Short communication

The improved discharge performance of Li/CF$_x$ batteries by using multi-walled carbon nanotubes as conductive additive

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ABSTRACT

The discharge performance of Li/CF$_x$ ($x = 1$) battery is improved by using multi-walled carbon nanotubes (MWCNTs) as an alternative conductive additive. Compared with the battery using acetylene black as conductive additive at the same amount, the Li/CF$_x$ battery using MWCNTs as conductive additive has higher specific capacity and energy density as well as smoother voltage plateau, especially at higher discharge rate. The specific capacity at discharge rate of 1 C is improved by nearly 26% when MWCNTs are employed as conductive additive. Meanwhile, it is also found that the discharge performance is able to be tuned by the amount of MWCNTs and the battery containing more MWCNTs is favorable to be discharged at higher rates. The specific capacity of Li/CF$_x$ battery with 11.09 wt.% MWCNTs is approximately 712 mAh g^{-1} at the discharge rate of 1 C. It is proposed that the formed three-dimensional networks of MWCNTs in cathode, which enlarges the contact area of interphase and facilitates electrons delivery, accelerates the rates of lithium ion diffusion into the fluorinated layers and electrons transport in cathode at the same time, which improves the discharge performance of Li/CF$_x$ battery subsequently, especially at higher rates.

1. Introduction

A primary battery based on fluoride and lithium is theoretically the optimum redox system for high energy density power source, and such battery has been realized commercially by the use of graphite fluoride CF$_x$ as cathode material for lithium battery with electrolyte organic solvent system [1,2], whose theoretical specific energy is 2.2 kWh kg^{-1} and is the highest of common lithium primary batteries, such as Li/MnO$_2$ or Li/SOCl$_2$ batteries [3]. Besides the high theoretical specific energy, the Li/CF$_x$ battery has high average operating voltage, long shelf life, stable operation and wide operation temperatures. However, the practical energy is only about 10% of the theoretical value for small cells and the delivered capacity is approximately 30% of the theoretical at very low rates for large capacity Li/CF$_x$ cells (∼1000 Ah) [4]. Moreover, the discharge voltage of real Li/CF$_x$ battery is much lower than the theoretical value of open circuit potential (3.2–3.5 V vs. Li$^+$/Li), showing significant polarization [5]. In addition, the voltage delay at the beginning of the discharge, poor low temperature performance and the heat generation during the discharge process and so on are other problems of Li/CF$_x$ batteries. These problems are mainly caused by poor electrical conductivity of CF$_x$ induced by the strongly covalent C–F bond as well as the formed ionic and electronic insulating LiF at the surface of cathode pores [6,7]. In order to solve these problems, Yazami et al. synthesized a series of subfluorinated carbon materials and improved the power capability of Li/CF$_x$ at the expense of specific capacity [8,9]. Zhang et al. demonstrated that the carbothermal treatment of CF$_x$ below the decomposition temperature could improve the discharge performance of Li/CF$_x$ battery because of the significant reduction in the cell reaction resistance [10,11]. Recently, Zhang et al. reported that Li/CF$_x$ battery whose cathode was coated by a uniformed carbon layer exhibited better discharge performance, especially at high current rate, due to the exterior connectivity between particles provided by the carbon coating [12].

Carbon nanotubes (CNTs) are candidate materials for the use in batteries field due to their unique electrical and mechanical properties, such as the excellent electrical conductivity at room temperature and the high aspect ratio [13,14]. Therefore, the use of CNTs as an additive for electrodes has several advantages compared to other carbon additives like carbon black and acetylene black, such as the significant reduction in additive mass compared to conventional carbon additives for sufficient percolation network to achieve appropriate conductive paths. Multi-walled carbon nanotubes (MWCNTs) have been employed as the conductive additive

Table 1
The composition of different Li/CF$_x$ batteries' cathodes.

Sample	Conductive additive (wt.%)		CF$_x$ (wt.%)	Binder (wt.%)
1	Acetylene black	10	80	10
2	MWCNTs	10	80	10
3	MWCNTs	8.16	81.63	10.21
4	MWCNTs	11.07	79.05	9.88

in the cathodes of rechargeable lithium ion batteries, such as LiCoO$_2$ [15], LiFePO$_4$ [16–18], and LiNi$_{0.7}$Co$_{0.3}$O$_2$ [19,20], showing about 10% improvement in the reversible capacity of the electrodes compared to carbon black counterparts.

