Short communication

Carbothermal treatment for the improved discharge performance of primary Li/CF$_x$ battery

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ABSTRACT

Carbothermal treatment was used to improve the discharge rate performance of primary lithium/carbon monofluoride (Li/CF$_x$ with $x=1$) batteries. The treatment was carried out by heating a mixture of CF$_x$ and carbon black (CB) just below the decomposition temperature of CF$_x$ under nitrogen for 2 h. In the treatment, poly(vinylidene fluoride-co-hexafluoropropylene) (Kynar) was used as a fluorinated polymer binder to press the CF$_x$/CB mixture into pellets. It was shown that the content of Kynar significantly affected the discharge performance of the resulting treated-CF$_x$ (T-CF$_x$). This can be attributed to the catalytic effect of HF formed by the pyrolysis of Kynar on the decomposition of CF$_x$ and on the reaction of CB with the volatile fluorocarbons formed by the decomposition of CF$_x$. The discharge performance of T-CF$_x$ cathode was also affected by the temperature of carbothermal treatment and by the ratio of CF$_x$ to CB. In this work the best result was obtained from a treatment conducted at 470 °C on a 87CF$_x$/10CB/3Kynar (by weight) mixture. In the discharge condition of C/5 and 20 °C, the Li/CF$_x$ cell with such-obtained T-CF$_x$ cathode showed about 95 mV higher voltage than the control cell while retaining nearly the same specific capacity. Impedance analyses indicate that the improved discharge performance is mainly attributed to a reduction in the cell reaction resistance (R_{cr}) that includes an ohmic resistance related to the ionic conductivity of the discharge product shell and a Faradic resistance related to the processes of charge-transfer and Li$^+$ ion diffusion in the CF$_x$ reaction zone.

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1. Introduction

Lithium/carbon monofluoride (Li/CF$_x$ with $x=1$) batteries are known to have the highest theoretical specific capacity among all commercially available primary lithium batteries. However, these batteries suffer voltage delay in the beginning of discharge and show high polarization during the discharge, especially at high rate or at low temperature [1]. The former is due to the intrinsic electrical insulating property of CF$_x$ ($x=1$) material, while the later is related to the slow kinetics of cell reaction because of the high activation energy for the conversion from the C–F covalent bonds to Li–F ionic bonds. Impedance analyses indicated that the overall resistance of a Li/CF$_x$ battery is mainly contributed by the CF$_x$ cathode, whose impedance is further dominated by a so-called cell reaction resistance (R_{cr}) including an ohmic resistance and a Faradic resistance [2]. In addition to causing voltage polarization, the high R_{cr} results in a huge I^2R heat. Due to these reasons, the current applications of Li/CF$_x$ batteries are mainly limited to the devices that need low-to-medium power such as

computer memory/clock backups and implantable medical equipments.

Many approaches have been attempted to solve the problems of Li/CF$_x$ batteries. To reduce or eliminate the initial voltage delay, small amount of a second cathode material that does not show voltage delay such as metal oxides [3–6] or subfluorinated carbons [7] was mixed with the CF$_x$ cathode. In this way, the voltage delay was eliminated by the second cathode material discharging first so that the cell passes the voltage delay region of CF$_x$ cathode. In addition, the controlled defluorination of CF$_x$ materials by KI [8] or alkali metal alkyl compounds [9] has been attempted to improve the discharge performance. More simply, a pre-discharging process was proposed to remove first 2–3% of capacity where voltage delay occurs [8,10]. Obviously, these approaches more or less resulted in the loss of battery capacity. For the improvement of discharge rate performance, the efforts were previously focused on the development of subfluorinated carbon materials [10–12] and the modification of electrode processing such as reducing the thickness of CF$_x$ electrodes [13,14]. These improvements are made at the expense of energy density due to a decrease either in the content of fluorine or in the loading of cathode active material. Other approaches included the enhancement of the electronic conductivity of CF$_x$ electrode by the addition of highly conductive carbon

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fibers [15] or by the coating of a highly conductive metal layer on the surface of CF_x particles [16,17]. These approaches have proven to be effective in increasing the rate capability of Li/CF_x batteries without adverse capacity loss.

