Enhanced Low-Temperature Performance of Li–CF_x Batteries

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This work describes the continued examination of the low-temperature performance of the Li–CF_x electrochemical couple in a −40°C or colder environment. Previously, the efficacy of subfluorinated CF_x (SFCF_x) cathode active materials was demonstrated; preliminary results indicated that the material was functional at rates up to C/20 at −40°C. However, there were often substantial voltage fluctuations during discharge, accompanied with inconsistent capacity yields and sometimes dramatic polarization events. In the research described herein, an investigation of various electrolyte and cathode compositions was conducted in an effort to optimize performance. In particular, several different electrolyte solvent formulations were examined using a salt content of either 1 M LiBF_4. A further modification consisted of addition of an anion receptor to the electrolyte that was intended to be a LiF-solvating agent. The most promising electrolyte was tested with several different SFCF_x compositions created using either graphic or multiwall nanotube precursor materials. Electrochemical evaluation showed that the best SFCF_x-based test cells were able to deliver specific capacity values up to five times greater than control cells (containing conventional CF_1.08 powder) at −40°C under discharge currents as high as C/5 with composite electrodes thicker than 100 μm. © 2007 The Electrochemical Society. DOI: 10.1149/1.2735823 All rights reserved.


Recently, it has been reported that subfluorinated CF_x (SFCF_x) materials (where 0.3 < x < 0.66) are capable of supporting discharge rates as high as 5C at room temperature with excellent utilization. It was unknown, however, whether these cathodes would possess the same characteristics at very low temperatures at aggressive rates (i.e., greater than C/100). The significantly slower cathode reaction kinetics and/or lower electrolyte ionic conductivity values at these temperatures could mitigate the benefits observed at room temperature. Furthermore, the factors that cause the voltage delay effect in Li–CF_x batteries are likely to be more prominent under high-rate, low-temperature conditions and therefore must be examined if a functional battery is to be eventually produced. Preliminary results have been published recently, where it was indicated that the subfluorinated CF_x materials did exhibit superior low-temperature performance at −40°C compared to baseline CF_1.08, though at current levels not exceeding a C/20 rate. Two electrolyte blends were compared: 1 M LiBF_4 solvated in a DME/PC mix to a ratio of either 80:20 or 50:50 v/v %. The 80:20 v/v % 1,2-dimethoxyethane (DME)/propylene carbonate (PC)-based electrolyte had superior performance at low temperatures, though there were still significant variations in cell performance at higher rates at −40°C. It was unclear whether this erratic behavior was due to the inherent properties of the electrolyte, interfacial properties (i.e., cathode surface wettability), or the redistribution of reaction by-products (LiF) upon discharge.

The focus of the work presented in this letter is to further improve low-temperature functionality by matching the highest capacity subfluorinated cathode active material with the proper electrolyte blend and electrode form factor. In particular, three different electrolytes were tested at low temperatures with a standard Li–CF_0.65 cell. The best electrolyte was then used to test several variations of subfluorinated CF_x cathode material. These results were compared to those obtained from cathodes produced using commercially available CF_1.08. In some cells, a solvating anion receptor additive was also inserted into the electrolyte with the intention of reducing cathode surface Li–F passivation, thereby increasing the electrode functionality. The most promising test cells were able to support substantial discharge currents at temperatures colder than −40°C, with composite cathode thicknesses exceeding 110 μm.

Experimental

A standard test vehicle was adopted that consisted of a spray-deposited cathode layer containing 10% poly(vinylidene difluoride) (PVDF) binder, 10% carbon black, and 80% active material on a 1 mil thick Al current collector foil heated. These composite cathodes ranged in thickness from 10 to 120 μm, with the most commonly tested thickness being about 40 ± 5 μm. The relationship between electrode mass and thickness was determined using a precision caliper on the thicker samples (>50 μm). The standard test cell consisted of 2032 coin cells with a Li metal anode and a single layer of polypropylene (Tonen) separator. The control electrode, based on CF_1.08 as received from a commercial vendor, contained 30 wt % carbon black and 10 wt % PVDF. This resulted in a composite electrode capable of similar room-temperature performance (per unit mass of the total composite electrode) as a CF_0.35-containing electrode.

