Lithium Dinitramide as an Additive in Lithium Power Cells

This inorganic additive appears to act as a superior SEI promoter.

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Lithium dinitramide, $LiN(NO_2)_2$ has shown promise as an additive to nonaqueous electrolytes in rechargeable and non-rechargeable lithium-ion-based electrochemical power cells. Such non-aqueous electrolytes consist of lithium salts dissolved in mixtures of organic ethers, esters, carbonates, or acetals. The benefits of adding lithium dinitramide (which is also a lithium salt) include lower irreversible loss of capacity on the first charge/discharge cycle, higher cycle life, lower self-discharge, greater flexibility in selection of electrolyte solvents, and greater charge capacity.

The need for a suitable electrolyte additive arises as follows: The metallic lithium in the anode of a lithium-ion-based power cell is so highly reactive that in addition to the desired main electrochemical reaction, it engages in side reactions that cause formation of resistive films and dendrites, which degrade performance as quantified in terms of charge capacity, cycle life, shelf life, first-cycle irreversible capacity loss, specific power, and specific energy. The incidence of side reactions can be reduced through the formation of a solid-electrolyte interface (SEI) — a thin film that prevents direct contact between the lithium anode material and the electrolyte. Ideally, an SEI should chemically protect the anode and the electrolyte from each other while exhibiting high conductivity for lithium ions and little or no conductivity for electrons. A suitable additive can act as an SEI promoter.

Heretofore, most SEI promotion was thought to derive from organic molecules in electrolyte solutions. In contrast, lithium dinitramide is inorganic. Dinitramide compounds are known as oxidizers in rocket-fuel chemistry and until now, were not known as SEI promoters in battery chemistry. Although the exact reason for the improvement afforded by the addition of lithium dinitramide is not clear, it has been hypothesized that lithium dinitramide competes with other electrolyte constituents to react with lithium on the surface of the anode to form a beneficial SEI. Apparently, nitrides and oxides that result from reduction of lithium dinitramide on the anode produce a thin, robust SEI different from the SEIs formed from organic SEI promoters. The SEI formed from lithium dinitramide is more electronically insulating than is the film formed in the presence of an otherwise identical electrolyte that does not include lithium dinitramide. SEI promotion with lithium dinitramide is useful in batteries with metallic lithium and lithium alloy anodes.

This work was done by Alexander A. Gorkovenko of Material Methods LLC for Glenn Research Center.

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-17983-1.

Accounting for Uncertainties in Strengths of SiC MEMS Parts

Fracture strength of a part can be predicted as one statistical distribution.

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A methodology has been devised for accounting for uncertainties in the strengths of silicon carbide structural components of microelectromechanical systems (MEMS). The methodology enables prediction of the probabilistic strengths of complexly shaped MEMS parts using data from tests of simple specimens. This methodology is intended to serve as a part of a rational basis for designing SiC MEMS, supplementing methodologies that have been borrowed from the art of designing macroscopic brittle material structures.

The need for this or a similar methodology arises as a consequence of the fundamental nature of MEMS and the brittle silicon-based materials of which they are typically fabricated. When tested to fracture, MEMS and structural components thereof show wide part-to-part scatter in strength. The methodology involves the use of the Ceramics Analysis and Reliability Evaluation of Structures Life (CARES/Life) software in conjunction with the ANSYS Probabilistic Design System (PDS) software to simulate or predict the strength responses of brittle material components while simultaneously accounting for the effects of variability of geometrical features on the strength responses. As such, the methodology involves the use of an extended version of the ANSYS/CARES/PDS software system described in “Probabilistic Prediction of Lifetimes of Ceramic Parts” (LEW-17682-1/4-1), *Software Tech Briefs* supplement to *NASA Tech Briefs*, Vol. 30, No. 9 (September 2006), page 10.

The ANSYS PDS software enables the ANSYS finite-element-analysis program to account for uncertainty in the design-and-analysis process. The ANSYS PDS software accounts for uncertainty in material properties, dimensions, and loading by assigning probabilistic distributions to user-specified model parameters and performing simulations using various sampling techniques. The CARES/Life code predicts the time-dependent probabilities of failure of brittle material structures under thermomechanical loads.

In the present methodology, CARES/Life is used with ANSYS/PDS to simulate the effect of variations of dimensions on the predicted probabilities of failure of SiC specimens. A special ANSYS macroinstruction code was developed for this purpose. This macroinstruction code simulates fracture strengths of specimens by use of a combination of a random-number generator (for probability of failure), CARES/Life, and ANSYS finite-element modeling for specimens having randomly chosen dimensions based on a statistical distribution and parameters thereof specified by the user. A unique contribution of this macroinstruction code is that given multiple stochastic input variables, including those pertaining to the strength of the material and the geometry of the part, one can now predict the fracture strength of a complexly shaped part as a single statistical distribution, and can predict a single value of probability of failure for a given load. This capability makes it possible to directly compare predictions made by use of CARES/Life with data from tests of specimens while accounting for the significant amounts of variability that are common in dimensions of MEMS structures.

