

ADVANCED CARBON FLUORIDES FOR PRIMARY LITHIUM BATTERIES

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ABSTRACT

Li-CFx battery using a specific fluorinated nanocarbon as cathode material exhibits a capacity exceeding the expected theoretical value when used as an electrode material in primary lithium battery. Carbon nanodiscs were partially fluorinated by atomic fluorine released by thermal decomposition of TbF₄, and the capacity of this material was up to 1180 mAh.g⁻¹, whereas a theoretical value of 847 mAh.g⁻¹ for the CF_{0.95} sample was calculated. The obtained value is also higher than the maximum one of 865 mAh.g⁻¹ expected for CF₁ carbon fluorides. The discharge mechanism was investigated using mainly SEM and solid state NMR in order to understand this “extracapacity”. Both the unfluorinated carbon and the LiF covering, which is formed outside the carbon lattice during the discharge mechanism, play a key role for the achievement of the extracapacity by the consumption of Li⁺ to form Li₂F⁺ species stabilized by the carbon host structure formed after the electrochemical defluorination.

RESULTS AND DISCUSSION

Carbon nanodiscs CND were fluorinated by atomic fluorine release by TbF₄ decomposition at different temperatures. The fluorination progressively turns the structure as a function of the reaction temperature into a (CF)*n* one. SEM images underlined the maintaining of the geometry for fluorination, whatever the reaction temperature. Nevertheless, as revealed by atomic force microscopy, the swelling due to the accommodation of the fluorine atoms differs according to the fluorination route as underlined by AFM, which was performed in tapping mode. The disc surface is smooth and cracks are observed on the whole surface. The accommodation of fluorine atoms in the sample is then homogeneous across discs thus leading to a homogeneous non-localized swelling. This therefore generates cracks on the material surface to accommodate the volume expansion associated with this process. Fluorinated CND were used as cathode material in primary lithium batteries. The two samples obtained by those fluorination way (C-500 and C-550 with atomic ratio F/C = 0.72 and 0.95, obtained at fluorination temperatures of 500 and 550°C, respectively) were used as cathode in primary lithium batteries. Samples

having F/C of about 0.7-0.8 were investigated because of its known good performances. [1, 2, 3].

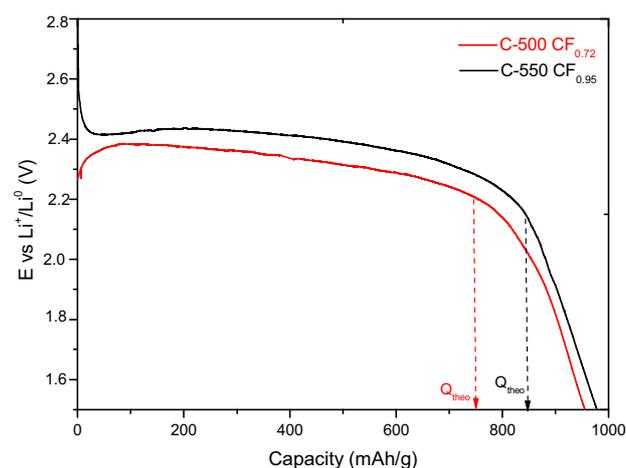


Figure 1. Galvanostatic discharge curves in EC/PC/3DMC LiPF₆ 1 M electrolyte at a current density of 10 mA.g⁻¹ of fluorinated carbon nanodiscs (C-500 and C-550)

Figure 1 shows the galvanostatic discharge curves of C-500 and C-550 samples with EC/PC/3DMC LiPF₆ electrolyte. Both samples exhibit the behavior usually expected for carbon fluorides with a well-defined plateau and initial overvoltage because of its insulating behavior. The voltage initially drops and then increases steadily to reach the main voltage plateau after few minutes; such a behavior has been already observed for graphite fluorides. [4, 5] The average potential is stable during the discharge in agreement with the unique C-F bonding (determined by ¹³C and ¹⁹F solid state NMR), which is still covalent whatever the fluorination conditions. The most unexpected observation is that the experimental capacity (Q_{exp}) significantly exceeds the theoretical value (Q_{theo}), for those two materials. Indeed, for C-550, the theoretical capacity is 847 mAh.g⁻¹ while an experimental capacity of 978 mAh.g⁻¹ is measured. This is also the case for C-500 sample, where 955 mAh.g⁻¹ as experimental capacity is measured instead of 751 mAh.g⁻¹.

