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Fluorocarbon materials produced by the thermo destruction of polytetrafluoroethylene and possibility of theirs application in Li/$(CF_x)_n$ batteries

S.V. Gnedenkov, A.K. Tsvetnikov, D.P. Opra*, S.L. Sinebryukhov, V.I. Sergienko

Institute of Chemistry of FEB RAS, 159 pr. 100-let Vladivostoku, Vladivostok 690022, Russia

Abstract

A few fluorocarbon compounds $(CF_x)_n$ were produced by the original thermo-gas-dynamic destruction (TD) of polytetrafluoroethylene (PTFE) at the high temperatures 530 and 550 °C. The chemical composition, electrochemical and morphological properties of such materials were characterized by electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM)/X-ray energy dispersive spectroscopy (XEDS) and compared to commercial fluorinated petroleum coke $(CF_1)_n$. The possibility of the application of the new obtained compounds as the cathode materials in primary lithium batteries was estimated. The differences of the investigated samples properties, which observed during electrochemical tests, are discussed.

Keywords: primary lithium batteries; fluorocarbon materials; thermo-gas-dynamic destruction of polytetrafluoroethylene

1. Introduction

It is well known that lithium batteries are the mostly applied power sources in the world at present time. A quite rapid progress of our society, world industry, military forces, and other applications set very high requirements to modern energy and power sources. So they must have following features: high

* Corresponding author. Tel.: +7-423-231-1889; fax: +7-423-231-2590.
E-mail address: ayacks@mail.ru.

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specific energy, maximum of specific power, minimum weight and size, wide temperature range of operation, fire and environmental safety.

According to these requirements the lithium fluorocarbon system Li/$(CF_x)_n$ is a good choice for many applications, but also it has some problems. First of all, Li/$(CF_x)_n$ batteries is low power density devices, because the $(CF_x)_n$ possesses a low electroconductivity. Usually it is not possible to apply such compounds as cathodes without some additives (for example, carbon black or various modifications of graphite) in different quantities (generally 5-15 % of a total cathode weight). Many famous scientists from all over the world are trying to solve this problem, and the very interesting results are presented [1, 2]. However it is still a topical disadvantage for modern Li/$(CF_x)_n$ batteries. The second problem of a Li/$(CF_x)_n$ battery is money- and labour-intensive synthesis of $(CF_x)_n$ compounds, which recently realized by direct fluorination of carbon, graphite, grapheme, petroleum coke, etc.

Here we present the qualitatively new fluorocarbon compound, prepared in the Fluoride Materials Laboratory of the Institute of Chemistry of FEB RAS, which can help to solve the Li/(CFx)n system problems.

2. Experiment

Two $(CF_x)_n$ materials (A and B) were prepared by the original thermo-gas-dynamic destruction of polytetrafluoroethylene at the high temperatures (530 and 550 °C, respectively) [3]. The A compound have a very big amounts of F (F/C=1.7), so the specific energy of Li/A battery may be higher than one for commercial Li/$(CF_1)_n$. The B fluorocarbon is sub-fluorinated material (F/C=0.3), that's why specific power of Li/B battery may be much better as compared to used at present time. In addition the conductivity of A and B samples also may be higher than one of the commercial $(CF_1)_n$, because of free nanosized carbon particles, which present in the $(CF_x)_n$ bulk. Furthermore, TD technique is energy-low method and it can be used for effective PTFE wastes recycling.

The sample particles morphology and their composition were analyzed by SEM and XEDS (Hitachi S5500 microscope). The conductivity of A and B samples was measured by EIS on Impedance/Gain-phase analyzer SI 1260.

A two electrodes cells were assembled to test the electrochemical behavior of the obtained $(CF_x)_n$ materials. Typical electrodes were prepared by mixing of 90 wt.% fluorocarbon powder (A or B) and 10 wt.% polytetrafluprpethylene-based binder F-4D on a steel mesh disc substrate. In this work the carbon black was not used to increase a conductivity of A and B compounds. The thin cathodes (1-3 mm thickness) were vacuum-furnace dried for 12-36 h at 150 °C. The thickness of lithium metal disc anode was ~ 0.2 mm. The diameters of the cathode, anode and separator were 13, 14, and 16 mm, respectively. The microporous polypropylene membrane was used as separator. The electrolyte was 1 mol $LiBF_4$ in γ-butyrolactone. The cells were assembled in an argon filled glove box. Relaxation was performed for at least 5 h until open circuit potential (OCP) stabilization.

Potentiostatic discharge was carried out on the potentiostat/galvanostat 1470E (Solartron) at room temperature during 1 h with applying various operating voltages (2.3 V, 2.5 V, and 2.8 V).

Electrochemical impedance spectroscopy measurements were potentiostatically performed at the cell's OCP with an ac oscillation of 10mV amplitude over the frequencies from 1 MHz to 0.01 Hz on frequency response analyzer 1455 (Solartron) combined with 1470E to study steady state of Li/$(CF_x)_n$ batteries.

A minimum of three cells were used for each test condition.

3. Results and discussions

The SEM-images of A and B powders and commercial $(CF_1)_n$ [4] are shown in Fig. 1a, b and c, respectively. It is clearly that A and B size particles less than 5 μm, while the $(CF_1)_n$ size particles ranges from 10 to 35 μm according to Ref. [4].

