

Entry

# Graphene Nanocomposite Materials for Supercapacitor Electrodes

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**Definition:** Graphene and related materials (graphene oxide, reduced graphene oxide) as a subclass of carbon materials and their composites have been examined in various functions as materials in supercapacitor electrodes. They have been suggested as active masses for electrodes in electrochemical double-layer capacitors, tested as conducting additives for redox-active materials showing only poor electronic conductivity, and their use as a coating of active materials for corrosion and dissolution protection has been suggested. They have also been examined as a corrosion-protection coating of metallic current collectors; paper-like materials prepared from them have been proposed as mechanical support and as a current collector of supercapacitor electrodes. This entry provides an overview with representative examples. It outlines advantages, challenges, and future directions.

**Keywords:** graphene; reduced graphene oxide; nanocomposite; supercapacitor; electrochemical energy storage



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## 1. Introduction

Following the enthusiastic reports about the properties of graphene and later of graphene-related materials like graphene oxide (GO), reduced graphene oxide (rGO) and further materials like crumpled graphene [1–4], suggestions of their use in electrochemistry—wherein carbon in its numerous forms has been a popular material for electrodes or as components of electrode materials has been around for decades—and in particular in devices for electrochemical energy conversion and storage (EES) [5,6] followed. These suggestions later included their use in supercapacitors [5,7–18]. As an electrode material in the latter application (as well as in battery applications), materials should meet some general requirements:

- Large surface area, more specifically electrochemically active surface area (EASA) [19,20], which will result in large interfacial capacitance;
- Defined porosity, which translates into accessibility of the EASA, enabling its use in particular at high current densities (the defining property of a supercapacitor) and thus improved capacitance retention [21];
- High electronic conductivity supporting large current densities without excessive Ohmic losses and associated Joule heat generation (with heating of a supercapacitor known to contribute to ageing [22]);
- Sufficient chemical, electrochemical, mechanical, and thermal stability affordability.

Further development beyond the pristine materials mentioned above has resulted in 3D materials like graphene foam or monoliths [3,23] and porous graphene films prepared

with a sacrificial template [24,25]. Nanocarbon materials (or carbon nanostructures) for application in energy conversion and storage including the ones addressed in this entry have been reviewed [26–28] for applications in flexible storage devices [29]; for further graphene nanomaterials, see [30]. For other nanostructured materials in energy-related applications, see [31].

Combining graphene and its relatives with other redox-active materials may result in composites having advantageous properties of both constituents, possibly without some of their flaws. These materials and their use in supercapacitors are the focus of this entry. Graphene and its relatives and their use in supercapacitors has been studied extensively and has been reviewed broadly; the respective literature is introduced in the respective sections. Use of these materials beyond supercapacitors is beyond this entry.

## 2. Graphene and Related Materials

In supercapacitors, some of the impressive properties of graphene as a quintessential 2D material are exploited: its large surface area (whether the BET-surface area or the expected EASA is another question), its high electronic conductivity, and its stability [8]. When processing the freshly made and most likely sheet-like shaped graphene into an electrode material, almost inevitably, agglomeration or restacking (sometimes very illustratively called graphitization [1]—although this term has a different and well-established meaning in the industry) caused by van der Waals and  $\pi$ - $\pi$ -interactions happens [32]. This way many advantages, in particular the large accessible surface area, are lost. Among the many approaches tried to suppress this process, the use of non-flat, i.e., crumpled, graphene has been suggested and studied extensively [1–4,33]. For enhanced ion transport even through the 2D-layers of graphene, porous graphene [4,34] and Holey graphene [35] have been suggested [36]. When combined with the defined porosity of the electrode material as tried with graphene (see, e.g., [24]), further benefits beyond avoiding restacking may become available.

Green methods for graphene preparation have been reviewed [37].

### 2.1. Graphene

The history of graphene and its relatives, with attention to the specific properties, advantages, as well as disadvantages for various possible applications beyond electrochemical energy storage and conversion, has been reviewed repeatedly [4–8,14–18,38]. In reviews, the use of graphene in numerous applications beyond energy storage and electrochemistry has been addressed [39–43].

