



Short communication

Enhancement of discharge performance of Li/CF_x cell by thermal treatment of CF_x cathode material

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ABSTRACT

In this work we demonstrate that the thermal treatment of CF_x cathode material just below the decomposition temperature can enhance discharge performance of Li/CF_x cells. The performance enhancement becomes more effective when heating a mixture of CF_x and citric acid (CA) since CA serves as an extra carbon source. Discharge experiments show that the thermal treatment not only reduces initial voltage delay, but also raises discharge voltage. Whereas the measurement of powder impedance indicates the thermal treatment does not increase electronic conductivity of CF_x material. Based on these facts, we propose that the thermal treatment results in a limited decomposition of CF_x, which yields a subfluorinated carbon (CF_{x-δ}), instead of a highly conductive carbon. In the case of CF_x/AC mixture, the AC provides extra carbon that reacts with F₂ and fluorocarbon radicals generated by the thermal decomposition of CF_x to form subfluorinated carbon. The process of thermal treatment is studied by thermogravimetric analysis and X-ray diffraction, and the effect of treatment conditions such as heating temperature, heating time and CF_x/CA ratio on the discharge performance of CF_x cathode is discussed. As an example, a Li/CF_x cell using CF_x treated with CA at 500 °C under nitrogen for 2 h achieved theoretical specific capacity when being discharged at C/5. Impedance analysis indicates that the enhanced performance is attributed to a significant reduction in the cell reaction resistance.

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1. Introduction

Primary Li/CF_x batteries are recently being developed as soldier portable power sources by the Army due to their high theoretical capacity in comparison to other lithium batteries such as Li/SOCl₂ and Li/MnO₂ batteries [1]. The overall discharge reaction of a Li/CF_x cell is expressed as “CF_x + xLi → C + xLiF”. According to this reaction, the specific capacity of a CF_x cathode is determined by the content of fluorine, i.e., *x* value in the formula. Theoretically, a CF_x with *x* = 1 has a specific capacity of 865 mAh g⁻¹, about twice that of SOCl₂ used in Li/SOCl₂ batteries. However, the content of fluorine in CF_x adversely affects electronic conductivity of the material [2,3]. For example, CF_x becomes an electrical isolator when the *x* value approaches to 1.0 [4]. Therefore, there is a trade-off between the specific capacity and power capability of the Li/CF_x cells. A high energy density Li/CF_x cell that requires high *x* value suffers initial voltage delay and poor rate capability. These problems are mostly related to the low electronic conductivity of CF_x cathode and to the slow kinetics of cell reaction. Especially, the slow kinetics that behaves as a significantly high cell reaction resistance in the impedance spectrum of

a Li/CF_x cell leads to another problem, i.e., huge heat generation accompanying with the discharge process, due to the effect of I²R heat [5].

Many approaches have been attempted to solve these problems. In order to improve cell power capability, Yazami et al. [6,7] developed a series of subfluorinated carbon materials with lower content of fluorine. The Li/CF_x cells using such CF_x materials demonstrated much higher power capability and better low temperature discharge performance. However, such successes were achieved at the expense of specific capacity. Both physical and chemical approaches have been reported to eliminate the initial voltage delay. The physical approaches were mainly to mix CF_x cathode with other cathode materials that have slightly higher discharge voltage than CF_x cathode, such as MnO₂ [8], MoO₃ [9], Ag₂V₄O₁₁ [10], and subfluorinated carbon [11]. In each case, the added cathode is discharged first and the CF_x cathode is followed until it passes the early capacity region that normally suffers voltage delay. The chemical approaches were mainly focused on the controlled defluorination (reduction) of CF_x materials by reacting with a reductive agent such as KI [12] and alkali metal alkyl compounds [13]. In this process, parts of fluorine on the surface of CF_x particles were removed to form subfluorinated carbon that hence offsets the initial voltage delay. The simplest approach for the elimination of initial voltage delay could be pre-discharging about 10% of cell's capacity so as to pass the initial

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voltage delay region [12]. However, this approach is costly because it wastes capacity and requires an additional pre-discharging step in the production process.

In this work we explored an alternative approach for the improvement of discharge performance of Li/CF_x cell by thermal treatment of CF_x cathode just below the decomposition temperature. This paper studies the process of thermal treatment, and discusses the relationship between treatment conditions and discharge performance of CF_x cathodes.

