

Increasing Discharge Capacities of Li-(CF)_n Cells

Electrolyte additive could open new applications for Li-(CF)_n batteries.

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An electrolyte additive has shown promise as a means of increasing the sustainable rates of discharge and, hence, the discharge capacities, of lithiumpoly(carbon monofluoride) electrochemical power cells. Lithium-poly(carbon monofluoride) [Li-(CF)_n] cells and batteries offer very high specific energies practical values of about 600 W·h/g and a theoretical maximum value of 2,180 W·h/kg. However, because Li-(CF) $_n$ cells and batteries cannot withstand discharge at high rates, they have been relegated to niche applications that involve very low discharge currents over times of the order of hundreds to thousands of hours. Increasing the discharge capacities of Li- $(CF)_n$ batteries while maintaining high practical levels of specific energy would open new applications for these batteries.

During the discharge of a Li-(CF)_n

causes LiF to precipitate at the cathode. LiF is almost completely insoluble in most non-aqueous solvents, including those used in the electrolyte solutions of Li-(CF), cells. LiF is electrochemically inactive and can block the desired transport of ions at the cathode, and, hence, the precipitation of LiF can form an everthickening film on the cathode that limits the rate of discharge.

The present electrolyte additive is a member of a class of fluorinated boronbased compounds that function as anion receptors, helping to increase the discharge capacity in two ways:

- 1. They render LiF somewhat soluble in the non-aqueous electrolyte solution, thereby delaying precipitation until a high concentration of LiF in solution has been reached.
- 2. When precipitation occurs, they promote the formation of large LiF

cell, one of the electrochemical reactions 3.0 2.5 With Additive 2.0 Cell Potential, Volts 1.0 Without Additive 0.5 0 1×10^5 2×10^5 3×10^5 4×10^5 5×10^5 6×10^5

Potential as a Function of Time was measured in constant-current (1-mA) discharges of two Li-(CF)_n cells that were nominally equivalent except that one contained tris(hexafluoroisopropyl) borate as an electrolyte additive.

Time, Seconds

grains that do not conformally coat the cathode.

The net effect is to reduce the blockage caused by precipitation of LiF, thereby maintaining a greater degree of access of electrolyte to the cathode.

The fluorinated boron-based anion receptor most commonly used heretofore tris(pentafluorophenyl) borane - has been found to sharply increase the viscosities of electrolyte solutions. Increases in viscosities generally contribute to reductions in discharge capacities. In contrast, the present additive - tris(hexafluoroisopropyl) borate — can be mixed with such conventional lithium-cell solvents as propylene carbonate and dimethoxyethane to obtain solutions that have much lower viscosities and accept greater concentrations of LiF.

The promise of tris(hexafluoroisopropyl) borate as an additive was demonstrated in an experiment on two Li- $(CF)_n$ cells in standard commercial button-style packages. The cells were identical with one exception: the electrolyte solution in one cell contained 24 weight percent of tris(hexafluoroisopropyl) borate. The cells were tested at discharge currents of 1 mA. As shown in the figure, the cell containing the additive outperformed the one without the additive by a wide margin.

This work was done by Jay Whitacre and William West of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

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