured more rapidly and at lower cost. These materials and methods could also be used to make improved TPSs for general aerospace, military, and industrial applications.

The ablative materials belong to two families. One family comprises filled,

fiber-reinforced elastomeric carbon phenolics with mass densities that range from 18 to 40 lbm/ft³ (288 to 641 kg/m³); these materials are designed to protect against heating rates up to about 1,300 Btu/(ft²s) [\approx 15 MW/m²]. The other family comprises filled, fiber-reinforced silicones with mass densities that range from 12 to 50 lbm/ft³ [192 to 800 kg/m³]; these materials are designed to protect against heating rates from 5 to about 400 Btu/(ft²s) [about 0.06 to about 4.5 MW/m²]. The fillers in these materials help to minimize their mass densities, while the fibers help to maximize their strengths.

Design and manufacture of TPSs according to the present approach involve the use of computer-aided design

and computer-aided manufacturing (CAD/CAM) methods, including computer numerically controlled (CNC) laser milling. This approach eliminates the labor-intensive steps of machining, fitting, and trimming heat-shield parts in the prior approach to manufacturing. In the present approach, molded panels of the ablative materials are CNC-laser-milled to precise final sizes and shapes and are thus made ready for bonding to heat-shield structures.

This work was done by William M. Congdon of Applied Research Associates, Inc., for Johnson Space Center. For further information, contact the Johnson Technology Transfer Office at (281) 483-3809. MSC-23141

PETIs as High-Temperature Resin-Transfer-Molding Materials PETI-matrix/carbon-fiber composites made by resin-transfer molding have excellent properties.

Langley Research Center, Hampton, Virginia

Compositions of, and processes for fabricating, high-temperature composite materials from phenylethynyl-terminated imide (PETI) oligomers by resin-transfer molding (RTM) and resin infusion have been developed. Composites having a combination of excellent mechanical properties and long-term high-temperature stability have been readily fabricated. These materials are particularly useful for the fabrication of high-temperature structures for jet-engine components, structural components on high-speed aircraft, spacecraft, and missiles.

Phenylethynyl-terminated amide acid oligomers that are precursors of PETI oligomers are easily made through the reaction of a mixture of aromatic diamines with aromatic dianhydrides at high stoichiometric offsets and 4-phenylethynylphthalic anhydride (PEPA) as an end-capper in a polar solvent such as *N*-methylpyrrolidinone (NMP). These oligomers are subsequently cyclodehydrated — for example, by heating the solution in the presence of toluene to remove the water by azeotropic distillation to form low-molecular-weight imide

oligomers. More precisely, what is obtained is a mixture of PETI oligomeric species, spanning a range of molecular weights, that exhibits a stable melt viscosity of less than approximately 60 poise (and generally less than 10 poise) at a temperature below 300 °C. After curing of the oligomers at a temperature of 371 °C, the resulting polymer can have a glass-transition temperature (T_g) as high as 375 °C, the exact value depending on the compositions.

As an example, one PETI oligomer, denoted PETI-330, was synthesized as