# Increasing the Affinity Between Carbon-Coated LiFePO₄/C Electrodes and Conventional Organic Electrolyte by Spontaneous Grafting of a Benzene-Trifluoromethylsulfonimide Moiety

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S *Supporting Information*
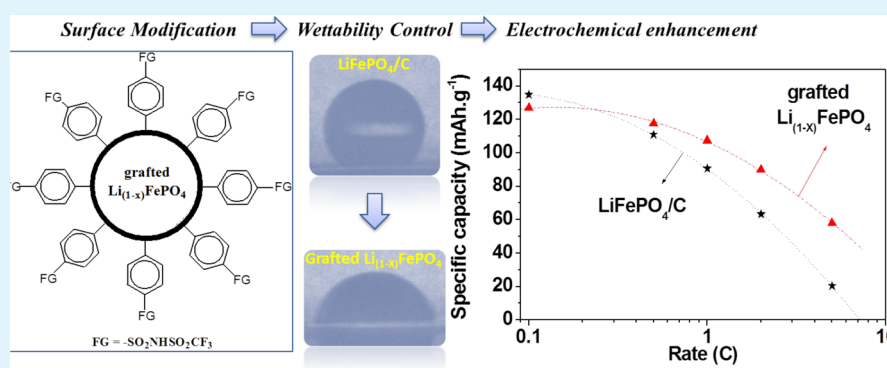
ABSTRACT: The grafting of benzene-trifluoromethylsulfonimide groups on LiFePO₄/C was achieved by spontaneous reduction of *in situ* generated diazonium ions of the corresponding 4-amino-benzene-trifluoromethylsulfonimide. The diazotization of 4-amino-benzene-trifluoromethylsulfonimide was a slow process that required a high concentration of precursors to promote the spontaneous grafting reaction. Contact angle measurements showed a hydrophilic surface was produced after the reaction that is consistent with grafting of benzene-trifluoromethylsulfonimide groups. Elemental analysis data revealed a 2.1 wt % loading of grafted molecules on the LiFePO₄/C powder. Chemical oxidation of the cathode material during the grafting reaction was detected by X-ray diffraction and quantified by inductively coupled plasma atomic emission spectrometry. Surface modification improves the wettability of the cathode material, and better discharge capacities were obtained for modified electrodes at high C-rate. In addition, electrochemical impedance spectroscopy showed the resistance of the modified cathode was lower than that of the bare LiFePO₄/C film electrode. Moreover, the modified cathode displayed superior capacity retention after 200 cycles of charge/discharge at 1 C.

KEYWORDS: surface modification, in situ generated aryl diazonium, wettability, olivine, cathode, lithium-ion battery

1. INTRODUCTION

Lithium-ion batteries are the most widely used secondary batteries for portable electronic devices. Among cathode materials that have been investigated so far, carbon-coated lithium iron phosphate (LiFePO₄/C) is one of the most interesting materials due to its low cost, nontoxicity, high specific capability, good cycle performance, and good rate capability, attributed to the presence of the carbon coating. With the appropriate synthesis methods and experimental conditions, it is possible to control the size and shape of the particles.[1] Microsized and agglomeration of particles must be avoided to improve the penetration of electrolyte in the bulk of the powder.[2,3] Intimate contact between electrolyte and active material is also crucial to achieve high performances. Concerning the electrolyte, the ionic conduction and the

thermal stability are major drawbacks limiting performances of batteries. Mixtures of salts, carbonate-based solvents, and various additives are used in commercial lithium batteries.[4] Adding one or more electrolyte additives (e.g., vinylene carbonate, vinyl ethylene carbonate, and fluoroethylene carbonate) to Li-ion batteries can dramatically improve the Coulombic efficiency and long-term stability of the batteries.[5] Electrolyte decomposition, especially in the presence of trace of water or other protic species, leads to metal dissolution and the formation of a passivation layer.[6−8] Scavengers such as Li₂CO₃ are also efficient to prevent the deterioration of the electrolyte—

material interface by limiting the metal dissolution (Fe dissolution is initiated by the mechanism of ion exchange between protons and iron ions, $2 H^+ \leftrightarrows Fe^{2+}$).[4] Furthermore, aging of LiFePO$_4$ upon exposure to ambient air was shown to be responsible for a decrease of performance.[9,10]

In order to limit the undesired effects of surface reactions and enhance the conductivity of the cathode material, numerous studies reported surface modification of cathode material for lithium-ion batteries.[11−21] Organic and inorganic coatings that were investigated include electroactive polymers such as (thiophene, poly(3,4-ethylenedioxythiophene),[11] polypyrrole,[12] and polyaniline[13]), as well as metal oxides (MgO,[14] TiO$_2$,[15] SiO$_2$,[16] and ZrO$_2$[17]). Ammonium poly(acrylic acid) dispersant[18] and surfactants like polyetheramine,[19] poly-(ethylenimine),[20] or anionic Avanel S-150[21] were used to promote better electrolyte wettability of the particle surface. Another well-known method for surface modification is based on the reduction of diazonium ions at the surface of the substrate.[22,23] This technique allows surface grafting either electrochemically[23−33] or spontaneously[34−37] by covalent molecules. Bélanger and co-workers investigated grafting onto various substrates,[38−40] in organic[41] and aqueous media.[42−44] Diazonium-based functionalization was previously reported for stabilizing carbon anodes in Li-ion batteries by the formation of lithium benzoate[45] and grafted nitrophenyl layers.[46] Silicon anodes[38,47−49] modified by organic molecules derived from a diazonium ions precursor showed superior cycling stability. The pioneering works on diazonium-modified positive electrodes concerned grafting of nitrophenyl groups on Li$_{1.1}$V$_3$O$_8$,[50] and later, LiFePO$_4$ powders were functionalized with redox molecules to assist the insertion of Li$^+$ ions.[51]

Recently, the synthesis of a diazonium (perfluoroalkyl) benzenesulfonimide monomer from Nafion monomer for proton exchange membrane fuel cells was reported.[52] Similarly, Creager et al.[53] carried out the electrochemical grafting of an aryl trifluoromethanesulfonimide moeity to enhance the penetration of electrolyte in a proton-exchange membrane (PEM) fuel cell electrode, which is crucial to achieve a high activity and a long life.[54,55] As part of our research program on Li-ion battery technology, we reported the grafting of aminophenyl and bromophenyl moieties on the carbon surface of LiFePO$_4$/C electrode materials.[56] Grafting of these organic groups was confirmed by energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), and thermogravimetric analysis (TGA) and elemental analyses. The cathodes fabricated with these materials showed improved rate capability, relative to unmodified LiFePO$_4$/C, at high charge/discharge current densities in half-cells vs Li. This proof of concept needed to be further investigated by the use of more relevant grafted molecules to increase ionic conductivity and electrolyte/electrode interface wettability and to obtain a LiFePO$_4$/C material with optimized properties. Our recent work with new organic-based Li-salts demonstrated that a family of aryl-trifluoromethanesulfonylimide Li-salts (Li-ATFSI) showed good ionic conductivities in carbonate-based solvent, were electrochemically stable enough to be used with standard electrode materials like LiFePO$_4$, lithium titanate oxide, and graphite, and gave similar cycling performance with LiPF$_6$ salt at high C-rate.[57] Inspired by these interesting results, we wanted to investigate the properties of such an aryl-trifluoromethanesulfonylimide moiety grafted on carbon-coated LiFePO$_4$.

