



DMAC and NMP as Electrolyte Additives for Li-Ion Cells

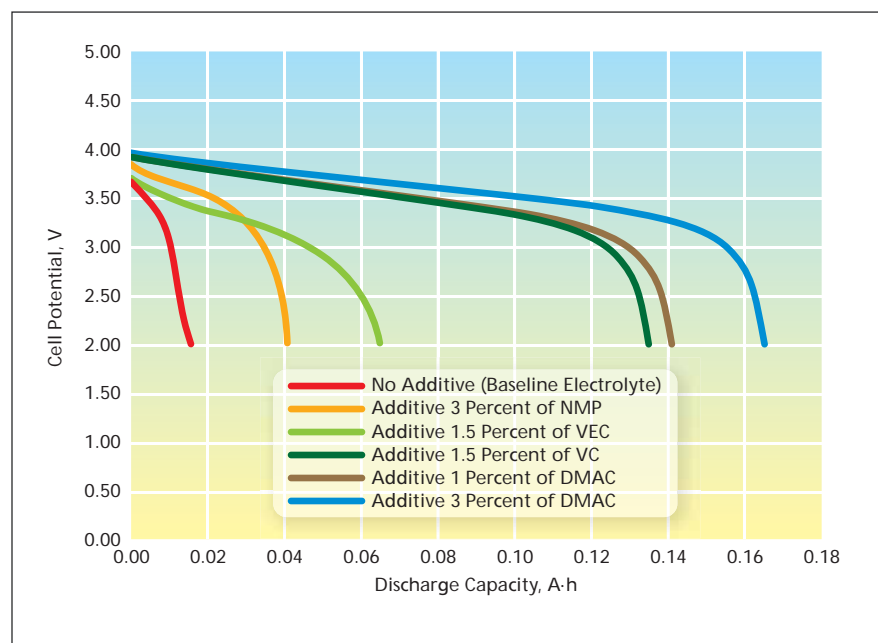
High-temperature resilience is increased.

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Dimethyl acetamide (DMAC) and N-methyl pyrrolidinone (NMP) have been found to be useful as high-temperature-resilience-enhancing additives to a baseline electrolyte used in rechargeable lithium-ion electrochemical cells. The baseline electrolyte, which was previously formulated to improve low-temperature performance, comprises LiPF_6 dissolved at a concentration of 1.0 M in a mixture comprising equal volume proportions of ethylene carbonate, diethyl carbonate, and dimethyl carbonate. This and other electrolytes comprising lithium salts dissolved in mixtures of esters (including alkyl carbonates) have been studied in continuing research directed toward extending the lower limits of operating temperatures and, more recently, enhancing the high-temperature resilience of such cells. This research at earlier stages, and the underlying physical and chemical principles, were reported in numerous previous *NASA Tech Briefs* articles.

Although these electrolytes provide excellent performance at low temperatures (typically as low as -40°C), when the affected Li-ion cells are subjected to high temperatures during storage and cycling, there occur irreversible losses of capacity accompanied by power fade and deterioration of low-temperature performance. The term "high-temperature resilience" signifies, loosely, the ability of a cell to resist such deterioration, retaining as much as possible of its initial charge/discharge capacity during operation or during storage in the fully charged condition at high temperature. For the purposes of the present development, a temperature is considered to be high if it equals or exceeds the upper limit (typically, 30°C) of the operating-temperature range for which the cells in question are generally designed.

Prior studies focusing on the reactivity of electrolytes like the ones of interest here had established that LiPF_6 can thermally decompose to form LiF and PF_5 , the later product being a strong Lewis acid that further reacts with alkyl carbonates to form a number of byprod-



Reversible Capacities, after storage at a temperature of 65°C of cells containing the baseline electrolyte plus various additives were measured at 20°C at a discharge rate of 25 mA [numerically equal to 1/16 of (the nominal capacity in A-h)] after the cells had been charged to a potential of 4.1 V at a rate of 25 mA.

ucts. The present additives — DMAC and NMP — are Lewis bases that act as stabilizing agents in that they reversibly bind with PF_5 , thereby preventing decomposition of the carbonate solvents at high temperature.

To enable testing of these additives, rechargeable carbon-anode/ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -cathode cells containing the baseline electrolyte plus various proportions of these additives were assembled. For comparison, cells containing, variously, the baseline electrolyte alone or the baseline electrolyte plus either of two previously known additives [vinylene carbonate (VC) and vinylene carbonate (VEC)] were also assembled. The cells were subjected to charge-discharge cycling tests and other electrochemical tests at various temperatures from room temperature (23°C) down to -20°C . The cells were also evaluated with respect to high-temperature resilience by measuring the capacities retained after storage for 10 days at a temperature of 55°C , followed by 10 days at 60°C , followed by 10

days at 65°C . The greatest retention of capacity was observed in a cell containing 3 percent of DMAC as the additive. Other cells, in order of decreasing retained capacity, included those containing 1 percent of DMAC, 1.5 percent of VC, 1.5 percent of VEC, 3 percent of NMP, and no additive (see figure).

This work was done by Marshall Smart and Ratnakumar Bugga of Caltech and Brett Lucht of the University of Rhode Island 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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