2. Experimental

Carbon monofluoride (CF_x, $x=0.99\text{--}1.08$, FluorStar Grade F, made from carbon fiber) was obtained from Lodestar Inc., Howell, New Jersey. Citric acid (CA, >99.5%, Fluka), propylene carbonate (PC, electrolyte grade, Ferro), 1,2-dimethoxyethane (DME, electrolyte grade, Ferro) and LiBF₄ (Stella) were used as received. A Lindberg/Blue Tubular furnace was used for thermal treatment that was conducted under nitrogen by a programmed heating schedule consisting of: (1) heating to the treatment temperature in 5 h, (2) remaining at the treatment temperature for a pre-determined period, and (3) turning off electric power for naturally cooling to room temperature. X-ray diffraction (XRD) pattern of the resulting product was recorded at 2° min⁻¹ on a Rigaku Ultima III diffractometer. Thermogravimetric analysis (TGA) was run at 5 °C min⁻¹ under nitrogen on a PerkinElmer TGA-7.

CF_x electrode was prepared by coating a slurry composed of 85% CF_x, 9% carbon black, 1% carbon fiber and 5% poly(vinylidene fluoride-co-hexafluoropropylene) (Kynar Flex™ 2801, Elf Atochem North America) in N-methylpyrrolidone solvent onto a Al foil. The coating was dried in an 80 °C-oven to evaporate solvent, and the resulting electrode film was punched into small disks with a diameter of 1.27 cm² for coin cell test. The electrode disks were further dried at 100 °C under vacuum for 8 h, and then transferred into a glove-box for cell assembly. In the glove-box Li/CF_x coin cells were assembled by using a 0.5 m LiBF₄ 1:1 (wt.) PC/DME electrolyte and a 0.4 mm thickness filtering paper as the separator. Coin cells were discharged on a Maccor Series 4000 cycler with a 1.5 V cutoff voltage and a C/5 constant current. The C-rate for each cell was respectively calculated from the weight and theoretical specific capacity of CF_x (865 mAh g⁻¹, based on $x=1$). A Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer was used for impedance measurements. A frequency range from 100 kHz to 0.01 Hz and an ac oscillation of 10 mV was used for the measurement of Li/CF_x cells, whereas a frequency range from 100 kHz to 10 Hz and an ac oscillation of 2.0 V was used for the measurement of CF_x powder samples. In order to measure the impedance of powder samples, the powder was filled into a Teflon O-ring with a 0.32 cm⁻¹ cell constant (i.e., having a 0.81 cm internal diameter and a 0.16 cm height), sandwiched between two soft Al foils, and pressed constantly for good electric contact. All electrochemical tests, including discharge and impedance, were carried out at 20 °C by using a Tenney Environmental Oven Series 942.

3. Results and discussion

3.1. Thermal treatment of CF_x alone

Fig. 1 shows TGA curves of CF_x material, which were recorded at 5 °C min⁻¹ under nitrogen atmosphere. Sample 1 (curves 1 and 1') was heated consecutively to 850 °C. It is shown that dramatic decomposition of CF_x occurs between 550 °C and 780 °C, and that in the end of experiment left was 21 wt.% of black carbon, about half of the carbon content in the pristine CF_x. This result reveals that some volatile subfluorinated carbon with small molecular weight

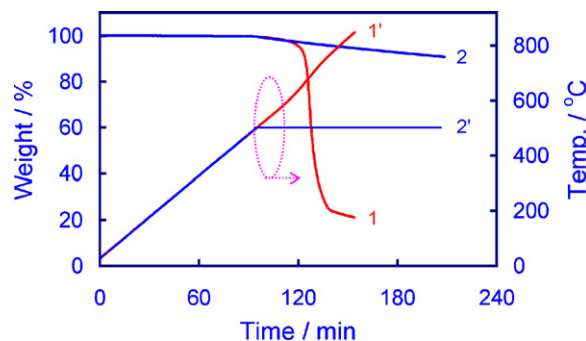
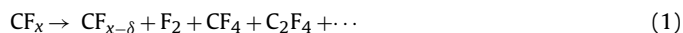


Fig. 1. TGA curves of CF_x material at a heating rate of 5 °C min⁻¹ under nitrogen flow. (1) Heating consecutively to 850 °C and (2) heating to 500 °C and remaining at 500 °C for 3 h.