### 2.2. Graphene Oxide

As compared to graphene, this material contains substantial amounts of oxygen, mostly in the form of functional groups; the carbon to oxygen ratio may be up to 2:1 [44]. This has some beneficial effects when comparing the properties and behavior of GO with those of pristine graphene, in particular with respect to usage as supercapacitor electrode material [45].

### 2.3. Reduced Graphene Oxide

This material obtained by chemical (hydrazine, hydroquinone etc.) or electrochemical reduction of GO still contains substantial amounts of oxygen-containing functional groups with the actual amount depending on the reducing agents and experimental parameters of the reductive treatment. Typical values of a carbon to oxygen ratio around 10:1 have been reported [44]. The functional groups may provide redox-storage; they also increase wettability and thus EASA [45]. They may further work as anchoring sites for the deposition of metal oxides [46]. The diminished oxygen content (as compared to GO) also results in a significantly increased electronic conductivity, higher by five orders of magnitude than that of GO, but still about three orders of magnitude lower than that of graphene [47]. The

surface area of GO at  $705 \text{ m}^2 \cdot \text{g}^{-1}$  [48] is significantly smaller than that of graphene, at  $2630 \text{ m}^2 \cdot \text{g}^{-1}$ .

#### 2.4. Three-Dimensional Graphene Materials

For a successful application of graphene and its relatives in a supercapacitor electrode they must be processed into an electrode. Graphene as well as rGO can be made into paper-like materials by simple suction filtration processes [38]. Such materials can be used straightforwardly as electrodes (see Section 3.1) or as support for electrodes subsequently being coated with an active material (see Section 3.5). Whether the latter combination of graphene paper as a current collector coated with an intrinsically conducting polymer ICP should be called a composite, as in [49], appears to be doubtful. Further developments of the use of graphene and its relatives either as active mass or as a support and current collector may be based on 3D structures like foams and monoliths [18,23].

### 3. Graphene in Supercapacitors

Some of the highly promising properties of graphene and its relatives have recommended their use in supercapacitors rather early, in particular in supercapacitor electrodes. This may happen in various functions ranging from being the sole active material to being an auxiliary material as reported in the following sections. General overviews on graphene in the various types of supercapacitors are available [23,50].

#### 3.1. Graphenes as Active Materials

Utilizing its large surface area and its high electronic conductivity, graphene alone is already an attractive electrode material for an electrochemical double-layer capacitor EDLC [51]. Unfortunately, aggregation, i.e., restacking, of graphene sheets tends to reduce the actually available surface area, and in addition this also makes wetting and ion transport more difficult. Mixing with other carbon materials like activated carbon, carbon black, carbon nanotubes, and mesoporous carbon has been tried [48]. These constituents act as spacers in the composites thus formed, prohibiting restacking and creating more accessible interparticle volume for electrolyte ingress and ion transport. In a typical example of graphene blended with carbon black [52], indeed, the BET surface area of the graphene nanosheets of  $267 \text{ m}^2 \cdot \text{g}^{-1}$  increased to  $531 \text{ m}^2 \cdot \text{g}^{-1}$  (GNS/CB-1) and  $586 \text{ m}^2 \cdot \text{g}^{-1}$  (GNS/CB-2) depending on the actual method of preparation. Electrodes made with these materials showed gravimetric specific capacitances of  $122.6 \text{ F} \cdot \text{g}^{-1}$  for graphene and  $150.4 \text{ F} \cdot \text{g}^{-1}$  (GNS/CB-1), respectively,  $175 \text{ F} \cdot \text{g}^{-1}$  (GNS/CB-2). Contributions from the carbon black are negligible because of its low specific surface area ( $15\text{--}42 \text{ m}^2 \cdot \text{g}^{-1}$ ). Capacitance retention with growing scan rate was not changed, as apparently the composites already provided an optimum internal morphology for ion transport.

Sometimes deplored poor ion transport between graphene layers can be remediated by using Holey graphene [35]. Performance of this material in terms of electronic conductivity and wetting can be further improved by heteroatom doping.

