

Short communication

Performance of carbon-fiber-containing LiFePO₄ cathodes for high-power applications

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Abstract

This paper describes the fabrication and testing of LiFePO₄ cathodes for hybrid vehicle applications. The cathodes contained combinations of three different carbon conductivity additives: vapor-grown carbon fibers (CF), carbon black (CB) and graphite (GR). Cells of different carbon composition and active-material loading were tested with 10 s charge and discharge pulses and found under certain conditions to meet the HEV power goals for the U.S. Advanced Battery Consortium. With all other factors held constant, cathodes with a mixture of CF+CB were found to have the best power-performance, followed by cells containing CF only and then by CB+GR. Thus, the use of carbon fibers as conductive additive was found to improve the power performance of cells compared to the baseline (CB+GR). The enhanced electrode performance due to the fibers also allows an increase in energy density while still meeting power goals. The best specific-power performance for each of the compositions investigated was found to occur around an active material loading of 1 mAh cm⁻². About one-third of the available energy was lost to irreversible processes when cells were pulse-charged or discharged at the maximum rate allowed by voltage-cutoff constraints.

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1. Introduction

Lithium-ion batteries are being considered for application in hybrid electric vehicles (HEVs) and electric vehicles (EVs) because these batteries have relatively high cell potentials, which in turn permits high energy and power densities [1–3]. According to the goals [4] set by the United States Advanced Battery Consortium (USABC), rechargeable lithium-ion batteries for vehicles need both high capacity and power. This paper describes the development of a cathode with carbon fiber as a conductive additive to enhance power performance for such applications.

Among several materials under development for use as cathodes in lithium-ion batteries, LiFePO₄ appears to be a promising candidate because of its high theoretical capacity (170 mAh g⁻¹), low cost, excellent cycling stability, low toxicity, and environmentally benign nature [5–10]. As an alternative to presently used LiCoO₂, other transition metal oxides such

as LiNiO₂ and LiMn₂O₄ have also received attention, but are generally more costly than LiFePO₄.

Two of the challenges of using LiFePO₄ are its poor electronic conductivity (around 10⁻⁹ S cm⁻¹) and low Li diffusivity (around 8 × 10⁻¹⁸ m² s⁻¹) [9,11,12]. These difficulties are typically overcome by using smaller particle sizes and sufficient amounts of conductivity additive. In fact, in the fabrication of LiFePO₄, nanometer-scale particles of active material are naturally embedded in a porous matrix of residual carbon to form larger-particle aggregates [13]. Nevertheless, there is still need for significant added carbon in the composite cathode to achieve desired electrical performance.

Our objective here is to examine the influence of carbon fibers on the electrical connections between active material and current collector, leading to improved power performance. Mandal et al. [14] showed that both the electronic conductivity and the discharge capacity of LiMn₂O₄ cathodes depended on conductive-additive content. Sastry and coworkers [15,16] have shown theoretically that the shape of the conductive material has a substantial effect on the conductivity of the network formed. In particular, an increase in the aspect ratio of the filler improves the conductivity of the network for a given volume fraction of

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additive. Zaghbi and coworkers found that good cyclability can be obtained using vapor-grown carbon fibers in carbon-based anodes [17].

It is important to realize that there is not only a need for a conductive network to facilitate electron transfer, but also good connections of the active-material particles to that network. Recent work in our group showed that the use carbon nanotubes (CNTs) as the conductive filler in thick-film cathodes significantly reduced the measured resistance of aluminum-doped spinel cathodes, increased active-material accessibility, and improved cycling and power performance of the electrode [18]. Unfortunately, CNTs remain quite expensive for EV and HEV applications. As an alternative, in the present work we used less-expensive vapor-grown carbon fibers with an aspect ratio of around 400 and a length close to the thickness of the electrode (around 70 μm).