Different depths of discharge DoD, 0%, 25%, 50%, 100% (relative to the theoretical capacity extracted from the fluorine content) and 127% (corresponding to the extracapacity), have been applied for a primary lithium battery with C-500 as cathode in EC/PC/3DMC LiPF₆ 1 M. After the discharge, the cathode material was dried under dynamic primary vacuum, transferred and ground in the argon-filled glove box and put into a rotor that allows NMR spectra to be recorded (without exposure to air) in order to investigate the discharge using ¹⁹F nucleus. After the recording of the NMR spectra, the electrode was investigated by EPR and SEM also without exposition to air.

SEM images of the C-500 composite electrode before and after discharges are shown in Figure 2. The good dispersion of PVDF binder is well highlighted for the raw electrode composite. The disc surface is covered with a film made with binder fibril (Figure 2a). In accordance with the well-known mechanism of formation of LiF with the reduction of CF_x [1, 6, 7], these particles can be attributed to LiF. The high concentration on the surface and edges suggests that LiF is formed outside the carbon lattice during the discharge. By analogy with lithium-graphite intercalation compounds, such as LiC₆, F⁻ ions, which are formed during the fluorocarbon reduction, diffuse within the interlayer and combine with solvated Li⁺ on the sheet edges. [8, 9] A recent study on the discharge mechanism of fluorinated carbon nanofibres showed that such particles made of LiF, are formed outside the carbonaceous matrix. [1] After the full theoretical discharge (100% of faradic yield), the fluorocarbon matrix is totally converted into carbon. The peak related to the (CF)_n phase disappeared. No diffraction peak of ordered carbon lattice is observed meaning that amorphous carbon is formed. LiF peaks are observed at 39, 45 and 65° in 2θ values. The formation of crystalline LiF particles is underlined by the sharpness of the peaks. It is to note that the discharge mechanism is nearly similar regardless the nanocarbon used, discs of fibres. [1] The LiF covering becomes thicker with increasing the discharge rate (DoD) up to 100%.

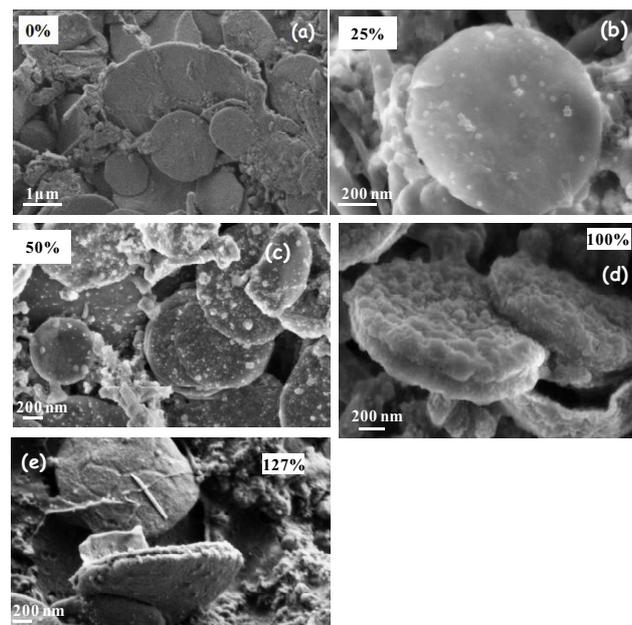


Figure 2. SEM images of C-500 at 0 (a), 25 (b), 50 (c) and 100% discharge (d and e). Figure (e) shows the sample with extracapacity (DoD of 127%)

After half of the discharge, discs and cones are still observed and are covered by particles with 20-30 nm size. The amount of these particles is higher on the cone and discs edges.

