

## DISCHARGE CHARACTERISTICS OF A LITHIUM BATTERY WITH FIBROUS CARBON FLUORIDE

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### Summary

Fluorine intercalated carbon fibres,  $(CF)_n$ , have been prepared from benzene-derived, vapour-grown carbon fibres, and have a high degree of preferred orientation of the carbon layers along the fibre axis. The  $(CF)_n$  fibres have been obtained through direct reaction with elemental fluorine at temperatures as low as 300 °C, using carbon fibres of diameter 0.1 - 1.0  $\mu\text{m}$ . The fibres have been used as the cathode material in a lithium battery with 1 M  $\text{LiClO}_4$ -propylene carbonate solution. The discharge potential of  $(CF)_n$  fibres is about 0.5 V higher than that of conventional graphite fluoride  $(CF)_n$  at a load of 0.5  $\text{mA cm}^{-2}$  and with a cathode utilization of ~80%. It is suggested that this high performance is due to the chemical and physical characteristics of the fibrous compounds.

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### Introduction

Vapour-grown carbon fibres (VGCFs) have been prepared by the pyrolysis of hydrocarbons such as benzene and methane, at temperatures around 1100 °C, using the catalytic effect of ultra-fine metal particles with diameters less than several tens of nanometers. The carbon fibres consist of concentric stackings of carbon layers around the fibre axis, *i.e.*, similar to the annual growth rings of trees. It is possible to change the properties of the fibres from a turbostratic carbon to a highly-ordered graphite; this procedure is not possible with PAN-based carbon fibres. By virtue of their structural properties, VGCFs have been regarded as an appropriate host material for fibrous graphite intercalation compounds (GICs). Well staged, ionic-bonded GICs with useful physical properties have been synthesized by the insertion of alkaline metals, metal chlorides [1 - 4], and  $\text{AsF}_5$ .

Using VGCFs, fibrous fluorine intercalation compounds, with covalent bonds between the carbon and the fluorine atoms, have also been prepared by direct reaction of the fibres with fluorine gas. A well controlled fibrous

compound has been synthesized [5, 6] with an aspect ratio (length/diameter) of more than 100 and a composition of  $(CF)_n$  (*i.e.*, corresponding to a stage-1 compound). A lithium battery has been constructed with a cathode consisting of fibrous fluorine-intercalation compounds of VGCFs and with an electrolyte of 1 M  $LiClO_4$ -propylene carbonate. Tests have shown that this cathode exhibits a high degree of performance. VGCF-fluorine compounds gave a higher open-circuit voltage and also higher discharge potentials than those of flaky compounds made from natural graphite powder [6]. This behaviour may be related to both the chemical and physical characteristics of the fibrous compounds. It has been suggested [6] that the performance of the lithium battery could be further improved by reducing the fibre diameter of the starting carbon used in the fluorination process.

Very thin VGCFs with diameters in the range 0.1 - 1.0  $\mu m$  have been successfully prepared by employing a floating catalyst system of ultra-fine iron particles [7, 8]. Both the structural properties of these VGCFs and their application in lithium batteries are reported in this paper.

## Experimental

Vapour-grown carbon fibres have been prepared using a floating catalyst system of ultra-fine iron particles of diameter 10 nm or less, using benzene as a hydrocarbon source [4]. This involves introducing a mixture of hydrogen, benzene vapor, and ultra-fine iron particles into a reaction tube kept at 1100 °C. A scanning electron micrograph of the VGCFs obtained by this floating catalyst system is shown in Fig. 1. The diameters of the carbon fibres used in the present work were 0.1 - 1.0  $\mu m$ .

Intercalation of fluorine into the VGCFs was achieved by direct reaction between the above pristine VGCF and elemental fluorine under a pressure of 1 atm and at a temperature around 300 °C.

A nickel vessel containing 50 mg of the VGCFs was placed on the bottom of a nickel reaction tube and the total system was evacuated by a rotary pump. After raising the temperature of the reaction vessel to the

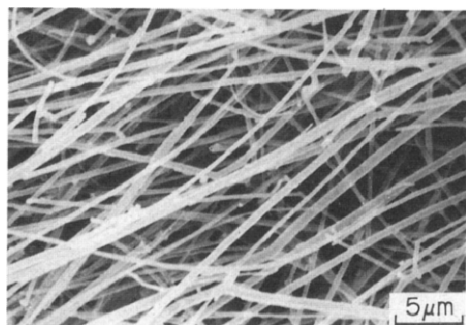


Fig. 1. Electron micrograph of very thin VGCFs prepared using a floating catalyst system of ultra-fine iron particles.

required value, fluorine gas was slowly introduced. After standing for the required time, the reaction tube was cooled to a temperature below 100 °C and the fluorine was replaced by argon gas. Elemental determinations of carbon and fluorine content were performed by a conventional gravimetric method and by an electrometric method using a fluoride-ion electrode, respectively [5]. No residual carbon was detected in any of the compounds.

