Expanded graphitic materials prepared from micro- and nanometric precursors as anodes for sodium-ion batteries

Alberto Ramos*, Ignacio Cameán, Nuria Cuesta, Cristina Antuña, Ana B. García

Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe 26, 33011-Oviedo, Spain

ABSTRACT

A series of expanded graphitic materials are prepared from two different precursors: micrometric synthetic graphite and graphitized carbon nanofibers, and tested as anodes for sodium-ion batteries. The materials preparation involves the oxidation of the precursors followed by partial thermal reduction. Overall, the expanded synthetic graphite materials show better electrochemical performance as anode than the expanded graphite nanofibers, providing higher specific capacity, leading to lower capacity losses in the first charge-discharge cycle and exhibiting outstanding cycling stability. Specific capacities of ~150 mA h g\(^{-1}\) at 37 mA g\(^{-1}\) and ~110 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) are attained, and up to 50 % of initial capacity at 19 mA g\(^{-1}\) is kept at 372 mA g\(^{-1}\). Unexpectedly, higher capacity losses are measured for the nanostructured electrodes by progressively increasing the current density. These differences are attributed to the lower surface area and porosity of expanded synthetic graphite materials which favors the formation of thinner and more stable SEI, thus reducing the electrode resistance and enhancing Na\(^+\) ions accessibility to surface oxygen groups with the consequent increase of the surface capacity which was found to be the main contribution to the total specific capacity.

KEYWORDS: Expanded graphitic materials; anodes; sodium-ion batteries

* Corresponding author. Tel. 34 985119090 E-mail: alberto.ramos@incar.csic.es
1. Introduction

Since their introduction in the market in the early 1990s, rechargeable lithium-ion batteries (LIBs) have been the batteries of choice for portable electronic devices (cell phones, tablets, laptops, etc.). LIBs are also being used for other applications, such as powering electric vehicles, or in stationary large scale electrical energy storage (EES) systems from renewable energy resources (e.g., wind turbines or solar cells). However, among other considerations, the scarcity of lithium in Earth’s crust (only 20 ppm) [1], together with the uneven distribution of lithium resources (mainly found in South America) and the increasing lithium minerals cost (~ $5000/ton of lithium carbonate in 2010) [2] as a consequence of the growing demand have made the scientific community turn their attention to the development of sodium-ion batteries (SIBs), as shown by an exponential increase in the number of research articles on this topic since 2010 [1].

SIBs were initially studied alongside LIBs in the 1970s and 1980s [3, 4], but after that they were overshadowed for a long time by the commercial success of their LIBs counterparts, with higher energy density. However, in the present world energetic situation, the natural abundance resources (4th most widely abundant element on earth) and low cost ($135–165/ton of mineral trona, from which sodium carbonate is produced) of sodium [2] as compared with lithium made these batteries an attractive alternative to LIBs, particularly for application in systems such as EES in which the cost is the overriding issue as they are made up of a great number of batteries, whereas the energy density at the battery unit level is not a critical factor.
Recent research on SIBs has benefited from the maturity reached after 30 years of R&D on LIBs. Thus, some of the cathodic materials investigated are analogous to those utilized in LIBs, only replacing lithium by sodium in the corresponding compound, these including layered oxides, phosphates, pyrophosphates, or fluorophosphates of transition metals, with promising results in some instances [1, 2, 5-10]. Similarly, the electrolyte formulations tested for these batteries consist mainly of sodium salts (NaPF₆, NaClO₄) dissolved in organic carbonates [11], which are also analogous to those employed in LIBs.

In contrast, development in the field of anodic materials for SIBs has been somewhat more limited, especially regarding carbon-based materials [12, 13], since intercalation of Na⁺ ions is practically hampered in graphite, anode of choice in most commercial LIBs. For example, intercalation compounds of the formula NaC₆₄ were obtained in low current density experiments for electrochemical intercalation of Na⁺ in graphite [14], amounting to a reversible capacity ~35 mA h g⁻¹, which contrasts with the stage-I graphite intercalation compound, LiC₆, attained for Li⁺ ions (theoretical capacity of 372 mA h g⁻¹). This limitation is partly due to the ionic radius of Na⁺, which is ~0.3 Å larger than Li⁺, as well as the stressed induced in the graphite structure when Na⁺ ions are intercalated [15]. Interestingly, this has been circumvented in part in recent studies by the use of ether-based electrolyte systems allowing the co-intercalation of Na⁺ ions with solvent molecules between the graphene layers, thus moderately increasing the reversible capacity delivered by graphite-based electrodes (100–150 mA h g⁻¹) [16, 17].

However, most of the studies on carbon-based materials as anodes for SIBs have been focused on those with mean interlayer distances > 0.37 nm, the
minimum value required for Na\(^+\) insertion in graphite-like structures according to theoretical calculations \[18\]. Thus, different carbon materials with diverse structures (micro- and nanostructures) and varied morphologies, usually with a certain degree of porosity and low-ordered structure consisting of few-layer graphite nanocrystallites, have been investigated for this application \[12\]. Among them, hard carbons are arguably the most promising candidates thus far \[19\text{-}34\], being able to deliver reversible capacities \(>300\) mA h g\(^{-1}\) at low-to-moderate current rates with remarkable stability along cycling, although some aspects need to be improved for their implementation as anodes for SIBs, such as their relatively low coulombic efficiency in the first cycle, which is related to their high surface area and porosity, or their modest rate performance. The turbostratic structure of these materials, consisting in few-layer-stacked graphite nanocrystallites with high interlayer distances (0.37–0.40 nm), together with their inherent porosity (i.e. nanopores and nanovoids formed between different turbostratic domains) account for their dual mechanism of interaction with Na\(^+\) ions: (i) reversible insertion of Na\(^+\) in the turbostratic domains, which usually occurs in the potential range 1.0–0.2 V vs Na/Na\(^+\) resulting in sloping potential vs capacity profiles; (ii) Na\(^+\) filling of nanopores and nanovoids in the structure, in a process similar to adsorption, giving rise to plateaus below 0.2 V vs Na/Na\(^+\) in the same profiles \[33\]. From both mechanisms, the former would be preferable since pore-filling occurs at very low potential and may be accompanied by sodium plating which could lead to battery failure upon cycling due to electrical shorting. In fact, other carbon materials, such as carbon nanofibers \[35\] or reduced graphene oxides \[36, 37\], showed no plateaus below 0.2 V indicating that their specific capacity was mainly due to Na\(^+\) insertion into the graphene layers. However, very low coulombic efficiencies in the
first cycle were calculated for these materials due to their large surface area make them impractical as potential anodes for commercial SIBs.

From the latter studies it can be concluded that an ideal carbon material for this application should have a long-range ordered layered structure with high interlayer distances and low porosity and surface area. In this regard, Wen et al. [38] prepared an expanded graphite (EG) through a facile synthetic route, involving the oxidation of a commercial graphite followed by a thermal treatment at 600 °C. This material had a relatively low surface area (~30 m² g⁻¹), a mean interlayer distance ~0.43 nm and was able to deliver high reversible capacities (~300 m A h g⁻¹) at low current densities, in the order of those delivered by hard carbons, with the advantage that most of this capacity was due to Na⁺ intercalation/deintercalation processes (i.e., short sloping plateau below 0.2 V in the potential profiles). However, rate capability tests revealed a modest performance at high current densities, which is most likely attributed to the micrometric size of this material, hampering Na⁺ ion diffusion within its turbostratic structure.

