Short communication

Carbon-coated fluorinated graphite for high energy and high power densities primary lithium batteries

Q. Zhang [a,*], S. D'Astorg [a], P. Xiao [b], X. Zhang [c], L. Lu [b]

[a] Department of Materials, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK
[b] Department of Mechanical Engineering, National University of Singapore, Singapore, 117576, Singapore
[c] Ultralife Corporation, Ultralife Batteries Brand, 2000 Technnology Parkway, Newark, NY 14513, USA

ARTICLE INFO

ABSTRACT

The electrochemical performances of fluorinated graphite have been improved by coating a uniform carbon layer on commercial CF_x ($x = 1$) powder used as cathode material in lithium battery. In comparison with the cell using un-coated CF_x as cathode, the cell using carbon coated CF_x cathode has a higher energy density and higher power density, particularly at higher discharge current rates (1C above). This is because the conductive carbon coating provides the exterior connectivity between particles for facile electron conduction, resulting in high rate performance.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Primary lithium batteries are commonly used for many applications such as cameras, electrical lock, electronic counter, electronic measurement equipment, emergency power source, memory back-up, military and implantable medical devices. These applications require power sources with high energy densities, good reliability, safety and long life. Li/graphite fluoride (CF_x) cells are known to have the highest theoretical capacity when compared to other primary lithium batteries such as $Li/SOCl_2$ and Li/MnO_2 batteries. The overall discharge reaction of a Li/CF_x cell is expressed as "$CF_x + xLi \rightarrow C + xLiF$". According to this reaction, the specific capacity of this cell increases with the increase of fluorine content, x [1]. The theoretical specific discharge capacity Q_{th}, expressed in $mAh\,g^{-1}$, is given by Eq. (1) [2].

$$Q_{th} = \frac{xF}{3.6(12 + 19x)} \quad (1)$$

where F is the Faraday constant (96,485 C/mol) and 3.6 is a unit conversion constant. Theoretically, a CF_x with $x = 1$ has a specific capacity of 865 mAh g^{-1}, about twice that of $SOCl_2$ currently used in primary $Li/SOCl_2$ batteries. Therefore, carbon fluorides CF_x with x close to unity have been actively studied as cathode materials in

high energy density lithium batteries [3,4]. Two types of synthesis are usually performed to form graphite fluorides: high temperature synthesis at 600 °C and low temperature synthesis at <100 °C. The commercial CF_x materials are normally synthesized at high temperature. The most important features of the Li/CF_1 (synthesized at high temperature) batteries are: high average operating voltage (around 2.4 V vs. Li^+/Li), long shelf life (>10 years at room temperature), stable operation and wide operating temperatures (−40 to 170 °C) [1]. In most non-aqueous liquid electrolytes, CF_1 cathode materials obtained at low temperature has an open circuit voltage (OCV) of 3.2–3.5 V vs. Li^+/Li. However, discharge voltage of a real Li/CF_x cell ($x = 1$) is much lower than this value, showing significant polarization [5] and average discharge voltage is lower for more covalent materials [6]. One reason for this high polarization is the low electronic conductivity of strongly covalent CF_1 materials. This kinetic limitation leads to the batteries being able to sustain only low to medium range discharge currents. In order to develop such batteries for new applications such as for soldier portable power sources [7] and for space long term exploratory missions, the range of achievable discharge currents should be extended, so as to increase the power density. To reach this goal, many efforts have been made. For example, Yazami et al. [1,2] synthesized a series of subfluorinated Li/CF_x ($x < 1$) cells with much improved power capability. However, their success was made at a cost of specific capacity.