The electrolyte comprised 1 M LiClO<sub>4</sub> in propylene carbonate. A glass cell used for the studies was designed so that a lithium anode was situated either side of a (CF)<sub>n</sub> cathode pellet. The potential of the (CF)<sub>n</sub> cathode was monitored against a lithium reference electrode via a Luggin capillary [9]. The cell voltage was measured with an operational amplifier having an internal impedance of 10<sup>12</sup> Ω, and was corrected for the small ohmic drop between the cathode and the tip of the Luggin capillary by employing a current-interrupter method. All experiments were carried out in a glove box filled with high-purity argon and maintained at 25 ± 1 °C. The cell was discharged at a constant current of 0.636 mA using a galvanostat. The apparent current density, calculated from the surface area of the cathode pellet, was 0.5 mA cm<sup>-2</sup>. The potential of the cathode was measured by a high precision d.c. voltmeter, and automatically recorded at regular intervals using a microcomputer system. The end-point of discharge was taken as the stage at which the cathode potential was 1 V *versus* the lithium reference electrode.

### Structure of fluorine-intercalated VGCFs

After fluorination to form (CF)<sub>n</sub>, the colour of the thin carbon fibres changed to white. An electron micrograph of the (CF)<sub>n</sub> is shown in Fig. 2. After intercalation of fluorine, the fibres became fragile, but the fibrous nature and the concentric-layer structure (which is peculiar to VGCFs) was still maintained.

Figure 3 shows a high-resolution lattice image of (CF)<sub>n</sub> fibrous material corresponding to stage 1. The interlayer spacings of the wrinkled fringes are

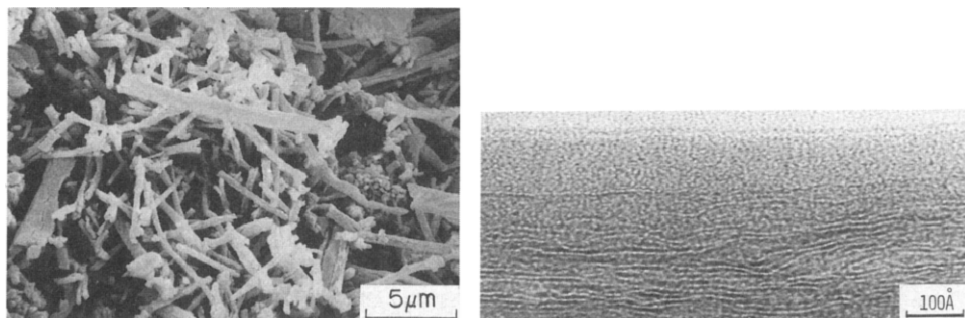


Fig. 2. Electron micrograph of fibrous carbon fluorides, (CF)<sub>n</sub>-VGCF, obtained from very thin carbon fibres.

Fig. 3. High resolution lattice image of stage 1 (CF)<sub>n</sub> fibre.

about 0.8 nm. This value is in good agreement with those determined by X-ray diffraction [6]. The characteristic wrinkled layers are well aligned, with a preferred orientation that is almost parallel with the fibre axis. This preferred orientation is derived from pristine carbon layers by insertion of covalent-bonded fluorine atoms. On the other hand, the layer structure of the present compound is very different from that of ionic-bonded intercalation compounds consisting of straight fringes.

The reaction conditions and the chemical compositions of fluorine intercalated VGCFs are summarized in Table 1. It can be seen that the fluorination temperature drops to 300 °C with decrease in the fibre diameter, and is also considerably below that for natural graphite (*i.e.*, about 600 °C).

TABLE 1

Pristine fibres, reaction conditions and composition of fluorinated carbon fibres

(CF) <sub>n</sub>	Pristine	Fluorinated temperature (°C)	Fluorinated time (h)	F/C ratio
Sample A	thick-VGCF (10 μm φ)	340	72	1.09
Sample B	thick-VGCF (5 - 8 μm φ)	340	72	1.06
Sample C	thin-VGCF (0.1 - 1 μm φ)	300	96	1.09
Flake	natural graphite	594	24	1.00

### Discharge characteristics of lithium battery

The typical discharge characteristics of (CF)<sub>n</sub>-fibre electrodes are shown in Fig. 4, and are compared with those of thick (CF)<sub>n</sub>-fibres and flaky natural graphite. Table 2 presents the respective average values of the discharge potential, the overpotential, the energy density (output energy/weight of electrodes), and the open-circuit voltage (OCV) both just before discharge and after 25% discharge. The initial OCV was measured after maintaining the cell at open-circuit for 24 h. The value of the initial OCV is influenced by >CF<sub>2</sub> and -CF<sub>3</sub> groups localized at the periphery of the graphite fluoride crystallites [5].

