Fluorinated exfoliated graphite as cathode materials for enhanced performances in primary lithium battery

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ARTICLE INFO

ABSTRACT

Accordion-like graphites prepared by exfoliation of a low temperature graphite fluoride were fluorinated using F_2 gas at various temperatures. The fluorinated exfoliated graphite exhibits unusual dual C—F bonding, i.e. weakened covalent and covalent. This bonding allows the discharge potential at the beginning of the electrochemical processes to be increased. Moreover, the accordion-like texture avoids partial exfoliation and loss of the electrical contact for some parts of the electrode, and allows the growth of LiF particles in the opened macro-porosity.

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1. Introduction

Although fluorinated carbons are used since long time as electrode material in primary Li batteries [1–4], the electrochemical mechanism of carbon fluoride defluorination is still discussed. This discussion does not concern the nature of the products after the electrochemical defluorination, namely amorphous carbon and LiF, but the process to form those products. A graphite intercalation compound (GIC) intermediate with solvated lithium is formed on the graphite sheet edges and acts as a diffusion layer [3,5]. Moreover, the concentration of lithium ions decreases rapidly with the distance from the electrode surface meaning that lithium ions stay out of the fluorocarbon matrix. On the sheet edges, the GIC subsequently decomposes into the final discharge products, carbon and LiF. The discharge is accompanied by significant electrode swelling due to the formation of volumetric LiF crystals as reported by Abraham et al. [6]. Based on the discharge and Open Circuit Voltage (OCV) recovery characteristics, Zhang et al. [7] proposed a discharge through a "shrinking core" model consisting of a CFx core and a product shell. The product shell is composed of an intermediate GIC, carbon and lithium fluoride. The product shell

grows with the discharge process, and its composition varies with the decomposition of GIC intermediate. The growth and accumulation of formed LiF particles on the sheet edge may result in a partial exfoliation of the layered carbon and the electrical contact into the electrode of some partially defluorinated parts is lost. In other words, some C-F bonds become inactive for the battery and the faradic yield (i.e. the ratio between the experimental and theoretical capacities) decreases. In order to avoid such process, fluorinated carbons with large cavities, which act as container for LiF, may be considered. The growth of LiF can be contained into such containers and would not lead to exfoliation.

Thus, for such aim, we design new materials using the versatility of the fluorination that allows the exfoliation of graphite. Thanks to a two-step process of fluorination/thermal defluorination performed on a selected room temperature graphite fluorides (obtained using a catalytic fluorination [8]), exfoliated graphite was prepared. The intercalated residual catalysts (its content has been optimized by a post-fluorination in F_2 gas) and the presence of two types of C—F bonds, covalent and weakened covalent [9,10], the simultaneous exfoliation and quasi-total defluorination of graphite occurred simultaneously when a thermal shock was applied. Both the fast gas evolution during the deintercalation of iodinated catalysts from the weakened covalent part of the sample and breaking of the graphene sheets in the covalent regions with evolution of CF_4 and C_2F_6 gas (underlined by FTIR) result in accordion-like texture. Details on the synthesis of

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the exfoliated graphite used as precursor in this work are described elsewhere in a recent paper [11]. The gap between multilayers of this latter may act as the container for LiF. Moreover, a quasi-total defluorination takes place during the thermal shock; F/C lower than 0.05 was demonstrated by EDX and electrochemical discharge in lithium battery. The exfoliated graphite (denoted EXF) was refluorinated using a flux of pure F_2 gas. The re-fluorinated porous samples were used as cathode in primary lithium battery. Their properties in Li battery and the discharge mechanism will be compared to a conventional graphite fluorides.

2. Experimental

2.1. Synthesis

Exfoliated graphite (EXF) was obtained as described in a previous paper [12]. Fluorination conditions and the full physical-chemical characterization of the fluorinated samples were presented in a recent study [11]. The fluorination was performed by gas-solid reaction with a flux of pure F_2 gas into a nickel reactor covered with NiF_2 as a passivation layer. First, O_2 and moisture from air were purged thanks to a continuous flux of inert gas N_2 at 120 °C for 1 h. Then, a flow of molecular fluorine F_2 was maintained for 3 h at a fluorination temperature T_F range in between room temperature (RT), and 250 °C. Finally, the reactive atmosphere was eliminated under N_2 flow at 120 °C during 1 h. Obtained products will be named EXF-T_F.

2.2. Physical-chemical characterizations

X-ray diffractogramms were recorded using a PHILIPS diffractometer with a Cu (Kα) radiation (λ = 1.5406 Å).