In this study, we report the improvement of current density (2C) of Li/CF_x cell by coating a carbon layer on the commercial CF_x mate-
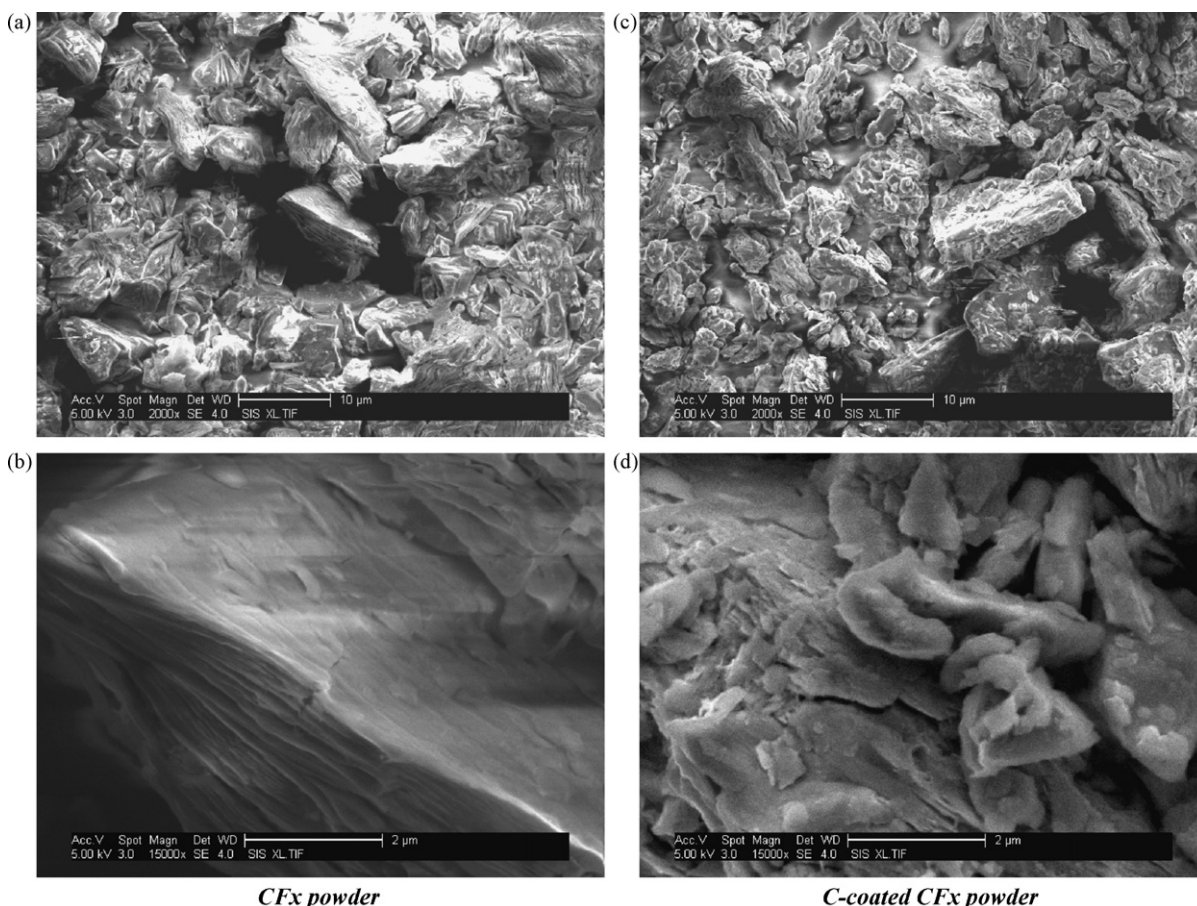

Fig. 1. SEM images of graphite fluoride at different magnifications: (a and b) CF_x and (c and d) CF_x/C.

rials aimed at increasing the electrical conductivity of CF_x cathode materials.

2. Experimental

2.1. Sample preparation

Fluorinated graphite (CF) powder with particle size of 6–10 μm was provided by Lodestar Inc. and used as the active cathode material. Polyvinylidene difluoride (PVDF) (Sigma, UK) material was used as the carbon precursor. The PVDF was first mixed with acetone and formed a slurry, and then the CF powder was well added to the PVDF–acetone slurry and stirred to form a homogeneous mixture and then allowed to be gradually dried. Finally, the PVDF–graphite mixture was heat-treated at various temperature up to 600 °C in nitrogen for 2 h, the PVDF converted to form a very thin layer of carbon coatings on each individual CF particle's surface. PVDF acts as the carbon source resulting in a uniform carbon coating on CF_x particles.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained using a Siemens D5005 diffractometer with Cu K_α radiation and a Goebel mirror. Scanning electron microscopy (S-FEG SEM) combined with an Oxford EDX analysis system was performed on a Philips XL30.

