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# Fluorinated Reduced Graphene Oxide as an interlayer in Li-S batteries

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## Abstract

We report on the synthesis of fluorinated reduced graphene oxide (F-rGO) by a direct fluorination of reduced graphene oxide (rGO) with XeF<sub>2</sub> or F<sub>2</sub>/BF<sub>3</sub> in anhydrous HF. Characterization performed by HAADF-STEM and NMR confirmed the formation of C–F bonds, which is also supported by the color change from graphite grey to light yellow. F-rGO has been used as an interlayer additive supported by a glass fiber separator in lithium-sulfur (Li-S) batteries in order to block the diffusion/migration of polysulfides from the porous positive electrode to the metallic lithium electrode and to prevent the redox shuttle effect. Electrochemical cycling of Li-S batteries has confirmed the beneficial role of F-rGO separators, with a more pronounced effect observed for high degrees of fluorination. X-ray Photoelectron Spectroscopy (XPS) studies have shown a direct effect on the amount of Li<sub>2</sub>S and polysulfides found on the lithium electrode, and evidenced a better reversibility of reduction/oxidation mechanisms of sulfur at the positive electrode upon discharge/charge.

## Keywords

Lithium-sulfur batteries, hydrophobic interlayer, graphene oxide, fluorination, XPS, Li<sub>2</sub>S

## 1. Introduction

The continuous demand for cheap batteries with higher energy density has pushed the alkali metal or alkali-earth metal anodes (Li, Na, Mg)<sup>1-3</sup> and sulfur based cathodes to the frontier of a battery research. Sulfur is cheap and sustainable cathode material. Used in combination with alkali metals constitutes a battery system which can be used in many different applications (from grid storage applications to battery driven cars).<sup>4,5</sup> Lithium anode and sulfur cathode is the most common system that has attracted researchers for several decades.<sup>6,7</sup>

Recent renewed interest in the lithium sulfur batteries was initiated by Nazar<sup>8</sup> due to increased demand of automotive industry for cheap, safe and sustainable batteries with high energy density. Since then it is a driving force for many research activities worldwide.<sup>9,10</sup> The majority of research activities in the field of Li-S batteries have been devoted to the development of a proper cathode host matrix, which can enable the full conversion of sulfur into Li<sub>2</sub>S during the reduction process.<sup>11,12</sup> While proper structuring of the cathode host matrices can lead to the high conversion of sulfur to Li<sub>2</sub>S, the morphology of the cathode composite is not capable of completely preventing the polysulfide diffusion out of the composite, primarily due to the high concentration gradient between electrodes. That can be at least partially improved by introducing sorption additives<sup>13,14</sup> in the cathode composite or by introducing double-coated cathodes. Both approaches improve capacity retention and stability; however, Coulombic efficiency is well below the level required for practical applications.

The need for the effective separation between the sulfur cathode and the lithium anode is in correlation with the reaction mechanism of Li-S batteries. Recent reports on the mechanism that was derived from different operando techniques<sup>15-17</sup> showed that the high voltage plateau at 2.4–2.3 V can be correlated to the reaction of sulfur with lithium to form long chain polysulfides which are highly soluble. The transition of voltage from 2.3 V to 2.1 V represents the conversion of long chain polysulfides to shorter polysulfides while the plateau at 2.1 V represents the precipitation of Li<sub>2</sub>S. Since there are high concentrations of soluble polysulfides in the electrolyte during the beginning of discharge, it can be expected that sorption additives should be very efficient, particularly if high sulfur loading is present in the composite cathode. Another approach to prevent polysulfide diffusion and/or migration to the lithium anode is a selective barrier for polysulfides. Different types of carbon-based barriers have been recently introduced as an additional interlayer between the glass fiber or polyolefin separator and sulfur cathode. Interlayers composed of reduced graphene oxide (rGO) mixed

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3 with an additional carbon black (CB)<sup>18,19</sup>, conductive multi-walled carbon nanotube  
4 (MWCNT)<sup>20</sup> or microporous carbon paper<sup>21</sup> have an effect on the capacity stabilization.  
5 These additional barriers prevent the migration of lithium polysulfides towards the lithium  
6 side and have an influence on the gravimetric and volumetric energy density.  
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10 An alternative to this approach is the use of separators which can effectively prevent the  
11 diffusion of polysulfides. We have recently showed that ion conductive ceramics (LATP from  
12 Ohara) increased the cycling stability on over 350 cycles at 99.95% Coulombic efficiency.<sup>22</sup>  
13 That result points out the need to design completely new types of separators that are repulsive  
14 for polysulfides<sup>22,23</sup> and permeable for lithium ions. At the same time, the separator has to act  
15 as a reservoir for the electrolyte since higher amounts of electrolyte are typically required in  
16 Li-S batteries compared to Li-ion batteries.<sup>24</sup>  
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22 Such approach was demonstrated in our previous work<sup>22</sup> where a hydrophobic interlayer  
23 prepared by chemically modified rGO was used. Chemical modification has been achieved by  
24 grafting organic molecules, such as *p*-fluorophenyl groups, onto rGO. Improved capacity  
25 stabilization was attributed to the lower reactivity of long-chain polysulfides with metallic  
26 lithium, due to reduced diffusion and/or migration through the separator.  
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31 A graphene derivative rGO, with the remaining oxygen and nitrogen functional groups, offers  
32 many possibilities for tailoring the surface.<sup>25</sup> The covalently modified graphene materials with  
33 halogen molecules have recently drawn attention for the use in electronic applications.<sup>26</sup> Nair  
34 et al.<sup>27</sup> prepared fully fluorinated graphene sheets by using XeF<sub>2</sub> as a fluorinated agent. As-  
35 prepared fluorinated graphene sheets possess insulating properties and show stability in  
36 different chemical and thermal conditions. The fluorinated graphene can be considered a 2D  
37 analogue of polytetrafluoroethylene (PTFE), which is a 1D fluorinated carbon chain.  
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43 In this work, we present a new synthesis route with direct fluorination of the surface of rGO  
44 with XeF<sub>2</sub><sup>28</sup> or fluorine gas in anhydrous hydrofluoric acid (aHF). As-prepared samples were  
45 thoroughly studied by solid-state NMR spectroscopy and HAADF-STEM. The degree of  
46 fluorination was additionally determined by X-ray Photoelectron Spectroscopy (XPS).  
47 Morphological changes during the fluorination process were assessed by SEM microscopy.  
48 As-prepared samples were deposited on the glass fiber sheets used as separators in the Li-S  
49 batteries. The impact of degree of fluorination on the capacity stability is presented. XPS  
50 analysis of both electrodes (composite cathode and lithium) has been performed in order to  
51 understand the differences in reaction mechanisms occurring with and without the interlayer  
52 containing fluorinated rGO.  
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## 2. Experimental part

### 2.1. Preparation of the fluorinated rGO samples

Graphene oxide (GO) and reduced graphene oxide (rGO) were prepared according to known procedures.<sup>29,30</sup> The rGO materials were fluorinated in perfluorinated ethylene propylene (FEP) reaction vessels constructed from 16 mm i.d. (19 mm o.d.) tubing equipped with a PTFE (polytetrafluoroethylene) valve encased in a brass casing and containing a PTFE-coated magnetic stirring bar.

The solvent, aHF, was prepared by treating commercial anhydrous HF (Linde, Fluorwasserstoff 3.5) with  $K_2NiF_6$  (Ozark-Mahoning, 99%) for several hours prior to use. Fluorine (Solvay Fluor, 98–99 vol%) and  $BF_3$  (Union carbide, 99.5%) were used as received. Xenon difluoride was prepared photochemically by UV irradiation of a xenon-fluorine gaseous mixture according to the published procedure.<sup>31</sup>

Volatile fluorides, HF,  $F_2$ , and  $BF_3$ , were transferred on a vacuum line constructed of PTFE, FEP, nickel and equipped with a monel Helicoid pressure gauge, a soda lime scrubber, liquid nitrogen cooled traps, and a two-stage rotary vane pump. The solid reagent,  $XeF_2$ , was stored and handled in an argon atmosphere in a glovebox with water content less than 0.5 ppm.

Reduced graphene oxide (rGO) was weighed in air into the FEP-reaction vessel which was attached to the vacuum line via a PTFE valve and evacuated. The solvent HF was condensed at liquid nitrogen temperature into the vessel. After the mixture had been warmed to room temperature, the resulting black slurry was agitated overnight on a laboratory platform shaker to ensure the homogeneity of a suspension. To a thoroughly homogenized rGO/HF slurry fluorine gas was added on a vacuum line at liquid nitrogen temperature. The reaction mixture was agitated on a laboratory shaker at room temperature for several days. Three different samples were synthesized with the aim obtaining different ratios of fluorine reacted with rGO. The schematic presentation of the reaction is given in Figure 1. More precisely, a sample **F-rGO\_2** was prepared by the fluorination of rGO (97 mg) with  $XeF_2$  (710 mg, 4.19 mmol) and catalytic amount of Lewis acid  $BF_3$  (0.63 mmol) in aHF (5.8 mL) for 25 days. A second sample, **F-rGO\_3**, was prepared by the fluorination of rGO (109 mg) with  $F_2$  (7.03 mmol in total, added in two portions) in aHF (5.8 mL) for 3 days. The third sample (**F-rGO\_4**) was prepared by the fluorination of rGO (102 mg) with  $F_2$  (8.19 mmol in total, added in two portions) in aHF (11.3 mL) for 51 days.

**Caution:** Fluorine and anhydrous hydrogen fluoride must be handled with great care in a closed system (i.e. vacuum line constructed of appropriate materials) located in a well-ventilated fume hood and protective gear must be worn at all times. Experimenters must familiarize themselves with hazards associated with the use of reactive inorganic fluorides and with the proper treatment procedures in the event of exposure.<sup>32,33</sup>

To prepare interlayers on the glass microfiber separator (Whatman), the fluorinated rGO samples were dispersed in the NMP and homogeneously deposited. The three different separator interlayers were prepared by the deposition of an F-rGO<sub>x</sub> dispersion (20 mg in 3 ml of NMP) on the top of glass microfiber, and dried for 4 days at 80°C, before being transferred into the glovebox and used for battery assembly. The estimated loading of F-rGO<sub>x</sub> on top of glass microfiber separator is between 0.3 to 0.4 mg/cm<sup>2</sup>.

