EVALUATION OF CATHODE MATERIALS FOR THE LITHIUM/ CARBONMONOFLUORIDE BATTERY

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Summary

The lithium–carbonmonofluoride $(CF)_n$ system is one of the most promising systems for high energy density primary batteries and is described in this paper. In this system, discharge performances mainly depend on cathode materials, $(CF)_n$, prepared by fluorinating various carbon materials at moderate temperatures. Two kinds of active carbons, graphite and coke, were chosen and tested in cells to determine the best carbon material for the carbonmonofluoride cathode. The $(CF)_n$ cathode made of coke has been shown to have excellent discharge performances, good storage behavior, and an energy density of 140 W h/kg in small button cell sizes.

Introduction

Much research on organic electrolyte lithium batteries has been carried out because these batteries have high energy density, long shelf-life, and excellent discharge capability over a wide temperature range. The most significant research has been in the area of cathode materials for such batteries.

Polycarbonmonofluoride, $(CF)_n$ is one of the most promising cathode materials because of its high theoretical energy density. The $(CF)_n$ system was originally developed by Matsushita Electric of Japan [1 - 3]. In the USA, Eagle Picher [4] and Yardney Electric [5] have been active in developing this system. Gunther [5] examined the fluorine content of the $(CF_x)_n$ system (where $x = 0.75$ - 1.35), and also the amount of conductive additives in the cathode mixture and surfactant added to the electrolyte. Malachesky *et al.* [6] examined the $Li/(C_2F)_n$ system compared with the $Li/(CF_{0.85})_n$ system and Watanabe *et al.* [7] with the $Li/(CF)_n$ system. $(C_2F)_n$ shows a higher level of discharge voltage than $(CF_{0.85})_n$ and $(CF)_n$, but from the viewpoint of energy density and flatness of discharge voltage, $(CF)_n$ is clearly superior to $(C_2F)_n$.

$(CF)_n$ can be prepared by the direct reaction of carbon and fluorine gas at temperatures ranging from about 200 to 600 °C [8]. The reaction is expressed as
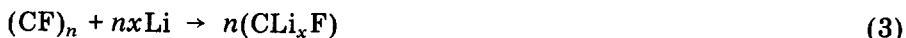
$$nC(s) + \frac{n}{2} F_2(g) \rightarrow (CF)_n(s) \tag{1}$$
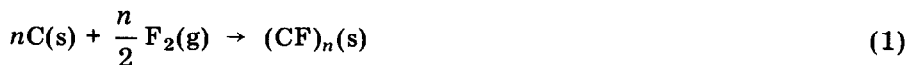
where n is an indefinite, large number.

The theoretical energy density of $(CF)_n$ is 2 600 W h/kg and is greater than those of CuF_2, NiF_2, and MnO_2. The cell reaction of the $Li/(CF)_n$ cell is generally shown as follows.

$$(CF)_n + nLi \rightarrow nC + nLiF. \tag{2}$$

The mechanism of reduction of the carbonmonofluoride cathode is shown as follows by Whittingham [9].

$$(CF)_n + nxLi \rightarrow n(CLi_xF) \tag{3}$$

where $x = 1$.

The $Li/(CF)_n$ cells show different discharge performances depending on the carbon materials used for synthesis of the $(CF)_n$ cathode. This paper presents our research to find the most suitable carbon starting material to be used for the preparation of $(CF)_n$ cathodes for lithium–organic electrolyte cells.

Experimental

Materials

Two kinds of active carbon, types 1 and 2, graphite and coke were examined as carbon starting materials. Artificial graphite was adopted as the example of graphite carbon because there were few impurities in it. Electron microscope photographs of these carbon materials are shown in Fig. 1. Carbon samples were fluorinated at temperatures ranging from 200 to 600 °C by Daikin Industrial Co. Ltd. of Japan. Electron microscope photographs of various $(CF)_n$ materials prepared by fluorination of the carbon are shown in Fig. 2 and, as can be seen, the shapes of $(CF)_n$ particles differ from those of the original carbon materials, though the starting material does have some effect on the morphology.