In the present paper, we describe the attachment via a covalent carbon−carbon bond of a benzene-trifluoromethane-sulfonylimide (BTFSI) moiety onto the carbon surface of the cathode material. This covalent bond was formed via the *in situ* formation of a diazonium ion, from the corresponding amine, and its spontaneous reduction to form a radical, which reacted with the carbon layer of LiFePO$_4$. Electrochemical measurements were used to investigate the kinetic of formation of the diazonium ion and its reduction. These results were used to guide the reaction conditions for the chemical grafting on LiFePO$_4$/C. After the grafting reaction, a set of characterization techniques, thermogravimetric analysis coupled to mass spectrometry, elemental analysis, inductively coupled plasma atomic emission spectrometry, and X-ray diffraction, were used to confirm and quantify the presence of the BTFSI groups on the surface of the cathode material. After the grafting step, partial oxidation of the LiFePO$_4$/C was observed, thus confirming that the reaction of diazotization occurred in solution leading to the formation of the new organic layer.[58] The electrode made with LiFePO$_4$/C-BTFSI was more homogeneous, and the electrical conductivity of the film was not affected although sp^3 defects are supposed to be present at the surface of the carbon coating.[59] The improved hydrophilicity of the powder promotes the wettability of the modified-electrode and a better discharge capacity at high C-rate in coin-cells. Moreover, the modified cathode displayed superior capacity retention after 200 charge/discharge cycles at 1 C.

2. EXPERIMENTAL SECTION

2.1. Surface Modification of LiFePO$_4$/C. LiFePO$_4$/C (2−3 wt % carbon) was provided by Hydro-Québec, Montréal, Canada. A recently reported procedure was adopted[56] for the surface modification process. Typically, 1.5 g of LiFePO$_4$/C was dispersed in 50 mL of acetonitrile (HPLC grade), followed by the direct addition of 1.25 mmol of the freshly synthesized 4-amino-benzene-trifluor-omethylsulfominide (ABTFSI; see the Supporting Information for the complete synthesis procedure and characterization of this compound). After a one-time addition of a volume corresponding to 1 equiv of *tert*-butyl nitrite (Aldrich), the mixture was stirred overnight at room temperature. The mixture was vacuum filtered using a Büchner assembly and a Nylon filter with a pore size of 0.47 μm. The modified powder was washed successively with an excess of acetonitrile (HPLC grade), DMF, methanol, and acetone (ACS grade). Finally, the modified powder was dried under vacuum at 70 °C for at least 12 h.

2.2. Characterization. Polycrystalline samples were characterized by X-ray powder diffraction (XRD) using a Philips X'Pert diffractometer θ−2θ with Cu Kα_1,α_2 radiation (λ_1 = 1.5405 Å, λ_2 = 1.5443 Å) and a monochromator to avoid the presence of K$_\beta$ radiation. The data were collected in the range between 15° and 60° in steps of 0.03° and an integration time of 5 s per step using an X'Celerator detector. Thermogravimetric analyses (TGA) were carried out under a constant air flow of 90 mL·min^{-1} from 30 to 750 °C with a heating rate of 10 °C·min^{-1}, using TA Instruments TGA (Q500)/Discovery MS. Mass spectrometry (MS) spectra were recorded during the thermogravimetric analyses, and all the fragments ranging from 30 to 300 m/z were analyzed. The hydrophilicity of the modified-sample and pristine LiFePO$_4$/C was determined by depositing 30 μL of water on the corresponding cathodes material. The water contact angle was measured by a homemade device, with lens to magnify the water droplets, and the contact angle (deg) was determined from a numerical image of the magnification with ImageJ software. The lithium content in the modified sample was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on Thermo Jarrelle Ash Trace Scan. An acidic digestion was necessary to prepare the samples. Typically, 40 mg of the cathode material was placed in 30

mL of 18 M nitric acid and the solution was boiled until a transparent solution was observed. After dilution to 100 mL with 5% HNO_3, the solution was injected in the plasma. The lithium content was obtained from a calibration curve of various Li concentrations prepared from a Lithium Atomic Spectroscopy Standard Solution Fluka ([Li] = 1000 ppm, prepared with $LiNO_3$ and HNO_3, 0.5 M). Elemental analyses were performed on an EAS1108, Fisons instruments S.p.A. (Italy). Approximately 2 mg of sample was placed in a tin cup and combusted at 1021 °C under He/O_2 flow. Combustion gases such as CO_2, H_2O, N_2, and SO_2 were transported under He flow to the chromatography to determine the C, H, N, and S concentrations, respectively. The cathode films (preparation described in Section 2.3.2) were observed with a scanning electron microscope (JEOL JSM-7600F) equipped with a field emission gun (FEG) at an acceleration voltage of 5 kV. The conductivity of the cathode films was determined by 4-point probe measurement using a Keithley 6220 DC precision current source (Signatone). The films were casted on glass slides to avoid the contribution of the aluminum current collector. The I−V DC potential sweeps were recorded at 100 mV·s^{-1} and yielded a linear I−V response. The electrical conductivity of the cathode film was calculated as follows:

$$\sigma_e = \frac{1}{R \times e}$$

where σ_e is the electrical conductivity (S/cm), R is the resistance of the film determined from the inverse slope of the I−V curve (Ω square), and e is the thickness of the film (cm).

2.3. Electrochemical Measurements. *2.3.1. Electrochemical Reduction of in Situ Generated Diazonium Ion of the Corresponding 4-Amino-Benzene-Trifluoromethylsulfonimide.* Potassium ferricyanide, potassium ferrocyanide, lithium perchlorate, and tetrabutylammonium hexafluorophosphate (NBu_4PF_6) were obtained from Aldrich. For the preparation of all aqueous solutions, Nanopure water (18.2 MΩ·cm) was used. Electrochemical experiments were performed at room temperature with a potentiostat/galvanostat Solartron model 1287 (Solartron Instruments) and an electrochemical interface SI1480 (Solartron Instruments). Glassy carbon (3 mm diameter) supplied by Bioanalytical Systems Inc. (BASi) was used as the working electrode. Before each measurement, the working electrode was polished with Buehler 1 μm alumina slurry (Tech-Met Canada) and then washed in ultrapure water by sonication for 5 min. All electrochemical measurements were carried out at a scan rate of 50 mV·s^{-1} in a one-compartment cell with a three-electrode configuration. Prior to the kinetic study of diazonium ion formation, a cyclic voltammogram was recorded every 10, 20, or 30 min and the experiment was stopped after 21 h. All potentials are reported versus Ag/AgCl reference electrode in aqueous electrolyte and Ag/AgNO$_3$ (0.01 M in acetonitrile) reference electrode in acetonitrile solution. Platinum gauze was used as counter electrode. All solutions were degassed by bubbling nitrogen (grade 4.8) for 30 min before each measurement.