## 2.2. Microscopy and NMR characterization

A field-emission scanning electron microscope (FE SEM Supra 35 VP Carl Zeiss) was used to obtain scanning electron microscope (SEM) images of the materials. For transmission electron microscopy (TEM) microscopy, the fluorinated F-rGO<sub>3</sub> sample was dispersed in ethanol and a drop of the dispersion was placed on a lacey-carbon-coated Cu grid and dried. Samples were examined with a Jeol ARM 200 CF, and a probe Cs-corrected scanning transmission electron microscope, equipped with a cold field emission electron source, operated at 80 kV. For electron energy loss spectroscopy (EELS) measurements GATAN Quantum ER dual-EELS system was used. Classical TEM-HRTEM and HAADF/ABF-STEM techniques were used for sample imaging. EELS spectra were collected in the STEM mode. To determine the ratio of intensities of individual fluorine atoms and carbon atoms from the substrate in HAADF images, models were constructed and HAADF images were calculated using the QSTEM computer program.<sup>34</sup>

<sup>13</sup>C MAS (Magic-Angle Spinning), <sup>19</sup>F-<sup>13</sup>C CPMAS (Cross-Polarization Magic-Angle Spinning) and <sup>19</sup>F-<sup>13</sup>C Lee-Goldburg (LG) CPMAS NMR spectra were recorded on a 600 MHz Varian NMR system equipped with a 3.2 mm Varian probe. Larmor frequencies for <sup>19</sup>F and <sup>13</sup>C were 564.10 MHz and 150.82 MHz, respectively. Sample rotation frequency in all experiments was 12 kHz. For MAS, CPMAS and LG-CPMAS NMR measurements, the number of scans was 6400, 50000 and 20000, and repetition delays between scans were 10 s, 0.5 s and 0.25 s, respectively. <sup>13</sup>C spectra were excited by a 90° excitation pulse of 1.9 μs. <sup>19</sup>F-<sup>13</sup>C CPMAS experiment employed RAMP<sup>35</sup> during 0.5 ms CP block and high-power XiX

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3 heteronuclear decoupling<sup>36</sup> during acquisition. In the <sup>19</sup>F-<sup>13</sup>C LG-CPMAS experiment, an  
4 additional tilt pulse of 0.725 μs was added prior to the 0.1 ms Lee-Goldburg<sup>37</sup> CP block. <sup>13</sup>C  
5 frequency axis was referenced to tetramethylsilane.  
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9 In the two-dimensional <sup>19</sup>F-<sup>13</sup>C LG-HETCOR experiment, <sup>19</sup>F nuclei were first excited by a  
10 90° pulse with a duration of 1.85 μs. Afterwards, their magnetization was allowed to evolve  
11 for *t*<sub>1</sub> before it was transferred to carbon nuclei by the 0.1 ms LG-CP block and the <sup>13</sup>C signal  
12 was detected. Prior to the LG-CP block, a tilt pulse of 0.725 μs was used. High-power XiX  
13 heteronuclear decoupling was applied on the fluorine channel during the acquisition. The  
14 number of increments along the indirectly detected dimension was 21 and the number of  
15 scans for each increment was 6000. The experiment was carried out in a hypercomplex  
16 mode.<sup>38</sup>  
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### 22 2.3. XPS characterization

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24 XPS measurements were carried out using a Kratos Axis Ultra spectrometer with focused  
25 monochromatic Al Kα radiation (hν=1486.6 eV). The spectrometer was calibrated using Ag  
26 3d<sub>5/2</sub> photoemission peak with full width at half maximum (FWHM) of 0.58 eV at 368.3 eV  
27 (binding energy) and each photoemission spectrum was recorded with a constant pass energy  
28 of 20 eV. The pressure in the analysis chamber was maintained at ~5.10<sup>-9</sup> mbar and the  
29 analyzed area of the samples was 300×700 μm<sup>2</sup>. Short scan spectra were measured before and  
30 after the usual long scan experiment to check for the possible degradation of sample surfaces  
31 due to X-ray beam. The photoemission peaks were calibrated using the hydrocarbon  
32 contamination peak at 285 eV in the C 1s spectra. The core level photoemission spectra were  
33 fitted using a Shirley type background with the linear combination of 70% Gaussian and 30%  
34 lorentzian line shapes<sup>39</sup> and the respective peaks were quantified using Scofield's relative  
35 sensitivity factors.<sup>40</sup> The process of battery opening, handling of electrodes and sample  
36 analysis was done either in a controlled argon atmosphere or an ultra-high vacuum. The  
37 vacuum sealed sample packages were carefully opened inside the argon purged glovebox  
38 which is directly connected to the XPS spectrometer to avoid any air/moisture exposure in the  
39 samples.  
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### 51 2.4. Electrochemical characterization

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53 Composite cathodes were prepared by mixing sulfur impregnated carbons<sup>41</sup> with a sulfur  
54 loading of 50 wt.%, PVdF and carbon black Printex XE2 from Degussa in a mass ratio of  
55 80:10:10 wt.%. The mixture was dispersed in N-methylpyrrolidone (NMP) and cast on  
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3 aluminum foil. The typical loading of the active material on the electrode was from 1.5 mg to  
4 2 mg of sulfur per  $\text{cm}^2$  electrode. The F-rGO\_x interlayer was faced against a cathode, wetted  
5 with a 1 M LiTFSI in sulfolane electrolyte (60  $\mu\text{L}$  per mg of sulfur) and placed into a battery  
6 sandwich together with metallic lithium (Aldrich) as a counter-electrode. The batteries were  
7 cycled in the potential range between 1.5 V and 3.0 V by using a Maccor 4200 or Biologic  
8 VMP3 galvanostat/potentiostat at C/10 ( $167.2 \text{ mA g}^{-1}$ ). All electrochemical measurements are  
9 given as a specific capacity calculated on the amount of sulfur in the cathode composite.  
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### 15 **3. Results and discussion**

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18 Different degrees of fluorination of the rGO were achieved by changing the reaction  
19 parameters and time. During the synthesis, the fluorination process could be visually observed  
20 by fading black color of rGO and resulting orange (F-rGO\_2), dark yellow (F-rGO\_3), and  
21 eventually light yellow color (F-rGO\_4) of extensively fluorinated material (Figure 1). The  
22 crucial step in the synthesis is to maintain the homogeneity of the suspension which over time  
23 becomes more thick and viscous due to the absorption of hydrogen fluoride on rGO, which  
24 necessitates the usage of relatively large amounts of HF solvent. Hydrogen fluoride also  
25 retards the subsequent reaction between rGO and fluorine. Furthermore, the aforementioned  
26 homogenization step is crucial for safety of the fluorination procedure, because dry reduced  
27 graphene oxide reacts violently with fluorine gas. Audible sparkling and local melting of  
28 fluorinated polymer occurred on inner walls of the FEP reaction vessel when dry flakes of  
29 rGO reacted with  $\text{F}_2$  that was added at liquid nitrogen temperature shortly after the addition of  
30 solvent. It noteworthy that the fluorination process of rGO with both in this study used potent  
31 fluorination reagents ( $\text{F}_2$  or  $\text{XeF}_2/\text{BF}_3$ ) is very slow in the presence of aHF; therefore, long  
32 reaction times were required.  
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#### 44 **3.1. Characterization of F-rGO\_x samples:**

##### 45 **3.1.1. Microscopy**

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48 Morphological changes of rGO after fluorination were checked by SEM and TEM  
49 microscopy. Figure 2 presents SEM micrographs of rGO and fluorinated derivatives of rGO.  
50 Morphological differences between rGO (Figure 2a) and low degree fluorinated sample F-  
51 rGO\_2 (Figure 2b) are minor, which suggests the non-destructive nature of the fluorination  
52 process. The use of fluorine gas in anhydrous HF influences the morphology of samples as the  
53 prepared F-rGO\_3 (Figure 2c) and F-rGO\_4 (Figure 2d) samples are more compact and  
54 dense.  
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3 Imaging the F-rGO\_3 sample with conventional TEM techniques revealed overlapping sheets  
4 of fluorinated rGO (Figure 3a). On thin areas where no obvious overlapping was present, we  
5 performed HAADF-STEM imaging at atomic resolution. Spots with higher contrast were  
6 observed (Figure 3b) and attributed to individual atoms or clusters of fluorine atoms. The  
7 presence of fluorine in this area was confirmed with EELS. In Figure 3c, the background  
8 subtracted EELS core-loss spectrum is shown where the edge at 685 eV that is characteristic  
9 for fluorine is clearly resolved. Due to a sub-angstrom resolution, single-atom imaging is  
10 possible, with C-corrected STEM even at 80 kV; however, the direct interpretation of the  
11 images is quite inaccurate. The diameter of the individual bright atoms in Figure 3b, defined  
12 as full-width at half maximum of line profile across the atoms, is in the order of 0.1 nm  
13 (Figures 3d and e). The covalent radius of fluorine is 71 pm, which is close to the measured  
14 value of 100 pm, but to be more exact it is necessary to compare the experimental image with  
15 a simulated (calculated) one. For this purpose, we construct the model consisting of 3  
16 misoriented parallel sheets of graphene (turbostratic graphene) with few bonded fluorine  
17 atoms (one single and one pair with the distance of 140 pm between atoms), as shown in  
18 Figure 3f. Using suitable instrumental parameters (such as Cs and Cc values, defocus, energy  
19 spread, convergence, etc.), we calculated the HAADF image of the constructed model using  
20 the QTEM code.<sup>34</sup> The simulated image is presented in Figure 3g. The dimensions and the  
21 ratio of intensity of carbon substrate and individual fluorine atoms in a simulated image are in  
22 quite good agreement with experimental images. Based on these results we can conclude that  
23 atoms observed in HAADF images are indeed fluorine atoms.  
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38 The number of graphene sheets in the observed area was estimated from low-loss EELS  
39 spectra. As described by Eberlein<sup>42</sup>, the position of the plasmon peak maximum is a function  
40 of number of sheets of graphene. The authors observed that  $\pi+\sigma$  surface plasmon maxima are  
41 around 15 eV for single-sheet graphene, 17 eV for 3 sheets and approaching 24 eV in the case  
42 of 10 or more sheets. We used a similar method and found that most of thinnest areas had 3-5  
43 graphene sheets (with  $\pi+\sigma$  surface plasmon maxima at around 17 eV (Figure 3h)) in  
44 turbostratic orientation. Figure 3i with low-loss EELS spectra and a local maximum at 22 eV  
45 is an example of an area with 5–10 graphene sheets.  
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### 52 3.1.2. NMR

53 <sup>13</sup>C MAS NMR spectra of our materials are presented in Figure 4. The spectra of the materials  
54 at different stages of preparation substantially differ from one another. <sup>13</sup>C MAS NMR  
55 spectrum of graphene oxide (GO) exhibits a number of partly resolved signals in the chemical  
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3 shift range between 0 and 200 ppm. As in previous NMR studies,<sup>25,43–48</sup> the signals resonating  
4 at 60 ppm and 70 ppm can be assigned to either C–O–C or tertiary C–OH groups, whereas the  
5 signals in the range between 110 ppm and 150 ppm belong to graphitic  $sp^2$  carbon atoms. A  
6 weaker signal at about 166 ppm can be assigned to ester carbonyl groups O=C–O and a signal  
7 at about 190 ppm to ketones C=O.  $^{13}\text{C}$  MAS NMR spectrum of the reduced material (rGO) is  
8 markedly different from the spectrum of the parent material. It contains one dominating broad  
9 signal extending from 90 ppm to 150 ppm and a weak signal of the O=C–O groups resonating  
10 at 166 ppm. Broad weak contributions below 60 ppm and above 200 ppm are the first-rank  
11 spinning sidebands of the main broad signal. The disappearance of the signals below 80 ppm  
12 indicates that the selected procedure for the preparation of rGO quite efficiently reduces the –  
13 C–OH and –C–O–C groups into the graphitic  $>\text{C}=\text{C}<$  carbon. The increased width of the  
14 obtained graphitic signal evidences that although the total fraction of the  $sp^2$  carbon increases,  
15 the average dimensions of the graphitic domains decrease upon reduction.<sup>25</sup>

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25 Fluorination of rGO again leads to large changes in the NMR spectrum. The  $^{13}\text{C}$  MAS NMR  
26 spectra of the three fluorinated samples F-rGO\_2, \_3, and \_4 (Figure 4) are very similar to  
27 one another and all exhibit at least four relatively narrow signals between 80 ppm and 170  
28 ppm. The small line width suggests that the above described procedure of fluorination leads to  
29 well-ordered materials with well-defined fluorinated graphene sheets. In all three spectra of  
30 fluorinated samples, the highest signals are those resonating at 84 ppm, lower and broader,  
31 but also quite intense are the signals extending between 95 ppm and 120 ppm. The spectra  
32 also exhibit a pronounced narrow signal at 135 ppm. This latter signal is accompanied by two  
33 strong spinning sidebands at about 50 ppm and 220 ppm, indicating that the corresponding  
34  $^{13}\text{C}$  nuclei experience quite strong chemical shift anisotropy. This fact and the value of the  
35 isotropic chemical shift of 135 ppm suggest that the contribution belongs to the graphitic (or  
36 graphene-like)  $sp^2$  carbon. This is in the agreement with observations in the TEM study,  
37 where we determined 5–10 layer thick graphene sheets. The fourth signal in the spectra of F-  
38 rGO resonates at 166 ppm and thus belongs to the remaining O=C–O groups. In all three  
39 fluorinated materials, the fraction of the O=C–O carbon atoms was small, below 3%.