In an effort to enhance the discharge performance of Li/CF_x batteries, we showed that both the initial voltage and discharge rate capability of the Li/CF_x batteries can be improved by the thermal treatment of CF_x material just below the decomposition temperature, especially in the presence of an organic compound as an extra carbon source [18]. We proposed that this improvement resulted from a process where CF_x was partially decomposed to form sub-fluorinated carbon and volatile fluorine-containing products (i.e., fluorine and fluorocarbons having low molecular weight), and that the carbon precursor formed by the pyrolysis of organic compound chemically combines with these volatile products. Based on this proposal, we used carbon black to react with the volatile fluorine-containing products generated by the decomposition of CF_x. In this paper, we report the results of such treatments and discuss the resulting impact on the discharge performance of Li/CF_x batteries.

2. Experimental

All materials, including carbon monofluoride (CF_x, $x = 0.99–1.08$, FluorStar Grade F, made from carbon fiber) from Lodestar Inc., carbon black (CB, 99.99%, acetylene, 50% compressed) from Alfa Aesar, propylene carbonate (PC, electrolyte grade, Ferro), 1,2-dimethoxyethane (DME, electrolyte grade, Ferro) and LiBF$_4$ (Stella), were used as received. Carbothermal treatment was carried out under nitrogen in a Lindberg/Blue Tubular furnace that was controlled by a programmed schedule consisting of: (1) heating to the pre-determined temperature in 5 h, (2) remaining at the pre-determined temperature for 2 h, and (3) turning off the electric power for naturally cooling to room temperature. In order to achieve efficient reaction, the mixture of CF_x and CB was pressed into pellets by using 3–8 wt.% of poly(vinylidene fluoride-co-hexafluoropropylene) (Kynar Flex^{TM} 2801, Elf Atochem North America) as the binder. X-ray diffraction (XRD) pattern of the starting materials and 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 PerkinElimer TGA-7.

Carbothermal treated CF_x (T-CF_x) cathode was prepared by coating a slurry composed of T-CF_x, CB, and Kynar in N-methylpyrrolidone solvent onto an Al foil. The composition for all cathodes and CF_x/CB mixtures was expressed in weight percentage, and the detailed composition for each was noted in figure captions. 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 cm^2 for coin cell tests. 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, a 0.5 m LiBF$_4$ 1:1 (wt.) PC/DME electrolyte was prepared, and using it Li/CF_x coin cells were assembled with Celgard$^®$ 3500 membrane as the separator. For comparison, a CF_x cathode consisting of 85% pristine CF_x, 9% CB, 1% carbon fiber, and 5% Kynar was prepared to build the control cell. In order to get accurate and reproducible results, four identical coin cells for each sample were assembled and 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 calculated from the exact weight and theoretical specific capacity of CF_x (865 mAh g^{-1}, based on $x = 1$). Using a Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer, impedance spectra of the cells were potentiostatically measured at open-circuit voltage with an ac oscillation of 10 mV over the frequency range from 100 kHz to 0.01 Hz. All electrochemical tests, including discharge and impedance, were carried out at 20 °C by using a Tenney
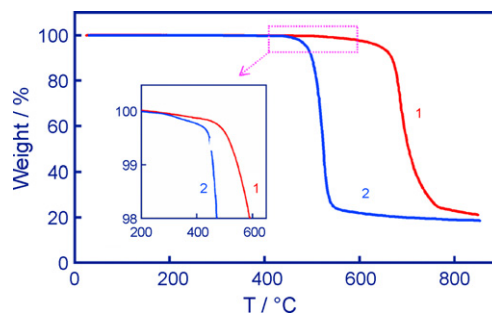

Fig. 1. TGA curves recorded at $5 °C$ min^{-1} under nitrogen. (1) Pristine CF_x, and (2) Kynar.

Environmental Oven Series 942 as the constant temperature environment provider.