Finally, when an extracapacity (DoD of 127%) is measured, the surface of the discs are covered by cracks that recall the disruptions observed on pristine fluorinated discs, well underlined by AFM images. Moreover, the discs seem to be split into two parts starting from their center.

Such data are in complete agreement with ¹⁹F MAS NMR, recorded at high spinning rate (34 kHz) (Figure 3). The PVDF used as a binder is characterized by the presence of a line at -94 ppm assigned to CF₂ groups. The amount of CF₂ groups in the fluorinated materials underlined by a chemical shift of -120 ppm/CFCl₃ on the ¹⁹F NMR spectra does not change upon discharge. These groups are electrochemically inactive. The lines near -80 ppm are related to phosphorous species. The spectrum of solid LiPF₆ is added for comparison and exhibits a line at -74 ppm.

The pristine fluorinated CND sample contains small amount of CF₂ groups, the lines for these groups being present with a very low intensity. As for the carbon

nanofibres, the decrease of the intensity of the C-F line at -190 ppm as a function of the depth of discharge, is in accordance with the electrochemical breaking of the C-F bonds during the discharge and it is accompanied by the formation of LiF. [1] For DoD of 100%, this line is no more present underlining the total conversion of the fluorocarbon matrix into carbon lattice. The line at -204 ppm is unambiguously assigned to the fluorine nuclei present in the particles of LiF. The two lines with a chemical shift at -153 and -147 ppm are observed for discharged fluorinated CND with DoD of 127% unlike fluorinated CND discharged at DoD of 0 and 100% (Figure 3). A fluorinated specie, which is Li_2F^+ is obtained. Thus, our hypothesis to explain unprecedented extracapacity involves an insertion phenomenon of lithiated species Li_2F^+ into the carbon newly formed by electrochemical defluorination. This additional process could be the origin of the obtained extracapacities.

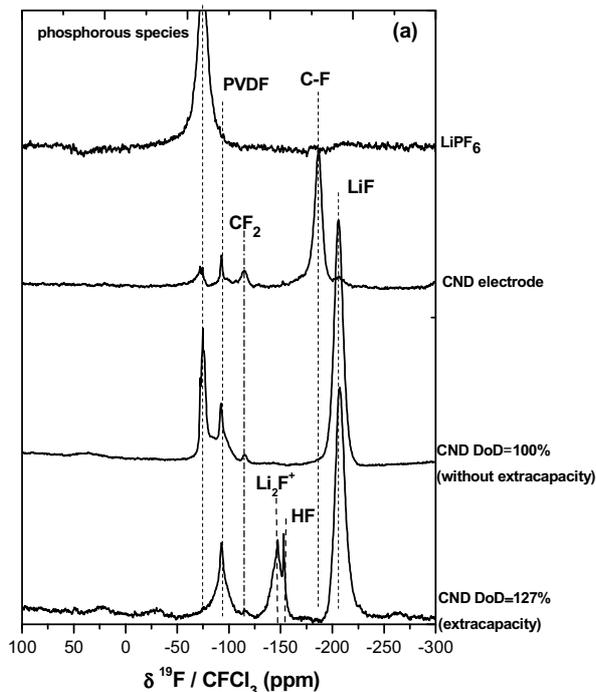
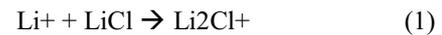


Figure 3. (a) ^{19}F MAS NMR spectra (34 kHz) of C-500/PVDF/CB (80/10/10 w/w) composite electrode before discharge (composite with simple contact with the electrolyte), and after discharge with and without extracapacity (depths of discharge DoD = 100 and 127% respectively). Lines at -74 ppm are related to phosphorous species as shown by the comparison with LiPF_6 powder