Figure 3 shows the X-ray diffraction patterns of $(CF)_n$ prepared from the four different starting materials. In each pattern, two peaks are found to exist at $2\theta = 12.5°$ and $2\theta = 45°$ and appear to characterize the $(CF)_n$. While the $(CF)_n$ peaks at 12.5° made from active carbon are blunt, those of $(CF)_n$ made from graphite and coke are relatively sharp. The morphology of the original coke is essentially amorphous, but when fluorinated to $(CF)_n$, it appears more crystalline than the material prepared from graphite. Fluorine contents and specific gravities of $(CF)_n$ are shown in Table 1. As can be seen
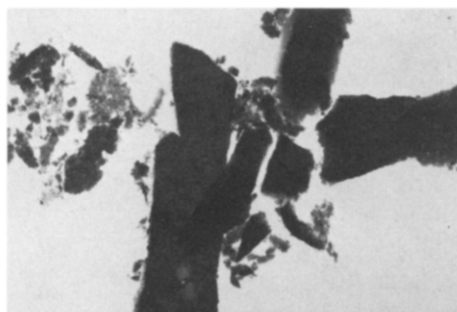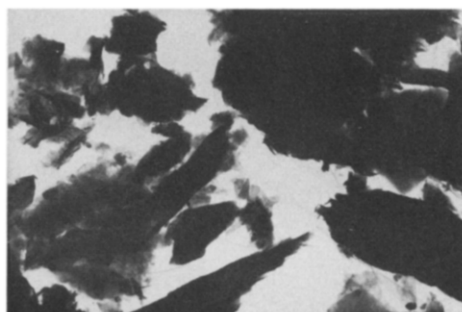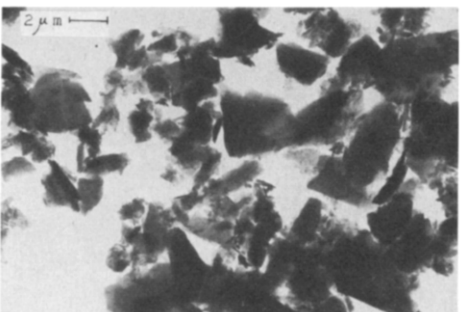
active carbon 1   graphite
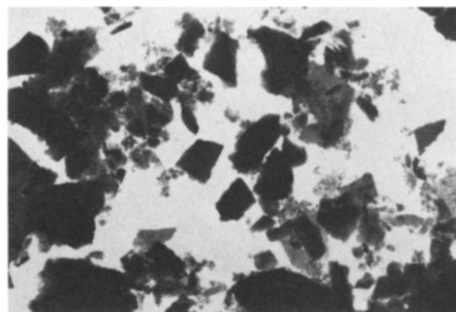
active carbon 2   coke

Fig. 1. Electron microscope photographs of carbon materials. (× 5 000)

from the Table, active carbon and coke are completely fluorinated, whereas graphite is not.

Theoretical gravimetric energy densities of the $(CF)_n$ are calculated and listed in Table 1. Since graphite $(CF)_n$ shows the highest specific gravity, it is likely to be the most advantageous of all from the viewpoint of volumetric energy density.

These four types of $(CF)_n$ were provided as cathode test materials. As a negative electrode, high-purity lithium sheet was used. For the electrolyte, propylenecarbonate (PC) and 1,2 dimethoxyethane (DME) were distilled with lithium metal under vacuum. The water remaining in the distilled PC and DME was kept below 20 ppm. Anhydrous, high grade lithium tetra-fluoroborate ($LiBF_4$) was dried in a vacuum oven at 110 °C for more than 48 h and dissolved in the mixture of PC and DME.

Specific conductivities of $LiBF_4$/PC–DME solution, shown in Fig. 4, were measured for several $LiBF_4$ concentrations over the range from 0.01M to 1.5M at 20 °C with the use of a conductivity meter (TOA Electronic Ltd. Model M-2A). The results show that the most suitable concentration of the electrolyte for optimum conductivity can be considered to be 1 - 1.2M $LiBF_4$ in PC and DME. Therefore 1M $LiBF_4$/PC–DME was used in the following experiments.
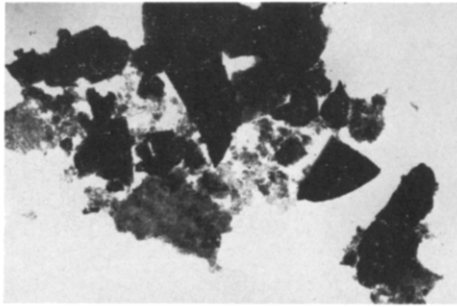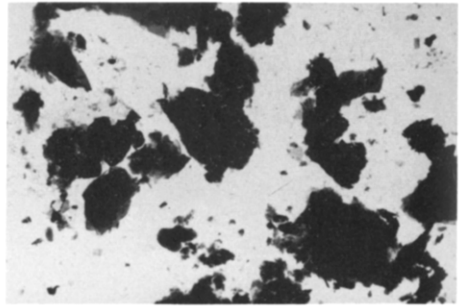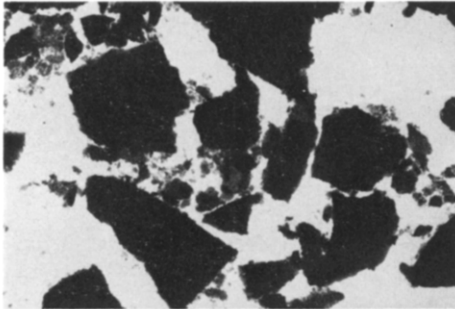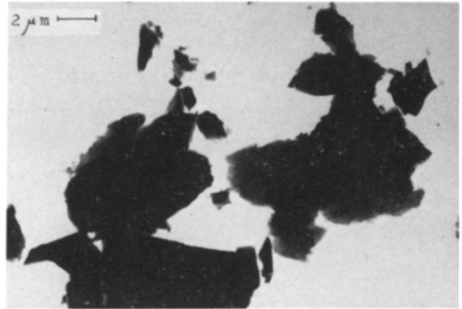
active carbon $(CF)_n$ 1

graphite $(CF)_n$

active carbon $(CF)_n$ 2

coke $(CF)_n$

Fig. 2. Electron microscope photographs of carbonmonofluorides. (×5 000)