In order to evaluate the effect of the fiber additive, we performed a series of experiments in which we constructed cathodes with different types of conductive additives, including mixtures. In each of the cells we kept the total mass fraction of carbon in the composite cathode constant at 8 wt.%. Previous work showed little change in internal electronic resistance for cathodes with carbon content above 8 wt.% [18]. The results are compared to the USABC goals for HEV power pulses [4]. We also show that the irreversible losses during each pulse are about one-third of total available energy, at the maximum allowable pulse-discharge rates for all the cells tested.

2. Experimental

2.1. Cell fabrication

The active material for the cathode was lithium iron phosphate (LiFePO_4) supplied by Hydro Québec, Montréal, Canada. Polyvinylidene fluoride copolymer (PVdF, 741 Kynar Corp.) was used as the binder for all of the cathodes fabricated in this study. Three different carbon-based conductivity additives were used: heat-treated vapor-grown carbon fibers (diameter: 100–200 nm, length: 30–100 μm , PR-19, Pyrograf Products Inc.), carbon black (diameter: 20–30 nm, XC-72R, Cabot Carbon Ltd.) and graphite (diameter: 5.5–7.5 μm , SFG-6, TIMCAL Group). For comparison purposes different combinations of these three additives were used as discussed below.

Each cathode used 84% active material, 8% PVdF, and 8% conductivity additive, all on a dry-weight basis. The cathodes were fabricated using the following steps. First, the PVdF binder was dissolved in *N*-methylpyrrolidene (NMP) with mild heating. For a particular composition, the respective amounts of carbon fiber (CF), carbon black (CB), graphite (GR) and lithium iron phosphate were dry-mixed by hand followed by mixing with an ultrasonic homogenizer. This mixture was then added to the PVdF-NMP solution and the resulting slurry was also stirred manually and by ultrasonic homogenizer. The composite slurry was spread uniformly on carbon-coated-aluminum current collector (Hydro Québec) using a doctor blade (Byk-Gardner, U.S.A.) and was dried overnight at 100 °C under vacuum (15 in Hg).

Individual cathodes were cut from dried sheet using a template of 4 cm^2 area and were then compressed to the desired thickness using a calendaring machine. Based on a mass balance and thickness measurements with a micrometer we determined the porosities before and after calendaring. Fiber-containing cathodes had their porosity reduced from about 80 to 65%. Baseline (non-fiber) cathodes had their porosity reduced from about 75 to 50%. We found that reducing the porosity of fiber-containing cathodes below about 65% led to poor cathode performance and the appearance of shiny compacted regions on the surface of the composite. Likewise, reduction of baseline-cathode porosity below 50% led to poor performance. For the cathodes fabricated as described above, the typical thickness for a fiber-containing cathode with loading 1 mAh cm^{-2} was 73 μm at 65% porosity.

Following fabrication of the composite cathodes, the batteries were assembled as follows. Each cathode was transferred to an Ar-atmosphere glove box (moisture content 0.9 ppm and oxygen content less than 0.25 ppm, VAC, Hawthorne, CA) where it was assembled into a cell with a Li-metal anode and three 25- μm -thick polypropylene separator layers (Celgard 2500, Celgard LLC, Charlotte, NC) for a total separator thickness of 75 μm . Three separator layers were used to discourage shorting of the cell by dendrite formation on the Li metal. A metallized polymer film (Class PPD Shield Pack, Inc., Los Angeles, CA) was used to package the cells. One molar LiPF_6 /ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte (LithDyne Elyte, LithChem International, Anaheim, CA) was added to the packages before sealing with an electric heat sealer (Impulse Sealer Tish 200, Electronic Heating Equipment Co.) before removal from glove box. External electric connections were formed with metal tabs protruding from the sealed enclosures.