2.3.2. Battery Preparation and Electrochemical Testing. The modified powders were mixed with conductive acetylene black carbon and polyvinylidenedifluoride (PVDF) in a weight ratio of 80:10:10 using 1-methyl-2-pyrrolidone (Alfa Aesar, 99%) as the solvent. The slurry was cast on aluminum foil (15 μm) and dried at 70 °C under vacuum for 24 h. The film was cut into circular discs (area = 1.767 cm^2) having a mass loading of ∼2.5 mg.cm^{-2}. Two-electrode electrochemical coin cells were assembled with lithium metal anodes, Celgard-2320 separator, 1 M $LiPF_6$ in ethylene carbonate (EC)/ diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:1:1 by vol.) electrolyte and LiFePO$_4$/C cathode. The cells were assembled in a dry argon-filled glovebox. The cells were controlled with a VMP3 potentiostat, and a charge/discharge cycling procedure was performed in galvanostatic mode between 2.0 and 4.0 V versus Li/Li$^+$ at different current densities after 1 h of rest at open circuit voltage (OCV). A current density of 170 mA·g^{-1} corresponds to a 1 C rate. For each current density ranging from C/10 to 5 C, 10 cycles were subsequently recorded with 1 min at OCV before each current density. Duplicate measurements with two independent coin-cells were performed.

Electrochemical impedance measurements were performed with amplitude of 10 mV and a frequency range of 200 kHz to 0.01 Hz at a depth of discharge of 50%. Electrochemical impedance measurements were carried out after five cycles of charge/discharge at a C/2 rate and then stabilized by applying a constant potential for 4 h. For cycling performance, 5 cycles in galvanostatic mode at low C rate (C/10) were performed before constant current tests with a current density corresponding to a 1 C rate at room temperature for 200 cycles.
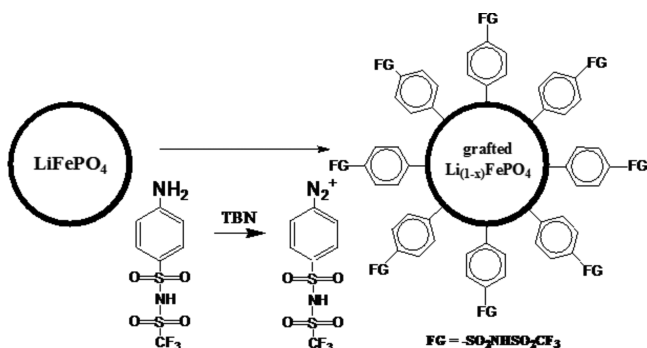
3. RESULTS AND DISCUSSION

3.1. Synthesis of the 4-Amino-Benzene-Trifluoromethanesulfonimide (ABTFSI). In our investigation of a family of new Li-salts for Li-ion batteries, we developed a synthesis procedure to obtain various aryl derivatives of the common lithium bis(trifluorosulfonimide), LiTFSI. These salts were evaluated as electrolyte and showed interesting properties in terms of ionic conductivity (ca. 1.70 mS·cm^{-1} at ca. 0.5 M in EC/DEC (3/7)), thermal stability (decomposition onset at ≥300 °C), and electrochemical window (≥4.5 V vs Li/Li$^+$ in EC/DEC (3/7) with a high surface carbon material electrode). More significant was the observation that they were inert to the aluminum current collector, compared to LiTFSI, which corrodes this material and limits its utilization.[60] Thus, these results prompted us to use the aryl-trifluoromethanesulfonimide moiety as a grafting unit on the carbon shell of a LiFePO$_4$ cathode material to increase the ionic conductivity in the vicinity of the LiFePO$_4$/C particles.

On the basis of our previous results, a new synthesis path was proposed to obtain a simple and low-cost reaction, the desired 4-amino-benzene-trifluoromethanesulfonimide (ABTFSI). Creager et al.[53] proposed an eight-step synthesis method that included the reduction of the nitro group to the corresponding diazonium salt. Mei et al.[52] proposed a shorter procedure, but still containing five different synthesis steps. The newly developed procedure comprises two steps (See Scheme S1, Supporting Information), using as starting compound the commercial 4-nitrobenzenesulfonyl chloride which was subjected to an amination reaction, and ABTFSI was obtained after reduction of the corresponding nitro group in good yield (See the Supporting Information for experimental details).

3.2. Investigation of the *in Situ* Formation and Reduction of Diazonium Ion. Our strategy also differs from previous reports[47−49,61] as we choose to generate the highly reactive and unstable diazonium ions *in situ* using *tert*-butyl nitrite directly in the presence of the material to be grafted. This one-pot method has the advantages of limiting the manipulation of unstable reactive species and reducing the number of synthesis steps and can be used for large−scale synthesis. The aim of this electrochemical investigation was to study the diazotization reaction of 4-amino-benzene-trifluoromethylsulfonimide (Scheme 1) in acetonitrile, first to demonstrate the feasibility of the grafting reaction, and second to determine the more suitable experimental conditions for the surface modification of LiFePO$_4$/C powders.

Figure 1A shows the first ten cyclic voltammograms at a scan rate of 50 mV·s^{-1} of a glassy carbon electrode in a solution of the *in situ* generated diazonium ions of ABTFSI after 180 min of reaction of equimolar amounts (25 mM) of ABTFSI and *tert*-butyl nitrite. A cathodic wave located at 0 V vs Ag/Ag$^+$ is observed in the first cycle that is in agreement with a previous literature report and corresponds to the reduction of the diazonium ions into radicals which then bind covalently to the glassy carbon surface.[23] Indeed, this cathodic peak is absent in
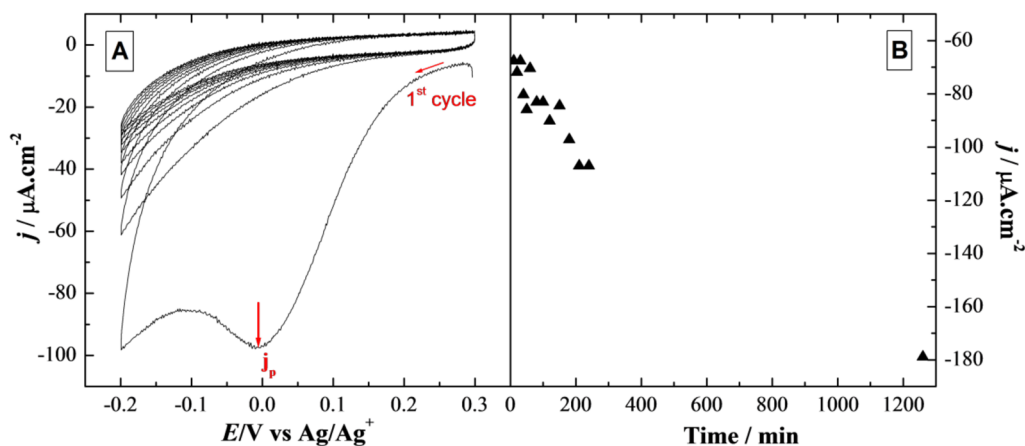
Scheme 1. Representation of the Grafting Reaction, with the Final Structure Representing the Organic Layer on the Carbon Coating of the Partially Delithiated $Li_{(1-x)}FePO_4/C$[a]