H-type glass test cell

To minimize the influence of the quantity of electrolyte, an H-type cell was employed in determining the most appropriate carbon material. Test electrodes consisted of 84 wt.% $(CF)_n$, 9 wt.% acetylene black and 7 wt.% styrene butadiene rubber. The above materials were mixed together and pressure molded on expanded titanium sheet. The test electrode was 20 mm × 20 mm × 1.0 mm in size. The finished cathodes were vacuum dried at 80 ℃ for 24 h. The $(CF)_n$ electrode was surrounded by a non-woven polypropylene separator and put into a model cell with a lithium anode pressed onto expanded nickel metal. The cell construction operations were all performed in Vacuum Atmospheres dryboxes filled with argon to prevent ingress of moisture into the cells.

Results and discussion

Figure 5 shows the typical polarization curves of cells constructed from $(CF)_n$ derived from the four different carbon starting materials. The two kinds of active carbon $(CF)_n$ show the same discharge polarization (rate)
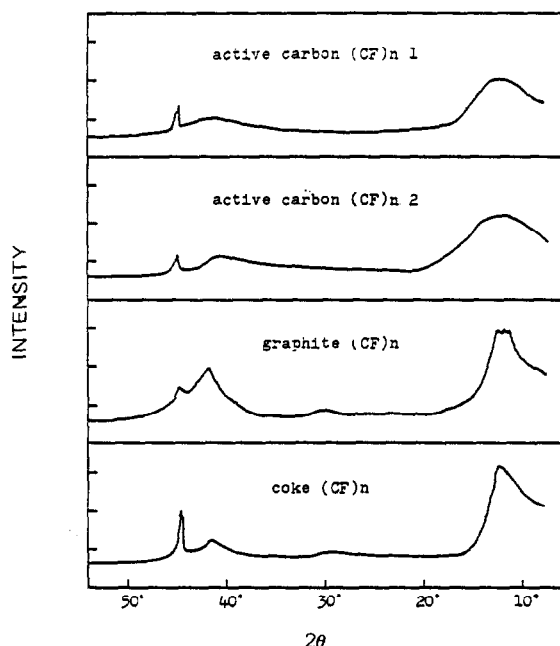
Fig. 3. X-ray diffraction patterns of carbonmonofluorides.

TABLE 1

Physical properties of various types of $(CF)_n$

Carbon material	Active carbon 1	Active carbon 2	Graphite	Coke
Fluorinated percentages (%)	100	100	96	100
Specific gravity	2.3	2.3	2.7	2.5
Theoretical energy density (mA h/g)	864	864	830	864

characteristics. The cell voltage characteristics of active carbon $(CF)_n$ show a higher level than graphite $(CF)_n$ or coke $(CF)_n$ at low current densities, but drop rapidly to show a lower level than graphite or coke $(CF)_n$ at high current densities.

Graphite and coke $(CF)_n$ show similar behavior. Figure 6 shows the effects of temperature on the voltage of the cell discharging at 1 mA/cm^2. The average discharge voltage of active carbon $(CF)_n$ shows a higher level at high temperatures, but drops rapidly to show a lower level than the coke or graphite $(CF)_n$ as the temperature decreases. The graphite and coke $(CF)_n$ show excellent behavior. From these results, graphite- and coke $(CF)_n$ are shown to be superior to active carbon $(CF)_n$.
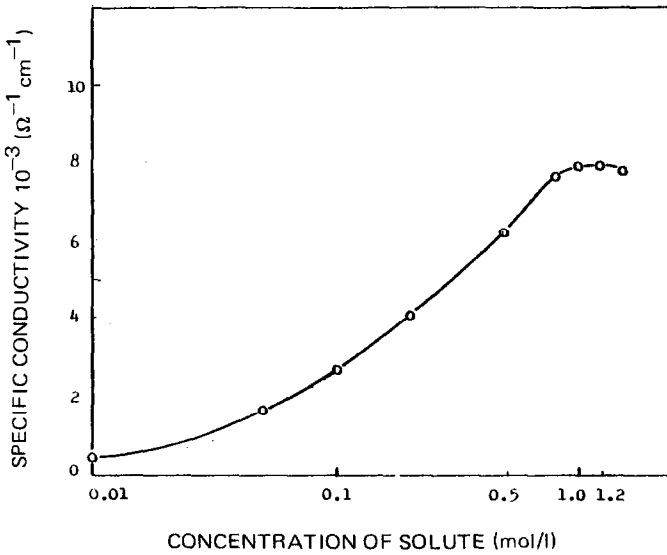
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Fig. 4. Specific conductivity of LiBF$_4$ in propylenecarbonate + 1,2-dimethoxyethane.
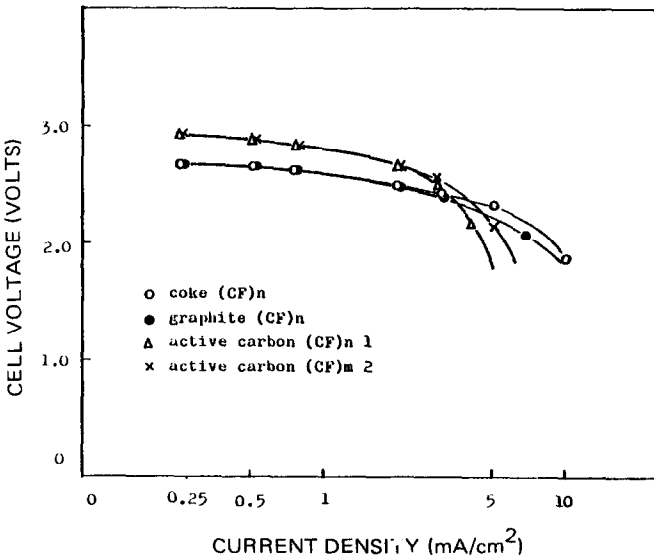

