



4-Vinyl-1,3-Dioxolane-2-One as an Additive for Li-Ion Cells

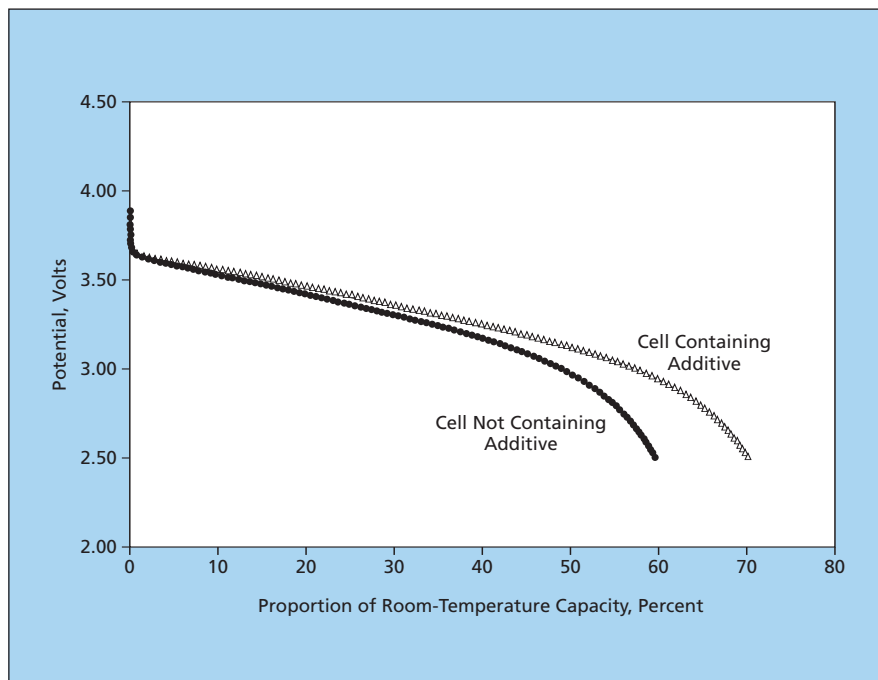
Low-temperature charge/discharge capacity is increased.

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Electrolyte additive 4-vinyl-1,3-dioxolane-2-one has been found to be promising for rechargeable lithium-ion electrochemical cells. This and other additives, along with advanced electrolytes comprising solutions of LiPF_6 in various mixtures of carbonate solvents, have been investigated in a continuing effort to improve the performances of rechargeable lithium-ion electrochemical cells, especially at low temperatures. In contrast to work by other researchers who have investigated the use of this additive to improve the high-temperature resilience of Li-ion cells, the current work involves the incorporation of 4-vinyl-1,3-dioxolane-2-one into quaternary carbonate electrolyte mixtures, previously optimized for low-temperature applications, resulting in improved low-temperature performance.

The benefit afforded by 4-vinyl-1,3-dioxolane-2-one can be better understood in the light of relevant information from a number of prior *NASA Tech Briefs* articles about electrolytes and additives for such cells. To recapitulate: The loss of performance with decreasing temperature is attributable largely to a decrease of ionic conductivity and the increase in viscosity of the electrolyte. What is needed to extend the lower limit of operating temperature is a stable electrolyte solution with relatively small low-temperature viscosity, a large electric permittivity, adequate coordination behavior, and appropriate ranges of solubilities of liquid and salt constituents. Whether the anode is made of graphitic or non-graphitic carbon, a film on the surface of the anode acts as a solid/electrolyte interface (SEI), the nature of which is critical to low-temperature performance. Desirably, the surface film should exert a chemically protective (passivating) effect on both the anode and the electrolyte, yet should remain conductive to lithium ions to facilitate intercalation and deintercalation of the ions into and out of the carbon during discharging and charging, respectively.

The additives investigated previously include alkyl pyrocarbonates. Those ad-



The **Proportion of Room-Temperature Capacity** retained at -20°C was determined, for each of two cells, from data obtained in the first five cycles of charge/discharge testing.

ditives help to improve low-temperature performances by giving rise to the formation of SEIs having desired properties. The formation of the SEIs is believed to be facilitated by products (e.g., CO_2) of the decomposition of these additives. These decomposition products are believed to react to form Li_2CO_3 -based films on the carbon electrodes.

The present additive, 4-vinyl-1,3-dioxolane-2-one, also helps to improve low-temperature performance by contributing to the formation of SEIs having desired properties, but probably in a different manner: It is believed that, as part of the decomposition process, the compound polymerizes on the surfaces of carbon electrodes.

The effectiveness of 4-vinyl-1,3-dioxolane-2-one as a performance-improving additive in several different LiPF_6 /carbonate-solvent-mixture electrolytes was investigated in a series of charge/discharge tests of rechargeable lithium-ion electrochemical cells containing the electrolytes, at room temperature and at

a temperature of -20°C . In one pair of tests, the electrolyte comprised LiPF_6 dissolved at a concentration of 1.0 M in a solvent mixture comprising 1 volume part of ethylene carbonate + 1 volume part of diethyl carbonate + 1 volume part of dimethyl carbonate + 2 volume parts of ethyl methyl carbonate. In one of the tests, no additive was included; in the other test, the electrolyte included 4-vinyl-1,3-dioxolane-2-one in the proportion of 1.5 weight percent. The results of these tests showed that the additive enhanced low-temperature performance: specifically, the results showed that at -20°C and at any given voltage, the cell containing the additive retained a greater proportion of its room-temperature capacity than did the cell that did not contain the additive (see figure).

*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).
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