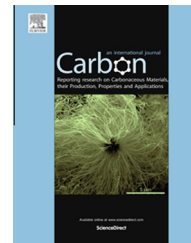


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Electrochemically exfoliated graphene oxide/iron oxide composite foams for lithium storage, produced by simultaneous graphene reduction and Fe(OH)₃ condensation

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ABSTRACT

We describe the production of graphene-based composites for energy storage, obtained by a combination of electrochemical and solution processing techniques. Electrochemically exfoliated graphene oxide sheets (EGO) are produced using an original setup that allows fast expansion of graphite flakes and efficient exfoliation of expanded graphite via an electrochemical route. The sheets are deposited on a sacrificial nickel foam together with an iron hydroxide colloidal precursor. Calcination treatment simultaneously renders the EGO foam conductive and transforms Fe(OH)₃ into hematite (α -Fe₂O₃), yielding a nanoporous Fe₂O₃ layer on the surface of the mesoporous EGO foam, creating an ideal structure for lithium storage. The obtained graphene/metal oxide hybrid is a continuous, electrically conductive three-dimensional (3D) composite featuring a hierarchical meso–nano porous structure. A systematic study of these composites, varying the Fe₂O₃:EGO ratio, is then performed to maximize their performance as nanostructured electrodes in standard coin cell batteries.

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1. Introduction

Lithium-based batteries are becoming increasingly popular for portable electronics applications, thanks to a growing demand for lightweight and flexible high-performance energy storage devices. A commonly used electrode is graphite, which has a limited theoretical capacity of 372 mA h g⁻¹ [1]. To meet the industrial demand for higher energy density

batteries, alternative anode materials based on transition metal oxides have been used to improve the storage capacity of electrodes, due to their reversible conversion reactions with lithium ($M_aX_b + (bn) Li \leftrightarrow aM + bLi_nX$, where M = transition metal, X = anion, and n = formal oxidation state of X) [2]. Among these metal oxides, Fe₂O₃ is a promising low-cost, abundant and non-toxic candidate for pseudo-capacitor electrodes with high theoretical capacity (1007 mA h g⁻¹,

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assuming ~ 6 Li per formula unit) [3]. However, the practical applications of Fe_2O_3 based electrodes suffer from their low electrical conductivity and inferior cycling stability [4].

Graphene, as a one-atom-thick layer of graphite, holds fascinating characteristics such as high surface area, excellent electrical conductivity, extraordinary elasticity and ultra-light weight. The integration of graphene sheets with metal oxides can efficiently enhance the electrical conductivity and improve the stability of these pseudo-capacitive materials [5–9]. Recently, three-dimensional (3D) graphene networks with porous architectures have been extensively investigated as excellent building blocks for electrochemically active metal particles. These freestanding 3D graphene-based foams (GF) couple a low density with the high flexibility and electrical conductivity of 2D graphene sheets. Meanwhile, the mesoporous or nanoporous [5,10] morphology of GF gives a large contact area between the electrolyte and the electrode, and provides multidimensional electron transport pathways to enhance the electrochemical performance. The production of porous electrodes using 2D sheets thus seems a very promising approach for energy storage, as demonstrated by the large number of papers published recently on this field [11–23]. However, the starting material used to prepare these foams is usually graphene oxide (typically produced by Hummers method), that requires many days of preparation and tedious purification [24]. Alternatively, graphene can be grown directly on the metal substrate by chemical vapor deposition (CVD), but this approach requires harsh reaction conditions like high temperature (800–1000 °C) and ultra-high vacuum.

To meet the urgent requirement of large scale fabrication of graphene from cheap raw materials, an alternative approach intensively studied in the last few years is to exfoliate graphite using an electric bias. Massive conversion of bulk graphite into soluble sheets of electrochemically exfoliated graphene oxide (EGO) can be obtained in a few minutes, compared to several tens of hours needed for chemical exfoliation of GO [25,26].

In particular, electrochemical exfoliation in aqueous solutions of inorganic salts can give a high yield of few-layers EGO ($>85\%$, ≤ 3 layers), a reduced amount of oxidative damage and a large lateral size ($>40 \mu\text{m}$) [25]. Furthermore, combining electrochemical exfoliation in acetonitrile and microwave-triggered expansion, we recently obtained $\approx 75\%$ yield of graphite exfoliation, with monolayer yield $>50\%$, and 72% of the sheets being larger than $1 \mu\text{m}$ [26].

The electrochemical exfoliation of graphite occurs so fast and efficiently because of the mechanical action due to gas production in the graphite bulk, which creates a pressure of several hundred bar, blister formation and delamination of graphene sheets [27]. However, the process can be used only with electrically continuous materials such as graphite rods or highly oriented pyrolytic graphite (HOPG), while the ideal starting material would be low-cost graphite powder, or microscopic graphite flakes. Furthermore, the electrochemical expansion is so fast and violent that large amounts of mesoscopic, unexfoliated graphite particles can be dispersed in solution, together with the monoatomic EGO sheets. These particles are no longer electrically connected to the working electrode, so do not exfoliate further.

