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APPLICATION OF GRAPHENES IN SUPERCAPACITORS (REVIEW)[1]

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Abstract. This review examines the literature, mainly of recent years, on the current topic of using graphenes in supercapacitors. The influence of the porous structure, doping and irradiation of graphenes is considered. Methods for producing graphenes, composites of graphenes with metal oxides, sulfides and selenides, with metal particles, with electron-conducting polymers, with MXenes, as well as quantum dots are considered. Electrochemical characteristics are given for the types of graphene considered.

Keywords: *graphenes, oxides, sulfides, selenides, electron-conducting polymers, polyaniline MXenes, quantum dots*

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LIST OF ABBREVIATIONS

AC – activated carbon
RGO – reduced graphene oxide
EDL – electrical double layer
SWCN – single-walled carbon nanotubes
PVA – polyvinyl alcohol
TEM – transmission electron microscopy
CNT – carbon nanotubes
SSA – specific surface area
CVA – cyclic voltammetry
EIS – electrochemical impedance spectroscopy
AC – activated carbon
CNT – carbon nanotubes
EDX – energy dispersive X-ray spectroscopy
EIS – electrochemical impedance spectroscopy
FESEM – Field emission scanning electron microscopy
FTIR – Raman infrared spectroscopy with Fourier transform
GCD – galvanostatic cycling
GO – graphene oxide
GQD – Graphene quantum dots
HRTEM – High-resolution transmission electron microscopy
PANi – polyaniline
PL – photoluminescence
PP – polyporphine
PPy – polypyrrole
PT – polythiophene
rGO – reduced graphene oxide
SEM – scanning electron microscopy
TEM – transmission electron microscopy
Uv-vis – ultraviolet visible spectroscopy
WSC – Wire supercapacitor
XRD – X-ray diffraction

INTRODUCTION

Recently, graphenes and their derivatives have been used as promising electrode materials for electrochemical supercapacitors [1, 2, 3–44]. Graphenes were discovered only about 15 years ago, for which their creators received the Nobel Prize, and almost immediately the remarkable properties of graphenes were discovered, which open up wide possibilities for their use in various sectors of the national economy, including chemical current

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[1] Based on the materials of the report at the 17th International Meeting “Fundamental and applied problems of solid state ionics”, Chernogolovka, June 16–23, 2024.

sources and electrochemical capacitors. A single layer of graphene sheet provides a specific external surface of up to 2,675 m^2/g available for liquid electrolyte, compared with an external specific surface of approximately 1,300 m^2/g for an individual single-walled carbon nanotube (SWNT). Graphene layers form plates of several single graphene layers, as a result of which the surface available for the electrolyte decreases. However, encouraging results have recently been obtained for ECSCs with graphene electrodes which often have the pseudo-capacity of Faraday redox reactions in addition to the capacity of the double electric layer (EDL).

Reduced graphene oxide (RGO) is usually obtained using a modified Hammers method. According to this technique, the initial graphite powder is added to a mixture of concentrated sulfuric acid and nitric acid during stirring and cooling, and after a while, three times the amount of potassium permanganate relative to graphite is added to the same mixture. Then a solution of hydrogen peroxide is added to it and after an hour it is diluted with three times the amount of distilled water. After settling for several hours, the upper transparent layer is decanted. The suspended sediment is filtered, washed with distilled water and dried at room temperature to a constant weight. As a result, a dry powdered graphite oxide is obtained, which is reduced by rapid heating to a temperature of 1000 °C. At the time of reduction, the material is stratified with a multiple increase in its volume (exfoliation). The final product is a powder of thin monolayers containing from 1 to 10 graphene monolayers in plates, which have a size range from 1 to 10 microns in the lateral direction. These monolayers, in turn, are grouped into agglomerates, between which pores with a wide (4–5 orders of magnitude) range of sizes are formed: micropores, mesopores, and macropores [8, 19–44].

It should be noted that the review analyzes many recent publications, from 2019 to 2024. In recent years, a number of reviews on the use of graphenes in supercapacitors have been published, for example [20, 21, 43]. However, they lacked the following important sections, which are systematically considered in this review: the effect of doping and irradiation, the effect of porous structure, quantum dots, graphene composites with metal oxides, with electron-conducting polymers, with MXenes.

An important place in the review is occupied by materials consisting of graphene composites with electron-conducting polymers (polyaniline, polypyrrole), with metal oxides and with MXenes. Supercapacitors with these materials have high electrochemical characteristics.

1. GRAPHENES AND THEIR COMBINATIONS WITH OTHER CARBON MATERIALS

Graphene electrodes are characterized by high reversibility of charge-discharge processes. This is clearly seen from Fig. 1, which shows the dependences of specific capacitance on specific current and on the number of galvanostatic charge/discharge cycles for two different electrodes with a specific surface area (SSA) of 450 and 520 m^2g^{-1}, made on the basis of RGO, which was applied to nickel felt. Electrochemical measurements were carried out at 30 wt.% KOH [45]. As you can see, when the specific current is changed by an order of magnitude, the capacity has hardly changed. It is also seen that for 500 cycles, the capacity remained practically constant.

In [18], it was found that graphene oxide has proton conductivity, and in [19], a supercapacitor consisting of a graphene oxide separator and two electrodes based on reduced graphene oxide was manufactured on this basis.

In [46], graphenes were obtained by three different methods and were investigated as electrode materials in electrochemical supercapacitors. The samples obtained by exfoliation of graphite oxide and nanodiamond transformation have a high specific capacity in H_2SO_4, the value reaches 117 F/g. When using an ionic liquid, the operating voltage was increased to 3.5 V (instead of 1 V in the case of an aqueous H_2SO_4 solution), the specific capacity and energy density are 75 F/g and 31.9 Wh/kg, respectively. The performance characteristics of graphenes, which are directly related to the number of layers and the size of the SSA, are superior to single-wall and multi-wall carbon nanotubes (CNTs).

Recently, many articles have been published on the use of graphenes in ECSCs. The study [47] is a summary of the latest developments in the use of graphene as a supercapacitor electrode in the form of foam (3D), thin layers (2D), nanofibers (1D) and nanodots (0D). This article provides a brief look at the discovery and advancement of graphene, followed by a study of the theoretical and experimental approaches used to produce top-quality graphene. In addition, the article focuses on the manufacture of electrodes while maintaining their basic characteristics. Their special effectiveness as an anode in supercapacitors is emphasized. The article concludes by identifying the main problems encountered and potential prospects.

Graphenic acid (GA) is a conductive graphene derivative dispersed in water that can be produced on a large scale from fluorographene. The paper [48] describes a study of synthesis with high reproducibility

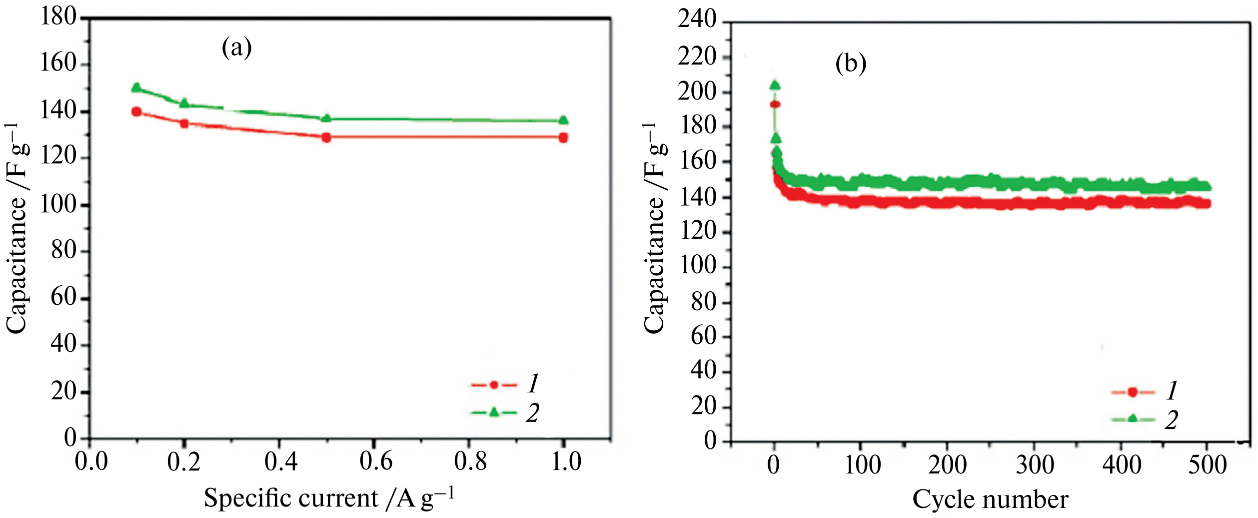

Fig. 1. Dependences of the specific capacitance on the specific current (a) and the dependences of the specific capacitance of 30 wt.% KOH on the number of galvanostatic charge/discharge cycles (b) at a specific current of 0.1 A/g for two RGO-based electrodes with different specific surface area values [45].

for the manufacture of GA. Charge/discharge cycling was performed. GA was tested in a two-electrode cell with a sulfuric acid electrolyte. The speed stability test showed that GA could be repeatedly cycled at a current density in the range from 1 to 20 A/g without loss of capacity. The cyclic stability experiment showed that even after 60,000 cycles, the material retained 95.3% of its specific capacity at a high current density of 3 A/g.

In [49], the concept of bipolar electrochemistry is used to develop a single-stage and controlled process for simultaneous exfoliation of a graphite source and for deposition of graphene oxide and reduced graphene oxide layers on conductive substrates. Electrochemical analysis performed on symmetrical cells showed a specific capacitance of 1.932 mF/cm^2 for high-quality reduced graphene oxide deposited on the negative electrode and 0.404 mF/cm^2 for graphene oxide deposited on the positive electrode at a scanning rate of 2 mV/s. The devices have also shown high stability to periodic and repetitive DC charge/discharge cycles, which is suitable for energy storage in supercapacitors. In the frequency domain, frequencies of 1820 and 1157 Hz were obtained with an impedance phase angle of –45° for devices based on positive and negative electrodes, respectively, which is a promising characteristic for AC filtration applications.

Recently, the rapid development of graphene-based supercapacitors has led to the need for devices with a certain adaptability, which will be a fundamental advantage in innovative electronic devices. Various materials are tested to ensure the appropriate properties. Graphene, which has unique properties such as high density and high conductivity, is considered as a potential candidate for use as a building material for superconductors. In [50], various aspects of graphene-based superconductors, their types, metal/nonmetal/polymer doping, as well as oxides and reduced oxides of superconductors incorporated into graphene were studied. To summarize, the processes followed by the researchers were compared to find out which of them is the most appropriate way to obtain the best electrochemical characteristics.