A representative SFCF_x electrode composition and thickness, CF_x65 and 40 ± 5 μm thick, was first used to identify promising electrolyte blends for low-temperature performance. The selected electrolyte blends are indicated in Table I.

The lithium tetrafluoroborate used was battery grade obtained from Mitsubishi Petrochemicals Co. and was vacuum dried prior to use. The PC and DME were also high-purity battery grade and obtained from Mitsubishi Petrochemicals Co. and were used as received. The trifluoroethyl ether (TEF) and trifluoropropylene carbonate (TFPC) were synthesized at the University of Southern California by a known method consisting of the acid-catalyzed dehydration reaction of 2,2,2-trifluoroethanol.

The rationale for incorporating ethers bearing fluoroalkyl groups in electrolyte formulations is twofold: (i) they are envisioned to

<table>
<thead>
<tr>
<th>Table I. Electrolyte solvent/salt blends initially tested for low-temperature efficacy in the Li/CF_x test cells. The performance of 1 M LiBF_4 solvated in 50:50 v/v % PC/DME at low temperatures is published elsewhere.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent (v/v %)</td>
</tr>
<tr>
<td>PC/DME (2:8)</td>
</tr>
<tr>
<td>PC/TEE/DME (2:2:6)</td>
</tr>
<tr>
<td>PC/DME (2:8)</td>
</tr>
<tr>
<td>PC/TFFC/DME (15:5:80)</td>
</tr>
<tr>
<td>VC (1.5) added to DME/PC (2:8)</td>
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impair beneficial physical properties to the electrolyte, due to their low viscosity, low melting points, and good solvating properties, and (ii) the hydrofluorocarbon ethers are anticipated to better wet the CF electrode, improving the interfacial properties. The optimization of the PC+DME blends is based upon the balance of having an adequate proportion of the high dielectric constant component (PC) and a sufficient proportion of the low-viscosity, good coordinating component (DME). During the course of optimization of these electrolytes for low-temperature operation, higher conductivity is observed with electrolyte formulations containing low PC content and low electrolyte salt concentration. In addition to these factors, the primary solvent, propylene carbonate or PC, needs to be in adequate proportion to impart passivation to the anode (and hence shelf life to the cell) but not high enough to contribute to higher viscosity at low temperatures.

Upon determining the highest performing electrolyte, at low temperatures, of those examined, test cells were made and tested using four different cathode active materials; three were SFCF₁x based, and the last was the CF₁₀₈₈-based standard. The SFCF₁x fabrication process is described elsewhere. The CF₁₀₆₈ electrodes used partially fluorinated Madagascar graphite precursor, while the other two SFCF₁x variations contained CF₀₅₉ or CF₀₃₂₂ material made using multiwall carbon nanotube material precursor materials supplied by MER Corporation (Tucson, AZ). Characterization data indicated that all of the SF CF₁x materials were comprised of pristine unfluorinated graphite domains mixed intimately with nanodispersed near-fully fluorinated graphitic regions and are consistent with data reported previously. The small scale of these regions dictates that the materials had a very high graphite-to-CF surface area and subsequently might possess excellent electronic/interfacial transport properties.

In seven of the 0.5 M LiBF₄ in DME/PC (80:20) containing cells, an anion receptor Lewis acid additive, tris(2,2,2-trifluoroethyl)borate (TTFEB), was also dissolved into the electrolyte solvent in an effort to decrease or eliminate the LiF (discharge reactant) electrode surface buildup via a F⁻ complexing reaction. Such an approach has been employed elsewhere, with a variety of anion receptor molecules in Li-ion electrolytes, mainly to enhance the solubility of lithium salts. The nominal TTFEB concentration in the electrolyte solution was 1.598 v/v % TTFEB/DME/PC (80:20).

Previous work indicated that a room-temperature predischarge step (consisting of a 1 h, discharge at a C/33 current level) was necessary to prepare the electrode interfacial regions to accommodate low-temperature discharge. This preparation was used here for most test cells; however, the necessity of this predischarge was re-examined for the most promising electrode/electrolyte combinations. In all cases, the C rate was calculated based on the expected room-temperature capacity of the cathode if discharged at a C/40 rate.