Hierarchical structuring of graphene-based electrode materials as a way to improve performance and stability, including some considerations already addressed in previous sections (e.g., 3D-materials), has been reviewed [23,53]. An rGO electrode with hierarchical porosity was prepared using hydrophobic spheres of  $\text{CaCO}_3$  as templates [54]. The obtained electrode kept 98.4% of its initial capacitance after 1000 cycles.

Doping of graphene, in particular substitutional doping with nitrogen, has been claimed to increase electronic conductivity of the obtained material [55]; see also [51]. Experimental data showing a much-increased specific capacitance (fourfold in [56], even after 200,000 cycles) but barely changed capacitance retention with increasing current density, do not provide clear evidence of significantly increased electronic conductivity in the absence of direct conductivity measurements but suggest otherwise changed properties, like less agglomeration or increased wetting. The major importance of nitrogen centers as a

reason of increased capacitance has been claimed without putting this claim into connection to electrochemical evidence [56].

An overview of the use of graphene in microsupercapacitors is available [51].

### 3.2. Graphenes as Conducting Additive

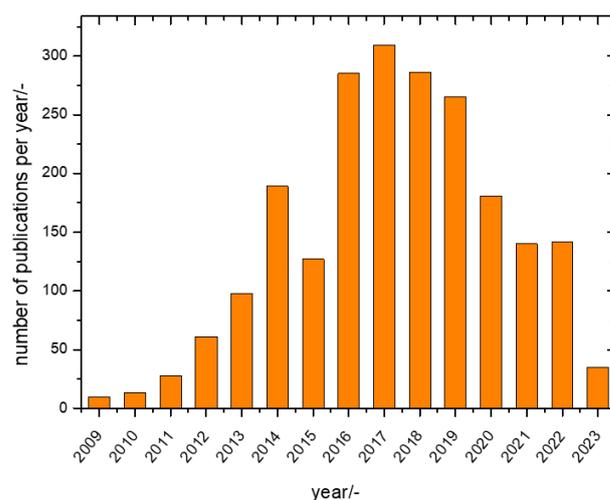
Addition of graphene or any of its relatives as a conductivity-enhancing constituent in a mixture can be implemented in various ways; in a popular procedure, the active material and the additive are dispersed aided by ultrasound. An even better effect in terms of even more increased conductivity and conceivably stability can be achieved by attaching the active materials like various metal oxides covalently to graphene nanosheets [57]. These moieties act further as spacers during processing of the material, inhibiting restacking. Capacitance retention after 6000 cycles ranges from 73 to 90%, leaving room for further improvement. The final claim that the noted improvements of the composite compared with plain graphene nanosheets could be attributed to the fact that in the composite, capacitive contributions from graphene dominate with the redox contributions from the metal oxides being negligible, flatly contradicts the reported experimental findings.

### 3.3. Graphenes in Nanocomposites

Another way to avoid restacking of graphene sheets proceeds via the combination of graphene with other materials into a composite or nanocomposite, and this avenue will be explored in this section. Whether a material qualifies as a composite or a nanocomposite has been discussed elsewhere; for examples see [58,59]. Basically, a composite can be understood as a mixture (blend) of two or more different materials aiming at combining desired properties of the components. In the case that at least one component is added with typical particle sizes on the nanometer scale, the material may be called a nanocomposite. Similar considerations may appear when considering the use of hybrid as in “hybrid nanomaterials”; this issue has been discussed before [60]. Hybrid nanocomposites with graphene have been discussed in [61].

Avoiding restacking is not the only reason; in addition and presumably as a more important reason, the combination with redox-active materials aims at increasing the charge-storage capability of the material. As pointed out above, graphene—just like every other carbonaceous material—stores charge only via accumulation of ions (whether without or with whatever type of adsorptive interaction with the electrode material is hardly relevant). Different from this, redox-active materials utilize Faradaic reactions just like in a battery electrode. To avoid negative effects of possibly slow kinetics, only thin layers and/or only superficial reactions are employed [60,62]. In such composites (the distinction addressed above is not pursued further) graphene or any of the related graphene-like materials serve mainly to increase electronic conductivity. This was already highlighted in an early review comparing electronic conductivities of some transition metal oxides showing low conductivity values, with RuO<sub>2</sub> being the only exception [46]. Further effects like corrosion protection or inhibition of dissolution of the redox-active material may also come into play, as discussed elsewhere [60,62].