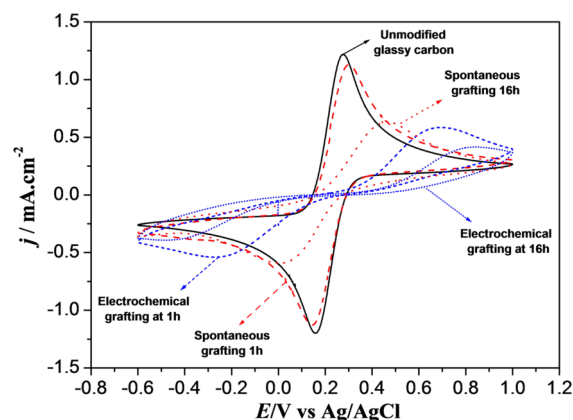[a]FG represents the functional group: $-SO_2NHSO_2CF_3$.

Figure 2. Cyclic voltammograms (2nd cycle) in 5 mM $K_3Fe(CN)_6$ + 5 mM $K_4Fe(CN)_6$ with 0.1 M $LiClO_4$ as aqueous electrolyte at a scan rate of 50 mV·s^{-1} with an unmodified glassy carbon electrode (solid line), modified by spontaneous grafting during 1 h (dashed line) and 16 h (dotted line) and by electrochemical reduction with 10 cyclic voltammograms at t = 1 h (short dashed line) and t = 16 h of diazotization reaction (short dotted line) in a 25 mM 4-amino-benzene-trifluoromethylsulfonimide + 25 mM tert-butyl nitrite solution with 0.1 M NBu_4PF_6 as supporting electrolyte in acetonitrile.

the subsequent scans due to passivation of the electrode surface with the attached organic groups.[22,23] Moreover, the reduction potential of the diazonium ions observed around 0 V vs Ag/Ag$^+$ suggests an efficient and easy spontaneous reduction reaction. In addition, the formation of the diazonium ions was followed by measuring the cathodic peak current density as a function of the reaction time between the amine and tert-butyl nitrite. Figure 1B shows an increase of the current density as a function of time, indicating that diazonium ions formation in acetonitrile with an equimolar amount of both reactants is slow. These electrochemical results demonstrate that the grafting process should be performed after several hours of reaction to maximize the grafting yield. They also highlight the importance of knowing the rate of formation of diazonium ions, which significantly depends on the nature of the amine and the reaction conditions.[41,62]

The presence of organic groups attached to the glassy carbon electrode surface was studied by observing its blocking properties in a soluble electroactive species solution like $Fe(CN)_6^{3-/4-}$ in water.[58] Figure 2 shows the cyclic voltammetry response for a glassy carbon electrode modified by spontaneous reaction during 1 and 16 h (method 1) and by electrochemical reduction with 10 cyclic voltammograms after reaction of the amine and tert-butyl nitrite for 1 and 16 h (to

form the in situ generated diazonium ions) (method 2). The $Fe(CN)_6^{3-/4-}$ redox couple presents a quasi-reversible system at the unmodified glassy carbon electrode with an apparent redox potential of 0.2 V vs Ag/AgCl. In contrast, the BTFSI-modified glassy carbon electrodes obtained by method 1 shows a significant blocking behavior for the redox reactions of the $Fe(CN)_6^{3-/4-}$ redox probe, which is even more evident for the glassy carbon electrode modified by electrochemical reduction (method 2). Thus, method 1 leads to a grafted layer that is obviously less compact than the one obtained by electro-chemistry (method 2). In both cases, the blocking effect caused by spontaneous grafting is dependent on the elapsed time for the formation of the diazonium ions. This is particularly obvious for the spontaneous grafting (method 1) where after 1 h only a small blocking effect was noted. This is consistent with the kinetic study that established that the formation of diazonium ions is slow (Figure 1B). Nevertheless, method 1 was used for this study, as the electrografting method (method

Figure 1. (A) Cyclic voltammograms (10 cycles) of glassy carbon electrode in 25 mM 4-amino-benzene-trifluoromethylsulfonimide + 25 mM tert-butyl nitrite in acetonitrile with 0.1 M NBu_4PF_6 as supporting electrolyte at a scan rate of 50 mV·s^{-1} recorded at t = 180 min. (B) Current density (j_p) of the reduction peak located at 0 V vs Ag/Ag$^+$ in the first cycle versus time of the diazotization reaction after addition of tert-butyl nitrite at t = 0 min.

2) would mainly lead to the functionalization of the electrode/electrolyte interface. More importantly, electrografting may be incompatible with other components of the electrode (current collector, binder, electronic conductor, etc.) and thus may be more difficult to apply on a larger scale. The spontaneous method allows chemical grafting of $LiFePO_4$/C particles directly in solution, and presumably, this would lead to a more uniformly grafted material. Finally, it was also established that a high concentration of precursors (e.g., amine and *tert*-butyl nitrite) is required to obtain good grafting yield (See Section 2 in the Supporting Information).

3.3. Surface Modification of $LiFePO_4$/C Powder. The attachment via a covalent bond of a benzene-trifluoromethyl-sulfonimide organic moiety onto the carbon surface of the $LiFePO_4$ cathode material (Scheme 1) was achieved as described in the Experimental Section.

The water contact angle decreased from 113° for the unmodified $LiFePO_4$/C (Figure 3, left) to 76° for the modified
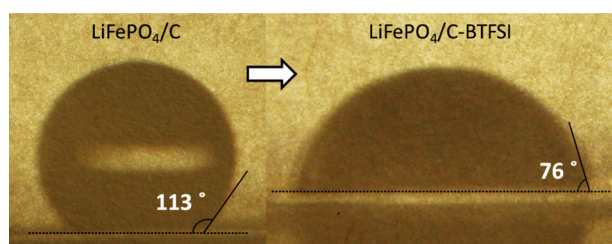
Figure 3. Images of a water drop on the unmodified $LiFePO_4$/C (contact angle = 113°) and on BTFSI-modified $LiFePO_4$/C (contact angle = 76°) composite cathodes.

(Figure 3, right) as a result of BTFSI grafting, which provides indirect evidence for surface grafting. Thus, after modification, the surface was clearly more hydrophilic. Furthermore, the affinity of benzene-trifluoromethylsulfonimide moieties for a conventional battery electrolyte was investigated by depositing a drop of the electrolyte (1 M $LiPF_6$ in EC/DEC/DMC (1:1:1 by vol)) onto a modified cathode disk (not shown). The experiment showed that the wettability was considerably enhanced by modification of the active electrode material as the electrolyte penetrated more rapidly into the cathode in comparison with the standard cathode.