Fig. 5. Voltage–current characteristics of Li/(CF)$_n$ H-type glass cells.

To evaluate the above results further, continuous discharge tests were carried out with the (CF)$_n$ electrode inserted between two lithium electrodes to make a unit cell. Figure 7 shows the discharge characteristics of these cathode materials under 500 ohm load at 20 °C, and Fig. 8 under 75 ohm load. As shown in Fig. 7, the two kinds of active carbon (CF)$_n$ show higher voltages than graphite and coke (CF)$_n$ at the beginning of the discharge, but
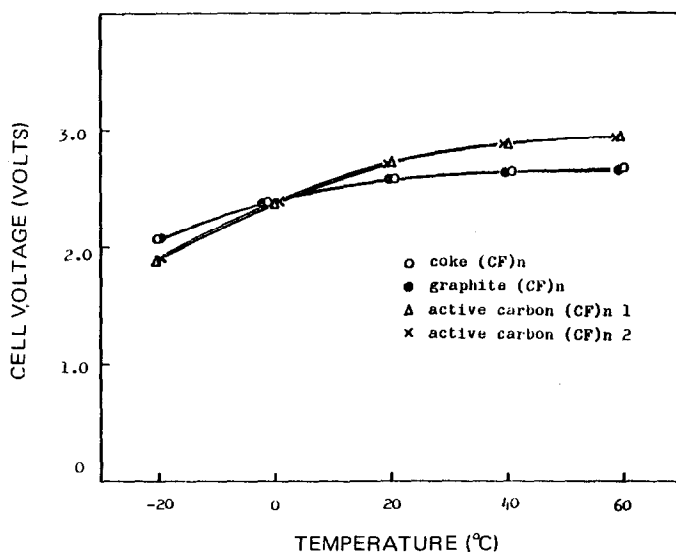
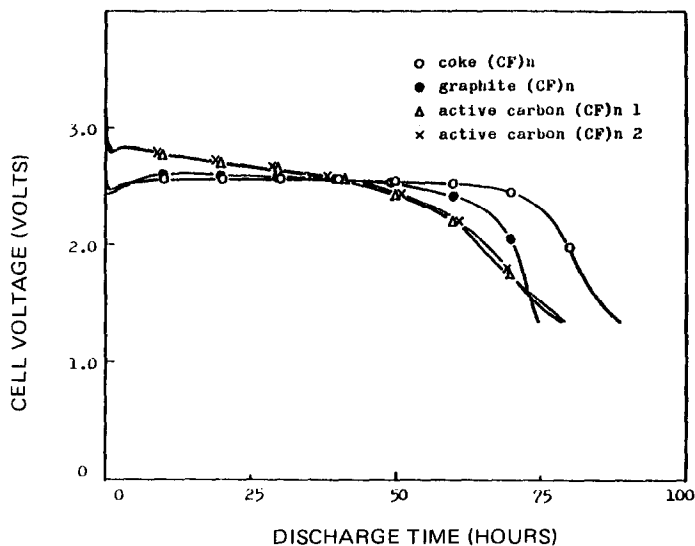Fig. 6. Effect of temperature on the discharge characteristics of the Li/(CF)$_n$ H-type glass cells under 1 mA load.

Fig. 7. Discharge characteristics of the (CF)$_n$ H-type glass cells under 500 Ω load at 20 °C.

gradually show lower voltages than graphite and coke (CF)$_n$ as the discharge proceeds. Graphite and coke (CF)$_n$ show consistently flat voltage curves. From the point of discharge capacity, coke (CF)$_n$ is superior to graphite (CF)$_n$ since the rate for the coke (CF)$_n$ is higher than that of the graphite

