



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/10 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 or 0.5 M LiBF₄. 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 graphitic 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.
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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.¹ 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)_n 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,² where it was indicated that the subfluorinated CF_x materials did exhibit superior low-temperature performance at -40°C compared to baseline CF₁, though at current levels not exceeding a C/20 rate. Two electrolyte blends were compared: 1 M LiBF₄ 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.² 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_{0.55}-containing electrode.²

A representative SFCF_x electrode composition and thickness, CF_{0.65} 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 (TEE) 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 I. Electrolyte solvent/salt blends initially tested for low-temperature efficacy in the Li/CF_x test cells. The performance of 1 M LiBF₄ solvated in 50:50 v/v % PC/DME at low temperatures is published elsewhere.²

| Solvent (v/v %) | Salt |
|--------------------------------|-------------------------|
| PC/DME (2:8) | 1 M LiBF ₄ |
| PC/TEE/DME (2:2:6) | 1 M LiBF ₄ |
| PC/DME (2:8) | 0.5 M LiBF ₄ |
| PC/TFPC/DME (15:5:80) | 1 M LiBF ₄ |
| VC (1.5) added to DME/PC (2:8) | 1 M LiBF ₄ |

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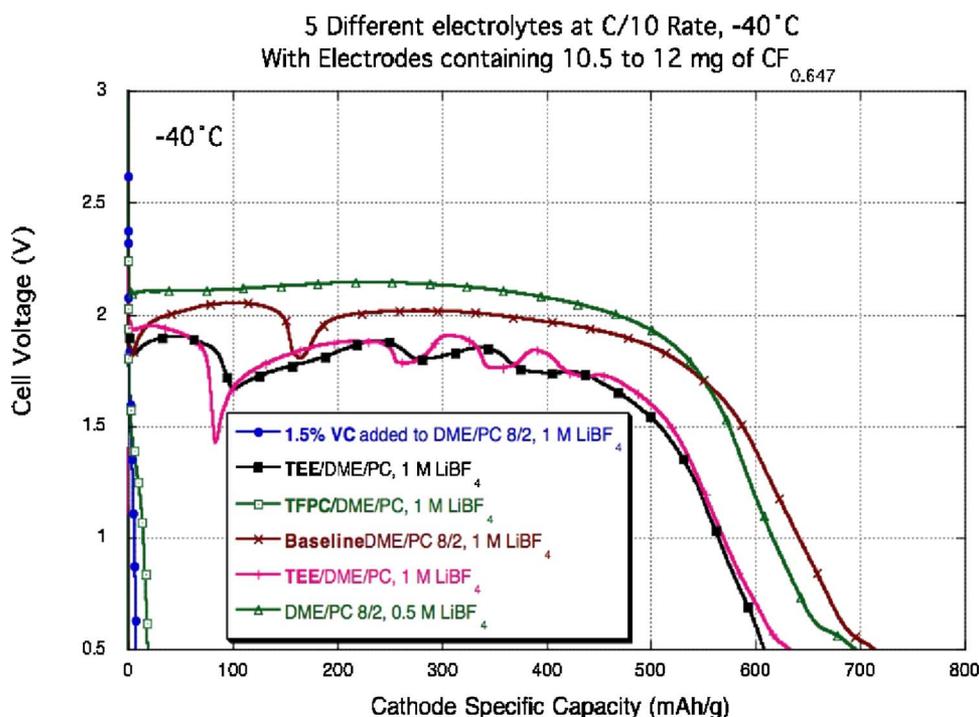


Figure 1. (Color online) Discharge data from $\text{Li}-\text{CF}_{0.65}$ test cells at -40°C at a C/10 rate. All electrodes were $40 \pm 5 \mu\text{m}$ in thickness. Five different electrolytes are compared here. The two cells that offered very little capacity at this discharge rate were then subsequently discharged at a C/40 rate and yielded full capacity (500 mAh/g above 1.5 V).