NMR experiments were carried out with a Bruker Avance spectrometer, with working frequencies for ^{13}C and ^{19}F of 73.4 and 282.2 MHz, respectively. A magic angle spinning (MAS) probes (Bruker) operating with 4.0 and 2.5 mm rotors were used. For MAS spectra, a simple sequence was performed with a single $\pi/2$ pulse length of 4.0 and 3.5 μs for ^{19}F and ^{13}C, respectively. ^{13}C chemical shifts were externally referenced to tetramethylsilane (TMS). ^{19}F chemical shifts were referenced with respect to $CFCl_3$.

The different samples were characterized by scanning electron microscopy (SEM) micrographs recorded using a Cambridge Scan 360 SEM operating at 1 kV.

Nitrogen adsorption isotherms were measured at 77 K by a Micromeritics ASAP 2020 automatic apparatus. Before measurements, samples were pre-treated under secondary vacuum at 300 °C for 12 h for sufficient removal of adsorbed impurities.

2.3. Electrochemical study

The electrochemical tests were determined through galvanostatic discharges. The electrodes were composed of the sample (about 80% by weight, w/w), acetylene black (from Mersen 10%, w/w) to ensure electronic conductivity and polyvinylidene difluoride (PVDF from Aldrich 10%, w/w) as binder. After stirring in propylene carbonate (PC), the mixture was spread uniformly onto a stainless steel current collector disk of 12 mm in diameter. Finally, after PC evaporation, the disk was heated under vacuum at 40 °C then 120 °C, during 1 h for each temperature, to remove traces of water and solvent. A two electrode cell was used, where lithium was both reference and counter electrodes. A polypropylene microporous film, wet with electrolyte composed of a lithium salt ($LiClO_4$ or $LiPF_6$) dissolved as 1 mol L^{-1} in PC (propylene carbonate) or a mixture of PC–EC (ethylene carbonate)-DMC(dimethyl carbonate), 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 the open circuit voltage (OCV) stabilization. Total galvanostatic discharges, carried out on a VMP2 from Biologic, under current density of 10 mA/g, were acquired at room temperature between the initial OCV and 2 V. For the sample EXF-200, discharges at various current rates: 6C, 5C, 4C, 2C and C/10 were made. When a plateau is clearly observed on the galvanostatic curve, the discharge potential is measured at half of the discharge and is noted $E_{1/2}$, for the other cases, the potentials of the pseudo-plateaus are extracted from the derivative curve dE/dx. The theoretical capacity Ctheo is obtained owing to the following equation:

Ctheo = x*96500/((12 + x*19)*3.6) where x is the atomic amount of fluorine in CFx composition.

3. Results and discussion

3.1. Physico-chemical characterizations of the fluorinated accordion like structure

EXF was fluorinated at different temperatures including room temperature which is scarce for graphitic materials. For all fluorination temperatures, fluorine grafting was efficient without any decomposition of the samples. Indeed, after fluorination, the accordion-like structure was preserved with no change in Specific Surface Area SSA [11]. These samples exhibit C—F bonding with both (strong) covalent bonds (denoted C—F) and weakened bonds (C···F) whatever the fluorination conditions. ^{13}C and ^{19}F NMR showed such dual C—F bonding (see Supplementary Information) and allow to determine their ratio (Table 1). C—F and C···F bonds are evidenced by the lines at −190 ppm and −150 ppm/$CFCl_3$ on NMR spectra, respectively.

3.2. Electrochemical properties

3.2.1. Galvanostatic discharges on fluorinated EXF

The samples were used as cathode materials in primary lithium battery using $LiPF_6$ 1M, PC-EC-3DMC as electrolyte by applying a discharge current of 10 mA/g (Fig. 1). First of all, OCV decreases with increasing F/C in accordance with the increase for the covalent character (Table 1). The electrochemical discharge curves are classical of carbon fluorides with an initial ohmic drop due to insulating behavior of highly fluorinated CFx materials. The behavior drastically differs in comparison with the precursor of the exfoliation in accordance with the huge changes in structure, porosity, C—F bonding and F/C ratio [12]. This overvoltage decreases with decreasing F/C value because of presence of sp^2 carbon atom ensuring electronic conductivity. The curve profile presents anomalous bi plateaus for low fluorination levels. The first plateau can be seen below capacities of 200 mAh/g and the second for higher capacities. So, with increasing fluorination temperature, the second plateau increases whereas the first one decreases to become null for fluorination temperature higher than 200 °C. To better evidence the discharge plateaus of EXF-RT and EXF-100,

Table 1
Summary of modus operandi, chemical composition, and ratio of weakened covalent/covalent bonding.

	Synthesis conditions	F/C (±0.03)	C···F/C—F[a] (±0.1)
EXF-RT	F_2, 3 h, RT	0.30	3.5
EXF-100	F_2, 3 h, 100 °C	0.40	1.9
EXF-200	F_2, 3 h, 200 °C	0.69	1.5
EXF-250	F_2, 3 h, 250 °C	0.74	1.7

[a] Calculated from ^{19}F MAS NMR.