In [51], it was found that a supercapacitor with graphene-based electrodes has a specific energy density of **85.6 Wh/kg** at room temperature and **136 Wh/kg** at 80 °C at 1 A/g. These energy densities are comparable to those of a nickel-metal hydride battery, but the supercapacitor can be charged or discharged in seconds or minutes. The key to success was the ability to take full advantage of the high density of single-layer graphene by preparing curved graphene sheets, which makes it possible to form mesopores accessible and wetted with environmentally friendly ionic liquids capable of operating at a voltage of >4 V.

1.1. The effect of porous structure

The characteristics of the porous structure significantly affect the electrochemical characteristics of graphene electrodes and corresponding supercapacitors. The characteristics of the porous structure include the specific surface area (SSA), the volume ratio of micro (hierarchical type of porous nano) pores, mesopores and macropores, the total porosity and structures of the electrodes. The hierarchical type of porous structure means that the smallest particles stick together into agglomerates, which, in turn, agglomerate into larger agglomerates, etc.

It was established in [52] that zinc chloride is an ideal pore forming agent, and in combination with capillary drying can set the specific surface area of graphene from 370 to more than 1000 m^2/g. With a good balance of porosity and density, a granular graphene electrode with a thickness of up to 400 microns provides a capacity of 150 F/cm^3 in an ion-liquid electrolyte corresponding to a volumetric energy density of **~65 Wh/l**. This study presents the principle of designing electrode materials for next-generation energy storage devices.

Graphene-based supercapacitors are attracting more and more attention due to the possible high SSA, high electron mobility and many other excellent properties of graphene. Nevertheless, in some experiments, contemporary graphene electrodes are considered in [53] in order to solve the problems of combining graphene with other types (for example, with EPP, metal oxides, atomic clusters, nanostructured electrodes, etc. to overcome obstacles such as small surface area, low electrical conductivity, and low capacitance, which significantly limits their electrochemical characteristics for supercapacitors. This review discusses various principles of hybridization (conductor hybridization), and recommendations on hybridization approaches to address these issues. It provides high values of SSA to 960, 1330, and 1530 m2/g and very high values of specific capacity of 530, 780, and 990 F/g.

Fiber supercapacitors (FSC) can be used to power flexible devices such as wearable electronics and smart textiles. [54] describes highly porous activated graphene (AG), which is embedded in graphene fibers to improve the electrochemical characteristics of FSC based on the capacitance of a double electric layer (EDL). Wet spinning of AG in a mixture with graphene oxide (GO) and subsequent chemical reduction of GO to reduced graphene oxide (rGO) make it possible to produce continuous and conductive graphene fibers. AG powders with a very high concentration significantly improve the electrochemical characteristics of FSC. In particular, an rGO/AG fiber with an 80/20 rGO/AG mass ratio reaches a specific surface capacity of **145.1 mF/cm^2** at a current density of 0.8 mA/cm^2 with a PVA/LiCl gel electrolyte. This corresponds to a surface energy and power density of 5.04 μWh/cm^2 and 0.50 mW/cm^2 for FSC, respectively. In addition, flexible FSCs using rGO/AG fibers demonstrate high cycling capacity with 91.5% capacity retention after 10,000 cycles. This work shows significant potential in the production of AG-based fibers for the development of highly efficient flexible FSCs.

In [55–57], it was described how the abundant bio-waste is efficiently converted into porous graphene sheets at a low temperature of 900 °C by using potassium hydroxide (KOH) as an activation agent to create porosity, as well as a catalyst to induce graphitization using a simple synthetic approach. The resulting carbon material has good textural properties, such as high SSA (2,308 m^2/g), large pore volume (1.3 cm/g), graphene sheet morphology with an interlayer d-distance of 0.345 nm and highly ordered sp-carbon, which is confirmed by detailed textural analysis. Due to its numerous synergistic properties, the material was tested as an effective electrode material for use in supercapacitors and provided a high specific capacity of **240 F/g at 1 A/g**. In addition, the assembled symmetrical supercapacitor demonstrated fast rate capability to retain 87% of capacity at high current (50 A/g), exceptional cyclic stability (93% capacity retention after 25,000 cycles) and a high energy density of **21.37 Wh/kg at a high power density of 13,420 W/kg**.

Obtaining a carbon electrode with high gravimetric and volumetric capacity under heavy loads is crucial for supercapacitors. At the same time, defective graphene nanospheres (GNS) meet the above requirements well [56–62]. The morphology and structure of the GNS are controlled by the microwave heating time and the iron content. A typical GNS with an SSA of 2,794 m^2/g, a pore volume of 1.48 cm^3/g and a packing density of 0.74 g/ cm^3 sets high gravimetric and volumetric capacities of **529 F/g and 392 F/cm^3 at 1 A/g** with a retention of 62.5% of the capacity at 100 A/g in a three-electrode system of 6 mol/l KOH. In a two-electrode system, the GNS has an energy density of **18.6 Wh/kg** (13.8 Wh/l) with a high specific power of 504 W/kg.

Redox covalent organic frameworks (COFs) represent a new class of energy storage materials due to their significant number of active sites, well-defined channels, and high surface area. However, their low electrical conductivity and low electrochemical accessibility to active centers seriously limit their practical application. The article [57] describes the manufacture of an electrode based on anthraquinone COFs/composite aerogel and graphene (DAAQ-COFs/GA) by electrostatic self-assembly between negatively charged graphene oxide (GO) nanolayers and modified positively charged DAAQ-COFs nanoflowers. Due to its hierarchical porous structure and fast reactions of redox centers, the electrode has a high specific capacity of **378 F/g at 1 A/g** and fast kinetics with a capacitive contribution of about 93.4% at 3 mV/s. In addition, the DAAQ-COFs /GA electrode, which does not contain a binder, and the pure graphene aerogel (GA) electrode were assembled into an asymmetric supercapacitor (ASC) with an energy density of up to 30.5 Wh/kg at a specific power of 700 W/kg. This work demonstrates the great potential for the development of high-performance energy storage devices based on COF.

[58] presents a simple method for obtaining graphene with a hierarchical porous structure by activating graphene oxide (GO) using a two-stage thermal annealing process. First, GO was processed at 600 °C by rapid thermal annealing in air, followed by thermal annealing in N_2. The prepared graphene powder contained a large number of slit nanopores with a high SSA of 653.2 m^2/g and a microporous surface area of 367.2 m^2/g. The porous structure could be easily adjusted by controlling the degree of oxidation of GO and the second annealing process. When graphene powder was used as a supercapacitor electrode, a specific capacity of **372.1 F/g** was achieved at **0.5 A/g** in electrolyte 1 M H_2SO_4. The performance of the supercapacitor was very stable, demonstrating a 103.8% retention of specific capacity after 10,000 cycles at 10 A/g. The effect of a porous structure on the performance of a supercapacitor has been systematically studied by varying the ratios between micro-, meso-, and macropores.

Activated reduced graphene oxide (a-rGO) is a material with a rigid 3D porous structure, high SSA, and a hierarchical type of porous structure. Using varying activation parameters and post-synthesis machining, in [59] two sets of materials with a wide range of SSA values of about 1000–3000 m^2/g were obtained, as well as significant differences in pore size distribution and surface oxygen content. The efficiency of activated graphene as an electrode in a supercapacitor with a KOH electrolyte correlated with the structural parameters of the materials and water absorption properties. It was found that a-rGO is a hydrophobic material, as evidenced by the negligible value of the BET concentration in H_2O, determined by analyzing the isotherms of water vapor sorption. However, the total pore volume determined by water vapor sorption and liquid water sorption practically did not differ from the volume obtained by analyzing nitrogen sorption isotherms. The best gravimetric and volumetric capacities in KOH electrolyte were not achieved for samples with the highest BET SSA (N_2) value for materials with 80–90% of the total pore volume in micropores and an increased BET SSA (H_2O). A comparison of the characteristics of electrodes made using rGO and a-rGO shows that a more hydrophilic surface is favorable for charge storage in supercapacitors with KOH electrolyte.

Fig. 2 shows the integral and differential curves of the pore size (width) distribution. As we can see, the differential curve has two obvious maxima and one weakly pronounced maximum. The SSA according to BET is equal to a very large value of **3,030 m^2/g**.

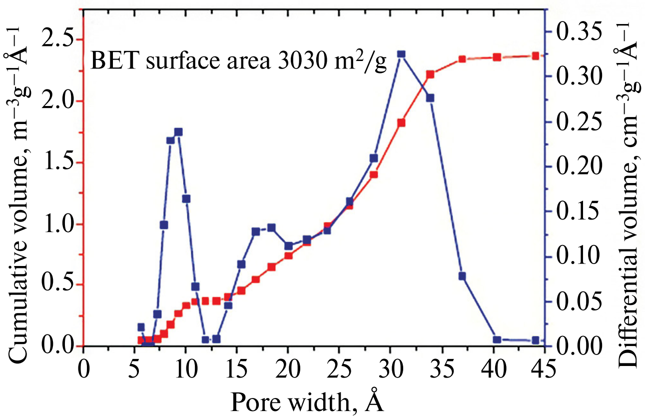

Fig. 2. Integral and differential curves of pore size (width) distribution [59].

In [60], it is reported about the development of a seamless **mesoporous carbon sheet** consisting of continuous graphene walls, which **exhibits** unusually high stability under high stress conditions. This material has a high SSA of 1,500 m^2/g and contains very few carbon edges (only 4% of the amount present in conventional activated carbons), and it can be used to assemble symmetrical supercapacitors with high stability for the electrolyte 1 MEt_3MeNBF_4/propylene carbonate. Operating at a high voltage of 4.4 V leads to a 2.7-fold increase in energy density compared to using conventional activated carbon.

The production of black liquor, lignin, carbon nanolayers, and multilayer graphene obtained by catalytic nickel graphitization was carried out in order to obtain electrode materials for supercapacitors (Ni@WE) in an environmentally friendly manner [61]. NaCO activation, nickel doping, and catalytic graphitization were performed synchronously; at the same time, the natural hierarchical porous structure of the wood was partially preserved. Cyclic voltammetry **(CV)**, galvanostatic charge-discharge spectroscopy and electrochemical impedance spectroscopy (EIS) Ni@WE confirmed that the sample sintered at 1000 °C has a specific capacitance of 163.7 F/g at a scanning frequency of 0.2 V/s. In addition, a higher energy density of **26.2 Wh/kg** with a power density of 124.6 W/kg was obtained in the ECSC, and 89.37% of the capacity remains even after 2000 cycles.

