



Review

An overview of graphene in energy production and storage applications

Dale A.C. Brownson, Dimitrios K. Kampouris, Craig E. Banks*

Faculty of Science and Engineering, School of Science and the Environment, Division of Chemistry and Environmental Science, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, Lancs, UK

ARTICLE INFO

Article history:

Received 24 December 2010
Received in revised form 27 January 2011
Accepted 2 February 2011

Keywords:

Graphene
Energy storage/generation
Electrochemistry
Super-capacitor
Battery
Fuel cell

ABSTRACT

Energy production and storage are both critical research domains where increasing demands for the improved performance of energy devices and the requirement for greener energy resources constitute immense research interest. Graphene has incurred intense interest since its freestanding form was isolated in 2004, and with the vast array of unique and highly desirable electrochemical properties it offers, comes the most promising prospects when implementation within areas of energy research is sought. We present a review of the current literature concerning the electrochemical application of graphene in energy storage/generation devices, starting with its use as a super-capacitor through to applications in batteries and fuel cells, depicting graphene's utilisation in this technologically important field.

© 2011 Elsevier B.V. All rights reserved.

Contents

1. Introduction.....	4873
1.1. Graphene: an introduction.....	4874
1.2. Graphene: a unique array of properties.....	4874
2. Graphene in energy storage devices.....	4875
2.1. Graphene as a super-capacitor.....	4875
2.2. Graphene as a battery/Li-ion storage.....	4878
2.3. Miscellaneous energy storage devices (solar power).....	4881
3. Graphene in energy generation devices.....	4882
3.1. Fuel cells.....	4882
3.2. Microbial bio-fuel cells.....	4883
3.3. Enzymatic bio-fuel cells.....	4884
4. Conclusions.....	4884
References.....	4885

1. Introduction

Current energy related devices are plagued with issues of poor performance and many are known to be extremely damaging to the environment [1–3]. With this in mind, energy is currently a vital global issue given the likely depletion of current resources (fossil fuels) coupled with the demand for higher-performance energy systems [4]. Such systems require the advantages of portability and

energy efficiency whilst being environmentally friendly [5,6]; this area of research is no doubt under constant strain, where advances and interest concerning the applicability of new, novel materials is required.

Attempts have been made at rectifying the current problems through the utilisation of electrochemical applications, and since the isolation of graphene in 2004 [7] there has been widespread excitement among scientists due to its exceptional physical attributes. Graphene is ideally suited for implementation in electrochemical applications due to its reported large electrical conductivity, vast surface area, unique heterogeneous electron transfer and charge carrier rates, widely applicable electro-catalytic

* Corresponding author. Tel.: +44 1612471196; fax: +44 1612476831.
E-mail address: c.banks@mmu.ac.uk (C.E. Banks).

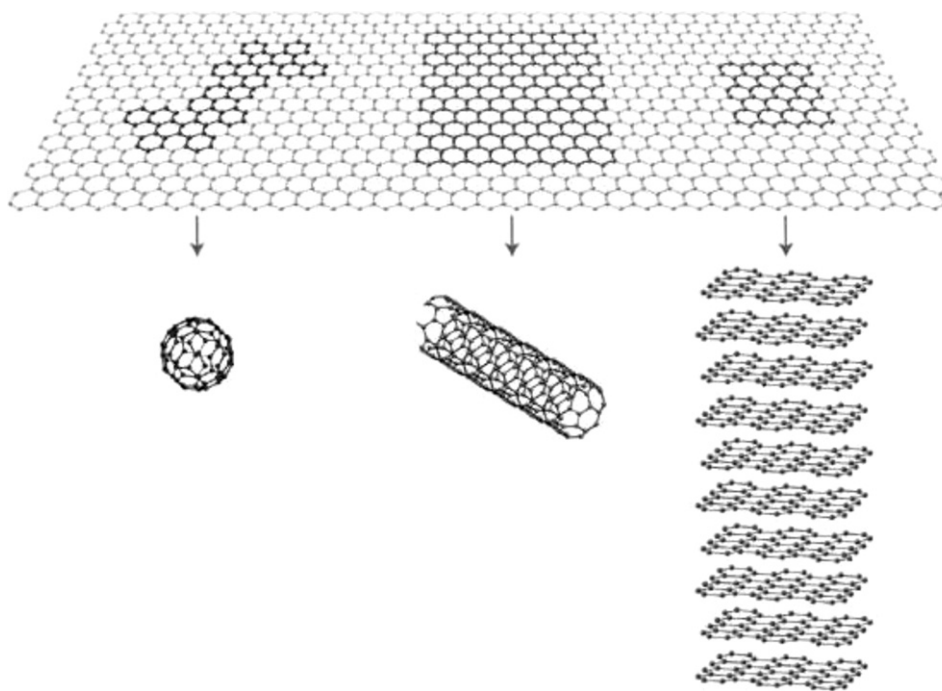


Fig. 1. Schematic representation of graphene, which is the fundamental starting material for a variety of fullerene materials; buckyballs, carbon nanotubes, and graphite. Re-modelled from Ref. [8].

activity, and low production costs [8–12]. Consequently graphene has been utilised beneficially as a promising alternate electrode material in many applications for enhancing specific technological fields and particularly the issues surrounding energy storage and generation – graphene is at the centre of future prospects where its unique attributes have begun to be utilised with astonishing outcomes when contrasted to current devices, that until now have dominated the field. Thus the utilisation of graphene in future applications to aid with technological advances within energy related fields holds great promise, where the years of research based upon various other carbon forms can be readily tailored to graphene. Utilising graphene to build on the existing wealth of knowledge and current techniques available, ground-breaking performance is expected to surpass that already achieved whilst at the same time proving to be a greener and more energy efficient alternative.

In this review we highlight the importance of graphene and present an overview of energy orientated literature. Note that there are many reviews exploring graphene's application within sensors and other selected applications [10–16], but there is distinct lack of reviews focusing specifically on energy storage/generation as a whole. This review fills this potential gap focusing solely on energy storage/generation with comprehensive tables provided. We first explore the unique properties of graphene whilst contrasting these to other electrode materials such as graphite and carbon nanotubes (CNTs), before detailing the application of graphene as a super-capacitor and noting the recent and exciting advancements reported in battery applications and other interesting areas of energy storage, after which we extend our overview into the subject area of energy generation and the utilisation of fuel cells.

1.1. Graphene: an introduction

Graphene is a two-dimensional one-atom-thick planar sheet of sp^2 bonded carbon atoms [8–10,17,18], which is considered as the fundamental foundation for all fullerene allotropic dimensionalities, as shown in Fig. 1 [11]. In addition to its planar state graphene can be 'wrapped' into zero-dimensional spherical bucky-

balls, 'rolled' into one-dimensional CNTs – further categorised into single- or multi-walled depending on the number of graphene layers present (SWCNTs/MWCNTs respectively), or can be 'stacked' into three-dimensional graphite – generally consisting of more than ten graphene layers [8,10,11,19]. Consequently graphene can be considered the 'mother of all carbon forms' – as a building block. A variation on graphene are nano-platelets which are characterised by stacks consisting of between two and ten graphene sheets, with another graphene existing in the form of graphene oxide (GO) – where the graphene has been oxidised within the employed fabrication process or spontaneously by contact with air, however, this form is usually chemically or electrochemically reduced before use [11]. It is important to clarify that a single graphene nanosheet (GNS) refers to graphene as its standard form – that is a single layer of graphene.

The fabrication process by which graphene is synthesised defines its properties and as a result its application, and therefore graphene fabrication is currently a heavily researched topic [10]. The vast array of current synthesis methodologies used for graphene manufacture include; exfoliation (either physical/mechanical or chemical) [20,21], epitaxial growth via Chemical Vapour Deposition (CVD) [22], the unzipping of CNTs (via electrochemical, chemical, or physical methods), and the reduction of sugars (such as glucose or sucrose) [23] to name just a few. Note however, there is no single method of graphene synthesis that yields graphene exhibiting the optimum properties for all potential applications [10].

1.2. Graphene: a unique array of properties

It is well known that graphene possesses unique physical, chemical and thermal properties [8–12], and with the applications of electrochemistry spanning far afield it is the properties of the electrode material itself that are most significant to the performance of the fabricated device.

An essential characteristic of an electrode material, particularly important in energy production and storage, is surface

area. The theoretical surface area of graphene is reported to be $\sim 2630 \text{ m}^2 \text{ g}^{-1}$, surpassing that of both SWCNTs and graphite which are reported to be $\sim 1315 \text{ m}^2 \text{ g}^{-1}$ and $\sim 10 \text{ m}^2 \text{ g}^{-1}$ respectively [10]. Additional cause for the excitement concerning graphene arises when examining the electrical conductivity of graphene, resulting from its extensive conjugated sp^2 carbon network, reported to be $\sim 64 \text{ mS cm}^{-1}$ which is approximately ~ 60 times more than that of SWCNTs [24,25] and which remains stable over a vast range of temperatures [8]; essential for reliability in many energy related applications. Of further importance to energy related devices and an additional indication of the extreme electronic quality that graphene possesses, is the fact that even at room temperature graphene displays the half-integer quantum Hall effect, with the effective speed of light as its Fermi velocity $v_F \sim 10^6 \text{ m s}^{-1}$ [26–28]; and more interestingly graphene is distinguished from its counterparts by its unusual band structure, rendering the quasiparticles in it formally identical to the massless Dirac Fermions. The charge density of graphene can be controlled by means of a gate electrode [27]; charge carriers can be tuned continuously between electrons and holes where electron mobility remains high even at high concentrations in both electrically and chemically doped devices, which translates to ballistic transport on the sub-micrometre scale [11]. For example, ultra-high electron mobility has been achieved in graphene by suspending a single GNS $\sim 150 \text{ nm}$ above a Si/SiO_2 gate electrode [29]. Here mobilities in excess of $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at electron densities of $\sim 2 \times 10^{11} \text{ cm}^{-2}$ are obtainable, in comparison the mobility of an electron in silicon is around $\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ indicating that the electron mobility in graphene is ~ 200 times higher. The fast charge carrier properties of graphene have been found not only to be continuous, but to exhibit high crystal quality [8], meaning charge carriers can travel thousands of inter-atomic distances without scattering – even with the presence of metallic impurities. This fact suggests that if graphene is used as a channel material, a transistor allowing extremely high-speed operation and with low electric power consumption could be obtained [8]. Furthermore, a pronounced ambipolar electric field effect is evident in graphene [11], and due to its unique credentials it has even been speculated that graphene can carry a super-current [11,28]. Further on this topic, GNSs offer a unique two-dimensional environment for electron transport and we have recently shown that the electron transfer of graphene resides from its edge rather than its side, where the former acts electrochemically akin to that of edge plane- and the latter to that of basal plane-like-sites/defects of highly ordered pyrolytic graphite, meaning that electron transfer at the edge is many orders of magnitude faster than at its side [30,31].