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51 To better understand the origin of the main signals in the NMR spectra of fluorinated  
52 materials,  $^{19}\text{F}$ - $^{13}\text{C}$  CPMAS and  $^{19}\text{F}$ - $^{13}\text{C}$  LG-CPMAS spectra were recorded. Examples of both  
53 spectra and their comparison to the directly excited  $^{13}\text{C}$  MAS NMR spectrum of the F-rGO\_3  
54 are shown in Figure 5. We can see that the  $^{19}\text{F}$ - $^{13}\text{C}$  CPMAS spectrum exhibits the same  
55 signals as the  $^{13}\text{C}$  MAS spectrum, except for the signal from the O=C–O groups. Obviously,  
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3 the latter groups are distant from fluorine nuclei so that the polarization transfer between  $^{19}\text{F}$   
4 and  $^{13}\text{C}$  is ineffective. Gao et al. showed in their graphite oxide material that  $^{13}\text{C}$  nuclei  
5 resonating at 169 ppm were spatially separated from the majority of the graphitic carbon.<sup>46</sup> If  
6 this was also the case in our materials, it would readily explain the disappearance of the 166  
7 ppm signal in the  $^{19}\text{F}$ - $^{13}\text{C}$  CPMAS NMR spectrum.  
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11 The  $^{19}\text{F}$ - $^{13}\text{C}$  LG-CPMAS experiment is more selective than the ordinary CPMAS experiment.  
12 In this type of experiment, the polarization transfer between  $^{19}\text{F}$  and  $^{13}\text{C}$  nuclei is efficient  
13 only for very proximal (e.g. directly bound) nuclei. Polarization transfer to carbon nuclei that  
14 are more than one bond apart from fluorine is already substantially hampered and leads to a  
15 notable reduction of the  $^{13}\text{C}$  NMR signal. The  $^{19}\text{F}$ - $^{13}\text{C}$  LG-CPMAS NMR spectrum of F-  
16 rGO\_3 clearly shows that only the narrow signal at 84 ppm and the broad signal between 95  
17 ppm and 120 ppm belong to the fluorinated carbon atoms. The graphitic  $sp^2$  carbon atoms  
18 resonating at 135 ppm, on the other hand, are not directly bound to fluorine. Based on the  
19 values of the isotropic chemical shifts, the 84 ppm  $^{13}\text{C}$  signal could be assigned to the  
20 fluorinated carbon atoms within the core of the modified graphene sheets ( $-\text{C}-\text{F}$ ), and the  
21 signal between 95 ppm and 120 ppm could be ascribed to the fluorinated carbon atoms on the  
22 edges of such sheets. This assumption was further verified by the two-dimensional  $^{19}\text{F}$ - $^{13}\text{C}$   
23 heteronuclear correlation (LG-HETCOR) experiment. The LG-HETCOR NMR spectrum of  
24 F-rGO\_3 in Figure 5 shows four distinct  $^{19}\text{F}$ - $^{13}\text{C}$  cross peaks. The most intense one resonates  
25 at 84 ppm and -145 ppm along the  $^{13}\text{C}$  and  $^{19}\text{F}$  dimensions, respectively, and, as already  
26 mentioned, belongs to the  $-\text{C}-\text{F}$  motifs within the fluorinated sheets. The graphitic carbon  
27 nuclei resonating at 135 ppm also yield a weak cross peak with the fluorine nuclei resonating  
28 at about -145 ppm. This indicates that the non-fluorinated  $sp^2$  carbon and the  $-\text{C}-\text{F}$  carbon  
29 share the same fluorinated graphene sheets and that the two types of carbon are quite  
30 homogeneously dispersed throughout the sheets. Careful inspection of the slices through the  
31 LG-HETCOR spectrum along the  $^{19}\text{F}$  dimension shows that the most intense cross peak is  
32 actually accompanied by a pronounced low-frequency shoulder. This shoulder with  $^{19}\text{F}$   
33 chemical shift of about -170 ppm could be due to  $-\text{C}-\text{F}$  pairs, whose nearest neighbors in the  
34 fluorinated graphene sheets are again  $-\text{C}-\text{F}$  pairs. The large intensity of the shoulder suggests  
35 that such fluorine-rich parts of the sheets are quite big or quite abundant, and that the extent of  
36 fluorination in the F-rGO samples is large.  
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56 The remaining two distinct cross peaks in the LG-HETCOR spectrum resonate at about 105  
57 ppm and -130 ppm, and at 111 ppm and -50 ppm along the  $^{13}\text{C}$  and  $^{19}\text{F}$  dimensions,  
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3 respectively. The  $^{19}\text{F}$  chemical shift of the former cross peak is very close to the  $^{19}\text{F}$  chemical  
4 shift of the most intense signal in the LG-HETCOR spectrum, suggesting that it most  
5 probably also corresponds to the  $-\text{C}-\text{F}$  type of fluorine. The different  $^{13}\text{C}$  chemical shifts  
6 between the two  $-\text{C}-\text{F}$  contributions could stem from the difference in the aromatic character  
7 of the corresponding carbon rings; whereas the 84 ppm signal can be assigned to  $-\text{C}-\text{F}$  groups  
8 in the parts of the fluorinated sheets with the predominantly non-aromatic character, the 105  
9 ppm signal could be ascribed to the  $-\text{C}-\text{F}$  groups in the parts of the sheets with a more  
10 aromatic character. The cross peak resonating at 111 ppm and -50 ppm along the  $^{13}\text{C}$  and  $^{19}\text{F}$   
11 dimensions, respectively, exhibits a very different fluorine chemical shift and this is most  
12 probably the contribution of the fluorinated  $-\text{CF}_2$  groups at the edges of the fluorinated  
13 graphene sheets. A tentative model of F-rGO materials is sketched in an inset in Figure 5.  
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22 The  $^{19}\text{F}$  chemical shift of about -50 ppm could also perhaps be assigned to fluorine bonded to  
23 nitrogen. Reduction of GO by hydrazine can, namely, create some hydrazine, amine or  
24 aziridine groups on the surface of rGO.<sup>25</sup> During the subsequent fluorination, hydrogen atoms  
25 in such groups could be substituted by fluorine, and the obtained  $-\text{C}-\text{N}-\text{F}$  motifs could  
26 perhaps contribute to NMR signals with a  $^{13}\text{C}$  chemical shift above 100 ppm and  $^{19}\text{F}$  chemical  
27 shift above -60 ppm. However, a relatively large distance between C and F in such functional  
28 groups would make their contribution hardly detectable in the LG-CPMAS and LG-HETCOR  
29 experiments, meaning that the  $-\text{C}-\text{N}-\text{F}$  motifs are not consistent with our NMR spectra.  
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38 A quantitative analysis of  $^{13}\text{C}$  MAS NMR spectra of the F-rGO materials allows one to  
39 estimate the degree of fluorination of these materials. In fact, a brief look at the spectra and  
40 comparison of the heights of the  $-\text{C}-\text{F}$  and the  $sp^2$  signals already suggests that the degree of  
41 fluorination is the lowest for F-rGO\_2, and that F-rGO\_3 and F-rGO\_4 are fluorinated to  
42 approximately the same extent (Figure 4). The detailed decomposition of the  $^{13}\text{C}$  MAS NMR  
43 spectra into individual contributions enables an even more precise estimation (Figure 5).  
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46 Summing up the contributions of the  $-\text{C}-\text{F}$  and  $-\text{CF}_2$  groups, we can see that in F-rGO\_2  
47 there are 67%, in F-rGO\_3 there are 74% and in F-rGO\_4 there are 76% of fluorinated carbon  
48 atoms. Obviously, the extent of fluorination is rather high in all three samples.  
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## 52 **3.2. Use of F-rGO samples in Li-S batteries:**

### 53 **3.2.1. Electrochemical characterization**

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56 To evaluate the impact of fluorination, we prepared four different sets of batteries. All tested  
57 batteries were prepared by using cathodes from the same batch while the amount of  
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3 electrolyte was normalized to the amount of sulfur in the cathode. The difference between  
4 cells was in the interlayer between the cathode and lithium metal. A typical cross-section and  
5 top view of a separator interlayer is presented in Figure 6. Based on many cross-section  
6 thickness measurements, we can estimate that the average thickness is approximately 3  $\mu\text{m}$   
7 (Figure 6a). We need to emphasize that the preparation procedure for the deposition of  
8 fluorinated reduced graphene oxide was not optimized and some imperfections can be  
9 observed from the top-down view in Figure 6b.

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11 During assembly of the Li-S cells, the interlayer was faced to the surface of the cathode. A  
12 typical open circuit potential (OCP) of the Li-S cells with fluorinated interlayer was between  
13 3.3 and 3.4 V versus metallic lithium. The OCP voltage is about 200–300 mV higher than the  
14 OCP in our previous paper where chemically modified graphene oxide was used as an  
15 interlayer.<sup>22</sup> The observed voltage could be an indirect confirmation for the presence of the  
16 elemental fluorine since the OCV voltage fits very well with the OCV voltage of Li (C–F)<sub>n</sub>  
17 batteries.<sup>49,50</sup> The presence of free fluorine is additionally confirmed by the presence of a  
18 plateau at 3.1 V during the first discharge. The length of the plateau is correlated with a  
19 degree of fluorination (Figure S1); however, according to the quantity of fluorine in the  
20 interlayer, only a minor part of fluorine electrochemically reacts with lithium. We assume that  
21 the observed electrochemical reaction in the first discharge is correlated to the amount of  
22 “free” fluorine in the interlayer. The reduction of fluorine is accomplished during the first  
23 discharge and batteries are cycled as normal Li-S cells from the second cycle.