2.2. Testing protocol

All cells were tested at 298 K using an Arbin 2048 battery cyclor controlled with Mits' 97 software (Arbin, College Station, TX). The testing protocol was as follows. Five formation cycles were used for all cells. For each of the first four cycles, the cells were charged at a $C/2$ rate to 4.0 V, followed by trickle charging at 4.0 V until current dropped below $C/50$. Following a 1-h rest, the cells were discharged at a $C/2$ rate to 2.2 V. At this stage the C -rate was based on the theoretical capacity. For the fifth cycle, the cells were charged in the same manner; however, the discharge rate was $C/10$. Typical open-circuit voltage prior to this discharge was 3.4 V. The $C/10$ discharge was used to estimate the effective capacity of each cell and all subsequent cycles are based on this value. We note that the faster $C/2$ formation cycles yielded substantially the same discharge-capacity results as did slower $C/10$ charging and discharging rates for all five cycles, and so the faster charging scheme was used in this work. The discharge end-point voltage of 2.2 V was selected to be 55% of the maximum charge voltage of 4.0 V, according to the protocol of the U.S. Department of Energy BATT program.

Following the formation cycles, a series of EV and HEV tests was performed. For the EV tests, each cell was charged at $C/2$ to 4.0 V followed by trickle charging and 1-h rest, and then fully

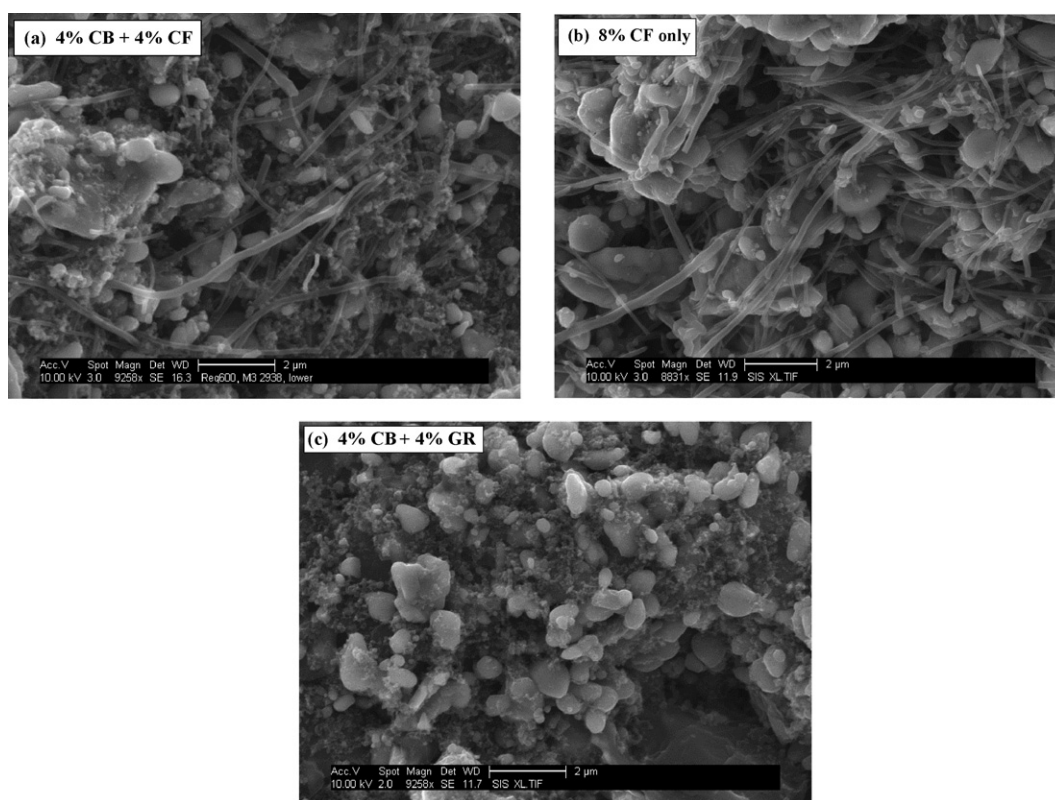


Fig. 1. SEM images of cathodes with differing conductive additives: (a) 4% carbon black + 4% carbon fiber, (b) 8% carbon fiber, and (c) 4% carbon black + 4% graphite.

