

The role of graphene for electrochemical energy storage

Rinaldo Raccichini^{1,2,3}, Alberto Varzi^{2,3}, Stefano Passerini^{2,3*} and Bruno Scrosati^{2,4*}

Since its first isolation in 2004, graphene has become one of the hottest topics in the field of materials science, and its highly appealing properties have led to a plethora of scientific papers. Among the many affected areas of materials science, this 'graphene fever' has influenced particularly the world of electrochemical energy-storage devices. Despite widespread enthusiasm, it is not yet clear whether graphene could really lead to progress in the field. Here we discuss the most recent applications of graphene — both as an active material and as an inactive component — from lithium-ion batteries and electrochemical capacitors to emerging technologies such as metal-air and magnesium-ion batteries. By critically analysing state-of-the-art technologies, we aim to address the benefits and issues of graphene-based materials, as well as outline the most promising results and applications so far.

Graphene, a carbon monolayer packed into a 2D honeycomb lattice, was for a long time considered to be merely a building block for carbonaceous materials of other dimensionalities (that is, graphite, fullerenes and carbon nanotubes)¹. Initially labelled as an 'academic material', graphene was thought not to exist in a free state until 2004, when Novoselov and co-workers isolated a single-atom-thick layer of carbon². Since then, interest in graphene has grown continuously, giving rise to what might be called the 'graphene gold rush'¹. Recently, intense research efforts — motivated by graphene's many appealing properties — have been boosted by multimillion-dollar funding from both the European Union and China³. Despite its wide range of potential applications⁴ and very promising array of features⁵ with respect to other structurally different forms of carbon (Table 1)^{5,6}, it is not yet clear whether graphene has the potential to revolutionize many aspects of our lives. In recent years, a large number of publications have discussed the application of graphene in electrochemical energy-storage devices (EESDs). However, although such discussions always highlight the advantages of graphene, they often lack an objective analysis of its limitations and drawbacks. This leaves us with a number of key questions. Will the employment of graphene be limited to niche applications, or will next-generation batteries and capacitors be graphene-based? Graphene's properties vary strongly as a function of its production method. Hence, which typologies of graphene can be produced with today's available technologies? Could these significantly outperform state-of-the-art materials? Furthermore, which performance metrics are more relevant for predicting the potential use of graphene in EESDs? This Progress Article aims to address these open questions.

Properties and production methods

Graphene — a defect-free flat carbon monolayer — is the only basic member of a much larger family of 2D carbon forms. As carefully reviewed in a *Carbon* Editorial⁷, this 'graphene family' includes materials with very different properties in terms of morphology, lateral dimensions, number of layers and defects (Tables 2 and 3)^{1,7,8}. Among these characteristics, the presence of defects is the factor that primarily affects the quality of the end material⁸ and, consequently, its electrochemical features. The methods adopted for graphene production^{5,6,9}, the most common shown in Fig. 1, play a crucial role in determining the properties of the final product.

Owing to limited scalability and high production costs, methods such as mechanical exfoliation^{2,10}, synthesis on SiC^{5,10} and bottom-up synthesis from structurally defined organic precursors^{9,10} necessarily restrict the use of graphene to fundamental research and niche applications, such as touch screens and high-frequency transistors. Similarly, chemical vapour deposition of hydrocarbons⁵, although a well-established technique in industry, seems generally unsuitable for mass-production of graphene for electrochemical energy storage because of its high cost, moderate product purity and rather low yield¹⁰. Nevertheless, chemical vapour deposition has been reported as an efficient method for producing vertically oriented graphene nanosheet electrodes¹¹, although the packing density of the as-obtained graphene is very low¹². Beyond the aforementioned techniques, two methods are widely employed for the bulk production of graphene: liquid-phase exfoliation, and reduction of graphene oxide. In liquid-phase exfoliation, pristine or expanded graphite particles, obtained by thermal expansion of graphite intercalation compounds (usually known as 'expandable graphite'), are first dispersed in a solvent to reduce the strength of the van der Waals attraction between the graphene layers. Afterwards, an external driving force such as ultrasonication¹³, electric field¹⁴ or shearing¹⁵ is used to induce the exfoliation of graphite into high-quality graphene sheets^{5,13}. Unfortunately, the low yield of this process leaves a considerable amount of unexfoliated graphite, which must be removed¹⁵. Nevertheless, the high scalability and low cost of liquid-phase exfoliation¹³ make it suitable for producing graphene in bulk quantities¹⁶. In the second method, graphene oxide (GO), a highly defective form of graphene with a disrupted sp^2 -bonding network, is produced by strong oxidation of pristine graphite^{17,18} followed by stirring or ultrasonication in liquid media¹⁹. Graphene oxide must be reduced in order to restore the π network, which is the characteristic of conductive graphene²⁰. Chemical, thermal and electrochemical processes are commonly employed in this order to produce reduced graphene oxide (RGO)^{10,20,21}. Despite the low-to-medium quality of the obtained material due to the presence of both intrinsic defects (edges and deformations) and extrinsic defects (O- and H-containing groups), these methods allow the production of bulk quantities with high yield and contained costs. Although liquid-phase exfoliation and reduction of GO are the primary methods for producing commercially available graphene for EESDs, other

¹Institute of Physical Chemistry, University of Muenster, Corrensstrasse 28/30, D-48149 Muenster, Germany. ²Helmholtz Institute Ulm, Helmholtzstrasse 11, D-89081 Ulm, Germany. ³Karlsruhe Institute of Technology, PO Box 3640, D-76021 Karlsruhe, Germany. ⁴Istituto Italiano di Tecnologia, Graphene Labs and Nanochemistry Department, Via Morego 30, I-16163 Genova, Italy. *e-mail: stefano.passerini@kit.edu; bruno.scrosati@gmail.com

Table 1 | Graphene properties compared with other carbonaceous materials.

	Graphene	Carbon nanotube	Fullerene	Graphite
Dimensions	2	1	0	3
Hybridization	sp^2	Mostly sp^2	Mostly sp^2	sp^2
Hardness	Highest (for single layer)	High	High	High
Tenacity	Flexible, elastic	Flexible, elastic	Elastic	Flexible, non-elastic
Experimental SSA ($m^2 g^{-1}$)	~1,500	~1,300	80–90	~10–20
Electrical conductivity ($S cm^{-1}$)	~2,000	Structure-dependent	10^{-10}	Anisotropic: $2-3 \times 10^{4*}$, 6^{\dagger}
Thermal conductivity ($W m^{-1} K^{-1}$)	4,840–5,300	3,500	0.4	Anisotropic: 1,500–2,000*, 5–10 [†]

*a direction, †c direction.

Table 2 | Dimension-based graphene nomenclature.

Thickness (n , number of layers)	Lateral dimension D (nm)		Aspect ratio (length:width)		
	$2 \leq n \leq 10$	$D \leq 100$	$100 \leq D \leq 10^5$	≤ 10	> 10
Single-layer monolayer	Few-layer multilayer	Nano-	Micro-	-Sheet -Flake -Plate -Platelet	-Ribbon

Table 3 | Graphene's structural defect typologies.

Intrinsic (removal or introduction of carbon atoms in graphene's chemical composition)	Extrinsic (introduction of non-carbon atoms in graphene's chemical composition)
Vacancies	O, H and other foreign atoms
Edges	
Deformations	
Hybrid structures	

techniques are available (such as carbon nanotube unzipping²² or direct arc-discharge²³). However, owing to their higher costs, these techniques remain relatively marginal and thus unsuitable for bulk production.

In their review, Novoselov *et al.*⁵ perfectly summarized the current state of affairs: “Graphene will be of even greater interest for industrial applications when mass-produced graphene has the same outstanding performance as the best samples obtained in research laboratories.” As a matter of fact, the large-scale production of ‘outstanding performance’ graphene is the most ambitious challenge to address before its widespread application⁵. This aspect is particularly relevant with regard to the introduction of graphene in EESDs for powering millions of electric cars in the near future.

Over the past few years, many studies have explored graphene-based materials for electrochemical energy storage²⁴. In most of these, graphene was produced from graphite. As shown in Fig. 2, expandable graphite can be thermally expanded and subsequently exfoliated to obtain graphene. Pristine graphite can also be directly exfoliated to give graphene through liquid-phase methods or, alternatively, oxidized to obtain graphite oxide^{25,26}. The latter, after liquid-phase exfoliation, yields GO, which is then reduced to form RGO²⁰. This approach is different from other types of application as it is particularly useful for energy-storage materials. In fact, although oxidation introduces defects that cannot be entirely removed during the reduction process²⁰, this synthetic pathway facilitates the preparation of composites. In contrast with graphene (including RGO), GO can be easily dispersed in a wide range of solvents¹⁰. This peculiarity enables, through different chemical routes, the functionalization of GO with electroactive materials (such as conductive polymers and metal oxides) to form GO-based composites²⁷. These composites can be used as such, or alternatively can be further reduced to obtain RGO-composites²⁸.