Taking into account structural (NMR and EPR) and morphological (SEM and AFM) characterizations, the discharge mechanism, quasi-independent of the electrolyte may be described as follows. The discharge occurs successively according to the following steps: i) the growth of LiF particles because the breaking of C-F bonds and the recombination with Li^+ ions to form a continuous shell on the surface of the discs at 100% of discharge ii) carbon lattice is rebuilt onto the central disc, which serves as a reinforcement, iii) to exceed the theoretical capacity, an insertion process into the reformed carbon lattice may occur; the access of the ions into the carbon host takes place through the edges of discs but also via cracks on the initial fluorinated discs highlighted by AFM. The shell of LiF formed seems to have a major role in extracapacity; it seems to allow the diffusion of the lithium ions, either Li^+ or Li_2F^+ through the edges or the surface after the full discharge. As a matter of fact, the LiF shell seems to be locally consumed on the access areas for insertion. This mechanism is similar to that of the lithium-thionyl chloride batteries (Li/SOCl_2) where the LiCl layer reacts with lithium ions to give Li_2Cl^+ cations according to the reaction:



which improves the performance of the cell. The splitting in two parts of the discs exactly on their center may be explained by two phenomena: either consumption of LiF as in the surface cracks or a volumic expansion because of the insertion.

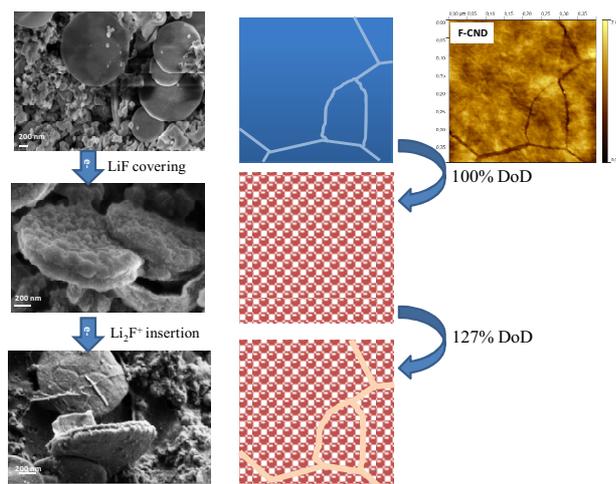
The extracapacity may be obtained because of the maintaining of the geometry of the carbon lattice. This point must be explained taking into account the intrinsic properties of CND. Using freezing fracture, Naess et al [10] observed for the same nanodiscs from N-Tec an in-plane cleavage that was usually parallel to the disc surface. The particles were fractured in a plane close to the geometrical centre of the disc. To establish this conclusion, a large number of TEM images (185) were analyzed. The histogram of the thickness ratio x_1/x_2 (x_1 is the height of the lower part of the disc and x_2 the height of the entire disc) shows that a significant number of discs rupture in an area close to the core. The splitting occurs between the graphitic layers, which are only bonded by weak van der Waals forces, and not in the amorphous carbon surrounding the disc. The authors concluded then the as-synthesized discs can be described as graphitic core within an envelope of non-crystalline carbon. The graphitic core is first grown to its full size, whereupon layers of amorphous carbon are deposited, the thickness of the graphitic core being estimated to only 2-5 nm. Moreover, if the material is

heat-treated at 2700°C, the graphitization takes place simultaneously in different parts of the amorphous carbon. Thus the temperature-induced conversion from amorphous carbon to layers of graphite is not fully coupled geometrically to the original graphite core. Central discs are more organized than the outer discs after graphitization. The higher the graphitization, the lower the reactivity with fluorine. So the fluorination is higher in the outer parts than in the central discs, not or less fluorinated.