As reported previously [6], the fibrous compounds exhibit a higher discharge potential as the diameter of the carbon fibre is decreased. The discharge potential of the thin carbon fibres under test here (Sample C) is 0.1 - 0.2 V higher than that of other types, and 0.5 V higher than conventional (CF)<sub>n</sub> compounds. This performance results in the energy density of the (CF)<sub>n</sub> fibre being about 20% higher than other (CF)<sub>n</sub> fibres, and about 40% higher than conventional (CF)<sub>n</sub> flake. Since thin and thick fibres have the same OCV, the higher discharge potentials are due to lower electrode overpotentials. The latter is directly influenced by the diffusivity of Li<sup>+</sup> ions into the fibre compound. The smooth insertion of Li<sup>+</sup> into the layered

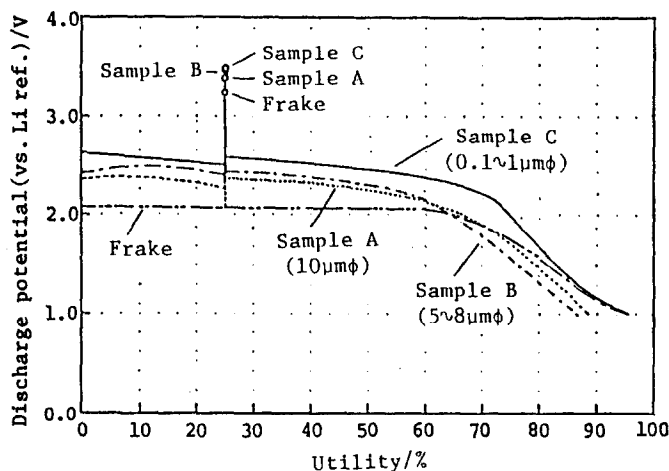


Fig. 4. Discharge characteristics of  $(CF)_n$  fibre electrodes based on thin and thick vapour-grown carbon fibres. (Discharge current:  $0.5 \text{ mA cm}^{-2}$ .)

TABLE 2

Discharge characteristics under a fixed current density ( $0.5 \text{ mA cm}^{-2}$ ) and OCVs of  $(CF)_n/\text{Li}$  batteries

$(CF)_n$	OCV (just before discharge) (V)	OCV (after 25% discharge) (V)	Discharge potential (V)	Over- potential (V)	Energy density ( $\text{Wh kg}^{-1}$ )
Sample A	3.21	3.38	2.44	0.94	1620
Sample B	3.23	3.46	2.48	0.98	1625
Sample C	3.37	3.48	2.57	0.91	1920
Flake	3.22	3.28	2.09	1.19	1400

structure of the fibres may be due to the high degree of preferred orientation of the small  $(CF)_n$  crystallites arranged parallel to the fibre axis. This structural feature may also account for the stable discharge of the electrode. The  $\text{Li}^+$  diffusion process through the solid phase, as well as the subsequent decomposition of the intercalation compounds, have a marked influence on the cell reaction rate [6 - 11].

It has been reported [5, 6] that the structural properties of the pristine carbon material exert a strong influence both on the synthesis of fluorinated carbon compounds and on their resultant electrochemical behaviour. Therefore, the physicochemical properties of the thin, fluorinated, vapour-grown carbon fibres reported here may account for the low overpotential and high discharge potentials observed when these materials are incorporated in lithium cells.

## Conclusions

Very thin, vapour-grown carbon fibres (VGCFs) have been successfully prepared by the thermal decomposition of hydrocarbons under the catalytic effect of floating, ultra-fine iron particles. Using these fibres as the starting material for fluorine intercalation, fibrous carbon fluorides,  $(CF)_n$ , have been obtained and then used in a primary cell with a lithium anode. This cell has exhibited a high discharge potential and a high material utilization, leading to a high energy density. The carbon fibres are discontinuous, and are therefore more useful as the precursor material for fluorination than is the continuous yarn formed from PAN-based and mesophase pitch-based carbon fibres. Furthermore, because of the inherent high degree of graphitization of the present VGCFs,  $(C_2F)_n$  types of thin, fibrous compounds can be formed using high-temperature materials treated at 3000 °C; these provide lithium batteries with high output potentials [9, 10] and with an improved stability (*i.e.*, "flatness") in discharge characteristics.

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