2.3. Electrochemical study

Typical electrodes are composed of graphite fluoride (with or without carbon pre-coating, 75% by weight, w/w), carbon black (15%, w/w) to insure electronic conductivity and PVDF (10%, w/w) as binder. The mixture was rolled into a thin film onto an aluminum foil current collector disk of 10 mm in diameter. Finally, the disk was dried in a vacuum oven at 120 °C for 12 h, to remove traces of water. The mass of active material was 0.28–0.48 mg for all the experiments. A two electrodes cell was used (Swagelok cell type), where lithium was used as both reference and counter electrode. A Celgard separator wet with 1.0 M $LiPF_6$ EC:DEC (1:1 by weight) electrolyte, was sandwiched between the composite electrode and a lithium metal foil. The cells were assembled in an argon filled dried glove box. Relaxation was performed for at least 5 h until open circuit voltage being stable. Galvanostatic discharges were carried out on a Neware battery test station at room temperature (24 °C), where 1C rate equals 865 mA g^{-1}. Discharge capacities detailed in this article have been obtained for a cell cut-off of 1.5 V.

3. Results and discussion

The color of commercial CF_x is white-grey and the carbon-coated CF_x is black. The XRD patterns (not shown here) for CF_x and carbon-coated CF_x are identical, indicating that carbon coating does not change the basic crystal structure of CF_x. Fig. 1 shows the SEM images of both un-coated and coated CF_x. The particle sizes of both samples range from 2 to 6 μm. The carbon coated CF_x powders tend to aggregate, which may be caused by the interaction of static electricity of small carbon particles coated on the surface of CF_x. The morphology of two samples seems to differ. The un-coated CF_x particles (Fig. 1a and b) have a smoother surface with sharper edges in comparison with coated CF_x (Fig. 1c and d). The elemental analysis by EDX on both coated and un-coated samples shows that there is
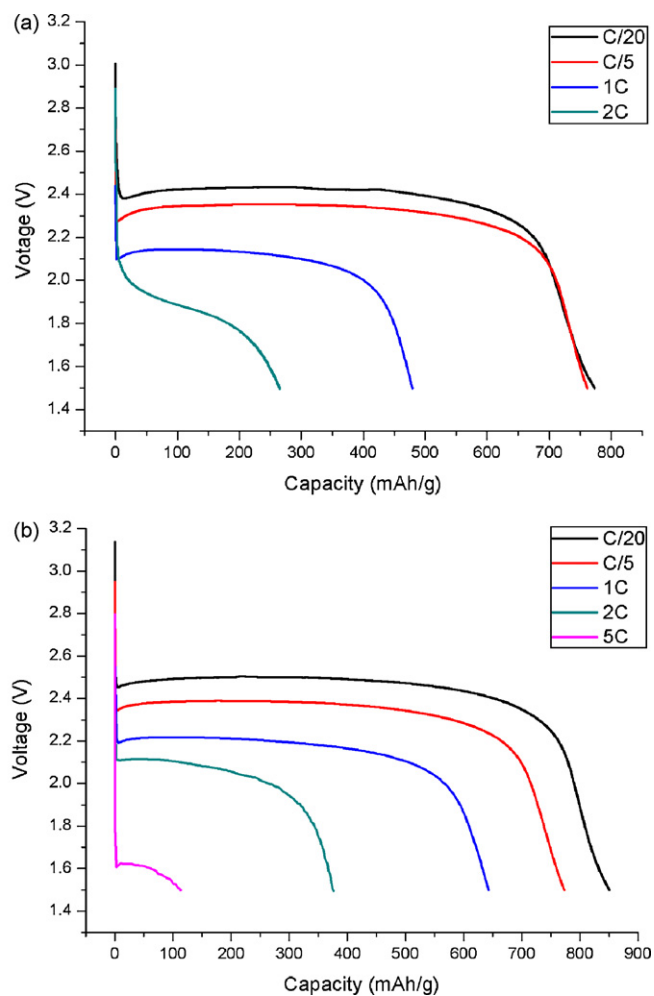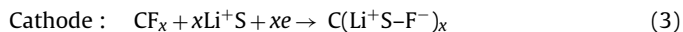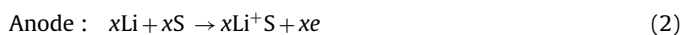
Fig. 2. Galvanostatic discharge curves at different current rates: (a) CF_x and (b) CF_x/C.
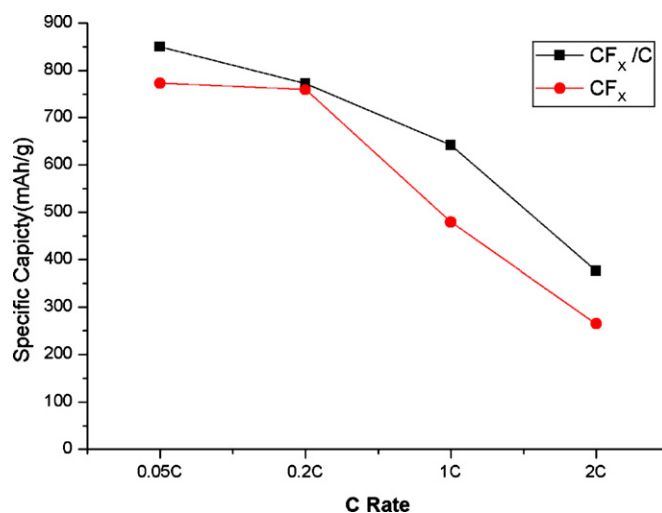