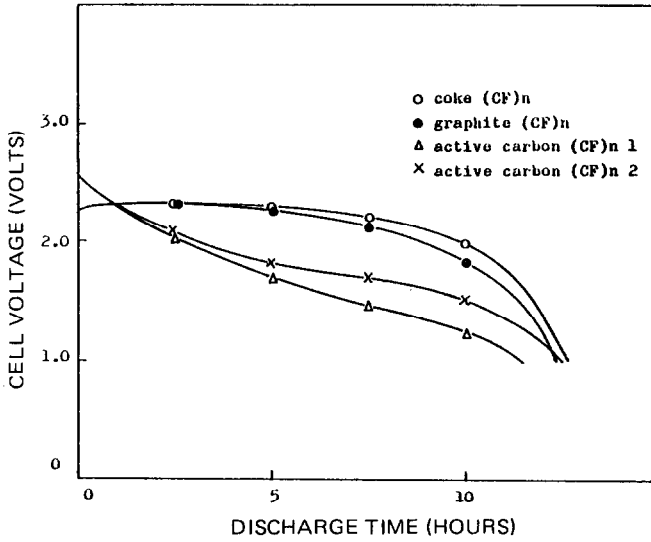Fig. 8. Discharge characteristics of the Li/(CF)$_n$ H-type glass cells under 75 Ω load at 20 °C.

(CF)$_n$. At a high rate discharge, as shown in the Fig. 8, the two kinds of active carbon (CF)$_n$ are evidently inferior to the others.

Finally, the coke (CF)$_n$ is excellent with regard to high rate capability, discharge capacity, and flat voltage curve. To examine the above results, a prototype cell was developed to confirm the practicability of the cell.

Prototype cell

A flat, button-type cell (diameter 23 mm and height 2.5 mm) has been developed as a prototype device. The construction of this cell is shown in Fig. 9.

The cathode and anode cases were made of stainless steel and insulated from each other by a polypropylene gasket. The cathode case was connected to the (CF)$_n$ electrode with a titanium collector and the anode case was connected directly to the lithium electrode. The cathode dimensions were 16.8 mm in diameter and 0.8 mm in thickness. The anode dimensions were 17.8 mm in diameter and 0.34 mm in thickness. These two electrodes were
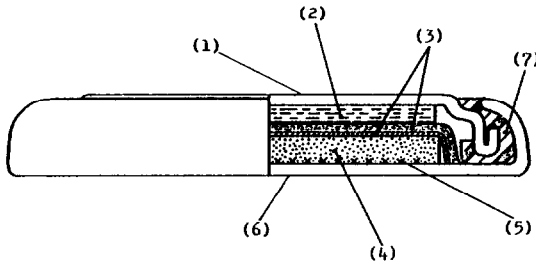

Fig. 9. A cross-sectional view of the Li/(CF)$_n$ flat, button-type cell. (1) Anode case, (2) anode, (3) separator, (4) cathode, (5) Ti screen, (6) cathode case, and (7) gasket.

separated by a porous polypropylene cloth. The electrolyte consisted of 1M LiBF$_4$ dissolved in PC and DME (volume ratio of 1:1). All the cell construction operations were performed in the manner mentioned previously.

Figure 10 shows the discharge characteristics of cells under 1 kΩ load and Fig. 11 under 13 kΩ load, both at 20 °C. Results similar to those with the H-type glass cell were obtained in the experiments using prototype
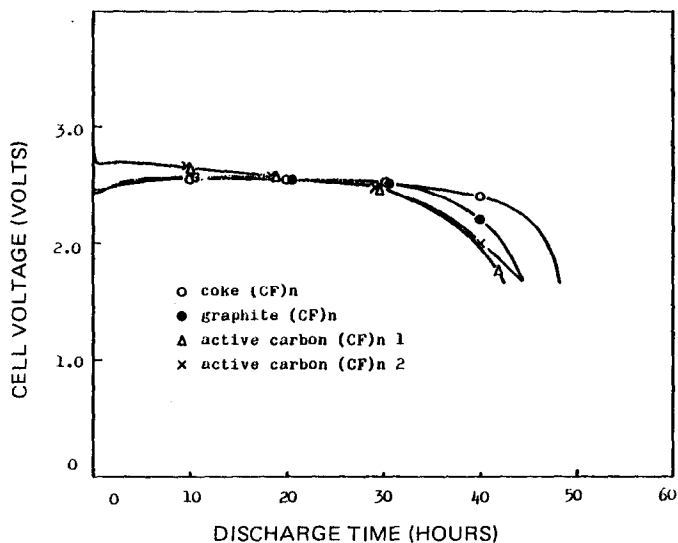

Fig. 10. Discharge characteristics of the Li/(CF)$_n$ flat, button-type cells under 1 kΩ load.

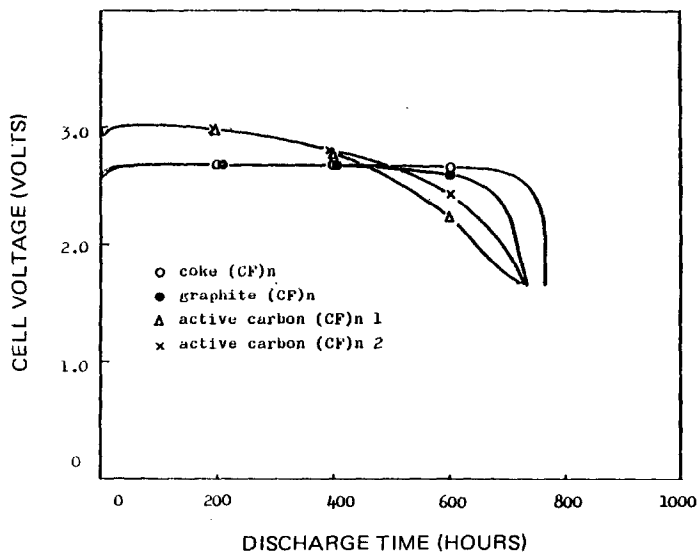Fig. 11. Discharge characteristics of the Li/(CF)$_n$ flat, button-type cells under 13 kΩ load.