A significant advantage graphene has over CNTs is that it generally does not possess the same disadvantages that have plagued them, such as residual metallic impurities that are inherent to the CVD fabrication process and have hindered their exploitation, for example in the manufacture of reliable energy devices [32,33]. Graphene has largely precluded this problem because methods of graphene synthesis that involve CVD [22,34] generally use non-metallic catalysts, note however, in cases where graphene is synthesised in this manner, control experiments may still need to be performed [11], and as with CNTs the control of defects and reproducibility of fabrication are likely to be issues common to graphene [11]. Further advantageous characteristics of graphene for their application in energy related devices emerge when comparing graphene to graphite – note that GNSs are flexible which is beneficial for use in flexible electronic and energy storage devices, as opposed to the brittle nature of graphite [10].

Another major advantage of graphene, greatly influencing its electrochemical performance in terms of the heterogeneous electron transfer rate, is the presence of oxygen-containing groups at its edges or surface [11]. When controlled attachment of functional

elements are required, such oxygen-containing groups may provide convenient attachment sites, which are expected to be similar to that observed for CNTs [16], thus specific groups can be introduced that play vital roles in electrochemical battery and fuel cell applications [10]; for example, oxygenated species can be used as ‘anchoring’ sites for the attachment of glucose oxidase (GOx) for use in a range of energy generation applications [35]. It is noteworthy that the electrochemical properties of graphene-based electrodes can hence be modified or tuned by chemical modification, and tailored to suit its application [19]. It is heavily debatable however, whether the presence of oxides upon graphene’s surface, in addition to the defect sites within graphene, may change its electronic and chemical properties beneficially or detrimentally [11].

Having considered each of graphenes inimitable electrochemical properties in turn, it is clear that graphene exhibits the largest surface area, fastest electron mobilities, highest conductivity, and the most exceptional electronic qualities when contrasted against other possible electrode materials (graphite, CNTs, and traditional noble metals), and its subtle electronic characteristics (attractive π – π interactions, and its strong absorptive capability) [36] suggest a long and viable future in energy production and storage; thus ‘theoretically’ in many applications graphene’s performance has the potential to be far superior than its counterparts.

2. Graphene in energy storage devices

Current electrochemical energy storage devices are becoming less appropriate for the ever increasing range of high demand applications utilising them today, as technology becomes increasingly more advanced and powerful the requirements of energy storage systems increase, thus in order to produce energy storage devices that can sufficiently meet the mounting demands of consumers, the exploration and exploitation of new electrode materials must occur. Graphene is extremely attractive for energy storage applications due to its unique reported properties (see above) [15].

2.1. Graphene as a super-capacitor

Electrochemical super-capacitors are passive and static electrical energy storage devices, utilised in applications such as portable electronics (mobile phones), memory back-up systems, and hybrid cars, where extremely fast charging is a valuable feature [15,37]. Super-capacitors have high power capabilities, fast charge propagation and charge-discharge processes (within seconds), long cyclic life (usually greater than 100,000 cycles), require low maintenance, and exhibit low self-discharging [15]; they have larger energy densities when compared to conventional capacitors, although, energy densities are lower than batteries and fuel cells [15]. A super-capacitor unit cell is usually comprised of two porous carbon electrodes that are isolated from electrical contact by a porous separator, the current collectors of metal foil or carbon impregnated polymers are used to conduct electrical current from each electrode [38]. The separator and the electrodes are impregnated with an electrolyte, this allows ionic current to flow between the electrodes whilst preventing electronic current from discharging the cell [38]. In super-capacitors, energy is stored due to the formation of an electrical double layer at the interface of the electrode (electrical double layer capacitors) [39] or due to electron transfer between the electrolyte and the electrode through fast Faradiac redox reactions (pseudo-capacitors) [40], often the capacitance of a super-capacitor is dependent on its ability to utilise both of the previous energy storage capabilities with high efficiency, where these two mechanisms can function simultaneously depending on the nature of the electrode material [15]. To develop a super-capacitor device, an active electrode material with high capacity performance is indispensable

Table 1
Overview of specific capacitance and power outputs of a range of graphene based materials and various other comparable materials for use as super-capacitors.

Electrode material	Performance parameter		Cyclic ability	Comments	Ref.
	Specific capacitance (F g^{-1})	Power density (kW kg^{-1})			
CNT/PANI	780	NT	After 1000 cycles the capacitance decreased by 67%	Obtained from CV measurement at a SR of 1 mV s^{-1}	[37]
GNS	150	NT	Specific capacitance was maintained with the specific current of 0.1 A g^{-1} for 500 cycles of charge/discharge	N/A	[39]
GNS	38.9	2.5	NT	Synthesised using a screen-printing approach and ultrasonic spray pyrolysis. Data obtained from CV measurement at a SR of 50 mV s^{-1}	[45]
GNS-cobalt (II) hydroxide nano-composite	972.5	NT	NT	N/A	[48]
GNS/CNT/PANI	1035	NT	After 1000 cycles the capacitance decreased by only 6% of the initial	Obtained from CV measurement at a SR of 1 mV s^{-1}	[37]
GNS/PANI	1046	70 @ 39 W h kg^{-1}	NT	Synthesised using in situ polymerisation. Capacitance obtained from CV measurement at a SR of 1 mV s^{-1}	[41]
GNS-nickel foam	164	NT	Specific capacitance remains 61% of the maximum capacitance after 700 cycles	Obtained from CV measurement at a SR of 10 mV s^{-1}	[43]
GNS-SnO ₂	42.7	3.9	NT	Synthesised using a screen-printing approach and ultrasonic spray pyrolysis. Data obtained from CV measurement at a SR of 50 mV s^{-1}	[45]
GNS-ZnO	61.7	4.8	NT	Synthesised using a screen-printing approach and ultrasonic spray pyrolysis. Data obtained from CV measurement at a SR of 50 mV s^{-1}	[45]
Graphene	205	10 @ 28.5 W h kg^{-1}	~90% specific capacitance remaining after 1200 cycles	Graphene was prepared from graphite oxide	[42]
MWCNT/PANI	463	NT	NT	Synthesised using in situ polymerisation. Capacitance obtained from CV measurement at a SR of 1 mV s^{-1}	[41]
Nickel (II) hydroxide nano-crystals deposited on GNS	1335	NT	NT	Obtained at a charge/discharge density of 2.8 A g^{-1}	[46]
PANI	115	NT	NT	Synthesised using in situ polymerisation. Capacitance obtained from CV measurement at a SR of 1 mV s^{-1}	[41]
PANI/GOS	531	NT	NT	Nanocomposite with a mass ratio of PANI/graphene, 100:1. Capacitance obtained by charge-discharge analysis	[1]
RuO ₂ /GNS	570	10 @ 20.1 W h kg^{-1}	~97.9% specific capacitance remaining after 1000 cycles	N/A	[47]

Key: CNT – carbon nanotube; CV – cyclic voltammetry; GNS – graphene nano-sheet; GOS – graphene oxide sheets; MWCNT – multi-walled carbon nanotube; N/A – not applicable; NT – not tested; PANI – polyaniline; RuO₂ – hydrous ruthenium oxide; SR – scan rate.

[41], however, all of the components are important factors. Current research on electrochemical capacitors is aimed at increasing both power and energy densities as well as lowering fabrication costs – whilst using environmentally friendly materials. The core materials studied for super-capacitor electrodes are carbons, metal oxides, and conducting polymers [1], with recent advancements having focused on CNTs. However, graphene based materials have shown immense theoretical and practical advantages, such as a high surface area, excellent conductivity and capacitance, and relatively low production costs (mass production).

The use of graphene as a super-capacitor material has been widely reported, with many studies reporting graphene as a far superior super-capacitor material than existing carbon and polymer based materials; Table 1 overviews a selection of recent literature reports where graphene has been utilised as a super-capacitor material in comparison to existing materials, for example graphite and CNTs.

According to the energy-storage mechanisms noted above, the key to enhancing specific capacitance is to enlarge the specific surface area and control the pore size, layer stacking, and distribution of the electrode material, thus Du et al. [39] investigated graphene as a potential electrode material. The authors mass-produced

GNSs with a narrow mesopore distribution of ~4 nm from natural graphite *via* oxidation and rapid heating processes, and found the GNSs to maintain a stable specific capacitance of 150 F g^{-1} under the specific current of 0.1 A g^{-1} for 500 cycles of charge/discharge [39]. Wang et al. [42] also investigated graphene as a potential super-capacitor electrode material, where a maximum specific capacitance of 205 F g^{-1} was measured with a power density of 10 kW kg^{-1} at a energy density of 28.5 Wh kg^{-1} , excellent cyclic ability was obtained also with ~90% specific capacitance remaining after 1200 cycles. Interestingly, other work [43] has shown that using an electrophoretic deposition method to deposit GNSs onto nickel foams with three-dimensional porous structures, the high specific capacitance of 164 F g^{-1} is obtained from cyclic voltammetric (CV) measurement at a scan rate of 10 mV s^{-1} , and it was noted that after 700 cycles the specific capacitance remains 61% of the maximum capacitance; FESEM images of their modified nickel foam are shown in Fig. 2. Furthermore, work encompassing the deposition of silver nanoparticles onto graphene sheets has shown that increased specific capacitance and improved charge transfer occurs with evidence of a reduced resistance [44]. Yet further exciting prospects emerge when considering work by Vivekchand et al. [40] who have shown graphene prepared *via* graphitic oxide