Graphene-based materials have been proposed for use in all kinds of EESD, either as an active material or an inactive component.

Graphene as an active material

Graphene can be considered to be an active material when it takes part in an energy-storage mechanism. This can range from hosting ions (such as Li^+ or Na^+ in metal-ion batteries) to storing electrostatic charges on the electrode double-layer (as in electrochemical double-layer capacitors, EDLCs), or functioning as a catalyst in metal–air batteries.

Lithium-ion batteries. In lithium-ion batteries (LIBs), Li^+ ions continuously shuttle between a lithium-releasing cathode (commonly a layered lithium metal oxide) and a lithium-accepting anode (commonly graphite)²⁹. The amount of ions hosted per gram of material determines the capacity — and thus the energy — of the battery. Similar to graphite, graphene can be used as an anode for hosting Li^+ , both as such and as a carbonaceous matrix in composites with other materials also capable of storing lithium.

Graphene as an Li^+ host. As originally suggested by Dahn *et al.* in 1995, an anode comprising single layers of graphene can host two times as many Li^+ ions as conventional graphite^{30,31}. The storage of one lithium ion on each side of graphene results in a Li_2C_6 stoichiometry that provides a specific capacity of 744 mAh g^{-1} — twice that of graphite (372 mAh g^{-1})³⁰. This primeval concept of lithium hosting in graphene-like carbons was retrieved following the first isolation of graphene in 2004². Differently from graphite, in which lithium is intercalated between the stacked layers³², single-layer graphene can theoretically store Li^+ ions through an adsorption mechanism, both on its internal surfaces and in the empty nanopores that exist between the randomly arranged single layers (accordingly to the ‘house of cards’ model)^{30,31}. Similarly to other disordered carbons, such a process mainly takes place at low potentials ($<0.5 \text{ V}$ versus Li/Li^+). However, it differs from the characteristic staging behaviour of graphite because graphene provides electronically and geometrically non-equivalent sites³². As a result of this unique mechanism,

the amount of lithium stored by graphene-based anodes is more strongly dependent on the production method of both the material and the electrode.

In most reported studies, RGO is the material of choice for lithium-ion storage³³. During the first Li⁺ insertion, RGO exhibited incredibly high-capacity values of >2,000 mAh g⁻¹ (ref. 33), which is higher than the theoretical capacity of single-layer graphene. However, this amazing capacity is not fully released after de-insertion due to the massive irreversibility of the first lithiation step³³. This phenomenon, also observed for other Li-ion anode materials^{32,34}, can be attributed mainly to the irreversible reduction of the electrolyte to form a surface passivation layer on the active particles; namely, the 'solid electrolyte interphase'³². As shown in Fig. 3a, the solid electrolyte interphase strongly depends on the specific surface area (SSA) of the active material. Accordingly, the extremely high SSA of graphene, when compared with common graphite (Table 1), results in a very high initial irreversible capacity⁶ (Fig. 3b). In the following de-insertion cycle, graphene displays a high reversible capacity, although delivered mostly at potentials of 1–3 V versus Li/Li⁺, which is rather higher than typical graphite values (0–0.4 V versus Li/Li⁺). This leads to the occurrence of a large voltage hysteresis upon insertion and de-insertion of Li⁺ (Fig. 3b), which results in poor energy efficiency for cells employing such electrodes. Such a drawback, together with the large cathode quantities needed to supply the initial charge for the irreversible capacity, makes graphene-based cells unfeasible. The voltage hysteresis, also observed in several nanotube-shaped materials³⁵ and high-specific-charge carbons³², is caused, among other reasons, by Li storage on defects such as edges and/or oxygen- and hydrogen-containing surface groups^{32,36}. It is thus advisable to limit the number of such defects in graphene-based anodes, particularly because they are also responsible³⁶ for the low Coulombic efficiency in the first cycle. In addition, the progressive reduction of oxygen-containing groups (for example, in RGO) leads to graphene layer re-stacking, which lowers the storage capacity over repeated cycling³³. All of these aspects affect the value of the reversible capacity, which, after a few tens of cycles, is rarely comparable to that of commercially available graphites³³.

Graphene quality is therefore a crucial issue that must be addressed before the graphite in LIBs can be replaced. Even when graphene is finally available in large quantities at reasonable cost, graphite will probably still be the active material of choice for widespread hard-case batteries, unless we develop effective strategies to prevent initial lithium ion consumption and avoid graphene layer re-stacking. In this regard, pre-lithiation^{37,38}, controlled surface functionalization⁶ and the use of composites³⁹ might be promising strategies. At the same time, the development of flexible LIBs, which require lightweight and ultrathin active materials, could benefit from the use of graphene. However, even if different studies demonstrate graphene as a promising anode in flexible LIBs, the aforementioned drawbacks still represent major obstacles for practical applications⁴⁰.

Graphene-based composite anodes. Several composites have recently been developed in an effort to overcome the energy-storage limitations and poor cycling behaviour of bare graphene negative electrodes⁴. The addition of electroactive materials, such as metal (or metal oxide) nanoparticles, provides reversible alloying (with SnO₂ or Si nanoparticles), insertion (with TiO₂) or conversion (with Fe₂O₃ or Co₃O₄) reactions with lithium, thus allowing considerably higher storage capacities than those of bare graphene or graphite^{6,41}. During the composite preparation, graphene can act as a support for the growth of electroactive nanostructures that, in turn, hinder re-stacking by lowering the van der Waals forces among the layers. As a result, graphene-based composites are less affected by agglomeration during electrode preparation, as well as by capacity fading during cycling⁶. Moreover, the extensive and highly conductive carbon matrix established by graphene layers improves the electrical

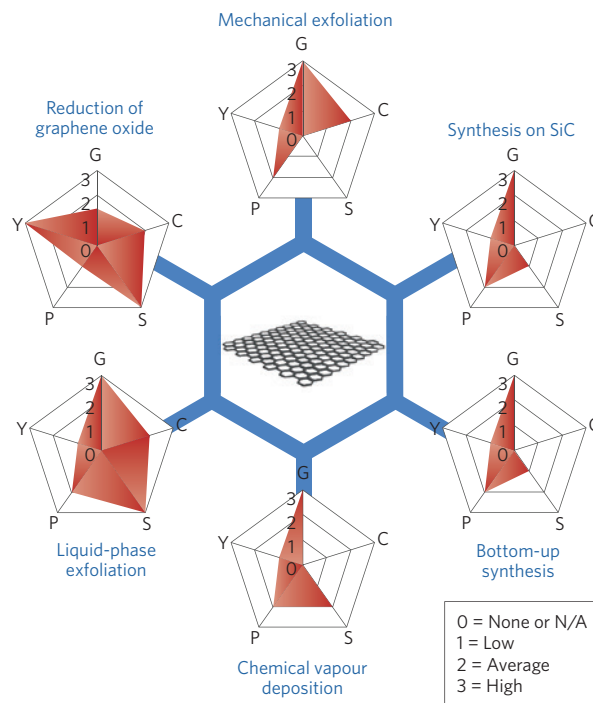


Figure 1 | Schematic of the most common graphene production methods.

Each method has been evaluated in terms of graphene quality (G), cost aspect (C; a low value corresponds to high cost of production), scalability (S), purity (P) and yield (Y) of the overall production process.

conductivity of the composite and buffers eventual volume changes taking place in electrodes based on alloying or conversion materials during cycling⁴². Despite these promising properties, however, graphene-based composites suffer, similarly to bare graphene, from the huge irreversible charge consumption of 30–50% during the first charge/discharge cycle^{6,43}. Results achieved so far with graphene composite anodes are very encouraging towards not only the development of high-energy LIBs, but also future applications such as wearable EESDs⁴⁰. Among the proposed composite graphene-based materials, some of the most promising in terms of reversible capacity are Co₃O₄/RGO (1,500 mAh g⁻¹)⁴⁴, silicon nanoparticles/RGO (1,150 mAh g⁻¹)⁴⁴, N- and S- co-doped RGO (900 mAh g⁻¹)⁴⁵ and SnO₂/RGO (700 mAh g⁻¹)⁴⁶. Nevertheless, the optimization of structural arrangement and weight ratio distribution between the composite components are still key issues that must be addressed to achieve good electrochemical performance and extended cycle life⁶.