However, as far as we know, there was no report about employing CNTs as conductive additives in the cathodes of lithium primary batteries. The discharge mechanism of lithium primary battery is not the same with that of lithium ion battery and they are irreplaceable in some cases [21]. Therefore, we started the research about employing MWCNTs as the conductive additive of Li/CF$_x$ battery. We found that the specific capacity, energy density and power density of Li/CF$_x$ battery using MWCNTs as conductive additive were obviously higher than those using acetylene black as conducting additive in the same amount and the discharge performance at high current rate was improved by increasing the amount of MWCNTs. The mechanism of these phenomena was discussed in this study as well.

2. Experimental

2.1. The treatment of MWCNTs

MWCNTs (The TsingHua University, ≥80%) went through a mild hydrochloric acid treatment to remove metal catalyst without destroying their structure. The mild hydrochloric acid treatment was processed as follows: a certain mass of MWCNTs was weighed in the beaker, and then added the hydrochloric acid (concentration of 36%), ultrasonic treatment for 60 min, filtered and washed to neutral, then dried for 24 h in a vacuum oven at 50 °C.

2.2. Preparation of electrode

CF$_x$ (x = 1, Alfa Aesar, A Johnson Matthey Company) was used as cathode material and MWCNTs or acetylene black was used as conductive agents. Poly (vinylidene fluoride) (PVDF) was dissolved in N,N-dimethyl formamide (NMP) as binder. The CF$_x$ electrode film was prepared by coating slurries composed of certain ratios (listed in Table 1) in NMP solvent on an Al foil. The coating was dried in an 80 °C oven to evaporate solvent, and the resulting electrode film was cut into small disks with a diameter of 1.27 cm for test in button cells. The shaped electrode pieces were further dried at 100 °C under vacuum for 8 h, and then transferred to a glove-box for cell assembly. The other reagents were purchased from Tianjin Chemical Company and used without further treatment.

2.3. Preparation of primary lithium batteries

Button cells were assembled in a dry glove-box filled with argon (Mikrouna Co., Advanced 2440/750) with a metallic lithium disc for the anode, a microporous polypropylene/polyethylene/polypropylene film soaked with 1 M LiPF$_6$ in the solution of ethylene carbonate:dimethyl carbonate:diethyl carbonate (1:1:1 vol.) as electrolyte, and the CF$_x$ based cathode.
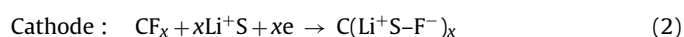
2.4. Characterization

The room temperature conductivities of MWCNTs and acetylene black were measured by a standard four-probe method using a Jandel Model RMs instrument, for which the powder of MWCNTs or acetylene black was pressed into pellet with thickness of ~1 nm under the pressure of 10 MPa for 5 min. The morphologies of electrode material were observed by scanning electron microscope (SEM, PhilipsXL-30). The button cells were discharged at constant current density (Land CT2001A, Wu Han Jin Nuo Electronics Co., China) at room temperature and the discharge measurement termination voltage was 1 V. Electrochemical impedance spectroscopy (EIS) was performed from 0.01 to 10 kHz frequency range using Advanced Electrochemical System Parstat 2263 when the Li/CF$_x$ battery was discharged under the rate of 1 C completely.