In this work, we describe a new approach to exfoliate abundant and cheap graphite flakes with an electrochemical approach, with a high exfoliation yield (50%) of non-monolithic EGO flakes.

To demonstrate a potential application of this method, the EGO sheets were deposited together with an $\text{Fe}(\text{OH})_3$ precursor on a sacrificial metal template, and then thermally annealed to obtain monolithic, conductive Fe_2O_3 /reduced graphene oxide (RGO) composite networks [28,29]. The material obtained in this way was characterized by Scanning Electron Microscopy (SEM), Raman Spectroscopy, Energy dispersive X-ray spectroscopy (EDX), and used as an electrode in lithium batteries.

2. Experimental

2.1. Materials

Graphite Flakes (+100 mesh series) were purchased from Aldrich. Sodium perchlorate (Sigma–Aldrich, 98%) and sulfuric acid (Sigma–Aldrich, 95–97%) were used as electrolytes; acetonitrile (Sigma–Aldrich, 99%), N,N-Dimethylformamide (Sigma, 99%) and Deionized (DI) water were used as solvents. A platinum foil (99.99%) with the size of $5 \text{ mm} \times 10 \text{ mm} \times 0.1 \text{ mm}$ was used as an anode connector. A platinum wire (99.99%, 0.3 mm) was used as a counter electrode. Nickel foams (380 g m^{-2} in areal density and 1.5 mm in thickness, compressed to 0.2 mm) were used as 3D templates for graphene coating. PMMA (950 K, 4% in anisole), obtained from Micro Resist Technology GmbH., was used as a support polymer for Ni etching step. PTFE (47 mm , $0.2 \mu\text{m}$) membrane filters (47 mm , $0.2 \mu\text{m}$) were purchased from GVS.

2.2. Synthesis of graphene based compounds

2.2.1. Electrochemical preparation of EGO

Graphite flakes (1 g) were put into a Nylon filter bag (200 mesh porosity, corresponding to a pore size of $\approx 75 \mu\text{m}$), and inserted into a porous plastic tube to keep the whole material coherent. The flakes were compressed by pressing a plastic cap on the top of the tube (Fig. 1). The plastic tube with filter mesh had a mechanical containment role, keeping the graphite flakes compressed inside the tube to ensure that they were all electrically connected to the metal electrode, and thus subject to exfoliation. This method allowed to perform electrochemical exfoliation on non-monolithic powder samples.

A platinum foil was connected to graphite on the top of the tube through a slot of the plastic cap, to act as working electrode. A platinum wire outside the tube was used as a counter-electrode. The ionic solution was prepared dissolving 1.3 g of sodium perchlorate in 10 mL of acetonitrile (1 mol L^{-1}). Then, exfoliation was performed following an approach already described in previous work [26]. In brief, uncharged acetonitrile molecules were intercalated in graphite by electrochemical treatment, due to the synergistic action of perchlorate ions dissolved in the acetonitrile. Then, the CH_3CN molecules were decomposed with microwaves, causing gas production and rapid graphite exfoliation. This method uses the gas produced by the decomposition of

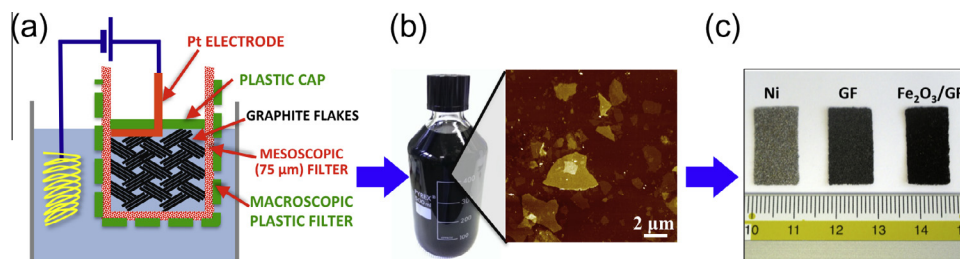


Fig. 1 – (a) Schematic illustration of EGO preparation by electrochemical processing. (b) Photograph of the EGO solution. In the inset, a representative AFM image of EGO flakes spin-coated on a SiO₂/Si substrate (Z-range: 20 nm). (c) Photograph comparing the original Ni foam, the GF and the Fe₂O₃/GF samples. (A color version of this figure can be viewed online.)

acetonitrile molecules as a powerful blowing agent to foster graphite exfoliation in a few seconds [26].

The first electrochemical intercalation/exfoliation stage was carried out for 30 min by applying a DC bias on the graphite electrode at a voltage of +5 V. After reaction, the partially exfoliated graphite samples were washed with acetonitrile several times and blow-dried with dry nitrogen for 2 min.