3. Results and discussion

3.1. Idea for carbothermal treatment

Carbon fluorides (CF_x) are a type of nonstoichiometric compounds, whose thermal stability depends on the content of fluorine, the nature of carbon precursor, and the method of synthesis [19]. In order to determine the decomposition temperature, TGA of CF_x was run and plotted along with that of Kynar in Fig. 1. It is shown that major decomposition of CF_x occurs between 550 °C and 780 °C, and that in the end of the experiment 21 wt% of black carbon, about half of the theoretical content of carbon in CF_x, is left. This result reveals that during the decomposition, some volatile fluorocarbons have been formed and evaporated. According to previous publications [20,21], the primary volatile products of the thermal decomposition of CF_x are CF_4 and C_2F_4, which are formed through a fluorocarbon radical process. That is, the C—C bonds at the edges of the CF_x particles where the carbon atoms already bonded to multiple fluorine atoms are broken, and the resulting radicals take up additional fluorine atoms from the interior of the CF_x particles. By this process, subfluorinated carbon ($CF_{x-\delta}$) having higher power capability can be formed by a limited decomposition of CF_x, as described by Eq. (1):

$$CF_x \rightarrow CF_{x-\delta} + CF_4 + C_2F_4 + \cdots \tag{1}$$

In order to recycle these volatile fluorocarbons, CF_x is mixed with carbon black (CB) and heated, which is proposed to result in the following reaction:

$$CF_x + C \rightarrow CF_{x-\delta} + CF_\delta \tag{2}$$

Since HF is a known catalyst and reaction media for the fluorination of graphite by elemental fluorine and fluoride complexes with high oxidation state [22–25], we can employ a fluorinated polymer as the in situ HF provider to promote reaction (2). For this purpose, Kynar was chosen as the binder to press CF_x/CB mixture into pellets. As Fig. 1 shows, major decomposition of Kynar occurs between 460 °C and 550 °C, about 30 °C lower than that of CF_x. Therefore, the temperature window between the decomposition temperatures of CF_x and Kynar can be used for the carbothermal treatment of CF_x.

Fig. 2 shows XRD patterns of CB, CF_x, and T-CF_x obtained by heating a pellet of 87CF_x/10CB/3Kynar mixture at 470 °C under nitrogen for 2 h. It is shown that the pattern of T-CF_x is a typical mixture of CF_x and CB. There are no extra diffraction peaks, indicating that the carbothermal treatment does not result in a new phase. In order to examine the effect of Kynar on the carbothermal treatment, the same conditions (including CF_x/CB ratio, reaction temperature and time) were used to treat CF_x/CB mixture in the forms of powder and pellet, respectively. The discharge curves of these two $Li/T-CF_x$ cells
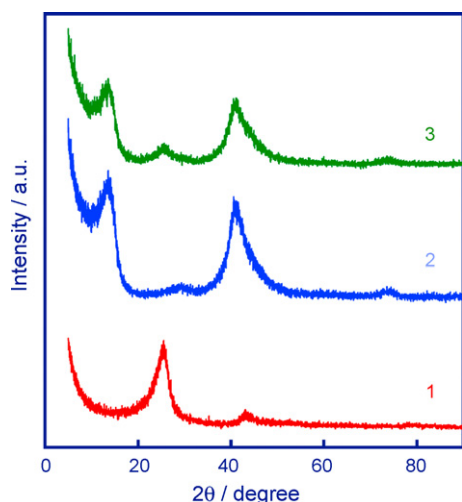
Fig. 2. XRD patterns of (1) CB, (2) Pristine CF_x, and (3) T-CF_x obtained by heating a pellet of 87CF_x/10CB/3Kynar mixture at 470 °C under nitrogen for 2 h.