Electrochemical properties and characteristics of high-density energy storage of a solid-state supercapacitor based on graphene nanolayers are described in [3]. The graphene electrode is made in an electrolyte containing 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) (ionic liquid) $LiClO_4$. The doping additive was enclosed in a polymer matrix in the form of a gel. The mesoporous graphene electrode was formed by dispersion in amorphous polyvinylidene fluoride, resulting in graphene with a minimum number

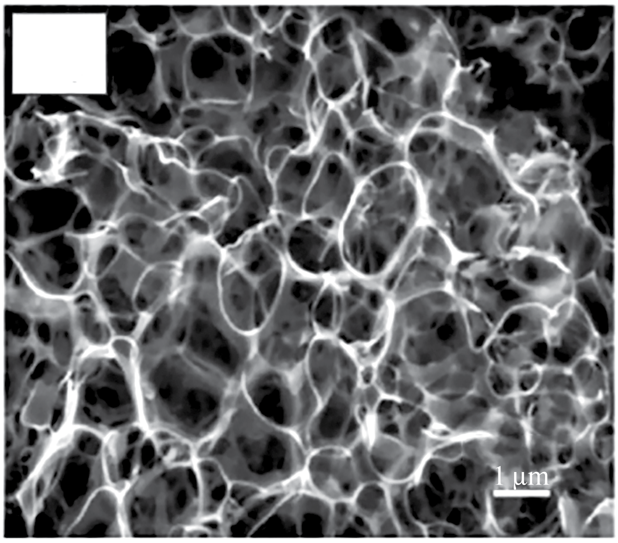

Fig. 3. SEM image of 3D graphene with macropores formed by removing the Na_2CO_3 pore forming agent [48].

of layers (<5 layers). Using the abundance of ions in an ion-liquid gel electrolyte and their efficient access to graphene layers through mesopores, a high specific capacity of **214 F/g** was obtained based on cyclic voltammetry data. Impedance studies show low charge transfer resistance and Warburg impedance, which indicates a high diffusion capacity for ion transport. The charge-discharge data show that the graphene supercapacitor, due to the presence of a wide (~ 2 V) potential window in the ion-liquid electrolyte gel, significantly increased the energy density to **33.3 Wh/kg at a power density of 3 kW/kg with a high ~ 3 A/g** discharge current density. It is reported about the integration of graphene supercapacitors with solar cells and the storage of electricity generated by light.

Three-dimensional (3D) porous graphene with planar nanopores and a hierarchical porous structure attracted great interest in [48] due to its use in supercapacitors because of its high SSA, very high conductivity, and unique porous structure. Combining the advantages of both porous materials and graphene, 3D porous graphene is considered as the embodiment of the idea to create a hierarchical hybrid with complex electrochemical characteristics in order to obtain high specific energy. In this review, the achievements of recent years in the field of manufacturing 3D porous graphene-based structures with micro-, meso- and macropores were summarized, as well as the relationship between structure and electrochemical properties was investigated, and their application in supercapacitors was discussed. Fig. 3 shows a SEM image of 3D graphene with macropores formed by removing the Na_2CO_3 pore forming agent.

In [48], porous particles with a hierarchical porous structure of activated carbon coated with graphene were obtained by spray drying of an aqueous suspension of GO/maltodextrin followed by carbonation and activation. The manufactured core-shell particles had a **high specific surface area (up to 2,457 m^2/g) and showed very high specific capacity (up to 405 F/g at 0.2 A/g**, 299 F/g at 1 A/g and 199 F/g at 50 A/g) along with excellent cycling stability, high energy density and high power density in KOH electrolyte. In addition, the spontaneous formation of the core-shell structure during spray drying was confirmed by calculations using the DFT method with XPS chemical analysis and the TEM method. This designed and controlled spray drying strategy can be implemented to develop new core-shell composite materials for potential applications in energy storage, catalysis, and adsorption.

Fig. 4 shows the differential pore size (width) distribution curves for various materials with a hierarchical porous structure described in [48].

1.2. The effects of doping and radiation

One of the effective ways to increase the electrochemical characteristics of graphenes is to dope them with various chemicals. According to [50], nitrogen-doped graphene is produced by the microwave method with EDA (ethylenediamine) as a nitrogen source. The experimental results show that nitrogen atoms from grafted EDA molecules on the graphene surface are effectively doped into graphene lattices. The NGS sample (nitrogen-doped graphene nanosheets) demonstrates high specific capacities of **197 and 151 F/g** at current densities of 0.5 and 5 A/g in an aqueous solution of 6.0 mol KOH, respectively. In addition, the supercapacitor demonstrates a high ability to operate at high currents: saving 77 and 70% at current densities of 5 and 40 A/g, respectively. In addition, this results in a capacity reduction below 2% after 5,000 charge and discharge cycles, which indicates long-term electrochemical stability.

In [51], N-doped graphenes based on graphene oxide and 3,3’,4,4’-tetraaminodiphenylox (TADPO) were obtained using a single-stage hydrothermal method. The data obtained indicate that benzimidazole rings were formed during the reaction, and the nitrogen content by weight in the resulting material ranged from 12.3 to 14.7%, depending on the initial concentration of TADPO. Due to the redox activity of benzimidazole rings, the new N-doped graphene materials demonstrated a high specific capacity, reaching **340 F/g** at 0.1 A/g, which was significantly higher than that of a sample of reduced graphene oxide obtained under similar conditions without the use of TADPO

(169 F/g at 0.1 A/g). The resulting supercapacitor also demonstrated good cyclic stability after 5,000 cycles.

In [52], the two-stage sol-gel method was used to obtain graphene samples doped with nitrogen with a large surface area, differing in the values of the SSA and nitrogen content. In some electrolytes, the specific surface area and porosity had a higher effect on the capacitance characteristics of graphene than the nitrogen content. All samples had higher capacitance characteristics than graphene oxide and a sample without nitrogen, but with a higher acidic electrolyte content than an alkaline one, which gives a volumetric specific capacity of ~118 F/cm^3 with Coulomb efficiency >99% and capacity retention >80% after 10,000 consecutive cycles. Based on the weight of the active material, the maximum gravimetric energy density reached **39 Wh/kg** in an acidic electrolyte at 0.1 A/g, which is almost 2.6 times higher than that of graphene oxide without nitrogen used in this study.

In [63], single-chamber instantaneous Joule heating was developed for the synthesis of nitrogen-doped graphene, which does not use solvents and catalysts, and graphene flash-doped with nitrogen (FNG) was obtained. Precursors of amorphous carbon black and urea rapidly transform into high-quality graphene in less than 1 s under the action of a short electrical pulse with a bright flash of blackbody radiation. The finished FNG product is characterized by high graphitization and hierarchical porous structure. It provides a high surface area-normalized capacity of 152.8 μF/ cm^2 at 1 A/g, a high speed of charging and discharging processes with a high capacity retention of 86.1% even at a **very high current of 128 A/g, and a relaxation time of 30.2 ms.** In addition, the assembled symmetrical quasi-solid state supercapacitor has a **high energy density of 16.9 Wh/kg and a maximum specific power of 16.0 kW/kg**, as well as great cyclic stability (91.2% of the initial capacity is retained after 10,000 cycles). These high characteristics show that FNG is a promising candidate for the use of high-performance supercapacitors.

3D sponge graphene doped with nitrogen (NG) was economically prepared in [53] using a new one-step method from polyethylene terephthalate (PET) waste mixed with urea at various temperatures. The effect of temperature and the amount of urea on the formation of NG has been investigated. Measurements using cyclic voltammetry and impedance spectroscopy have shown that nitrogen fixation, which affects the structure and morphology of the prepared materials, improves charge propagation and ion diffusion. The obtained materials demonstrate high characteristics of supercapacitor electrodes with a specific capacity of up to **405 F/g at 1 A/g**. For an optimal sample, **high values of energy density of 68.1 Wh/kg and specific power of 558.5 W/kg** in 6 M KOH were recorded. The NG samples showed high cyclic stability with 87.7% capacity retention after 5,000 cycles at 4 A/g. Thus, the prepared NG is considered a promising, cheap material used in energy storage systems, and the method used is a cost-effective and environmentally friendly method of mass production of NG, and also opens up waste recycling opportunities for a wide range of applications. Fig. 5 shows the CVA curves, which show that they have a shape close to rectangular, which corresponds to the charge of the EDL. At low currents, the influence of Faraday reactions is also visible, which is expressed in the characteristic deviation of the shape of these curves from the rectangular one.

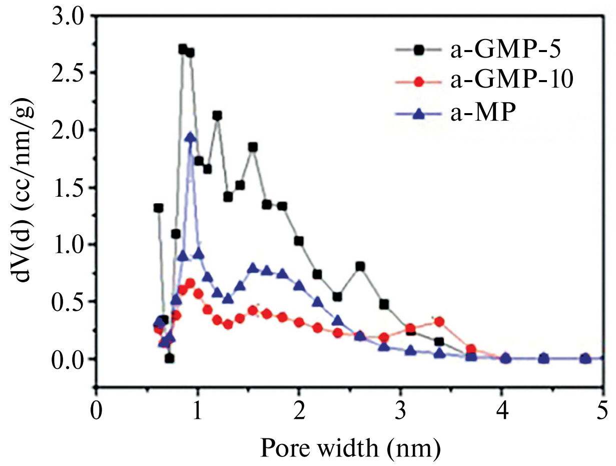

Fig. 4. Differential pore size (width) distribution curves for various materials with hierarchical porous structure described in [48].

[64] describes a highly oriented graphene film electrode (NGF), efficiently doped with nitrogen, including its design. NGF has a unique structure that provides high packing density (up to 1.64 g/cm^3) and efficient ion transport at the same time. Symmetrical NGF-based supercapacitors (NGF-SC) showed a specific capacity of 370 F/cm3 **or 226 F/g** with a weight of 11.2 mg/cm^2 in an aqueous electrolyte. In this case, capacity retention was 90.1% after 100,000 cycles. In an ionic liquid, NGF-SC showed a high capacity of 352 F/cm3 or 215 F/g at 11.2 mg/cm2 and with a potential window of 0–3.5 V, providing an **ultra-high energy density of 138 Wh/l**. With a 3H design and high mass load, the energy density of the entire NGF-SC ECSC reaches 65 Wh/L, which is much higher than that of commercial supercapacitors. Notably, this NGF-SC has demonstrated a **long service life of up to 50,000 cycles with 84.8% retention, which is a record**.