discharged at rates of $C/2$, $1C$, $2C$, $5C$, $10C$, $15C$, and $20C$, respectively, on consecutive cycles. Following these cycles, the cell was discharged to 50% DOD at a $C/5$ rate and rested for 1 h. HEV pulse tests were then performed. A sequence of 10 s discharge and charge pulses was performed at different C -rates (5–25 C , in 5 C increments); each discharge pulse was followed by a charge pulse (to restore the state of charge to 50%). A 10-min rest period was used between each type of pulse.

3. Results and discussion

3.1. Cathodes with different conductive additive

Cathodes with three different carbon compositions were tested: 4% CB + 4% CF, 8% CF, and 4% CB + 4% GR. The cathodes not containing carbon fibers were intended as a control or baseline from which to compare the influence of the fibers. Fig. 1 shows SEM images of the cathode surface with these three different compositions. The pictures show the cathodes to be well-mixed on the microscale. The cathodes containing carbon fibers (CB + CF and CF only) show the fibers quite clearly. The fibers appear to be in good contact with other particles. The fibers are believed to enhance the electrical conduction and contact throughout the cathode and also provide mechanical strength to the solid matrix.

Following formation cycles, the cathodes described in this study achieved $C/10$ discharge capacities (discharging from 3.4 to 2.2 V versus lithium) that were around 85–90% of their respective theoretical capacities.

3.2. Determination of maximum C -rate and specific power

As described in the experimental section, we conducted a series of 10-s pulse tests at different C -rates on each cell in order to assess HEV power performance. Our objective was to calculate the maximum power obtainable during the 10-s pulse within the constraint that the voltage must remain within the specified window of 2.2–4.0 V. We define pulse power as the total energy of the pulse divided by the pulse time (10 s). Fig. 2 illustrates the process we used to calculate the maximum allowable pulse

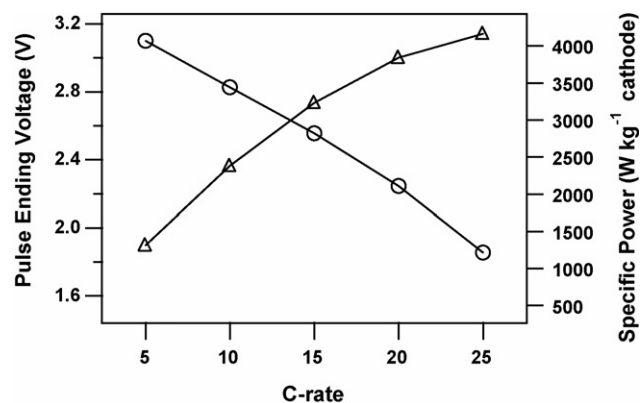


Fig. 2. Representative results from a series of 10-s pulse-discharge tests on a single cell at 50% DOD. Voltage at end of each pulse (circles) is compared to resulting specific power (triangles) as a function of pulse C -rate. Maximum pulse power for the cell is obtained for the C -rate that corresponds to 2.2 V ending voltage.

power, in this case for a representative cell in discharge. The maximum power occurs at the maximum-magnitude charge or discharge rate that does not cause the voltage to go outside the allowable voltage window during the pulse. In the case of Fig. 2, the maximum discharge rate that leads to 2.2 V at the end of the pulse is around 20.6C, obtained by interpolation. The specific power corresponding to that maximum rate is 3882 W kg⁻¹ cathode, again obtained by interpolation. All the “max power” calculations in subsequent figures were determined in this manner.