A commercial microwave oven (Whirlpool JT379) with rotating tray was used for further expansion. The graphite samples were placed in a porcelain crucible (capacity 50 mL) and heated in the microwave oven for 30 s under 90 W. Then, the expanded foam-like graphite was compressed again to make the whole material coherent. The material was fixed a second time in a porous plastic tube, connected to a Pt foil and further exfoliated in 0.1 M H₂SO₄ solution as an anode at +10 V for 2 h. Then, the graphene sheets were collected by vacuum filtration onto a PTFE membrane and cleaned several times by repeated washing with DI water. Afterwards, the exfoliated flakes were redispersed in DMF by sonication for 30 min (37 kHz, ≈100 W effective ultrasonic power, Model ELMA P70H Ultrasonic). The graphene oxide solution was centrifuged at 2000 rpm for 30 min to remove any re-aggregated particles.

2.2.2. Preparation of Fe(OH)₃ solution

6.5 g of FeCl₃ was dissolved in 20 mL DI water (2 mol L⁻¹). 1 ml of the prepared solution was dropped into 100 mL of 1:1 boiling distilled water/isopropyl alcohol (IPA). The solution was kept boiling for 2 h to obtain Fe(OH)₃ solution. After centrifugation at 10,000 rpm and repeated washing with water and IPA several times to remove the chloride ions, Fe(OH)₃ (10 mg mL⁻¹) was obtained and redispersed in 20 mL IPA.

2.2.3. Preparation of graphene foam (GF) and Fe₂O₃/GF

EGO solutions (0.7 mg mL⁻¹ in DMF) were deposited onto a Ni foam (10 mm × 5 mm × 0.2 mm) positioned on a hot-plate at 150 °C by drop casting method, and allowed to slowly infiltrate into the foam to give graphene oxide/Ni foam.

A freestanding foam (GF) was obtained by etching the Ni foam substrate. First, the foam was soaked in a poly(methyl-methacrylate) (PMMA) solution (4% in anisole) and baked at 150 °C for 30 min, then GF/Ni foam was etched in 10% HCl solution for 24 h at 80 °C to fully dissolve the Ni metal. The PMMA support layer is important to prepare this free-standing GF; without PMMA support, GF broke down or collapsed

during the HCl acid etching step. PMMA was removed by immersing the foam in hot acetone. Energy Dispersive X-ray spectroscopy (EDX) confirmed the complete removal of Ni after this treatment.

Fe₂O₃/EGO composites were prepared by drop-casting a dilute Fe(OH)₃ solution (1 mg mL⁻¹ in IPA) onto a GF placed on a hot-plate at 100 °C. The ratio of Fe(OH)₃ and EGO could be changed by casting different amounts of Fe(OH)₃ solution.

The samples were heated at 400 °C for 2 h to reduce the EGO, decompose the Fe(OH)₃ (if present) and obtain GF or Fe₂O₃/GF composites. A different weight ratio of Fe₂O₃:GF (from 1:5 to 5:1 with the fixed total amount of 3 mg) was obtained by coating different amounts of EGO and Fe(OH)₃, and measuring the weight difference after each coating. The weight loss measured for our EGO after heating was ≈30%. The weight loss from Fe(OH)₃ to Fe₂O₃ was around 27%, which is consistent with the calculation (2Fe(OH)₃ → Fe₂O₃ + 3H₂O, weight loss of water is 25.2%). In all cases, the weight loss of EGO and Fe(OH)₃ was accounted for in the calculation to obtain the correct Fe₂O₃/GF ratio. This procedure was performed either on samples still having the underlying Nickel substrate, or on pure, freestanding GF.

2.3. Electrochemical measurements and characterization

Cyclic voltammetry (CV) studies were carried out using a 1.0 mol L⁻¹ Na₂SO₄ solution in ultra pure water (0.56 μS cm⁻¹) with an AMEL 5000 three electrode system setup. Foams partially immersed in the solution acted as the working electrode (only the immersed volume was used for calculations). The reference electrode was an aqueous Saturated Calomel Electrode (SCE), and the auxiliary electrode was a Pt wire separated from the working electrode by a glass frit.

Specific capacitance values were calculated from the CV curves using the following equation: $C = (\int Idt)/(m\Delta V)$, where I is the oxidation or reduction current, dt is time differential, m is the mass of the active graphene foam, and ΔV is the voltage range of one sweep segment.

Standard 2032 coin cells were assembled inside a MBRAUN glovebox (H₂O < 2 ppm, O₂ < 10 ppm) using GF or Fe₂O₃/GF samples with varying Fe₂O₃/GF ratios. In such a primary lithium battery, lithium foil is used as the anode with a polymer electrolyte composed of high molecular weight poly(ethylene glycol) borate ester. The Lewis acid centers of the borate esters interact with the anion resulting in enhanced lithium

ion transport, and the resulting performance of such polymer electrolytes is comparable with conventional liquid organic electrolytes at room temperature. The prepared graphene foams were used directly as the cathode.

The electrical resistance of the graphene foams was measured with a four-point probe system (Keithley 2700 Multimeter). Scanning Electron Microscopy (SEM) images were obtained with a ZEISS 1530 instrument. Raman scattering measurements were carried out with a micro-Raman spectrometer (Model: LabRAM from Horiba Jobin-Yvon), using a 100× objective (laser spot diameter $\approx 5 \mu\text{m}$), laser excitation wavelength of 632.8 nm and laser power $\sim 4 \text{ mW}$. XRD measurements were collected with a PANalytical X'PertPro instrument in Bragg-Brentano reflection mode ($\lambda = 0.1542 \text{ nm}$, X'Celerator detector).