Porous graphene fibers doped with nitrogen and sulfur (NS-GFs) were synthesized by hydrothermal self-assembly followed by thermal annealing,

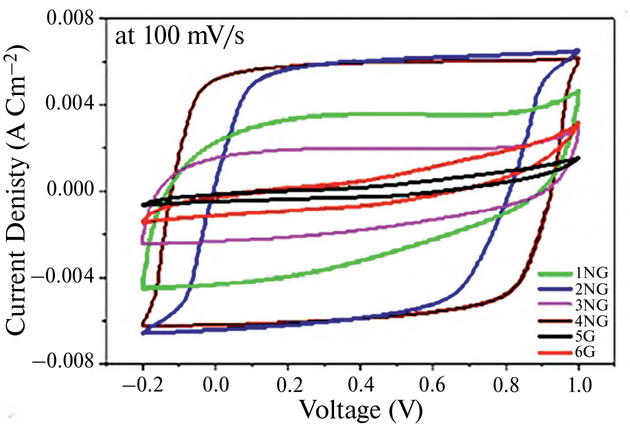

Fig. 5. CVA curves for a supercapacitor based on electrodes developed in [53].

demonstrating high capacitance characteristics of **401 F/cm^3 at 400 mA/cm^3** due to the synergistic effect of double doping by heteroatoms [65]. The manufactured symmetrical fully solid-state supercapacitor with polyvinyl alcohol/H_2SO_4 gel electrolyte and graphene oxide had a high capacity of 221 F/cm^3 and a high energy density of 7.7 MWh/cm^3 at 80 mA/cm^3. Interestingly, the conversion of solar-thermal energy from 0.1 wt.% graphene oxide extends the operating temperature range of the supercapacitor to 0 °C. In addition, the effect of photocatalysis of heteroatoms with double doping increases the capacity of NS-GFs. At an ambient temperature of 0 °C, the capacity increases to 182 F/cm^3 under solar radiation due to the excellent absorption of sunlight and the efficient conversion of solar-thermal energy by graphene oxide, preventing the freezing of the aqueous electrolyte.

[20] presents a porous carbon/graphene composite (PCG) obtained from pollen doped with nitrogen and sulfur with an interconnected “sphere in a layer” structure, in which carbon microspheres with a hierarchical structure can serve as “porous pads” preventing agglomeration of graphene nanolayers. Optimized PCG composite, manufactured with 0.5 wt.% graphene oxide (PCG-0/5), demonstrated **high specific capacity (420 F/g at 1 A/g), speed characteristics (280 F/g at 20 A/g) and excellent cyclic stability with 94% capacity retention after 10,000 cycles**. The symmetrical ECSC **provides a high energy density of 31.3 Wh/kg** in a neutral environment.

In [66], supercapacitor characteristics with phosphorus-doped graphene electrodes were studied, which were synthesized in one stage using Yucel’s method. The formation of graphene layers in the mesopore structure was observed by scanning electron microscopy. X-ray photoelectron spectroscopy has been used to identify ordinary phosphorus and phosphorus included in the functional groups -[(–P O)] and -(PO) formed on the inner surface of the electrode. Cyclic voltammetry and electrochemical impedance spectroscopy were used for electrochemical characterization of the electrodes. Cyclic charge-discharge tests were also performed for 1000 cycles to determine the cyclic stability of the electrode materials. As the number of cycles in the electrode synthesis process increased, the number of different molecular functional groups on the surface increased. The largest capacity is 301.3 mF/cm^2 at a current density of 10 mA/cm^2 in a sulfuric acid solution.

A simple approach to obtaining phosphate-functionalized carbon composites based on graphene is presented in [67]. Homogeneous deposition of a thin layer of phenolic resin onto the surface of graphene oxide (GO) layers was achieved using orthophosphoric acid as a polymerization catalyst and functionalization agent. As a result of subsequent pyrolysis of the composite, homogeneous lamellar microstructured porous carbon-graphene composites were obtained, combining accelerated molecular diffusion and accelerated electron transfer. To determine the effect of GO and porosity on the operation of the supercapacitor, a graphene-free sample and a KOH-activated composite using aqueous and organic electrolytes were also obtained and tested. It was found that the presence of GO and KOH activation leads to an increase in specific surface area in combination with progressive pore expansion. As a result, the KOH-activated composite reached specific capacities of 211 and 105 F/g when using 1 M H_2SO_4 and 1.5 M Et_4NBF_4 electrolytes, respectively. It has also been found that phosphorous functionalization of the electrodes makes it possible to achieve an operating voltage of 1.3 V in an aqueous electrolyte, which leads to a significant increase in the energy density of the cell. Finally, both non-activated and activated graphene-based composites provide very good conservation of capacitance, energy density and power, as well as cycling stability.

[68] describes the use of graphene aerogels doped with boron (B-GA), which were produced by a simple hydrothermal method. These B-GA are characterized by high SSA and high mesoporosity. B-GA supercapacitors have a **high specific capacity of 308.3 F/g at 1 A/g**. Moreover, B-GA provides high stability during cycling, namely 92% of capacity retention after 5000 cycles at 1 A/g, which is higher than that of undoped graphene aerogels (86%). The performance improvement is due to a combination of a mesoporous structure, high SSA, and an abundance of B-GA defects. This study demonstrates the significant potential of B-GA electrodes for high-performance

supercapacitors. Fig. 6 shows a schematic representation of the molecular structure of graphene aerogel doped with boron (B-GA).

In [69], boron-doped diamond (BG/BDD) was synthesized by chemical deposition from the gas phase using electron filaments (EA-HFCVD). Boron atoms efficiently dope graphene and diamond, and boron graphene (BG) sheets are grown vertically on boron diamond (BDD). The boron content in BG affects the characteristics of the BG/BDD electrode, and the electrode has a high specific capacity. The electrochemical behavior of the BG/BDD electrode was analyzed at both positive and negative potential windows in three-electrode electrochemical cells using saturated aqueous NaCl as an electrolyte. A symmetrical supercapacitor (SSC) was then manufactured to evaluate the practical application of the BG/BDD electrode. The BG/BDD-based device operates at a high voltage of 3.2 V. The SSC provides a **high energy density of 79.5 Wh/kg** with a specific power of 221 W/kg and a **high specific power of 18.1 kW/kg** with an energy density of 30.7 Wh/kg. It also retains 99.6% of its specific capacity in the range of 0–2.5 V. Therefore, this ECSC has a significant advantage in stability at high operating voltages.

Thus, it has been shown that supercapacitors using boron doping of graphenes have high electrochemical characteristics.

In the study [70], a one-step method was implemented for manufacturing various electrodes from graphene oxide doped with S, N, and Cl heteroatoms as electrode materials for high-capacity supercapacitors. X-ray photoelectron spectroscopy has revealed the formation of -ClO$_2$, -ClO$_3$, -SO$_x$ (x:2, 3) and -NO$_2$ groups in graphene oxide-based electrodes. The detailed mechanisms of formation of these groups are investigated. Graphene oxide electrodes doped with sulfur, nitrogen, and chlorine were used as electrode materials for supercapacitors. The capacitances of graphene oxide electrodes doped with -S, -N, and -Cl were determined to be 206.4, 533.2, and 1098 mF/cm^2, respectively, at a current density of 10 mA/cm^2.

In [71], the stability and electrochemical properties of graphene doped with B, N, P, and S atoms were investigated. The B, N, P, and S atoms bind strongly to graphene, and all the studied systems exhibit metallic behavior. While graphene with large SSA can increase the capacity of EDL, its low quantum capacity limits its use in supercapacitors. This is a direct result of the limited density of states near the Dirac point in the original graphene. It has been established that the doping of N and S with one vacancy has a relatively stable structure and a high quantum capacity. It is assumed that such electrodes can be used as ideal electrodes for symmetrical supercapacitors. The advantages of some codoped graphene systems have been demonstrated by calculating the quantum capacity. It was found that graphene doped with N/S and N/P with one vacancy is suitable for asymmetric supercapacitors. The increased quantum capacity contributes to the formation of localized states near the Dirac point and/or shifts in the Fermi level due to the introduction of a doping and vacant complex. Fig. 7 shows a Ragone diagram for symmetrical BG/BDD-based ECSCs and other graphene-based ECSCs studied. As we can see, high characteristics were obtained in [71].

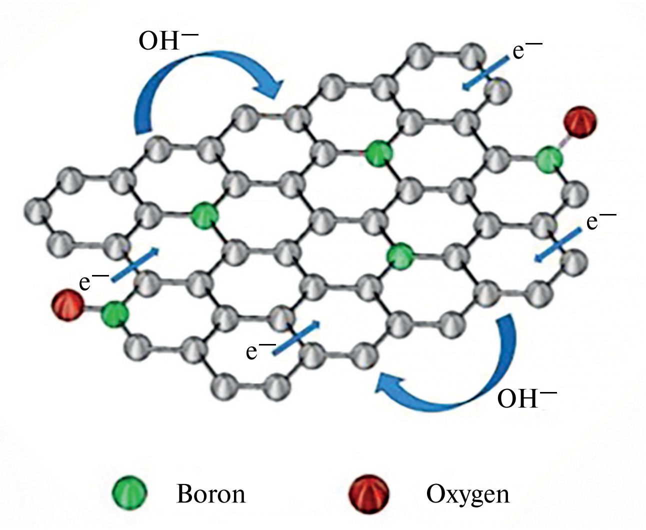

Fig. 6. Schematic representation of the molecular structure of graphene aerogel doped with boron (B-GA) [68].

1.3. Methods for obtaining reduced graphene oxide

Obtaining high-quality graphene-like structures and materials in an environmentally friendly way is still difficult to achieve. Recent studies have shown that laser irradiation of the corresponding precursors represents great potential and versatility for the realization of high-quality graphene-like materials at low cost. [72] presents a detailed study of the laser transformation of homogenized dried Corinthian raisins (Vitisvinifera L., var. Apyrena) into graphene-like material. This is a one-step process, as the conversion of raw materials from biomass takes place in the environment. Diffraction, Raman scattering, and electron microscopy have shown that the structure of the laser-irradiated product differs significantly from that of graphite carbon. XPS analysis shows a very high C/O ratio of 19 after decomposition of the crude biomass. The combination of the turbostratic structure and the almost complete removal of oxygen forms leads to an ultra-low resistance,

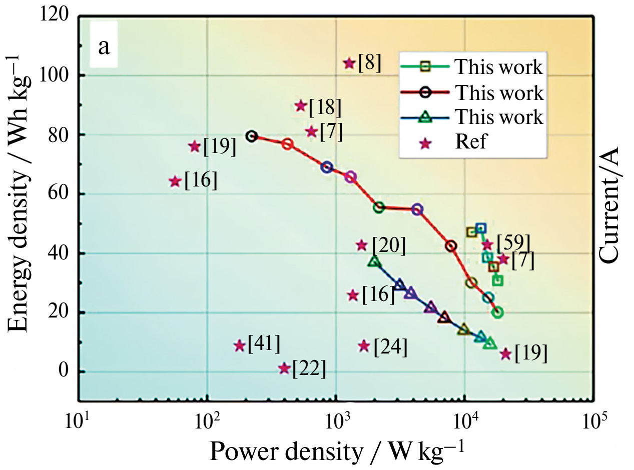

Fig. 7. Ragone diagram for symmetrical BG/BDD-based ECSCs and other graphene-based ECSCs studied [71].

which confirms the successful modification of the raw material to a graphene-like structure with a high degree of sp hybridization. An additional advantage of this approach is that this process can induce both the growth of graphene-like structures on the irradiated target and produce high-quality graphene-like powders. The latter were used to prepare electrodes for symmetrical supercapacitors, which demonstrate higher performance compared to graphene-based supercapacitors prepared by other laser methods.