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25 The degree of fluorination was additionally measured by XPS, which confirmed the trend  
26 observed by NMR, namely F-rGO\_2 contains 17 mol% of fluorine while F-rGO\_3 and F-  
27 rGO\_4 contain 43 mol% of fluorine (hydrogen is not taken into account because not detected  
28 by XPS). The C1s spectrum of F-rGO\_3 sample is shown in Figure S2. According to XPS, F-  
29 rGO\_3 mainly contains C–F groups (~95%) and a few CF<sub>2</sub> groups (~5%), which is in good  
30 agreement with NMR data.

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32 With the aim of determining how different degrees of fluorination and different reaction times  
33 influence the electrochemical stability of Li-S batteries, we prepared 4 different sets of  
34 batteries using the same cathode material and electrolyte (quantity of electrolyte was  
35 normalized per sulfur mass in the electrode). Figure 7 shows the capacities obtained during  
36 discharge process for four different separators. The highest discharge capacities were obtained  
37 within batteries without an rGO interlayer and with samples with the lowest degree of  
38 fluorination (sample F-rGO\_2). Despite high starting capacities in both measurements, we  
39 observed relatively fast fading in the first 3 cycles; however, remarkable differences between  
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3 capacities have to be pointed out. The capacity drop in the battery containing separator with  
4 the interlayer of F-rGO\_2 is only half of the capacity drop in the battery without interlayer.  
5 Much better cycling stability in the formation cycles was obtained with more fluorinated  
6 graphene interlayers; however, starting discharge capacities were lower compared to batteries  
7 with an F-rGO\_2 interlayer or without any interlayer. This is correlated to the transport  
8 properties for lithium ions. A higher degree of fluorination is expected to result in a more  
9 hydrophobic nature of the interlayer as well as denser and more compact sample  
10 morphologies. Thus, it is not surprising that the battery with the interlayer prepared from  
11 sample F-rGO\_4 showed the lowest capacity at the beginning. The optimal cycling behavior  
12 (cycling stability and specific capacity) was obtained with the interlayer prepared from the F-  
13 rGO\_3 sample. That set of measurements confirms the blocking nature of fluorinated rGO  
14 samples and points out the need for proper design of the blocking interlayer on the separator.  
15 A higher degree of fluorination leads to low specific capacities due to transport properties,  
16 while a lower degree of fluorination slightly improves capacity fading. By adjusting the  
17 degree of fluorination (that can be correlated to the hydrophobicity) and by optimization of  
18 the interlayer morphology and deposition, we assume that stable cycling properties can be  
19 obtained. So far, the electrochemical properties of Li-S batteries containing F-rGO\_3 are  
20 optimal and are very similar to the cycling properties with an interlayer prepared by the  
21 chemical modification of rGO shown recently.<sup>22</sup> The observed capacity fading can be  
22 correlated to the imperfections in the deposited interlayers (Figure 6a).

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Comparison of the galvanostatic curves reveals further differences in the electrochemical properties of tested separator interlayers. Figure 8 shows selected voltage profiles for all battery configurations tested in this study for the 2<sup>nd</sup>, the 10<sup>th</sup>, the 50<sup>th</sup> and the 100<sup>th</sup> cycles. It should be noted that the first cycle was not reported in the voltage profiles since it corresponds to the reaction of lithium with free fluorine, as stated above. As a result, the second cycle can be considered the reference cycle.

The battery with the glass fiber separator exhibits galvanostatic curves with a relatively short high voltage plateau and ill-defined low voltage plateau, suggesting high internal resistance inside the cell, which is probably connected to a high capacity drop in the first cycle (Figure 8a). Much smaller increase of polarization, but still remarkable, were observed in the battery using F-rGO\_2 sample as the interlayer (Figure 8b). Comparison between those two samples confirms blocking nature for the polysulfides of the fluorinated interlayer. The use of interlayers with a higher degree of fluorination (Figure 8c,d) improves capacity stability and capacity drop is mainly connected with a capacity fading related to a low voltage plateau

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3 (characteristic to formation of the short polysulfides and  $\text{Li}_2\text{S}$ ). Here, we need to pinpoint that  
4 voltage plateau is more sloping in the batteries with a higher degree of fluorination (with F-  
5 rGO\_3 and F-rGO\_4 interlayers) compared to the battery with an F-rGO\_2 interlayer. The  
6 difference can be explained by a decrease of ionic pathways for lithium ions due to the higher  
7 hydrophobicity and denser layers. The latter property is also the reason for different specific  
8 capacities between F-rGO\_3 and F-rGO\_4 interlayers, while the cycling stability is not  
9 affected. That was expected, since both samples have the same degree of fluorination;  
10 however, much longer reaction times for F-rGO\_4 sample correspond to denser samples.  
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### 18 **3.2.2. Study of mechanisms by XPS**

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21 In order to understand the mechanisms and the origin of the electrochemical improvements of  
22 the Li-S batteries using F-rGO samples, we carried out the XPS study of electrodes from  
23 batteries with and without F-rGO in the separator. Both electrodes (composite cathode and  
24 lithium) were analyzed at the end of discharge and charge of the first and second cycle.  
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28 The main interest of XPS analysis in our approach is that it allows a clear distinction between  
29 the different chemical environments of sulfur, and therefore between the different sulfur-  
30 containing species in the system, due to the wide binding energy range of S 2p core peak as a  
31 function of oxidation state and local environment of sulfur atoms. As shown in our previous  
32 work, the salt LiTFSI, polysulfides  $\text{S}_n^{2-}$ , lithium sulfide  $\text{Li}_2\text{S}$  and possible extra species  
33 coming from side reactions can be distinguished in S 2p spectra.<sup>13</sup> Moreover, it is possible to  
34 distinguish terminal and bridging sulfur atoms in polysulfides, and thus obtain information  
35 about the mean length of polysulfides from the terminal vs. bridging sulfur intensity ratio.  
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39 The XPS study was carried out on the F-rGO\_3 sample which gave the best electrochemical  
40 performances in Li-S batteries, as shown above. The first and the second cycles were studied.  
41 In order to have full information on sulfur species present in the electrolyte, which are the  
42 electrochemically active species, the electrodes were not washed before XPS analysis but just  
43 dried in an ultra-high vacuum after battery opening without removing the salt.  
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#### 49 **First cycle**

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51 The S 2p XPS spectra of the composite cathode, just after simple contact with the electrolyte,  
52 and after the first discharge, with the reference glass fiber separator and with the F-rGO\_3  
53 interlayer, respectively, are plotted in Figure 9. The cathode that was only in contact with the  
54 electrolyte (soaked electrode) shows the S 2p signal of the salt LiTFSI at very high binding  
55 energy (S  $2p_{3/2}$  at around  $169.4 \text{ eV}^{51}$ ) together with the signal of the starting elemental sulfur  
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3  $S_8$  (S  $2p_{3/2}$  at  $\sim 164$  eV). Note that due to spin-orbit coupling, all S 2p components consist of  
4 doublets ( $2p_{3/2}$  -  $2p_{1/2}$ ) separated by  $\sim 1.2$  eV with a 2/1 intensity ratio. Only the position of the  
5 S  $2p_{3/2}$  component will be further analyzed. After the first discharge, the S 2p spectrum of the  
6 cathode from the battery using the reference glass fiber separator is very different from the  
7 soaked electrode. New components appear which are assigned to  $Li_2S$  ( $\sim 160.5$  eV), to  
8 terminal sulfur ( $\sim 162$  eV) and bridging ( $\sim 163.6$  eV) sulfur atoms from  $Li_2S_n$  polysulfides,  
9 respectively. The contribution of bridging sulfur is very weak, showing that the mean length  
10 of polysulfides is very short in this case (mainly  $Li_2S_2$ ). This is the result of a reduction of  $S_8$   
11 upon discharge, leading to the final reduction product  $Li_2S$  and to very short chain  
12 polysulfides. Note that an additional peak appears at  $\sim 167$  eV. This binding energy value is in  
13 the range of S(IV) oxidation state, and can be assigned to sulfite compounds arising from the  
14 reduction of the salt  $(F_3C-SO_2)_2N, Li^+$  (LiTFSI) in which sulfur is originally in the S(VI)  
15 oxidation state. Several side reaction products can be considered to explain this peak, such as  
16  $LiSO_2CF_3$  after breaking the S–N bond of LiTFSI, or  $(F_3C-SO_2-N-SO_2)^{2-}, 2Li^+$  after breaking  
17 the S–C bond, or even  $Li_2SO_3$ , as already mentioned by Aurbach *et al.*<sup>52</sup>

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28 On the other hand, the S 2p spectrum of the cathode coming from the battery using the F-rGO  
29 interlayer shows a main contribution of bridging sulfur atoms ( $\sim 163.6$  eV) with a bridging to  
30 terminal sulfur intensity ratio  $\sim 4$ , and no signal for  $Li_2S$ . Therefore, at the end of the first  
31 discharge, a rather weak proportion of  $S_8$  has been reduced. Note that the electrodes were not  
32 washed before XPS analysis, as said above, and thus the S 2p signal of the salt may fluctuate  
33 as a function of the amount of electrolyte remaining at the surface of the electrode, depending  
34 on the wettability of it, which may change after cycling.

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40 At the same time, analysis of F 1s spectra of the separator provides interesting information, as  
41 shown in Figure 10. After the first discharge, the F 1s spectrum of the reference glass fiber  
42 separator shows two peaks (Figure 10a). The first at 688.6 eV corresponds to the LiTFSI  
43 salt.<sup>51</sup> The weak one at 685 eV is attributed to LiF, coming from the degradation of salt. The  
44 F 1s spectrum of the separator containing the F-rGO interlayer has a very different shape  
45 (Figure 10b) since the LiF signal shows a much greater intensity (5% of the global XPS  
46 intensity, vs. 0.8% for the reference glass fiber separator). For comparison, the F 1s spectrum  
47 of the pristine F-rGO\_3 sample is plotted in Figure 10c. We can conclude that the peak  
48 observed at 685 eV after discharge cannot be attributed to fluorinated species from F-rGO, but  
49 results from reaction of lithium towards F-rGO. This allows understanding of the mechanisms  
50 occurring upon the first discharge: «activation» process of the F-rGO interlayer occurs which  
51 consists of the reaction of lithium with the free fluorine remaining in the separator to produce  
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3 LiF. As a result, a rather weak proportion of  $S_8$  is reduced. Therefore, the battery can be  
4 considered operational only after this «activation» cycle, and the second cycle can be  
5 considered the true reference cycle for cycling evolution upon aging. That is why we propose  
6 a detailed analysis of the second cycle.  
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### 10 11 **Second cycle**