This history of the nanodiscs has important consequence during the fluorination/defluorination. An analogy between thermal and electrochemical defluorination is interesting. Ahmad et al. described the preparation of multilayer carbon nanomaterials obtained by thermal treatment (defluorination) of these sub-fluorinated nanocarbons obtained by the controlled fluorination process. [11] The defluorination occurs with a progressive thinning of the discs because of evolution of gaseous CF_4 and C_2F_6 species. Some carbons reorder onto the non or less fluorinated central discs resulting in very thin discs (thickness in the 5-20 nm range) which fold up on themselves. Homogeneous dispersion of fluorine atoms into the outer discs thanks to the controlled fluorination and lowering of the structural defects result in equivalent thinning in the whole discs. Any thinning occurs during the electrochemical defluorination but reduced carbon rebuilt onto the central discs, which act as a reinforcement to preserve the discotic geometry.

An insertion of lithiated ions may takes place into the complex structure of defluorinated carbon discs covered with LiF. The LiF covering may acts both as lithium ions source and as diffusive layer for those ions. LiF is then probably consumed during the additional electrochemical process, assimilated as an insertion of lithiated ions Li^+ or Li_2F^+ (in accordance with the additional line observed in ^{19}F and ^7Li NMR spectra and charge transfer seen by EPR). LiF layer is then thinner at any zones of insertion, i.e. onto the sheet edges and onto the disruptions of carbon sheets, initially present in the raw fluorinated materials (well underlined by AFM).

Scheme 1 summarizes the electrochemical discharge mechanism and the insertion phenomenon which leads to extracapacity.



Scheme 1. Mechanisms explaining the extracapacity obtained with fluorinated CND

Since the LiF layer and the formation Li_2F^+ species play a major role in extracapacity, the thicker the LiF layer is, the greater the insertion of lithiated species and the extracapacity.

Taking into account that the ternary mixture of alkylcarbonates used as solvent for EC/PC/3DMC LiPF_6 1M electrolyte is able to dissolve higher quantity of LiF ($\text{SLiF} = 9.08 \text{ g.L}^{-1}$) compared to PC solvent (where $\text{SLiF} = 0.13 \text{ g.L}^{-1}$), extracapacity should be higher with PC LiClO_4 1M electrolyte rather than EC/PC/3DMC LiPF_6 1M electrolyte.

Thus, galvanostatic discharges at low current density (10 mA/g) were performed in 1M LiClO_4 PC electrolyte. A capacity up to 1180 mAh/g was observed, higher than 847 mAh/g expected for $\text{CF}_{0.95}$ composition and enhanced in comparison with the one obtained in EC/PC/3DMC LiPF_6 1M electrolyte. Such experimental facts clearly underline that the extracapacity is related to the LiF covering and it can be improved via the choice of the electrolyte to reach 140% faradic yield.

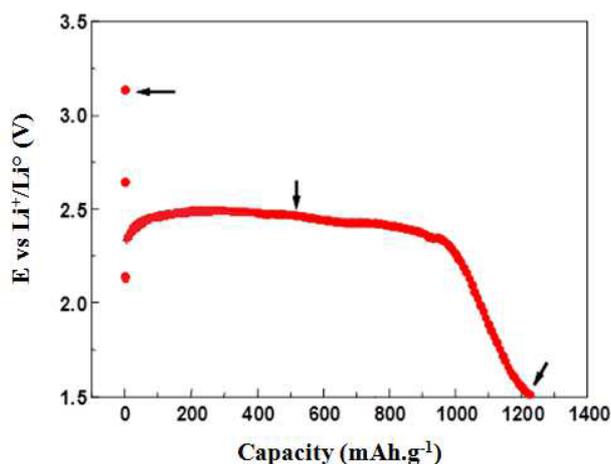


Figure 4. Galvanostatic discharge curve in PC LiClO₄ 1M electrolyte at a current density of 10 mA.g⁻¹ of CND fluorinated by controlled fluorination (C-550).

The extracapacity obtained there is the higher ever known in CFx primary lithium battery.

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