3. Results and discussion

Li/CF$_x$ batteries using MWCNTs or acetylene black as conductive additives in the same mass ratio (10.00 wt.%) were discharged at different current density and their galvanostatic discharge curves are represented in Fig. 1(a) and (b) respectively. An obvious increase in capacity is observed in the sample used MWCNTs as conductive additive compared to the one used acetylene black as conductive additive, the capacity of the former gets close to the theoretical value (865 mAh g^{-1}) while the latter delivers about 93% of theoretical capacity at the discharge rate of 0.05 C. Moreover, the specific capacity of the former at higher discharge rate is significantly larger than the latter, and there is nearly 26% improvement in the specific capacity of Li/CF$_x$ battery added MWCNTs as conductive agent when discharge rate is 1 C. In addition, the discharge profile of Li/CF$_x$ using MWCNTs as conductive additive is flatter than that of battery using acetylene black as conductive additive at the same discharge. The voltage plateau of batteries whose conductive additive is MWCNTs is also higher than the ones using acetylene black as conductive additive at high discharge rate (more than 0.5 C), though the voltage plateau is not significantly improved at low discharge rate, which is caused by the slow diffusion of solvated lithium ions [12]. The SEM images of these two cathodes are shown in Fig. 2 and it can be observed that pieces of MWCNTs connected CF$_x$ particles in series and MWCNTs interlaced all particles together to form a three-dimensional network wiring in the cathode whose conductive additive is MWCNTs from Fig. 2(a). These features are accordant with the previous reports which employed MWCNTs as conductive additives in the rechargeable lithium ion batteries [15–20,22,23].

Meanwhile, the effects of MWCNTs' amounts on the discharge performance of Li/CF$_x$ battery were also investigated and the galvanostatic discharge curves of Li/CF$_x$ batteries with different amount of MWCNTs at various discharge rates were shown in Fig. 1(c) and (d) respectively. From these curves, it is found that the specific capacity, energy density and voltage plateau of Li/CF$_x$ batteries with different amount of MWCNTs exhibit few differences at low discharge rate, while at high discharge rate the Li/CF$_x$ battery containing more MWCNTs shows obviously better discharge performance than battery containing fewer MWCNTs. The voltage plateau is nearly 2.2 V and the specific capacity is approximately 712 mAh g^{-1} of Li/CF$_x$ battery whose cathode contains 11.09 wt.% MWCNTs as conductive additive at the discharge rate of 1 C.

A widely accepted discharge reaction of Li/CF$_x$ battery is described as follows [24]:
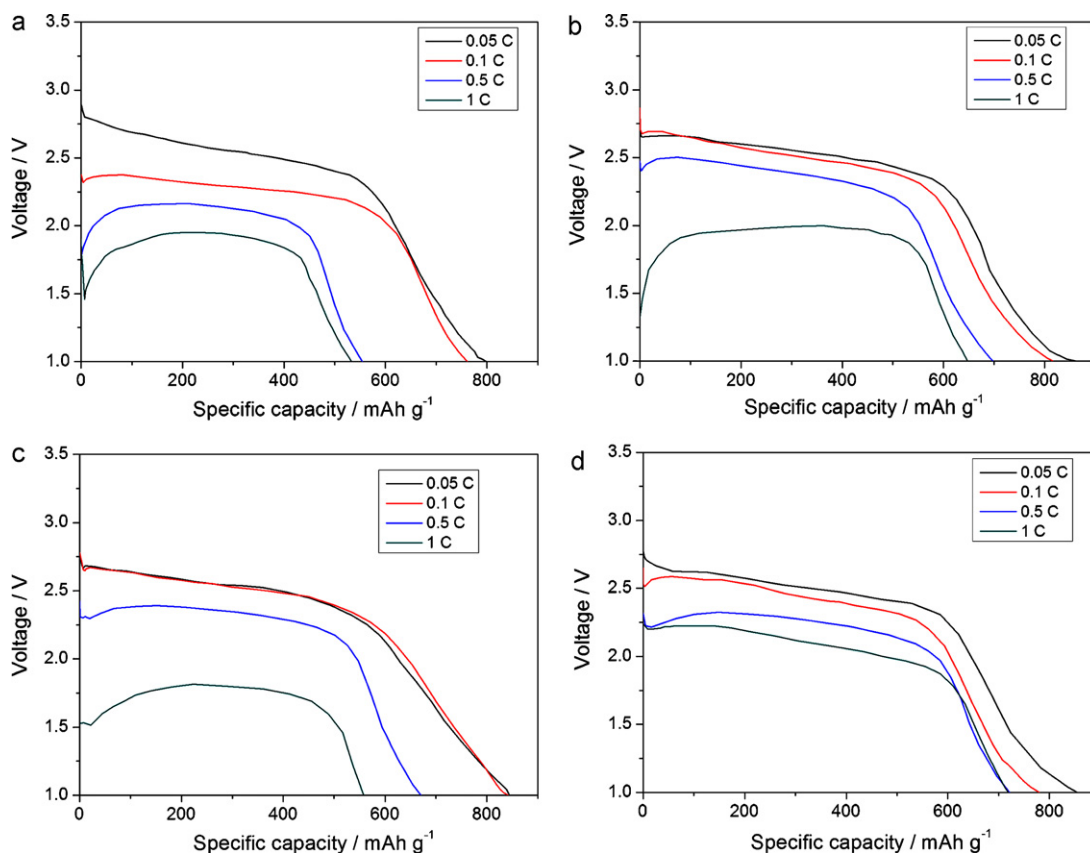
$$\text{Anode}: \quad x\text{Li} + x\text{S} \rightarrow x\text{Li}^+\text{S} + xe \tag{1}$$