With these precedents in mind, in this paper the electrochemical performance as anode for SIBs of novel expanded graphite nanofibers materials (EGNFs) is investigated by means of galvanostatic cycling at constant and variable (from 18.2 to high 372 mA g⁻¹) current density. The use of these expanded nanomaterials, prepared for the first time in our laboratory from graphitized carbon nanofibers (GNFs), should improve, a priori, the battery rate performance since they would allow faster insertion/de-insertion processes by reducing the diffusion length of Na⁺ ions. In addition, expanded synthetic graphite materials (ESGs) obtained from micrometric synthetic graphite (SG) were also studied. Both types of expanded graphitic materials (EGs) were prepared by a two-step method involving oxidation
of the graphitic material precursor, followed by thermal treatment of the graphite oxides (GOs). The anodic behavior of the different nano and micro EGs materials are discussed in terms of the battery reversible capacity, irreversible capacity in the first cycle, capacity retention and cycle efficiency by considering the influence of composition, graphitic structure, surface area and porosity. The mechanism of interaction of Na\textsuperscript{+} ions with the EGs was also analyzed through cyclic voltammetry experiments at different sweep rates.

2. Experimental

2.1. Materials: source and preparation

The expanded graphitic materials (EGs) were prepared from two precursors: a synthetic micrometric graphite (SG), Timrex SLP50, from TIMCAL (www.timcal.com) which, according to the supplier, is a highly pure graphite (ash content <0.10 wt.%) with a perfect crystalline structure (interplanar distance, $d_{002}$, 0.3354–0.3356 nm, crystallite size $L_c$ >250 nm) and a Potato@Shape particle morphology that is commercialized as active material for negative electrodes of lithium-ion batteries, and (commercial carbon nanofibers, PR-24-XT-PS, supplied by Pyrograf Products Inc. (http://pyrografproducts.com), that were subjected to a graphitization thermal treatment at 2800 °C (GNFs) [39], with $d_{002}$ ~0.3389 nm and $L_c$ ~15 nm.

The preparation of the EGs, namely expanded synthetic graphite (ESGs) or expanded graphite nanofibers (EGNFs) materials, was carried out by a two-step process: (1) oxidation of the SG and GNFs precursors through a slightly-modified
Hummers method [40] to obtain the corresponding oxides (SGO and GNFO), especially so in the case of GNFO, which was based on the oxidation of related carbon nanofibers and nanotubes in the literature [41-46] and (2) thermal treatment to partially reduce the oxides at three different temperatures (300, 600 and 900 ºC).

In a typical experiment to prepare SGO, NaNO$_3$ (1.5 g) was dissolved in H$_2$SO$_4$ (69 mL). Then, 3 g of SG were added to the solution and the suspension thus formed was vigorously stirred for 1 h at room temperature. Afterwards, KMnO$_4$ (9 g) was slowly added to the suspension, keeping the temperature below 20 ºC with a water/ice bath. After heating at 35 ºC for 1 h, the suspension color changed from black to dark brown and distilled water (200 mL) was then slowly added, keeping the temperature < 98 ºC. Once the addition was completed, the suspension was further stirred for 30 min at 98 ºC, during which time the suspension color changed again from dark brown to light brown. Then, after leaving the reaction mixture cool down to room temperature, distilled water (140 mL) and H$_2$O$_2$ (30 wt.%, 30 mL) were added, successively, and the suspension was left standing overnight to decant. After removing the supernatant liquid, the remaining brown slurry was washed with distilled water, the suspension was then centrifuged (4000 rpm, 30 min), decanting the supernatant liquid afterwards. This procedure was repeated several times until the supernatant reached the pH of distilled water (pH ~ 5–6). The aqueous slurry thus obtained was dried overnight in an oven at 60 ºC to obtain a dark brown film which was ball-milled for the minimum amount of time required to obtain SGO as an homogeneous powdery dark brown solid.

GNFO was prepared in an analogous way with slight variations as regards the reagent quantities and proportions while the order of addition remained the same.
Thus, 200 mL of H$_2$SO$_4$, 0.5 g of NaNO$_3$, 1 g of GNFs and 6 g of KMnO$_4$ were used. The higher proportion of H$_2$SO$_4$ is due to the lower tap density of the GNFs as compared to the SG, giving rise to more viscous slurries in H$_2$SO$_4$ at the same concentrations. Moreover, higher reaction temperatures (55–70 °C) were employed. After the addition of KMnO$_4$, the suspension was heated at 55 °C for 45 min, then at 65 °C for 30 min and finally at 70 °C for 30 more min until a suspension color change, from black to dark brown, was perceived. Then, after the addition of distilled water (200 mL), the suspension was kept at 98 °C for 15 min until its color turned light brown. The rest of the procedure was reminiscent of that already described for SGO.

As mentioned, SGO or GNFO oxides were subjected to heat treatment, in a tube furnace, at three different temperatures: 300, 600 and 900 °C, under a constant N$_2$ flow of 50 mL min$^{-1}$, for 1 h at a heating rate of 2 °C min$^{-1}$. The resulting expanded graphitic materials were identified as ESG3, ESG6, ESG9 and EGNF3, EGNF6, EGNF9, respectively.

2.2. Characterization techniques

The diffractograms were recorded in a Bruker D8 X-ray powder diffractometer as described elsewhere [47]. For each material, three diffractograms were obtained, using a different representative batch of sample for each run. The mean interlayer spacing, $d_{002}$, was evaluated from the position of the (002) peak, or the (001) peak for the graphite oxides, SGO and GNFO, applying Bragg’s equation. The mean crystallite size along the c axis, $L_c$ was calculated from the (002) peak using the Scherrer formula, with a value of K = 0.9 [48]. The broadening of
Diffraction peaks due to instrumental factors was corrected with the use of a silicon standard. Typical standard errors of the XRD parameters are <2 % and <0.5 % of the reported values for \( L_c \) and \( d_{002} \), respectively. Raman spectra were obtained in a Raman microspectrometer HR 800 Jobin Yvon Horiba as described previously [49]. Extended scans from 1750 to 950 cm\(^{-1} \) were performed to obtain the first-order Raman spectra of the samples, with typical exposure times of 15 s. The intensity \( I \) of the Raman bands was measured using a mixed Gaussian-Lorentzian curve-fitting procedure. The relative intensity of the Raman D-band (\( I_D/I_I \) with \( I_I = I_I + I_D + I_{2D} + I_G \)) was calculated with standard errors lower than 2 %.

The oxygen and carbon contents of the materials were determined directly by elemental microanalysis in a LECO VTF-900 oven and a LECO CHNS-932 oven, respectively. For both analyses ~1 mg of dry samples were used.

XPS measurements were performed in a SPECS spectrometer with a Phoibos 100 analyzer at a pressure of 10\(^{-7} \) Pa, with a non-monochromated Mg K\( \alpha \) X-ray source (1486.6 eV) operated at 11.86 kV and 100 W. For SGO and GNFO samples, the charge was in situ compensated with an electron gun. The total atomic percentages (at.%) of the different elements present in the ~10 nm upper layers were calculated from the survey spectra by considering the integrated areas of the main XPS peaks (C1s and O1s) and their respective sensitive factors. Casa XPS software was used for data processing, allowing Shirley-type background subtraction, peak fitting using mixed Gaussian-Lorentzian functions and quantification for the high-resolution C1s spectra.

Thermogravimetric analyses (TGA) of the oxides, SGO and GNFO, were performed in a TG SDTQ600c analyzer. The samples were heated at a heating rate of 2 °C min\(^{-1} \) up to 1000 °C in an argon flow (100 mL min\(^{-1} \)). The eluted gas
was analyzed by mass spectroscopy (MS), detecting H$_2$O ($m/z = 18$), CO ($m/z = 28$) and CO$_2$ ($m/z = 44$).

Temperature programmed desorption (TPD) analyses of SGO and GNFO were performed in an Autochem II 2920 apparatus. The samples were heated at a heating rate of 2 °C min$^{-1}$ up to 1000 °C in an argon flow (50 mL min$^{-1}$). The amounts of CO and CO$_2$ evolved were monitored by MS from the intensities of $m/z$ at 28 and 44, respectively.

