Graphite Fluoride Prepared at Mild Temperature for High Energy/High Power Density Lithium Batteries

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GRAPHITE FLUORIDE PREPARED AT MILD TEMPERATURE FOR HIGH ENERGY/HIGH POWER DENSITY LITHIUM BATTERIES

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ABSTRACT

We used a two-step fluorination of natural or synthetic graphites, the one at the ambient temperature in the presence of F_2 + IF_5 + HF and the second in the temperature range of 100 - 350°C in F_2 atmosphere. This led to graphite fluorides characterized by the planarity of the carbon hexagons (sp^2 hybridization), by the iono-covalent character of the C-F bondings and by the high F/C ratio, close to unity. These graphite fluorides were compared to conventional, highly covalent CF_x (sp^3 hybridization) in their electrochemical performances in lithium batteries, especially regarding the high rate discharge capability.
We found a large advantage with the iono-covalent CF_x that is they sustain a 5 C rate discharge where the covalent ones failed to discharge under 4 C. The difference is tentatively related to the internal structure and to the higher electrical conductivity of iono-covalent CF_x.

Keywords: Carbon fluoride, lithium batteries, high rate capability.

INTRODUCTION

Carbon fluoride of general composition CF_x (x ~ 1) and MnO_2 are the most widely used cathode materials for primary lithium/organic electrolyte batteries. CF_x features: 1) a high specific capacity (>700 mAh/g), 2) a long shelf life (or low self discharge rate) and 3) a good stability at high temperature. Commercial CF_x is prepared at moderatly high temperature

($\geq$ 350 °C) by direct fluorination of synthetic or ungraphitized coke. Such class of CF_x will be denoted HT-CF_x (high temperature).

The drawback of HT-CF_x compared to MnO_2 is a lower discharge voltage (2,4 ~ 2,6 V [1] compared to 2,8 ~ 3,0 V [2]) and a higher cost. The former is due to the high cathodic overvoltage during the fluorine displacement from carbon to lithium to form lithium fluoride [3]. The strong covalency of the C-F bonding affects the electrical conductivity that is HT-CF_x is considered as an insulating material rather than a semi-conducting one.

Since many years, we have been conducting some basic research aimed at understanding the mechanism of the fluorination of graphite at mild temperature and at establishing the relationship between the physico-chemical characteristics and the electrochemical properties of CF_x [4-6]. In this work we show that CF_x obtained in two successive fluorination steps show outstanding electrochemical behavior in lithium batteries, especially regarding high rate discharge performances.

EXPERIMENTAL

1) Two steps fluorination

Natural graphite and graphitized petroleum coke were used in fine powders (10 to 30 µm) and introduced into the fluorination reactor. After evacuation at 350 °C for several hours, and cooling to the ambient temperature, a gas mixture composed of F_2 + IF_5 (formed in-situ) + HF was flown into the reactor during 4 hours. Then only pure fluorine was introduced while the temperature in the reactor was gradually increased to a fixed value denoted T_{ref} (refluorination temperature, $T_{ref} \leq 500$ °C). After 6 hours of reaction at T_{ref}, nitrogen was flown until unreacted fluorine was totally removed. The reactor was then opened and the sample was stored in dry atmosphere. Because of the lower temperature used to prepare such samples, they will be designed hereafter LT-CF_x.

The HT-CF sample was provided by Daikin industries, Ltd. (Japan).

2) Characterizations and electrochemical studies:

LT-CF_x were analyzed by means of XRD and ESCA. The electrodes were prepared by spreading a mixture of CF_x (62,5 wt %) + polyvinylidene fluoride (PVDF - Elf-Atochem 2821) (12,5 wt %) + dibutyl phthalate (DBP 16,7 wt %) + acetylene black (8,3 wt %) in acetone suspension. After evaporation a film was obtained with a typical thickness of 150-250 µm. A disc of 20 mm in diameter was cut from the film then it was washed with

methanol to remove the DBP platicizer, dried and weighted then it was mounted into a coin-type cell (2430). The cell used metallic lithium foil (20 mm in diameter) as the anode and 1 M solution of $LiClO_4$ in propylene carbonate (PC) / ethylene carbonate (EC) / Dimethoxyethane (DME) vol 1:1:2 mixture as electrolyte. Galvanostatic discharge with rate ranging between C/10 to 5C (80 mA/g to 4000 mA/g of CF_x) was applied between the initial open circuit voltage ($\sim$ 3,5 V) and 1,5 V cut-off voltage.