$$\text{Cathode}: \quad \text{CF}_x + x\text{Li}^+\text{S} + xe \rightarrow \text{C(Li}^+\text{S–F}^-)_x \tag{2}$$

Fig. 1. The galvanostatic discharge curves at different discharge rates of sample 1 (a), sample 2 (b), sample 3 (c) and sample 4 (d) Li/CF$_x$ batteries. The cathode components of these samples are accordant to Table 1.

where S represents one or more solvent molecules coordinated with each Li$^+$ ion and C(Li$^+$S–F$^-$) the graphite intercalation compound (GIC) intermediate that subsequently decomposes into the final discharge products, carbon and lithium fluoride, as shown as below:

$$C(Li^+S–F^-)_x \rightarrow C + xLiF + xS \tag{3}$$

The cathode reaction contains three steps, which are the diffusion of solvated lithium ions in fluorine layer, the formation of GIC intermediate and the injection of electrons from current collector into CF$_x$ and the dissociation of GIC intermediate. It has been demonstrated that the lithium ion diffusion is the key step in controlling the cathode reaction progress and the inefficient solvated lithium ion intercalating into fluorinated layers is the main reason blocking the discharge performance of Li/CF$_x$ battery at high discharge rate [25]. The diffusion rate of lithium ion in the solid phase can be represented by the Fick diffusion law:

$$N'_A = -DA\frac{dC_A}{d\delta} \tag{4}$$

where N'_A is the diffusion rate of component, D is the diffusion coefficient, A is the contact area of interphase mass delivery, δ is the diffusion distance, and $dC_A/d\delta$ is the concentration gradient. In the case of employing MWCNTs to alternate traditional carbon materials as conductive additive, it has been found that the formed resilient networks of MWCNTs, shown in Fig. 2(a), can expand the cathode's volume of lithium ion batteries, providing broader surface area for lithium ion diffusion [22,23]. In addition, MWCNTs can contact with active materials by point-contact pattern just like ultrafine carbon suspension [26]. Therefore, the contact area of interphase is enlarged remarkably by using MWCNTs as conductive additive, improving the diffusion of solvated lithium into the fluorinated layers and the discharge performance of Li/CF$_x$
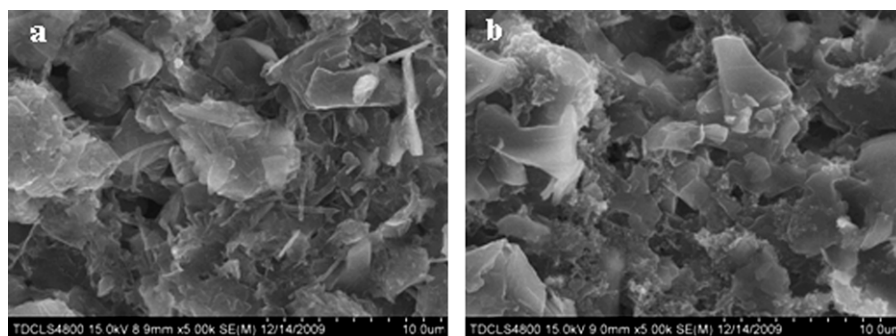