3. Results and discussion

3.1. Morphology and structure

In this work we used cheap, natural graphite flakes as starting materials instead of the expensive, highly oriented pyrolytic graphite (HOPG) previously employed. After intercalation, expansion and exfoliation steps, EGO solutions were obtained with good yield ($\sim 35\%$) and concentration (0.7 mg mL^{-1}). Moreover, the yield was further improved to 50% by recycling the sediment and repeating the mild sonication/centrifugation step.

The high yield is due to the high density of material present and the confinement role of the polypropylene tube, which keeps the graphitic sheets associated even during electrochemical processing in sulfuric acids. The exfoliation of graphite anode at +10 V promotes the intercalation of bisulfate ions into graphite, and the delamination of graphite inner layers due to gas evolution (O_2 and CO_2 from electrolysis of water and oxidation of graphite) [27]. At the end of the process, we obtain a black-colored EGO slurry, which is solubilized very effectively by a mild sonication (30 min) in DMF. A comparison of the sheets obtained by electrochemical exfoliation as compared to classical, extended sonication in DMF has been already reported in previous papers [26,27]. Prolonged sonication in DMF yields non-defective graphene sheets [30], but sheet size is less than $1 \mu\text{m}$, and sonication time should be $>400 \text{ h}$ to obtain high concentration. The approach described here gives sheets spanning 1–10 μm in length, mostly mono- or bi-layers (for statistics see Refs. [26,27]), with concentration around 0.7 mg mL^{-1} .

The pre-expansion of graphite using acetonitrile and microwaves is fundamental to obtain a good yield [26]. After the rapid expansion process, the volume of graphite

crystallites increased hundreds of times (see SEM images in Fig. S1), which vastly facilitated the electrochemical intercalation of the bisulfate anion in the last step. Meanwhile, the mesoscopic Nylon mesh kept all the graphite electrically connected, and efficiently avoided the detachment of non-exfoliated flakes from the electrolysis of water and the following gas evolution.

By comparison, simple exfoliation of expanded graphite flakes with only a plastic tube and no Nylon filter produced exfoliated graphene with $\sim 20\%$ yield due to the dispersion of flakes in the solution. After exfoliation and solubilization, the EGO sheets were deposited on a meso-porous nickel foam holder ($\sim 0.2 \text{ mm}$ thick) acting as a sacrificial hard template [11,31]. EGO solution was drop cast onto the foam, forming a continuous graphene layer on the nickel surface. After this, the Ni template could be removed by filling the foam with PMMA, etching the metal in acid, and removing the PMMA in hot acetone. Fig. 2 shows a schematic representation of the synthesis steps for this 3D structure.

A freestanding GF was obtained with size $20 \text{ mm} \times 10 \text{ mm} \times 0.2 \text{ mm}$, featuring low bulk resistance ($22 \Omega \text{ cm}^{-2}$) and areal density ($\approx 1.0 \text{ mg cm}^{-2}$). This corresponds roughly to a volume density of $\approx 50 \text{ mg cm}^{-3}$, significantly greater than what is typically attainable with graphene foams grown by CVD on nickel templates (20 mg cm^{-3} , Ref. [12]).

The prepared free-standing GF forms an interconnected and monolithic 3D network structure (Fig. 3). The weight of GF could be easily adjusted by varying the loading amount of EGO solution on Ni. By using an EGO loading greater than 0.5 mg cm^{-2} , a continuous framework was formed, without the formation of cracks or collapse of the structure. A comparison of the GF before and after Ni etching is reported in Fig. 3. The morphology with and without Ni is similar at both low and high magnification, confirming that the etching of the Ni template damages neither the foam nor the (possibly present) Fe_2O_3 coating. Few parts of the hollow internal branches are cracked, maybe due to escaped H_2 gas during the metal etching step ($2\text{HCl} + \text{Ni} \rightarrow \text{NiCl}_2 + \text{H}_2$). Besides this, the whole structure appears uniform and continuous, demonstrating the good coating properties of the EGO solution due to good affinity with the nickel surface.

To decorate the graphene network structure, a $\text{Fe}(\text{OH})_3$ solution (3 mg mL^{-1}) was used as a precursor for $\alpha\text{-Fe}_2\text{O}_3$ particles. A controlled amount of $\text{Fe}(\text{OH})_3$ was drop cast onto the foam on a hot plate, then $\text{Fe}(\text{OH})_3$ dehydration was induced simultaneously with reduction of EGO [32] by thermal annealing at 400°C , much below the temperature required for graphene production by CVD ($T = 1000^\circ\text{C}$) [11].