[73] reports on the simultaneous exfoliation and reduction of graphene oxide (GO) and graphene nanolayers (GNPs) by rapid microwave irradiation in order to overcome the obstacles associated with low electrical conductivity and a tendency to re-aggregation, as well as realize their full potential as materials for supercapacitor electrodes. Morphological studies revealed the porous structure of microwave graphene oxide (MW-GO) and microwave graphene nanolayers (MW-GNPs), which showed the exfoliation of graphene-based materials. The supercapacitor was manufactured using a mixture of MW-GO, MW-GNP and polypyrrole and showed a specific capacity of 137.2 F/g during cycling, stability of 89.8% after 1000 charge/discharge cycles.

In [74], graphene was obtained by irradiating graphite oxide dissolved in an aqueous electrolyte with an excimer laser at various laser energies and irradiation times. The morphology and structure of laser-reduced graphene were characterized using scanning electron microscopy, small-angle X-ray diffraction (XRD), and X-ray photoelectron spectroscopy. The results of X-ray diffraction confirm that deoxygenation of graphite oxide layers occurred almost completely for all laser irradiation conditions used. Graphene obtained by this method is a chaotically aggregated, crumpled, disordered and fine sheet-like solid material. Graphene recovered by a laser was used as the electrode active material for supercapacitors, and its specific capacity was evaluated in a two-electrode cell with an aqueous solution of 0.5 M Na_2SO_4 or in 1 M electrolyte based on tetraethylammonium tetrafluoroborate acetonitrile. It has been established that the specific capacity of graphene produced using a laser depends on the energy and time of laser irradiation. The highest specific capacitance was determined to be 141 F/g at 1.04 A/g and 84 F/g at 1.46 A/g in aqueous electrolytes and electrolytes with ACN (acetonitrile), respectively. Comparing the characteristics of graphene-based supercapacitors is difficult due to the variety of methods for obtaining materials.

Graphenes obtained by several methods are compared in [75]. These include anodic and cathodic electrochemically expanded graphene, liquid-phase expanded graphene, graphene oxide, reduced graphene oxide, and graphene nanoribbons. The reduced graphene oxide showed the highest capacity of about **154 F/g in 6 M KOH at 0.5 A/g**, which was explained by the influence of functional oxygen-containing groups providing additional pseudo-capacity. However, the storage capacity was poor due to low conductivity. In comparison, anodic electrochemically expanded graphene showed a capacity of about 44 F/g and demonstrated excellent capacity retention due to its higher conductivity. These results highlight the importance of matching the graphene production method to a specific application. For example, graphene oxide and anodic electrochemically expanded graphene are best suited for high-energy and high-power ECSC applications, respectively.

Graphene synthesis often involves the use of toxic chemicals that threaten the environment. Due to the recent shift due to the recent shift in focus to to the synthesis of nanomaterials from agricultural waste due to their easy accessibility, cost-effectiveness, and, most importantly, environmental friendliness, [76] presented for the first time a new and "green" synthesis of multilayer graphene layers using pomegranate peel as a precursor at a low temperature of 80 °C. Surface morphology and microstructural properties were determined using transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), UV-visible spectroscopy (UV-Vis), and electrical properties were determined by Hall effect measurements. The supercapacitor was also investigated using cyclic voltammetry (CV), galvanostatic charge-discharge cycling (GCD) and electrochemical impedance spectroscopy (EIS). The resulting supercapacitor provided a capacity of 3.39 mF/cm^2 at a current density of 15.6 μA/cm^2, which makes such graphene a good material for electrochemical storage devices.

In [77], a simple and economical method of manufacturing water-soluble graphene layers using coal is reported. The synthesized carbon graphene (CDG) layers were characterized by X–ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), Raman infrared (FTIR) with Fourier transform (FTIR), ultraviolet visible (UV-vis) spectroscopy, and photoluminescence (PL). The presence of marginal oxygen functions in CDG sheets leads to the induction of fluorescent properties. To determine the electrochemical properties of CDG, measurements of cyclic voltammetry (CV), charge-discharge, and electrochemical impedance spectroscopy (EIS) in various electrolytes were performed. The value of the CDG specific capacitance in 1 M Na_2SO_4 turned out to be **277 F/g** at a scan rate of 5 mV/s. CDGs demonstrate stability over long cycles, i.e. the value of the specific capacitance remains at ~91% after 2000 cycles at a current density of 10 mA/g.

Given the non-biodegradable nature of plastic, its recycling is crucial to ensure effective waste management and resource conservation. [78] reports on a low-cost and environmentally friendly method of recycling plastic waste to produce a large number of graphene nanolayers (GN) using a two-stage pyrolysis process. To analyze the usefulness of GNs synthesized by this method, their capacitive behavior with various current sinks was studied, such as copper tape (CuT), indium tin oxide (ITO) glass, graphite sheet (GS) and aluminum sheet (AlS) in PVA (polyvinyl alcohol)-H_3PO_4 in a gel electrolyte. The results obtained confirm that the AlS current collector provided the highest specific capacity of 38.78 F/g. Thus, the present study shows a cost-effective option for achieving a closed-loop economy by recycling plastic waste using energy storage systems.

[79] reports on processing plastic waste into graphene nanolayers (GN) and their subsequent use in dye-sensitized solar cells (DSSC) and supercapacitors. Bentonite nanoclay was used as an agent for the decomposition of plastic waste using two-stage pyrolysis methods at 450 and 945 °C in an inert N_2 atmosphere to produce GN. The presence of GN with a small number of layers was confirmed by Raman spectroscopy, XRD and HRTEM. In addition, IR Fourier and EDX analyses were also performed to identify and quantify functional groups in GN. The use of GN as the material of the active layer of the supercapacitor electrodes provided a **high specific capacity of 398 F/g** at a sweep rate of 0.005 V/s. The supercapacitor also showed **significant energy and power densities of 38 Wh/kg and 1009.74 W/kg**, respectively. Thus, this method has shown the benefits of recycling plastic waste to preserve the environment and high electrochemical characteristics.

Many types of agricultural waste can be considered as an abundant and inexpensive carbon source for large-scale production of graphene-type materials. It was shown in [80] that widely available coconut waste can be efficiently converted to reduced graphene oxide by a simple catalytic process using ferrocene as an efficient and inexpensive catalyst. The structure and morphology of the manufactured materials were characterized by XRD, SEM, and TEM methods. The results obtained confirmed the formation of high-quality reduced graphene oxide. It was found that this material showed high ECSC performance and excellent cyclic stability. Thus, reduced graphene oxide, obtained in a simple, environmentally friendly way from this type of agricultural waste, may be a good candidate for the role of supercapacitor electrodes.

Wood, as a type of biomass materials, has potential application value in many aspects. In [81], a composite material made of carbonized graphene oxide@PVA (CWCC-rGO@PVA) with a high specific capacity, high flexibility, deformability, and the ability to generate electricity from the environment using carbonized wood cell chamber (CWCC) as a base was designed and manufactured. GO, as an intermediate, binds to CWCC in the form of C–C bonds, and the resulting CWCC-rGO intermediate combines with PVA (polyvinyl alcohol) to form hydrogen bonds. The resulting final hybrid is CWCC-rGO@PVA demonstrates high electrochemical characteristics, including a high specific capacity of **288 F/g**, a capacity retention of 91%, an energy density of **36 Wh/kg** and a power density of **3600 W/kg**.

In [82], the design and assembly method of nanocellulose-graphene composite materials used for flexible supercapacitors are considered. Mechanical flexibility, specific capacity, electrochemical characteristics, cyclic stability, renewability and biodegradability are taken into account in order to evaluate the characteristics of composite materials and better evaluate the advantages of this material.

The article [83] describes a new technique for producing high-density graphene flakes (HDGF) for high-performance supercapacitors. HDGF are produced by crushing into small pieces of a thermally reduced graphene oxide film. The high packing density, as well as the rapid transfer of electrons and ions, were achieved simultaneously by disrupting the continuity of the graphene film while maintaining its dense structure. The manufactured HDGF had a high gravimetric capacity (**237 F/g**) and a volumetric capacity of **261 F/cm**^{3}, as well as excellent cycle stability with 98% of the initial capacity after 10,000 cycles. In addition, a symmetrical supercapacitor using HDGF as electrode materials can obtain a volumetric capacity of up to 16 Wh/l with a power density of 88 W/l in an aqueous system. This strategy provides a new way to develop high-volume supercapacitors for energy storage in the future.

Miniaturization of energy storage is crucial for the development of next-generation portable electronic devices. Microsupercapacitors (MSCs) have great potential to work as embedded micro-power sources and energy storage devices that complement batteries and energy harvesting systems. Scalable production of materials for supercapacitors using cost-effective and high-performance processing methods is crucial for the widespread use of MSCs. It was reported in [84] that wet-jet milling of graphite makes it possible to increase the production of graphene as a material for supercapacitors. The formulation of water-based/alcohol-based graphene ink makes it possible to screen print flexible MSCs that do not contain metals. These MSCs have a surface capacity of up to 5,296 mF/cm^2 for one electrode, which corresponds to a very high volumetric capacity of 1,961 F/cm^3. Screen-printed MSCs can operate at a power density of more than 20 MW/cm^2. The devices demonstrate excellent resistance to charge-discharge cycles (10,000 cycles), bending cycles (100 cycles with a bending radius of 1 cm) and folding (up to 180° angles).

Recently, printing technologies have become promising methods for manufacturing electrochemical energy storage devices (ECSD), while newly developed printers have significantly improved printed electrodes due to lower cost, easier preparation, higher productivity, and improved electrochemical and mechanical properties. In [85], an overview of printing technologies for the production of ECSD is presented and the main attention is paid to graphene-based materials. Inkjet, aerosol, screen, roll and 3D printing were considered, the latest literature was reviewed, illustrative examples of the technical application of printing technologies for energy storage and electrochemical characteristics were presented.