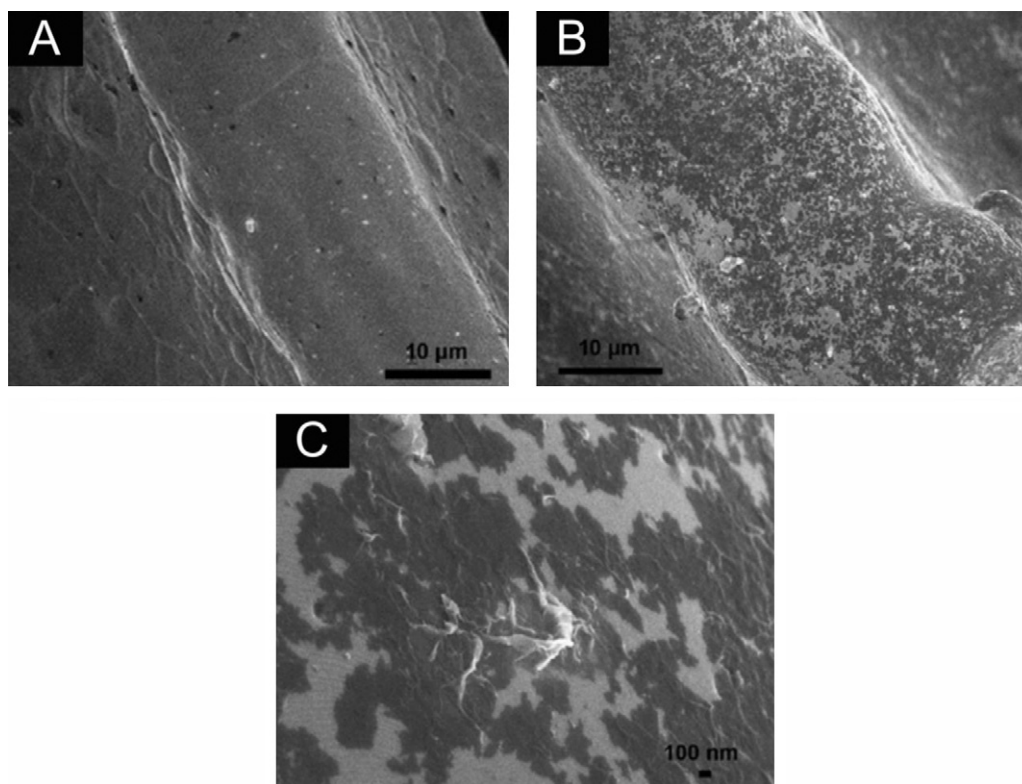


Fig. 2. FESEM images of (A) bare nickel foam, and (B) and (C) graphene nanosheets deposited on nickel foam. Reprinted from Ref. [43] with permission from Elsevier.

whilst utilising an ionic liquid, thus enabling the operating voltage to be extended up to 3.5 V, exhibits a specific capacitance and energy density of $\sim 75 \text{ F g}^{-1}$ and 31.9 Wh kg^{-1} respectively, surpassing those of both SW- and MWCNTs, 64 and 14 F g^{-1} respectively; the authors claim that the energy density is one of the highest values reported to-date of this kind, inferring that the performance characteristics of graphene are directly related to its quality in terms of numbers of graphene layers and the inherent surface area. It is likely however that the 'highest energy value' claimed in this case will most probably be surpassed in coming months given the intense research in this area. These comparable results suggest potential for GNS based electrochemical capacitors to be fabricated, but scalability might be an issue.

However, it is evident that the general specific capacitance of graphene is not as high as expected, and thus it is notable that many researchers have turned to the incorporation and fabrication of graphene based hybrid materials in the pursuit for improved capacitance performance. In one notable example Wang et al. [1] report a novel high performance electrode material based upon fibrillar polyaniline (PANI) doped with graphene oxide sheets. The authors obtained a nanocomposite with a mass ratio of PANI/graphene, 100:1, which exhibited a high specific capacitance of 531 F g^{-1} , obtained by charge-discharge analysis, and when compared to individual PANI (216 F g^{-1}) it was clear that doping (and the ratio of graphene oxide) has a profound effect on the electrochemical capacitance performance of nanocomposites; graphene exhibits great potential for application in super-capacitors and other power source systems of the future.

Further work was conducted by Yan et al. [41] reporting that a GNS/PANI composite synthesised using in situ polymerisation could obtain a high specific capacitance of 1046 F g^{-1} (examined using CV and galvanostatic charge/discharge analysis), which compared to 115 F g^{-1} for pure PANI, 463 F g^{-1} for SWCNT/PANI, and 500 F g^{-1} for MWCNT/PANI; additionally, the energy density of the GNS/PANI composite could reach 39 Wh kg^{-1} at a power density

of 70 kW kg^{-1} . It is apparent that GNS/PANI modifications offer a highly conductive support material where the well-dispersed depositions of nanoscale PANI particles are attributable to the GNSs large surface area and flexibility. Other work on this topic [37] has investigated the effect of a GNS/CNT/PANI composite, claiming responses similar to the composites mentioned above, and that after 1000 cycles the capacitance decreased by only 6% of the initial (compared to 52 and 67% for GNS/PANI and CNT/PANI respectively); demonstrating that a hybrid-graphene material may exhibit the ultimately desired properties required for superior energy related devices to be realised [4,37].

In addition to these reports, further work has indicated that graphene has the potential to outperform its counterparts as a capacitor material; for example it has been highlighted that a graphene-ZnO composite exhibits enhanced capacitance when compared to CNTs, as well as an enhanced reversible charge/discharge ability [2,42,45]. One notable example [45] concerns the fabrication of GNS-ZnO and GNS-SnO₂ electrode materials, where a screen-printing approach was employed to fabricate the graphene film onto a graphite substrate whilst the ZnO or SnO₂ was deposited onto the graphene film *via* ultrasonic spray pyrolysis. The performances of these electrodes were then tested through electrochemical impedance spectroscopy, CV, and chronopotentiometry. Results demonstrated that the inclusion of either ZnO or SnO₂ improved the capacitive performance of the graphene electrode. The GNS-ZnO composite electrode exhibited a higher capacitance value, 61.7 F g^{-1} , and maximum power density, 4.8 kW kg^{-1} , when compared to the GNS-SnO₂ and pure graphene electrodes, exhibiting capacitances of 42.7 and 38.9 F g^{-1} and power densities of 3.9 and 2.5 kW kg^{-1} respectively. In another notable example Zhang et al. [2] prepared a graphene-ZnO composite film and investigated its electrochemical characteristics. Their results showed that the composite exhibited enhanced capacitance behaviour/values with better reversible charging/discharging ability by comparison to pure graphene and pure ZnO electrodes. One

explanation for this, in addition to graphene's enhanced surface area (and other qualities discussed earlier), has been ascribed to the increase in lattice defect density exhibited by graphene (such as the fracture of graphene layers and the ratio of edge to basal carbon surface), where it is believed that increased edge plane increases the capacitance of a material [39]. However, work by Stoller et al. [38] stated that on chemically modified graphene electrodes the super-capacitor performance does not depend on a rigid porous structure to deliver its large surface area but on graphenes flexibility, where graphene sheets adjust their position depending on the electrolyte used. Stoller and co-workers [38] found the weight specific capacitance of chemically modified graphene to be up to 135 F g^{-1} [38].

Other work has been explored where inorganic nanomaterials have been anchored onto graphene's surface, resulting in high performance super-capacitors [46–48]. Wang et al. [46] have grown nickel (II) hydroxide nano-crystals on graphene sheets, finding that the resultant material exhibits a high specific capacitance of $\sim 1335 \text{ F g}^{-1}$ at a charge/discharge density of 2.8 A g^{-1} and $\sim 953 \text{ F g}^{-1}$ at 45.7 A g^{-1} respectively, as well as exhibiting excellent cyclic ability; the authors demonstrated that their graphene based nano-composite outperformed the utilisation of small nickel (II) hydroxide nano-particles grown on graphite oxide [46]. For comparison, a physical mixture of pre-synthesized nickel (II) hydroxide nano-plates and graphene exhibited lower specific capacitance, highlighting the importance of direct growth of these nanomaterials on graphene to enhance the intimate interactions and charge transport between the active nanomaterials and the conducting underlying network [46]. Such results suggest the importance of rational design and synthesis of graphene-based nano-composite materials for high-performance energy applications where high specific capacitance and remarkable rate capability are promising for applications in supercapacitors with both high energy and power densities [46]. Further work by Wu et al. [47] has demonstrated that hydrous ruthenium oxide/graphene composites exhibit a high specific capacitance of $\sim 570 \text{ F g}^{-1}$ (for 38.3% ruthenium weight loading) with enhanced rate capability and excellent electrochemical stability ($\sim 97.9\%$ retention after 1000 cycles), in addition to a high energy density of 20.1 Wh kg^{-1} at a low operation rate of 100 mA g^{-1} or a power density of $10,000 \text{ W kg}^{-1}$ at a reasonable energy density of 4.3 Wh kg^{-1} . Interestingly, it was found that the total specific capacitance of the composite material was higher than the sum of specific capacitances of pure graphene and pure ruthenium oxide in their relative ratios, which was ascribed to be indicative of a positive synergistic effect of graphene and ruthenium oxide on the improvement of the electrochemical performance [47]. Moreover, Chen et al. [48] have reported on the utilisation of a graphene-cobalt (II) hydroxide nano-composite and shown the electrochemical specific capacitance of the graphene composite to reach 972.5 F g^{-1} , leading to a significant improvement in relation to each individual component (137.6 and 726.1 F g^{-1} for graphene and cobalt hydroxide respectively). These findings again demonstrate the importance and great potential of graphene-based composites in the development of high-performance energy-storage systems [46–48].

Considering the data presented above however, it is important to note that elegant work by Pumera et al. [49] has shown that it is not always beneficial to exfoliate graphitic structures to single layer graphene, GNS, to achieve maximum electrochemical performance and capacitance. Pumera has demonstrated, using electrochemical impedance spectroscopy, that multilayer (>10 layers) graphene nanoribbons with cross sections of $100 \times 100 \text{ nm}$ provide a larger capacitance (15.6 F g^{-1}) than few-layer (3–9 layers) graphene nanoribbons (14.9 F g^{-1}) and a far greater capacitance than single layer GNSs (10.9 F g^{-1}) with the same cross section, likely caused by graphene layers laying flat on top of one another

blocking/concealing the edge plane as has been shown previously where basal plane based electrodes have greatly reduced charge storage when compared to edge plane surfaces, thus vertically orientated GNSs are believed to be a near-ideal structure [49,50], likely due to a higher edge plane content available and larger inter-layer spaces allowing for improved capacitance due to the complete utilisation of available space [49,50]. This of course does not account for the use of hybrid materials however, where the combination of graphene with various other materials could possibly lead to the increased availability of the graphene's edge-plane sites and surface area, as well as influencing other factors such as inter-layer spacing leading to an improved capacitance performance; this argument is also relevant for graphene within the fabrication of lithium ion (Li-ion) batteries – see below. Furthermore, when considering this argument it is interesting to observe that few layer graphene samples have been shown to exhibit superior characteristics when they are disordered in nature. For example, Pan et al. [20] have reported the fabrication of highly disordered graphene nanosheets which exhibit promising possibilities in high-capacity Li-ion batteries because of their high reversible capacity (1054 mA h g^{-1}) and good cyclic performance, exhibiting a far superior performance when compared to highly ordered GNSs (540 mA h g^{-1}) [5] and graphite samples (372 mA h g^{-1}) [5], thus in addition to being attributed to larger inter-layer spacing by Pan and colleagues, these findings concur with the above suggestion that increased edge plane and surface area availability results in enhanced performance [20]. The disorder of GNSs can be achieved *via* a variety of methods including the introduction of hybrid materials or for example by electron-beam irradiation as utilised in the work by Pan and co-workers [20]; there is a strong possibility that increasing the inter-planar spaces between graphene sheets in addition to the edge plane sites available could lead to numerous advantageous prospects in capacitance and energy storage applications.