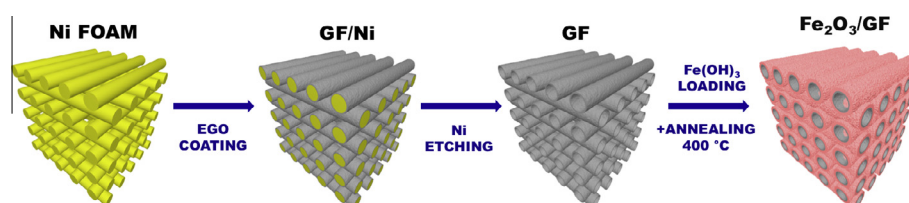


Fig. 2 – Schematic illustration of GF and $\text{Fe}_2\text{O}_3/\text{GF}$ synthesis routes. (A color version of this figure can be viewed online.)

The previously smooth graphene surface (Fig. 4a and b) thus became uniformly covered by a porous Fe_2O_3 layer with pore sizes well below 100 nm (Fig. 4c and d), formed during the condensation reaction at 400 °C and subsequent generation of vapor ($2\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$).

Fig. 5 reports the Energy Dispersive X-ray spectroscopy (EDX) maps obtained on a segment of $\text{Fe}_2\text{O}_3/\text{GF}$ foam. Fig. S2 in the Supporting Information shows the EDX spectrum from a small region on the foam. Both figures show clearly only the signal of carbon, oxygen, and iron, therefore confirming the complete removal of the nickel foam. Despite the low spatial resolution of the EDX maps (few μm), and the noise due the

low acquisition time used to prevent sample damaging, the combination of EDX measurements and imaging shows that the nanoporous Fe_2O_3 layer is uniformly distributed on the GF foam (Fig. 4c and d).

The structure of the composite was characterized by X-ray diffraction (Fig. 6) and Raman spectroscopy (Fig. 7), given that both Fe_2O_3 and GF reveal a strong Raman signal and a typical XRD periodicity. Raman spectra of GF and $\text{Fe}_2\text{O}_3/\text{GF}$ both showed the characteristic D peak ($\approx 1329\text{ cm}^{-1}$) and D' shoulder peak ($\approx 1605\text{ cm}^{-1}$) typical of GO and RGO, related to carbon defects in both spectra [33]. $I_{\text{D}}/I_{\text{G}}$ ratio for GF and $\text{Fe}_2\text{O}_3/\text{GF}$ were 0.5 and 1.4 respectively. The large, broad appearance

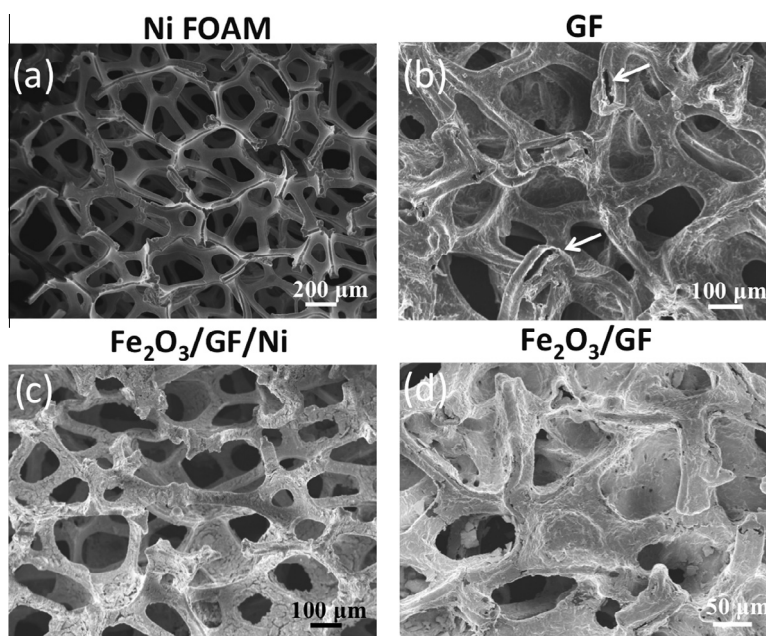


Fig. 3 – SEM images of: (a) Pristine Nickel foam. (b) GF, (c) $\text{Fe}_2\text{O}_3/\text{GF}/\text{Ni}$ foam and (d) $\text{Fe}_2\text{O}_3/\text{GF}$. Arrows in (b) indicate rare cracks due to the etching of the nickel substrate.