has been formed and evaporated during the thermal decomposition. According to previous literature [14,15], the major volatile products of the thermal decomposition of CF_x materials were CF₄ and C₂F₄, which were formed through a fluorocarbon radical process in which the C–C bonds at the edges of the CF_x particles were broken and the resulting radicals subsequently took up additional fluorine atoms from the interior of the CF_x. A later work by Hung [16] showed that F₂ was the main volatile products when heating a subfluorinated CF_x with $x=0.68$ at 300–400 °C under nitrogen. Sample 2 was heated to 500 °C, a little lower than the decomposition temperature of CF_x, and remained at 500 °C for 3 h (see curves 2 and 2'). In this case we still observed 13% weight loss, implying that CF_x suffered slow decomposition. Combining the results of Refs. [14–16], we express this process as



Since subfluorinated carbon (CF_{x-δ}) has better power capability than the pristine CF_x, we may employ a controlled thermal decomposition to improve discharge performance of Li/CF_x cells.

To reduce defluorination of CF_x, we shortened heating time at 500 °C to 2 h and prepared a subfluorinated CF_x with black color. Fig. 2 compares discharge curves of two Li/CF_x cells with pristine and subfluorinated CF_x cathode, respectively. It can be seen that the subfluorinated CF_x has almost same capacity as the pristine CF_x, i.e., about 90% of the theoretical capacity based on CF_{1.0} formula, although it contains less fluorine content. Furthermore, the subfluorinated CF_x does not show voltage delay in the beginning of discharge while providing slightly higher discharge voltage.

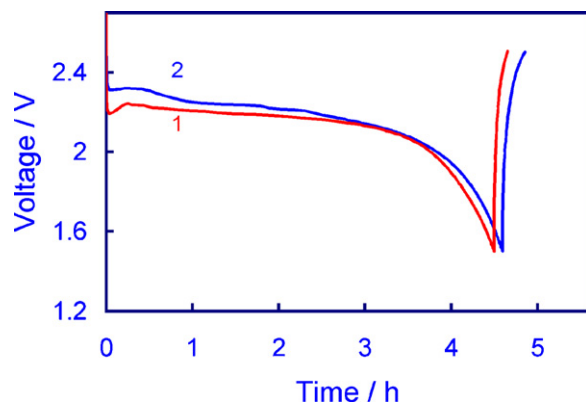


Fig. 2. Discharge curves of Li/CF_x cells. (1) Pristine CF_x and (2) CF_x heated at 500 °C under nitrogen for 2 h.

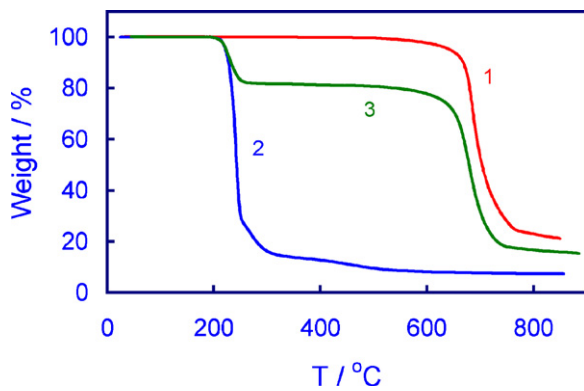


Fig. 3. TGA curves of (1) CF_x , (2) CA, and (3) A 5:1 CF_x/AC mixture, which were recorded at 5°Cmin^{-1} under nitrogen flow.