impart 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_x 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 SFCF_x -based, and the last was the $\text{CF}_{1.08}$ -based standard. The SFCF_x fabrication process is described elsewhere.³ The $\text{CF}_{0.65}$ electrodes used partially fluorinated Madagascar graphite precursor, while the other two SFCF_x variations contained $\text{CF}_{0.59}$ or $\text{CF}_{0.82}$ material made using multiwall carbon nanotube material precursor materials supplied by MER Corporation (Tucson, AZ). Characterization data indicated that all of the SF CF_x materials were comprised of pristine unfluorinated graphite domains mixed intimately with nanodispersed near-fully fluorinated graphitic regions and are consistent with data reported previously.^{1,3} 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 several of the 0.5 M LiBF_4 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 battery electrolytes, mainly to enhance the solubility of lithium salts.⁴⁻⁶ The nominal TTFEB concentration in the electrolyte solution was 1.5:98 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.² 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 $\text{CF}_{0.64}$ SFCF_x 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 LiBF_4 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 $\text{Li}/\text{CF}_{0.64}$ 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 CF_x cathodes (of similar mass/thickness) as discharged at the C/5 rate using the 0.5 M LiBF_4 solvated in 8:2 v/v % DME/PC electrolyte. The thickness of the $\text{CF}_{1.08}$ -based cathode was $35 \mu\text{m}$, while the thickness of the SFCF_x cathodes was