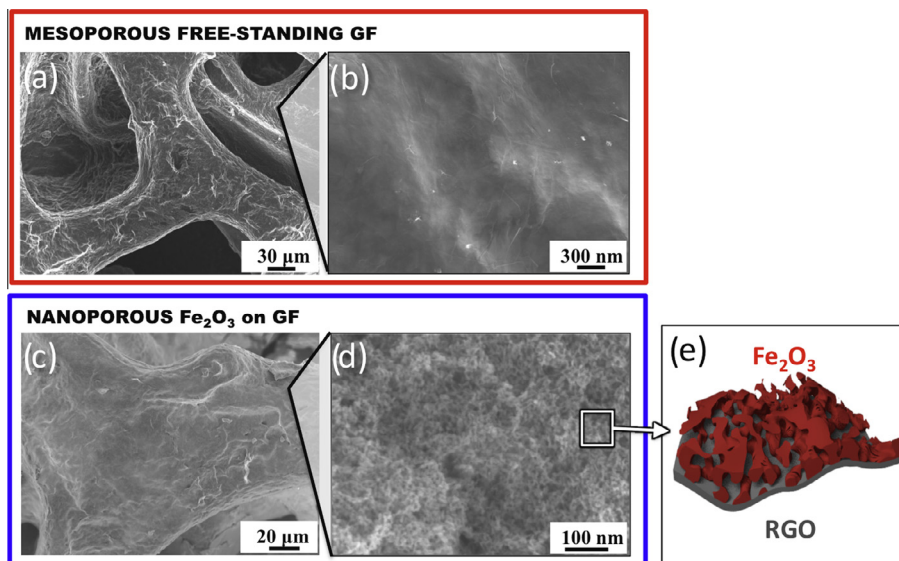


Fig. 4 – SEM images of: (a) GF, and (c) $\text{Fe}_2\text{O}_3/\text{GF}$, 1:2 weight ratio. (b and d) are zoom-in of (a) and (c), respectively. (e) Cartoon showing the hierarchical structure of the $\text{Fe}_2\text{O}_3/\text{GF}$ porous layer. (A color version of this figure can be viewed online.)

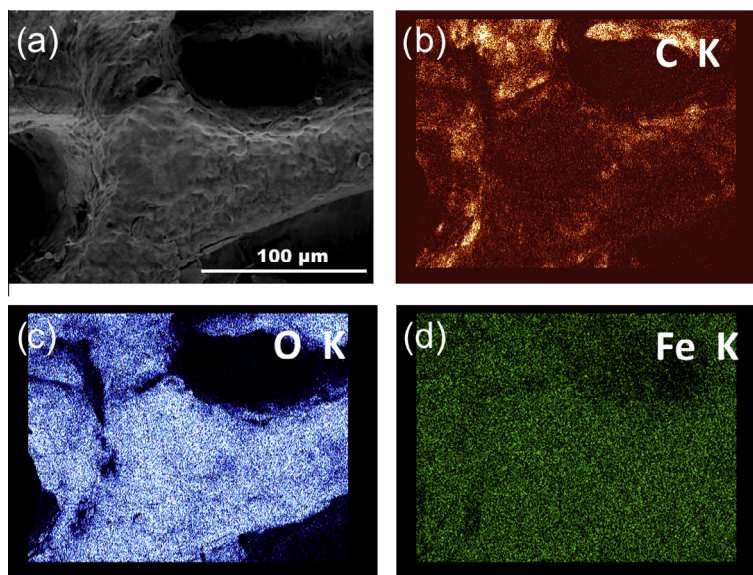


Fig. 5 – SEM image and EDX mapping of C, O, Fe elements on a segment of Fe₂O₃/GF foam. (A color version of this figure can be viewed online.)

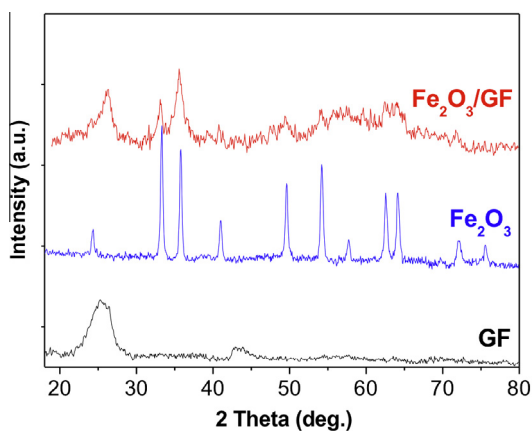


Fig. 6 – XRD signal of Fe₂O₃ powder, GF and Fe₂O₃/GF. (A color version of this figure can be viewed online.)

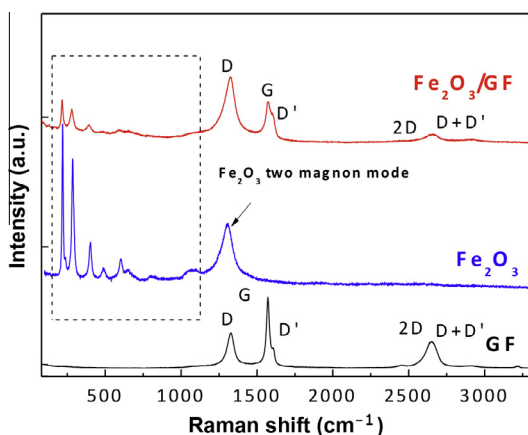


Fig. 7 – Raman spectra of Fe₂O₃ powder, GF and Fe₂O₃/GF. (A color version of this figure can be viewed online.)