The textural properties of the materials were determined by N$_2$ adsorption-desorption at −196 °C in a Micromeritics ASAP 2420 apparatus. The samples were outgassed at 25 °C (oxides) or 120 °C (EGs). The textural parameters, BET surface area ($S_{BET}$) and total pore volume ($V_t$), were calculated by applying the BET equation to the adsorption isotherms. Micropore volume (<2 nm) was calculated from the Dubinin-Radushkevich equation [50]. Narrow microporosity (< 0.7 nm) was also determined for the non-porous sample EGNF3 by applying the Dubinin-Radushkevich equation to the CO$_2$ adsorption isotherm at 0 °C, obtained from a Quantacrome Instruments NOVA 4200e.

2.3. Cell preparation and electrochemical measurements

The electrochemical measurements were performed in two- and three-electrode Swagelok-type laboratory cells. The working electrodes were prepared by the drop-casting method from slurries formed by adding the active material (EGs) to a ~0.8 wt.% solution of the binder, polyvinylidene fluoride (PVDF), in 1-methyl-2-pyrrolidone, (EG:PVDF, 92:8, w/w) and stirring vigorously for over 20 h. Then, a drop of this slurry was spread on a copper disc of 12 mm of diameter and
25 μm of thickness and was dried under vacuum at 120 °C for 2 h. Finally, the electrode was hydraulically pressed at a pressure ~40 MPa, and the load (active material + binder) was calculated by weight difference, being in the range 1.5–4.3 mg cm⁻². One or two sodium metal discs of 12 mm of diameter were used as counter and/or reference electrodes, depending on the cell configuration. The electrodes were separated by two micro-fiber glass discs impregnated with the electrolyte solution, 1 M NaPF₆ in ethylene carbonate (EC):diethylcarbonate (DEC), 1:1, w/w. The cell assemblage was carried out in a dry box with O₂ and H₂O contents below 0.1 ppm. The initial potential (Eᵢ) of these cells was always in the range 2.8–3.1 V vs Na/Na⁺.

The electrochemical measurements of the cells were conducted in a Biologic multichannel VMP2/Z potentiostat/galvanostat. Galvanostatic cycling and cyclic voltammetry experiments were carried out in two-electrode cell configurations, whereas three-electrode cells were used for electrochemical impedance spectroscopy (EIS) measurements. The galvanostatic cycling of the working electrodes was carried out in the 2.0–0.003 V potential range vs Na/Na⁺ at constant (37.2 mA g⁻¹ for 50 cycles) or variable (from 18.2 to 372 mA g⁻¹, 10 cycles at each current density, starting and finishing at the lowest one) current densities. Prolonged cycling (200 cycles) at 100 mA g⁻¹ was also conducted with some electrodes after the end of cycling at constant or variable current density. The cyclic voltammograms (CV) were collected in the 2.0–0.003 V potential range vs Na/Na⁺ at increasing scan rates, from 0.05 to 50 mV s⁻¹. EIS measurements were performed prior to galvanostatic cycling, and after 10 and 50 discharge-charge cycles at 37.2 mA g⁻¹, allowing cells to relax in open potential circuit for at least 4
hours to get a quasi-equilibrium system. The EIS experiments were then carried out by applying an AC voltage signal of 5 mV from 100 KHz to 2 mHz.

3. Results and discussion

3.1. Expanded graphitic materials properties

To help discussing the results of the performance of the EGs materials prepared in this work as anode for SIBs, their properties as regards graphitic structure, porosity and both bulk and surface compositions are firstly considered and compared with those of the corresponding raw GOs. Moreover, to determine the most suitable temperatures for the second step involved in the preparation of EGs, the thermal stability of GOs was previously studied by TGA and TPD.

The TG (weight vs temperature) and DTG (derivative weight vs temperature) profiles of SGO and GNFO are shown in Figure 1. As can be seen, there is a weight loss below 140 °C ($T_{\text{max}} \sim 70$ °C) for both materials ascribed to water desorption [51-53], amounting ~17 % for GNFO and ~12 % for SGO. The nature of the eluted gas was confirmed in the TGA/MS profiles (Figure S1, supporting information) by the presence of broad peaks for $m/z = 18$, with maximum ion currents at 70 °C, as well. A dramatic weight loss of ~33 % which is typical of graphite oxides, associated with the release of oxygen functional groups, mainly as H$_2$O, CO$_2$ and CO gases [53], was measured in the range 140–300 °C with $T_{\text{max}}$ (temperature of maximum weight loss rate) at ~190 °C for GNFO and ~200 °C for SGO; whereas it was much more attenuated and continuous for both
materials at temperatures above 300 ºC, amounting to ~18 %, mostly due to CO and CO₂ elimination, as corroborated by MS (Figure S1).

TPD analyses on GOs were conducted in order to quantify the total amount of CO and CO₂ desorbed during heat treatment (Figure 2), this being 8.4 and 7.7 mmol g⁻¹, respectively, for SGO and 6.5 and 9.5 mmol g⁻¹ for GNFO. As observed in Figure 2, a significant proportion of the total CO (~30 %) and CO₂ (~70 %) released is desorbed in the temperature range 100–300 ºC, with sharp bands in the TPD profiles at ~190 ºC, reminiscent of those found in the TG/MS analyses (Figures 1, S1). Focusing on CO profiles, several overlapping broad bands of lower intensity are clearly observed over 300 ºC for both oxides, attributed to decomposition of carboxylic anhydrides (300–500 ºC), phenols and ethers (550–800 ºC) and quinones and carbonyls (800–1000 ºC), [54, 55] accounting for the rest of the gas eluted (~70%). CO₂ desorbed over 300 ºC (~30%) can be mainly associated with the decomposition of carboxylic anhydrides (300–480 ºC), and lactones (480–700 ºC) [54, 55]. From these thermal stability tests, it can be concluded that the amount of oxygen-containing functional groups in GNFO and SGO decreases dramatically between 140 and 300 ºC and more gradually over 300 ºC. With these results in mind, three different treatment temperatures were selected to prepare the expanded graphitic materials: 300, 600 and 900 ºC, ensuring this way that the EGs thus prepared, among other characteristics, will have a wide range of oxygen content (from ~25 % to ~2 %), as will be shown below, whose impact on the electrochemical performance of the materials will be discussed.

The graphitic structure of the materials was assessed by XRD and Raman spectroscopy and the main structural parameters obtained from these techniques
are collected in Table 1. As regards XRD, both oxides, SGO and GNFO, display a peak owing to the (001) reflection plane at ~11° (Figure S2 in supporting information), for which interlayer distances ($d_{002}$) of ~0.8 nm are calculated. After heat treatment of these materials to obtain the different EGs, this peak shifts to higher angles (22–26°), owing to the (002) graphite reflection this time, leading to $d_{002}$ values in the range 0.404–0.343 nm. This interlayer contraction is caused by the loss of an important amount of oxygen-functional groups and partial recovery of the graphitic structure. The major differences between the two EGs series (ESGs and EGNFs) are observed for those materials prepared at 300 °C (ESG3 and EGNF3). Thus, the (002) reflection peaks in the diffractogram of ESG3 could be easy deconvoluted in two peaks, which denotes the heterogeneous nature of this material, composed of two phases with $d_{002}$ values of 0.4038 and 0.3616 nm, respectively, in a 1:4 ratio. In contrast, EGNF3 is a more homogeneous material with a lower $d_{002}$ value of 0.3570 nm. In both series, increasing the oxide treatment temperature from 300 to 600 or 900 °C slightly reduces the interlayer spacing to 0.34–0.35 nm in the resulting materials, with no significant differences between the latter two temperatures. The $L_c$ values calculated for all these materials are well below 10 nm, this implying their low degree of structural order due to the inclusion defects from oxygen-type functional groups and partial exfoliation of the graphitic structure of the precursors after oxidation and pyrolysis.