cells in which the quantity of electrolyte is limited. In the case of low rate discharge under 13 kΩ load, the discharge voltage of the active carbon $(CF)_n$ cells is higher than that of the graphite or the coke $(CF)_n$ cell at the beginning, but in the case of a comparatively high discharge rate under 1 kΩ load, the phenomenon is not so distinguishable. On the other hand, the coke $(CF)_n$ cell shows a flat discharge curve and the graphite $(CF)_n$ cell a fairly flat discharge curve, even at a high rate discharge. In each case, coke $(CF)_n$ gives the best performance of the cathode materials studied. In the button-cell-size used for the prototype test, the coke $(CF)_n$ cell delivered about 140 W h/kg at 20 °C under a 13 kΩ load.

One of the most important performance criteria of primary cells is long shelf life, even at high temperatures. Figure 12 shows the discharge characteristics at 20 °C under a 1 kΩ load and Fig. 13 under a 13 kΩ load after one month storage at 60 °C. No noticeable loss of capacity was observed after a month of storage, as indicated in Figs. 12 and 13, showing the good storage capability of the Li/$(CF)_n$ system. This is because $(CF)_n$ cathodes are chemically stable in the organic electrolyte.

The phenomenon of voltage delay is observed in all carbon materials, that is, the cell voltage drops initially below the operating level on load and recovers gradually as the discharge progresses. This phenomenon may be attributed to the fact that although $(CF)_n$ is an insulator, the $(CF)_n$ cathode gradually changes to conductive carbon as the reaction proceeds. This fact is shown by employing as a cathode material conductive $(CF)_n$ which has been fluorinated far below 100%.
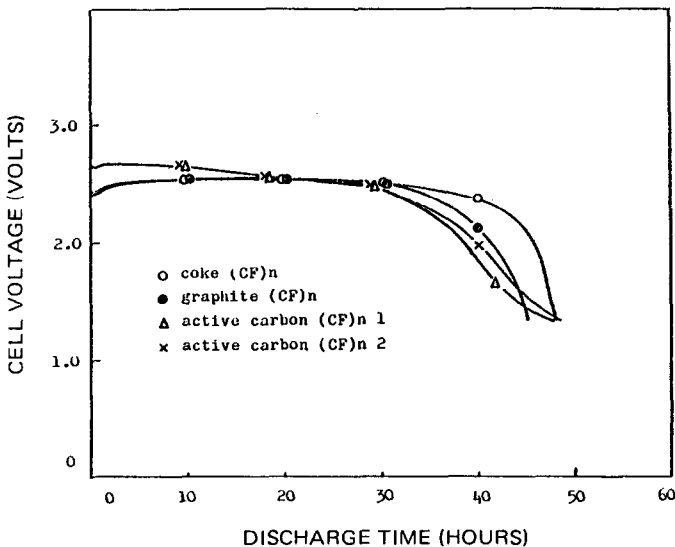

Fig. 12. Effect of high temperature storage, 1 month at 60 °C, on cell discharge characteristics of flat, button-type cells under 1 kΩ load.
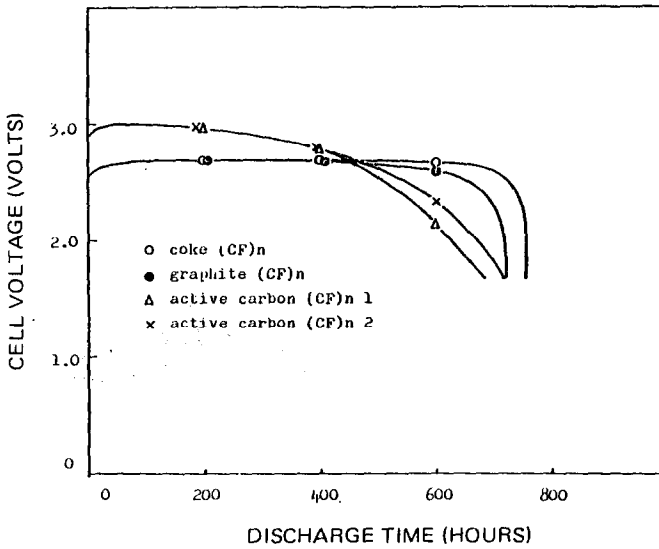
Fig. 13. Effect of high temperature storage, 1 month at 60 °C, on cell discharge character-istics of flat, button-type cells under 13 kΩ load.
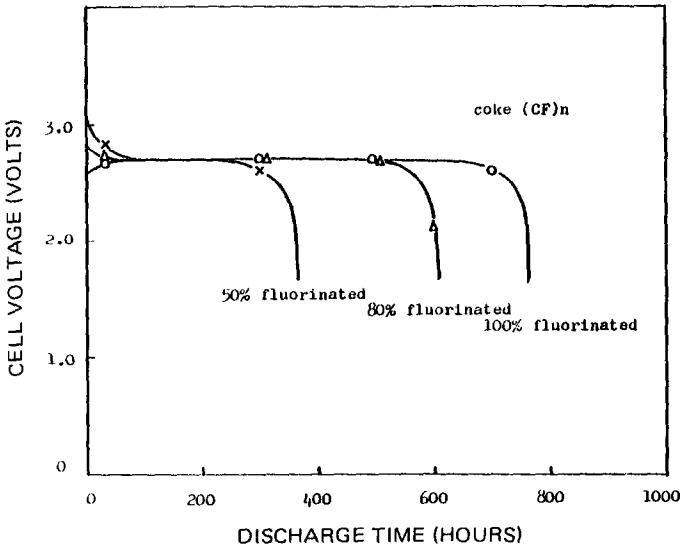