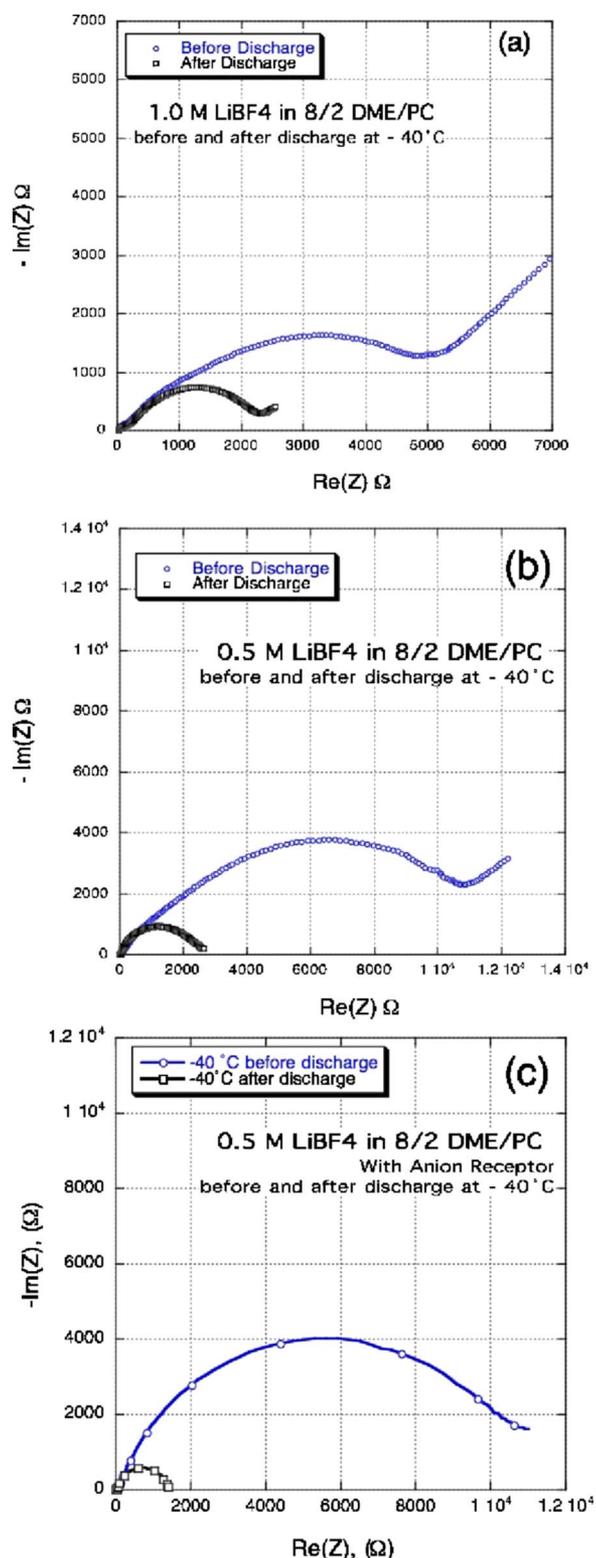


Figure 2. (Color online) EIS data collected from Li-CF_{0.65} cells before and after full discharge at -40°C with 8:2 v/v % DME/PC electrolyte solvent using (a) 1 M LiBF₄, (b) 0.5 M LiBF₄, and (c) 0.5 M LiBF₄ with anion receptor. The frequency range was 100,000 Hz to 50 mHz, while the cells were held at open-circuit potentials as measured after 30 min of equilibration.

40–60 μm. The delivered capacities for the SFCF_x cathodes were as much as 300% greater with the subfluorinated cathodes than that of

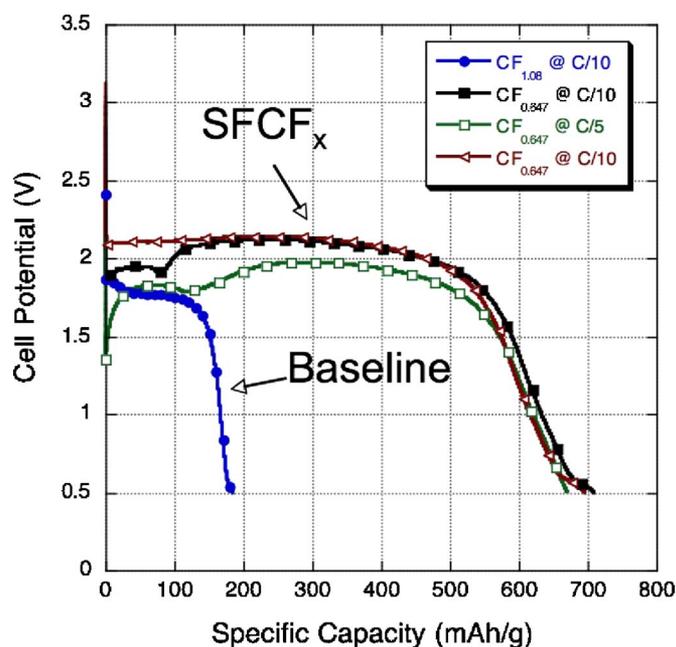


Figure 3. (Color online) Discharge data from various Li-CF_x test cells at -40°C at a C/5 rate. All cells were 40 ± 5 μm in thickness. The cells containing SFCF_x yielded significantly more capacity at higher discharge potentials than that for the cell containing commercially available CF_{1.08}. The highest capacity material was CF_{0.82} (multiwalled nanotube, MWNT, precursor), which delivered over 650 mAh/g above 1.5 V. The open squares are data from the thickest of the SFCF_x electrodes (57 μm).

the CF_{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_x chemistry and was therefore examined here under low-temperature conditions.^{7,8} Figure 4 shows the behavior of CF_{0.65} composite cathodes with thicknesses varying from 4 to 118 μm at a C/5 discharge