2. COMPOSITES WITH GRAPHENES

2.1. Composites with metal oxides

Graphene composites with transition metal oxides, as a rule, have high electrochemical characteristics due to both the effective characteristics of graphene and the pseudo-capacitance properties of transition metal oxides [41, 86–137]. Metal oxides are common materials for supercapacitor electrodes, demonstrating high energy and power density, as well as long service life. In composites, graphene and metal oxides have demonstrated a combination of high cyclic stability of graphene and high capacity of metal oxides, which significantly improve the complex properties of nanocomposites. In [41], modern developments of graphene composites with metal oxides (MGr) (and nitrogen doping) in the field of electrochemical capacitors are highlighted, taking into account their synergetic properties. It is shown that MGr composites, in comparison with individual materials, have achieved a significant increase in the speed, capacity and stability of cycling. An overview of the characteristics, approaches to the preparation and application of graphene (Gr) is presented. The mechanism of implementation of various types of electrochemical capacitance is described in detail. Finally, the future prospects and problems of MGr composites for energy storage were discussed.

In the study [86], a metal current-removing film was deposited on a flexible substrate in the form of a microgrid by selective laser sintering of silver nanoparticles. The specific capacity was 5.8 mF/cm^2 at 1.5 mA/cm^2 with the electrolyte PVA-H_3PO_4. Then, electrodeposition of manganese dioxide (MnO_2) nanoparticles was carried out, which further increased the capacity to 49.1 mF/cm$_2$ at 1 mA/cm$_2$ in 0.5 M Na_2SO_4. As a result, the capacity reduction remained below 10% for 10,000 charge/discharge cycles.

In [87], a new approach was presented to the creation of electrodes with a hierarchical structure that allows supercapacitors to maintain their capacity under mechanical deformation. The electrodes are manufactured first by growing vertical graphene nanolayers (VGN), and then by depositing manganese dioxide (MnO_2) on plastic nickel wires. Two such electrodes are used to make a symmetrical supercapacitor using a solid-state electrolyte containing carboxymethylcellulose and sodium sulfate. This supercapacitor achieves a high capacity of up to 56 mF/cm^2, a high energy density of 7.7 MWh/cm^2 and a high power density of 5 MWh/cm^2. These exceptional properties are due to the synergy between the VGN and MnO_2, where the highly porous VGNs fulfill the important function of a mechanically robust platform with a large surface area that allows the application of a pseudo-high-capacity MnO_2 material. Supercapacitors made from these electrodes can be shaped into different forms by bending and twisting with little loss of performance. The promising results presented in this study open up a new path for manufacturing high-performance energy storage devices for wearable electronics and wireless communications.

In [88], electrodes were created from carbon fiber (CF) modified with vertically oriented graphenes (VG) and manganese dioxide (MnO_2), as well as with nitrogen doping. The results show that the hybridization of VG and MnO_2 creates a significant synergistic effect, leading to an increase in the surface capacity of the electrode. This synergistic effect is explained by the double effect on VG increase in effective surface area and electrical conductivity, which provide a better distribution of MnO_2, as well as a highly conductive network. A supercapacitor based on a CF/VG/MnO_2 hybrid electrode and a polymer electrolyte has a specific capacity per surface area of 30.7 mF/cm_2, an energy density of 12.2 MW/kg, and a power density of 2210.3 MW/kg. In addition, the mechanical characteristics demonstrate a tensile strength of 86 MPa and a bending strength of 32 MPa for this supercapacitor design.

Work [89] is devoted to the production of composite thin films of manganese dioxide (MnO_2)/graphene oxide (GO) doped with silver (Ag) and nitrogen. A BET study showed that MnO_2–Ag_3/GO nanosheets have a specific surface area of 192 m_2/g. A specially defined morphology in the form of a flower and interconnected nanolayers of MnO_2–Ag_3/GO electrodes made it possible to achieve high electrochemical characteristics. The maximum specific capacity of **877 F/g** at a scanning speed of 5 mV/s was obtained for the MnO_2–Ag_3/GO electrode tested in 1 M Na_2SO_4 with 94.57% capacity retention after 5000 cycles. A flexible solid-state symmetrical supercapacitor based on MnO_2Ag_3/GO composite produced a specific energy of **57 Wh/kg** with a specific power of **1.6 kW/kg** and maintaining 94% capacity after 10,000 cycles.

In [39], CuMnO nanocrystals and a composite CuMnO/graphene quantum dot (GQD) (with phosphorus doping) were synthesized by the hydrothermal method, and they were used to create a new type of supercapacitor. GQDs have been applied to increase the specific capacity and increase the efficiency of the supercapacitor. As you know, a quantum dot is a fragment of a conductor or semiconductor whose charge carriers are limited in space in all three dimensions. The size of a quantum dot is so small that the quantum effects are significant. Various methods were used to identify the synthesized nanocomposite and study its morphology, structure, and surface area. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to record and track the electrochemical behavior of the synthesized nanocomposite used as an electrode material. A study of changes in the capacitance of CuMnO/GQD and $CuMnO_2$ electrodes during 5,000 consecutive charge/discharge cycles showed that the stability of the nanocomposite electrode is higher and its capacity after this number of cycles reaches 83.3%, while the capacity of the electrode made of CuMnO nanoparticles reaches 65.4% of the initial one. The specific capacity of the CuMnO/GQD nanocomposite and CuMnO nanoparticles at a current density of 1 A/g was 520.2 and 381.5 C/g, respectively. The maximum specific energy of the asymmetric supercapacitor SIMPO/GQD/AC, obtained with a specific power of 1108.1 W/kg, is equal to a large value of **47.9 Wh/kg**. The capacity of the asymmetric supercapacitor decreased by only 13.3% after 5,000 charge and discharge cycles, which is a very good service life compared to similar materials. All these results indicate that the CuMnO/GQD nanocomposite can be considered as a possible option for a high-speed and stable supercapacitor.

Miniature graphene-based supercapacitors obtained by laser conversion of suitable precursors have recently attracted attention for the production of small-sized energy storage devices. In [90], LightScribe technology was used to perform single-chamber synthesis of TiO nanoparticles embedded in porous graphene-based electrodes by converting precursor materials by absorbing infrared laser irradiation. Improved electrochemical characteristics of supercapacitors have been achieved by combining Faraday reactions occurring with metal oxide nanoparticles with conventional EDL charging occurring in porous graphene. Microsuperapacitors consisting of TiO-graphene electrodes were tested using two hydrogel polymer electrolytes based on polyvinyl alcohol/HPO and polyvinyl alcohol/HSO, respectively. In devices based on TiO-graphene, a specific capacity of up to 9.9 mF/cm^2 has been obtained, which corresponds to a volumetric capacity of 13 F/cm3 and doubles the characteristics of graphene-based supercapacitors. The microsupercapacitors have achieved specific surface energy and specific surface power of 0.22 and 39 μW/cm^2, as well as a cycle capacity of more than 3,000 cycles. These high results suggest that laser-produced TiO graphene nanostructures are excellent candidates for microsupercondensors for environmentally friendly, large-scale, and low-cost applications. Fig. 8 shows a change in capacitance over 3,000 charge-discharge cycles at a current of 5 mA/cm^2 for microsupercondensors developed in [90].

[91] demonstrates a simple method for obtaining a functionalized spongy graphene nanocomposite/titanium dioxide (FG-$HTiO_2$) hydrogenated from nanotubes, doped with boron (in the form

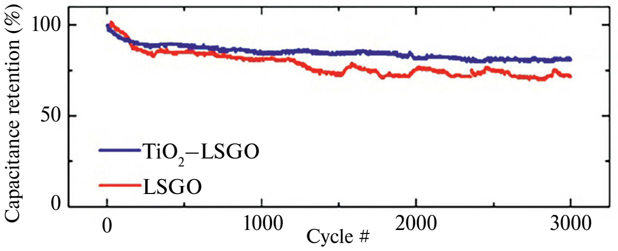

Fig. 8. Capacitance change over 3000 charge-discharge cycles at a current of 5 mA/cm^2 for microsupercondensors developed in [90].

of interconnected, porous 3-dimensional (3D) network layers. This 3D network structure provides better contact at the electrode/electrolyte interface and accelerates the kinetics of charge transfer. The manufactured FG-TiO_2 composite was characterized by X-ray diffraction (XRD), IR Fourier, scanning electron microscopy (FESEM), Raman spectroscopy, thermogravimetric analysis (TGA), absorption spectroscopy, and transmission electron microscopy (TEM). The synthesized materials were evaluated in relation to their use in 0.5 MH_2SO_4 supercapacitors using cyclic voltammetry (CV) at various potential scanning speeds and galvanostatic charge/discharge tests at various current densities. The FG-$HTiO_2$ electrodes showed a maximum specific capacity of **401 F/g** at 1 mV/s. The energy density was **78.66 Wh/kg** at a power density of 466.9 W/kg at 0.8 A/g.

[92] describes a simple and binder-free technique for obtaining layered double hydroxides of β-$Ni(OH)_2$/Nickel-cobalt (β-$Ni(OH)_2$/NiCo) in combination with graphene modified with fluorine (FG) as a supercapacitor electrode. Electrodes (β-$Ni(OH)_2$/NiCo) were obtained by the hydrothermal method by synchronous electrochemical stratification of graphite into fluor-modified graphene and the use of a composite (β-$Ni(OH)_2$/NiCo). This hybrid structure (β-$Ni(OH)_2$/NiCo) of modified graphene as a supercapacitor electrode demonstrates high conductivity, rapid ion diffusion, and high mechanical strength. As a result, the β-$Ni(OH)_2$/NiCo@FG electrode has a very high capacity (3996 mF/cm^2 at 1 mA/cm^2), high speed capability and extended service life. β-$Ni(OH)_2$/NiCo in combination with undoped electrochemically stratified graphene demonstrates significantly improved cyclic stability (79% capacity retention after 1000 cycles at a current of 5 mA/cm^2), surpassing that of β-Ni(OH). Thus, this technique has great potential to improve the performance of electrodes.

[93] reports on the simple synthesis of porous graphene-NiO (PGNO) nanocomposites using a unique system of mixed solvents using a solvothermal approach. Microscopic characterization of porous graphene (PG) shows the presence of pores in graphene sheets; NiO (NO) shows a scaly structure, and the PGNO composite shows the fixation of NO nanocapsules on PG sheets. A series of electrode materials were obtained by varying the percentage of PG (and the materials were designated as 5–30 PGNO, respectively). An electrochemical study showed **a high capacitance value of 511 F/g** at a scan rate of 5 mV/s for a 10 PGNO composite in the 3-electrode method and 80% retention of the initial capacitance after 10,000 cycles at a current density of 8 A/g. The manufactured symmetrical hybrid supercapacitor using PGNO electrodes also showed a good capacity value of 86.0 F/g at a sweep speed of 5 mV/s. The manufactured device retained 84% of the initial capacity at the end of 10,000 cycles at a current density of 8 A/g, demonstrating good electrochemical stability and high-speed ability of the material. The percentage contribution of the EDL capacity and pseudo-capacity to the total specific capacity of the PGNO supercapacitor was also estimated.