Having overviewed the application of graphene as a super-capacitor, it is clear that it has already made a significant impact and revealed itself to be a promising material for future research within this area. With the possibility of hybrid graphene materials emerging in the near future, we may witness the fabrication of a super-capacitor composite that is able to acquire currently unachievable capacitance levels and greatly improved cyclic abilities; of course a major limitation is the current cost of graphene, reproducibility, scalability, and characterisation, where drawing from the latter many reports are emerging where claims of the utilisation of graphene are made without adequate characterisation being performed and in such cases perhaps graphene is not present, rather multiple layer or greater – thus appropriate control experiments need to be performed where results are compared to other appropriate carbon forms such as graphite or activated carbons. This is an issue evident throughout each aspect of graphene's utilisation within energy related applications, and consequently should be borne-in-mind when considering each topic covered below.

2.2. Graphene as a battery/Li-ion storage

Lithium (Li) based rechargeable batteries are a further class of energy storage devices where graphene has been employed due to its reported superior physical attributes. As with super-capacitors, there is an increasing worldwide demand for advanced Li-ion batteries with higher energy capacities and longer cycle lifetimes, which are promising with regards to their application within electric vehicles [20,51,52]. Li-ion batteries can store and supply electricity over a long period of time, where electrode materials (i.e. anode/cathode) play dominant roles in the performance, although each component of the battery is essential to its performance capabilities [12,53]. Currently the anode material employed for lithium based batteries is usually graphite because of its high

Table 2

Overview of the specific capacitance and cyclic stabilities of a range of graphene based materials and various other comparable materials for the application of graphene as a Lithium-ion battery electrode.

Compound	Specific capacitance (mA h g ⁻¹)	Cyclic stability	Comments	Ref.
GNS	540	300 after 30 cycles at 50 mA g ⁻¹	N/A	[5,55]
GNS	1264	848 after 40 cycles at 100 mA g ⁻¹	GNSs in coin-type cells versus metallic lithium	[51]
GNS	1233	502 after 30 cycles at the current density of 0.2 mA cm ⁻²	GNSs were prepared from artificial graphite by oxidation, rapid expansion and ultrasonic treatment	[52]
GNS/Fe ₃ O ₄	1026	580 after 100 cycles at 700 mA g ⁻¹	N/A	[53]
GNS/SnO ₂	860	570 after 30 cycles at 50 mA g ⁻¹	GNSs were homogeneously distributed between the loosely packed SnO ₂ nanoparticles in such a way that a nanoporous structure with a large amount of void spaces could be prepared	[5]
GNS/SnO ₂	840	590 after 50 cycles at the current density of 400 mA g ⁻¹	The optimum molar ratio of SnO ₂ /graphene was 3.2:1	[62]
GNS/with C ₆₀ spacer molecules	784	NT	N/A	[55]
GNS/with CNT spacer	730	NT	N/A	[55]
Graphite	372	240 after 30 cycles at 50 mA g ⁻¹	N/A	[5,55]
Mn ₃ O ₄ /RGO	~900	~730 after 40 cycles at 400 mA g ⁻¹	N/A	[60]
Ox-GNSs	~1400	Cyclic stability within the range of 800	Capacity loss per cycle of ~3% for early cycles; this decreasing for subsequent cycles	[57]

Key: C₆₀ – carbon 60; CNT – carbon nanotube; GNS – graphene nanosheet; N/A – not applicable; NT – not tested; Ox – oxidised; RGO – reduced graphene oxide.

Coulombic efficiency (the ratio of the extracted Li to the inserted Li) [12] where it can be reversibly charged and discharged under intercalation potentials with a reasonable specific capacity [5]. However, to improve battery performance the relatively low theoretical capacity associated with graphite batteries (372 mA h g⁻¹) and the long diffusion distances of the Li-ions need to be overcome [12]. Graphene has already shown itself as a beneficial replacement, for example papers have emerged boasting graphene based electrodes to have higher specific capacities than many other electrode materials (including graphite), and in addition to this many theoretical papers have emerged [5,10,20,51,54]. One particular report states that graphene's two-dimensional edge plane sites should aid Li-ion adsorption and diffusion, consequently reducing charging times and increasing power outputs. An overview of various graphene based electrode materials reported in the literature for use as a lithium based battery are listed and compared to other electrode materials, namely graphite and CNTs, in Table 2.

In one interesting example Yoo and colleagues [55] fabricated a graphene based electrode using CNTs as spacers to prevent the restacking of the graphene sheets. The modified electrode was demonstrated to possess a specific capacitance towards lithium of 730 mA h g⁻¹ [55], which is greatly improved when compared to the existing graphite (372 mA h g⁻¹) [10] and an alternate graphene modified electrode without the use of spacers (540 mA h g⁻¹). Note that the use of graphene without spacers exhibits a largely superior response over that of comparable graphite. When Yoo et al. utilised C₆₀ molecules in addition to spacers between graphene sheets, the capacitance increased to 784 mA h g⁻¹ [55]. Moreover, graphene's advantageous application in lithium storage devices was partly explained by Takamura et al. [56] whom linked the high rate discharge capability of Li-ion batteries to nano-sized holes identified within the graphene sheets. However, this is not the only issue when looking at the performance of batteries, as discharge rates and cyclic abilities also need to be considered.

Bhardwaj and co-workers [57] have reported upon the electrochemical Li intake capacity of carbonaceous one-dimensional GNSs obtained by unzipping pristine MWCNTs. The authors showed that oxidised-GNSs (ox-GNSs) outperformed all other materials tested (GNSs and MWCNTs) in terms of energy density, obtaining a first charge capacity of ~1400 mA h g⁻¹ with a low Coulombic efficiency for the first cycle, ~53%, and ~95% for subsequent cycles, which was shown to be notably superior to MWCNTs and GNSs and similar to that of graphite. The cyclic capacity of the ox-GNSs was within

the range of 800 mA h g⁻¹, with an early capacity loss per cycle of ~3% (decreasing upon subsequent cycles) [57]. The cyclability is the capacity loss per cycle, and is a useful parameter to evaluate battery performance, where here, MWCNTs and GNSs perform better than the proposed ox-GNSs (capacity losses of ~1.4% and ~2.6% respectively), however, due to the higher initial capacitance of the ox-GNSs the performance of this material can still be regarded as superior, as can be observed in Fig. 3 [57].

In another interesting example Lian et al. [51] evaluated the electrochemical performance of GNSs in coin-type cells versus metallic lithium. The authors reported a large reversible capacity where high quality graphene sheets were used as an anode material for Li-ion batteries, showing that the GNSs possess a curled morphology with a large specific surface area. The first reversible specific capacity of the prepared GNS was as high as 1264 mA h g⁻¹ at a current density of 100 mA g⁻¹, where even at high current densities of 500 mA g⁻¹ the reversible capacity remained at 718 mA h g⁻¹. After 40 cycles the reversible capacity remained at 848 mA h g⁻¹ at a current density of 100 mA g⁻¹.

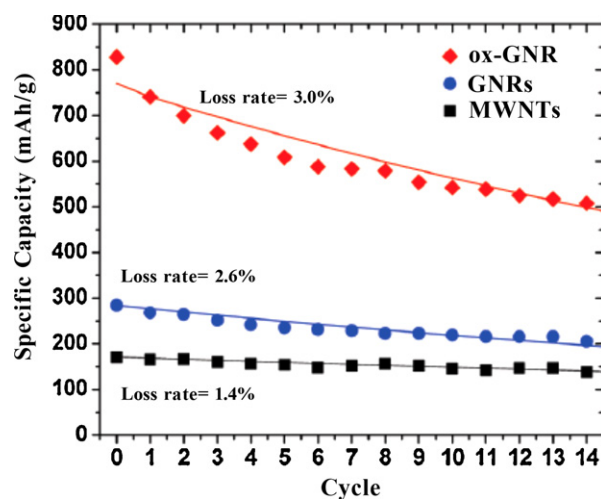


Fig. 3. Cyclability of three different carbonaceous electrodes materials; oxidised graphene (ox-GNR); graphene (GNR); and multi-walled carbon nanotubes (MWCNTs). Symbols represent experimental measurements, whilst bold lines represent values extrapolated at the indicated loss rate. Reproduced with permission from Ref. [57]. Copyright (2010) American Chemical Society.

These results indicate that the GNSs possess electrochemical performances suitable for their application within lithium storage devices [51].

One notable study [58] was performed where non-annealed graphene paper, prepared *via* reduction of prefabricated graphene oxide paper with hydrazine hydrate, was employed as the sole component of a binder-free Li-ion battery anode. The fabricated anode possessed excellent cyclic ability, whilst exhibiting a voltage versus capacity profile similar to that of a polymer-bound graphene powder anode (the reversible capacity was 84 mA h g^{-1} at a 50 mA g^{-1} current rate). However, it must be stated that the overall capacity of this and other examples using graphene paper [59] as the electrode material are poor when contrast to the emerging hybrid graphene materials is sought (see below) [5,53,60].

As is the case for super-capacitor devices, it is emerging that current research regarding Li-ion batteries is focused towards the fabrication of hybrid graphene composite materials when looking for improved battery performance. For example, previous work by Paek et al. [5] has demonstrated that a graphene/SnO₂ based nano-porous electrode exhibited a higher reversible capacity when compared to bare SnO₂, bare graphene, and bare graphite electrodes, and in addition to this, the graphene/SnO₂ electrode exhibited a much improved cyclic performance when compared to the same electrodes [5]. The graphene/SnO₂ based nano-porous electrode was synthesised and shown to exhibit a reversible capacity of 810 mA h g^{-1} [5]. Furthermore, its cyclic performance was drastically enhanced in comparison to bare SnO₂ nanoparticles, where after 30 cycles the charge capacity of the graphene/SnO₂ based electrode remained at 570 mA h g^{-1} (70% retention of the reversibility capacity), whereas the bare SnO₂ nanoparticles first charge capacity was 550 mA h g^{-1} which dropped rapidly to 60 mA h g^{-1} after only 15 cycles at 50 mA g^{-1} . Paek and co-workers [5] also reported superior cyclic performances over graphite modified nanoparticles, where the initial capacitance was $\sim 500 \text{ mA h g}^{-1}$, which dropped slightly during cycling – the bare graphene electrode resides only slightly above this level; Fig. 4 demonstrates the capacities and cyclic abilities of the mentioned composites along with a schematic representation of the fabricated graphene electrodes [5]. Other work on SnO₂–graphene hybrid based Li-ion batteries has yielded similar results with regards to capacitance and obtained good cyclic abilities (retaining 520 mA h g^{-1} after 100 cycles) [61,62].

