



# Tuning fluorine and oxygen distribution in graphite oxifluorides for enhanced performances in primary lithium battery

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## ABSTRACT

Fluorine Graphite Intercalation Compounds are one of the most common cathode used in primary lithium batteries, mainly for their high delivering potential. Nevertheless, to increase their capacities, fluorine can be partially substituted by oxygen. Oxifluorides offer then versatility to design cathode materials delivering the upmost performances. Combining the choice of the precursor (either graphite oxide or sub-fluorinated graphite fluoride) and two-step synthesis processes, which include Hummers' oxidation and direct fluorination, allow the tuning of the fluorine and oxygen atoms distribution. According to the sequence, i.e. fluorination/oxidation or oxidation/fluorination, several oxifluorides were then prepared. On one hand, direct fluorination using F<sub>2</sub> gas resulted in homogeneous fluorine dispersion when precursor was graphite oxide. On the other hand, Hummers' oxidation was modulated according to the temperature parameter. C–OH, C–O–C, COOH, CF, CF<sub>2</sub> and CF<sub>3</sub> were identified through multinuclear solid-state MAS-NMR. Covalence and environment, especially in-plane organization of those chemical groups, were assessed. When oxifluorides are then used as cathode in primary lithium battery, the better performances are obtained for 3 phases compounds where fluorinated part insured high potential whereas oxygenated part allowed durability to be reached; carbonaceous region providing conductivity. A maximum of about 2400 Wh/kg of energy density is attempted.

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## 1. Introduction

Graphite has numerous advantages for energy storage applications. Its availability and versatility thanks to both its lamellar structure and its reactivity explain that graphite is widely used as an anode in secondary lithium batteries. It could also be used as a cathode material in primary lithium batteries after undergoing oxidation or fluorination. Thus graphite intercalation compounds (GICs) were extensively studied [1,2]. Covalent GICs appear as the most promising for this latter application as shown by Hunger and Heymach [1–3]. They have explicitly identified graphite oxide (GO) synthesized by Brodie in 1859 [4], and graphite fluoride (GF) discovered in 1934 by Ruff et Bretschneider [5] as interesting

candidates.

Studies of graphite fluoride (GF) being contemporary with lithium batteries research, quick development of this material and understanding of its discharge mechanisms as cathode occurred. Ruff's identification of (CF)<sub>n</sub> structural type [5] and then discoveries of (C<sub>2</sub>F)<sub>n</sub> type by Kita et al. [6] and (C<sub>4</sub>F)<sub>n</sub> by Rüdorff et al. [7] drove to deep structural understanding. Since Braeuer proved their stability in organic electrolytes [8–10], graphite fluorides were actively tested in electrochemical cell by Hunger, Heymach, Fukuda and Gunther [3,11–13]. More works led to commercialization of Lithium - fluorinated carbons (CF<sub>x</sub>) with valuable advantages in commercial systems i.e. delivering high energy density 700 Wh.kg<sup>-1</sup> (1000 Wh.l<sup>-1</sup>), flat voltage plateau at 2.6 V vs Li<sup>+</sup>/Li, broad operating temperature range [-40 to 90 °C] and reliability on long term (20 years) [14]. 800 Wh.kg<sup>-1</sup> energy density, together with a high power density of 9860 W kg<sup>-1</sup> was achieved thanks to a ball-milling of GF [15]. On the contrary, in spite of once shown promising results, graphite oxide did not meet the same success, being forgotten by electrochemists [3]. Relying on oxygen and fluorine similarities, Lagow et al. [16] initiated graphite

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oxyfluorides synthesis. Nazarov et Yakovlev developed them in 70s, and Gornostayev patented them [17]. Electrochemical tests using them in primary lithium battery as cathode material were first performed by Hamwi's group. Marchand et al. [13] obtained one stable compound, delivering 1347 Wh.kg<sup>-1</sup>. Then, Al Saleh et al. [18] improved the synthesis conditions and a 2265 Wh.kg<sup>-1</sup> energy density was reached, thus exceeding in-lab results of about 2000 Wh.kg<sup>-1</sup> for classical graphite fluorides. Fluorination of GO prepared using Staudenmaier's method results in a C<sub>8</sub>O<sub>2.17</sub>H<sub>0.63</sub>F composition [19,20]. The capacity and energy density were 820 mAh.g<sup>-1</sup> and 1950 Wh.kg<sup>-1</sup>, respectively. Interestingly, fluorinated oxides were highly capacitive while oxidized fluorides have the highest discharge potential. So, it was demonstrated that engineering, the synthesis enabled to modulate the electrochemical properties. Recently, the discovery of graphene and research for their derivatives revived the interest for graphite oxyfluorides.

One-pot synthesis of graphene oxyfluorides was exclusively performed through electrochemical oxidation in aqueous HF solution [18,21,22]. It enabled *in situ* exfoliation of graphite and its functionalization [23]; nevertheless, resulting oxygen and fluorine contents were too limited for high energy density cathode. For instance, stage 1 type oxygenated C<sub>x</sub>F was obtained by the oxidation of graphite in 47% HF aqueous solution. The discharge profile of this sample as a cathode of lithium primary battery was similar to that of (C<sub>2.5</sub>F)<sub>n</sub> prepared under F<sub>2</sub> gas atmosphere but with a slightly higher capacity of 550 mAh.g<sup>-1</sup> (539 mAh.g<sup>-1</sup> for (C<sub>2.5</sub>F)<sub>n</sub>). This strongly indicated that not only fluorinated groups but also oxygenated ones in this sample were electrochemically active [22].