The methodology was tested by applying it to submillimeter-sized single-crystal SiC tensile specimens fabricated by deep reactive-ion etching. The specimens had large thickness-to-width ratios (high-aspect-ratios). Some of the specimens contained, variously, elliptical or circular through-thickness holes, which served as stress concentrators. The roughness of the sidewalls left by etching was greater than that of the top and bottom specimen surfaces. There was a large amount of scatter in the measured fracture strengths (typical for ceramics), but the average fracture strength was observed to increase with greater concentration of stress. Variations in dimensions among specimens were measured. The aforementioned macroinstruction code was used to predict the fracture strengths of the specimens with the stress-concentrating holes and the variations in dimensions.

The predictions were found to correlate well with data from tests of the specimens containing circular holes but not quite as well with data from tests of the specimens containing elliptical holes. The results were interpreted as signifying, in part, that (1) the Weibull distribution, which is used in the CARES/Life software, adequately characterizes the distribution of strengths of MEMS parts; (2) the surface areas of the relatively rough etched sidewalls likely controlled the observed failure responses; (3) the methodology enables accounting for part-to-part variations in dimensions and other properties; and (4) at least at moderate levels of concentration of stress, the methodology can be used to enable successful design of complexly shaped parts on the basis of data from tests of simply shaped specimens.

This work was done by Noel Nemeth, Laura Evans, Glen Beheim, and Mark Trapp of Glenn Research Center; Osama Jadaan of the University of Wisconsin; and William N. Sharpe, Jr., of Johns Hopkins University. 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, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4–8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-18095-1.

Ion-Conducting Organic/Inorganic Polymers

Properties can be tailored through a choice of starting alkoxysilane and diamine ingredients.

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Ion-conducting polymers that are hybrids of organic and inorganic moieties and that are suitable for forming into solid-electrolyte membranes have been invented in an effort to improve upon the polymeric materials that have been used previously for such membranes. Examples of the prior materials include perfluorosulfonic acid-based formulations, polybenzimidazoles, sulfonated polyetherketone, sulfonated naphthalenic polyimides, and polyethylene oxide (PEO)-based formulations. Relative to the prior materials, the polymers of the present invention offer greater dimensional stability, greater ease of formation into mechanically resilient films, and acceptably high ionic conductivities over wider temperature ranges. Devices in which films made of these ion-conducting organic/inorganic polymers could be used include fuel cells, lithium batteries, chemical sensors, electrochemical capacitors, electrochromic windows and display devices, and analog memory devices.

The synthesis of a polymer of this type (see Figure 1) starts with a reaction between an epoxide-functionalized alkoxysilane and a diamine. The product of this reaction is polymerized by hydrolysis and condensation of the alkoxysilane group, producing a molecular network that contains both organic and inorganic (silica) links. The silica in the network contributes to the ionic conductivity and to the desired thermal and mechanical properties.

Examples of other diamines that have been used in the reaction sequence of Figure 1 are shown in Figure 2. One can

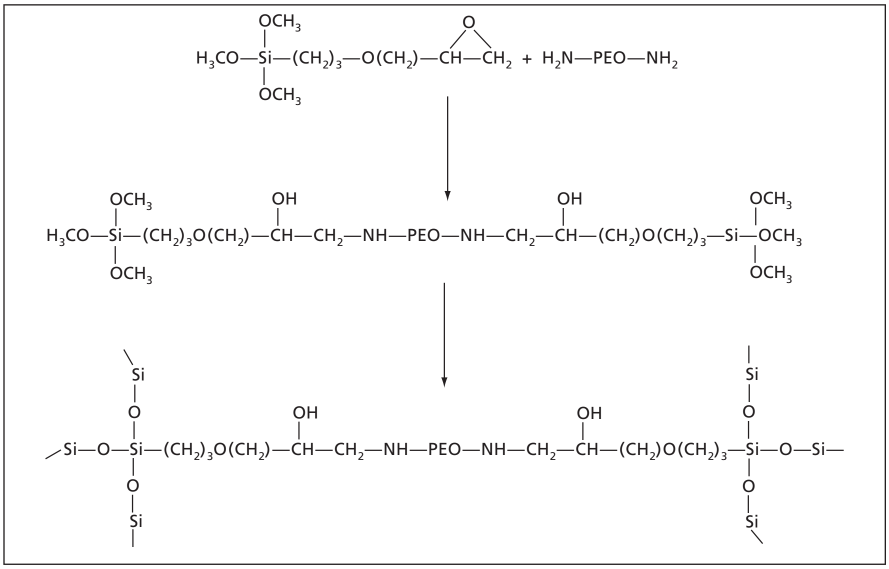

Figure 1. A **Molecular Network of Organic and Inorganic Moieties** is produced in this representative reaction sequence. The starting alkoxysilane and diamine can be other than the ones shown here.