RESULTS AND DISCUSSION

1) XRD and ESCA characterizations:

The main effect of the second fluorination on the XRD charts (not presented here) is the progressive disappearance of the 002 line associated with residual stage-1 GIC formed with iodine fluoride species during the first step of fluorination [4]. In addition the 100 line of CF_x appeared at $2\theta \sim 42°$ (Cu K_α) leading to an in-plane parameter a= 2,46 Å close to that of the parent graphite. This indicates that the carbon remains in the sp^2 hybridization and therefore that the fluorinated graphenes remain planar even after the refluorination at 350 °C. The 001 line remained unchanged or slightly moved to lower diffraction angles as T_{ref} was increased. The interlayer spacing (d_{001} of CF_x) varied between 6,3 and 6,2 Å as T_{ref} was increased between the ambient temperature and 350 °C.

The most significant changes in the LT-CF_x structure was observed in C_{1s} ESCA spectra as shown in figure 1. They are typically composed of two main lines: a first at binding energies 284 eV< C_{1s} < 287 eV and a second in the 287 eV< C_{1s} < 292 eV. The relative intensity of the first line decreases and the line is centered at higher binding energy as T_{ref} increased. Concomitantly, the second line appeared at higher energy with a stronger intensity. For comparison, the spectrum obtained with HT-CF_x is given and shows a main line at 290,5 eV in agreement with previous studies [7]. The first line is generally associated with non fluorinated carbon C-C bonding and the second one to C-F bonding. As T_{ref} increased, the amounts of non fluorinated carbon decreases and the C-F bonding has increased energy. The covalent character is enforced. However, from XRD the sp^2 hybridization is still maintained at least for $T_{ref} \leq 350$ °C. At 500 °C, a large part of the C-F bondings is covalent.
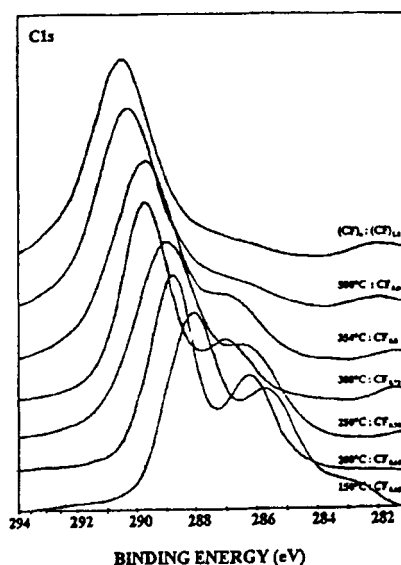
FIGURE 1: Refluorination temperature (T_{ref}) dependance of the C_{1s} ESCA spectra of LT-CF_x. (CF)$_n$ denotes HT-$CF_{1.1}$.

2) Electrochemical performances:

The discharge curves at different rates (C/10 to 5C for LT-$CF_{0.92}$ and C/10 to 3C for HT-$CF_{1.1}$) are shown respectively in figures 2 a and 2 b. Noteworthy is the higher discharge voltage obtained under the same rate with HT-CF_x and LT-CF_x.
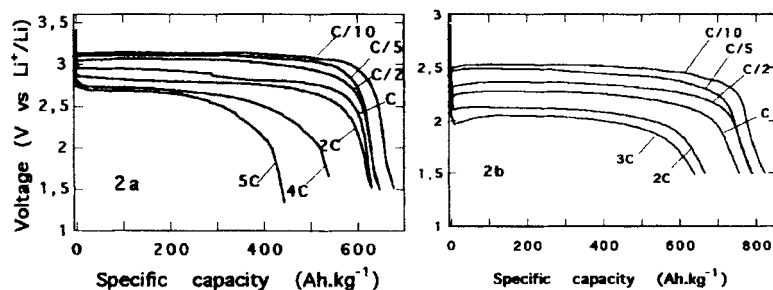

FIGURE 2: Galvanostatic discharge curves of (a) Li/LT-$CF_{0.92}$ and (b) Li/HT-$CF_{1.1}$ under different rates.