A significant difference between the BTFSI-modified and the unmodified samples was observed in contact with water. After 10 min in water, the unmodified $LiFePO_4$/C powder, as shown Figure 4a, deposited on the bottom of the erlenmeyer, whereas the $LiFePO_4$/C-BTFSI powder remained in suspension after 10 min (Figure 4b).

3.4. Characterization of the Modified-$LiFePO_4$/C Powders. *3.4.1. TGA-MS Analysis.* The unmodified and modified $LiFePO_4$/C powders were characterized by thermo-gravimetric analysis coupled with a mass spectrometry analyzer to determine the loading of grafted molecules and to obtain some evidence for the chemical nature of the grafted species.[56]

The thermogravimetric analysis curve for the unmodified $LiFePO_4$/C shown in Figure 5 consists of two regions.[63] In the first region between 300 and 400 °C, the weight gain (2.3%) corresponds to the oxidation of $LiFePO_4$ and the formation of $Li_3Fe_2(PO_4)_3$ and Fe_2O_3. In the second region from 430 to 600 °C, the weight loss (0.5%) is due to the burnoff of the carbon shell of the $LiFePO_4$/C particle. The variation of mass in the
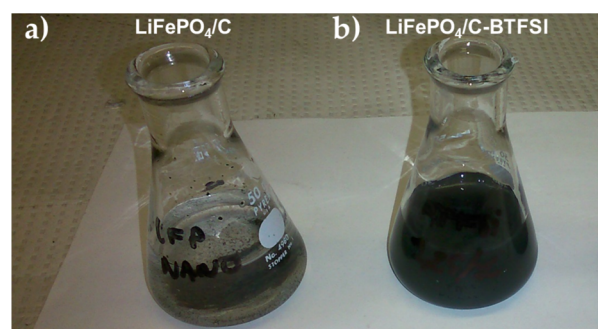
Figure 4. Images of (a) unmodified $LiFePO_4$/C and (b) $LiFePO_4$/C-BTFSI powders dispersed in water for 10 min.

latter region can be used to evaluate the weight of grafted functionality on the carbon shell.[64]

The thermogravimetric curves for $LiFePO_4$/C-BTFSI and the unmodified sample show significant differences. Between 100 and 340 °C, a continuous weight loss of 1.14% was recorded with the modified sample, which is probably due to adsorbed humidity by the powder because of the increased hydrophilicity. This is confirmed by the detection of water (H_2O, m/z = 18) in the mass spectrometry profile of the modified sample (Figure 6b). Furthermore, the onset of oxidation for the grafted powder occurs at a slightly higher temperature (about 40 °C) than the unmodified $LiFePO_4$/C. The same trend was observed in our previous work and was attributed to the presence of a protective layer on the $LiFePO_4$ core by the organic species.[56] Moreover, the weight gain due to the oxidation of $LiFePO_4$ between 340 and 440 °C for the grafted sample is lower compared to the unmodified powder. In fact, during the grafting reaction, partial oxidation of $LiFePO_4$ occurs in order to assist the reduction of the *in situ* generated diazonium ions. This partial oxidation explains the smaller weight gain of the modified sample.[61]

Careful examination of the MS spectra recorded during thermogravimetric analyses of the unmodified $LiFePO_4$/C powder (Figure 7a) and $LiFePO_4$/C-BTFSI (Figure 7b) revealed that the onset of CO_2 generation occurs at lower temperature for the modified powder. This suggests that the BTFSI layer starts degrading at 300 °C and thus leads to an underestimation of the weight gain associated with oxidation of $LiFePO_4$. A significant difference is a larger weight loss between 440 and 600 °C of the grafted sample compared to the unmodified $LiFePO_4$/C. This leads to an additional weight loss of only 0.02 wt % (Table 1) which is assigned to the loss of benzene-trifluoromethylsulfonimide-grafted groups. This value would point to a particularly low loading of grafted groups. Nonetheless, we believe that this evaluation is clearly an underestimation due to the low thermal stability of the BTFSI layer and other evidence (MS and contact angle) that suggests the presence of this layer. As a consequence, elemental analysis was used to assess more accurately the loading of the grafted groups.

3.4.2. Elemental Analysis. Elemental analysis was used to quantify the loading of the grafted molecules on the $LiFePO_4$/C particles. The loading of each element is given in Table 2 for the 4-amino-benzene-(trifluoromethyl)sulfonimide molecule, the bare $LiFePO_4$/C, and the modified $LiFePO_4$/C powder. The composition of the amine precursor is in good agreement with that expected on the basis of chemical formula (See Section 1.4 in the Supporting Information).
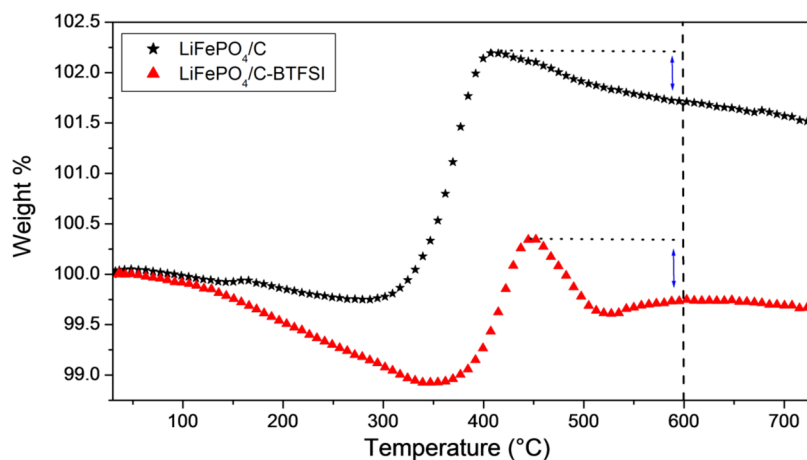
Figure 5. Thermogravimetric curves for the BTFSI-modified and the unmodified LiFePO₄/C powders.