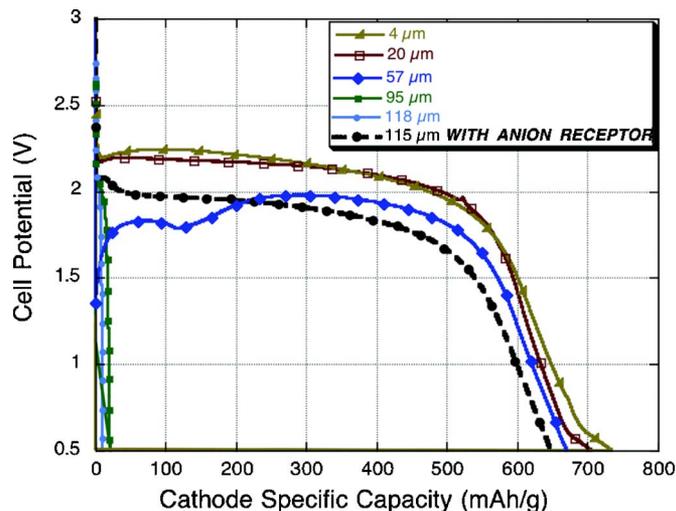


Figure 4. (Color online) Discharge behavior at a C/5 rate, -40°C as a function of composite cathode thickness, for CF_{0.65}-based test cells. The 0.5 M LiBF₄ with 8:2 v/v % DME/PC electrolyte was used in all cases, and the TTFEB anion acceptor was added in the thick electrode case (115 μm thick).

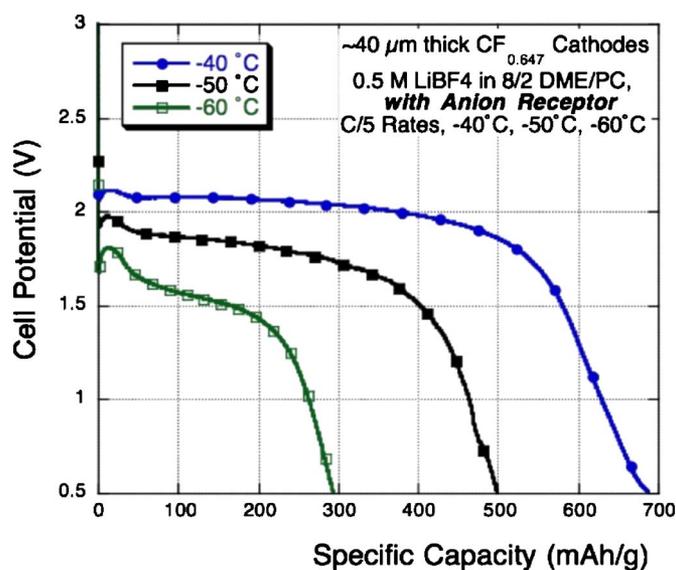


Figure 5. (Color online) High-rate, low-temperature performance of $\text{LiCF}_{0.65}$ cells with anion receptor added to the 0.5 M LiBF_4 with 8:2 v/v % DME/PC electrolyte. At -60°C , over 250 mAh/g was delivered at a C/5 rate. The composite cathode structures were approximately $40\ \mu\text{m}$ thick for these tests.

rate. The cells delivered nearly full capacity, with some polarization and voltage delay, up to a thickness of at least $57\ \mu\text{m}$. Cathodes as thick as $95\ \mu\text{m}$ or higher were severely polarized upon discharge under these conditions but were able to deliver full capacity at reduced discharge rates, for example at a C/10 rate for the $95\ \mu\text{m}$ cathode and at a C/40 rate for the $118\ \mu\text{m}$ thick cathode (these results are not shown).