Wang et al. [60] have reported Mn₃O₄–graphene hybrid materials as a suitable high-capacity anode material for utilisation in Li-ion batteries. Wang and co-workers [60] have developed a two-step solution-phase reaction to form Mn₃O₄ nanoparticles on reduced graphene oxide (RGO) sheets. The authors claim that their selective growth of Mn₃O₄ nanoparticles onto the RGO sheets (in contrast to free particle growth in solution) allowed for the electrically insulating Mn₃O₄ nanoparticles to be ‘wired-up’ to a current collector through the underlying conducting graphene network. The Mn₃O₄/RGO hybrid material demonstrated a high specific capacity up to $\sim 900 \text{ mA h g}^{-1}$, near the theoretical capacity of Mn₃O₄ ($\sim 936 \text{ mA h g}^{-1}$), with a good rate capability and cycling stability (a capacity of $\sim 730 \text{ mA h g}^{-1}$ at 400 mA g^{-1} was retained after 40 cycles), owing to the intimate interactions between the graphene substrates and the Mn₃O₄ nanoparticles [60]. Even at a high current density of 1600 mA g^{-1} the specific capacity was $\sim 390 \text{ mA h g}^{-1}$, which is higher than the theoretical capacity of graphite – commonly utilised within Li-ion batteries (372 mA h g^{-1}). Control experiments were performed utilising the synthesis of free Mn₃O₄ nanoparticles by the same process, however without the presence of graphene, where the performance was much worse; at a low current density of 40 mA g^{-1} the free Mn₃O₄ nanoparticles exhibited a capacity lower than 300 mA h g^{-1} , which further decreased to $\sim 115 \text{ mA h g}^{-1}$ after only 10 cycles. Conse-

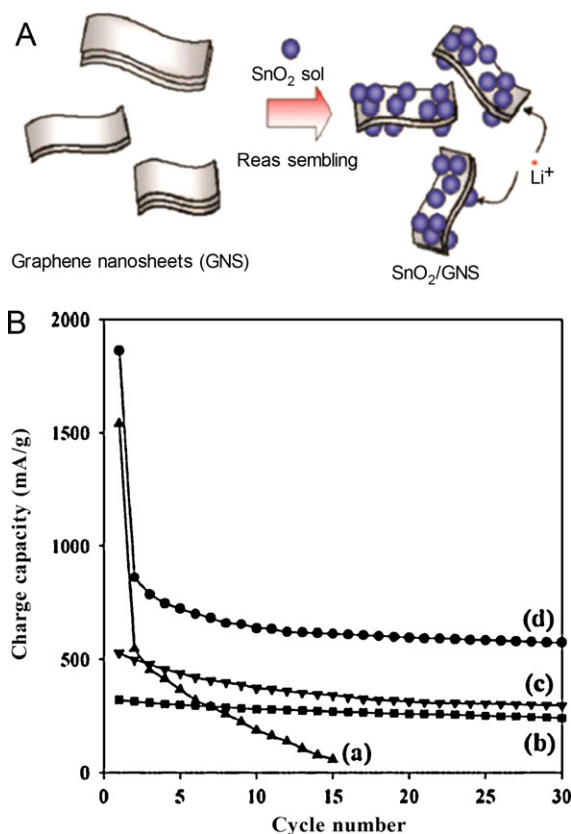


Fig. 4. (A) Schematic representation for the synthesis and structure of SnO₂ on graphene nanosheets (GNS). (B) Cyclic performances for (a) bare SnO₂ nanoparticle, (b) graphite, (c) GNS, and (d) SnO₂/GNS. Reproduced with permission from Ref. [5] Copyright (2009) American Chemical Society.

quently Wang et al. claim that the above hybrid material could be a promising candidate for high-capacity, low-cost, and environmentally friendly anode materials for Li-ion batteries of the future, since the observed performance surpasses that of graphite [60].

Whilst on the theme of hybrid materials, Fe₃O₄ exhibits great potential for use as an anode material with high capacity, low cost, eco-friendliness, and natural abundance. However because of the problem of rapid capacity fading during cycling, it has attracted the attention of scientists for use in the creation of hybrid materials [53]. Cause for excitement comes from elegant work by Zhou et al. [53] who fabricated a well-organised flexible interleaved composite of GNSs decorated with Fe₃O₄ particles through in situ reduction of iron hydroxide between GNSs; the interleaved network of GNSs produce a pathway for electron transport as shown in Fig. 5. The GNS/Fe₃O₄ composite exhibits a reversible specific capacity approaching 1026 mA h g^{-1} after 30 cycles at 35 mA g^{-1} and 580 mA h g^{-1} after 100 cycles at 700 mA g^{-1} , as well as improved cyclic stability and an excellent rate capability [53]. When comparison is sought towards the capacities of bare Fe₂O₃ and commercial Fe₂O₄ particles after 30 cycles at 35 mA g^{-1} (the cyclic abilities are also highlighted in Fig. 5) a decrease from 770 and 760 mA h g^{-1} to 475 and 359 mA h g^{-1} occur respectively, thus demonstrating poor cyclic abilities [53]. The authors inferred the multifunctional features of the GNS/Fe₃O₄ composite to be as follows: (i) GNSs play a ‘flexible confinement’ function to enwrap Fe₃O₄ particles, which can compensate for the volume change of Fe₃O₄ and prevent the detachment and agglomeration of pulverised Fe₃O₄, thus extending the cycling life of the electrode; (ii) GNSs provide a large contact surface for individual dispersion of well-adhered Fe₃O₄ particles and act as an excellent conductive agent to provide a highway for electron transport, improving the accessible capac-

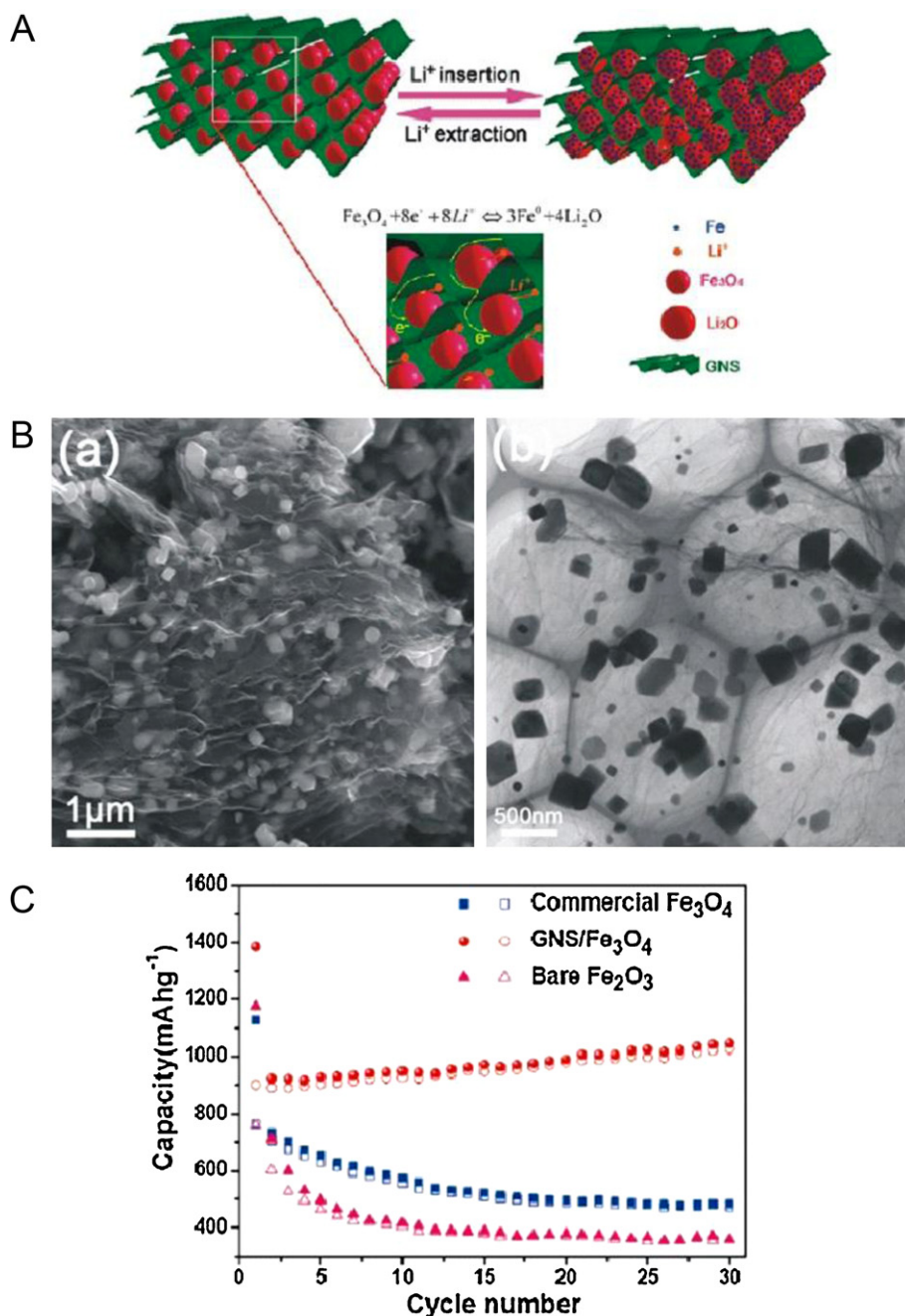


Fig. 5. (A) Schematic of a flexible interleaved structure consisting of graphene nanosheets (GNS) and Fe₃O₄ particles. (B) (a) SEM image of the cross-section of GNS/Fe₃O₄ composite, and (b) TEM. (C) Cycling performance of commercial Fe₃O₄ particles, GNS/Fe₃O₄ composite, and bare Fe₂O₃ particles at a current density of 35 mA g⁻¹ – solid symbols, discharge; hollow symbols, charge. Reproduced with permission from Ref. [53]. Copyright (2010) American Chemical Society.

ity; (iii) Fe₃O₄ particles separate GNSs and prevent their restacking thus improving the adsorption and immersion of electrolyte on the surface of electro-active material; and (iv) the porosity formed by lateral GNSs and Fe₃O₄ particles facilitates ion transportation [53]. As a result, this unique laterally confined GNS/Fe₃O₄ composite can dramatically improve the cycling stability and the rate capability of Fe₃O₄ as an anode material for lithium ion batteries [53].