Fig. 2 and subsequent figures give specific power in terms of W kg⁻¹ of cathode. The mass of cathode includes the dry composite material and the current collector (both have superficial area 4 cm²) and excludes metal connection tabs to the current collector. For comparison purposes, the USABC power goals shown on the plot are converted to the same specific-power basis using the simple assumption that the total battery mass for hypothetical large-size commercial cells (including cathode, anode, separator, electrolyte, and packaging material) is exactly three times the cathode-only mass. This estimate is not intended to be definitive, but instead to suggest how our small laboratory-scale cells perform relative to the goals established for vehicle-size batteries.

3.3. Power performance of composite cathodes

Fig. 3 shows the pulse-discharge power performance of cathodes with different compositions of carbon additives. Cathodes with three different combinations of carbon additives (CF + CB, CF only and CB + GR) were tested. The ordinate represents pulse specific power. The abscissa represents active material loading (mAh cm⁻²) on the cathode. The USABC power goals for HEV are represented by the horizontal line. The maximum pulse-discharge specific power occurs at loading values around 1 mAh cm⁻² for all three compositions tested. The cathode containing both fiber and carbon black appears to have the best performance, followed by the carbon-fiber-only cathode and the baseline cathode. The scatter in the power data is most likely due to slight cell-to-cell fabrication variations.

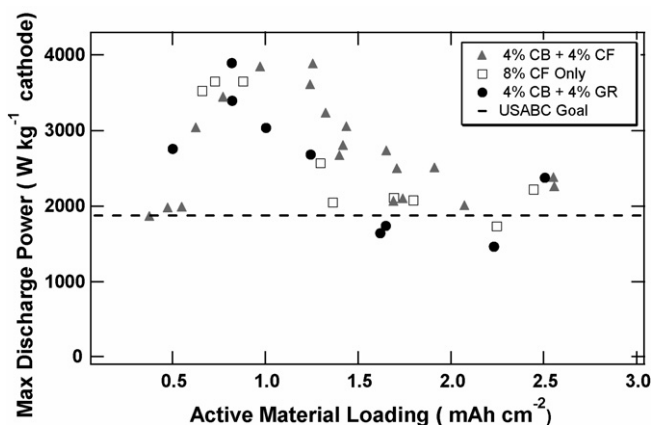


Fig. 3. Maximum-specific power for 10-s pulse discharge of cathodes with different conductive carbon additives and at 50% DOD. Carbon-additive amounts are given in the key. The USABC power goal for HEV applications is represented by the horizontal line.

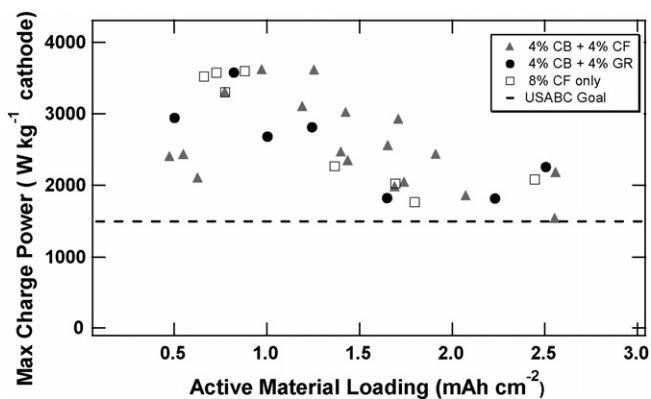


Fig. 4. Maximum-specific power for 10-s pulse charge of cathodes with different conductive carbon additives and at 50% DOD. Carbon-additive amounts are given in the key. The USABC power goal for HEV applications is represented by the horizontal line.

Fig. 4 shows pulse-charge power performance for cathodes with different compositions of carbon additives. Similar to Fig. 3, it shows that the optimum pulse-charge specific power occurs for loadings around 1 mAh cm⁻² for all three compositions tested. Again, the cathode with carbon fiber and carbon black showed the best performance. All three cathode compositions appear to be capable of satisfying the regenerative pulse-charge power goals set by USABC.