Fig. 3. Comparison of specific capacities of both cells vs. discharge current rate.

final discharge products, carbon and lithium fluoride, as shown below:

$$C(Li^+S-F^-)_x \rightarrow C + xLiF + xS \qquad (4)$$

The cathode reaction takes place in three basic steps: (a) the diffusion of solvated lithium ions in fluorine layer, (b) the formation of GIC intermediate and (c) the injection of electrons from current collector, aluminum foil, into CF_x and the dissociation of GIC intermediate. The mechanism above has shown that the slow diffusion of solvated lithium ions in the GIC intermediate layer is the controlling step in cathode reaction. The slow diffusion would not be improved by coating a carbon layer on the surface of CF_x because the mechanisms in both coated and un-coated cases should remain the same. This has reflected in the results of similar specific discharge capacities and discharge voltage plateaus at low current rates in both cases. An interesting observation is the storage performance at high rates (>1C) (Fig. 3). The specific discharge capacity for the cell using carbon-coated cathode is about 650 mAh g^{-1} at 1C and 370 mAh g^{-1} at 2C while it is only 480 mAh g^{-1} at 1C and 260 mAh g^{-1} at 2C for the cell using un-coated cathode. These results emphasize the need for optimizing the morphology in order to increase the power density. The existence of conducting carbon coating on the surface of CF_x improves the particle connection and favors the electron pathway through the electrode and thus increases the power density, though the whole enhancement of power density is limited. This limited increase in power density of CF_x by coating a carbon layer indirectly indicates that the lithium ion diffusion is a key step in controlling the cathode reaction progress. Table 1 shows the electrochemical performances of carbon-coated graphite fluoride compared with the ones of commercial graphite fluoride. The energy density and average power density of the cells obviously increase after the carbon coating, par-