12 The same batteries were studied, one with the reference glass fiber separator and the other one  
13 with the F-rGO\_3 interlayer. Both the composite cathode and the lithium anode were  
14 analyzed, at the end of the second discharge, and at the end of the second cycle (second  
15 charge). The results obtained for the cathode are shown in Figure 11a (2<sup>nd</sup> discharge) and 11b  
16 (2<sup>nd</sup> charge).  
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21 The S 2p spectra of both cathodes after the 2<sup>nd</sup> discharge show the expected profile, *i.e.* the  
22 main contribution of the  $Li_2S$  signal, which is the final reduction product, together with the  
23 presence of very short chain polysulfides (bridging to terminal sulfur intensity ratio close to  
24 0.16 corresponding to a mean  $Li_2S_n$  length  $n \sim 2.3$ ). The signals of the salt LiTFSI and its  
25 reduction product(s) are also detected. On the other hand, the S 2p spectra of both cathodes  
26 after the 2<sup>nd</sup> charge (Figure 11b) exhibit some interesting differences. Both cathodes display  
27 the two signals of bridging ( $\sim 163.5$  eV) and terminal ( $\sim 162$  eV) sulfur atoms from  
28 polysulfides, but with different intensity ratios. Note that, as said above, the amount of  
29 remaining salt at the surface may fluctuate and, for that reason, the signal of the polysulfides  
30 for the cathode using the F-rGO interlayer was zoomed. For the cathode using the reference  
31 glass fiber separator, the contribution of terminal sulfur atoms is much greater, which  
32 corresponds to an estimated mean polysulfide length  $Li_2S_{4.2}$ , whereas for the cathode using  
33 the F-rGO\_3 interlayer separator the contribution of terminal sulfur atoms is rather weak. The  
34 great bridging to terminal sulfur intensity ratio  $\sim 4.6$ , together with the slightly greater binding  
35 energy observed for the bridging sulfur peak (164 eV), shows that elemental sulfur is present  
36 at the end of charge for this sample. Therefore, the reversibility of the electrochemical  
37 reaction appears to be much better for the cathode using the F-rGO\_3 interlayer separator:  
38 more short-chain polysulfides have been re-oxidized into long-chain polysulfides and  
39 elemental sulfur upon charge.  
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53 Analysis of the lithium electrode provides additional information about the mechanisms. S 2p  
54 spectra of the two lithium electrodes using the two kinds of separators are shown in Figure  
55 12a (2<sup>nd</sup> discharge) and 12b (2<sup>nd</sup> charge). These spectra display the same S 2p components as  
56 cathodes.  
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3 The spectrum of the lithium electrode using the reference glass fiber separator after the 2<sup>nd</sup>  
4 discharge shows the presence of Li<sub>2</sub>S (~160.2 eV) and of very short-chain polysulfides  
5 (estimated mean length Li<sub>2</sub>S<sub>2.2</sub>). These species are the result of longer-chain polysulfides  
6 reduction at the surface of metallic lithium, ensuing from the diffusion/migration of  
7 polysulfides from the cathode to the lithium electrode, and represent a loss of reversible  
8 capacity for the following charge at the cathode side. When it comes to the Li electrode using  
9 the F-rGO interlayer separator, no Li<sub>2</sub>S signal can be detected, and the amount of polysulfides  
10 is weaker. This is the proof that the F-rGO interlayer has been very efficient in blocking the  
11 diffusion/migration of polysulfides, although some of them have reached the lithium electrode  
12 to be reduced at its surface.

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19 After the 2<sup>nd</sup> charge (full 2<sup>nd</sup> cycle) the Li<sub>2</sub>S signal is still present at the surface of the lithium  
20 electrode using the normal glass separator. The slight variation of the amount of  
21 Li<sub>2</sub>S/polysulfides at the surface of this electrode compared to the discharge may be due to the  
22 surface reconstruction of metallic lithium upon charge. Concerning the lithium electrode  
23 using the F-rGO interlayer, still no Li<sub>2</sub>S signal could be detected. Therefore, this confirms that  
24 the F-rGO plays a role in blocking the diffusion/migration of polysulfides from one electrode  
25 to the other and preventing the redox shuttle effect.  
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#### 32 4. Conclusions

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35 In this work, we have synthesized F-rGO by direct fluorination of reduced graphene oxide and  
36 obtained different degrees of fluorination. Characterization by NMR and TEM confirmed the  
37 formation of C–F bonds in as-prepared samples. We have used F-rGO as a separator  
38 interlayer in Li-S batteries and showed that it improves the electrochemical performances of  
39 the batteries, with a more beneficial effect for fluorine-rich F-rGO samples. XPS investigation  
40 of the action mechanisms of this interlayer additive, by comparison of the relative amounts of  
41 Li<sub>2</sub>S, and polysulfides, by determination of the mean length of polysulfides at both electrodes,  
42 has proven the efficiency of this kind of separator interlayer in blocking the  
43 diffusion/migration of polysulfides from the porous positive electrode to the metallic lithium  
44 electrode. Above mentioned shows a better reversibility of the sulfur electrochemical reaction,  
45 and better capacity retention upon cycling. The results of this work open the way to designing  
46 better selective separator interlayers in order to reach better capacity retention and finally  
47 meet requirements for the commercialization of Li-S batteries.  
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3 **Figure 1:** Synthesis scheme of fluorinated reduced graphene oxide samples preparation (a)  
4 and photographs of reduced graphene oxide and fluorinated samples (b).  
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6 **Figure 2:** SEM micrographs of rGO (a), F-rGO\_2 (b), F-rGO\_3 (c) and F-rGO\_4 (d).  
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8 **Figure 3:** TEM micrograph of fluorinated graphene sheets (a). HAADF image of a thin area  
9 in the sample where individual atoms and clusters of fluorine atoms are visible (b), EELS  
10 spectrum of the area shown in Fig. 3b with characteristic fluorine K edge at 685 eV. Enlarged  
11 image of the fluorine atom (d) with the diameter (full width at half maximum) of around 0.1  
12 nm as measured from the line profile of the intensities (e). Model of 3 layered graphene with  
13 one isolated atom and one two-atom clusters of fluorine (f) used for HAADF image  
14 calculations, shown in (g). Thickness (number of graphene layers) was estimated from the  
15 local maximum at the low loss between 12 and 30 eV as in the case of 3 – 5 layers with  
16 maximum around 17 eV (h) and 5 – 10 layers with a maximum around 22 eV (i).  
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24 **Figure 4:**  $^{13}\text{C}$  MAS NMR spectra of materials at different stages of preparation. Asterisks  
25 denote spinning sidebands.  
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28 **Figure 5:** A more detailed NMR analysis of F-rGO\_3. (a) compares  $^{13}\text{C}$  MAS,  $^{19}\text{F}$ - $^{13}\text{C}$   
29 CPMAS and  $^{19}\text{F}$ - $^{13}\text{C}$  LG-CPMAS NMR spectra. Vertical lines are guides for eyes and mark  
30 positions of the O=C-O, graphitic,  $\text{CF}_2$  and C-F carbon signals (with aromatic  $\text{C}^{\text{a}}$  and non-  
31 aromatic  $\text{C}^{\text{na}}$  character). Below the  $^{13}\text{C}$  MAS NMR spectrum, decomposition of this spectrum  
32 into individual contributions is presented. The thin red line represents the model spectrum. (b)  
33 shows  $^{19}\text{F}$ - $^{13}\text{C}$  LG-HETCOR NMR spectrum; inset shows a tentative model of the fluorinated  
34 graphene.  
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40 **Figure 6:** SEM micrograph of separator cross section showing thickness of the F-rGO\_X  
41 thickness (a) and bird's eye view of the homogeneity of deposited F-rGO\_X interlayer on the  
42 fiber glass separator (b).  
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45 **Figure 7:** Cycling performance of 4 different sets of Li-S batteries (left y axis) and  
46 corresponding coulombic efficiency (right y axis).  
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49 **Figure 8:** Galvanostatic discharge/charge curves for the 2<sup>nd</sup>, 10<sup>th</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycle for a  
50 battery with a glass fiber separator (a), a separator with an F-rGO\_2 interlayer (b), a separator  
51 with an F-rGO\_3 interlayer (c) and a separator with an F-rGO\_4 interlayer (d).  
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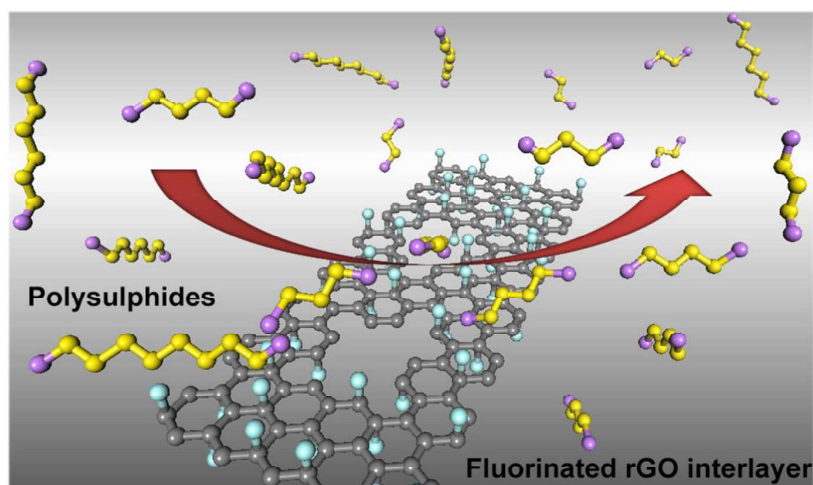
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3 **Figure 9:** S 2p spectra of the composite cathode after simple contact with the electrolyte  
4 (soaked), after the first discharge with the reference glass fiber separator and with the  
5 F-rGO\_3 interlayer.  
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8 **Figure 10:** F 1s spectra of the separator recovered from the battery after the first discharge:  
9 reference glass fiber separator (a) and separator including the F-rGO\_3 interlayer (b).  
10 Comparison with pristine F-rGO\_3, as prepared by direct fluorination of rGO (c).  
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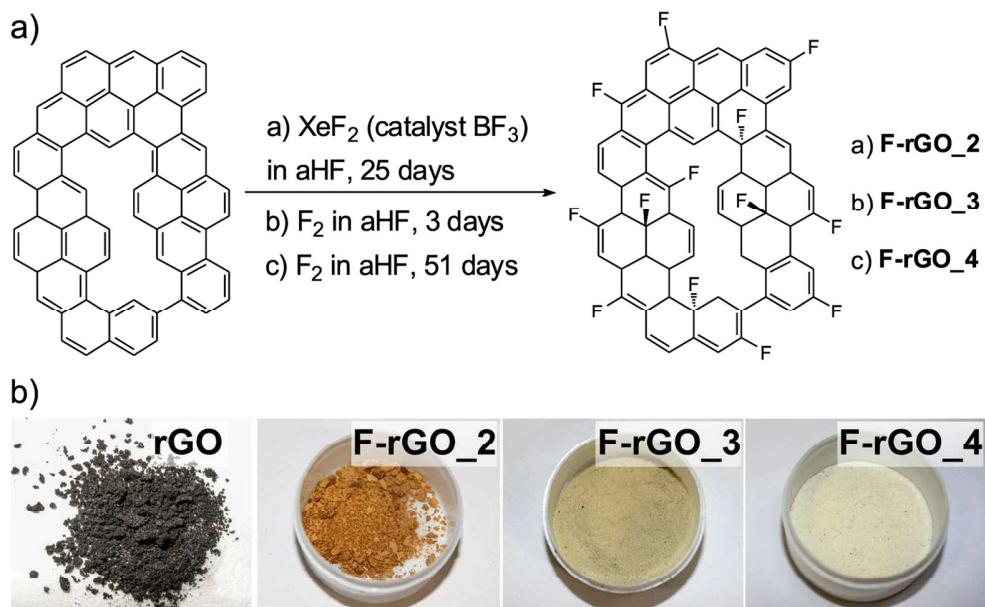
13 **Figure 11:** S 2p spectra of the composite cathode with the reference glass fiber separator and  
14 with the F-rGO\_3 interlayer after the 2<sup>nd</sup> discharge (a) and after the 2<sup>nd</sup> charge (b).  
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17 **Figure 12:** S 2p spectra of the lithium electrode with the reference glass fiber separator and  
18 with the F-rGO\_3 interlayer after the 2<sup>nd</sup> discharge (a) and after the 2<sup>nd</sup> charge (b).  
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Schematic view of Lithium polysulfide repulsion from the fluorinated rGO interlayer in a Li-S battery