Sodium-ion batteries. The development of sodium-ion batteries (SIBs), seen as a cheaper alternative to LIBs, is promoting extensive research to identify a suitable anode active material because, owing to their large ionic radius, Na⁺ ions do not intercalate into graphite⁴⁷ (Fig. 3c). In this regard, graphene seems to be a good candidate as an active anode in SIBs.

Graphene as an Na⁺ host. The use of RGO as an anode material in SIBs was first reported in 2013⁴⁸, where it showed promising electrochemical behaviour, good cycle life and excellent rate capability. Such remarkable performance is related to the presence of defects (for example, residual oxygen-containing groups), which increase the graphene interlayer distance (0.37 nm, compared with 0.34 nm in graphite). However, as observed in LIBs, the presence of defects represents a serious drawback in term of Coulombic efficiency for SIBs⁴⁸. Recently, Ding *et al.* reported the synthesis of different kinds of few-layer graphene (produced from biomass precursors) and their performance as anode materials in SIBs⁴⁹. Interestingly, the obtained

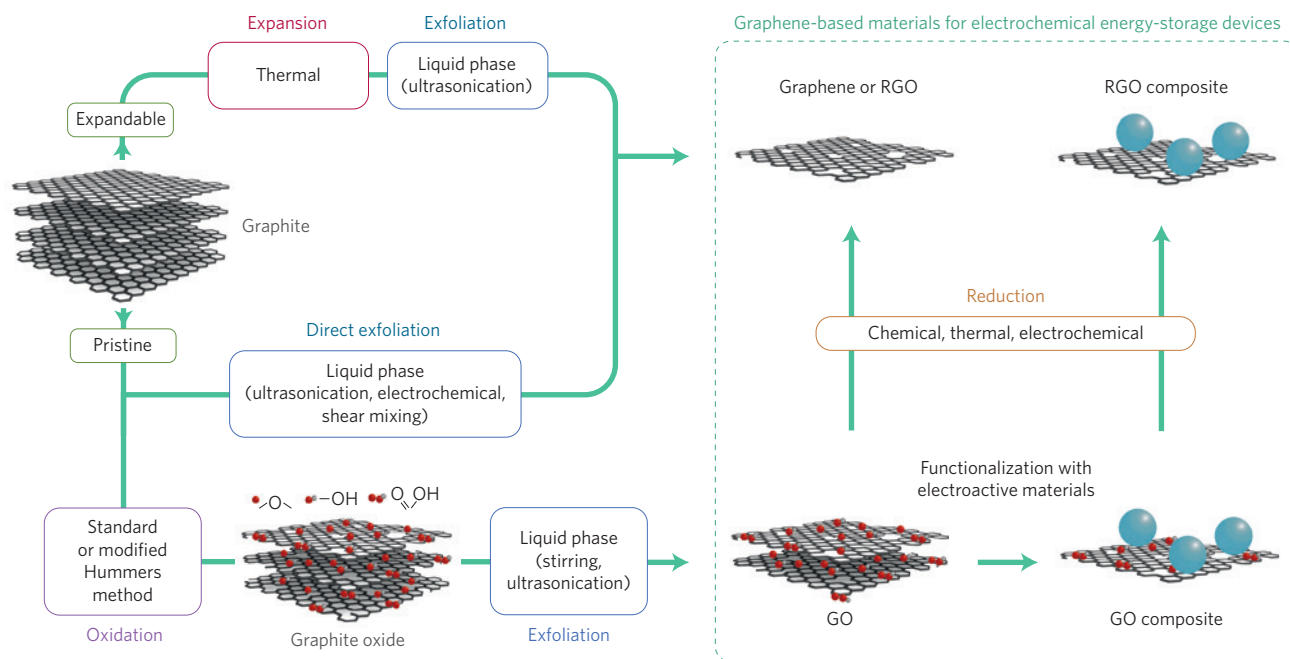


Figure 2 | The most common synthetic pathways for producing graphene-based materials (GO, RGO, GO- and RGO-based compounds) for use as electrode active materials in EESDs.

graphenes exhibited different Na^+ ion host mechanisms depending on the synthesis temperature (600–1,400 °C). Lower temperatures yielded average-quality graphenes with an Na^+ storage capacity similar to that of RGO. In contrast, higher temperatures enabled the formation of better quality graphene, with an interlayer spacing of 0.38 nm and promising insertion performance. Indeed, this report discloses one of the best-performing graphene-like materials for SIB anodes⁴⁹, showing up to 300 mAh g^{-1} specific capacity and good retention over 200 cycles, even though the Coulombic efficiency for the first cycle remains poor. Such results give hope for the successful employment of graphene in SIBs, insofar as it can compete with other recently developed anode materials⁵⁰. Additionally, the lower insertion potential of graphene-based anodes makes it more advantageous in terms of specific energy^{49,50}.

Similarly to LIBs, graphene-based composites enable SIBs with higher specific capacity, better rate capability and longer cycle life than bare graphene^{51–55}.

Electrochemical capacitors. Electrochemical capacitors (also called supercapacitors) exploit fast charge-storage mechanisms to enable considerably higher power densities than those available in LIBs or SIBs. Electrochemical capacitors can be subdivided into two classes: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, the energy is physically stored through the adsorption of ions on the surface of the electrodes, whereas in pseudocapacitors, electrochemical energy storage is enabled by fast redox reactions occurring between the electrode active material and the electrolyte⁵⁶.

Electrochemical double-layer capacitors. In EDLCs, the electrode's active materials are electrochemically stable, do not undergo any Faradaic processes and, above all, possess large SSAs⁵⁶. The amount of charge stored per unit mass (F g^{-1}), volume (F cm^{-3}) or area (F cm^{-2}) is indeed directly proportional to the surface available for the formation of the double layer (that is, the area in contact with the electrolyte)⁵⁷. In principle, graphene, with its theoretical SSA of 2,675 $\text{m}^2 \text{g}^{-1}$ (ref. 8) and capacitance of 550 F g^{-1} (ref. 58), would be a perfect candidate for boosting the energy density of such devices⁵⁹. However, this does not seem to be the case in practice, as the difficulty of even approaching the theoretical SSA of graphene (for instance,

average values for RGO are in the range of 300–1,000 $\text{m}^2 \text{g}^{-1}$)⁴³ results in a lower practical gravimetric capacitance (100–270 F g^{-1} and 70–120 F g^{-1} with aqueous and organic electrolytes, respectively)^{43,58}. Additionally, spontaneous graphene layer re-stacking, which occurs during both electrode manufacturing and cycling, strongly reduces the practical surface available for charge storage (Fig. 3d,e). Different approaches have been introduced to mitigate these detrimental effects. As reported by Ruoff *et al.*, RGO can be chemically activated to create an extended 3D meso- and microporous network (with an SSA of up to 3,100 $\text{m}^2 \text{g}^{-1}$) of highly curved graphene walls that prevent re-stacking during cycling. Such 'activated graphene' enables high gravimetric capacitances with both organic (166 F g^{-1}) and ionic liquid electrolytes (200 F g^{-1})⁶⁰ and, moreover, operates across a wide temperature range of -50 °C to 80 °C⁶¹. Alternatively, graphene layer re-stacking can be minimized by optimizing the electrode-manufacturing process. In this regard, RGO sheets could be vertically aligned with respect to the current collector plane, thus granting better ion accessibility and enabling higher packing density. Moreover, high and reversible volumetric (171 F cm^{-3}) and areal (1.83 F cm^{-2}) capacitances in aqueous electrolyte could be obtained¹².

In summary, although activated graphene and vertically aligned RGO show promising performance, the large majority of graphene-like materials cannot yet compete with the cheaper and well-established activated carbons⁶². The majority of the results reported for graphene-based supercapacitors were obtained with very low density electrode materials (for example, aerogels and foams), which possess a large number of void spaces (macropores). These pores are filled by the electrolyte, thus increasing both the weight and volume of the final device to a point where they are unsuitable for use in EDLCs^{58,63}. In contrast, graphene would probably fit in the approaching era of small-scale supercapacitors required to power the next generation of wearable- and micro-electronic devices⁶⁴.