The use of the TTFEB anion-receptor additive resulted in even thicker composite electrodes that could be made functional at these temperatures. Figure 4 also contains the results from a $115\ \mu\text{m}$ thick $\text{CF}_{0.65}$ cathode discharged at a C/5 rate at -40°C with the anion-receptor additive. Figure 5 contains plots of $\text{Li}-\text{CF}_{0.65}$ cells made using the TTFEB anion receptor in 0.5 M LiBF_4 , 8:2 PC/DME electrolyte and discharged at progressively lower temperatures at a C/5 rate. Even at -60°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 predischage 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 Li/CF_x electrochemical couple compared to previously published results. This improvement can be attributed to one of several mechanisms, including enhanced low-temperature electrolyte conductivity,⁹ 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 ohmic 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°C for the three different blends examined. 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.² 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 predischage 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 predischage step. It is also possible that lowering the salt content results in an electrolyte with a more favorable viscosity at -40°C , as has been shown elsewhere.⁹ 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 $50\ \mu\text{m}$ in thickness), a substantial voltage delay was observed for cells without any anion receptor, such as that for the $57\ \mu\text{m}$ thick $\text{CF}_{0.65}$ cathode discharged at a C/5 rate at -40°C (Fig. 4). In this case, the voltage delay lasted about half of the discharge, though eventually the cell became fully functional, albeit slightly polarized. This reproducible voltage delay behavior was not observed in any of the anion-receptor-containing cells, even when discharged at a C/2.5 rate or at temperatures colder than -40°C . These observations (when combined with the EIS results that indicate large fluctuations of the cathode impedance before and after discharge) are consistent with the idea that the voltage delay observed in the $\text{Li}-\text{CF}_x$ couple is related to a cathode surface film that is only partially affected when using the predischage step. The anion receptor apparently mitigates all of the negative affects of this layer and may do so by dissolving some of the interfacial layer assumed to primarily be comprised of LiF, thereby allowing high-rate discharge at relatively cold temperatures without catastrophic cell polarization.

The type of graphitic precursor used did not have a significant impact on test cell performance at low temperatures. The data in Fig. 6 indicate a roughly linear relationship between degree of fluorination and capacity, and there did not appear to be a strong correlation showing that either the graphitic or the MWNT materials offered more favorable low-temperature performance. This result is not entirely unexpected, as X-ray diffraction and electron microscopy results indicate a similar microstructure in these two types of subfluorinated carbons.³ The degree of fluorination was the strongest indicator of energy density, even at low temperatures. Because the baseline $\text{CF}_{1.08}$ delivered much lower capacity (less than 300 mAh/g) under these same conditions, there must be a point between $x = 0.82$ and 1.08 where the low-temperature efficacy of this cathode is substantially reduced, even when implemented with the better-performing electrolyte blend and anion receptor identified in this work.

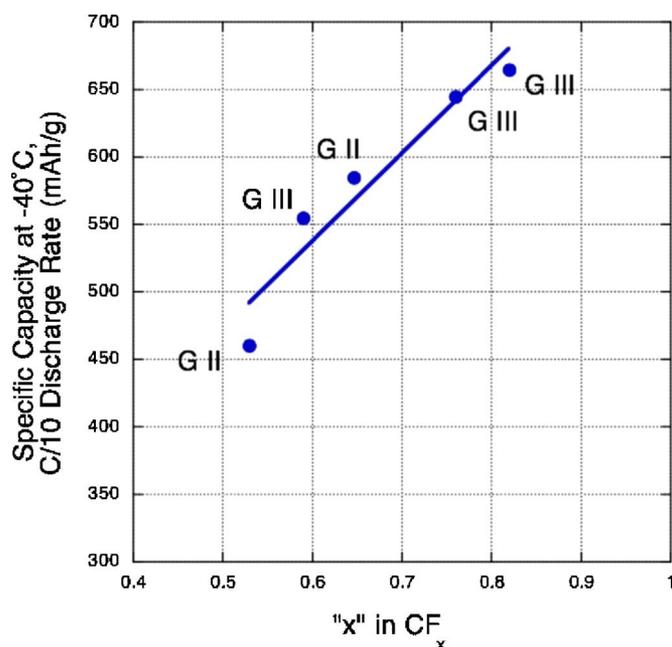


Figure 6. (Color online) Capacity yielded at -40°C from SFCF_x test cells based on either graphitic (GII) or MWNT (GIII) precursor material. A C/10 discharge was used in all cases, and all cells were approximately $40\ \mu\text{m}$ in thickness.

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 $\sim 40\ \mu\text{m}$ thick composite electrode structures and tested at -40°C using several different electrolyte blends. The $\text{CF}_{0.65}$ - and $\text{CF}_{0.82}$ -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 $115\ \mu\text{m}$ 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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