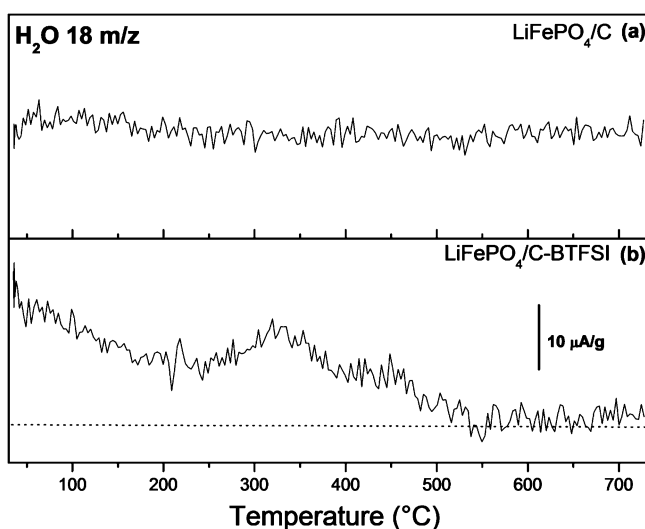**Figure 6.** Mass spectra recorded during thermogravimetric analyses for (a) the pristine LiFePO₄/C powder and for (b) LiFePO₄/C-BTFSI. H₂O was detected at $m/z = 18$.
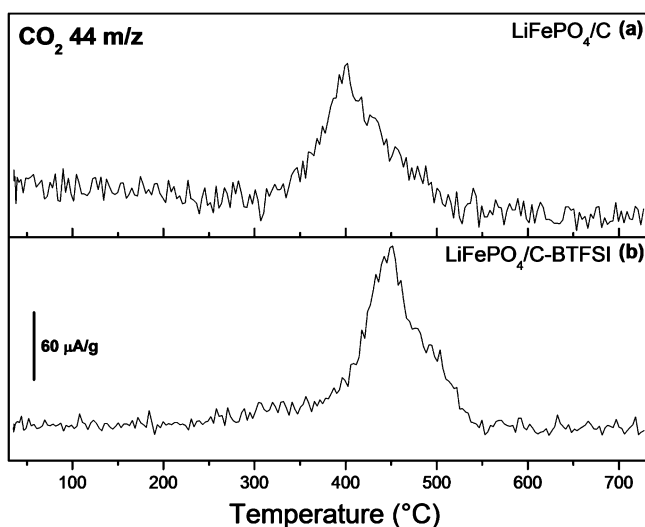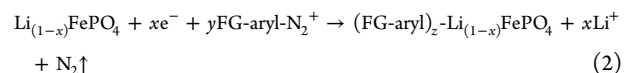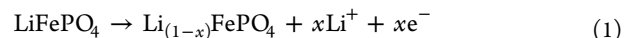

Figure 7. Mass spectra recorded during thermogravimetric analyses for: (a) unmodified LiFePO₄/C and (b) LiFePO₄/C-BTFSI. The CO₂ formed during the decomposition of the carbon coating was detected at $m/z = 44$.

The carbon content of the unmodified LiFePO₄/C powder is 2.33 wt % (Table 2). The modified LiFePO₄/C powder shows an additional weight of carbon of 0.9 wt %, for a total of 3.23 wt %. The C/N and C/S molar ratios for the modified LiFePO₄/C powder, deduced from the sulfur and nitrogen content, did not agree with the expected ratio of 7 and 3.5, respectively (Scheme 1). However, the low nitrogen content (less than 0.3 wt %) is not very reliable. Furthermore, the presence of adsorbed reactants or solvents used in the grafting reaction may also be the origin of higher N/S and C/S molar ratios. Therefore, the sulfur content from elemental analysis was used to estimate the loading of the grafted groups; i.e., the only source of sulfur is from the BTFSI-grafted moieties. On the basis of the molecular formula of 4-amino-benzene-trifluoromethylsulfonimide and the elemental analysis data for the modified sample, 0.29 wt % of sulfur in the LiFePO₄/C-BTFSI material would correspond to approximately 2.1 wt % of grafted groups (Table 1).

3.4.3. Partial Oxidation of LiFePO₄ in Solution. As observed by thermogravimetric analysis, partial oxidation of the modified powder occurs after the grafting reaction. The loss of lithium from the bare LiFePO₄ sample (eq 1) is associated with the reduction of diazonium ions in solution[56,61] (eq 2):

$$LiFePO_4 \rightarrow Li_{(1-x)}FePO_4 + xLi^+ + xe^- \tag{1}$$

$$Li_{(1-x)}FePO_4 + xe^- + yFG\text{-}aryl\text{-}N_2^+ \rightarrow (FG\text{-}aryl)_z\text{-}Li_{(1-x)}FePO_4 + xLi^+ + N_2\uparrow \tag{2}$$

The amount of grafted functionality, z, was determined by elemental analysis. ICP-AES was used to determine the lithium content of the modified and unmodified LiFePO₄/C powders. The values of x in $Li_{(1-x)}FePO_4$ are presented in Table 1 for the unmodified and grafted samples. A loss of 0.12 Li was observed for LiFePO₄/C-BTFSI. The corresponding expected amount of grafted groups of 21.9 wt % is much higher than the experimental values (2.1 wt %). Thus, approximately only 10% of the oxidized LiFePO₄ contribute to the formation of the grafted layer, as also observed for bromophenyl-modified LiFePO₄/C powder.[65] These results suggest that the oxidation of the cathode material is involved in side reactions (e.g., oxidation by *tert*-butyl nitrite) and the complete mechanism of the grafting reaction that is currently under investigation will be published later.[65]

Table 1. Summary of ICP Experiments, Thermogravimetric and Elemental Analyses of Unmodified and BTFSI-Modified LiFePO$_4$/C Powders To Estimate the Amount of Deinserted Li$^+$ Ions, and the Loading of Grafted Groups after the Grafting Reaction[a]

| sample	wt % of grafted molecules by TGA	wt % of grafted molecules by elemental analysis	x in Li$_{(1-x)}$FePO$_4$ by ICP	electronic conductivity (S·cm^{-1})[b]
LiFePO$_4$/C			∼0	0.24 ± 0.06
LiFePO$_4$/C-BTFSI	0.02	2.1	0.12	0.28 ± 0.04

[a]Electronic conductivity values for corresponding cathode films are also provided. [b]Measurements ($N = 20$) performed on films casted on glass slides as described Section 2.2.

Table 2. Weight Content (%) of N, C, H, and S of 4-Amino-Benzene-Trifluoromethylsulfonimide, Unmodified and Modified LiFePO$_4$/C Powders

	weight (%)			
sample	% N	% C	% H	% S
4-amino-benzene-(trifluoromethyl)sulfonimide[a]	6.13 (9.21)	19.74 (27.63)	3.48 (2.32)	14.08 (21.07)
LiFePO$_4$/C	0	2.33	0	0
LiFePO$_4$/C-BTFSI	0.18	3.23	0	0.29

[a]Values in parentheses refer to theoretical values.

The XRD pattern of the organic grafted cathode material is presented Figure 8. All of the diffraction peaks corresponding
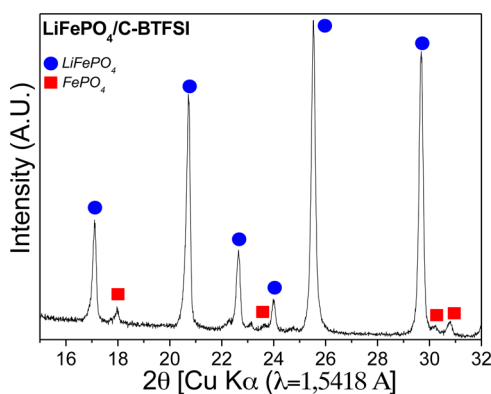

Figure 8. XRD pattern of LiFePO$_4$/C-BTFSI powder. LiFePO$_4$ (blue ●) and FePO$_4$ (red ■) phases are identified.

to the LiFePO$_4$/C phase are indexed (blue ●) and belong to the *Pnmb* orthorhombic space group (JCPDS 01-081-1173).[66] Additional low intensity peaks (red ■), associated with the delithiated FePO$_4$ phase, are also identified. The presence of

this second phase confirms that LiFePO$_4$ was slightly oxidized during the grafting reaction.