Pseudocapacitors. In pseudocapacitors, the presence in the active material of electroactive species such as oxygen-containing functional groups, conducting polymers or transition metal oxides enables higher energy densities with respect to EDLCs^{58,59}. Nevertheless, pseudocapacitors are inferior to EDLCs in terms of power density (limited by the poor electrical conductivity of the active materials)

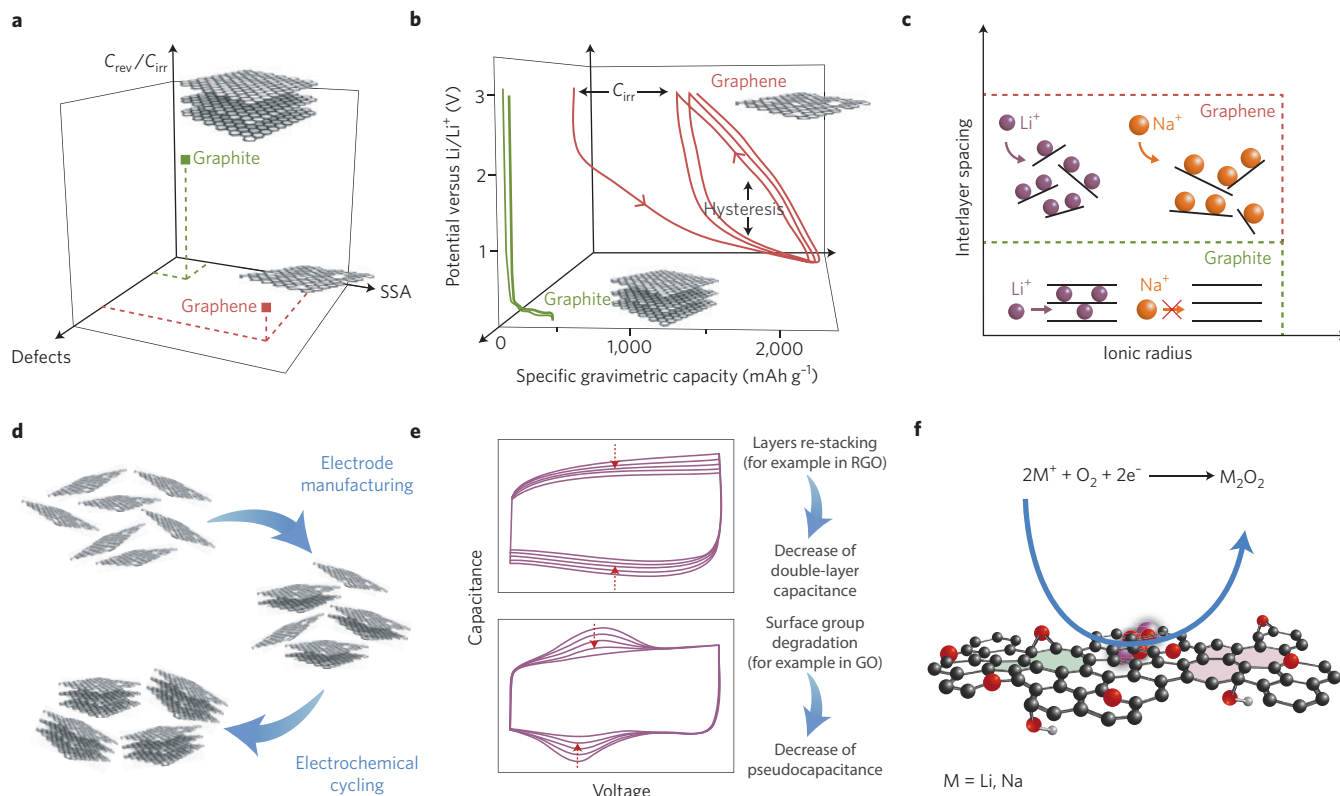


Figure 3 | Features and limitations of graphene as an active material in different EESDs. **a**, Graphite and graphene in LIB anodes. Correlation of characteristics in terms of defect amount, SSA and ratio between reversible (C_{rev}) and irreversible (C_{irr}) capacity during the first charge/discharge cycle. **b**, Typical voltage profiles of graphite and graphene (RGO) during constant current Li^+ insertion/de-insertion. **c**, Li^+ and Na^+ insertion mechanisms in graphene and graphite. **d**, Layers re-stacking in graphene during electrode manufacturing and electrochemical cycling. Re-stacking is a serious issue that affects the performances of all graphene-based EESDs. **e**, Generic voltammetric behaviour of graphene-based electrochemical capacitors over prolonged cycling. Top: Effect of graphene layers re-stacking (such as in RGO) on the double-layer capacitance. Bottom: Effect of surface group degradation (such as in GO) on pseudocapacitance. **f**, Catalytic effect of graphene defects (vacancies, deformations and presence of surface groups) in metal-air batteries.

and cycle life⁶². In this regard, graphene-based electrodes could be viable candidates for improving the performance of pseudocapacitors⁶². Despite its lower electrical conductivity, GO, owing to its large number of oxygen-containing groups, has a higher pseudocapacitance than RGO⁶⁵. However, as previously discussed, these groups may negatively affect the electrochemical behaviour of the electrode by reducing the cycling stability and reversibility^{62,65} (Fig. 3e). Various graphene-conducting polymer and graphene-metal-oxide composites have also been developed and investigated for use as pseudocapacitors^{6,62}. In these composites, graphene provides a support matrix for the growth of the electroactive species at the nanoscale, which results in a larger SSA and thus enhances the electrochemical performance by increasing electrical conductivity and mechanical stability^{62,66}.

It seems the key to exploiting the full potential of graphene in pseudocapacitors relies on the development of composite materials that offer the synergistic effect of the graphene substrate and the electroactive component, along with an optimized spatial orientation of the graphene sheets^{12,39,66}.

Lithium-air batteries. The growing demand for energy has led to the development of new EESDs with higher energy densities than metal-ion batteries. In this regard, the lithium-air battery (LAB), which offers a theoretical energy density of $5,200 \text{ Wh kg}^{-1}$ (ref. 67), represents one of the best candidates. Although lithium-air chemistry was introduced in 1976, the rechargeability of this system was brought to the attention of the scientific community only in 2006 by Bruce and colleagues⁶⁸. Although different LABs may employ

different typologies of electrolyte, they are generally composed of metallic lithium and oxygen (or air) as, respectively, the anode and cathode. The rechargeability of the system relies on the conversion of reduction products (LiO_2 and, mainly, Li_2O_2) formed during discharge (oxygen-reduction reaction), back to the original reagents during charge (oxygen-evolution reaction)³⁹. Unfortunately, the entire system suffers from a low energy efficiency, short lifetime and low rate capability (discharge capacity of 400 mAh g^{-1} after 50 cycles at a specific current of 100 mA g^{-1})^{68–70}. Reports indicate a maximum of only 100 capacity-limited ($1,000 \text{ mAh g}^{-1}$) cycles⁷¹. Among the various factors that influence the performance of LABs, the morphology of the air electrode (cathode) is particularly important for obtaining high discharge capacity. In fact, the SSA and porosity of the air electrode determine the morphology and amount of discharge products. It was demonstrated that RGO, with its large SSA, could deliver higher capacities than other carbon substrates (for example, $8,700 \text{ mAh g}^{-1}$ with respect to $1,000–2,000 \text{ mAh g}^{-1}$ in the first cycle). Defects and functional groups can also play a catalytic role for the formation of discharge products⁶⁹ (Fig. 3f). So far, the use of RGO as a bare material or substrate for other catalyst⁷² in LAB cathodes has improved performance, although achieving the theoretical energy density is still far away. Different aspects are still unclear and further studies are needed to demonstrate an effective role of graphene in LABs. Further investigations of graphene with stable electrolytes are needed before we can assess its effective role in such batteries⁶⁹.

Sodium-air batteries. Over the past five years, sodium-air batteries (SABs), despite having an energy density half that of LABs,

have been increasingly proposed owing to their low production cost and the availability of the required raw materials⁷³. In contrast with lithium, sodium is capable of reversibly forming during discharge a stable superoxide (NaO_2) with low overpotentials⁷³. This enables SABs to cycle with a charge efficiency of 80–90% after the first cycle. The formation of peroxide (Na_2O_2), however, is kinetically hindered as it requires a suitable catalyst. RGO has demonstrated, under dry air conditions, remarkable catalytic properties towards the formation of Na_2O_2 (ref. 74), which are not exhibited by conventional carbon. As reported by Liu *et al.*⁷⁴, the micro- and nanostructures of the graphene air electrode enable one of the highest specific discharge capacities for SABs. These results suggest that RGO can efficiently function as a catalyst for both oxygen-reduction and oxygen-evolution reactions. Nitrogen-doped RGO nanosheets have also been investigated in this respect. The defective sites introduced by nitrogen doping enable a more uniform and smaller size distribution of the discharge products and, therefore, a higher specific discharge capacity with respect to the undoped graphene⁷⁵. Even though this technology is in the very early stages of development, the few reports available in this field depict a quite promising scenario for graphene in SABs.