**Results**

Figure 1 shows discharge data from CF₁₀₆₄ SFCF₁x active-material cells using a C/10 discharge rate at −40°C with the different electrolytes listed in Table I. The best (highest power, smoothest discharge curve) result was obtained with 0.5 M LiBF₄ solvated in an 8:2 v/v % DME/PC blend. Test cells made with electrolytes that had a higher salt content (1 M), were more rate-limited and had erratic potential variations during discharge at these low temperatures. Repeated testing supports this finding. Those cells that polarized rapidly were still functional and displayed smooth discharge curves and good discharge capacities at lower rates (C/20 or slower) at −40°C.

The execution of the predischarge step in the 0.5 M salt content cells was found to have no beneficial effect on low-temperature performance, in contrast to the results obtained using electrolytes containing higher salt concentrations. Electrical impedance spectroscopy (EIS) data collected from test coin cells with stainless steel blocking electrodes indicate that the 1 M salt-content electrolyte had approximately twice the high-frequency, real-axis intercept at −40°C compared to the 0.5 M salt-containing blend. Figure 2 shows EIS data from Li/CF₁₀₆₄ cells with either a 1 or 0.5 M salt content. Figure 2c contains the same data for a 0.5 M salt-content cell with the anion-receptor additive. All of these cells had similar active material masses and similar impedance characteristics after discharge.

Figure 3 shows a comparison between the −40°C temperature performances of various CF₁x cathodes (of similar mass/thickness) as discharged at the C/5 rate using the 0.5 M LiBF₄ solvated in 8:2 v/v % DME/PC electrolyte. The thickness of the CF₁₀₈₈-based cathode was 35 μm, while the thickness of the SFCF₁x cathodes was...
40–60 μm. The delivered capacities for the SFCF\textsubscript{x} cathodes were as much as 300% greater with the subfluorinated cathodes than that of the CF\textsubscript{1.08} baseline cathode under identical discharge conditions. Multiple electrodes were tested for each electrode composition with consistent results.

The composite cathode thickness has previously been found to have a strong negative correlation with the maximum usable discharge rate or realized discharge capacity in the Li–CF\textsubscript{x} chemistry and was therefore examined here under low-temperature conditions. Figure 4 shows the behavior of CF\textsubscript{0.65} composite cathodes with thicknesses varying from 4 to 118 μm at a C/5 discharge rate, −40°C as a function of composite cathode thickness, for CF\textsubscript{0.65}-based test cells. The 0.5 M LiBF\textsubscript{4} with 8:2 v/v % DME/PC electrolyte was used in all cases, and the TTFEB anion acceptor was added in the thick electrode case (115 μm thick).
The cathode impedance is substantially reduced after discharge, in solutions with either 0.5 or 1.0 M salt concentration, with or without the anion-receptor additive. Furthermore, previous results on three-electrode cells indicate that much of the change in series resistance occurs on the cathode side of the cell under these conditions. Even though the series resistance, reflected in the $x$-axis intercept at high frequencies, does not change, the low-frequency impedance is significantly reduced after discharge. This may be due to inadequate wetting of the interface before discharge (an effect that would be related to electrolyte viscosity) or could be due to the insulating nature of a native film that forms on the cathode before discharge.

The fact that a room-temperature predischarge is not required using the lower salt content electrolyte blend can be attributed to one of several possible mechanisms. In the first, it is assumed that some portion of the electrolyte salt reacts with the cathode material upon contact to form interfacial film that impedes the cathodic reaction in some way, particularly at discharge commencement. Lowering the salt content may result in a less robust cathode surface film, because a lower salt concentration lowers the chemical driving force responsible for the formation of any interfacial layer between a CF surface and the Li-ion-containing electrolyte. A thinner cathode surface film may subsequently reduce or negate the need for a predischarge step. It is also possible that lowering the salt content results in an electrolyte with a more favorable viscosity at $-40^\circ{\text{C}}$, as has been shown elsewhere. The lowered viscosity allows for a more uniform wetting of the cathode surface as well as for a more robust discharge current without polarization. It is not known if either (or a combination) of these mechanisms are responsible for the observed effects.