The benefits of such composites were noticed some time ago, as measured in numbers of publications per year. The initially rapid growth of activity has apparently decreased more recently (see Figure 1).



**Figure 1.** Annual publication numbers of reports with “graphene” and “supercapacitor” and “composite” anywhere in the title, keywords or abstract (data from Web of Science<sup>®</sup> retrieved on 11 September 2023). Further publications addressing this topic (mentioning the keyword(s)) somewhere in the text could not be counted; when noticed and considered relevant in the present context they were evaluated below nevertheless. The very few publications on “electrochemical capacitors” or “double layer capacitors” instead of “supercapacitors” were included; the associated confusion suggests once more systematic use of technical terms. More on this topic can be found in [63,64].

Graphene has been combined with metal chalcogenides and intrinsically conducting polymers, and reviews on specifically such combinations including applications are available [46,51,59,65–86]. The electrochemical redox behavior of metal chalcogenides has been discussed repeatedly; it may range from a behavior showing in cyclic voltammetry CV and galvanostatic charge/discharge GCD curves a battery-like or a capacitor-like behavior. The latter behavior has been called pseudo-capacitive because it only looks like the behavior of a capacitor without having the respective cause. Pseudo-capacitive behavior is certainly not due to “weakly attached surface ions” as stated in [46]. Neither are “rapid Faradaic reactions within the electrode material” utilized as claimed in [8]. For a more focused discussion of charge storage associated with pseudocapacitive electrode behavior see [87]. Beyond enhanced electronic conductivity, addition of a second component to a metal chalcogenide has further benefits: because of said poor conductivity and because of volume changes during the redox processes, small particles are used. A second component may buffer these changes. In addition, a carbonaceous constituent may prevent agglomeration of the chalcogenide particles as noticed with NiO, resulting in a significantly increased specific capacitance of the composite five times that of the pristine chalcogenide [88]. NiO is attractive because of its large theoretical charge storage capability  $C_{th} = 2583 \text{ F}\cdot\text{g}^{-1}$  [21] but has a very low electronic conductivity limiting its suitability as a single electrode material. Whether use of this oxide is limited to an electrode potential window of only 0.5 V as attributed by these authors to a previous report [89] wherein this oxide was not even studied as a single compound remains inexplicable. How the formation of a composite shall mitigate this flaw is not addressed. Results of an examination of the stability of this material are not provided. Further examples of composites with nickel oxides can be found in [90]. Whether further names of devices are of any help appears to be at least questionable generally.

Among the chalcogenides, layered transition metal dichalcogenides with the composition  $\text{MX}_2$  ( $\text{M} = \text{Mo}, \text{W}, \text{Re}$  and  $\text{X} = \text{S}, \text{Se}$  or  $\text{Te}$ ) have attracted attention because of favorable properties for electrochemical storage applications [91]; for an overview see [49]. Their structure, providing pathways for fast ion movement, enables swift electrochemical reaction kinetics suggesting their use in particular for supercapacitor electrodes. Unfortunately, the materials tend to agglomerate; in addition, some of them are present as crystallographi-

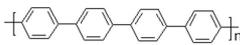
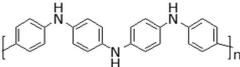
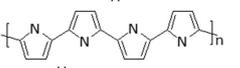
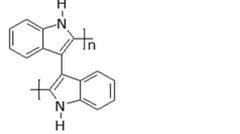
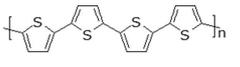
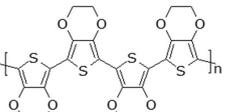
cally different phases with frequently very low electronic conductivity. Combining with graphene in particular can remedy these flaws. In addition, electronic interactions between graphene as a typical 2D-material with these layered chalcogenides also result in improved electronic transport. Data obtained with WS<sub>2</sub> [92] and MoS<sub>2</sub> [93,94] showed promising performance data, and beyond specific storage capability remarkable capacitance retentions with cycling of up to 94.7% after 10,000 cycles were stated. Layered double hydroxides (LDHs) have attracted much interest as supercapacitor electrode material because of their extremely high theoretical storage capabilities [95–97]. Unfortunately, they show low electronic conductivities. Further improvements were achieved by combining them with graphene [98]. Stability data beyond 500 cycles seem to be scant. In a more extensive review almost no capacity losses after 10,000 cycles were reported [97,99]. Composites of LDHs with rGO have also been studied with 80% of the initial capacitance left after 20,000 cycles in the best case [100]. Details of preparation have been collected [101].