3.2. Thermal treatment of CF_x with citric acid

As shown by Eq. (1), the thermal decomposition of CF_x loses expensive fluorine in the form of F_2 and other volatile fluorocarbons such as CF_4 and C_2F_4 . In order to recycle these fluorides, an extra carbon source was added into the pristine CF_x for thermal treatment. For this purpose, we choose citric acid as the carbon source since CA has a melting point (153°C) lower than its decomposition temperature. This feature allows CA to melt and form a thin liquid film on the CF_x particles right before thermal decomposition of CA. Therefore, we mixed pristine CF_x and CA (in an appropriate ratio) in solid and then conducted thermal treatment as usual. Fig. 3 shows TGA curves of pristine CF_x , CA, and a 5:1 (in weight) CF_x/CA mixture, respectively. The CA is shown to decompose dramatically between 200°C and 260°C . In this stage, CA loses 74% weight in forms of many small molecules, such as H_2O , CO_2 , CO , to condense into short carbon chains that normally contain significant amount of hydrogen and oxygen [17]. Slow weight loss continues between 260°C and 600°C , during which additional 18% weight loss was observed. In this stage, the short carbon chains lose residual hydrogen and oxygen in the form of H_2O and H_2 , and crosslink into a large carbon sheet, or called as carbon precursor. In this stage the carbon still contains a small amount of hydrogen and oxygen, and carbon-carbon are bonded covalently in the sp^3 hybridized state. Therefore, the carbon precursor is either non-conductive or with very low electronic conductivity. Above 600°C , very little weight loss was observed and highly conductive carbon was formed. Since the temperature for the thermal treatment cannot exceed the decomposition temperature (550°C) of CF_x , the carbon formed by pyrolysis of CA under the present conditions should be non-conductive. In other words, the presence of CA in the thermal treatment of CF_x will not add electronic conductivity.

Fig. 4 shows XRD patterns of the pristine CF_x and subfluorinated carbon made by heating a 5:1 (wt.) CF_x/CA mixture at 500°C under nitrogen for 2 h. These two XRD patterns are exactly same, indicating that no new phase was formed in the thermal treatment although the color had been changed from gray to black. Fig. 5 compares the impedance of CF_x before and after thermal treatment. As a reference, the commercial carbon black as used in the CF_x electrode is also plotted in Fig. 5. It can be observed that the impedance of carbon black is independent of frequency and constantly remained at $16\text{--}17\Omega$, showing a typical characteristic of electronic conductor. The impedances of the pristine CF_x and subfluorinated carbon are almost same, and furthermore the logarithms of their impedance and frequency exhibit an excellent linear correlation (Fig. 5). This is a characteristic of pure capacitor, and means that they are entirely non-conductive. Based on the results of Figs. 3–5, the process of thermal treatment of CF_x/CA mixture can briefly

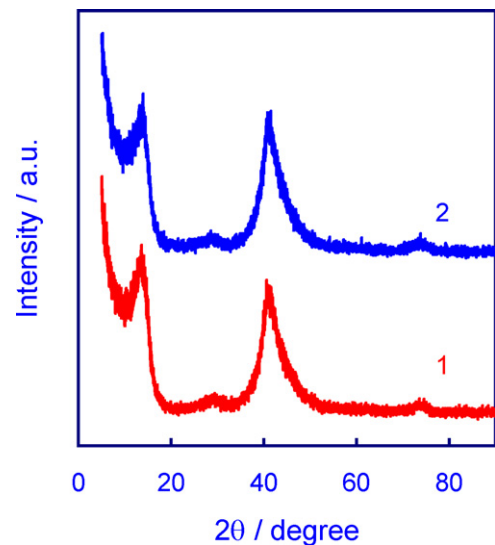
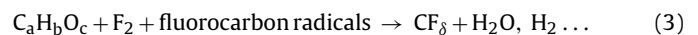
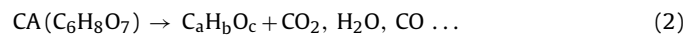


Fig. 4. XRD patterns of CF_x before and after thermal treatment by heating a 5:1 CF_x/CA mixture at 500°C under nitrogen for 2 h. (1) Pristine CF_x and (2) treated CF_x .

described as



Eq. (2) expresses that CA was decomposed to form carbon precursor ($\text{C}_a\text{H}_b\text{O}_c$), and that the resulting carbon still contains significant amount of hydrogen and oxygen atoms. Eq. (3) expresses that the carbon precursor either reacts with F_2 or terminates fluorocarbon radicals generated by the thermal decomposition of CF_x to form electrochemically active subfluorinated carbon (CF_δ) and other small molecules such as H_2O and H_2 . According to the equations above, the thermal treatment does not yield highly conductive carbon, instead recycles fluorides to generate subfluorinated carbon.