3.5. Electrochemical Measurements. The contact angle measurements unequivocally demonstrated that surface modification improved the wettability of the cathode. Hence, a better affinity between the active material and the electrolyte and improved performance at higher cycling rates are expected. This was confirmed in coin-cells with the bare and modified LiFePO$_4$/C electrodes.

Figure 9 presents the charge/discharge profiles for: (A) the unmodified and (B) the modified LiFePO$_4$/C-BTFSI electrodes cycled at different rates ranging from C/10 to 5 C. At low discharge currents (below C/2), both electrodes display the typical plateau of a LiFePO$_4$ cathode at around 3.4 V vs Li/Li$^+$.[21] Interestingly, a larger irreversibility is noted for the modified electrode during the first cycle at C/10, quite similar to results reported previously for LiFePO$_4$/C electrodes following modification with bromophenyl and aminophenyl groups.[56] The discharge voltage sharply decreased with the increase in cycling rate for the unmodified LiFePO$_4$/C (Figure 9A) due to the higher resistance and polarization than for the modified LiFePO$_4$/C-BTFSI electrode (Figure 9B), consistent with an improvement of the Li$^+$ extraction for the latter. As a consequence, the discharge capacities of the unmodified
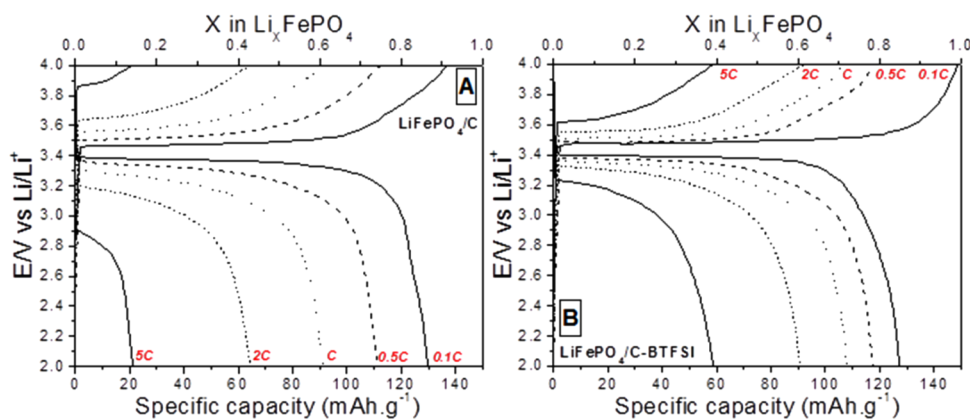
Figure 9. Charge/discharge profiles at various rates (identified in red characters) for (A) the unmodified and (B) the modified LiFePO$_4$/C-BTFSI electrodes.

electrode are smaller for high charge/discharge currents. In fact, at 5C the modified LiFePO$_4$/C-BTFSI electrode is able to deliver a discharge capacity of about 60 mAh·g^{-1} similar to the unmodified LiFePO$_4$/C electrode at a cycling rate of 2 C.

Figure 10 shows the rate capability for unmodified and modified LiFePO$_4$/C electrodes. For the lowest current density
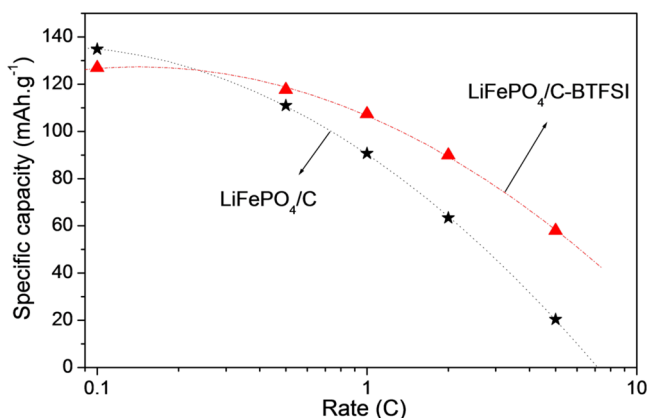

Figure 10. Rate capability for unmodified LiFePO$_4$/C and LiFePO$_4$/C-BTFSI electrodes.

(C/10), the specific capacity delivered by LiFePO$_4$/C-BTFSI was slightly lower, (126 mAh·g^{-1}) compared to the bare LiFePO$_4$/C (135 mAh·g^{-1}). This difference may be due to the uncertainty in the loading of grafted groups, which thus directly influences the value of specific capacity since the same discharge capacities were obtained for another independent coin-cell. When the cycling rate was increased, the grafted sample showed better discharge capacities than the unmodified LiFePO$_4$/C electrode, as discussed above. At 5 C, LiFePO$_4$/C-BTFSI retains 46.1% of its initial discharge capacity at C/10, while the unmodified LiFePO$_4$/C electrode retained only 14.8%. A similar trend was previously observed for bromophenyl-modified LiFePO$_4$/C electrodes with a loading of 0.4 wt %, but poor electrochemical performances were obtained with higher loading (1.1 wt %).[56] The improved performance reported here for a higher loading of grafted groups (2.1 wt %) might be associated with the chemical nature of the grafted groups, with the BTFSI species favoring ion transport due to improved wettability. In fact, the electronic conductivity of the modified cathode film, reported in Table 1, was not adversely affected although the BTFSI grafting on the carbon coating of LiFePO$_4$ particles is supposed to generate sp^3 carbon.[59] The impact of the loading of the BTFSI moiety was not fully evaluated in this study, but is the subject of ongoing research.