Graphene as an inactive component

Graphene could play an important role in EESDs, even without being actively involved in the electrochemical reaction. Owing to its impressive electrical conductivity (Table 1), graphene was proposed as a conductive agent in metal-ion battery electrodes as well as an encapsulating carbon matrix in, for example, lithium–sulphur batteries. Besides enabling efficient electron transport, its superior thermal conductivity (Table 1) may be advantageous for dissipating the heat generated in the case of high current loads or/and abuse conditions⁵. This would result in devices with improved intrinsic safety. The variety of structures reported can be classified into six different models (Fig. 4a)⁶.

Lithium-ion batteries. LiCoO_2 , LiMn_2O_4 and LiFePO_4 (hereafter referred to as LMO) are some of the most commonly used cathode materials in LIBs. The cycle life and rate capability of these materials are generally limited by their poor electrical conductivity. Introducing low-cost conductive additives (for example, carbon black) into the composite electrodes commonly solves this issue. Nevertheless, owing to their amorphous structure, carbon blacks possess a rather low electrical conductivity, with respect to more crystalline carbons such as graphene^{5,76}.

Recently, Kucinskis *et al.*⁷⁶ reviewed state-of-the-art graphene-based composite cathode materials. Among the vast number of reports, most employ GO as a source for the formation of graphene conductive networks. Additionally, in a large part of these works, GO is reduced to RGO simultaneously with the LMO precursors (one-pot synthesis) to produce graphene-based composites. This approach, which is different from simply mixing the carbon additive with the LMO active material during electrode preparation, promotes the formation of small-size LMO particles (leading to improved Li^+ diffusion) directly onto the RGO matrix⁷⁶. Moreover, the RGO 3D network is reportedly capable of preventing the dissolution of some LMOs³⁹, thus extending the cycle life of the batteries. However, it was also suggested that when RGO is mixed in a manner similar to conventional carbon additives during electrode preparation, it could negatively affect the Li^+ mobility, thus worsening the electrochemical performance of the composite cathode⁷⁶ (Fig. 4b). Regardless of this fact, RGO is generally reported to enhance the rate capability of the cathode with respect to conventional carbon additives. Depending on the active material, improvements of up to 160% of the discharge capacity (at the same current rate) have been observed⁷⁶. Nevertheless, it is not yet clear whether RGO may replace carbon blacks, which are much cheaper and easier to handle⁷⁶.

Sodium-ion batteries. As explained previously for the negative electrode, the larger size of Na^+ with respect to Li^+ restricts the choice of available cathode material for SIBs⁴⁷. Several layered oxides with promising electrochemical performance have recently been developed⁵⁰. However, like their LIB analogues, they usually possess poor electrical conductivity and thus limited rate capability. So far, only a few reports are available on graphene-containing composite cathodes for SIBs^{77–80}. However, in all cases, the RGO matrix seems to enhance the electrical conductivity of the composite, thus improving the rate capability compared with bare cathode materials^{77–80}.

Lithium–sulphur batteries. Lithium–sulphur batteries (LSBs), through the redox reaction of metallic lithium (anode) and elemental sulphur (cathode), could provide a remarkably high theoretical specific energy of up to 2,600 Wh kg^{-1} (ref. 39). Despite the intrinsic advantages of sulphur in terms of low cost, abundance, low toxicity and high theoretical specific capacity (1,672 mAh g^{-1}), LSBs are affected by several drawbacks: (1) slow kinetics owing to the low electrical conductivity of the redox reaction products; (2) low energy efficiency; (3) poor cycle life as a direct result of the dissolution of the intermediate reaction products (polysulphides) in the electrolyte; and (4) large volume changes during the electrochemical reaction⁶⁹. Graphene has been proposed as a good candidate to address these issues because of its high electrical conductivity and capability of trapping the charge/discharge products³⁹. Several studies have reported that RGO and GO are suitable substrates for the deposition of sulphur micro- and nanoparticles^{39,69}. Good encapsulation seems to be achieved in both cases; however, the presence of epoxy and hydroxyl groups in GO promotes the immobilization of sulphur and thus prevents its dissolution³⁹. Promising performance — with specific capacities $>1,000$ mAh g^{-1} — has also been obtained with hybrid graphene–polymer–sulphur composites, although an acceptable capacity retention during cycling has not yet been achieved⁴¹. Recently, different graphene–sulphur composites have been synthesized and tested in LSBs^{81–83}. They exhibit a good performance in terms of capacity, Coulombic efficiency and stability during cycling^{81–84}, even if the values reported are not higher than those obtained with other carbon-encapsulated sulphur cathodes, such as ordered mesoporous carbon⁸⁴.

From these results, graphene might be a possible candidate for encapsulating sulphur on LSB cathodes. However, real advances in the field require improvements to the sulphur/graphene interface in order to achieve stable electrochemical performance³⁹.

Developing applications of graphene

The recent outbreak of graphene in the field of electrochemical energy storage has spurred research into its applications in novel systems such as magnesium-ion batteries (MIBs), which is one of the newest members of the metal-ion battery family. MIBs have been proposed as a high-energy-density and environmentally friendly replacement for LIBs⁸⁵. Although research in this field is still at an early stage, a few graphene-based composites have recently been proposed as MIB cathode materials^{86,87}. Although the results obtained so far show very poor electrochemical behaviour, they could represent the first attempts to use graphene in MIBs. Interestingly, Wang *et al.* have already patented a rechargeable magnesium-ion cell based on graphene active materials⁸⁸.

The employment of graphene has also been considered for the improvement of vanadium redox-flow batteries (VRFBs). Patented in 1986⁸⁹, VRFBs enable energy storage using $\text{V}^{3+}/\text{V}^{2+}$ and $[\text{VO}_2^+]/[\text{VO}_2^+]$ redox couples as negative and positive acid electrolytic solutions, respectively⁹⁰. Carbon-based materials, such as cloths or graphite felts, are used as electrodes because of their electrochemical stability and wide operating potential⁹¹. Unfortunately, despite their high SSAs, these electrodes do not exhibit satisfactory electrochemical properties⁹². Accordingly, the use of graphene-based materials has