Figs. 3 and 4 both show that the specific-power performance declines for active-material loading above about 1 mAh cm⁻². On the other hand, the specific energy of the cathodes (not shown) increases with active material loading. This is because the fraction of cathode mass devoted to current collector decreases with higher loading. For instance, for our cathodes at 1 mAh cm⁻² the current collector itself has a mass equal to 46% of the composite mass (active material, carbon, and binder), with both based on the same superficial area. Therefore, the amount of active material loading controls the trade-off between specific energy and specific power that can be extracted from the cathode. Cathodes with greater specific power at a given loading can therefore be operated at correspondingly greater overall energy density and still satisfy minimum pulse-power goals. Thus, the marginally higher specific power of the CF + CB cathodes can be used to effect increased specific energy if desired for specific applications.

The respective active-material-loading ranges for the best charge and discharge power performance coincide. This observation is consistent with the expectation that, neglecting phase-change hysteresis in the active material, the internal resistance in the cathode affects charging and discharging similarly. Hence, the optimization of pulse discharge power automatically helps to attain the optimization of pulse charge power.

3.4. Irreversible power loss

Fig. 5 shows the variation of discharge-pulse efficiency with active material loading. Here, pulse efficiency is defined as the ratio of the actual power obtained to the power that would be obtained if there were no irreversible losses during the 10-s

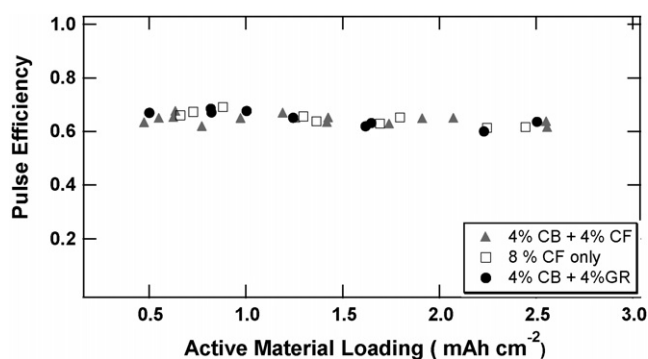


Fig. 5. Effects of loading and carbon-additive composition on discharge-pulse efficiency. Pulse efficiency is defined as the ratio of the actual power obtained to the power that would be obtained if there were no irreversible losses during the pulse.

pulse, at the same discharge rate. Interestingly, the efficiency of all the cells tested lies in a narrow band between 60 and 70%. In other words, when operated at maximum allowable power about one-third of the available energy or power is lost to irreversible processes independent of the type of conductive additive, for the cells investigated.

4. Summary and analysis

4.1. Optimal power

Cathodes with varying composition of the carbon additives (CB+CF, CF only and CB+GR) were fabricated and tested. The cathodes containing CF+CB were observed to have the best power performance, followed by cathodes containing CF only and CB+GR. The best pulse-power performance for each composition tested was found to be at active material loading of around 1 mAh cm^{-2} . Loading values greater than the optimum point lead to a trade-off between specific power and specific energy. The use of carbon fibers permits increased energy density while satisfying the HEV power goals established by USABC. All cells investigated were found to have 30–40% irreversible power loss at the maximum allowable pulse current rates, independent of the composition of cathodes.

In this work we chose not to use area-specific impedance (ASI) as a metric for power performance. ASI is the voltage change during a pulse or transient experiment (ΔV), divided by the impressed current density (i). The current density for a given cell is typically some prescribed multiple of the C -rate. The difficulty with this is that the numerator (ΔV) and denominator (i) scale differently with electrode loading. The net result for the cells here is that ASI decreases with increasing loading throughout the studied range, and thus has a presumed minimum at a loading value far in excess of the point for maximum power density. While ASI as commonly defined does allow one to compare different cathode chemistries or compositions at the same approximate loading, it is less useful in determining an optimal battery loading for a given chemistry or composition.