a 30% increase in C/F ratio for C-coated CF_x sample, indicating there is really a layer of carbon coated on the CF_x. Commercial CF_x contains 39 wt% of carbon, and a 30% increase in C/F ratio for C-coated CF_x sample indicates that the C-coated CF_x contains ~50 wt% of carbon and all the increased carbons are on the surface of the original CF_x. The contribution of the fluorine from PVDF to the capacity is smaller in comparison with the contribution of the carbon from PVDF. Fig. 2 represents the galvanostatic discharge curves of CF_x and CF_x/C samples, obtained at various discharging current densities. While the discharge profile of the Li/CF_x cell exhibits the characteristic plateau around 2.4 V, the discharge profile of Li/CF_x/C shows a slightly higher voltage of 2.5 V. An obvious increase in capacity is showed for the coated sample compared to the uncoated sample and the value of capacity of coated sample gets close to the theoretical one (865 mAh g^{-1}) while the uncoated cell delivers about 90% of theoretical capacity. The voltage of both cells shows a small and current-related delay in the beginning of discharge, and then the voltage slowly recovers to the normal voltage (2.4–2.5 V) until the discharge ends.

A widely accepted discharge reaction of Li/CF_x cell can be described as [8]:

$$\text{Anode}: \quad xLi + xS \rightarrow xLi^+S + xe \qquad (2)$$

$$\text{Cathode}: \quad CF_x + xLi^+S + xe \rightarrow C(Li^+S-F^-)_x \qquad (3)$$

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

Table 1
Electrochemical performances of both cells.

Samples	Theoretical capacity (mAh g^{-1})	C-rate	Energy density (Wh kg^{-1})	Average power density (W kg^{-1})
CF_x	865	0.05C	1815	~110
		0.2C	1743	~387
		1C	1001	~1793
		2C	475	~3081
CF_x/C	865	0.05C	2036	~102
		0.2C	1775	~394
		1C	1379	~2068
		2C	764	~3526

ticularly at high current rates. These results are also better than those in earlier reports on primary Li/CF$_x$ cells, at high rates [1,8]. The reason of discharging rate improvement is because the conductive carbon coating provides the exterior connectivity between particles for facile electron conduction, resulting in high rate performance. However, further optimizing the morphology of the carbon coating is needed, for example, the thickness of carbon coating, in order to obtain the maximum increase of the electron conduction. In another aspect, reducing the commercial CF$_x$ particle size from micrometer to nanometer is an efficient way to shorten the lithium ion diffusion lengths. All of these works are in progress and the results will be reported in another paper.

4. Conclusions

Carbon layer has been coated on the commercial CF$_x$ particles by decomposing PVDF at high temperature in N$_2$ gas. The exterior conductive carbon coating provides connectivity for facile electron conduction, resulting in high rate performances. Carbon coating on the electrode materials thus improves the storage performance of lithium batteries and the specific discharge capacity reaches the theoretical capacity at lower discharge rates. Further optimizing the thickness of the carbon layer is needed in order to further enhance the storage performance at high current rates, and also the

reduction of particle size may provide a shorter length of lithium ion diffusion. We believe that combination of the reduction of particle size and the exterior connectivity by optimized carbon coating would result in a high energy and high power density primary lithium battery.

Acknowledgements

References

[1] R. Yazami, A. Hamwi, K. Guerin, Y. Ozawa, M. Dubois, J. Giraudet, F. Masin, Electrochem. Commun. 9 (2007) 1850.
[2] P. Lam, R. Yazami, J. Power Sources 153 (2006) 354.
[3] R. Yazami, in: T. Nakajima (Ed.), Chemistry, Physics and Applications of Fluorine-Graphite and Fluoride-Carbon Compounds, Marcel Dekker, 1995, p. 251.
[4] N. Watanabe, Solid State Ionics 1 (1980) 87.
[5] D. Linden, T.B. Reddy (Eds.), Handbook of Batteries, third ed., McGraw-Hill, 2002, p. 9, Chapter 4.
[6] J. Giraudet, C. Delabarre, K. Guérin, M. Dubois, F. Masin, A. Hamwi, J. Power Sources 158 (2006) 1365.
[7] A. Suszko, R. Thompson, D. Stevens, Workshop on Carbon Fluorides for Lithium Batteries, Pasadena, CA, February 26, 2006.
[8] S.S. Zhang, D. Foster, J. Wolfenstine, J. Read, J. Power Sources 187 (2009) 233.