The fact that the addition of an anion receptor, tris(2,2,2-trifluoroethyl borate), known to dissolve LiF, results in a further performance enhancement is consistent with the idea that solvating a surface LiF film on the cathode enhances performance. In intermediate cases (i.e., C/10 or higher rates, or around 50 $\mu$m in thickness), a substantial voltage delay was observed for cells without any anion receptor, such as that for the 57 $\mu$m thick CF$_{0.65}$ cathode discharged at a C/5 rate at $-40^\circ{\text{C}}$ with the anion-receptor additive. Figure 5 contains plots of Li–CF$_{0.65}$ cells made using the TTFEB anion receptor in 0.5 M LiBF$_4$, 82 PC/DME electrolyte and discharged at progressively lower temperatures at a C/5 rate. Even at $-60^\circ{\text{C}}$, smooth discharges were observed and a specific capacity of nearly 275 mAh/g was obtained. In all cases, those cells made with the anion-receptor additive did not exhibit any noticeable voltage delay effects, even without the execution of a room-temperature predischarge step. There was, instead, a characteristic positive voltage excursion upon discharge.

Discussion

A decrease in the electrolyte salt content from 1 to 0.5 M in an 80:20 v/v % DME/PC solution has further enhanced the low-temperature performance of the LiCF$_x$ electrochemical couple compared to previously published results. This improvement can be attributed to one of several mechanisms, including enhanced low-temperature electrolyte conductivity, an improvement in the low-temperature electrolyte viscosity, or a relative decrease in surface precipitation on the active cathode material surfaces when the cells are fabricated. There is not as yet conclusive proof as to which of these mechanisms (if any) are at work, and this effect bears further examination. The impedance spectroscopy data indicate, however, that there is not a substantial difference between the electrode impedance as a function of salt content, which in turn indicates that the enhancement mechanism is not directly related to the ionic losses associated with an electrode surface layer. The real impedance axis intercept is under 20 $\Omega$ for all cells and does not change significantly after discharge, showing that the bulk electrolyte has similar conductivity at $-40^\circ{\text{C}}$ for the three different blends examined. The
Conclusion

The results are consistent with previously published suggestions that the nanoscale intermixing of pristine graphitic domains and partially fluorinated domains observed in SFCF \(_x\) materials greatly enhance the specific capacity of these materials at low temperatures at aggressive rates.\(^2\) Electrolyte screening identified that blends consisting of 20:80 v/v \% PC/DME with 0.5 M LiBF\(_4\) offered superior low-temperature performance compared to the baseline formulations, based on 1 M LiBF\(_4\) in either 50:50 or 20:80 v/v \% PC/DME. This may be attributed to enhanced low-temperature electrolyte viscosity and/or a diminished tendency to form a resistive native cathode/electrolyte SEI. Three variations of SFCF \(_x\) cathode materials were inserted into similar \(110 \mu\m\) thick composite electrode structures and tested at −40°C using several different electrolyte blends. The CF\(_{0.65}\) and CF\(_{0.82}\)-based cells could deliver well over 600 mAh/g above 2 V under a C/5 discharge rate at −40°C with the proper electrolyte blend. To further increase rate capability and/or functional cathode thickness, an anion-receptor electrolyte additive, TTFEB, was evaluated and proved to be effective. With this additive, composite cathode structures 115 \(\mu\m\) thick yielded over 500 mAh/g at a C/5 discharge rate at −40°C. These results indicate that the CF/electrolyte interfacial area, the viscosity of the electrolyte, and the nature of any surface film that may form on these active areas are critical to low-temperature performance. The modifications implemented resulted in a greatly enhanced low-temperature performance for this useful electrochemical couple and have enabled cells that are functional to temperatures −60°C and possibly colder.

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References


Figure 6. (Color online) Capacity yielded at −40°C from SFCF \(_x\) test cells based on either graphitic (GII) or MWNT (GIII) precursor material. A C/10 discharge was used in all cases, and all cells were approximately 40 \(\mu\m\) in thickness.