are plotted along with that of the control cell in Fig. 3. Obviously, the treatment in the form of pellet (curve 3) gives more significant improvement than that in the form of powder (curve 2). This can be attributed to two factors that are present in the form of pellets: (1) better contact between the particles of CF_x and CB, which favors solid-state reaction, and (2) the catalytic effect of HF formed by the pyrolysis of Kynar on the reaction of CB and fluorocarbons, which accordingly promotes reaction (2). Since the HF catalyst promotes both directions of fluorination and defluorination, there should be an optimum content for Kynar to give the best combination in the discharge voltage and specific capacity of T-CF_x cathode. To find the optimum content of Kynar, four CF_x/CB/Kynar pellets containing 0%, 3%, 5%, and 8% of Kynar were prepared and heated at 500 °C for 2 h. The discharge curves of resulting Li/T-CF_x cells are plotted in Fig. 4, from which the best combination of the discharge voltage and specific capacity is observed for the case with 5% Kynar (curve 3).

3.2. Relationship of treatment conditions and discharge performance

The treatment conditions were optimized in terms of heating temperature and CF_x/CB ratio. To find the optimum temperature, three pellets with the same composition of 87CF_x/10CB/3Kynar were respectively heated at 450 °C, 470 °C, and 500 °C under nitrogen for 2 h. With the increase of temperature, these treatments

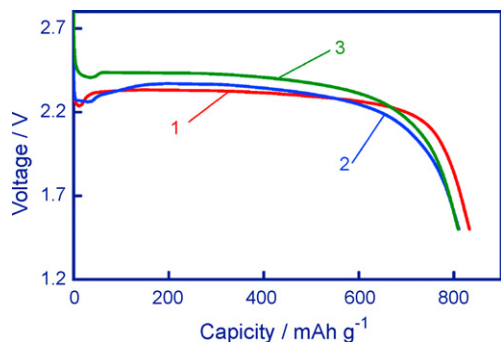**Fig. 3.** Discharge curves of Li/CF_x cells at C/5. (1) Control cell, (2) T-CF_x obtained by treating a powder of 90CF_x/10CB mixture, and (3) T-CF_x obtained by treating a pellet of 85CF_x/10CB/5Kynar mixture. Both treatments were conducted at 500 °C under nitrogen for 2 h, and the cathodes had a composition of 95T-CF_x/5Kynar.
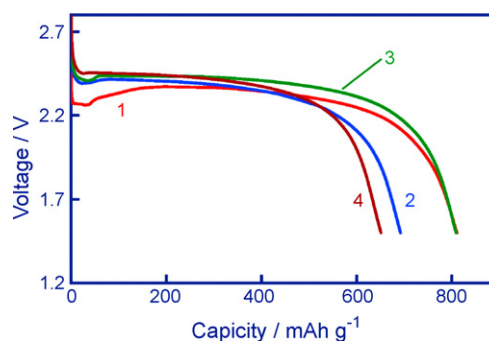

Fig. 4. Discharge curves of Li/T-CF_x cells at C/5. (1) T-CF_x obtained from a powder of 90CF_x/10CB mixture, (2) T-CF_x obtained from a pellet of 87CF_x/10CB/3Kynar mixture, (3) T-CF_x obtained from a pellet of 85CF_x/10CB/5Kynar mixture, and (4) T-CF_x obtained from a pellet of 82CF_x/10CB/8Kynar mixture. All T-CF_x were obtained by heating the mixture at 500 °C under nitrogen for 2 h, and the cathodes had a composition of 95T-CF_x/5Kynar.
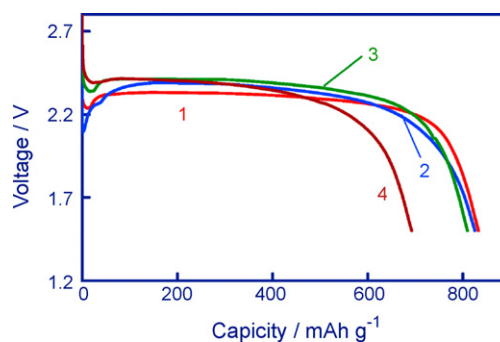

Fig. 5. Discharge curves of Li/CF_x cells at C/5. (1) Control cell, (2) T-CF_x treated at 450 °C, (3) T-CF_x treated at 470 °C, and (4) T-CF_x treated at 500 °C. All T-CF_x were obtained by heating a pellet of 87CF_x/10CB/3Kynar mixture under nitrogen for 2 h, and the cathodes had a composition of 95T-CF_x/5Kynar.