28 Figure 1: Synthesis scheme of fluorinated reduced graphene oxide samples preparation (a) and photographs  
29 of reduced graphene oxide and fluorinated samples (b).  
30 129x80mm (300 x 300 DPI)

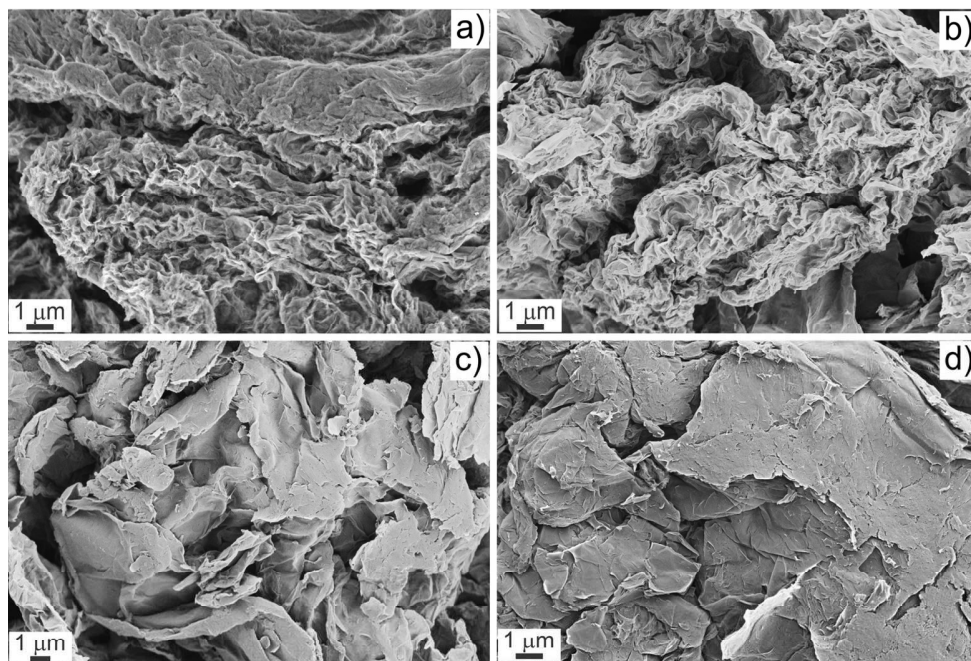


Figure 2: SEM micrographs of rGO (a), F-rGO\_2 (b), F-rGO\_3 (c) and F-rGO\_4 (d).  
140x94mm (300 x 300 DPI)

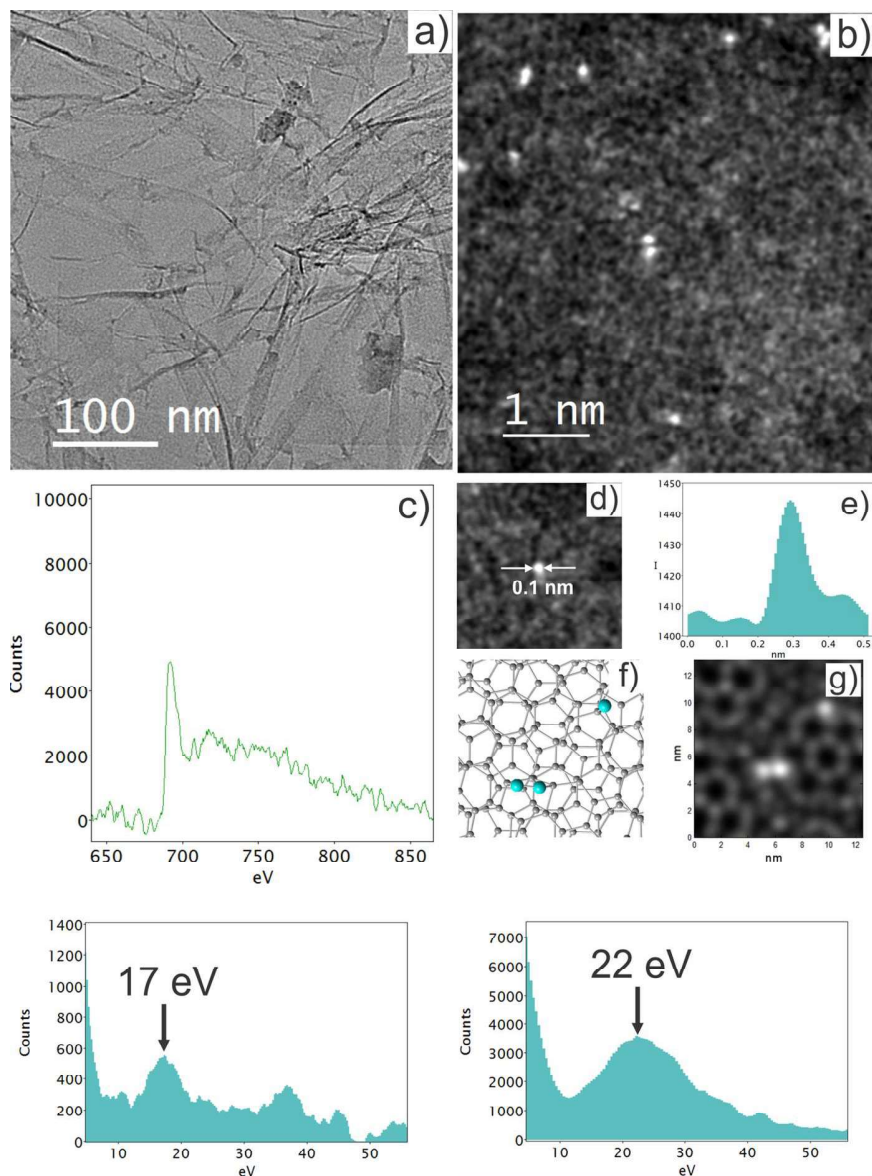


Figure 3: TEM micrograph of fluorinated graphene sheets (a). HAADF image of a thin area in the sample where individual atoms and clusters of fluorine atoms are visible (b), EELS spectrum of the area shown in Fig. 3b with characteristic fluorine K edge at 685 eV. Enlarged image of the fluorine atom (d) with the diameter (full width at half maximum) of around 0.1 nm as measured from the line profile of the intensities (e). Model of 3 layered graphene with one isolated atom and one two-atom clusters of fluorine (f) used for HAADF image calculations, shown in (g). Thickness (number of graphene layers) was estimated from the local maximum at the low loss between 12 and 30 eV as in the case of 3 – 5 layers with maximum around 17 eV (h) and 5 – 10 layers with a maximum around 22 eV (i).  
127x170mm (300 x 300 DPI)

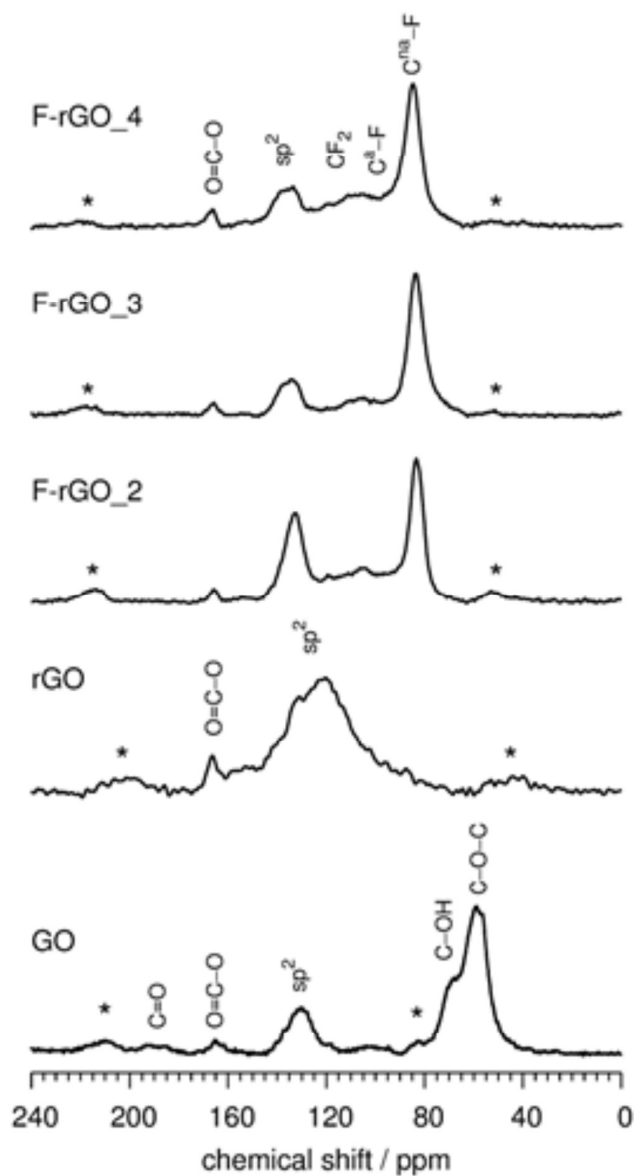
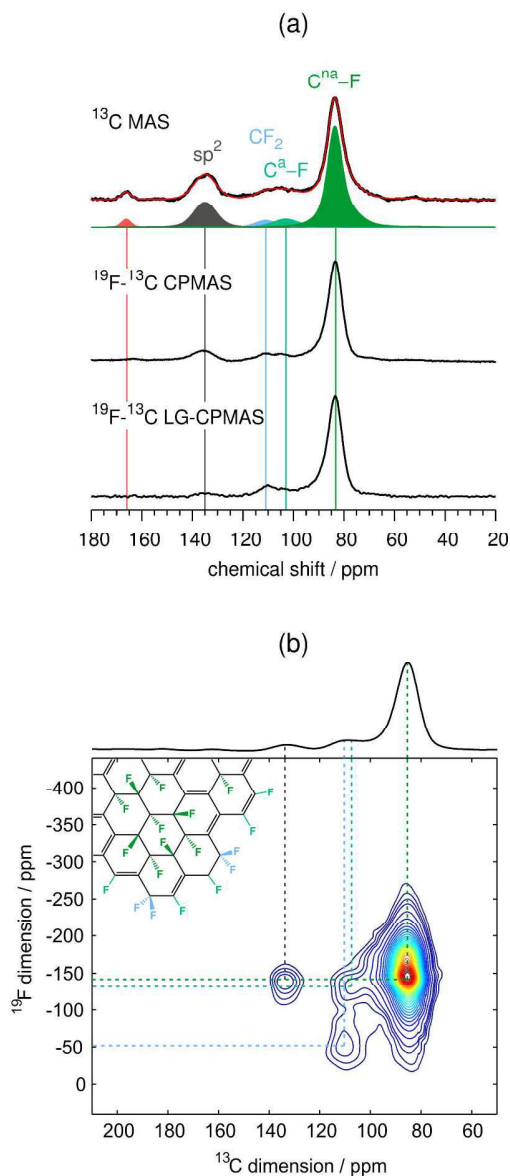