of the D peak of the Fe₂O₃/GF sample is due to the contribution of the Fe₂O₃ two magnon scattering of hematite ($\approx 1305 \text{ cm}^{-1}$), which also influence the different I_D/I_G ratio compared to the pure GF sample. The G peak ($\approx 1572 \text{ cm}^{-1}$) and 2D peak ($\approx 2650 \text{ cm}^{-1}$) are typically associated with graphitic carbon. In comparison, bare Fe₂O₃ powder shows distinctive peaks (219 cm^{-1} , 285 cm^{-1} , 402 cm^{-1}) attributed to 2A_{1g} and 4E_g Raman modes for the hematite phase [34]. These bands were also clearly observed in Fe₂O₃/GF sample, confirming that the iron oxide formed has a hematite structure. The XRD patterns of Fe₂O₃ agree also with the rhombohedral phase of hematite (JCPDS No. 33-0664). An XRD peak at 26°, corresponding to a spacing of $\approx 3.4 \text{ \AA}$, is observed for GF and for Fe₂O₃/GF, in good agreement with what was previously observed for EGO [27]. Noteworthy, the XRD diffraction peaks were relatively broad for Fe₂O₃/GF composites, indicating that the iron oxide particles are non-crystalline or sub nanocrystalline and that EGO sheets are poorly stacked, a favorable condition to enhance lithium intercalation. XRD peaks of nickel were not detected in either Fe₂O₃/GF or bare GF samples, confirming that the etching process successfully removed the nickel template.

3.2. Energy storage application

Thanks to the approach based entirely on solution processing, the Fe₂O₃:EGO w/w ratio could be easily tuned allowing optimization of the capacitance of the material. Using this approach, different weight ratios of Fe₂O₃:EGO (1:5, 1:2, 1:1, 2:1, 5:1 w/w with a fixed total amount of 3 mg) were loaded into the Ni foam by separately drop casting EGO and Fe(OH)₃ onto the Ni template. The electrochemical properties of Fe₂O₃/GF/Ni composite were measured with a three-electrode system in a 1 M Na₂SO₄ aqueous solution (Fig. S3 in SI). The cyclic voltammetry (CV) profile of the GF/Ni foam sample at a scan rate from 5 to 200 mV s⁻¹ suggests a typical

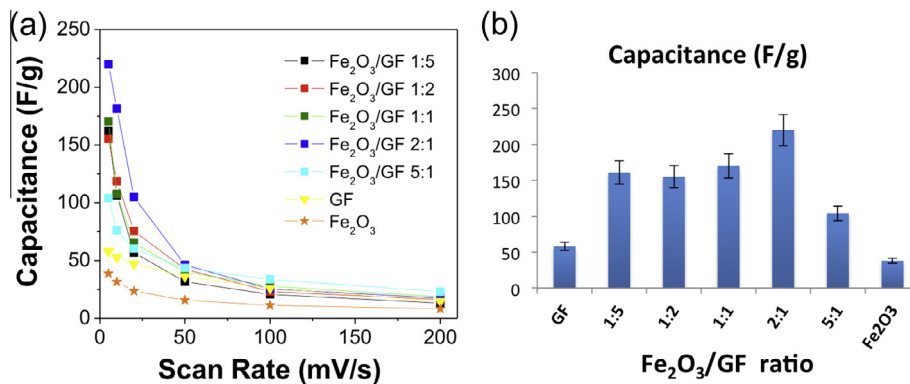


Fig. 8 – (a) Comparison of specific capacitance values from the different materials tested. (b) Specific capacitance values at the scan rate of 5 mV/s obtained for GF, Fe₂O₃ and for different composites with varying Fe₂O₃:GF ratio. (A color version of this figure can be viewed online.)

electrical double layer behavior at all sweeping rates. For comparison, simple GF/Ni and Fe₂O₃/Ni foams were prepared as control samples. The capacitor value of GF/Ni foam was 58 F g⁻¹ at 5 mV s⁻¹. After the decoration of iron oxide nanoparticles, the current response increased at least twice even at the lowest Fe₂O₃:EGO ratio tested (1:5). The highest capacitance was obtained with a Fe₂O₃:EGO ratio 2:1, demonstrating that the meso-porous structure of graphene and the nanostructured iron oxide nanoparticles interact well to ensure a low resistance and short-range diffusion pathways for ions. Conversely, bare Fe₂O₃/Ni foam samples showed low initial capacitance that dropped significantly at high scan rates.

An Fe₂O₃/EGO ratio of 2:1 exhibited the highest specific capacity of 220 F/g at a scan rate of 5 mV s⁻¹. Further increase of the iron oxide up to 5:1 (Fe₂O₃:GF) gave worse specific capacitances, possibly due to the poorly conducting upper layer of iron oxide (Fig. 8).

The Fe₂O₃/GF composite could be used in Li storage materials as the cathode without a Ni or Cu based current collector and without any polymer binder. The prepared foams were thus used directly as the working electrode (cathode) to

construct standard 2032 coin-cell batteries with the Li-foil as the counter electrode (anode) and poly(ethylene glycol) borate ester as polymer electrolyte [35].