More intriguingly graphene composites have been utilised as both anode and cathode materials, such as in the case of graphene/LiFePO₄ [63], and graphene/Li₄Ti₅O₁₂ [64], where their application is promising for Li-ion secondary batteries, however, such outputs are not as high as previous reports, questioning their suitability into this field.

In light of the literature discussed above current research regarding graphene as a Li-ion storage device indicates it to be beneficial over graphite based electrodes, exhibiting improved cyclic performances and higher capacitance for applications within Li-ion batteries. Again, exciting future developments within this area are expected and there is no doubt that among the greatest performers to materialise within the near future, a hybrid graphene based material will reside.

2.3. Miscellaneous energy storage devices (solar power)

Of further interest and significant importance in the development of clean and renewable energy is the application of graphene in solar power based devices, where photoelectrochemical solar

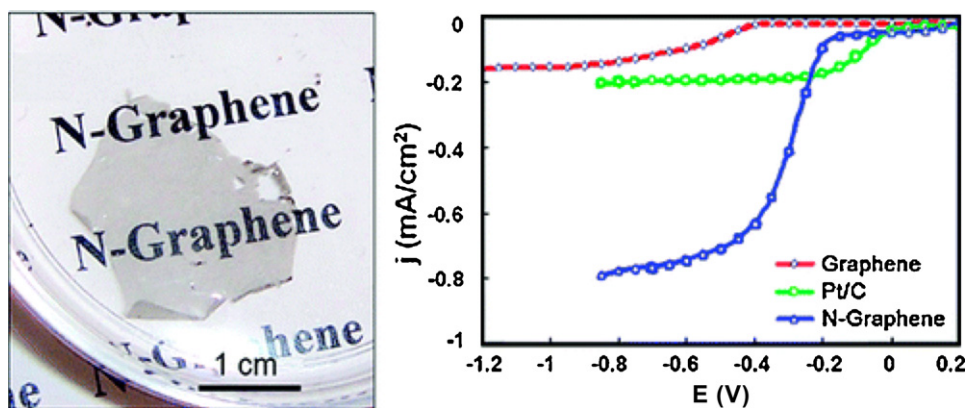


Fig. 6. Digital photo image of transparent nitrogen doped graphene film floating on water. Rotating disc voltammograms for electrochemical reduction of oxygen in air-saturate 0.1 M KOH. Rotation speed 1000 rpm, scan rate 0.01 V s⁻¹, all masses of the material the same = 7.5 μg. Reproduced with permission from Ref. [3]. Copyright (2010) American Chemical Society.

energy conversion plays an important role in generating electrical energy [65,66].

Recently Chang et al. [66] developed a novel photoelectrochemical cell (PEC) based on a graphene/poly(3-octyl-thiophene) (POT) nanocomposite for use within photovoltaic energy conversion where their composite provides a general platform for next generation solar energy conversion, photoconductivity, and photodetectors. Chang et al. [66] have demonstrated that the doping of graphene in the POT film significantly improves the photocurrent generation rate as well as the photovoltaic conversion efficiency of the PECs by over 10 folds than that of pure POT [66]. Moreover, the electron transfer resistance of the graphene/POT nanocomposite decreased significantly and was only 10% of pure POT, suggesting that the graphene composite may serve as a promising platform for solar energy conversion within the future. It was noted that the performances of the PECs were largely dependent on the graphene content and morphology, with the highest efficiencies obtained at a graphene content of 5 wt% in the nanocomposite [66], and the greatly improved responses being attributed to graphene's high capability as an electron acceptor in addition to its large surface area and high electron mobility; all of which are essential to the performance of higher energy conversion solar cells.

Some reports have criticised the use of graphene use as a transparent conductor stating that its conductivity ratio is too small, but it has been suggested that substrate-induced doping can potentially increase the two-dimensional direct-current conductivity enough to make graphene a viable transparent conductor [67]. For example, Valentini et al. [68] have reported a facile method to use GNSs as part of a transparent electrode for the preparation of polymer solar cells. It is claimed that the application of GNSs in a polymer solar cell is plausible where functionalised graphene is cheap and easily prepared, and graphene is expected to be used as a hole acceptor material in polymer photovoltaic applications because the ideal monolayer of graphene has a transparency of 98% and a sheet resistance of 6 kΩ sq⁻¹, making it suitable for transparent and conducting electrodes that are essential to many areas of modern electronics and commonly found in touch-panels and solar cells [68].

3. Graphene in energy generation devices

In addition to the tremendous impact that graphene has undoubtedly had when utilised in the field of energy storage, graphene has also made a significant impact in the fabrication and application of energy generation devices. With the World's climate on the conscience of many and the depletion of non-renewable energy sources ever-nearing, the search for replacements has

resulted in great interest in fuel cell applications and consequently the examination and development of new electrode materials. Graphene is attractive as an electrode material for use within fuel cells because of its large surface area, improved enzymatic binding ability, unique electrical conductivity, widely applicable electro-catalytic activity, and low production costs [8–12]. Table 3 summarises the various applications of graphene in fuel cell devices.

3.1. Fuel cells

One notable contribution has been from Dai and co-workers [3] who explored graphene and nitrogen doped graphene formed *via* CVD towards the electrochemical reduction of oxygen (oxygen reduction reaction (ORR)), comparing it with commercially available platinum (Pt) loaded carbon. Platinum has long been regarded as one of the best catalysts for the electrochemical ORR, and is consequently utilised in fuel cells, but has the drawback of being expensive and exhibiting time-dependent drift due to the poisoning/deactivation of the Pt surface with carbon monoxide [3]. As depicted in Fig. 6, Dai et al. have reported that nitrogen-doped graphene acts as a metal-free electrode with a greatly enhanced electro-catalytic activity, long-term operation stability, and tolerance to crossover effect than Pt for oxygen reduction *via* a four-electron pathway in alkaline solutions producing water as a product [3]. However, note that the over-potential is less on the Pt surface, and therefore the observed high current density in Fig. 6 might be due to incorrect normalisation of surface area [11].

In proton exchange membrane fuel cells (PEMFCs) Pt based electro-catalysts are widely used as anode and cathode electro-catalysts for hydrogen oxidation and for ORRs respectively. In recent work Jafri et al. [69] utilised GNS and nitrogen doped-GNSs as the catalyst support for Pt nanoparticles for ORRs in PEMFCs. The authors constructed a fuel cell with Pt loaded GNS where the power densities 440 and 390 mW cm⁻² were obtained for nitrogen doped-GNS-Pt and GNS-Pt respectively [69]. Jafri and co-workers comment on the improved performance inferring that the nitrogen doping process creates pyrrolic nitrogen defects acting as anchoring sites for the deposition of Pt nanoparticles, and is also likely due to increased electrical conductivity or improved carbon-catalyst binding [69]. Contrasting earlier work by Zhang et al. [70] has demonstrated that the fabrication of low-cost graphite submicron-particles (GSP) can be employed as a possible support for polymer electrolyte membrane (PEM) fuel cells, where Pt nanoparticles were deposited on GSP in addition to carbon black and CNTs *via* a ethylene glycol reduction method. Zhang and colleagues report that the Pt/GSP showed the highest electro-catalytic activity towards

Table 3

Overview of the power and current densities obtained by the utilisation of a range of graphene based materials and various other comparable materials as an electrode material in fuel cells.

Type of substrate	Fuel/oxidant	Current/power density at maximum power	Power density vs. time	Comments	Ref.
Au/GNS/GOx	Glucose	$156.6 \pm 25 \mu\text{A cm}^{-2}$	$24.3 \pm 4 \mu\text{W}$ at 0.38 V (load 15 k Ω)	Tested every day with a 15 k Ω external load. After the first 24 h, it had lost 6.2% of its original power output. Later, the power output was found to decay slowly and became 50% of the original value after 7 days	[24]
Au/SWCNT/GOx	Glucose	$86.8 \pm 13 \mu\text{A cm}^{-2}$	$7.8 \pm 1.1 \mu\text{W}$ at 0.25 V (load 15 k Ω)	N/A	[24]
GNS–Pt	H ₂ /O ₂	390 mW cm ⁻²	NT	PEMFC	[69]
GO–Pt	H ₂ /O ₂	161 mW cm ⁻²	NT	N/A	[71]
Nitrogen doped-GNS–Pt	H ₂ /O ₂	440 mW cm ⁻²	NT	PEMFC	[69]
Pt	H ₂ /O ₂	96 mW cm ⁻²	NT	N/A	[71]

Key: Au – gold; GNS – graphene nanosheet; GO – graphene oxide; GOx – glucose oxidase; N/A – not applicable; NT – not tested; PEMFC – proton exchange membrane fuel cell; Pt – platinum; SWCNT – single walled carbon nanotube.

the ORRs and that a durability study indicated the Pt/GSP was 2–3 times more durable than the CNT and carbon black alternatives [70]. However, recently [71] the dispersion of Pt on GO has been shown to be useful for achieving relatively enhanced performance in fuel cells, essentially the use of GO as a support material for the distribution of Pt nanoparticles provides new ways to develop advanced electro-catalyst materials for hydrogen fuel cells; here a partially reduced GO–Pt based fuel cell delivered a maximum power of 161 mW cm⁻² compared to 96 mW cm⁻² for an unsupported Pt based fuel cell.

Direct methanol fuel cells have drawn great attention recently due to their high energy density, low pollutant emission, ease of handling the liquid, and low operating temperatures (60–100 °C), however, low electro-catalytic activity towards methanol oxidation is hindering exploitation [72]. Graphene has been linked to the enhanced electro-catalytic activity of catalysts for fuel cell applications, in-particularly Xin et al. [72] have recently demonstrated that the utilisation of a platinum/GNS (Pt/GNS) catalyst revealed a high catalytic activity for both methanol oxidation and the ORR when compared to Pt supported on carbon black (C). Xin and co-workers deposited Pt nanoparticles onto GNS via synchronous reduction of H₂PtCl₆ and GO suspension using NaBH₄; Their results, CV profiles, are depicted in Fig. 7 where the peak current towards methanol electro-oxidation is shown and it is apparent that the current density of the Pt/GNS catalyst (182.6 mA mg⁻¹) outperforms the response of Pt/C (77.9 mA mg⁻¹). However, it is noted that the prior

heat treatment of the Pt/GNS catalyst improved the performance further by ~3.5 times over that of the Pt/C response; a response supported by previous literature [72,73]. Moreover, chronoamperometric analysis was performed to analyse the stability of the fabricated catalysis towards methanol oxidation, and it was depicted that all of the catalysts decayed rapidly in the initial stages, gradually reaching a steady state where it was clear that the greatest activity and stability was achieved by the heat treated Pt/GNS with an ending current of 55.5 mA mg⁻¹, followed by Pt/GNS and Pt/C respectively – suggesting that the heat treatment of a Pt/GNS catalyst provides greatly improved methanol oxidation than current materials [72]. Other similar work [74] has demonstrated that using a GNS supported Pt–Ruthenium (Ru) nano-composite, improved catalytic activity is achievable towards the oxidation of methanol when contrasted to a Pt–Ru/Vulcan base alternative. Moreover, work by Dong et al. [6] has demonstrated that Pt and Pt–Ru nanoparticles synthesised onto GNSs exhibit high electro-catalytic activity towards methanol and ethanol when contrasted against graphite alternatives, leading to a greatly reduced over-potential and increased reversibility, thus these findings favour the use of graphene sheets as catalyst supports for both direct methanol and ethanol fuel cells [6]. Additionally, Shang et al. [75] have investigated the application of uniform and porous GNSs as a support for catalytic Pt nanoclusters in direct-methanol electro-oxidation, where again, as observed throughout the energy related field, it appears that hybrid materials exhibit distinctly superior electrochemical characteristics than the standard components, particularly in the fabrication of fuel cells, as this novel graphene supported Pt based nanostructure has the potential to serve as a low-cost and highly efficient electrode material for methanol fuel cells.