Fig. 14. Discharge characteristics of the Li/(CF)$_n$ (insufficiently fluorinated) flat, button-type cells under 13 kΩ load.

Figure 14 shows the discharge characteristics of insufficiently fluorinated (CF)$_n$ cathodes (fluorinated percentages are 50 and 80%). The cathodes maintained a high level of voltage at the beginning of the cell discharge, that is, the lower the degree of fluorination, the higher the initial value of the voltage. The same (CF)$_n$ cathodes, however, show a lower discharge capacity, as one might expect from the incomplete fluorination. In general use, such a

degree of voltage delay will be negligible. The practical cells using coke $(CF)_n$ as a cathode, are now described.

Practical cell performance

Performances for one type of lithium/$(CF)_n$ practical cell (23 mm dia., 2.5 mm height) for commercial use are shown and summarized in Figs. 15 and 16. Figure 15 shows the discharge characteristics and Fig. 16 the effect of temperature on the discharge characteristics. Several other cells are also available.

The various lithium cells are illustrated in Fig. 17. Specifications of various types of mainly commercial cells are shown in Table 2. Three types of cylindrical cell (BR-C, BR-2/3A, BR-1/2A) have been developed with spirally wound, flexible electrodes. In such cells, containing a fairly large amount of electrolyte, each sealing cap made from a polypropylene disk functions both as a safety vent and as a complete sealing device. These cylindrical type cells have been used in professional wireless transmitters, measuring instruments, surveying equipment, etc.

Miniature pin-type cells (BR435, BR425) consist of a cylindrical cathode and a central anode in an aluminum case. This type of cell has been used mainly as an energy source in LED fishing floats and for microelectronic equipments.

Button-type cells (BR2325, BR2320, BR2016) have been used as a power source for electronic watches and portable calculators. Typical discharge curve and storage characteristics of cylindrical "C" size cells are shown
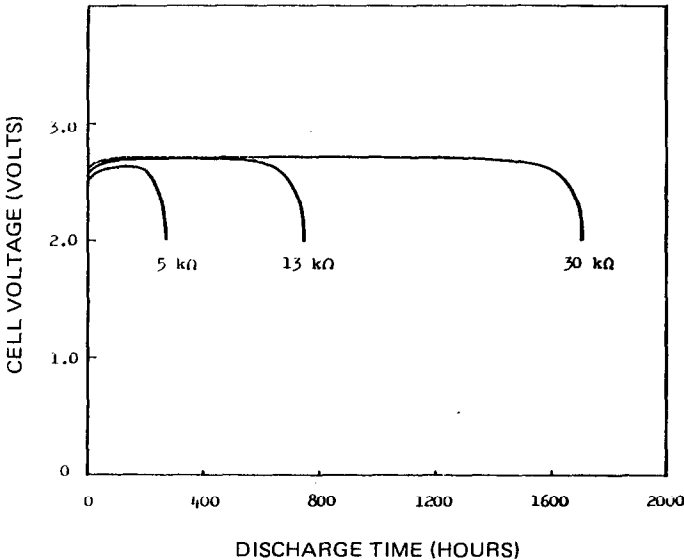

Fig. 15. Discharge characteristics of the practical Li/$(CF)_n$ flat, button-type cells under various loads at 20 °C.
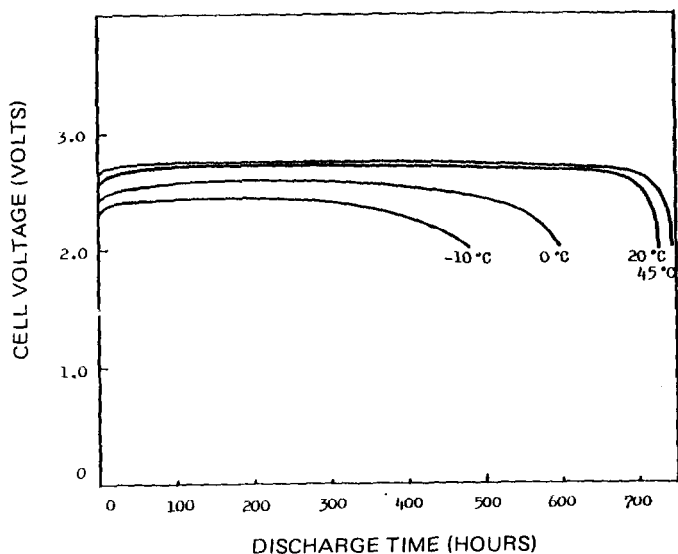
Fig. 16. Effect of temperature on the discharge characteristics of the practical Li/(CF)$_n$ flat, button-type cells under 13 kΩ load.