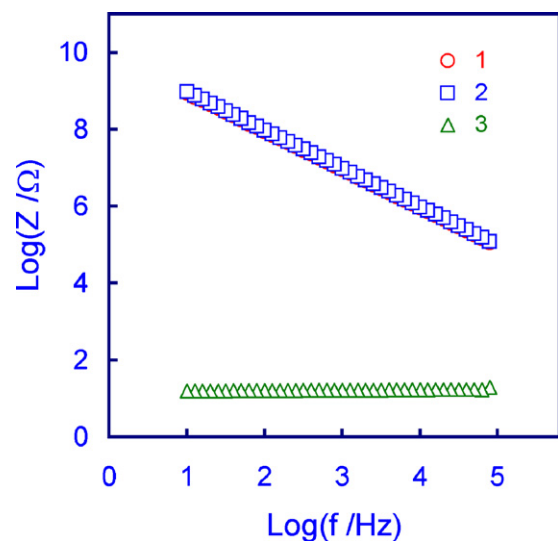


Fig. 5. Responses of impedance to AC-frequency for (1) pristine CF_x , (2) treated CF_x and (3) carbon black, which were recorded by filling powder in a holder with a 0.32 cm^{-1} cell constant.

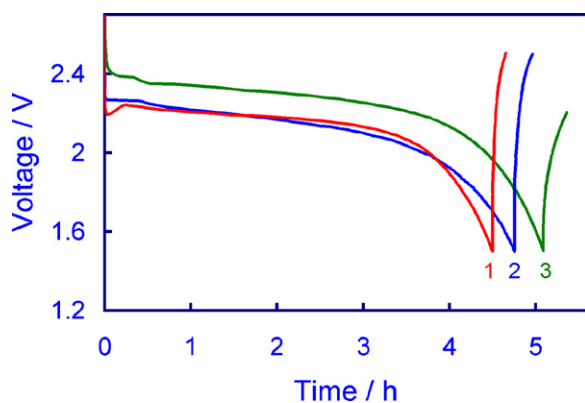


Fig. 6. Discharge curves of Li/CF_x cells. (1) Pristine CF_x, (2) CF_x treated by heating a 5:1 CF_x/AC mixture at 400 °C under nitrogen for 3 h, and (3) CF_x treated by heating a 5:1 CF_x/AC mixture at 500 °C under nitrogen for 2 h.

3.3. The effect of treatment conditions on discharge performance

The same mixtures of 5:1 (wt.) CF_x/CA were used to study the effect of heating temperature on the discharge performance of CF_x cathode. Fig. 6 displays discharge curves of the Li/CF_x cells with pristine CF_x and subfluorinated carbons made by different temperatures, respectively. By comparing cells 1 and 2, we see that the performance improvement is very little when the thermal treatment was conducted at 400 °C although the treatment time was extended for an additional 1 h. This is due to that the carbon formed by CA decomposition is non-conductive, and that the temperature is not high enough to decompose CF_x. When the temperature was elevated to 500 °C, both discharge voltage and capacity were improved significantly (cell 3). In this case, about 100% of theoretical capacity based on CF_{1.0} formula was achieved. This merit can be attributed to the formation of subfluorinated carbon as shown by Eq. (1) and to the recycle of fluorides as shown by Eq. (3). In addition, we have observed that further increase in the heating temperature, for example rising to 550 °C, resulted in a significant weight loss. Therefore, it is reasonable to control the treatment temperature not higher than 500 °C.

The effect of CF_x/CA ratio on discharge performance was studied by thermal treatment at 500 °C under nitrogen for 2 h, and the results are shown in Fig. 7. Comparison of cell 1 and cell 2 shows that the improvement is not obvious when a 10:1 (wt.) CF_x/CA ratio was used. This is likely because the carbon formed by CA decomposition is not sufficient to recycle fluorides, and in this case the result is similar with the thermal treatment of CF_x alone, as showed by

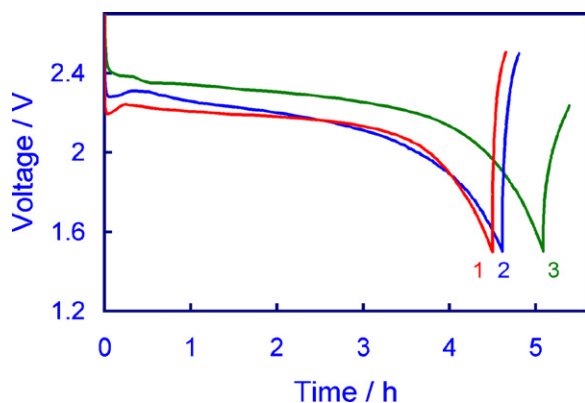


Fig. 7. Discharge curves of Li/CF_x cells. (1) Pristine CF_x, (2) CF_x treated by heating a 10:1 CF_x/AC mixture at 500 °C under nitrogen for 2 h, and (3) CF_x treated by heating a 5:1 CF_x/AC mixture at 500 °C under nitrogen for 2 h.