As demonstrated in the above examples, GNSs pose as a good candidate for use as a supporting material in high-loading metal catalysts for potential applications in the fabrication of high-energy ‘greener’ solutions to current issues surrounding fuel cells; we expect the fundamental processes to be determined for metal immobilisation onto graphene, which is currently still not fully understood.

3.2. Microbial bio-fuel cells

Microbial fuel cells (MFCs) have emerged within recent years offering great opportunities for cleaner more sustainable energy whilst at the same time utilising waste products and meeting increasing energy needs [76]. MFCs are essentially bioreactors that generate electricity from the degradation of organic substances with the aid of the metabolic activity of microorganisms (bacteria) [76,77]. As with other low-temperature fuel cells the slow kinetics of the ORR at the cathode has limited the performance and energy

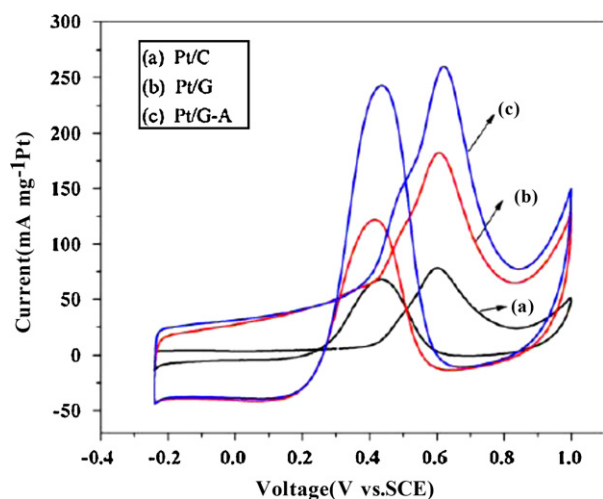


Fig. 7. Cyclic voltammograms of methanol oxidation on (a) Pt/carbon black, (b) Pt/graphene, and (c) Pt/graphene-heat treated modified composites. Scan rate: 20 mV s⁻¹, 0.5 M H₂SO₄ and 0.5 M CH₃OH. Reprinted from Ref. [72] with permission from Elsevier.

production of the MFC, thus in order to improve the cathodic performance the development of catalysts is essential [77]. Recently Wu and colleagues [77] identified the need to investigate the catalytic activity of graphene upon the ORR in neutral media for its potential application in MFCs. Wu and co-workers demonstrated that reduced graphene sheets (RGSs), prepared *via* chemical reduction of graphite oxide, are an excellent potential electrode material for MFCs, showing that the modification of a glassy carbon electrode (GCE) with RGSs (using the electrolyte 3.5% NaCl) resulted in an obvious positive shift of the peak potential (lowering the overpotential) and a larger current density [77].

It is clear that graphene has not yet been fully explored within this area, but we expect many more examples and applications within this field to appear in the not so distant future, building on the already vibrant examples available utilising graphite and CNTs, for instance in the treatment of domestic and industrial wastewater for the generation of energy [76].

3.3. Enzymatic bio-fuel cells

Recently, there has been substantial interest towards the development of enzymatic biofuel cells (EBFCs) as they possess the potential to be employed as an *in-vivo* power source for implantable medical devices such as pacemakers [24]. The most striking feature of the EBFC is that they can utilise glucose or other carbohydrates copiously present in the human body as a fuel. However, EBFCs have major issues to be rectified including low power densities and poor stability. The low power density of the EBFC in comparison with conventional inorganic fuel cells is due to the location of the active site of the enzyme buried deep under the protein shell; hindering the electron transfer pathway between the enzyme's active site and the electrode. Previously CNTs have been employed to improve electron transfer to sites 'buried' deep within the enzyme and other approaches involve the covalent binding of the enzyme, for example, GOx for use in bio-fuel cells with glucose as a fuel – however, a complex chemical treatment process of CNTs has to be performed in order to create active binding sites on the edge of the CNTs. Such a process however, likely hinders mass production [24]. Furthermore, a number of redox mediators are widely used to boost electron transfer rates between the species involved. Due to graphene's excellent conductivity, ballistic electron mobilities at room temperature [24], large surface area, and other unique properties (as discussed above) it is thought of as an optimal replacement and starting platform for further research, where high performance EBFCs are expected soon. It is also worth mentioning that graphene can be synthesised to possess a number of surface active functional moieties; such as carboxylic, ketonic, quinonic and C=C. Of these, the carboxylic and ketonic groups are reactive and can easily bind covalently with, for example, GOx. The presence of extended C=C conjugation in graphene is also expected to shuttle electrons [24].

Although this is a relatively new area of graphene research and consequentially there is limited literature available, one of the few papers currently available is highly exciting. The most compelling advancement within this area of electrochemistry concerns the use of GNSs within the construction of membraneless EBFCs, as reported by Liu et al. [24] who employed graphene to fabricate the anode and cathode in a biofuel cell; Fig. 8 depicts their experimental set-up. The anode of the biofuel cell consisted of a gold electrode on which the authors co-immobilised graphene with GOx using a silica sol-gel matrix whilst the cathode was constructed in the same manner except they employed bilirubin oxidase (BOD) as the cathodic enzyme. Voltammetric measurements were conducted to quantitatively evaluate the suitability and power output of employing a GNS as an electrode dopant and its performance was compared with a similar EBFC system constructed using SWCNTs. Upon com-

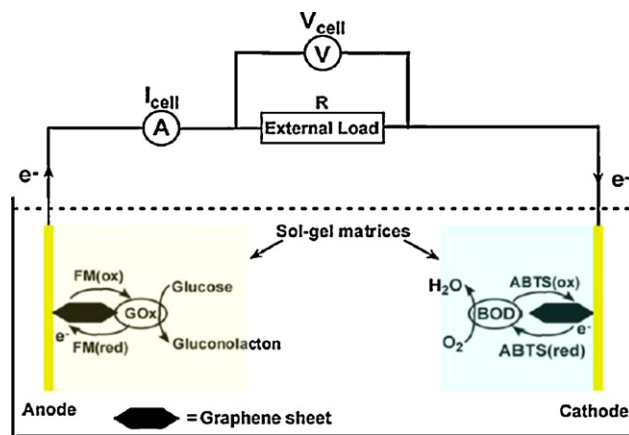


Fig. 8. Graphene based membraneless EBFC components employing GOx/FM and BOD/ABTS functionalised electrodes as biocatalytic anode and cathode, respectively. Reprinted from Ref. [24] with permission from Elsevier.

parison, the graphene based biofuel cell exhibited a maximum power density of $24.3 \pm 4 \mu\text{W}$ at 0.38 V (load $15 \text{ k}\Omega$), which is nearly two times greater than that of the SWCNTs EBFC ($7.8 \pm 1.1 \mu\text{W}$ at 0.25 V (load $15 \text{ k}\Omega$)). The maximum current density of the graphene based EBFC was found to be $156.6 \pm 25 \mu\text{A cm}^{-2}$, and for the SWCNT based EBFC $86.8 \pm 13 \mu\text{A cm}^{-2}$. Therefore, it is evident that the graphene based electrode is better suited for applications in EBFCs. To evaluate the stability of the graphene based EBFC, the system was stored in pH 7.4 phosphate buffer solution at 4°C and tested every day with a $15 \text{ k}\Omega$ external load. After the first 24 h, it had lost 6.2% of its original power output. Later, the power output was found to decay slowly and became 50% of the original value after 7 days; which is substantially longer than other EBFC devices, and outperforms the SWCNT based EBFC [24]. The authors stated that the enhanced performance was based upon; (i) the larger surface area of graphene in comparison to SWCNTs; (ii) graphenes greater sp^2 character than other materials within its field (responsible for shuttling the electrons and assisting in the better performance of the EBFC); (iii) and the larger number of dislocations and electro-active functional groups present in graphene.

4. Conclusions

Research concerning the search for elevated energy permitting devices and cleaner alternatives for energy generation has journeyed down an interesting path. The investigation of graphene within the context of energy thus far has led to the development of devices with great potential for utilisation and exploitation within the near-future, where perhaps the emergence of hybrid materials or the utilisation of nano-architectonics will be of paramount importance to aid in the development of state-of-the-art nanotechnology and its utilisation within energy related themes. It must be noted where the utilisation of graphene is inferred, adequate characterisation of the graphene must be performed and is of great importance when ensuring that inaccurate claims are not boasted where graphene is absent and rather another derivative of carbon such as 'multi-layer graphene' *viz* graphite is the true origin; and in light of this we suggest that appropriate control experiments in the form of various other carbon based materials such as graphite and activated carbons are performed. Having summarised the current literature regarding the use of graphene in various energy related applications including batteries, super-capacitors, and fuel cells, it is clear that although graphene is still a relatively new material it has already made a wide and diverse impact, and with the contribution of current literature portraying graphene as far-superior than its rival materials, much more is expected from this novel material

within the near future – graphene looks to be a likely candidate for utilisation in energy storage/generation applications through frantic and intense interest. For such applications to be adopted into commercial entities there are still many hurdles to overcome such as; scalability, reproducibility, continuity of energy outputs and storage capabilities, the reproducibility and characterisation of graphene itself, and its inherent cost.

