



A **Monomer Molecule** suitable for photopolymerization contains a generic spacer group between an *ortho*-methylbenzophenone and a maleimide group.

nected to a dienophile (in this case, a maleimide) through a generic spacer group. Irradiation with ultraviolet light gives rise to a photochemical intermediate — the aforementioned *ortho*-quinodimethane — from the *ortho*-methylbenzophenone. This group may react with the dienophile on another such monomer molecule to produce an

oligomer that, in turn may react in a step-growth manner to produce a polyimide.

This approach offers several advantages in addition to those mentioned above:

- The monomer can be stored for a long time because it remains unreactive until exposed to light.
- Because the monomer is the only active starting ingredient, there is no need for

mixing, no concern for ensuring correct proportions of monomers, and the purity of the final product material is inherently high.

- The use of solvents is optional: The synthesis can be performed using the neat monomer or the monomer mixed with one or more solvent(s) in dilute or concentrated solution.
- The solubility of the monomer and the physical and chemical properties of the final polymer can be tailored through selection of the spacer group.

*This work was done by Michael A. Meador of Glenn Research Center and Daniel S. Tyson and Faysal Ilhan of Ohio Aerospace Institute. 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-18174-1.*

## Optimized Carbonate and Ester-Based Li-Ion Electrolytes

**This technology can be used in portable electronics, cell phones, and electric vehicles.**

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To maintain high conductivity in low temperatures, electrolyte co-solvents have been designed to have a high dielectric constant, low viscosity, adequate coordination behavior, and appropriate liquid ranges and salt solubilities. Electrolytes that contain ester-based co-solvents in large proportion (>50 percent) and ethylene carbonate (EC) in small proportion (<20 percent) improve low-temperature performance in MCMB carbon-LiNiCoO<sub>2</sub> lithium-ion cells. These co-solvents have been demonstrated to enhance performance, especially at temperatures down to -70 °C. Low-viscosity, ester-based co-solvents were incorporated into multi-component electrolytes of the following composition: 1.0 M LiPF<sub>6</sub> in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + X (1:1:8 volume percent) [where X = methyl butyrate (MB), ethyl butyrate EB, methyl propionate (MP), or ethyl valerate (EV)]. These electrolyte formulations result in improved low-temperature performance of lithium-ion cells, with dramatic results at temperatures below -40 °C. [See "Ester-Based Electrolytes for Low-Temperature Li-Ion Cells," (NPO-41097) *NASA Tech Briefs*, Vol 29, No. 12 (December, 2005), p. 59.]

Improved low-temperature performance can also be realized with ester-based electrolytes containing high salt concentrations and by using mixed salt formulations — specifically with (a) 1.0 M LiPF<sub>6</sub> + 0.40 LiBF<sub>4</sub> and (b) 1.40 M LiPF<sub>6</sub> dissolved in EC+EMC+MP (1:1:8 volume percent) and EC+EMC+MB (1:1:8 volume percent) solvent mixtures. The rate capability has been observed to increase dramatically at low temperatures (i.e., -60 °C) using this approach. It is anticipated that increased salt concentrations and the use of mixed salt systems will also improve the low-temperature performance characteristics of other solvent blends of carbonates and esters. ["Mixed-Salt/Ester Electrolytes for Low-Temperature Li + Cells" (NPO-42862), *NASA Tech Briefs*, Vol. 30, No. 11 (November 2006), p 66.]

A number of these electrolytes have been demonstrated in both experimental and aerospace-quality, high-capacity prototype cells. In more recent work, these ester-containing electrolytes have been further optimized to provide both good low-temperature performance (down to -60 °C) while still offering reasonable high-temperature resilience. This has primarily been achieved by fix-

ing the EC-content at 20 percent and the ester co-solvent at 20 percent, in contrast to the previously developed ultra-low temperature systems, which have the EC-content and ester-content at 10 percent and 80 percent, respectively. Using this approach, a prototype cell containing a 1.0 M LiPF<sub>6</sub> EC+EMC+MP (20:60:20 volume percent) electrolyte was capable of delivering over six times the amount of capacity delivered by the baseline ternary, all-carbonate blend, and was able to support reasonably aggressive rates at low temperature (-50 and -60 °C). Cells containing other esters also performed well at low temperature, with the lower-molecular-weight, lower-viscosity co-solvents generally yielding better performance at low temperatures.

Although slightly less favorable in terms of electrolyte conductivity, the higher-molecular-weight esters [i.e., propyl butyrate (PB), and butyl butyrate (BB)] are expected to result in cells with more favorable high-temperature resilience (>40 °C), compared to the lower-molecular-weight esters.

This technology has relevance for manned and unmanned space missions, aircraft batteries, and Land Warrior applications, as well as for terrestrial applica-

tions that require good performance and a high level of safety over a range of temperatures, including portable electronics like camcorders, cellular phones, laptop computers, and radio communication sets. Electric vehicle applications can also use this innovation where high-power batteries must operate at low temperatures, such as in monitoring stations in Antarctica.

*This work was done by Marshall Smart and Ratnakumar Bugga 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 invention. Inquiries concerning rights for its commercial use should be addressed to:*

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