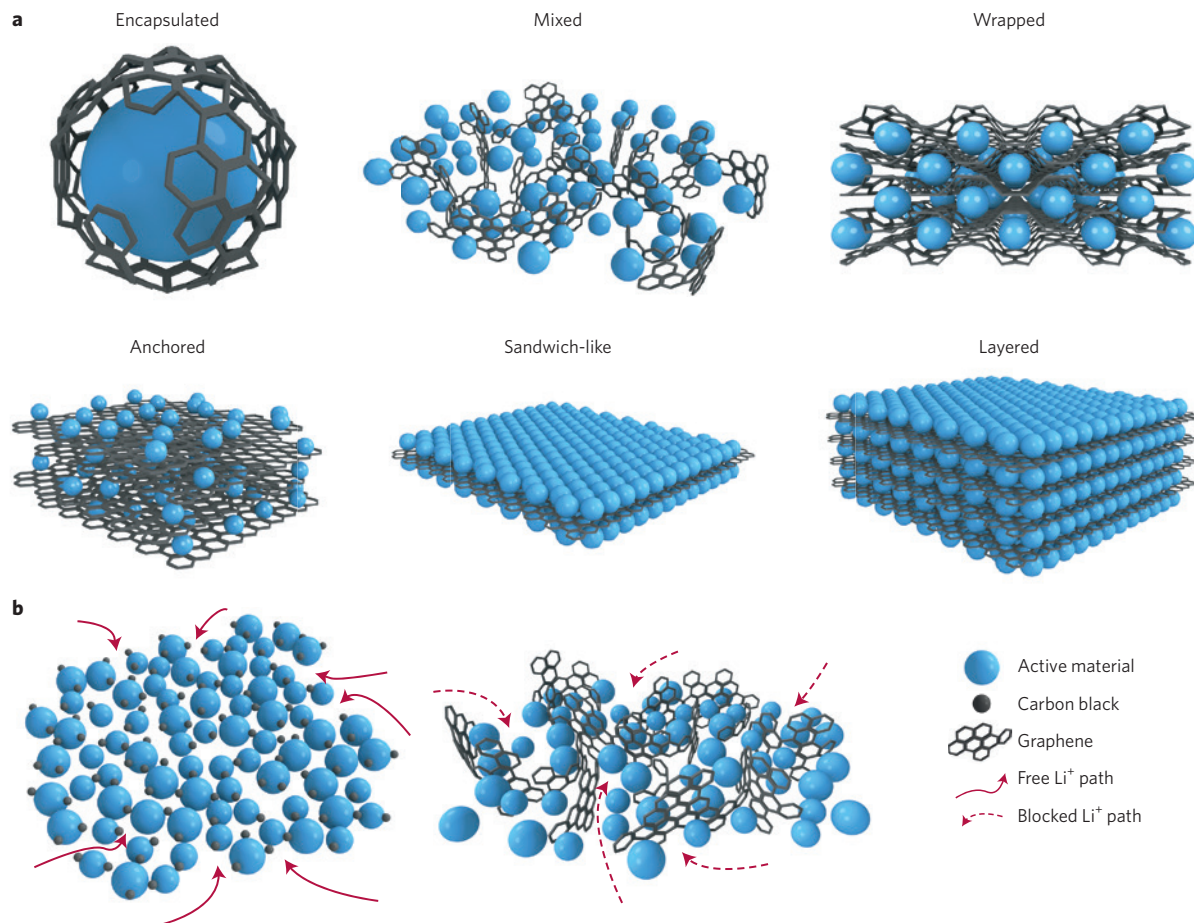


Figure 4 | Structural models and a possible drawback of graphene composites. **a**, Schematic of the different structures of graphene composite electrode materials. All models (except where specifically indicated) refer to composites in which graphene and the active material are synthesized through one-pot processes. Encapsulated: Single active-material particles are encapsulated by graphene, which acts as either an active (for example, LIB anodes) or an inactive (for example, LIB cathodes) component. Mixed: Graphene and active materials are synthesized separately and mixed mechanically during the electrode preparation. In this structure, graphene may serve as an inactive conductive matrix (for example, LIB cathodes) or an active material (for example, LIB anodes). Wrapped: The active-material particles are wrapped by multiple graphene sheets. This structure well-represents pseudocapacitor electrodes, in which graphene is the active material, as well as metal-ion battery cathodes, where graphene is an inactive component. Anchored: This is the most common structure for graphene composites, in which electroactive nanoparticles are anchored to the graphene surface. This structure is very relevant for metal-ion battery anodes and pseudocapacitors, where graphene serves as an active material, as well as for metal-ion battery cathodes and in LSBs, where graphene acts as an inactive component. Sandwich-like model: Graphene is used as a template to generate active material/graphene sandwich structures. This graphene-composite model, although not widespread, is used for LIB cathodes. Layered model: Active-material nanoparticles are alternated with graphene sheets to form a composite layered structure, which has been proposed for use in metal-ion battery anodes and cathodes. **b**, Li^+ paths in carbon black- (left) and graphene- (right) based electrodes in the mixed structural model. The figure highlights a possible drawback of graphene in terms of Li^+ mobility.

been proposed to improve electrical conductivity, kinetic reversibility and electrochemical activity of these electrodes^{91,92}. Over the past few years, a small number of studies have investigated the electrochemical properties of GO-based⁹¹, RGO^{90,92} and RGO-based composites^{93–95} for application in VRFBs. All of these reports show promising electrochemical performance for graphene-supported carbon electrodes, specifically in terms of high peak current density, reduced overpotential and decreased charge-transfer resistance. Additionally, GO⁹⁶ and commercial graphene⁹⁷ have recently been tested as additives in VRFB ion-exchange membranes, with the aim of reducing the vanadium permeation and preventing ionic cross-mixing. The results achieved so far seem promising when compared with those obtained with bare membranes. However, the development of a successful commercial VRFB containing graphene is still far away.

Conclusions

It has been ten years since the beginning of the graphene era, and the rush to find new applications for this exciting material is more

vibrant than ever. However, despite the enormous amount of data produced throughout research laboratories across the globe, it is still not clear whether graphene has the potential to revolutionize many aspects of our lives. This is particularly appropriate for the field of electrochemical energy storage, in which ‘graphene fever’ has reached rather high levels due to the continuous need for new materials that can meet the market’s performance requirements.

Graphene promises to increase substantially the energy- and power-density of practical systems, as well as enable the development of next-generation devices. However, the results so far tend to suggest that real breakthroughs are still to come. As was the case for many other innovative materials in the past, the main task is to close the gap between laboratory-scale research and practical applications. The first challenge lies in the production of graphene. Owing to its peculiar nature, the electrochemical properties of this material are strictly dependent on its method of production, and so are its chances of finding an application in EESDs. Nowadays, the vast majority of graphene-based materials are produced by the reduction

of GO to RGO. This method is relatively cheap and has the potential for scalability — mandatory properties for widespread adoption — but introduces both intrinsic and extrinsic defects, which strongly affect electrochemical properties. Although for some applications the defects function as catalyst sites to improve cell kinetics (for example, in lithium–air and sodium–air batteries), in other cases they strongly reduce the performance. For example, RGO cannot compete with the widespread carbonaceous materials commonly employed in commercial LIBs. In fact, despite their very promising initial performance, RGO electrodes show a limited cycle life⁹⁸ compared with well-established graphite electrodes. With respect to EDLCs, the limited cycle life and low density of RGO-based electrodes prevents their transition to the commercial stage. However, some strategies for improving the packing density of graphene-based materials have been proposed. Nevertheless, the macroporous nature of graphene, in general, seriously affects its volumetric energy density. In this case, the common practice of evaluating EDLC performance through gravimetric data might lead to misleading conclusions. Because low-density and few-micrometre-thick electrodes are often reported, volumetric data are surely more appropriate⁶³.

In view of the funding and human resources devoted worldwide to this unique material, we may expect to see a turnover in the not-too-distant future. Some important results support this vision. In fact, a growing body of research into graphene-based full LIBs^{37,38,99,100} is continuing to prove the benefits of graphene for this important application. In addition, it has been demonstrated that graphene (or RGO) may find its true role when employed in composite electrodes. Here, graphene layers and electroactive particles work symbiotically, with the former providing a stiff and conductive matrix, which can buffer eventual volume changes, and the latter helping to avoid layer re-stacking. Graphene-based composites have, in fact, shown outstanding performance in LIBs^{44–46}, SIBs^{51–55}, pseudocapacitors^{58,59,62,66} and LSB^{81–83}. Moreover, a few preliminary studies into full SIBs^{51,55} have confirmed graphene exploitation in the ‘beyond lithium’ battery generation. Nevertheless, the most crucial point is the nano-architecture of the composite. Indeed, if proper nanoscale engineering is achieved, such compounds will surely play a crucial role in the progress of the field.

Winning the graphene ‘gold rush’ requires consistent investment and commitment from industry and research-funding institutions. In this scenario, research scientists are those who occupy the most prominent position, by highlighting the benefits and, most importantly, addressing the issues that still hinder the large-scale application of graphene in EESDs.

Received 4 March 2014; accepted 7 November 2014; published online 22 December 2014