The first-order Raman spectra for these materials (Figure S3 in Supporting Information) could be satisfactorily deconvoluted into four different bands (for an example, see Figure S4 in Supporting Information). Thus, apart from the main G (for graphite) and D (for defects) bands, at ~1595 and ~1355 cm$^{-1}$, respectively, two more bands could be also assigned, denoted as I (1235 – 1260 cm$^{-1}$) and D$''$
(1505 – 1515 cm$^{-1}$). The origin of the latter two bands is not entirely clear, but they are usually attributed to impurity ions and in-plane defects, respectively, which are typically found in disordered carbon materials [55-57]. The degree of structural order of these materials was evaluated by the relative intensity of the D band in these spectra ($I_D/I_t$, see Table 1), with no significant differences between them, all presenting relatively high values, ~40%, as expected for disordered carbons with multiple defects. However, the D band clearly sharpens and shifts to slightly lower wavenumbers upon treatment at 900 ºC (see $\omega_D$ and $\nu_D$ in Table 1), which could be linked to a modest increase of the structural order at the surface level due to the loss of most of the oxygen-containing functional groups confirmed through elemental analysis and XPS measurements (see below).

As expected, the oxidation of the precursors materials (SG and GNFs) provokes an increase of the surface area ($S_{BET}$), of one order of magnitude, approximately (e.g. from 30 m$^2$ g$^{-1}$ for GNFs [39] to 246 m$^2$ g$^{-1}$ for GNFO), due to the introduction of defects, increase of the interlayer spacing and partial exfoliation. Focusing on the surface area ($S_{BET}$) and porosity values of the GOs and EGs materials in Table 2 (the nitrogen adsorption-desorption isotherm from which these parameters have been calculated are given in Figure S5), it can be concluded that, with the exception of EGNF3, EGNFs have higher $S_{BET}$ (85–119 m$^2$ g$^{-1}$) than ESGs (20–42 m$^2$ g$^{-1}$), which is not at all surprising since the value of the GNFO oxide is more than 6 times higher than that of SGO. Although a decrease in this parameter occurs after heat treatment at 300 ºC of both GOs under study to obtain EGs, it is rather remarkable for GNFO, as EGNF3 shows a $S_{BET} < 1$ m$^2$ g$^{-1}$. This could be related to the dramatic contraction of the mean interlayer spacing experienced by these two expanded materials, ESG3 and
EGNF3, as commented above. In contrast, heat treatment of the graphite oxides at higher temperatures results in materials with larger $S_{\text{BET}}$. On the other hand, both EGs series show little porosity ($V_T < 0.1 \text{ cm}^3 \text{ g}^{-1}$), being the micropore volume ($V_{\text{MICRO}}$) higher for EGNFs materials, with the exception of the mentioned non-porous EGNF3. However, a CO$_2$ adsorption study of this material revealed the presence of a substantial volume of narrow micropores ($<0.7 \text{ nm}$), amounting to 0.207 cm$^3$ g$^{-1}$. This type of behavior has been reported for other carbon materials (e.g. carbon fibers or activated carbons with low degree of activation) for which N$_2$ adsorption also proved to be useless to determine the micropore volume of the narrowest microporosity [58].

The carbon and oxygen elemental analyses (bulk composition) of the materials are reported in Table 3. As seen, the oxygen content decreases upon increasing the treatment temperature of the GOs, in good agreement with the thermal stability results (Figure 1) and with no significant differences within both series (SG-based and GNF-based). Thus, an important amount of oxygen is lost at 300 ºC (from ~47 wt.% in GOs to ~24 wt.% in ESG3 or EGNG3), whereas a more attenuated oxygen loss occurs after elevating the temperature to 600 and 900 ºC (~13 wt.% for ESG6 and EGNF6, and ~3 wt.% for ESG9 and EGNF9). Conversely, the carbon content increases proportionally, reaching values up to 95 wt.% for the EGs prepared at 900 ºC. In line with this, the surface C/O atomic ratio of the EGs, calculated from the XPS spectra, increased progressively with treatment temperature (Table 3). This time, a comparison between both series shows slightly higher surface C/O ratios for the SG-based materials (e.g., 5.1 and 3.5 for SGO and GNFO; 18.6 and 14.2 for ESG9 and EGNF9). The high-resolution C1s spectra confirm the progressive loss of oxygen-containing functional groups experimented by the GOs.
after increasing treatment temperature (Figure S6 in Supporting Information). Thus, three different peaks were obtained after curve fitting, corresponding to the binding energies of C=C bonds in graphitic carbon (284.5–285.0 eV), C–O bonds from phenols, alcohols, or ethers (286.0–287.1 eV) and C=O bonds from ketones and carboxylic groups (288.5–288.9 eV) [59]. As can be seen in Table 3, the contribution of C=C bonds in the materials increases remarkably after the heat treatment of the graphite oxide (e.g. from 37.9 % for GNFO up to 69.9% for EGNF9), indicating a partial recovery of the graphitic structure. At the same time, the contributions of C–O and C=O bonds, despite fluctuating more within each series, have a clear tendency to decline (e.g, C–O contribution from 30.0 % for SGO to 24.5 % for ESG3; or C=O contribution from 8.0 % for EGNF6 to 4.6 % for EGNF9).

In sum, expanded graphitic materials, namely ESGs and EGNFs, have been prepared from micro (synthetic graphite) and nanometric (graphitized carbon nanofibers) precursors by treatment of the corresponding oxides, SGO and GNFO, at 300, 600 or 900 ºC. These expanded graphitic materials have mean interlayer distances in the range 0.404–0.343 nm, a low degree of 3-D and 2-D structural order, as indicated by the low $L_c$ values calculated, <5 nm, and the elevated relative intensities of the D-band in the Raman spectra ($I_D/I_t \sim 40\%$), respectively. In terms of textural properties, generally speaking, higher surface areas and microporosities were measured for the EGNFs materials, whereas the oxygen content within each series, which is in the range 25–2 %, diminishes with the oxide treatment temperature, both in the bulk and the surface (e.g., % O: ESG3 > ESG6 > ESG9), as measured by elemental analysis and XPS, with no significant differences between ESGs and EGNFs materials (e.g, %O: ESG3 ~ EGNF3).
3.2. Electrochemical performance as anodes of the expanded graphitic materials