resulted in a weight loss of 4.0%, 6.1%, and 11.9%, respectively. The discharge curves of the resulting Li/T-CF_x cells are plotted along with that of a control cell in Fig. 5. As compared with the control cell, all three cells show higher discharge voltage. However, the cell with T-CF_x treated at 500 °C (curve 4) gives significantly lower specific capacity due to more loss of fluorine, as suggested by its high weight loss (11.9%). Therefore, the suitable temperature for carbothermal treatment should be in a range between 450 °C and 470 °C, which is about 30 °C lower than the thermal treatment without the addition of fluorinated polymer [18].
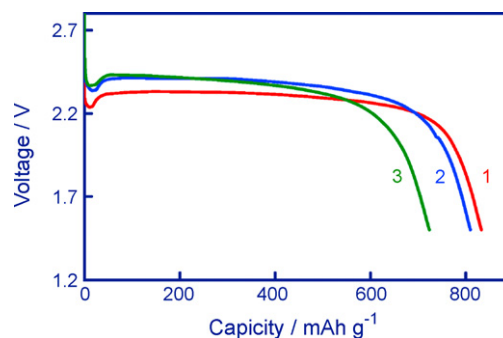

Fig. 6. Discharge curves of Li/CF_x cells at C/5. (1) Control cell, (2) T-CF_x cathode having a composition of 95T-CF_x/5Kynar in which the T-CF_x was made from a pellet of 87CF_x/10CB/3Kynar mixture, and (3) T-CF_x cathode having a composition of 90T-CF_x/5CB/5Kynar in which the T-CF_x was made from a pellet of 92CF_x/5CB/3Kynar mixture. Both T-CF_x were obtained by heating a pellet mixture at 470 °C under nitrogen for 2 h.
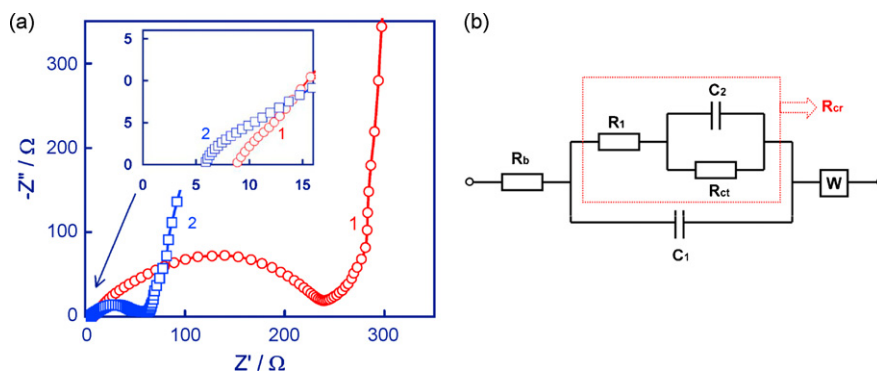
(a)

(b)

Fig. 7. (a) Impedance spectra of Li/CF_x cells at 20% DOD. (1) Control cell, (2) Li/T-CF_x cell in which the cathode had a composition of 95T-CF_x/5Kynar and the T-CF_x was obtained by heating a pellet of 87CF_x/10CB/3Kynar mixture at 470 °C under nitrogen for 2 h. (b) Equivalent circuit for analysis of a Li/CF_x cell, in which R_1 is the ohmic resistance of the discharge product shell of CF_x cathode and R_{ct} is the charge-transfer resistance of cell reaction.

