Additive for Low-Temperature Operation of Li-$(CF)_n$ Cells

Tris(2,2,2-trifluoroethyl) borate as an electrolyte additive increases low-temperature capacity.

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Some progress has been reported in continuing research on the use of anion-receptor compounds as electrolyte additives to increase the sustainable rates of discharge and, hence, the discharge capacities, of lithium-poly(carbon monofluoride) [Li-$(CF)_n$, where n >1] primary electrochemical power cells. Some results of this research at a prior stage were summarized in "Increasing Discharge Capacities of Li$(CF)_n$ Cells" (NPO-42346), *NASA Tech Briefs*, Vol. 32, No. 2 (February 2008), page 37. A major difference between the present and previously reported results is that now there is some additional focus on improving performance at temperatures from ambient down to as low as –40 °C.

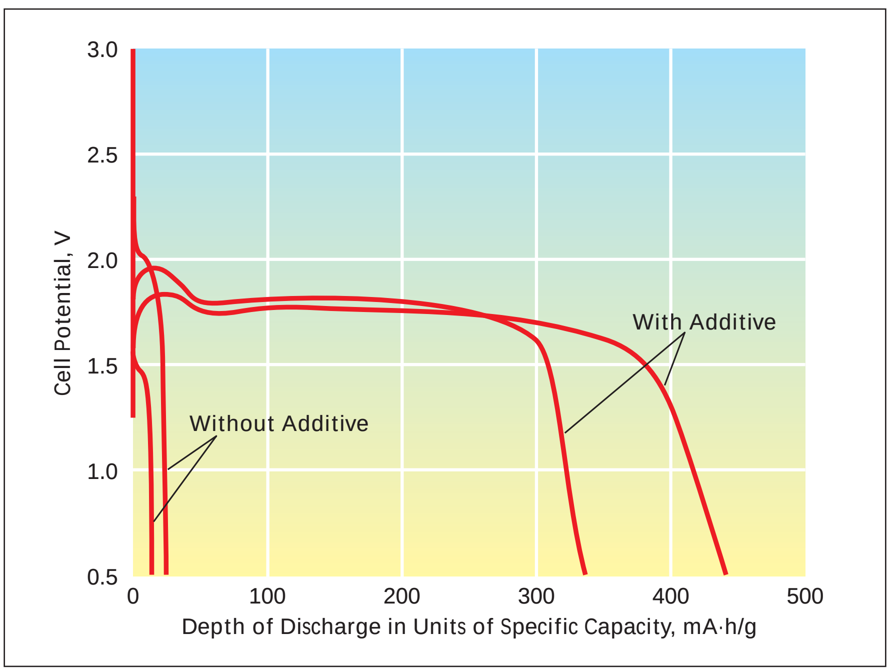
To recapitulate from the cited prior article: During the discharge of a Li-$(CF)_n$ cell, one of the electrochemical reactions causes LiF to precipitate at the cathode. LiF is almost completely insoluble in most non-aqueous solvents, including those used in the electrolyte solutions of Li-$(CF)_n$ cells. LiF is electrochemically inactive and can block the desired transport of electrons at the cathode, and, hence, the precipitation of LiF can form an ever-thickening film on the cathode that limits the rate of discharge. An anion-receptor electrolyte additive helps to increase the discharge capacity in two ways:

- It renders LiF somewhat soluble in the non-aqueous electrolyte solution, thereby delaying precipitation until a high concentration of LiF in solution has been reached.
- When precipitation occurs, it promotes the formation of large LiF 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 and greater electronic conductivity.

The anion-receptor compounds studied in this line of research have been fluorinated boron-based compounds. The specific compound mentioned in the cited prior article, in which there was no special focus on low-temperature performance, was tris(hexafluoroisopropyl) borate. The anion-receptor compound used in the more-recent research reported here — tris(2,2,2-trifluoroethyl) borate — was selected because of an expectation that it would reduce the viscosity of the electrolyte, thereby increasing the low-temperature conductivity and, consequently, increasing the low-temperature discharge-rate capability. One complicating observation made in this research was that tris(2,2,2-trifluoroethyl) borate does not improve the low-temperature performance of a cell containing a fully fluorinated $(CF)_n$ cathode, but does improve the low-temperature performance of a cell containing a sub-fluorinated $(CF)_n$ cathode — that is, a cathode made of $(CF_x)_n$ [where x<1].

The improvement in low-temperature performance can be considerable. For example, in one set of tests at a temperature of –40 °C, a pair of cells that did not contain the present anion-receptor additive and another pair of cells that did contain this additive were discharged at a current of $C/2.5$ (where C is the magnitude of the current, integrated for one hour, that would amount to the nominal charge capacity of a cell). The results of the tests (see figure) showed that the cells containing the additive performed much better than did the cells without the additive.



Two Pairs of Li-$(CF_x)_n$ Cells containing an electrolyte in the form of 0.5 M $LiBF_4$ in a non-aqueous solvent were discharged at a rate $C/2.5$ at a temperature of –40 °C. The cells not containing the electrolyte additive were essentially nonfunctional; those containing the additive were functional, retaining approximately half of their room-temperature discharge capacities.

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

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