3.2.1. Galvanostatic cycling at low electric current density

Galvanostatic cycling experiments were initially performed for EG-based electrodes at the relatively low current rate of 37.2 mA g\(^{-1}\) for 50 cycles. The main electrochemical parameters are summarized in Table 4, and specific discharge (sodiation)/charge (desodiation) capacities vs cycle number plots are shown in Figure 3. From a general perspective of this data, it can be concluded that the EGs materials prepared at 300 °C and 600°C provided the best electrochemical results, specifically as regards discharge capacity at the end of cycling. Moreover, as can be observed in Figure 3, higher specific capacities were delivered by ESGs as compared to EGNFs materials. Thus, maximum \(C_{\text{disc}}\) of \(~150\) and \(100\) mA h g\(^{-1}\) were reached for ESG3 and EGNF3 materials, vs values of only \(~58\) and \(~25\) mA h g\(^{-1}\) for ESG9 and EGNF9, respectively. This difference can be, \textit{a priori}, attributed to the higher \(S_{\text{BET}}\) and microporosity of EGNFs materials (Table 2) since an inverse relationship between these textural parameters and the specific capacity has been previously established in a study using hard carbons as anodes for SIBs [26]. Moreover, this could also be related to the fact that thicker SEI layers may be formed in materials with higher porosity and surface areas, which may disable the Na\(^+\) ion storage due to its electronically insulating nature and thus blocking the access of Na\(^+\) ions to the enclosed voids inside the carbon architecture [19]. To confirm this hypothesis, EIS analyses were performed on ESG3 and EGNF3
electrodes before cycling and after 10 and 50 discharge/charge cycles, respectively. The Nyquist plots obtained are given in Figure 4. The experimental data were fitted using two different equivalent circuits for the electrodes before and after cycling (see Figure S7 in Supporting Information), and the resistance values obtained thereof are shown in Table S1 (Supporting Information). As can be seen, Nyquist plots before cycling show a semicircle attributed to charge-transfer resistance ($R_{CT}$) and a Warburg tail ($Z_W$) due to Na$^+$ ion diffusion in the electrode. After cycling, two depressed semicircles can be appreciated, $R_{SEI}$ (due to SEI layer formation, at higher frequencies) and $R_{CT}$ (at middle frequencies), as well as a Warburg tail with a much lower slope, which is also attributed to the formation of a SEI layer [60]. Moreover, changes of the charge-transfer resistance values were also detected (Table S1). Thus, $R_{CT}$ of ESG3 electrode was reduced from $\sim 140 \ \Omega$ to a more or less stable value of $< 50 \ \Omega$, which contrasts with the significant increase for EGNF3 electrode (from $\sim 155$ to $\sim 766 \ \Omega$ after cycle 50). Consequently, EGS3 electrode is expected to allow faster charge transfer. $R_{SEI}$ follows a similar trend for both electrodes, although both the increase along cycling and the final values after cycle 50 are also much higher for EGNF3 than for ESG3 (1097 vs 196 $\Omega$), thus confirming the above mentioned hypothesis about the formation of a thicker and more unstable SEI layer of insulating nature for the former electrode, which, in addition, seems to be continuously growing. Unlike specific capacity, no differences between ESGs and EGNFs electrodes as regards cycling stability were observed (Figure 3), showing all of them relatively high capacity retentions at the end of cycling, in the range 70–80% (R in Table 4). Similar reversible capacities values ($150–200 \ mA \ h \ g^{-1}$ at current densities 20–40 mA g$^{-1}$) were previously measured by using pyrolytic carbons from graphite oxide [61] or
reduced graphene oxides [36, 37] as anodes in SIBs. However, other materials such as hard carbons or expanded graphite have been reported to provide larger capacities, with values >300 mA h g\(^{-1}\) after 60 cycles at C/10 [28] or 284 mA h g\(^{-1}\) after 30 cycles at 20 mA g\(^{-1}\) [38], respectively. In this context, it should be taken into account that the \(d_{002}\) values calculated for EGs materials were, in general, <0.37 nm (Table 1), which is considered to be the minimum interlayer distance between graphene layers to allow Na\(^+\) intercalation in graphitic materials, as mentioned in the introduction [18] (only the minor of the two phases comprising ESG3 possess higher \(d_{002}\), of 0.40 nm, as seen in Table 1), thus explaining the lower capacity delivered by these expanded graphitic materials. Furthermore, it is possible that an important part of this capacity may be related to the reaction of Na\(^+\) ions with surface oxygen-containing groups [24, 38, 62] since a direct relationship between these two parameters can be inferred by comparing the electrochemical data in Table 4 and the surface chemical analyses in Table 3 (see sum of atomic carbon distribution in C-O an C=O) of EGs materials. In this regard, a more detailed analysis on the mechanism of interaction of Na\(^+\) ions will be commented below.

As expected from the above discussed EIS results, the irreversible capacity in the first cycle (\(C_{irr}\)), which is mainly due to the SEI formation, for EGNF-based electrodes (72–85 %) is higher than for ESG-based electrodes (60–68 %). SEI formation in this type of electrodes is usually proportional to the surface area of the carbon material used [12], which is essentially in good agreement with the results obtained in this work (see Table 2). However, this is not applicable for EGNF3 which shows a \(C_{irr}\) as high as 77 %, despite possessing the lowest \(S_{BET}\) (<1 m\(^2\) g\(^{-1}\)). In this material, the low coulombic efficiency (CE) in the first cycle could be
related to its narrow microporosity as measured by CO$_2$ adsorption. Although we are not aware of any precedent in the literature relating these two parameters, previous work by Bommier et al. with hard carbon anodes for SIBs showed that increasing the anode materials $S_{BET}$ and pore volume (measured by N$_2$ sorption) results in larger $C_{irr}$ and lower reversible capacity [26]. In any event, the lowest $C_{irr}$ values in this work for ESG3 and ESG6 electrodes (~60 %) are still rather high, but only marginally higher than those obtained for related carbon materials such as other EGs [38] or pyrolytic carbons from graphite oxide [61] (both ~50 %), and even lower than those measured for reduced graphene oxides [36, 37]. It should also be noted that the CE increases rapidly along cycling for EGs obtained at 300 and 600 ºC, being ~80 % in the 2$^\text{nd}$ cycle for EGNF3 and EGNF6, and ~90 % for ESG3 and ESG6, but all of them reaching ~97 % by the 10$^\text{th}$ cycle, and >99 % by the end of cycling. Low CE in the first cycles has also been observed for other carbon materials [21, 63, 64] and may be linked to side irreversible reactions (e.g., continuously growing SEI due to electrolyte decomposition [60], or irreversible trapping of Na$^+$ ions in the bulk [65]). Overall, lower CEs along cycling were obtained for the EGs prepared at 900 ºC, only attaining ~96 % in the last cycle.

3.2.2. Mechanism of interaction with Na$^+$ ions: influence of oxygen-containing functional groups

In order to gain further insight into the mechanism of interaction of the Na$^+$ ions with the EGs materials during the galvanostatic process, the potential ($E$) vs discharge/charge capacities profiles for cycles 1, 2, 10 and 50, and the corresponding differential capacity ($dC/dE$) vs potential profiles, both for the ESGs
(Figure 5) and EGFNs (Figure S8 in Supporting Information) electrodes are analysed in depth. Since the profiles were very similar for both series of electrodes, only ESGs will be commented in detail. Firstly, the potential vs capacity profiles are typical of disordered carbons used as anodes for SIBs, showing sloping discharge and charge curves (Figure 5a, b, c). In all cases, the slope during the 1\textsuperscript{st} discharge is much less pronounced <0.7 V vs Na/Na\textsuperscript{+} compared to the other cycles, which is indicative of SEI formation due to decomposition of the electrolyte at low potentials. Focusing on the discharge curves, it can be observed that the potential at which the sodiation process begins tends to decrease as the temperature at which the expanded graphitic material was prepared from the oxide, in other words, as the oxygen content (bulk or surface) of the material decreases (Table 3). Thus, these potential values are 1.5, 1.2 and 0.7 V vs Na/Na\textsuperscript{+} for ESG3, ESG6 and ESG9, respectively. This trend would be consistent with a recent \textit{ab initio} study of sodium intercalation in disordered carbons [66], which predicts Na\textsuperscript{+} ion intercalation beginning at \(\sim0.7\) V vs Na/Na\textsuperscript{+}, attributing the higher values found in the literature (1.2–1.5 V vs Na/Na\textsuperscript{+}) to the strong bonding to oxygen functional groups on the materials surface. Another feature of these profiles is the absence of plateaus below 0.2 V, as no significant slope changes can be appreciated down to 0.003 V vs Na/Na\textsuperscript{+}, as opposed to those typically observed for hard carbons [33, 66]. This implies that only a small amount of Na\textsuperscript{+} ions is inserted into nanopores/nanocavities in the EGs materials prepared. Similar profiles have been observed in the literature for related expanded graphitic materials [38] and pyrolytic carbons prepared from graphite [61]. However, anomalous disruptions in the discharge slopes in the potential range 0.1–0.2 V vs Na/Na\textsuperscript{+} are also observed for the 2\textsuperscript{nd} and 10\textsuperscript{th} cycles. These
anomalies, which disappear by the 50th cycle, can be better appreciated in the differential capacity profiles (Figure 5d,e,f), as a sudden drop of the $dC/dE$ values, sometimes followed by a sharp peak around the aforementioned discharge potentials. Moreover, on the charge profiles, low-intensity sharp peaks appear at the beginning of desodiation (~0.1 V vs Na/Na$^+$), diminishing in intensity or disappearing after 50 cycles. These two phenomena at very low potentials may be ascribed to irreversible reactions such as Na$^+$ filling/depleting of nanopores or nanocavities which become inaccessible after several discharge/charge cycles, maybe due to continuous SEI formation in the first cycles (in agreement with EIS values in Table S1 and previous discussion), or metal electrodeposition and stripping occurring also in the first cycles [34]. In addition to this, there is some hysteresis in the potential profiles, typical of disordered carbons, with overpotentials of ~0.1–0.2 V between discharge and charge curves, which remain practically unchanged along cycling for all the EGs.