References

- [1] H. Wang, Q. Hao, X. Yang, L. Lu, X. Wang, *Electrochem. Commun.* 11 (2009) 1158.
- [2] Y. Zhang, H. Li, L. Pan, T. Lu, Z. Sun, *J. Electroanal. Chem.* 634 (2009) 68.
- [3] L. Qu, Y.J.-B. Baek, L. Dai, *ACS Nano* 4 (2010) 1321.
- [4] K. Zhang, L.L. Zhang, X.S. Zhao, J. Wu, *Chem. Mater.* 22 (2010) 1392.
- [5] S.-M. Paek, E. Yoo, I. Honma, *Nano Lett.* 9 (2009) 72.
- [6] L. Dong, R.R.S. Gari, Z. Li, M.M. Craig, S. Hou, *Carbon* 48 (2010) 781.
- [7] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* 306 (2004) 666.
- [8] A.K. Geim, K.S. Novoselov, *Nat. Mater.* 6 (2007) 183.
- [9] D. Chen, L. Tang, J. Li, *Chem. Soc. Rev.* 39 (2010) 3157.
- [10] M. Pumera, *Chem. Rec.* 9 (2009) 211.
- [11] D.A.C. Brownson, C.E. Banks, *Analyst* 135 (2010) 2768.
- [12] M. Liang, L. Zhi, *J. Mater. Chem.* 19 (2009) 5871.
- [13] D.R. Kauffman, A. Star, *Analyst* 135 (2010) 2790.
- [14] R. Liu, J. Duay, S.B. Lee, *Chem. Commun.* (2011), doi:10.1039/C1030CC03158E.
- [15] L.L. Zhang, R. Zhou, X.S. Zhao, *J. Mater. Chem.* 20 (2010) 5983.
- [16] G.G. Wildgoose, C.E. Banks, H.C. Leventis, R.G. Compton, *Microchim. Acta* 152 (2006) 187.
- [17] W. Yang, K.R. Ratinac, S.P. Ringer, P. Thordason, J.J. Gooding, F. Braet, *Angew. Chem.* 49 (2010) 2114.
- [18] R.L. McCreery, *Chem. Rev.* 108 (2008) 2646.
- [19] G.G. Wallace, J. Chen, D. Li, S.E. Moulton, J.M. Razal, *J. Mater. Chem.* 20 (2010) 3553.
- [20] D. Pan, S. Wang, B. Zhao, M. Wu, H. Zhang, Y. Wang, Z. Jiao, *Chem. Mater.* 21 (2009) 3136.
- [21] H.-L. Guo, X.-F. Wang, Q.-Y. Qian, F.-B. Wang, X.-H. Xia, *ACS Nano* 3 (2009) 2653.
- [22] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R.D. Piner, L. Colombo, R.S. Ruoff, *Nano Lett.* 9 (2009) 4359.
- [23] C. Zhu, S. Guo, Y. Fang, S. Dong, *ACS Nano* 4 (2010) 2429.
- [24] C. Liu, S. Alwarappan, Z. Chen, X. Kong, C.-Z. Li, *Biosens. Bioelectron.* 25 (2010) 1829.
- [25] X. Wang, L. Zhi, K. Mullen, *Nano Lett.* 8 (2008) 323.
- [26] B. Soodchomshom, *Physica B* 405 (2010) 1383.
- [27] H.B. Heersche, P. Jarillo-Herrero, J.B. Oostinga, L.M.K. Vandersypen, A.F. Morpurgo, *Nature* 446 (2007) 58.
- [28] S. Sato, N. Harada, D. Kondo, M. Ohfuchi, *Fujitsu Sci. Technol. J.* 46 (2009) 103.
- [29] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H.L. Stormer, *Solid State Commun.* 146 (2008) 351.
- [30] D.K. Kampouris, C.E. Banks, *Chem. Commun.* 46 (2010) 8986.
- [31] P.M. Hallam, C.E. Banks, *Electrochem. Commun.* 13 (2011) 8.
- [32] C.E. Banks, A. Crossley, C. Salter, S.J. Wilkins, R.G. Compton, *Angew. Chem. Int.* 45 (2006) 2533.
- [33] X. Ji, R.O. Kadara, J. Krussma, Q. Chen, C.E. Banks, *Electroanalysis* 22 (2010) 7.
- [34] W.-J. Lin, C.-S. Liao, J.-H. Jhang, Y.-C. Tsai, *Electrochem. Commun.* 11 (2009) 2153.
- [35] Y. Lin, F. Lu, Y. Tu, Z. Ren, *Nano Lett.* 4 (2004) 191.
- [36] X. Kang, J. Wang, H. Wu, J. Liu, I.A. Aksay, Y. Lin, *Talanta* 81 (2010) 754.
- [37] J. Yan, T. Wei, Z. Fan, W. Qian, M. Zhang, X. Shen, F. Wei, *J. Power Sources* 195 (2010) 3041.
- [38] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, *Nano Lett.* 8 (2008) 3498.
- [39] X. Du, P. Guo, H. Song, X. Chen, *Electrochim. Acta* 55 (2010) 4812.
- [40] S.R.C. Vivekchand, C.S. Rout, K.S. Subrahmanyam, A. Govindaraj, C.N.R. Rao, *J. Chem. Sci.* 120 (2008) 9.
- [41] J. Yan, T. Wei, B. Shao, Z. Fan, W. Qian, M. Zhang, F. Wei, *Carbon* 48 (2010) 487.
- [42] Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, Y. Chen, *J. Phys. Chem. C* 113 (2009) 13103.
- [43] Y. Chen, X. Zhang, P. Yu, Y. Ma, *J. Power Sources* 195 (2010) 3031.
- [44] K.-S. Kim, I.-J. Kim, S.-J. Park, *Synth. Met.* (2010), doi:10.1016/J.SYNTHMET.2010.1009.1011.
- [45] T. Lu, Y. Zhang, H. Li, L. Pan, Y. Li, Z. Sun, *Electrochim. Acta* 55 (2010) 4170.
- [46] H. Wang, H.S. Casalongue, Y. Liang, H. Dai, *J. Am. Chem. Soc.* 132 (2010) 7472.
- [47] Z.-S. Wu, D.-W. Wang, W. Ren, J. Zhao, G. Zhou, F. Li, H.-M. Cheng, *Adv. Funct. Mater.* 20 (2010) 3595.
- [48] S. Chen, J. Zhu, X. Wang, *J. Phys. Chem. C* 114 (2010) 11829.
- [49] M.S. Goh, M. Pumera, *Electrochem. Commun.* 12 (2010) 1375.
- [50] J.R. Miller, R.A. Outlaw, B.C. Holloway, *Science* 329 (2010) 1637.
- [51] P. Lian, X. Zhu, S. Liang, Z. Li, W. Yang, H. Wang, *Electrochim. Acta* 55 (2010) 3909.
- [52] P. Guo, H. Song, X. Chen, *Electrochem. Commun.* 11 (2009) 1320.
- [53] G. Zhou, D.-W. Wang, F. Li, L. Zhang, N. Li, Z.-S. Wu, L. Wen, G.Q. Lu, H.-M. Cheng, *Chem. Mater.* 22 (2010) 5306.
- [54] C. Uthaisar, V. Barone, *Nano Lett.* 10 (2010) 2838.
- [55] E.J. Yoo, J. Kim, E. Hosono, H.-S. Zhou, T. Kudo, I. Honma, *Nano Lett.* 8 (2008) 2277.
- [56] T. Takamura, K. Endo, L. Fu, Y. Wu, K.J. Lee, T. Matsumoto, *Electrochim. Acta* 53 (2007) 1055.
- [57] T. Bhardwaj, A. Antic, B. Pavan, V. Barone, B.D. Fahlman, *J. Am. Chem. Soc.* 132 (2010) 12556.
- [58] A. Abouimrane, O.C. Compton, K. Amine, S.T. Nguyen, *J. Phys. Chem. C* 114 (2010) 12800.
- [59] C. Wang, D. Li, C.O. Too, G.G. Wallace, *Chem. Mater.* 21 (2009) 2604.
- [60] H. Wang, L.-F. Cui, Y. Yang, H.S. Casalongue, J.T. Robinson, Y. Liang, Y. Cui, H. Dai, *J. Am. Chem. Soc.* 132 (2010) 13978.
- [61] J. Yao, X. Shen, B. Wang, H. Liu, G. Wang, *Electrochem. Commun.* 11 (2009) 1849.
- [62] X. Wang, X. Zhou, K. Yao, J. Zhang, Z. Liu, *Carbon* (2010), doi:10.1016/J.CARBON.2010.1008.1052.
- [63] Y. Ding, Y. Jiang, F. Xu, J. Yin, H. Ren, Q. Zhuo, Z. Long, P. Zhang, *Electrochem. Commun.* 12 (2010) 10.
- [64] L. Shen, C. Yuan, H. Luo, X. Zhang, S. Yang, X. Lu, *Nanoscale* (2011), doi:10.1039/C1030NR00639D.
- [65] M. Liang, B. Luo, L. Zhi, *Int. J. Energy Res.* 33 (2009) 1161.
- [66] H. Chang, Y. Liu, H. Zhang, J. Li, *J. Electroanal. Chem.* (2010), doi:10.1016/J.JELECHEM.2010.1010.1015.
- [67] S. De, J.N. Coleman, *ACS Nano* 4 (2010) 2713.
- [68] L. Valentini, M. Cardinali, S.B. Bon, D. Bagnis, R. Verdejo, M.A. Lopez-Manchado, J.M. Kenny, *J. Mater. Chem.* 20 (2010) 995.
- [69] R.I. Jafri, N. Rajalakshmi, S. Ramaprabhu, *J. Mater. Chem.* 20 (2010) 7114.
- [70] S. Zhang, Y. Shao, X. Li, Z. Nie, Y. Wang, J. Liu, G. Yin, Y. Lin, *J. Power Sources* 195 (2010) 457.
- [71] B. Seger, P.V. Kamat, *J. Phys. Chem. C* 113 (2009) 7990.
- [72] Y. Xin, J.-G. Liu, Y. Zhou, W. Liu, J. Gao, Y. Xie, Y. Yin, Z. Zou, *J. Power Sources* (2010), doi:10.1016/J.JPOWSOUR.2010.1008.1051.
- [73] Y.M. Li, L.H. Tang, J.H. Li, *Chem. Commun.* 11 (2009) 846.
- [74] S. Bong, Y.-R. Kim, I. Kim, S. Woo, S. Uhm, J. Lee, H. Kim, *Electrochem. Commun.* 12 (2010) 129.
- [75] N. Shang, P. Papakonstantinou, P. Wang, S.R.P. Silva, *J. Phys. Chem. C* 114 (2010) 15837.
- [76] D. Pant, G. Van Bogaert, L. Diels, K. Vanbroekhoven, *Bioresour. Technol.* 101 (2010) 1533.
- [77] J. Wu, Y. Wang, D. Zhang, B. Hou, *J. Power Sources* (2010), doi:10.1016/J.JPOWSOUR.2010.1007.1087.