Electrochemical impedance spectroscopy measurements were performed at 50% depth of discharge to better understand the electrochemical properties of the cathode materials. The Nyquist plots presented in Figure 11 show an intercept on the real axis at high frequency that is attributed to the resistance of the electrolyte. A semicircle in the high-middle frequency region is observed for all the electrodes, and the diameter on the Z$_{re}$ axis is approximately equal to the charge-transfer resistance through the electrode/electrolyte interface.[21] The 45° straight line domain in the low frequency region is associated with diffusion of lithium ions into the bulk of the electrode.[67] Good correlations between galvanostatic cycling performance and charge transfer resistance for the modified and
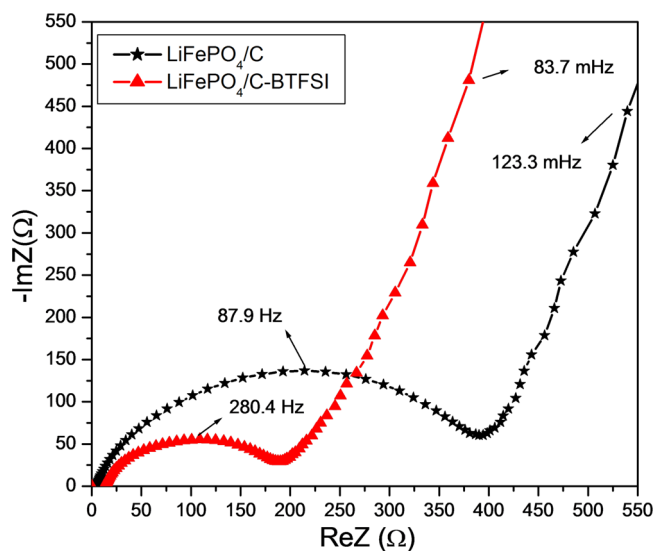

Figure 11. Electrochemical impedance spectroscopy measurements for unmodified and BTFSI-grafted LiFePO$_4$/C electrodes.

unmodified LiFePO$_4$/C electrodes were obtained. The LiFePO$_4$/C-BTFSI cathode that showed the best performance at high cycling rate also had lower charge transfer resistance (198 Ω) than the unmodified LiFePO$_4$/C electrode (410 Ω). A similar behavior was reported for bromophenyl-modified LiFePO$_4$/C electrodes.[56] Finally, these results with the LiFePO$_4$/C-BTFSI cathode are consistent with improved wettability of the cathode material and higher Li$^+$ diffusion at the active material/electrolyte interface.

The electrochemical behavior of the modified and unmodified LiFePO$_4$/C electrodes was also compared during the cycling tests as presented in Figure 12. Both the modified
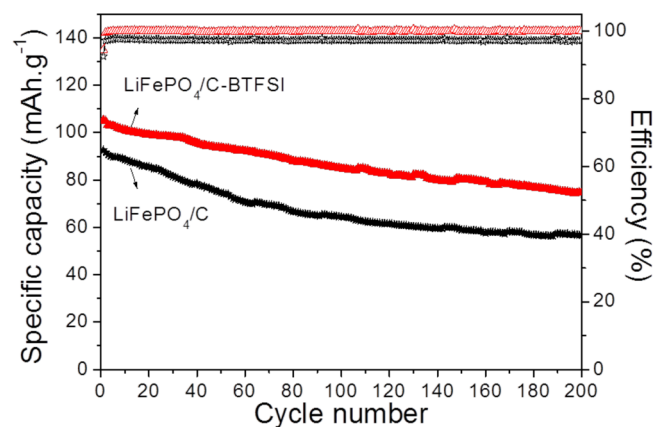
Figure 12. Cycling performance for unmodified LiFePO$_4$/C and LiFePO$_4$/C-BTFSI electrodes. The discharge capacity (filled triangles) and the charge/discharge efficiency (empty triangles) were recorded at room temperature and 1 C rate.

and the unmodified cathodes show a gradual loss of capacity during cycling, similar to that reported for electrodes made with LiFePO$_4$ submicrometer plates[1] or with microsized LiFePO$_4$/C[68] cycled at 1 C. Thus, the nature of the LiFePO$_4$ electrode material cannot explain solely this behavior. The LiFePO$_4$/C-BTFSI and the unmodified LiFePO$_4$/C cathodes displayed initial discharge capacity of 105 and 92 mAh·g^{-1}, respectively, for a discharge rate of 1 C. After 200 cycles, the unmodified

LiFePO$_4$/C electrode delivered a capacity of 57 mAh·g^{-1}, corresponding to an average capacity fade of 0.19% per cycle. A similar average capacity fade was obtained for cathode prepared with LiFePO$_4$/C and PVDF as binder.[68] On the contrary, the modified electrode presents a better capacity retention since the delivered capacity decreased to 75 mAh·g^{-1} after 200 cycles of charge/discharge at 1 C (capacity fade of 0.14% per cycle). The improved performances can be attributed to a more homogeneous cathode film[68] due to the presence of the BTFSI groups at the surface of LiFePO$_4$/C particles that leads to a better distribution of the electrode components and limits the formation of agglomerates (as shown in Figure S9 in the Supporting Information). Moreover, the Coulombic efficiency is higher for the LiFePO$_4$/C-BTFSI cathode (Figure 12) assuming a decrease of the parasitic reactions, such as electrolyte oxidation at the positive electrode which limits the lifetime of Li-ion cells.[69] Beyond the modulation of the surface properties (e.g., wettability enhancement, better homogeneity of cathode film), the grafting at the surface of the Li-ion battery material also may play a key role on the nature or stability of the passive layer as commonly reported following modification of graphite anode with nitrophenyl groups[70] or with the utilization of additive in the electrolyte.[71]

4. CONCLUSIONS

The diazotization of 4-amino-benzene-trifluoromethylsulfonimide was demonstrated, but the kinetic study revealed a slow reaction rate that required high concentrations of precursor to enhance the grafting reaction on the substrates. This study describes the grafting of benzene-trifluoromethylsulfonimide groups on the surface of carbon-coated LiFePO$_4$ through chemical reduction of the *in situ* generated diazonium ions. The grafted material was more hydrophilic than the unmodified LiFePO$_4$/C, and the wettability increased with the conventional carbonated-based electrolyte. The loading of the grafted groups was estimated by elemental analysis instead of thermogravimetric analysis which did not yield meaningful results. The XRD patterns indicated that the grafting reaction is accompanied by partial oxidation of LiFePO$_4$/C, which occurs with the reduction of the *in situ* generated diazonium ions. The amount of extracted lithium (e.g., level of oxidation) was determined by ICP-AES. No obvious relation between the level of oxidation and the loading of grafted groups was observed. Chemical grafting of BTFSI moieties improved the rate capability of LiFePO$_4$/C electrodes at high charge/discharge current densities, and the resistance of the cathode films was significantly decreased. Moreover, the modified cathode displayed superior capacity retention after 200 cycles of charge/discharge at 1 C. Additionally, the electrode made with the LiFePO$_4$/C-BTFSI was more homogeneous, and the electrical conductivity of the film was not affected although sp^3 defects are supposed to be present at the surface of the carbon coating.[59] The chemical nature of the grafted group was important because the BTFSI-modified cathode material showed superior performance compared to other organic-based modified LiFePO$_4$/C cathode. The nature of the interaction between this new organic grafted group and the electrolyte will be further evaluated to optimize the electrochemical performance in LiFePO$_4$-based Li-ion batteries.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Detailed organic syntheses of 4-nitro-*N*-((trifluoromethyl)-sulfonyl)benzenesulfonimide and 4-amino-*N*-((trifluoromethyl)sulfonyl)benzenesulfonimide, thermal stability of 4-amino-*N*-((trifluoromethyl)sulfonyl)-benzenesulfonimide, initial conditions for grafting on LiFePO$_4$/C particles, and characterization of cathode film electrodes by scanning electron microscopy. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06184.

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Notes
The authors declare no competing financial interest.

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