Graphene oxide (GO) nanosheets, as well as two-dimensional $Ni(OH)_2$ with very good uniformity were obtained by the Hammers method and the hydrothermal method, respectively [94]. $Ni(OH)_2$ nanosheets treated with cationic surfactants and graphene oxide with negative charges were mixed with each other by electrostatic self-assembly. After annealing, hybrid two-dimensional nanosheets of reduced graphene oxide NiO-(NiO-rGO) were obtained. Due to the synergistic effects, the NiO-rGO electrode has optimized electrochemical characteristics, unlike pure NiO or rGO. The results show that NiO nanosheets are uniformly dispersed on the surface of rGO nanosheets, and a hybrid electrode with NiO-rGO nanosheets can provide a **high capacity of 343 C/g (at 1 A/g)**. In addition, electrodes consisting of NiO-rGO nanosheets were used to assemble a symmetrical supercapacitor. The energy density of the manufactured supercapacitor device can reach 5.4 Wh/kg at a power density of 0.43 kW/kg when operating in the voltage range 0–1.4 V. In addition, the symmetrical supercapacitor also demonstrates excellent capacity retention at 90% after 10,000 cycles (10 A/g).

In [95, 96], composite structures made of nickel-cobaltite/graphene (NiCo O/GQD) were studied, which exhibit increased electrical conductivity and function as electrode materials with a higher energy density compared to GQD (graphene quantum dots) and NiCoO. The electrochemical characteristics of the NiCoO/GQD composite were obtained by galvanostatic charge-discharge method for three-electrode systems with 0.1 M potassium hydroxide electrolyte. It was found that the observed specific capacitance for the composite is a large value of **481.4 F/g** at 0.35 A/g. This is higher than that of graphene quantum dots (GQD) (45.6 F/g) and is associated with increased electrical conductivity and diffusion of ions, which move faster between the electrodes and the electrolyte. These results demonstrate the unique characteristics of the manufactured composites as promising electrode materials for use in supercapacitors.

The $W_{18}O_{49}$ nanocomposite with reduced graphene oxide (rGO) from nanowires (NW) is considered in [97] as a new active material for supercapacitor electrodes. It demonstrates high specific capacity and excellent speed characteristics in $AlCl_3$ aqueous electrolyte. Electrochemical studies show that the presence of rGO accelerates the diffusion of Al^{3+} ions in the nanocomposite, thereby providing more ions for the intercalation pseudo-capacity. The manufactured asymmetric supercapacitor $W_{18}O_{49}$NWs-rGO//rGO demonstrates a **high specific capacity of 365.5 F/g at 1 A/g** and excellent cyclic stability while maintaining 96.7% capacity at 12,000 cycles. It is important to note that it provides a **high energy density of 28.5 Wh/kg at a power density of 751 Wh/kg**, which is the highest energy density value for all known devices based on the $W_{18}O_{49}$ supercapacitor.

In [98], multilayer graphene films uniformly coated with a thin layer of V_2O_5 (graphene/V_2O_5 composite) were obtained by combining laser reduction and low-temperature atomic layer deposition. To test the effect of crystallinity on the electrochemical characteristics of the graphene/V_2O_5 composite, high-temperature annealing was first performed, followed by a detailed comparative study of the amorphous and crystalline coating of the composite. It has been shown that graphene coated with amorphous V_2O_5 can provide higher performance of a supercapacitor electrode (i.e., specific capacity, energy density, and cyclic stability) than its crystalline counterpart.

In [30], vanadium pentoxide (V_2O_5) was grown on graphene using the microwave method, which is simple, fast, energy-saving, and efficient. Thanks to this method of microwave synthesis, homogeneous V_2O_5 nanoparticles with a size of about 20 nm are evenly distributed over graphene. The resulting V_2O_5/graphene composite was used in symmetrical supercapacitors, showing specific capacitance of **673.2 and 474.6 F/g at 1 and 10 A/g**, respectively, and retention of 96.8% capacity after 10,000 cycles at 1 A/g. In addition, supercapacitors have demonstrated high energy and power density characteristics **(46.8 Wh/kg at 499.4 W/kg and 32.9 Wh/kg at 4746.0 W/kg)**, which outperform many similar devices.

Metal oxide nanoparticle (MONP)-graphene composites are highly valuable candidates as electrode materials for electrochemical supercapacitors (ECCS). In [99], the development of a universal approach to the manufacture of ECSC electrodes by impregnating MONP (M = Ti, Ni, Sn) synthesized by laser ablation in liquid on laser-induced graphene (LIG) was described. A typical SnO_2/LIG microsupercapacitor (MSC) provides a specific capacity of 18.58 mF/cm^2 at a scanning speed of 10 mV/s, which is 5.2 times higher than that of an unmodified LIG. In addition, the microsupercapacitor (MSC) demonstrates long-term cyclic stability (retains 82.15% of specific capacity after 5,000 cycles) and good mechanical flexibility (specific capacity decreases by 5% at a bending angle of 150°). MONP and LIG are manufactured using the same laser processing system, without the use of chemical ligands or reducing agents in the synthesis process, which is a cost-effective and environmentally friendly method. This simple and straightforward method provides a highly efficient solution for large-scale MSCs manufacturing.

In [100], nanocomposites of reduced graphene oxide/lanthanum oxide were obtained. The reduced graphene oxide with a large specific surface area was successfully doped with lanthanum oxide. The reduced graphene oxide/lanthanum oxide composites were manufactured as an electrode material for a supercapacitor, which demonstrated a significant specific capacity of 156.25 F/g at a current density of 0.1 A/g and high cycling stability. The material retains 78% of its original charge-discharge efficiency after 500 cycles. The high electrochemical characteristics of the composite material may be associated with the deposition of lanthanum oxide nanoparticles on the surface of the reduced graphene oxide, which increase the effective conductive area of the reduced graphene oxide and the contact area between the electrolyte and graphene. Graphene and lanthanum oxide composites can significantly improve the stability and electrical characteristics of supercapacitors and have great potential for chemical sensors, microelectronics, energy storage and conversion.

In [101], a hybrid type of energy storage device is presented, consisting of electrodes based on a composite of graphene and zinc oxide plates. This composite exhibits both the electrochemical characteristics of a supercapacitor with a high power density and a battery with a sufficiently high energy density compared to each individual material. The improved characteristics of the hybrid correlated with the structure of the electrodes. To improve the electrochemical characteristics of supercapacitors, it is necessary to have a well-defined mass, shape and surface area of the electrode materials. In this work, the original design of the mounting device was presented, which makes it possible to accurately determine all the critical parameters of the electrode materials: specific mass and surface area. With the initial installation, a supercapacitor device was created that could also act as a battery due to its high energy density values, which is why it was named *superbat*. In this work, 3D graphene foam was used as the first electrode due to its large surface, while ZnO nanocrystals were used for the second electrode due to their defective structure. A high specific capacitance value of **448 F/g** was obtained, which was associated not only with the quality of synthesis, but also with the choice of electrode and electrolyte materials. Moreover, each component used in the design of the hybrid supercapacitor also played a key role in achieving a high capacity value. The results demonstrated the high performance and stability of the device.

In [102], Ni3Si_2/NiOOH composites/graphene nanostructures were synthesized by chemical deposition from the gas phase at low pressure. In a carbon-rich atmosphere, high-energy atoms bombarded the surface of Ni and Si and reduced free energy during thermodynamic equilibrium of Ni-Si solids, significantly catalyzing the growth of Ni-Si nanocrystals. Electrochemical measurements have shown that these nanostructures have an **ultrahigh**

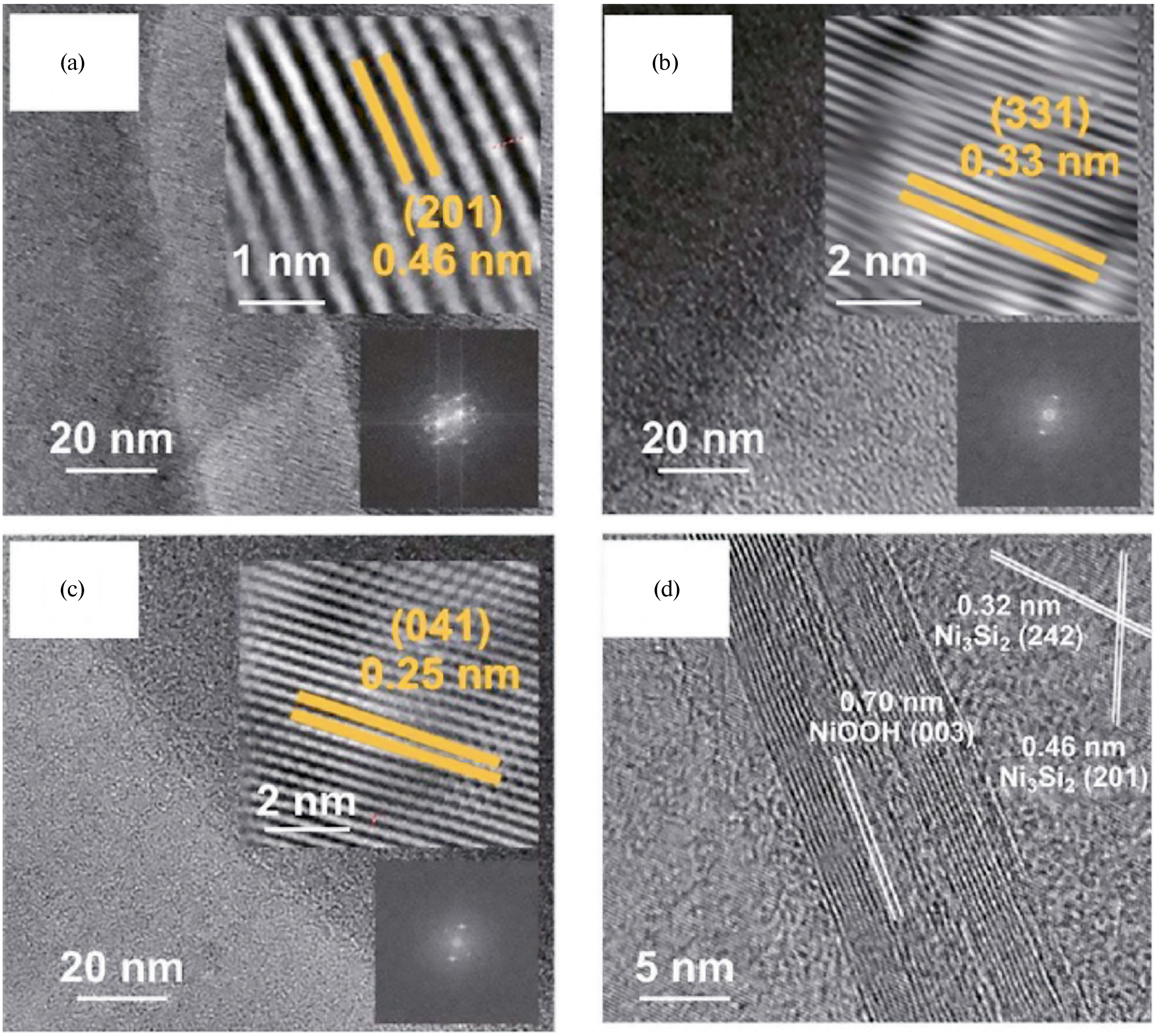

Fig. 9. TEM images of Ni_3Si_2/NiOOH/graphene nanostructures obtained in [102].

specific capacity of 1193.28 F/g at 1 A/g. When integrated into a solid-state supercapacitor, it provides a high energy density of up to **25.9 Wh/kg at a power density of 750 W/kg**, which can be attributed separately to the Ni3Si2/graphene skeleton, which provides high power, as well as to NiOOH in an alkaline solution. Fig. 9 shows TEM images of Ni_3Si_2/NiOOH/graphene nanostructures obtained in [102].