Nanostructuring of a composite may even further improve performance [18,102]. A molybdenum net served as a molybdenum source during a hydrothermal process in reducing GO and forming MoS<sub>2</sub> [103]. After 4000 cycles 98.8% of the initial capacitance of the prepared electrode was retained.

Covalent attachment of molecules or molecular species to GO or rGO via the more or less amply present oxygen-containing moieties provides an additional option to prohibit restacking, and the mode of attachment may further support and enhance electronic charge propagation [104] (different from the title wherein graphene is named rGO has actually been used). A covalent organic framework attached to rGO yielded a superior capacitance contributed by the redox-active framework retaining 88% of its initial capacitance after 20,000 cycles. Covalent attachment of metal oxide particles to graphene sheets by coupling via polyaniline has improved supercapacitor electrode performance [105]. Commonly covalent attachment and grafting seem to have the same meaning. Simple deposition of metal oxide particles, sometimes called decorating, may not qualify as grafting as claimed in [106]. The obtained composites were examined for stability up to 5000 cycles, and capacity retentions better than 90% were obtained. Whether the “decoration process” (as compared to other simpler processes) contributed to this was not reported.

Further examples of composites of graphene and its relatives with metal chalcogenides can be found in overviews and selective reviews [48,107–114]. Particular attention to preparation and fabrication processes has been paid in [115].

The second class of materials combined with graphene or its relatives has ICPs [116–120]. Figure 2 provides an overview and some representative examples of ICPs.

		conductivity/S·cm <sup>-1</sup>
	poly- <i>para</i> -phenylene (PPP)	10 <sup>2</sup> .. 10 <sup>3</sup>
	polyaniline (PANI)	30 .. 200
	polypyrrole (PPy)	10 <sup>2</sup> .. 7.5·10 <sup>3</sup>
	polyindole (PIND)	0.1 .. 1
	polythiophene (PTh)	10 .. 10 <sup>3</sup>
	polyethylenedioxythiophene (PEDOT)	300 .. 500

**Figure 2.** Representative ICPs and corresponding monomers (conductivity data apparently—although practically nowhere clearly stated—of the oxidized state of the ICP based on literature sources [most

of them secondary without providing original sources of data] [121–132]. In the neutral [not to be confused with the reduced] state, ICPs are insulators or semiconductors with conductivities around  $10^{-5}$  to  $10^{-10}$  S·cm<sup>-1</sup> [133]).

Their use as single materials or copolymers in devices for electrochemical energy storage and conversion has been studied and reviewed [134–142]. Their successful implementation in practical devices has been hindered by various factors:

- Volume change (swelling/shrinking) during oxidation/reduction caused by ingress/egress of charge-balancing counterions with their solvation shells.
- Electronic conductivity insufficient for high current densities typical of supercapacitors; in addition conductivity may change substantially as a function of state of oxidation.

ICPs can be electrodeposited directly on a substrate subsequently serving as current collector and mechanical scaffold in an electrode. This combination hardly qualifies as a composite as suggested for graphene paper used as support with a coating with PANI in [47]. They can also be prepared by chemical polymerization as powders; these are subsequently processed into an electrode following procedures well-established with other powdery electrode materials. In the latter case addition of a conducting ingredient (carbon powder, etc.) was almost a natural option to counter the second flaw addressed above. The first flaw can be mitigated to some extent by using small particles (nanostructuring [102], see also [62,143]). Considering the advantages of graphene and its relatives its use as such conducting additive was only a natural consequence. Composites of PANI for diverse applications including supercapacitors have been inspected [47,144–148]. A layer-by-layer composite of PANI and rGO kept 93% of its initial capacity after 1000 cycles, and this was attributed to the layered structure [97]. More on layered structures and their possibilities for supercapacitors can be found in [149]. The difficult to understand description in [61] casts unnecessary doubts on this construction. A porous graphene hydrogel filled with PANI by electropolymerization showed an optimum capacitance value at a moderate loading with PANI [150]. The conclusion that higher loadings result in poorer utilization because of Ohmic resistance of the ICP confirms considerations reported elsewhere [21].