Considering the results discussed so far, it seems obvious that there is a significant surface capacitive contribution ($C_s$) to the specific capacity delivered by the EGs electrodes (i.e. pseudocapacitance due to reaction between Na$^+$ ions and oxygen-containing functional groups on the materials surface). In order to quantify $C_s$, cyclic voltammetry (CV) experiments at different scan rates, from 0.05 to 50 mV s$^{-1}$, were carried out and the total sodiation capacity obtained from these experiments was plotted vs the reciprocal square root of scan rate, $\nu^{-1/2}$ (for ESG3 and EGNF3 electrodes, see Figure 6, for the other materials, see Figures S9 and S10 in Supporting Information). Since the potential vs capacity profiles in Figure 5 show a pseudocapacitive behavior (i.e. the capacity, $C$, depends on the change of the potential, $dE$), the total specific capacity ($\bar{C}$) calculated from the CV
experiments can be divided in two contributions, the surface capacitive contribution \((C_s)\) and the intercalation pseudocapacitive contribution \((C)\). Assuming semi-infinite linear diffusion, \(C_i\) is expected to be linearly related to \(v^{1/2}\) \((C_i = cv^{1/2})\), with \(c\) being a diffusion related coefficient constant, and therefore \(C = cv^{1/2} + C_s\) [63, 67]. Thus, two distinct regions can be appreciated in the \(C\) vs \(v^{1/2}\) plots: diffusion-controlled linear regions at high scan rates (>0.5 mV s\(^{-1}\), Region 2 in Figures 6a,d), which represent capacity limited by semi-infinite linear diffusion, and capacitive-controlled regions, independent of the sweep rate, at lower scan rates (<0.5 mV s\(^{-1}\), Region 1 in Figures 6a,d), for which Na\(^+\) ion diffusion is not the rate-limiting step for charge storage [68]. The \(y\)-intercept obtained by extrapolating the linear fitting for sweep rates <0.5 mV s\(^{-1}\) yields \(C_s\) (see Table 5). As can be seen, there is a direct correlation between the oxygen content of the EGs materials (as determined from elemental analysis and XPS measurements, see Table 3) and the \(C_s\) values of the corresponding EGs electrodes (Table 5). As an example, \(C_s\) values of ~60, 54 and 31 % were calculated for ESG3, ESG6, and ESG9 with oxygen content of ~23, 14 and 3 wt.%, respectively. Therefore, these results account for the larger specific capacity delivered by the expanded materials prepared at 300 or 600 °C (ESG3, ESG6, EGNF3, EGNF6) when compared to those obtained at 900 °C (ESG9, EGNF9) as have been seen in Table 4 and Figure 3. Moreover, a comparison between both electrode series reveals that, provided the same preparation temperature, \(C_s\) values for ESGs are almost two times higher than those of EGNFs (e.g. ESG3 and EGNF3 in Table 5). This is somewhat surprising since the relative amount of oxygen-containing functional groups for corresponding ESGs and EGNFs is not very different as discussed above (Table 3). A plausible explanation for these results may come from the
thicker and more unstable SEI layers formed in EGNFs electrodes, as concluded from the discussion of the SEI data in previous section (see Table S1 and Figure 4), which may hamper the accessibility to oxygen groups for Na$^{+}$ ions in order to form bonding interactions, thus reducing $C_{s}$ substantially. As the absolute sodiation capacity values owing to the intercalation contribution (see $C_{i}$, in mA h g$^{-1}$, in Table 5) for ESG3, ESG6, EGNF3 and EGNF6, are very similar, ~75 mA h g$^{-1}$, the inferior specific capacity delivered by the EGNFs electrodes fundamentally stems from their lower surface capacity contribution ($C_{s}$, in mA h g$^{-1}$, in Table 5). Overall, these results contrast with those of the other expanded graphite used as anode for SIBs reported in the literature, for which the contribution of $C_{s}$ represents only 10 % of the total sodiation capacity [38]. In this case, the higher interlayer spacing (~0.43 nm) measured for this material facilitates Na$^{+}$ ion intercalation allowing much higher $C_{i}$ values.

3.2.3. Effect of electrical current density on galvanostatic cycling

The cycling behaviour of ESG3, ESG6 and EGNF3 electrodes at increasing electrical current density (from 18.6 to 372 mA g$^{-1}$) is depicted in Figure 7. Among the different EGs prepared, these materials were selected because they showed the best electrochemical performance at low electrical current density (Table 4, Figure 3).

The increase of the current density has little to moderate repercussion on the specific capacity delivered by EGSs electrodes. As an example, losses of discharge capacity in the range of ~50 mA h g$^{-1}$ were detected by increasing four times the current density applied (from 18.6 to 74.4 mA g$^{-1}$). Even at the highest...
current density, of 372 mA g\(^{-1}\), ESG3 and ESG6 still retain ~40–50 % of the initial capacity provided at 18.6 mA g\(^{-1}\) with values of 76 and 86 mA h g\(^{-1}\), respectively. In contrast, under the same conditions, capacity losses of ~80 % were measured for EGNF3 whose nanostructured nature should, in theory, favor the diffusion of Na\(^+\) ions at higher cycling rates. This unexpected behavior can only be attributed to the thicker insulating SEI layer formed in EGNFs electrodes in the first cycles as was inferred from EIS analysis (Figure 4), thus affecting their performance, particularly, after increasing the current density since the surface capacitive contribution to the specific capacity, which should be dominant at higher current rates, is much lower for EGNFs materials. However, the initial capacity at 18.6 mA g\(^{-1}\) is basically recovered in the three electrodes studied after returning to these cycling conditions from the highest current density of 372 mA g\(^{-1}\) and, furthermore, all of them exhibit a remarkable stable capacity as well as efficiency along cycling in the whole range of current densities applied.

Prolonged galvanostatic cycling tests at moderate current density (200 cycles at 100 mA g\(^{-1}\)) were conducted for ESG3, ESG6 and EGNF3 electrodes after experiments at different current densities (Figure 7) and for EGNF6 after galvanostatic cycling at 37.2 mA g\(^{-1}\) (Figure 4). The plots of the discharge capacity vs cycle number are compiled in Figure 8. As expected from the above discussed results, ESGs electrodes deliver larger discharge capacity than EGNFs ones along cycling (values at the end of cycling were 85–110 mA h g\(^{-1}\) vs 44 mA h g\(^{-1}\), while the capacity retention was rather high (78–86 %) and the coulombic efficiency (>99 %) excellent in all of them.