References

- Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nature Mater.* **6**, 183–191 (2007).
- Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
- Graphene Flagship; <http://graphene-flagship.eu/>.
- Singh, V. *et al.* Graphene based materials: Past, present and future. *Prog. Mater. Sci.* **56**, 1178–1271 (2011).
- Novoselov, K. S. *et al.* A roadmap for graphene. *Nature* **490**, 192–200 (2012).
- Wu, Z.-S. *et al.* Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy* **1**, 107–131 (2012).
- Bianco, A. *et al.* All in the graphene family – A recommended nomenclature for two-dimensional carbon materials. *Carbon* **65**, 1–6 (2013).
- Ivanovskii, A. L. Graphene-based and graphene-like materials. *Russ. Chem. Rev.* **81**, 571–605 (2012).
- Sivudu, K. S. & Mahajan, Y. R. Challenges and opportunities for the mass production of high quality graphene: An analysis of worldwide patents. *Nanotech Insights* **3**, 6–18 (2012).
- Warner, J. H., Schäffel, F., Bachmatiuk, A. & Rummeli, M. H. *Graphene: Fundamentals and Emergent Applications* Ch. 4 (Elsevier, 2013).
- Miller, J. R., Outlaw, R. A. & Holloway, B. C. Graphene double-layer capacitor with ac line-filtering performance. *Science* **329**, 1637–1639 (2010).
- Yoon, Y. *et al.* Vertical alignments of graphene sheets spatially and densely piled for fast ion diffusion in compact supercapacitors. *ACS Nano* **8**, 4580–4590 (2014).
- Cai, M., Thorpe, D., Adamson, D. H. & Schniepp, H. C. Methods of graphite exfoliation. *J. Mater. Chem.* **22**, 24992–25002 (2012).
- Wei, D. *et al.* Graphene from electrochemical exfoliation and its direct applications in enhanced energy storage devices. *Chem. Commun.* **48**, 1239–1241 (2012).
- Paton, K. R. *et al.* Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nature Mater.* **13**, 624–630 (2014).
- Tour, J. M. Layered materials: Scaling up exfoliation. *Nature Mater.* **13**, 545–546 (2014).
- Hummers, W. S. Jr & Offeman, R. E. Preparation of graphitic oxide. *J. Am. Chem. Soc.* **80**, 1339 (1957).
- Kovtyukhova, N. I. *et al.* Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem. Mater.* **11**, 771–778 (1999).
- Li, D., Müller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. *Nature Nanotech.* **3**, 101–105 (2008).
- Dreyer, D. R., Park, S., Bielawski, C. W. & Ruoff, R. S. The chemistry of graphene oxide. *Chem. Soc. Rev.* **39**, 228–240 (2010).
- Park, S. & Ruoff, R. S. Chemical methods for the production of graphenes. *Nature Nanotech.* **4**, 217–224 (2009).
- Kosynkin, D. V. *et al.* Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature* **458**, 872–876 (2009).
- Wu, Y. *et al.* Efficient and large-scale synthesis of few-layered graphene using an arc-discharge method and conductivity studies of the resulting films. *Nano Res.* **3**, 661–669 (2010).
- Hou, J., Shao, Y., Ellis, M. W., Moore, R. B. & Yi, B. Graphene-based electrochemical energy conversion and storage: Fuel cells, supercapacitors and lithium ion batteries. *Phys. Chem. Chem. Phys.* **13**, 15384–15402 (2011).
- Hirata, M., Gotou, T., Horiuchi, S., Fujiwara, M. & Ohba, M. Thin-film particles of graphite oxide 1: high-yield synthesis and flexibility of the particles. *Carbon* **42**, 2929–2937 (2004).
- Gao, W., Alemany, L. B., Ci, L. & Ajayan, P. M. New insights into the structure and reduction of graphite oxide. *Nature Chem.* **1**, 403–408 (2009).
- Compton, O. C. & Nguyen, S. T. Graphene oxide, highly reduced graphene oxide, and graphene: Versatile building blocks for carbon-based materials. *Small* **6**, 711–723 (2010).
- Stankovich, S. *et al.* Graphene-based composite materials. *Nature* **442**, 282–286 (2006).
- Scrosati, B. & Garche, J. Lithium batteries: status, prospects and future. *J. Power Sources* **195**, 2419–2430 (2010).
- Dahn, J. R., Zheng, T., Liu, Y. & Xue, J. S. Mechanisms for lithium insertion in carbonaceous materials. *Science* **270**, 590–593 (1995).
- Liu, Y., Xue, J. S., Zheng, T. & Dahn, J. R. Mechanism of lithium insertion in hard carbons prepared by pyrolysis of epoxy resins. *Carbon* **34**, 193–200 (1996).
- Winter, M., Besenhard, J. O., Spahr, M. E. & Novák, P. Insertion electrode materials for rechargeable lithium batteries. *Adv. Mater.* **10**, 725–763 (1998).
- Vargas, C. O. A., Caballero, Á. & Morales, J. Can the performance of graphene nanosheets for lithium storage in Li-ion batteries be predicted? *Nanoscale* **4**, 2083–2092 (2012).
- Zhang, W.-J. A review of the electrochemical performance of alloy anodes for lithium-ion batteries. *J. Power Sources* **196**, 13–24 (2011).
- Landi, B. J., Ganter, M. J., Cress, C. D., DiLeo, R. A. & Raffaele, R. P. Carbon nanotubes for lithium ion batteries. *Energ. Environ. Sci.* **2**, 638–654 (2009).
- Xiang, H. F. *et al.* Graphene sheets as anode materials for Li-ion batteries: Preparation, structure, electrochemical properties and mechanism for lithium storage. *RSC Adv.* **2**, 6792–6799 (2012).
- Vargas, O., Caballero, Á. & Morales, J. Enhanced electrochemical performance of maghemite/graphene nanosheets composite as electrode in half and full Li-ion cells. *Electrochim. Acta* **130**, 551–558 (2014).
- Hassoun, J. *et al.* An advanced lithium-ion battery based on a graphene anode and a lithium iron phosphate cathode. *Nano Lett.* **14**, 4901–4906 (2014).
- Zhu, J., Yang, D., Yin, Z., Yan, Q. & Zhang, H. Graphene and graphene-based materials for energy storage applications. *Small* **10**, 3480–3498 (2014).
- Zhou, G., Li, F. & Cheng, H.-M. Progress in flexible lithium batteries and future prospects. *Energ. Environ. Sci.* **7**, 1307–1338 (2014).
- Xu, C. *et al.* Graphene-based electrodes for electrochemical energy storage. *Energ. Environ. Sci.* **6**, 1388–1414 (2013).
- Huang, X., Zeng, Z., Fan, Z., Liu, J. & Zhang, H. Graphene-based electrodes. *Adv. Mater.* **24**, 5979–6004 (2012).
- Sun, Y., Wu, Q. & Shi, G. Graphene based new energy materials. *Energ. Environ. Sci.* **4**, 1113–1132 (2011).
- Lee, W. W. & Lee, J.-M. Novel synthesis of high performance anode materials for lithium-ion batteries (LIBs). *J. Mater. Chem. A* **2**, 1589–1626 (2014).