A composite of rGO and PPy had twice the specific capacitance of plain PPy and kept 83% of its initial capacitance after 5000 cycles even at high current density [151]. For more examples of composites with PPy see [152]. A graphene paper coating deposited on carbon cloth and subsequently modified with a thin coating of PEDOT grown by electrooxidation of the monomer yielded an electrode which may qualify as not exactly a composite [153]. The highest specific gravimetric capacitance was obtained at the shortest deposition time suggesting best material utilization in line with early considerations of mass utilization in supercapacitor electrodes [21]. A major increase of specific capacitance with the graphene interlayer was attributed to differences in deposition mechanism and different porosities of the substrates. Stability was not examined. Further examples of ICPs with graphene and its relatives can be found [154–156].

These composites can be prepared by chemical polymerization, i.e., oxidation of monomers, in a solution containing also dispersed graphene, GO, or rGO. The actual composition of the composite depends on the experimental conditions, in particular composition of the reactant solution. Agglomeration of graphene, etc., as a potential problem with chemical polymerization—which is actually a volume reaction—is avoided with electropolymerization as an interfacial process with much lower room-time yields. Electropolymerization with the current collector as a substrate is another option. Again aniline monomers are dissolved and graphene, etc., is finely dispersed. As reported [157] this approach has rarely moved beyond the laboratory scale. Further examples of composites of graphene with ICPs can be found elsewhere [158–160], and composites with further carbon nanostructures have been discussed in [161].

Finally both redox-active constituents can be incorporated together with graphene in a ternary composite. Examples and advantages have been pointed out before [60,162,163]. As pointed out in the latter reports authors almost always hardly attempt a rational assignment

of whatever task to a constituent. This also applies to the composite of NiO (known for its large charge storage capability), graphene, and PPy as a final coating [164]. Using a polymeric binder and a solvent the powdery composite was made into a liquid which could be dropped on a copper foil current collector modified first with nanowires of  $\text{Cu}(\text{OH})_2$ . For unknown reasons the authors did not examine the stability and capacitance retention of this rather complex material.

A few composites of both metal chalcogenides and ICPs with Holey graphene used for enhanced electronic conductivity and better ion transport can be found in [35].

Composites of graphene with metal oxide frameworks (MOFs) have been reviewed with particular attention to synthetic aspects [165]. Capacitance retentions up to 99% after 10,000 cycles are noteworthy. Composites with metals are apparently rare; one with gold is noteworthy because of its exclusive ingredients, not because of performance [166].

Composites of graphene and GO with carbon nanotubes (CNTs) have been prepared in various ways as an option to avoid restacking of graphene and to generally improve properties of the single constituents [66,167]; for an example with a sandwich structure, see [168]. After 2000 cycles the initial capacitance was increased by 20%. A self-assembled composite of GO or rGO (the report is inconclusive on this detail; possibly the annealing of the rGO/CNT composite at 200 °C helped in this conversion) and CNTs kept 98% of its initial capacitance after 10,000 cycles [169]. Poly(ethyleneimine)-modified graphene was prepared by chemical reduction of GO in the presence of the cationic polymer; subsequent self-assembly with acid-oxidized multiwalled CNTs yielded a composite film [170]. CNTs grown directly on graphene showed promising electrochemical performance [171], but stability was not examined.

Theoretical work on graphene composites is scant. Mechanical properties which may become relevant during large scale manufacturing processes have been discussed [172,173].