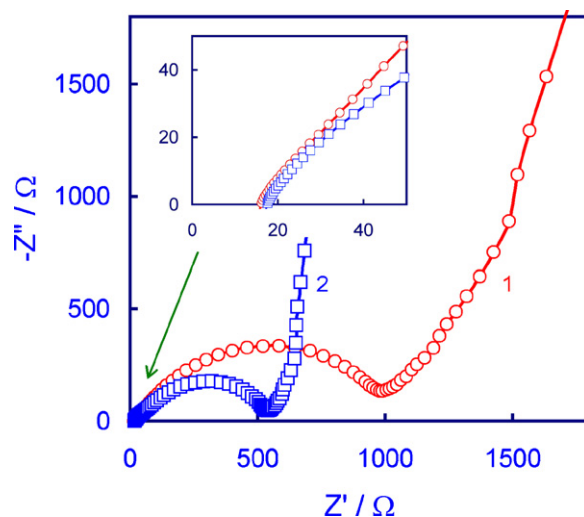


Fig. 8. Impedance spectra of Li/CF_x cells at 10% DOD. (1) Pristine CF_x and (2) CF_x treated by heating a 5:1 CF_x/AC mixture at 500 °C under nitrogen for 2 h.

comparing cell 2 in Fig. 6 and cell 2 in Fig. 7. It is indicated by cell 3 that significant improvement was obtained when the CF_x/CA ratio was increased to 5:1 (wt.). Considering the dilution of fluorine by extra carbon, we believe there must be an optimum CF_x/CA ratio, and we are currently working on this issue.

3.4. Understanding of performance enhancement

Mechanism of performance enhancement of CF_x cathode by thermal treatment can be explained by impedance data. Fig. 8 shows impedance spectra of two Li/CF_x cells with pristine CF_x and treated CF_x, respectively, which were recorded at 10% of depth-of-discharge (DOD). Both impedance spectra show a suppressed semicircle followed by a slopping straight line at low frequency end. According to our previous analysis [5], the impedance of a Li/CF_x cell is predominantly contributed by CF_x cathode, and the semicircle mainly reflects cell reaction resistance (R_{cr}) of the CF_x cathode that is affected by Li⁺ ion diffusion (conductivity) in the discharge product shell and by charge-transfer process of the cell reaction. It can be seen from Fig. 8 that cell 2 with treated CF_x has much lower R_{cr} than cell 1 using pristine CF_x. This advantage is attributed to the better power capability of the subfluorinated carbon formed by the thermal treatment. The intercept between the semicircle and real resistance (horizontal axes) at high frequency end represents a bulk resistance (R_b) of the cell, including those of the current collector, electrode, separator and electrolyte. The inset in Fig. 8 indicates that both cells have nearly same R_b (ca. 18 Ω). This result further confirms the conclusion that the thermal treatment does not increase electronic conductivity of CF_x material, instead results in the formation of subfluorinated carbon that has better power capability.

4. Conclusions

In conclusion, thermal treatment just below the decomposition temperature of CF_x materials offers an effective approach for the improvement of discharge performance of Li/CF_x cells. The thermal treatment causes a limited decomposition of CF_x to form subfluorinated carbon that has better power capability. The discharge performance of subfluorinated carbon is affected by the temperature and time of thermal treatment. Organic compounds, citric acid in this work, can serve as an extra carbon source to recycle fluorides that otherwise are evaporated in the form of F₂ and volatile fluorocarbons such as CF₄ and C₂F₄ during thermal decomposition of CF_x.

Based on the reversal correlation of the specific capacity and power capability with the content of fluorine, a sunfluorinated carbon with optimum discharge performance can be made by adjusting the ratio of CF_x to organic compound in the thermal treatment. In this work, the best result was obtained from the treatment of a 5:1 (wt.) CF_x/CA mixture at 500 °C under nitrogen for 2 h. It was shown that the discharge capacity of CF_x such-treated achieved the theoretical value (865 mAh g^{-1} , based on $CF_{1.0}$ formula) at C/5 and at 20 °C.

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