Figure 4:  $^{13}\text{C}$  MAS NMR spectra of materials at different stages of preparation. Asterisks denote spinning sidebands.  
131x244mm (300 x 300 DPI)



47 Figure 5: A more detailed NMR analysis of F-rGO\_3. (a) compares  $^{13}\text{C}$  MAS,  $^{19}\text{F}$ - $^{13}\text{C}$  CPMAS and  $^{19}\text{F}$ - $^{13}\text{C}$   
48 LG-CPMAS NMR spectra. Vertical lines are guides for eyes and mark positions of the O=C-O, graphitic, CF<sub>2</sub>  
49 and C-F carbon signals (with aromatic Ca and non-aromatic Cna character). Below the  $^{13}\text{C}$  MAS NMR  
50 spectrum, decomposition of this spectrum into individual contributions is presented. The thin red line  
51 represents the model spectrum. (b) shows  $^{19}\text{F}$ - $^{13}\text{C}$  LG-HETCOR NMR spectrum; inset shows a tentative  
52 model of the fluorinated graphene.

184x428mm (300 x 300 DPI)

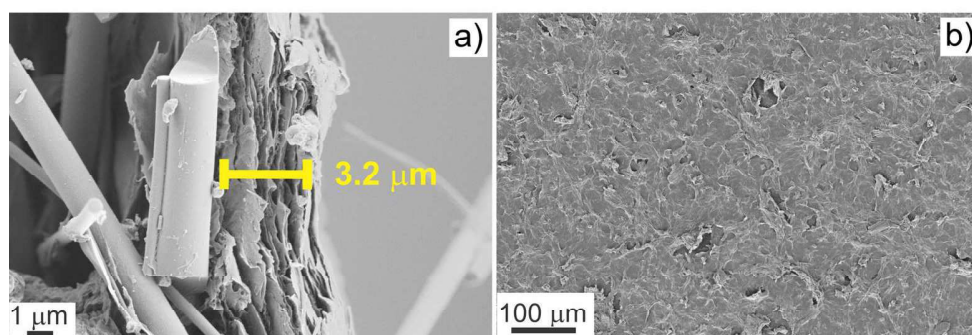


Figure 6: SEM micrograph of separator cross section showing thickness of the F-rGO\_X thickness (a) and bird's eye view of the homogeneity of deposited F-rGO\_X interlayer on the fiber glass separator (b).  
151x109mm (300 x 300 DPI)

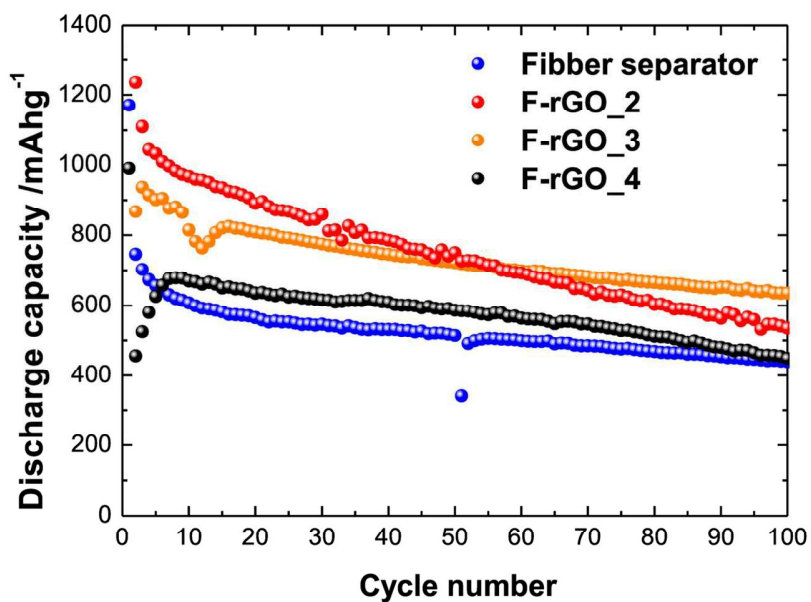


Figure 7: Cycling performance of 4 different sets of Li-S batteries (left y axis) and corresponding coulombic efficiency (right y axis).  
125x87mm (300 x 300 DPI)



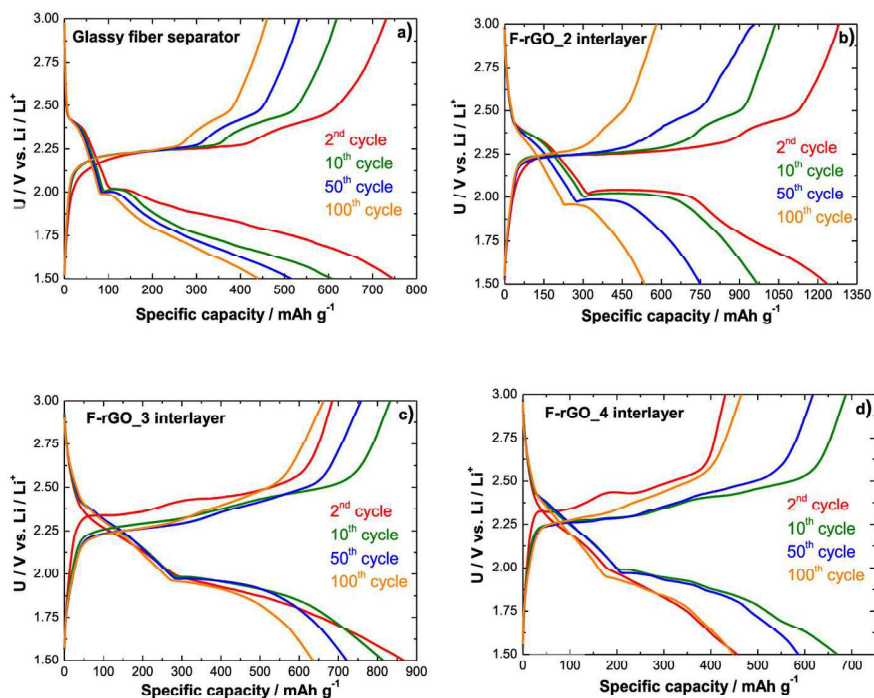


Figure 8: Galvanostatic discharge/charge curves for the 2nd, 10th, 50th and 100th cycle for a battery with a glass fiber separator (a), a separator with an F-rGO\_2 interlayer (b), a separator with an F-rGO\_3 interlayer (c) and a separator with an F-rGO\_4 interlayer (d).  
165x126mm (300 x 300 DPI)

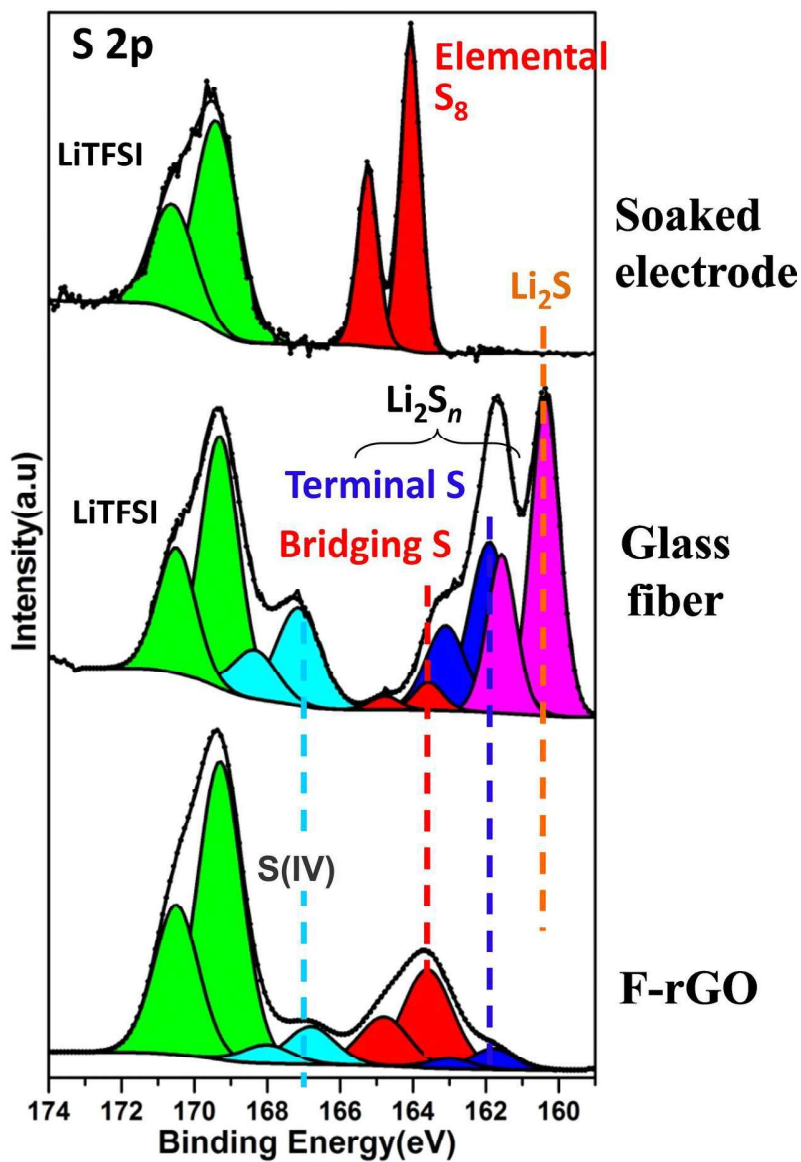


Figure 9: S 2p spectra of the composite cathode after simple contact with the electrolyte (soaked), after the first discharge with the reference glass fiber separator and with the F-rGO\_3 interlayer.  
166x243mm (300 x 300 DPI)