When the graphene foam (GF) was coated with Fe₂O₃ at = 2:1 ratio, we typically observed two voltage plateaus during the first charge and discharge step (Fig. 9a). Li insertion into the Fe₂O₃ hematite nanostructure gave the voltage plateau at ~1.6 V during charging, while the stepwise reduction Fe³⁺ → Fe due to the lithiation process during the discharge stage gave the long plateau observed at ~0.8 V. This discharge plateau obtained with Fe₂O₃/GF is much higher than the voltage plateau of the cell made of GF (ca. 0.4 V), indicating that much more energy can be retained in the Fe₂O₃/GF composite. Use of Fe₂O₃/GF also improves the stability of the energy capacity in the cycling performance.

With the decoration of Fe₂O₃ nanoporous coatings, the initial discharge capacities can be enhanced from 508 to 701 mAh g⁻¹, a value comparable to commercially available batteries, and a higher energy capacity could be retained after the first discharge/charge cycle. The 3D graphene foam matrix worked as an efficient current collector to transfer sufficient electrons to the active metal oxide, without any

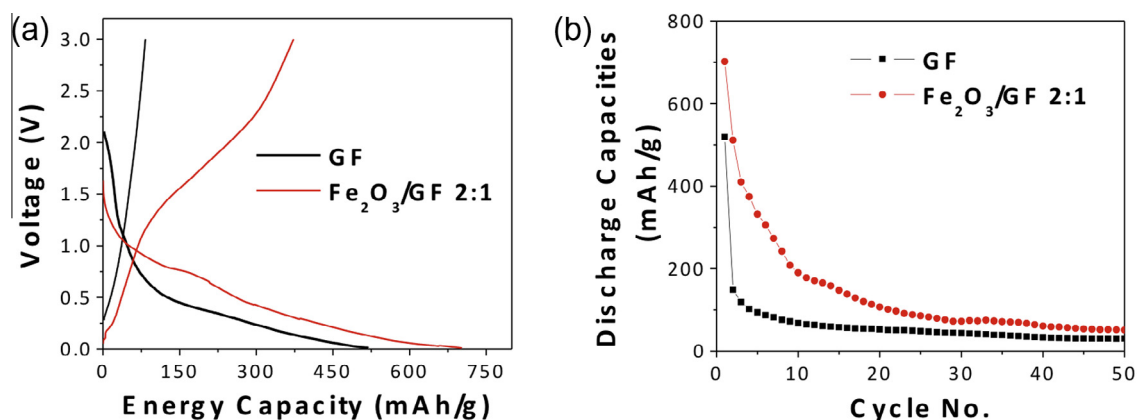


Fig. 9 – Electrochemical performance of GF and Fe₂O₃/GF 2:1 composite in coin-cell batteries, (a) first-cycle discharge (lithium insertion) and charge (lithium extraction) curves of the products. (b) Cycling performances of the products at the current density of 50 mA/g. (A color version of this figure can be viewed online.)

electrochemically non-active polymeric binder or conducting additives. Noteworthy, the cycling capability of the Fe_2O_3 :EGO electrodes was also significantly better than that of pure GF, even if a significant, irreversible capacity loss was observed after a few tens of cycles (Fig. 9b). This loss could be ascribed to the partial detachment of the Fe_2O_3 nanostructure during the lithiation and delithiation processes, and the formation of an electronically insulating solid electrolyte interface film on the Fe_2O_3 /GF surface during cycling [4,36]. SEM images comparing the quality of the coatings for all the different Fe_2O_3 :EGO ratios tested are available in Fig. S4. In all samples we observed the presence of a very rough and thick Fe_2O_3 layer, which tends to crack at large thicknesses. These materials should be further developed and optimized to improve the performance and cyclability; however, it should be noted that the approach described here has the additional benefit of using binder-free skeleton materials, differently from other commercial approaches.

4. Conclusions

In summary, we used a homemade setup to electrochemically exfoliate EGO sheets starting from graphite powders. The EGO sheets obtained in this way were highly soluble and processable, and could be processed together with an $\text{Fe}(\text{OH})_3$ precursor to produce monolithic, freestanding, electrically conductive three-dimensional (3D) networks. The $\text{Fe}(\text{OH})_3$ /EGO blend was then transformed by thermal annealing into Fe_2O_3 /RGO, which could be effectively used as an electrode in batteries. Preparation of Fe_2O_3 /RGO composites in this way helped to avoid traditional hydrothermal or solvothermal synthesis routes that usually require high pressures and long reaction times. Loading different amounts of the precursor solutions we could easily modulate the weight ratio between graphene foam and Fe_2O_3 , and thus maximize their performance when used in Lithium batteries. Combining nanoscale characterization with tests in commercial coin cells, the best results were obtained for an Fe_2O_3 :EGO ratio of 2:1, yielding a capacity of 701 mAh g^{-1} . Electron microscopy, X-ray diffraction and Raman spectroscopy of the Fe_2O_3 and EGO confirmed the 3D nano-crystalline structure of the network and the absence of contaminants coming from the metallic template or the exfoliation process. Overall, all the techniques described (exfoliation/filtration, infiltration, thermal treatments) are also suitable to produce samples larger than the $10 \times 20 \text{ mm}$ ones described herein, and thus may be easily up-scaled.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2014.12.007>.

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