Fig. 2. The SEM images of cathodes by using MWCNTs (a) and acetylene black (b) as conductive additive, respectively.
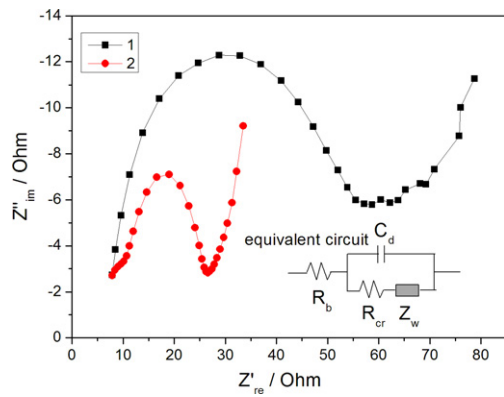
Fig. 3. The EIS spectra of Li/CF$_x$ batteries discharged completely by using acetylene black (1) and MWCNTs (2) as conductive additive in the three-electrode configuration at room temperature in the frequency range from 0.01 to 10 kHz. The components of cathode are accordant to the samples listed in Table 1 with the same number.

battery subsequently, especially at higher discharge rate. Furthermore, the obviously higher electronic conductivity of MWCNTs (1.67×10^3 S m^{-1}) than that of acetylene black (5.26×10^2 S m^{-1}) and the one-dimensional structures of MWCNTs favor electrons delivery through the electrode to CF$_x$ as well as the separated CF$_x$ particles connected by the three-dimensional networks of MWCNTs [27]. As a result, the rate of two main steps in the cathode reaction is accelerated by employing MWCNTs as the conductive additive. Additionally, MWCNTs also have outstanding thermal conductivity [26] and mechanical strength [28], which can dissipate the generated heat during the discharge process effectively and prevent the cracking and the swelled lithium fluoride blocking the diffusion of lithium ions [29]. Therefore, the discharge performance of Li/CF$_x$ battery improves subsequently by using MWCNTs as conductive additive.

In order to verify the proposed hypothesis of the improved discharge performance induced by using MWCNTs as conductive additive, especially at higher discharge rate, the impedance studies are performed. Fig. 3 shows the Nyquist plots of impedance for the Li/CF$_x$ batteries, using the same amount of acetylene black and MWCNTs as conductive additives respectively, after being completely discharged under the rate of 1 C, which are combinations of a depressed semicircle in high frequencies and a straight line in low frequencies. Interpretation of the impedance spectra was based on the equivalent circuit of the inset in Fig. 3. The symbols R_b, R_{cr}, C_d, and Z_w denote the ohmic resistance, cell reaction resistance, capacitance of the double layer, and Warburg impedance, respectively. The R_b represented by the intercept at high frequency is contributed by the current collector, electrode, separator and electrode [24]. Because of the completely discharging, the main conductive particles in cathode of Li/CF$_x$ battery are the produced carbon. Therefore, the R_b is small and dose not exhibits obviously differences of batteries, regardless of the employed conductive additives. However, the R_{cr}, represented by the semicircle of impedance spectrum, of Li/CF$_x$ battery containing MWCNTs is obviously smaller than that of the battery using acetylene black as the conductive additive. The R_{cr} is the combined effect of the contact resistance between conductive particles, product shell resistance and charge-transfer resistance [24]. It has been demonstrated that MWCNTs enable to facilitate the electrons delivery through the electrode to CF$_x$ and the separated CF$_x$ particles, so the charge-transfer resistance and the contact resistance between conductive particles decrease remarkably and the R_{cr} of battery using MWCNTs as the conductive additives reduces subsequently. In the low frequency region, the faradaic reaction is the main effect. It has been asserted that the slope of the impedance in the low frequency region can indi-
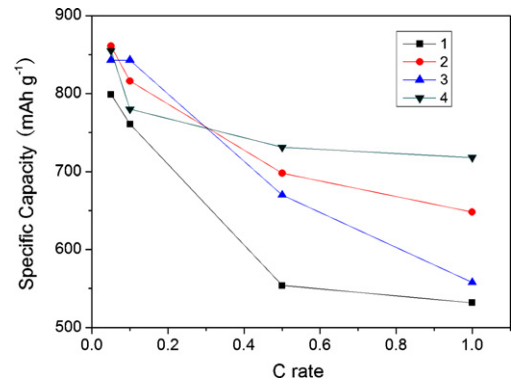