Fig. 17. Photographs of various practical cells.

in Fig. 18. Storage characteristics of several other commercial cells are similar to this.

Conclusions

Discharge performances of Li/(CF)$_n$ cells mainly depend on the starting materials used to synthesize the (CF)$_n$ cathode. Active carbon, graphite, and

TABLE 2

Specifications of various types of commercial cells

		Spiral type			Inside-out type		Flat type		
		BR-C	BR-2/3A	BR-1/2A	BR435	BR425	BR2325	BR2320	BR2016
Open circuit voltage (V)		3	3	3	3	3	3	3	3
Nominal capacity (mA h)		5000	1200	750	40	20	150	110	60
Dimensions	diameter (mm)	26.0	17.0	17.0	4.2	4.2	23.0	23.0	20.0
	height (mm)	50.0	33.5	23.0	35.9	25.9	2.5	2.0	1.6
Weight (g)		47.0	13.5	9.5	0.85	0.55	3.1	2.5	1.5
Energy density	W h/kg	320	260	230	140	110	140	130	120
	W h/l	560	470	430	290	210	430	400	360
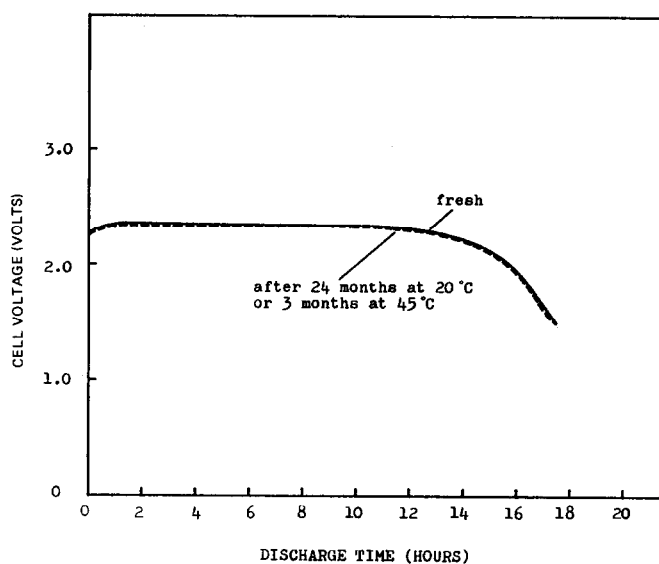
Fig. 18. Typical discharge curves of "C" size $Li/(CF)_n$ cell under 8 Ω load.

coke were tested as the raw materials for the synthesis of $(CF)_n$. Active carbon $(CF)_n$ shows a higher voltage than that of graphite $(CF)_n$ or coke $(CF)_n$ at the beginning of discharge, but shows a lower level as the discharge proceeds. Graphite and coke $(CF)_n$ show good performances in terms of flatness of voltage. While coke is easily fluorinated to 100%, graphite is not, and reaches only 96% of complete fluorination. Consequently graphite $(CF)_n$ has less discharge capacity than coke $(CF)_n$.

Further, coke is the best starting material for the synthesis of $(CF)_n$ with high performance and good chemical stability in organic electrolytes. Thus, coke $(CF)_n$ shows a superior storage performance at room and at high temperatures. In small button cells, it also demonstrates an energy density of 140 W h/kg. Various types of lithium $(CF)_n$ cells are now in commercial use in Japan.

References

1 *U.S. patent 3 536 532 and 3 700 502* to N. Watanabe and M. Fukuda.
2 M. Fukuda and T. Iijima, *Electrochemical Society Fall Meeting, Cleveland, Ohio, October 3 - 7, 1971*, Extended Abstracts No. 41.
3 M. Fukuda and T. Iijima, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 713.
4 D. Linden, N. Wilburn and E. Brooks, in D. H. Collins (ed.), *Power Sources 4*, Oriel Press, Newcastle upon Tyne, 1973, p. 483.
5 R. G. Gunther, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 729.
6 P. A. Malachesky, G. H. Newman and J. A. Shropshire, *Electrochemical Society Fall Meeting, Atlanta, Georgia, October 9 - 14, 1977*, Extended Abstracts No. 10.
7 N. Watanabe and K. Morigaki, *Denki Kagaku, 47* (1977) 35.
8 N. Watanabe and A. Shibuya, *Kogyo Kagaku Zassi, 71* (1968) 963.
9 M. S. Whittingham *J. Electrochem. Soc., 122* (4) (1975) 526.