Overall, ESGs electrodes show the best electrochemical performances at different current densities, particularly ESG6, which is the only expanded material
able to deliver specific capacities >100 mA h g\(^{-1}\) after 200 cycles at 100 mA g\(^{-1}\) (86 % of the initial capacity), and retain up to 50 % of the capacity delivered at 18.6 mA g\(^{-1}\) when cycling at 372 mA g\(^{-1}\) (~86 mA h g\(^{-1}\)). These results are close to those reported previously for related carbon materials at moderate current rates (100–400 mA g\(^{-1}\)) such as reduced graphene oxides [36, 37] or expanded graphite [38] (C\(_{\text{rev}}\) in the range 80–200 mA h g\(^{-1}\)), but somewhat inferior compared to some hard carbons [21, 24, 26], or other state-of-the-art carbons, including nanostructured ones [35, 63, 64, 69-74].

4. **Conclusions**

Overall, ESGs materials (expanded synthetic graphite) show better electrochemical performance as anode in sodium-ion batteries than their EGNFs counterparts (expanded graphite nanofibers), providing higher specific capacity, leading to lower capacity losses in the charge-discharge first cycle and exhibiting outstanding cycling stability. Thus, ESG3 and ESG6 electrodes deliver specific capacities of ~150 and 127 mA h g\(^{-1}\) after 50 cycles at 37.2 mA g\(^{-1}\), whereas only ~100 and 75 mA h g\(^{-1}\) are attained for EGNF3 and EGNF6, respectively. Unexpectedly, higher capacity losses are measured for the nanostructured EGNFs electrodes by progressively increasing the current density, reaching values up to 80 % vs 40–50 % for ESGs electrodes.

These differences can be attributed to the lower surface area and porosity of ESGs materials which favors the formation of thinner and more stable SEI layer, thus reducing the electrode resistance and enhancing Na\(^+\) ions accessibility to surface oxygen groups with the consequent increase of the surface capacity.
Since in the materials prepared in this work, the capacity provided as a consequence of Na\(^+\) intercalation is not very significant due to the relatively low interlayer distances, the surface contribution to the specific capacity is the dominant and differential factor. Furthermore the oxygen content was found to be directly proportional to this surface contribution of the capacity, thus providing an explanation for the differences found between materials within ESGs and ENFGs series that have been prepared at different temperatures.

In conclusion, improved electrochemical performances could be achieved by preparing expanded graphitic materials with higher interlayer distance in order to increase the intercalation capacity contribution, lower surface areas and porosities, to both decrease the capacity loss during the SEI formation and increase the specific capacity, and with a considerable amount of oxygen-containing functional groups (>10 wt.%) to keep a reasonably high surface capacity contribution.

**Acknowledgements**

Financial support from IBERDROLA SPAIN FOUNDATION ([www.fundacioniberdrola.org](http://www.fundacioniberdrola.org), Projects 2015-2016) and Spanish Ministry of Economy and Competitiveness MINECO (under Projects ENE2011-28318-C0-02 and ENE2014-52189-C2-2-R) is gratefully acknowledged. A. Ramos and N. Cuesta, respectively, thank the Spanish Research Council for Scientific Research (CSIC) for a JAE-Doc contract, co-funded by the European Social Fund (ESF), and the Spanish Ministry of Economy and Competitiveness (MINECO) for a pre-doctoral grant (BES-2012-052711).
REFERENCES


[9] V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J. Carretero-González, T. Rojo, Na-ion batteries, recent advances and present challenges to


W.S. Hummers Jr., R.E. Offeman, Preparation of Graphitic Oxide, Journal of the American Chemical Society, 80 (1958) 1339-.


### Table 1

Structural parameters of GOs and EGs materials calculated from XRD profiles: interlayer spacing ($d_{002}$) and crystallite size along the c axis ($L_c$), and from 1st order Raman spectrum: D-band position ($\nu_D$), D-band width ($w_D$) and relative D-band intensity.

<table>
<thead>
<tr>
<th>Material</th>
<th>$d_{002}$ (nm)</th>
<th>$L_c$ (nm)</th>
<th>$w_D$ (cm$^{-1}$)</th>
<th>$\nu_D$ (cm$^{-1}$)</th>
<th>$I_D/I_t$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGO</td>
<td>0.8000</td>
<td>8.9</td>
<td>116</td>
<td>1355</td>
<td>42.8</td>
</tr>
<tr>
<td>ESG3</td>
<td>{0.4038 / 0.3616}$^a$</td>
<td>{4.5 / 1.2}$^a$</td>
<td>111</td>
<td>1355</td>
<td>44.1</td>
</tr>
<tr>
<td>ESG6</td>
<td>0.3435</td>
<td>3.9</td>
<td>108</td>
<td>1355</td>
<td>38.9</td>
</tr>
<tr>
<td>ESG9</td>
<td>0.3432</td>
<td>2.2</td>
<td>89</td>
<td>1350</td>
<td>40.9</td>
</tr>
<tr>
<td>GNFO</td>
<td>0.8233</td>
<td>2.9</td>
<td>115</td>
<td>1356</td>
<td>40.8</td>
</tr>
<tr>
<td>EGNF3</td>
<td>0.3570</td>
<td>1.4</td>
<td>110</td>
<td>1353</td>
<td>40.3</td>
</tr>
<tr>
<td>EGNF6</td>
<td>0.3461</td>
<td>2.0</td>
<td>113</td>
<td>1352</td>
<td>38.4</td>
</tr>
<tr>
<td>EGNF9</td>
<td>0.3493</td>
<td>1.8</td>
<td>93</td>
<td>1350</td>
<td>37.8</td>
</tr>
</tbody>
</table>

$^a$ From the deconvolution into two (002) peaks.
Table 2

Textural parameters of GOs and EGs materials: BET surface area ($S_{\text{BET}}$), total ($V_T$), mesopore ($V_{\text{MESO}}$) and micropore ($V_{\text{MICRO}}$) volumes.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_T$ (cm$^3$ g$^{-1}$)$^a$</th>
<th>$V_{\text{MESO}}$ (cm$^3$ g$^{-1}$)$^b$</th>
<th>$V_{\text{MICRO}}$ (cm$^3$ g$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGO</td>
<td>37</td>
<td>0.023</td>
<td>0.008</td>
<td>0.015</td>
</tr>
<tr>
<td>ESG3</td>
<td>20</td>
<td>0.020</td>
<td>0.012</td>
<td>0.008</td>
</tr>
<tr>
<td>ESG6</td>
<td>42</td>
<td>0.041</td>
<td>0.024</td>
<td>0.017</td>
</tr>
<tr>
<td>ESG9</td>
<td>39</td>
<td>0.045</td>
<td>0.029</td>
<td>0.016</td>
</tr>
<tr>
<td>GNFO</td>
<td>246</td>
<td>0.111</td>
<td>0.009</td>
<td>0.102</td>
</tr>
<tr>
<td>EGNF3</td>
<td>&lt;1</td>
<td>0.004</td>
<td>0.003</td>
<td>{0.001} $^d$</td>
</tr>
<tr>
<td>EGNF6</td>
<td>85</td>
<td>0.045</td>
<td>0.009</td>
<td>0.036</td>
</tr>
<tr>
<td>EGNF9</td>
<td>119</td>
<td>0.077</td>
<td>0.031</td>
<td>0.046</td>
</tr>
</tbody>
</table>

$^a$ Calculated at $P/P_0 \sim 0.97$. $^b$ $V_{\text{MESO}} = V_T - V_{\text{MICRO}}$. $^c$ Calculated using Dubinin-Radushkevich equation for N$_2$ adsorption at −196 °C. $^d$ Narrow microporosity (<0.7 nm) calculated using Dubinin-Radushkevich equation for CO$_2$ adsorption at 0 °C.
Table 3