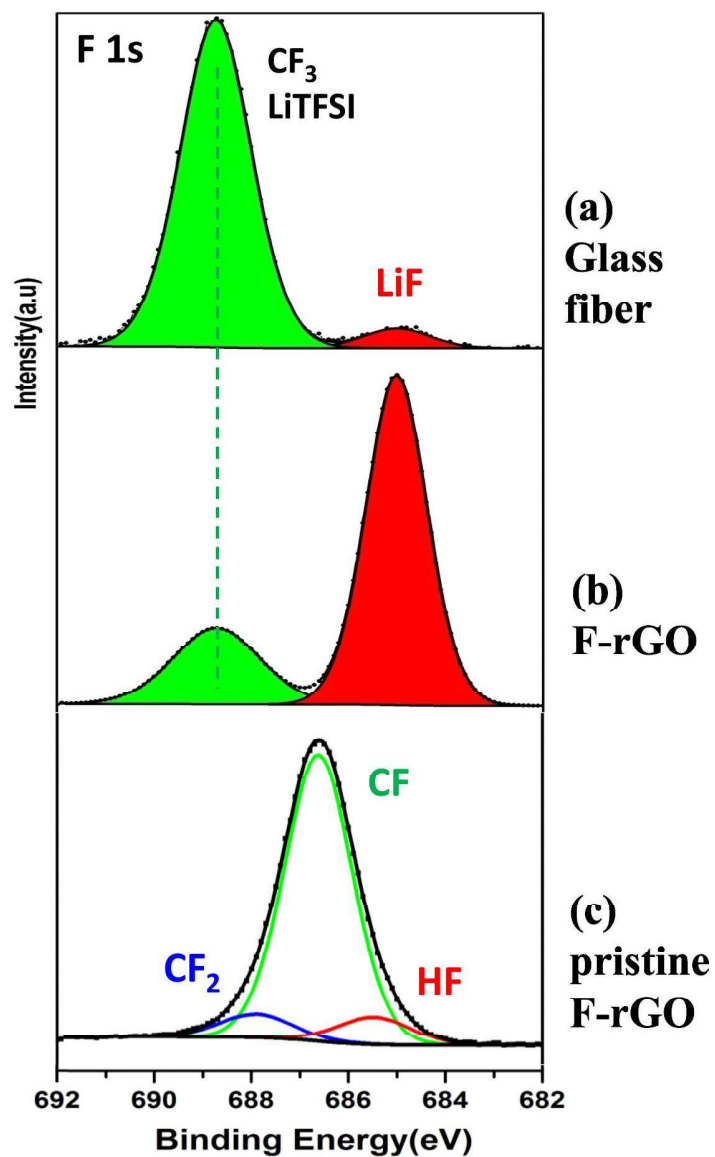


Figure 10: F 1s spectra of the separator recovered from the battery after the first discharge: reference glass fiber separator (a) and separator including the F-rGO<sub>3</sub> interlayer (b). Comparison with pristine F-rGO<sub>3</sub>, as prepared by direct fluorination of rGO (c).  
190x313mm (300 x 300 DPI)

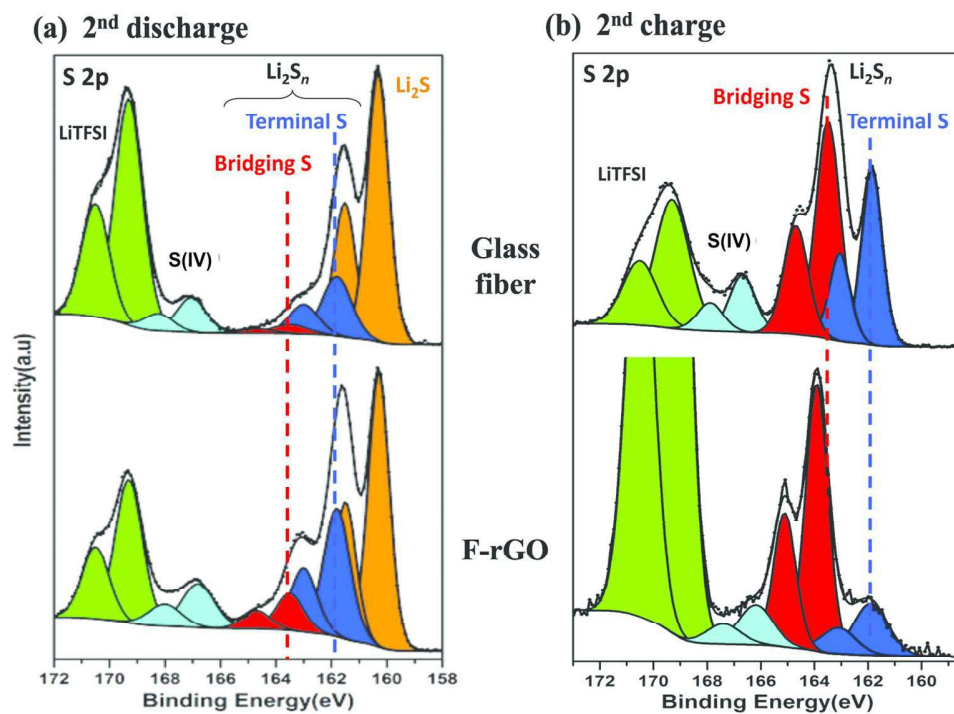


Figure 11: S 2p spectra of the composite cathode with the reference glass fiber separator and with the F-rGO\_3 interlayer after the 2<sup>nd</sup> discharge (a) and after the 2<sup>nd</sup> charge (b).  
143x104mm (300 x 300 DPI)

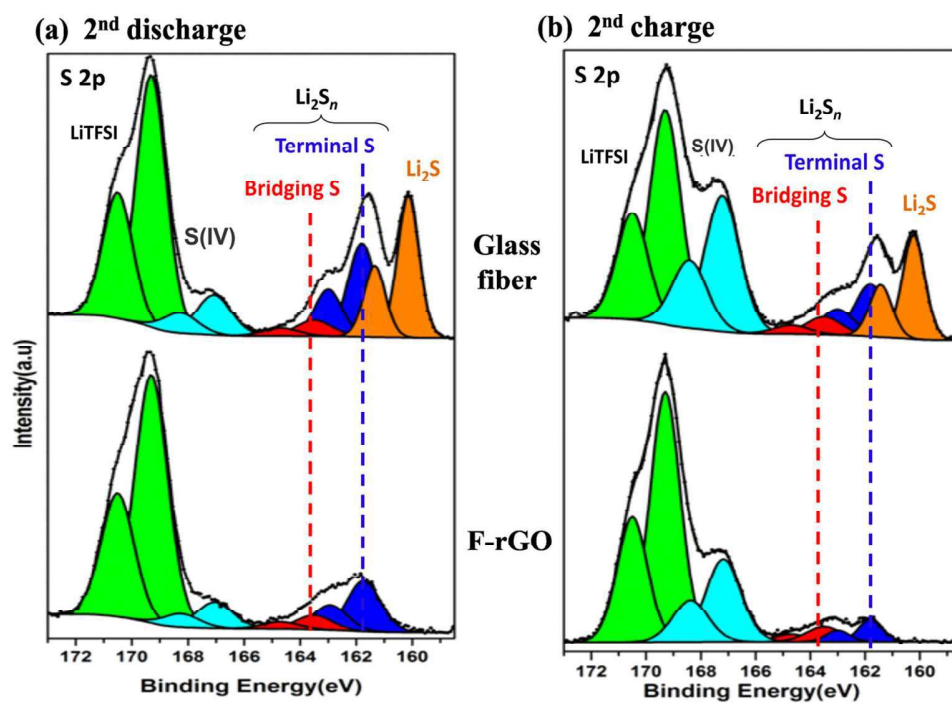


Figure 12: S 2p spectra of the lithium electrode with the reference glass fiber separator and with the F-rGO\_3 interlayer after the 2<sup>nd</sup> discharge (a) and after the 2<sup>nd</sup> charge (b).  
118x84mm (300 x 300 DPI)

## Supplementary Information

# Fluorinated Reduced Graphene Oxide as an interlayer in Li-S batteries

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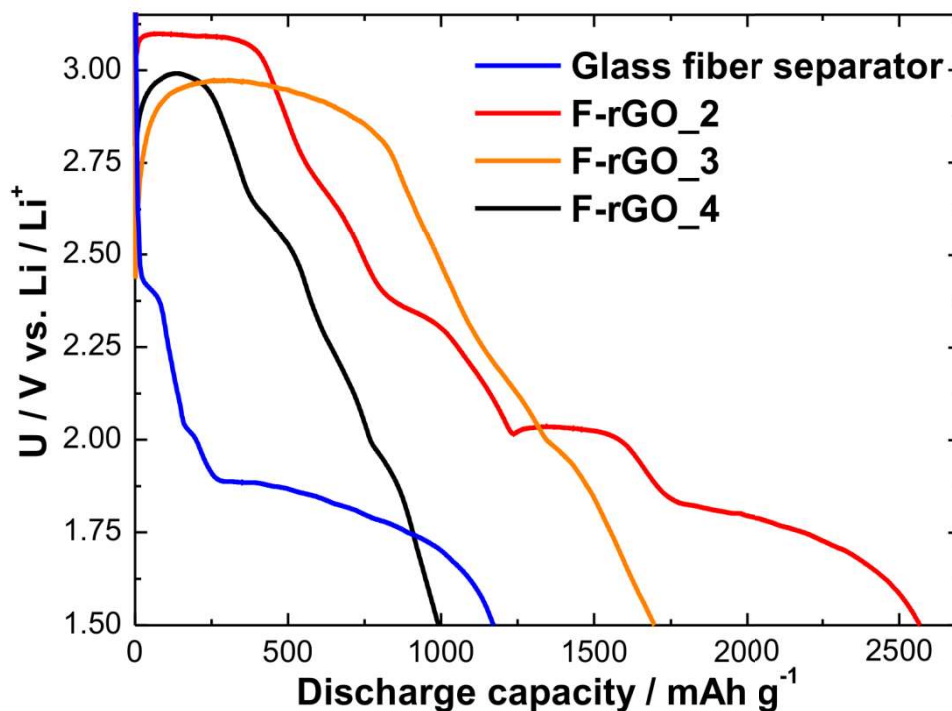


Figure S1: First discharge for 4 different sets of Li-S batteries.

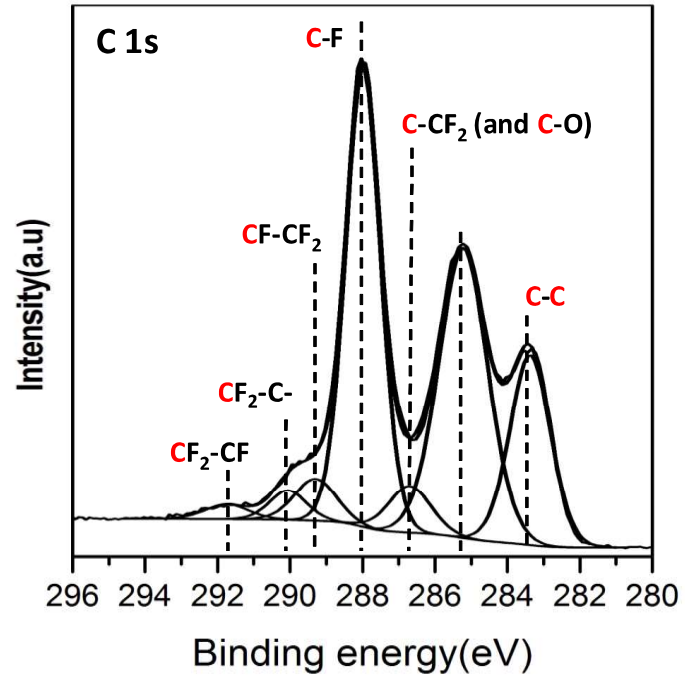


Figure S2: C 1s spectrum of F-rGO<sub>3</sub> sample