The effect of CF_x/CB ratio was examined by heating two pellets with a composition of 87CF_x/10CB/3Kynar and 92CF_x/5CB/3Kynar, respectively, under nitrogen for 2 h. After treatment, both cases showed a 6.1–6.2 wt.% loss. Since the latter contained only 5% CB, additional 5% CB was added to increase the electrical conductivity for the preparation of its resulting T-CF_x cathode. The discharge curves of these two cells are compared with that of a control cell in Fig. 6, which shows that both cells give higher discharge voltage. It is interesting to note that the case with 92CF_x/5CB/3Kynar (curve 3) has lower specific capacity than the other one although an additional 5% CB was already added to match the total content of conductive carbon in the preparation of the cathode. This means that for good discharge performance of Li/CF_x batteries, the conductive carbon is added rather in the carbothermal treatment step than in the preparation of CF_x cathode. In this work, the best discharge performance was observed from the T-CF_x obtained by heating a 87CF_x/10CB/3Kynar pellet at 470 °C under nitrogen for 2 h, and no additional conductive carbon is needed for the preparation of the cathode sheet. It can be estimated from Fig. 6 that this T-CF_x (curve 2) gives an averaged 95 mV increase in the discharge voltage without obvious capacity loss, as compared with the control cell (curve 1).

3.3. Understanding of the performance improvement

The performance improvement of CF_x material by carbothermal treatment was understood by impedance analyses. Fig. 7a compares the impedance spectra of a control Li/CF_x cell and a Li/T-CF_x cell, both of which were recorded at 20% of depth-of-discharge (DOD) and at 20 °C. These two impedance spectra have the similar profile showing a suppressed semicircle followed by a slopping straight line at the low frequency end. According to our previous analyses on each of the lithium anode, CF_x cathode and Li/CF_x cell [2], the semicircle mainly reflects cell reaction resistance (R_{cr}) of the CF_x cathode, including an ohmic resistance (R_1) and a charge-transfer process (R_{ct}/C_2) of the cell reaction, as indicated in the proposed equivalent circuit (Fig. 7b). The ohmic resistance is related to the ionic conductivity of the discharge product shell on the remaining CF_x core, and Warburg impedance (W) responds to the diffusion of Li$^+$ ions in the reaction zone between the remaining CF_x core and discharge product shell [2]. As shown in Fig. 7a, the significant difference between two impedance spectra is that the Li/T-CF_x cell (spectrum 2) has much lower R_{cr} than the control cell. Meanwhile, it was found that the Li/T-CF_x cell had higher frequencies in the onset between the semicircle and the slopping straight line than the control cell. This is another indication for the higher reaction kinetics of the Li/T-CF_x cell. Based on these results, the improved discharge performance by carbothermal treatment can be attributed to a reduction in the

cell reaction resistance (R_{cr}), or in other words to an increase in the cell reaction kinetics of the CF_x cathode. As indicated by the inset of Fig. 7a, in addition, the Li/T-CF_x cell has lower bulk resistance (R_b) that generally reflects the resistances of the current collector, electrode, separator and electrolyte. This improvement can be attributed to the better electrical contact between the particles of CF_x and conductive carbon, which was gained during pressing CF_x/CB/Kynar mixture into pellets for the carbothermal treatment.

4. Conclusions

In conclusion, carbothermal treatment provides an easy approach for the improvement of discharge performance of Li/CF_x cells. The treatment conducted just below the decomposition temperature of CF_x results in the formation of subfluorinated carbon ($CF_{x-\delta}$) having higher power capability, as expressed by the reaction of "$CF_x + C \rightarrow CF_{x-\delta} + CF_\delta$". The use of a fluorinated polymer binder to press CF_x/CB mixture into pellets can effectively promote the carbothermal reaction. The fluorinated polymer, Kynar in the present work, offers two functions of (1) serving as the binder to bond CF_x and CB together, and (2) providing HF to catalyze carbothermal reaction. In this work, the best result was obtained by heating a 87CF_x/10CB/3Kynar pellet at 470 °C under nitrogen for 2 h. When discharging at C/5 and at 20 °C, the cell with such-treated CF_x cathode showed a 95 mV increase in the discharge voltage without significant loss in specific capacity, as compared with the control cell. Impedance analyses indicate that the improvement of discharge performance by the carbothermal treatment is mainly attributed to an increase in the cell reaction kinetics of the CF_x cathode.

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