### 3.4. Graphenes as a Coating

A procedure to coat metal oxide particles initially for use in lithium ion batteries has been reported [174]. A coating with rGO of  $\text{V}_2\text{O}_5$  nanoribbons applied by a different procedure significantly improved their electrochemical performance as supercapacitor electrode material by enhancing the electronic conductivity of the composite [175]; an overview on composites with  $\text{V}_2\text{O}_5$  is available [176]. Similar benefits were observed with nanorods of  $\text{Mn}_2\text{V}_2\text{O}_7$  [177], nanoarrays of  $\text{FeNi}_2\text{S}_4@\text{Co}_9\text{S}_8$  [178] and nickel sulfide particles [179] all coated with rGO.

### 3.5. Graphenes as an Auxiliary Material

Graphene can be made into a foam which subsequently is filled with active materials like metal chalcogenides or ICPs [23]. The foam provides structural stability and efficient electron transport. Capacitance retentions up to 83% after 15,000 cycles for a filling with PANI nanofibers confirm this assumption [180]. A graphene foam filled with  $\text{NiCo}_2\text{O}_4$  showed 92% retention after 4000 cycles [181]. Graphene coating of current collectors can be used for corrosion protection [182]. It has also been identified as an advantageous interface between support/current collector and active electrode mass because of its capability to improve electronic coupling [183].

## 4. Trends and Developments

Given the frequently and always enthusiastically praised attractive properties of graphene and its relatives investigation of their utilization in the various functions outlined above will certainly continue and in the case attractive and economically viable procedures are developed, may even be intensified. Possibly the rather disillusioning conclusion including the statement in [184] that all these graphene-containing composites did not make it to the market will be overwritten. For another perspective from roughly the same point in supercapacitor development see [185]. Whether the claimed equivalence [23] with secondary batteries in terms of energy density (as usual not specified whether gravimetric

or volumetric) will be achieved remains doubtful because of a fundamental difference: in a battery the electrode material is utilized as far (and as deeply) as possible whereas supercapacitor electrodes mostly operate at the surface hardly utilizing any material deeper in the electrode. Possibilities to integrate supercapacitors into electronic circuits as miniature or even microsupercapacitors will grow with the development of suitable manufacturing technologies affecting the aspects addressed in the following sections.

#### 4.1. Graphenes as Active Material

Because approaches towards the inhibition of restacking and agglomeration of graphene have been identified, research and development of plain graphene as an active material will mostly pursue cheaper production methods. The use of crumpled graphene, already successfully commercialized, will continue and possibly grow in volume.

#### 4.2. Graphenes as Conducting Additive

Currently, the two roles of conducting additive and constituents of a composite are hard to distinguish. Other types of carbon will presumably stay popular in this use, and graphene and its relative will most likely be treated as constituents of a composite.

#### 4.3. Graphenes in Composites

Although the frequency of research publications with graphene, etc., as a constituent in a composite appears to have passed a maximum (see Figure 1), activities continue. They should—as addressed clearly before [60,62,162]—be examined for stability under realistic conditions (with respect to current densities and temperatures in two electrode setups).

#### 4.4. Graphenes as a Coating

When moving from discovery or optimization of an active material to an electrode mass and finally a complete device, practically as well as economically feasible current collectors must be carefully considered. Cheap but less corrosion-stable materials may become acceptable after coating with graphite or graphene; one more reason to pursue cheaper and more easily processable types of graphene further.

#### 4.5. Graphenes as an Auxiliary Material

Graphene and its relatives in various 3D shapes as host bodies for redox active materials may grow in importance with development of economically more viable processes and availability of more and promising stability data.

### 5. Conclusions and Prospects

Because of the remarkable width of application possibilities a unified perspective is hard to provide. Crumpled graphene will presumably grow in volume of its use in commercial devices, and other forms may also grow given long-term stable composites with spacers showing promising performance can be identified. In terms of possible combinations and thus conceivable further developments composites of graphene and its relatives will attract further researchers' activities. They should examine more carefully and extensively long-term stability of materials and devices (beyond the initial 500 or 1000 cycles); without reliable data on this from an engineering point of view, most important properties' success in the market will stay a distant aim. Claims for hybrid devices wherein one electrode takes care of energy density, the other of power density, may be unnecessary.

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