



Materials

Room-Temperature-Cured Copolymers for Lithium Battery Gel Electrolytes

Room-temperature curing offers an important advantage in room-temperature functionality.

John H. Glenn Research Center, Cleveland, Ohio

Polyimide-PEO copolymers ("PEO" signifies polyethylene oxide) that have branched rod-coil molecular structures and that can be cured into film form at room temperature have been invented for use as gel electrolytes for lithium-ion electric-power cells. These copolymers offer an alternative to previously patented branched rod-coil polyimides that have been considered for use as polymer electrolytes and that must be cured at a temperature of 200 °C. In order to obtain sufficient conductivity

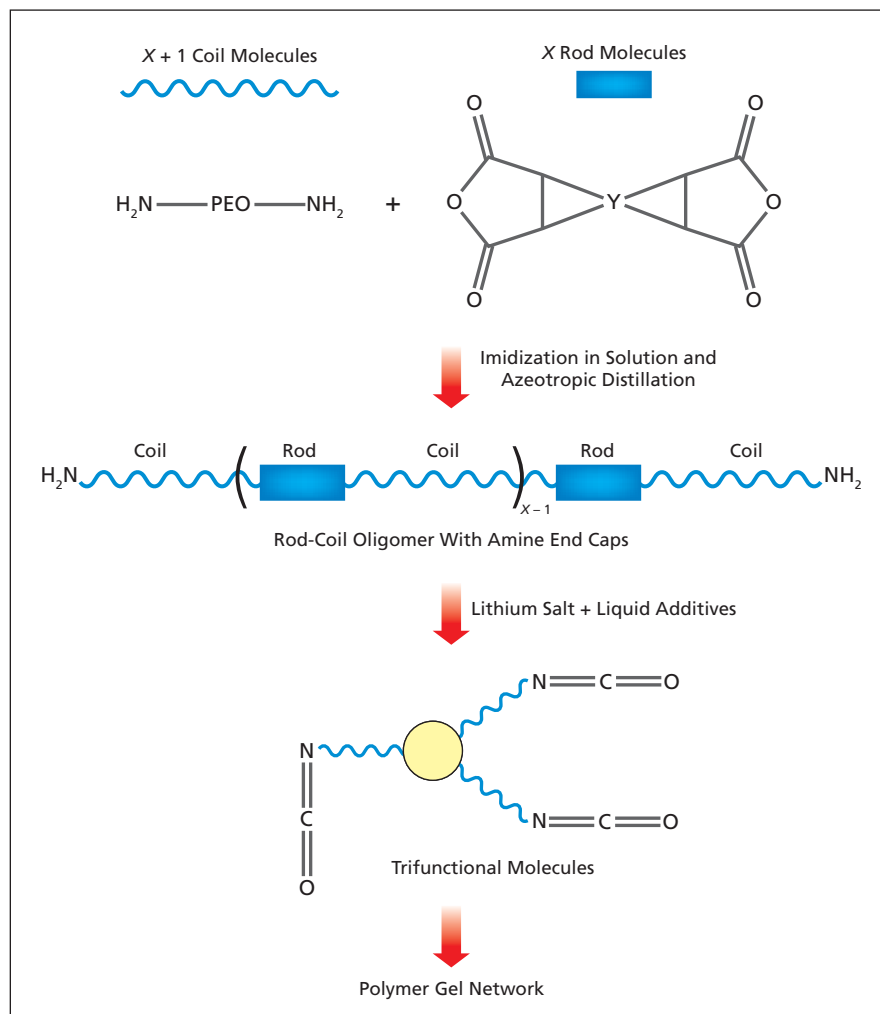
for lithium ions in practical applications at and below room temperature, it is necessary to imbibe such a polymer with a suitable carbonate solvent or ionic liquid, but the high-temperature cure makes it impossible to incorporate and retain such a liquid within the polymer molecular framework. By eliminating the high-temperature cure, the present invention makes it possible to incorporate the required liquid.

The curing of a polyimide-PEO copolymer according to the invention

results in formation of a gel network that is capable of conducting lithium ions. The PEO molecular segments provide the lithium-ion conductivity, while the imide segments and branching provide dimensional stability. The network can hold as much as four times its own weight of liquid while maintaining a high degree of dimensional stability. The liquid can aid significantly in the conduction of lithium ions, and in some circumstances, can increase cell cycle life. Electrolytes have been prepared that contain no volatile components, have a potential stability window of >4.5 V, and have exhibited stable Galvanic cycling between lithium metal electrodes in a coin cell for over 1,000 hours at 60 °C and 0.25 mA/cm² current density.