Gas-solid fluorination of graphite oxide was carried out with pure molecular fluorine F<sub>2</sub> [18] or a catalytic gaseous atmosphere made of F<sub>2</sub>-HF-IF<sub>5</sub> [21] as well as with gaseous HF [24,25]. Recent works by Jankovský et al. involved high pressure-high temperature process, with strong influence of the precursor [26]. Solid-liquid fluorination of graphite oxides [27], was performed in hot HF solution [18,21,28] or under irradiation as shown by Gong et al. [29]. Brodie's oxidation [18] as well as Hummers' [30] were once performed on graphite fluorides even if Lagow concluded that this latter was inert [16]. It is relevant to note that precursors were exclusively obtained from gas/solid fluorination.

Comprehensive work on both multiscale structure and chemistry of graphite oxyfluorides is scarce in literature. To fill the gap, in this paper, a wide range of materials was investigated thanks to two synthesis methods: direct fluorination (F<sub>2</sub>) and Hummers' oxidation, the safest and more efficient method for oxidation. In this paper, their combinations allowed both the fluorine and oxygen contents and their distributions to be tailored. Main design parameters for fluorination were its synthesis mode (static or dynamic), the reactive stoichiometry, the duration and the temperature according to the precursor (graphite or graphite oxide). Oxidation was performed equally on graphite and graphite fluoride. The temperature of oxidation was modulated as only few reports deal with the influence of this parameter. Only Ehrburger and Donnet studied in 1973 gas emission of oxidative medium at different temperatures [31]. Characterization of the final objects was achieved thanks to cross-checked data. In particular, functional and atomic formula came from multinuclear solid-state MAS-NMR.

Our final aim was both the tailoring of the oxygen and fluorine distribution, either homogeneous or with well separated regions of each type, with a deep knowledge of the involved functional groups, and the correlation of their amount with the electrochemical properties obtained when used as cathode in primary lithium battery.

## 2. Methods

### 2.1. Material

Commercial TIMREX KS15 Primary Synthetic Graphite was purchased from Imerys. The in-plane length is about 17 μm while thickness of each platelet is about 100–200 nm. Those data were confirmed by Scanning Electronic Microscopy (SEM).

### 2.2. Direct fluorination

Fluorination was performed by gas-solid reaction with a flux of pure molecular F<sub>2</sub> gas into a nickel reactor passivated with NiF<sub>2</sub>. Pure gaseous F<sub>2</sub> of 99% purity was purchased from Solvay.

#### 2.2.1. Fluorination of graphite

The fluorination of graphite was carried under static mode (closed reactor) to control the stoichiometry and to ensure homogeneity on 10 g-batch samples. Oxidation being known to mainly affect graphite phase, a low fluorine content was selected in order to achieve polyphasic compound. So, a F/C atomic ratio of 0.3 was selected, related compound being denoted **GF0.3**. First, the reactor was purged from O<sub>2</sub> and moisture with dynamic vacuum overnight. Then, a finite quantity of molecular fluorine F<sub>2</sub> was introduced and the reactor was heated up to 355 °C until consumption of fluorine (i.e. pressure decrease). Finally, the reactive atmosphere was eliminated under N<sub>2</sub> flow after cooling of the reactor. The atomic ratio was determined first by weight uptake and confirmed by quantitative solid state <sup>13</sup>C NMR.

#### 2.2.2. Fluorination of graphite oxide

Fluorinations of oxides were performed on 50 mg sample in dynamic mode (fluorination under a flow of F<sub>2</sub> gas). First, O<sub>2</sub> and moisture were purged thanks to a continuous N<sub>2</sub> inert gas flow at 120 °C for 1 h. This step allows also adsorbed water molecules to be removed. Then, a molecular fluorine F<sub>2</sub> flow was maintained during 120 min at 100 °C. Finally, the reactive atmosphere was eliminated under N<sub>2</sub> flow during 1 h at 120 °C. Two precursors, presented in 2.3.1, were used: conventional graphite oxide, denoted **cGO**, leading to **cGO-F** after fluorination, and ice-bath graphite oxide **iGO (iGO-F after fluorination)**. Fluorination treatments were also carried out at room-temperature for 15, 45, 90 and 240 min.

### 2.3. Hummers' oxidation

#### 2.3.1. Oxidation of graphite

**Conventional graphite oxide (cGO)**: 500 mg of KS15 graphite was mixed with 500 mg of NaNO<sub>3</sub> in an Erlenmeyer flask. After placing it in an ice-bath, 33 ml of concentrated H<sub>2</sub>SO<sub>4</sub> were added while stirring. 3.5 g of KMnO<sub>4</sub> were carefully introduced after what the medium was heated to 35 °C for 1 h. Then 50 ml of distilled water were poured on with caution since the reaction is strongly exothermic. Finally, the medium was heated at 98 °C for 45 min. 3 ml of H<sub>2</sub>O<sub>2</sub> (30%) were added before washing-filtration process.

**Ice-bath graphite oxide (iGO)** involved the same protocol in ice-bath all along the reaction.

#### 2.3.2. Oxidation of graphite fluoride

The same oxidative protocol was applied to **GF0.3** (2.2.1) giving **GF0.3-cO**. An ice-bath oxidation was also performed all along the reaction; the resulting compound was named **GF0.3-iO**.

**Table 1** summarizes the duration and notation according to the

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