45. Ai, W. *et al.* Nitrogen and sulfur codoped graphene: Multifunctional electrode materials for high-performance Li-ion batteries and oxygen reduction reaction. *Adv. Mater.* **26**, 6186–6192 (2014).
46. Chen, J. S. & Lou, X. W. D. SnO₂-based nanomaterials: Synthesis and application in lithium-ion batteries. *Small* **9**, 1877–1893 (2013).
47. Cao, Y. *et al.* Sodium ion insertion in hollow carbon nanowires for battery applications. *Nano Lett.* **12**, 3783–3787 (2012).
48. Wang, Y.-X., Chou, S.-L., Liu, H.-K. & Dou, S.-X. Reduced graphene oxide with superior cycling stability and rate capability for sodium storage. *Carbon* **57**, 202–208 (2013).
49. Ding, J. *et al.* Carbon nanosheet frameworks derived from peat moss as high performance sodium ion battery anodes. *ACS Nano* **7**, 11004–11015 (2013).
50. Hong, S. Y. *et al.* Charge carriers in rechargeable batteries: Na ions vs. Li ions. *Energ. Environ. Sci.* **6**, 2067–2081 (2013).
51. Yu, D. Y. W. *et al.* High-capacity antimony sulphide nanoparticle-decorated graphene composite as anode for sodium-ion batteries. *Nature Commun.* **4**, 2922 (2013).
52. Prikhodchenko, P. V. *et al.* Nanocrystalline tin disulfide coating of reduced graphene oxide produced by the peroxostannate deposition route for sodium ion battery anodes. *J. Mater. Chem. A* **2**, 8431–8437 (2014).
53. Nithya, C. & Gopukumar, S. rGO/nano Sb composite: A high performance anode material for Na⁺ ion batteries and evidence for the formation of nanoribbons from the nano rGO sheet during galvanostatic cycling. *J. Mater. Chem. A* **2**, 10516–10525 (2014).
54. Qin, G., Zhang, X. & Wang, C. Design of nitrogen doped graphene grafted TiO₂ hollow nanostructures with enhanced sodium storage performance. *J. Mater. Chem. A* **2**, 12449–12458 (2014).
55. Qu, B. *et al.* Layered SnS₂-reduced graphene oxide composite — A high-capacity, high-rate, and long-cycle life sodium-ion battery anode material. *Adv. Mater.* **26**, 3854–3859 (2014).
56. Simon, P. & Gogotsi, Y. Materials for electrochemical capacitors. *Nature Mater.* **7**, 845–854 (2008).
57. Stoller, M. D., Park, S., Zhu, Y., An, J. & Ruoff, R. S. Graphene-based ultracapacitors. *Nano Lett.* **8**, 3498–3502 (2008).
58. Chen, J., Li, C. & Shi, G. Graphene materials for electrochemical capacitors. *J. Phys. Chem. Lett.* **4**, 1244–1253 (2013).
59. Bose, S. *et al.* Carbon-based nanostructured materials and their composites as supercapacitor electrodes. *J. Mater. Chem.* **22**, 767–784 (2012).
60. Zhu, Y. *et al.* Carbon-based supercapacitors produced by activation of graphene. *Science* **332**, 1537–1541 (2011).
61. Tsai, W.-Y. *et al.* Outstanding performance of activated graphene based supercapacitors in ionic liquid electrolyte from –50 to 80°C. *Nano Energy* **2**, 403–411 (2013).
62. Huang, Y., Liang, J. & Chen, Y. An overview of the applications of graphene-based materials in supercapacitors. *Small* **8**, 1805–1834 (2012).
63. Gogotsi, Y. & Simon, P. True performance metrics in electrochemical energy storage. *Science* **334**, 917–918 (2011).
64. Beidaghi, M. & Gogotsi, Y. Capacitive energy storage in micro-scale devices: Recent advances in design and fabrication of micro-supercapacitors. *Energ. Environ. Sci.* **7**, 867–884 (2014).
65. Xu, B. *et al.* What is the choice for supercapacitors: Graphene or graphene oxide? *Energ. Environ. Sci.* **4**, 2826–2830 (2011).
66. Han, G. *et al.* MnO₂ nanorods intercalating graphene oxide/polyaniline ternary composites for robust high-performance supercapacitors. *Sci. Rep.* **4**, 4824 (2014).
67. Lee, J.-S. *et al.* Metal–air batteries with high energy density: Li–air versus Zn–air. *Adv. Energ. Mater.* **1**, 34–50 (2011).
68. Ogasawara, T., Débart, A., Holzapfel, M., Novák, P. & Bruce, P. G. Rechargeable Li₂O₂ electrode for lithium batteries. *J. Am. Chem. Soc.* **128**, 1390–1393 (2006).
69. Kim, H., Lim, H.-D., Kim, J. & Kang, K. Graphene for advanced Li/S and Li/air batteries. *J. Mater. Chem. A* **2**, 33–47 (2014).
70. Girishkumar, G., McCloskey, B., Luntz, A. C., Swanson, S. & Wilcke, W. Lithium–air battery: Promise and challenges. *J. Phys. Chem. Lett.* **1**, 2193–2203 (2010).
71. Jung, H.-G., Hassoun, J., Park, J.-B., Sun, Y.-K. & Scrosati, B. An improved high-performance lithium–air battery. *Nature Chem.* **4**, 579–585 (2012).
72. Jung, H.-G. *et al.* Ruthenium-based electrocatalysts supported on reduced graphene oxide for lithium–air batteries. *ACS Nano* **7**, 3532–3539 (2013).
73. Hartmann, P. *et al.* A rechargeable room-temperature sodium superoxide (NaO₂) battery. *Nature Mater.* **12**, 228–232 (2013).
74. Liu, W., Sun, Q., Yang, Y., Xie, J.-Y. & Fu, Z.-W. An enhanced electrochemical performance of a sodium–air battery with graphene nanosheets as air electrode catalysts. *Chem. Commun.* **49**, 1951–1953 (2013).
75. Li, Y. *et al.* Superior catalytic activity of nitrogen-doped graphene cathodes for high energy capacity sodium–air batteries. *Chem. Commun.* **49**, 11731–11733 (2013).
76. Kucinskis, G., Bajars, G. & Kleperis, J. Graphene in lithium ion battery cathode materials: A review. *J. Power Sources* **240**, 66–79 (2013).
77. Jung, Y. H., Lim, C. H. & Kim, D. K. Graphene-supported Na₃V₂(PO₄)₃ as a high rate cathode material for sodium–ion batteries. *J. Mater. Chem. A* **1**, 11350–11354 (2013).
78. Xu, M. *et al.* Na₃V₂O₂(PO₄)₂F/graphene sandwich structure for high-performance cathode of a sodium–ion battery. *Phys. Chem. Chem. Phys.* **15**, 13032–13037 (2013).
79. Zhu, H. *et al.* Free-standing Na_{2/3}Fe_{1/2}Mn_{1/2}O₂@graphene film for a sodium–ion battery cathode. *ACS Appl. Mater. Interfaces* **6**, 4242–4247 (2014).
80. Yang, D., Liao, X.-Z., Shen, J., He, Y.-S. & Ma, Z.-F. A flexible and binder-free reduced graphene oxide/Na_{0.25}Ni_{1/3}Mn_{2/3}O₂ composite electrode for high-performance sodium ion batteries. *J. Mater. Chem. A* **2**, 6723–6726 (2014).
81. Zu, C. & Manthiram, A. Hydroxylated graphene-sulfur nanocomposites for high-rate lithium–sulfur batteries. *Adv. Energ. Mater.* **3**, 1008–1012 (2013).
82. Zhao, M.-Q. *et al.* Unstacked double-layer templated graphene for high-rate lithium–sulfur batteries. *Nature Commun.* **5**, 3410 (2014).
83. Lu, S., Chen, Y., Wu, X., Wang, Z. & Li, Y. Three-dimensional sulfur/graphene multifunctional hybrid sponges for lithium–sulfur batteries with large areal mass loading. *Sci. Rep.* **4**, 4629 (2014).
84. Yin, Y.-X., Xin, S., Guo, Y.-G. & Wan, L.-J. Lithium–sulfur batteries: Electrochemistry, materials, and prospects. *Angew. Chem. Int. Ed.* **52**, 13186–13200 (2013).
85. Yoo, H. D. *et al.* Mg rechargeable batteries: An on-going challenge. *Energ. Environ. Sci.* **6**, 2265–2279 (2013).
86. Liu, Y. *et al.* Synthesis of rGO-supported layered MoS₂ for high-performance rechargeable Mg batteries. *Nanoscale* **5**, 9562–9567 (2013).
87. Chen, Q. *et al.* PTMA/graphene as a novel cathode material for rechargeable magnesium batteries. *Acta Physico-Chimica Sin.* **29**, 2295–2299 (2013).
88. Wang, Y., Zhamu, A. & Jang, B. Z. Rechargeable magnesium-ion cell having a high-capacity cathode. US Patent 2013/0302697 (2013).
89. Weber, A. Z. *et al.* Redox flow batteries: A review. *J. Appl. Electrochem.* **41**, 1137–1164 (2011).
90. González, Z. *et al.* Graphite oxide-based graphene materials as positive electrodes in vanadium redox flow batteries. *J. Power Sources* **241**, 349–354 (2013).
91. Han, P. *et al.* Graphene oxide nanosheets/multi-walled carbon nanotubes hybrid as an excellent electrocatalytic material towards VO²⁺/VO³⁺ redox couples for vanadium redox flow batteries. *Energ. Environ. Sci.* **4**, 4710–4717 (2011).
92. González, Z. *et al.* Thermally reduced graphite oxide as positive electrode in vanadium redox flow batteries. *Carbon* **50**, 828–834 (2012).
93. Flox, C., Skoumal, M., Rubio-García, J., Andreu, T. & Morante, J. R. Strategies for enhancing electrochemical activity of carbon-based electrodes for all-vanadium redox flow batteries. *Appl. Energ.* **109**, 344–351 (2013).
94. Han, P. *et al.* RuSe/reduced graphene oxide: An efficient electrocatalyst for VO²⁺/VO³⁺ redox couples in vanadium redox flow batteries. *RSC Adv.* **4**, 20379–20381 (2014).
95. Shi, L., Liu, S., He, Z. & Shen, J. Nitrogen-doped graphene: Effects of nitrogen species on the properties of the vanadium redox flow battery. *Electrochim. Acta* **138**, 93–100 (2014).
96. Dai, W., Shen, Y., Li, Z., Yu, L. & Qiu, X. SPEEK/graphene oxide nanocomposite membranes with superior cyclability for highly efficient vanadium redox flow battery. *J. Mater. Chem. A* **2**, 12423–12432 (2014).
97. Dai, W. *et al.* Sulfonated poly(ether ether ketone)/graphene composite membrane for vanadium redox flow battery. *Electrochim. Acta* **132**, 200–207 (2014).
98. Vargas, O. *et al.* Electrochemical performance of a graphene nanosheets anode in a high voltage lithium-ion cell. *Phys. Chem. Chem. Phys.* **15**, 20444–20446 (2013).
99. Choi, D. *et al.* Li-ion batteries from LiFePO₄ cathode and anatase/graphene composite anode for stationary energy storage. *Electrochem. Commun.* **12**, 378–381 (2010).
100. Chae, C., Noh, H.-J., Lee, J. K., Scrosati, B. & Sun, Y.-K. A high-energy Li-ion battery using a silicon-based anode and a nano-structured layered composite cathode. *Adv. Func. Mater.* **24**, 3036–3042 (2014).

Acknowledgements

R.R., A.V. and S.P. acknowledge the financial support of Bundesministerium für Bildung und Forschung (BMBF) within the project 'IES, Innovative Elektrochemische Superkondensatoren' (contract number 03EK3010). B.S. is grateful to the Helmholtz Institute Ulm for a six-month visiting professorship position.

Author contributions

R.R. and A.V. designed the outline of the Progress Article, wrote the manuscript and conceived the figures and tables. S.P. and B.S. supervised and revised the writing.

Additional information

Reprints and permissions information is available online at www.nature.com/reprints. Correspondence should be addressed to S.P. or B.S.

Competing financial interests

The authors declare no competing financial interests.