Elemental and XPS surface chemical analyses of GOs and EGs materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>C (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>O (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C/O atm. ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>C=C (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>C−O (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>C=O (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGO</td>
<td>50.2</td>
<td>47.4</td>
<td>5.1</td>
<td>60.2</td>
<td>30.0</td>
<td>9.8</td>
</tr>
<tr>
<td>ESG3</td>
<td>76.9</td>
<td>23.0</td>
<td>8.4</td>
<td>63.8</td>
<td>24.5</td>
<td>11.7</td>
</tr>
<tr>
<td>ESG6</td>
<td>86.0</td>
<td>13.6</td>
<td>12.9</td>
<td>66.4</td>
<td>26.2</td>
<td>7.5</td>
</tr>
<tr>
<td>ESG9</td>
<td>95.4</td>
<td>3.0</td>
<td>18.6</td>
<td>75.8</td>
<td>19.2</td>
<td>5.0</td>
</tr>
<tr>
<td>GNFO</td>
<td>48.2</td>
<td>46.1</td>
<td>3.5</td>
<td>37.9</td>
<td>44.5</td>
<td>17.6</td>
</tr>
<tr>
<td>EGNF3</td>
<td>74.5</td>
<td>25.1</td>
<td>7.2</td>
<td>63.7</td>
<td>25.4</td>
<td>10.9</td>
</tr>
<tr>
<td>EGNF6</td>
<td>85.3</td>
<td>13.1</td>
<td>10.8</td>
<td>65.7</td>
<td>26.3</td>
<td>8.0</td>
</tr>
<tr>
<td>EGNF9</td>
<td>94.5</td>
<td>2.2</td>
<td>14.2</td>
<td>69.9</td>
<td>25.5</td>
<td>4.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> From elemental analysis. <sup>b</sup> Surface atomic ratio and carbon distribution calculated from XPS measurements.
Table 4

Electrochemical parameters from the galvanostatic cycling at 37.2 mA g\(^{-1}\) of ESGs and EGNFs electrodes

<table>
<thead>
<tr>
<th>Material</th>
<th>(C_{\text{disc, 1st cycle}}) (mA h g(^{-1}))</th>
<th>(C_{\text{disc, 2nd cycle}}) (mA h g(^{-1}))</th>
<th>(C_{\text{disc, 50th cycle}}) (mA h g(^{-1}))</th>
<th>(C_{\text{irr, 1st cycle}}) (%)(^a)</th>
<th>(R) (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESG3</td>
<td>475</td>
<td>203</td>
<td>150</td>
<td>60</td>
<td>74</td>
</tr>
<tr>
<td>ESG6</td>
<td>427</td>
<td>165</td>
<td>127</td>
<td>63</td>
<td>77</td>
</tr>
<tr>
<td>ESG9</td>
<td>203</td>
<td>78</td>
<td>58</td>
<td>68</td>
<td>74</td>
</tr>
<tr>
<td>EGNF3</td>
<td>448</td>
<td>139</td>
<td>100</td>
<td>77</td>
<td>72</td>
</tr>
<tr>
<td>EGNF6</td>
<td>297</td>
<td>100</td>
<td>75</td>
<td>72</td>
<td>75</td>
</tr>
<tr>
<td>EGNF9</td>
<td>93</td>
<td>34</td>
<td>25</td>
<td>85</td>
<td>80</td>
</tr>
</tbody>
</table>

\(^a\) \left[ \frac{(C_{\text{disc, 1st cycle}} - C_{\text{charge, 1st cycle}})}{C_{\text{disc, 1st cycle}}} \right] \times 100

\(^b\) \left[ \frac{(C_{\text{disc, 50th cycle}} - C_{\text{disc, 2nd cycle}})}{C_{\text{disc, 2nd cycle}}} \right] \times 100
Table 5

Surface capacitive ($C_s$, in mA h g$^{-1}$ and %) and intercalation pseudocapacitive ($C_i$, in mA h g$^{-1}$ and %) contributions to the specific capacity delivered by ESGs and EGNFs electrodes.

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_s$ (mA h g$^{-1}$)</th>
<th>(%)</th>
<th>$C_i$ (mA h g$^{-1}$)</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESG3</td>
<td>111</td>
<td>60</td>
<td>73</td>
<td>40</td>
</tr>
<tr>
<td>ESG6</td>
<td>87</td>
<td>54</td>
<td>74</td>
<td>46</td>
</tr>
<tr>
<td>ESG9</td>
<td>28</td>
<td>31</td>
<td>62</td>
<td>69</td>
</tr>
<tr>
<td>EGNF3</td>
<td>34</td>
<td>30</td>
<td>78</td>
<td>70</td>
</tr>
<tr>
<td>EGNF6</td>
<td>31</td>
<td>28</td>
<td>81</td>
<td>72</td>
</tr>
<tr>
<td>EGNF9</td>
<td>7</td>
<td>15</td>
<td>39</td>
<td>85</td>
</tr>
</tbody>
</table>
CAPTIONS FOR FIGURES

**Figure 1.** TG and DTG plots for SGO (top) and GNFO (bottom).

**Figure 2.** CO and CO$_2$ profiles obtained by TPD for SGO (top) and GNFO (bottom). Inset: Magnification of the area below 1 $\mu$mol g$^{-1}$ s$^{-1}$.

**Figure 3.** Galvanostatic cycling at 37.2 mA g$^{-1}$ for ESGs (top) and EGNFs (bottom) electrodes.

**Figure 4.** Nyquist impedance plots from the EIS analysis of ESG3 (top) and EGNF3 (bottom) electrodes.

**Figure 5.** Potential vs Capacity (a, b, c) and Differential Capacity vs Potential (d, e, f) profiles for 1$^{st}$, 2$^{nd}$, 10$^{th}$ and 50$^{th}$ cycles for ESGs electrodes.

**Figure 6.** Normalized discharge capacities vs $v^{1/2}$ and voltammograms at different scan rates (from 0.05 mV s$^{-1}$ to 50 mV s$^{-1}$) for ESG3 (a, b, c) and EGNF3 (d, e, f) electrodes.

**Figure 7.** Cycling performance of ESG3, ESG6 and EGNF3 electrodes at different electrical current densities.

**Figure 8.** Prolonged galvanostatic cycling at 100 mA g$^{-1}$ for ESG3, ESG6, EGNF3 and EGNF6 electrodes.
FIGURES

Figure 1. TG and DTG plots for SGO (top) and GNFO (bottom).
Figure 2. CO and CO$_2$ profiles obtained by TPD for SGO (top) and GNFO (bottom). Inset: Magnification of the area below 1 $\mu$mol g$^{-1}$ s$^{-1}$. 
Figure 3. Galvanostatic cycling at 37.2 mA g\(^{-1}\) for ESGs (top) and EGNFs (bottom) electrodes.
Figure 4. Nyquist impedance plots from the EIS analysis of ESG3 (top) and EGNF3 (bottom) electrodes.
Figure 5. Potential vs Capacity (a, b, c) and Differential Capacity vs Potential (d, e, f) profiles for 1\textsuperscript{st}, 2\textsuperscript{nd}, 10\textsuperscript{th} and 50\textsuperscript{th} cycles for ESG electrodes.
Figure 6. Normalized discharge capacities vs $v^{-1/2}$ and voltammograms at different scan rates (from 0.05 mV s$^{-1}$ to 50 mV s$^{-1}$) for ESG3 (a, b, c) and EGNF3 (d, e, f) electrodes.
Figure 7. Cycling performance of ESG3, ESG6 and EGNF3 electrodes at different electrical current densities.
Figure 8. Prolonged galvanostatic cycling at 100 mA g⁻¹ for ESG3, ESG6, EGNF3 and EGNF6 electrodes.