The copolymer is synthesized in the following process (see figure):

1. A PEO oligomer that is terminated with primary aliphatic amines on both ends is reacted with a dianhydride to make a polyamide-acid prepolymer. The reaction takes place in a solvent, and the stoichiometry of the oligomer and the dianhydride is adjusted so that the resulting prepolymer is a linear polymer capped with amines on both ends. The solvent must be carefully chosen to solubilize the prepolymer, have a boiling temperature preferably between 150 and 200 °C, and to be inert to lithium metal and other cell ingredients.
2. The polyamide-acid prepolymer is imidized in solution. The water generated in the imidization reaction is removed by azeotropic distillation.
3. The appropriate additives (e.g., a lithium salt and a carbonate solvent) are dissolved in the polymer solution. A trifunctional molecule that reacts with the amine end caps at ambient temperatures to form a gel is then added to the solution. The gelation time and the properties of the resulting film can be adjusted by changing the length of the polymer chains. The properties of the film can also be ad-



A **Polymer Gel Network** based on a branched rod-coil polyimide-PEO copolymer is synthesized in a relatively simple process that can be adapted to tailoring the properties of the final product.

justed through choice of the dianhydride, the length of the starting PEO oligomer molecules, and partial replacement of the trifunctional molecule with a difunctional molecule.

4. The film can be packaged once gelation has occurred. Because the reaction solvent is inert toward all cell ingredients, it is not necessary to

remove this solvent. Optionally, because the reaction solvent boils at a temperature $\approx 100\text{ }^{\circ}\text{C}$ lower than does a typical cyclic carbonate solvent, the reaction solvent can be preferentially evaporated before packaging.

This work was done by Mary Ann B. Meador of Glenn Research Center and Dean M. Tigelaar of Ohio Aerospace Institute. Fur-

ther 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, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-18205-1.

Catalysts for Efficient Production of Carbon Nanotubes

Some alloys have been found to work at lower temperatures.

Lyndon B. Johnson Space Center, Houston, Texas

Several metal alloys have shown promise as improved catalysts for catalytic thermal decomposition of hydrocarbon gases to produce carbon nanotubes (CNTs). Heretofore almost every experiment on the production of carbon nanotubes by this method has involved the use of iron, nickel, or cobalt as the catalyst. However, the catalytic-conversion efficiencies of these metals have been observed to be limited. The identification of better catalysts is part of a continuing program to develop means of mass production of high-quality carbon nanotubes at costs lower than those achieved thus far (as much as \$100/g for purified multi-wall CNTs or \$1,000/g for single-wall CNTs in year 2002).

The main effort thus far in this program has been the design and implementation of a process tailored specifically for high-throughput screening of

alloys for catalyzing the growth of CNTs. The process includes an integral combination of (1) formulation of libraries of catalysts, (2) synthesis of CNTs from decomposition of ethylene on powders of the alloys in a pyrolytic chemical-vapor-decomposition reactor, and (3) scanning-electron-microscope screening of the CNTs thus synthesized to evaluate the catalytic efficiencies of the alloys. Information gained in this process is put into a database and analyzed to identify promising alloy compositions, which are to be subjected to further evaluation in a subsequent round of testing.

The promising alloys identified thus far have been the following (compositions in atomic percentages): 90 Co, 10 Ti; 20 Co, 70 Ni, 5 Ti, 5 Ta; 90 Co, 10 Mo; 20 Co, 75 Ni, 5 Mo; 80 Co, 10 Ti, 10 Al; 70 Co, 15 Ni, 15 Ti; 80 Co, 10 Ni, 10 Ti; 70 Co, 5 Ta, 5 Mo, 20 Mn; 80 Ni, 10 Mo, 10

A; 80 Co, 12 Ni, 8 Al; and 80 Co, 20 Cr.

Some of these alloys have been found to catalyze the formation of carbon nanotubes from ethylene at temperatures as low as 350 to 400 $^{\circ}\text{C}$. In contrast, the temperatures typically required for prior catalysts range from 550 to 750 $^{\circ}\text{C}$.

This work was done by Ted X. Sun and Yi Dong of Intermetrix Corp. for Johnson Space Center. 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 invention. Inquiries concerning rights for its commercial use should be addressed to:

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Refer to MSC-23477-1, volume and number of this NASA Tech Briefs issue, and the page number.

Amorphous Silk Fibroin Membranes for Separation of CO₂

Lyndon B. Johnson Space Center, Houston, Texas

Amorphous silk fibroin has shown promise as a polymeric material derivable from natural sources for making membranes for use in removing CO₂ from mixed-gas streams. For most applications of silk fibroin, for purposes other than gas separation, this material is used in its highly crystalline, nearly natural form because this form has uncommonly high tensile strength. However, the crystalline phase of silk fibroin is impermeable, making it necessary to convert the material to amorphous form to obtain the high permeability needed for gas separation.

Accordingly, one aspect of the present development is a process for generating amorphous silk fibroin by treating native silk fibroin in an aqueous methanol/salt solution. The resulting material remains self-standing and can be prepared as thin film suitable for permeation testing. The permeability of this material by pure CO₂ has been found to be highly improved, and its mixed-gas permeability has been found to exceed the mixed-gas permeabilities of several ultrahigh-CO₂-permeable synthetic polymers. Only one of the synthetic polymers — poly(trimethylsilyl-

propyne) [PTMSP] — may be more highly permeable by CO₂. PTMSP becomes unstable with time, whereas amorphous silk should not, although at the time of this reporting this has not been conclusively proven.

This work was done by Christopher M. Aberg, Anand K. Patel, Eun Seok Gil, and Richard J. Spontak of North Carolina State University and May-Britt Hagg of Norwegian University of Science and Technology for Johnson Space Center.

For further information, contact the JSC Innovation Partnerships Office at (281) 483-3809. MSC-24032-1