Fig. 4. Comparison of specific capacities of Li/CF$_x$ batteries with different conductive additives. The numbers are accordant to the samples listed in Table 1.

cate the level electrochemical activity and the lithium ion diffusion in the solid state [17,19,20]. The bigger slope of the impedance of the Li/CF$_x$ battery using MWCNTs as conductive additive than that of battery employing acetylene black as conductive additive indicates that MWCNTs can enhance the diffusion coefficient of lithium ion to fluorinated graphite and this effect is caused by the enlarged contact area and MWCNTs wiring [17]. Meanwhile, the frequency in the onset between the semicircle and the slopping straight line of Li/CF$_x$ containing MWCNTs is higher than that of the battery containing acetylene black, which indicates for the higher reaction kinetics when MWCNTs are employed as conductive additive [11].

Moreover, it can be observed from Fig. 4 that the specific capacity of Li/CF$_x$ battery is enhanced with the increase of MWCNTs' amount at high discharge rate (higher than 0.5 C), though this effect is not observed at lower discharge rate, which indicates that increasing the amount of conductive additive can promote the discharge performance at higher discharge rate. The energy density and average power density of the batteries also increase when MWCNTs are used as conductive additive and it can be found the average power density of Li/CF$_x$ battery is enhanced with the increase of MWCNTs' amount at high discharge rates, from the Ragone plot of all the batteries (Fig. 5). These results imply that the discharge performance of Li/CF$_x$ battery is mainly controlled by the active fluorinated graphite when discharge rate is low and the battery with more CF$_x$ exhibits better performance subsequently; whereas the discharge performance of Li/CF$_x$ battery is determined by lithium ion diffusion when discharge rate becomes higher and the battery with more amount of MWCNTs facilitates this diffusion and shows better performance. The batteries using MWCNTs as conductive additive in this study are comparable to the earlier reports concerning on improving the performance of Li/CF$_x$ bat-
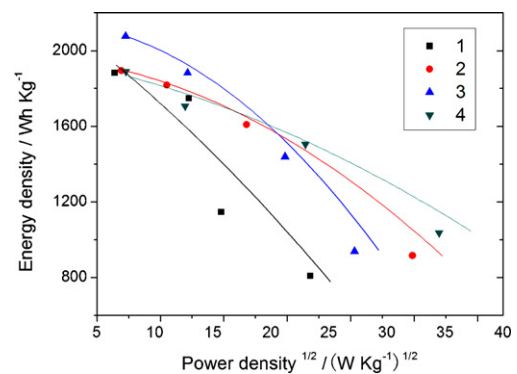

Fig. 5. Ragone plot of Li/CF$_x$ batteries with different conductive additives. The numbers are accordant to the samples listed in Table 1.

teries at higher discharge rate [12,24] and employing MWCNTs as conductive additive as well as increasing their amount in the cathode is convenient to improve the discharge performance of primary lithium batteries at high rate.

4. Conclusion

MWCNTs have been employed to be the conductive additive of Li/CF$_x$ battery as an alternative of traditional carbon materials. The storage performance of Li/CF$_x$ battery using MWCNTs as conductive additive is obviously improved, comparing to the one using acetylene black as conductive additive, and its specific capacity reaches the theoretical capacity at low discharge rates. The discharge performance of these batteries at high discharge rates improves with the increase of MWCNTs amount in the cathode. The enhanced rates of lithium ion diffusion into the CF$_x$ and the electrons transport in the cathode, caused by the formed three-dimensional networks of MWCNTs and the intrinsic excellent electrical conductivity of MWCNTs, are the main reasons of the improved discharge performance of Li/CF$_x$ battery and these effects are demonstrated by impedance spectra. This study provides a very facile and convenient way to enhance the electrochemical performances of lithium primary batteries and indicates that the discharge performance can be tuned by the amount of conductive additive based on the employed discharge rate.

Acknowledgments

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