In order to compare the energy density output (in Wh/kg of CF_x) achieved with each sample under the same power density (in W/kg of CF_x), we have

drawn the so called "Ragone Plot" for each type of CF_x in figure 3. The outstanding performances of $LT-CF_x$ are clearly shown, that is higher energy density was reached with $LT-CF_x$ at the same power density rate.
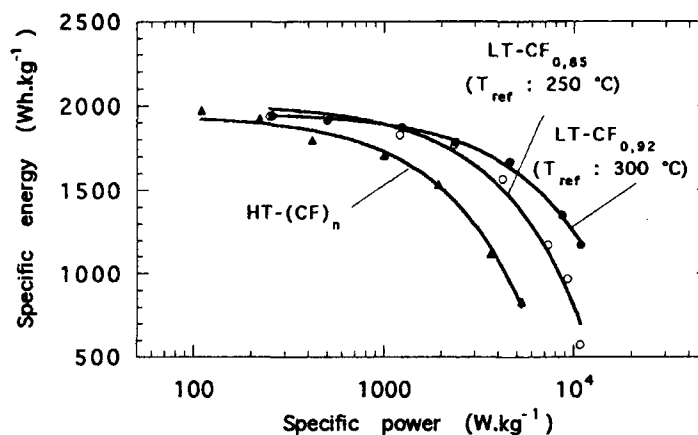

FIGURE 3: Ragone plots of Li/LT-CF_x (T_{ref} = 250°C and 300°C) and Li/HT-CF_x cells.

The cell polarization takes into account a series of overpotentials which tend to decrease the overall voltage during the lithium transfer from one the negative lithium pole to the positive CF_x one. In addition to the ohmic loss within the cell which is the same for LT and HT-CF_x , the main overpotentials actually result from the charge transfer and the diffusion impedances. Such impedances can be compared for LT and HT-CF_x based cells by complex impedance measurements as showed in figure 4 (Nyquist Plots). The spectra were taken after 10% discharge of the cell in order to form the diffusion layer [3]. One can roughly separate the spectra into high, medium and low frequencies areas. At high frequency ($\approx 10^4$ Hz), the first intercept of the Nyquist plot with real part axis of the impedance (Re (Z)) is the same for the two curves ($\approx 2 \ \Omega$). The difference is more pronounced in the second intercept at medium frequencies (1-10 Hz) which lies in the 40 Ω for LT-CF_x and 90 Ω for HT-CF_x . The frequency range is typically associated to the charge transfer reaction ($CF + Li^+ + e^- $——> LiCF). The higher resistance of HT-CF_x is mainly due to its lower electric conductivity and to the higher binding energy of the C-F bonding as shown by ESCA measurements.

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In the low frequency range (1-10^2 Hz) the diffusion is the predominant mechanism. Where LT-CF$_x$ shows a typical Warburg branch (≈ 45 ° with Re(Z) axis), the HT-CF$_x$ one has a more blocking electrode behavior. The higher conductivity and the planarity of the carbon layers in LT-CF$_x$ should be at the origin of higher diffusivity of lithium.
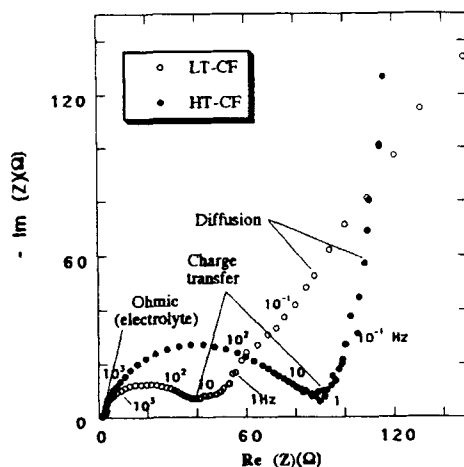

FIGURE 4. Nyquist plots of Li/LT-CF$_{0.92}$ and Li/HT-CF$_{1.1}$ cells.

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