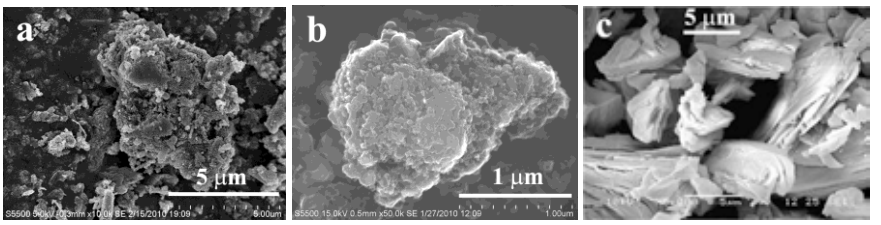

Fig.1. SEM-images of $(CF_x)_n$ compounds: (a) – A [4]; (b) – B [4]; (c) – $(CF_1)_n$ [5].

Thus, the dispersibility of obtained A and B fluorocarbons is rather high. Therefore, the active area of such cathodes is larger and battery discharge rate is faster than ones for $(CF_1)_n$.

Table 1. Characterization of A and B materials

Sample	F/C ratio	Specific capacity, (A·h/kg)	Specific energy, (Wt·h/kg)	Conductivity, (Ohm^{-1}/cm)
A	1,7	1100	3000	$3.4 \cdot 10^{-2}$
B	0,3	445	1250	$1.7 \cdot 10^{-2}$
$(CF_1)_n$	1	860	2200	10^{-12}-10^{-14}

According to XEDS data the F/C ratio was calculated for both samples (Table 1) and this result was used for calculation of theoretical specific capacity and energy (Table 1).

In conformity with impedance spectroscopy data the conductivity of A and B samples is much better than one for commercial $(CF_1)_n$ (Table 1). In addition in spite of B sample characterized by higher C content (XEDS) in compared with A, the values of their conductivity are nearly equal.

According to the obtained data it can be concluded that A material is very perspective as Li/$(CF_x)_n$ system cathode due to its high fluorine content, good conductivity, and small size particles.

For the batteries steady state investigation the impedance spectra were obtained by EIS (Fig. 2).

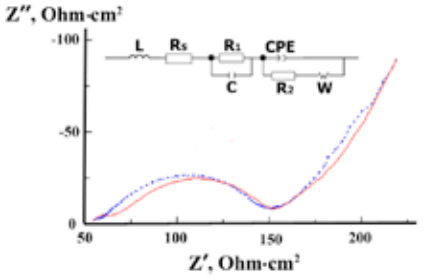

Fig.2. Impedance spectra of lithium batteries with on A (dashed line) and B (solid line) fluorocarbons.

Both spectra have a typical shape and composed of two partially depressed semicircles at high frequency and a straight line in the low frequency range. The battery parameters were estimated by simulation of the impedance data using the equivalent electric circuit (Fig. 2). The R_s is the overall cell resistance, which reflects conductivity of the electrolyte, separator, and electrodes; R_1 and C are resistance and capacitance of the solid electrolyte interface layer formed on the lithium anode; R_2 and CPE are charge-transfer resistance and double-layer capacitance; W is the Warburg impedance related to a diffusion effects of lithium ions in the solid $(CF_x)_n$ bulk.

The $Li/(CF_x)_n$ is discharging step by step and the slowest stage is the Li ions intercalation in the fluorocarbon structure. In the most of cases this solid-state diffusion limits the discharge rate. For the diffusional effects investigation the potentiostatic mode was applied and discharge curve was plotted (Fig. 3). It was shown that the maximum discharge current for such batteries is equal 0.5 mA.

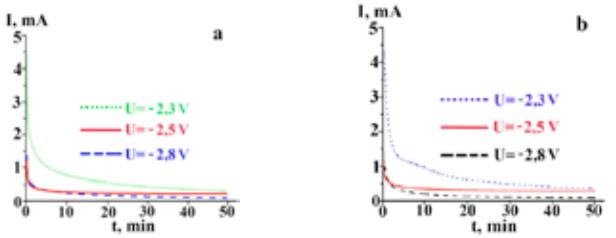

Fig.3. Potentiostatic curves of batteries with A (a) and B (b) materials at various discharge voltage (2.3 V – dotted line, 2.5 V – solid line and 2.8 V – dashed line).

4. Conclusions

In this work the several fluorocarbon materials with various F/C ratios have been produced by original thermo-gas-dynamic destruction of polytetrafluoroethylene at the high temperatures 530 and 550 °C. Their physical and electrochemical properties have been studied and compared with commercial $(CF_1)_n$. For the first time, a full analysis of this type of fluorocarbon materials has been made. Our results show that such compounds could excel the traditional fluorinated petroleum coke. In the samples the free atomic carbon is presented. It could acts as an intrinsic conductor between the fluorocarbon particles. In addition the A material is characterized by high fluorine content that provides the high values of specific capacity and energy.

Acknowledgements

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References

[1] Zhang Q, D'Astorg S, Xiao P, Zhang X, Lu L. Carbon-coated fluorinated graphite for high energy and high power densities primary lithium batteries. *Journal of Power Sources* 2010; **195:** 2914-2917.

[2] Delabarre C, Dubois M, Giraudet J, Guerrin K, Hamwi A. Electrochemical performance of low temperature fluorinated graphites used as cathode in primary lithium batteries *Carbon* 2006; **44:** 2543-2548.

[3] Gnedenkov SV, Sinebryukhov SL, Tsvetnikov AK, Opra DP, Sergienko VI. New fluorocarbon compounds as perspective cathodic materials. *Vestnik DVO RAN* 2010; **5:** 5-11, in Russian.

[4] Lam P, Yazami R. Physical characteristics and rate performance of $(CF_x)_n$ ($0.33 < x < 0.66$) in lithium batteries. *Journal of Power Sources* 2006; **153:** 354-359.