It should be noted that our maximum pulse-power results depend on the voltage constraints placed on the cell. At 50%

depth of discharge, the open-circuit potential (versus Li) of the cathode is 3.42 V. Potential was allowed to go down to 2.2 V for the 10-s discharge pulses, and up to 4.0 V for the 10-s charge pulses. The respective maximum rates were around 20C for discharge and 10C for charge, for cells at 1 mAh cm^{-2} . The use of a larger voltage window would of course permit greater rates and hence greater power densities.

The optimum cathode loading for power performance is a result of the fact that specific power is normalized by the mass of the cathode. At lower loadings, a greater proportion of cathode mass is devoted to the current collector, leading to decreased specific energy and power. On the other hand, transport losses (both ionic and electronic resistances) increase with cathode thickness. The competition between these two effects leads to an optimum loading point.

The focus of this work was on the performance limitations specific to the cathode and so we chose not to use a composite anode in order to better facilitate analysis. We recognize the cycle-life and safety limitations of Li-metal anode, although it is important to note that people are working on the problems inherent in Li-metal anodes [18] and so metal could one day be commercially viable.

4.2. The use of carbon fibers

Why do the fiber-containing cathodes perform better than the baseline composition, for the same total fraction of carbon additives? As already noted in the introduction, it is known that high-aspect-ratio additives are more efficient at increasing overall electronic conductivity for a given volume fraction and intrinsic material conductivity. By nature, the conductivity of networks of low-aspect-ratio materials such as carbon black and graphite are dominated by the degree of inter-particle resistance, which in turn depends on the degree of inter-particle contact. This is the reason that carbon-black networks have an effective conductivity that is a strong function of mechanical pressure [19]. On the other hand, high-aspect-ratio materials such as fibers are better able to maintain conductivity with less sensitivity to inter-particle contact. By analogy, fibers act as highways for electrons.

The conventional thinking with respect to the use of graphite and carbon black follows similar lines. The intrinsic electrical conductivity of graphite is more than that of carbon black because of its ordered structure—it acts as a comparatively good highway for the electrical network. However, carbon black establishes better electrical contacts between larger particles because of its smaller size and greater surface area. A combination of both graphite and carbon black allows for a highly conductive network that also connects to the active material particles. Like graphite, the heat-treated carbon fibers we used have good electrical conductivity, but additionally gain the benefit of high aspect ratio. Therefore, the combination of fibers and carbon black provides a highly conductive network that connects well to the active material particles and the current collector.

Even though the carbon fibers were found to enhance the power performance of the cells tested, it is important to recognize the difficulties related to their use. Using our casting procedure,

we found it difficult to reliably fabricate carbon-fiber-containing cathodes with thickness below 60 μm (thickness after drying and calendaring; corresponds to loading around 0.8 mAh cm^{-2}). We performed preliminary experiments with two cathodes where the fibers were manually chopped using a razor blade on a glass surface. The chopping did not significantly change the cell performance when compared to unchopped fibers. Shorter fibers could lead to improved processibility, however, and deserve further investigation.

The vapor-grown carbon fibers we used are significantly cheaper than carbon nanotubes, but they are nevertheless costlier than other carbon additives considered here. It may be the case that a significantly smaller fraction of fibers in the overall amount of carbon additive will nevertheless generate most of the observed benefit. Or perhaps the optimal composition will require all three carbon additives considered here. With a reduction in the fraction of carbon fibers used, the cost of the fibers becomes less of an issue. We are continuing investigation along these lines.

In addition, if the cycle life of carbon-fiber containing cells is improved then this would be an advantage that would offset increased cost. A potential advantage of using carbon fiber is this material's ability to impart mechanical strength and stability to the solid matrix in the cathode. Lack of mechanical stability has been associated with lithium-battery failure mechanisms by Kostecki and coworkers [20]. They found evidence of carbon-particle retreat and rearrangement in the cathode during extending battery cycling. Continued investigation in our group is underway to assess the long-term cycling performance of the cell compositions studied here.

Acknowledgments

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