In [113], positive electrodes without a binder were produced by electrochemical deposition, in which nanorods (CuONRs) grown directly on copper foam (CF) are decorated with bimetallic cobalt-zinc-sulfide (Co-Zn-S NAs) nanomatrices. The manufactured Co-Zn-S@CuO-CF composites have a very high specific capacity of **317.03 mAh/g at 1.76 A/g**, as well as very good cyclic stability (retention of 113% after 4,500 cycles). The negative electrodes were additionally manufactured by direct deposition of iron sulfide (Fe-S NSs) nanosheets graphene oxide (GO), showing a remarkable specific capacity of **543.9 F/g at 0.79 A/g**. Having the advantages of obtaining high values of specific energy and specific power (**25.71 Wh/kg and 8.73 kW/kg**) along with acceptable stability, the manufactured asymmetric supercapacitor is very promising.

[104] describes the manufacture of flexible microsupercondensators (MSCs) based on hybrid materials from single-walled carbon nanotubes (SWCNs) with laser-induced graphene fibers (LIGF) decorated with manganese dioxide (MnO_2) nanoparticles. SWCNs are applied to the surface of LIGF and the space between them, which can bind LIGF to form more conductive pathways and provide more active areas for the growth of MnO_2 nanoparticles. Due to the synergistic effect between the LIGF conductive network of single-walled nanocarbon nanoparticles and MnO_2 nanoparticles with high theoretical capacity, the obtained flexible MSCs based on LIGF-C4/MnO_2 hybrid electrodes provide a high capacity of 156.94 mF/cm^2, which is about 8 times higher than that of MSCs based on LIGF-MnO_2 (20 mF/cm$_2$). In addition, LIGF-C4/MnO_2 also exhibit significant specific energy of 21.8 MWh/cm$_2$, long-term cycling stability, significant modular integration, and very high mechanical flexibility (with 90.5% capacity retention after 1,200 bending cycles). Thus, the design of hybrid electrode materials proposed in this paper provides a simple and novel method for the development of flexible energy storage devices with high performance characteristics, which opens up great prospects for use in wearable electronics. Thus, it has been shown that supercapacitors using graphene composites with metal oxides have high electrochemical characteristics.

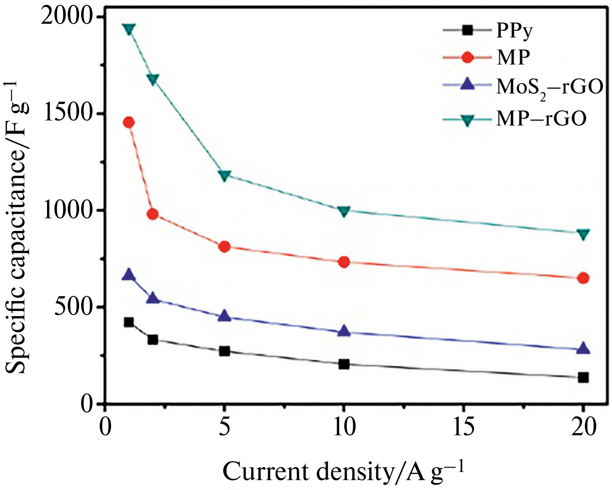

Fig. 10. Dependences of the specific capacitance on the specific current for the samples developed in [106].

2.2. Composites with metal sulfides and selenides

Other types of graphene composites that have been intensively developed recently are composites with transition metal sulfides and selenides. In [105–135], a system of co-dissolution in a deep eutectic solvent (DES) was developed by mixing water and acetonitrile with a typical DES electrolyte consisting of acetamide and lithium perchlorate. The addition of co-solvents not only solves the problems of high viscosity and low conductivity of DES, but also creates some unique properties. For example, the presence of water improves the fire-retardant properties of DES electrolyte. In contrast, the addition of acetonitrile further improves ionic conductivity without compromising the wide window of electrochemical stability (ESW). The effect of the amount of co-solvent in DES and the optimal molar ratio between the co-solvents was investigated. When the molar ratio of acetonitrile to water is 4.4:1, hybrid DES exhibits the best physical properties, including a wide ESW potential window (2.55 V), high conductivity (15.6 mS/cm) and low viscosity (5.82 MPa s). In addition, a series of spectroscopic measurements were performed to understand the interaction between the electrolyte components. On the other hand, the use of a hydrogel consisting of MoS_2 and reduced graphene oxide (rGO) as electrode materials for supercapacitors has been demonstrated. This hydrogel inherited the porous structure of the rGO hydrogel and the high conductivity of MoS_2. Finally, high-voltage symmetrical supercapacitors were manufactured using hybrid DES and hydrogel as the electrolyte and electrode, respectively. The optimized supercapacitor operates at a wide operating voltage range of 2.3 V and reaches a maximum energy density

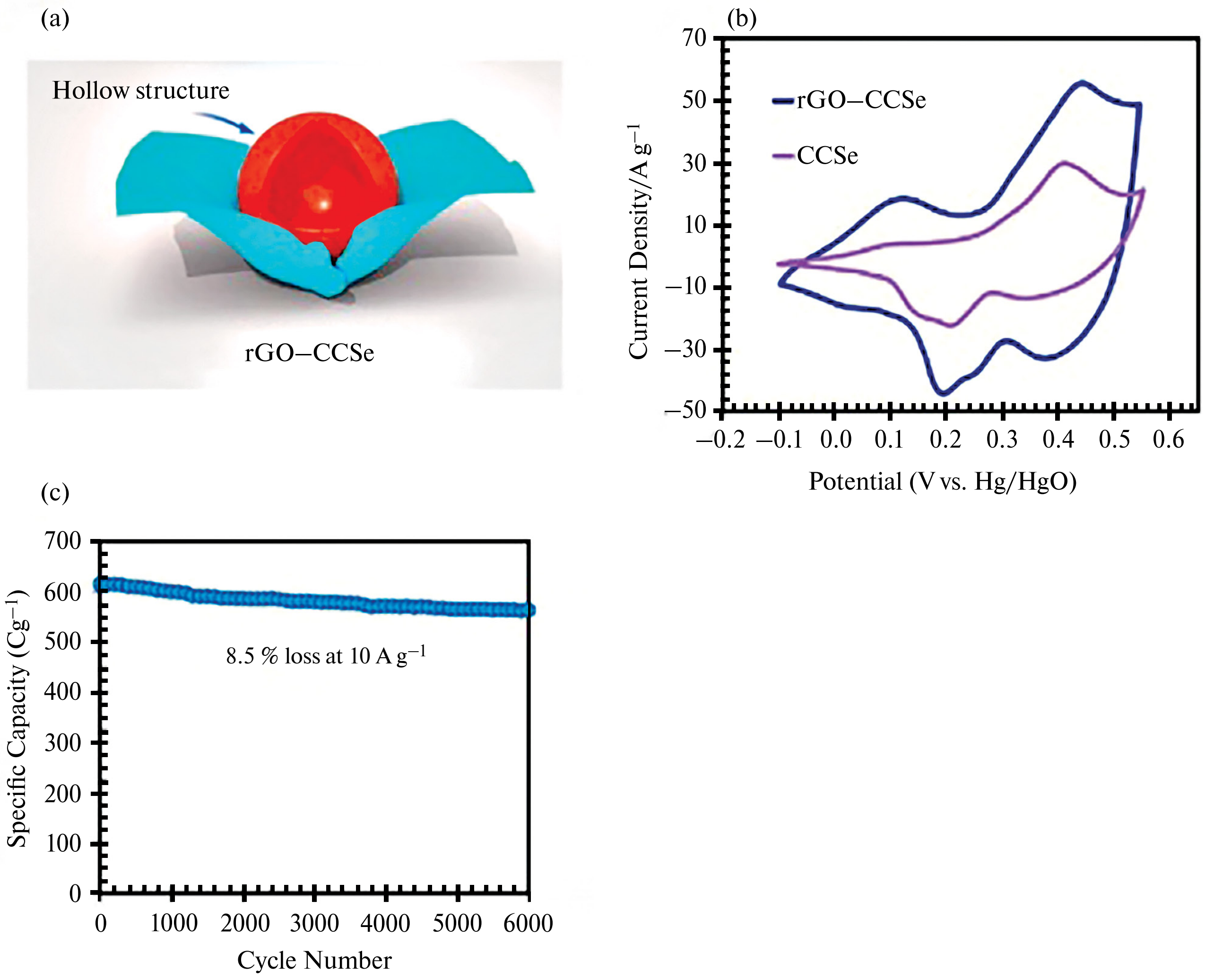

Fig. 11. (a) Schematic formation of hollow structures of cobalt and copper selenide (rGO-CCSe) wrapped in graphene; (b) CVA curves for rGO-CCSe and CCSe; (c) capacity change during rGO-CCSe cycling [109].

of **31.2 Wh/kg at a power density of 1164 W/kg**. In addition, this ECSC has demonstrated the retention of 91% capacity after **20,000 cycles**.

A composite of polypyrrole (PPy) on reduced graphene (rGO) with vertically oriented MoS_2 sulfide was produced in [106] using a single-stage hydrothermal method (MP-rGO). Ultrathin MoS_2 nanosheets mixed with PPy lamellae are well coated with rGO, forming a triple nanostructure. PPy lamellae are formed on rGO using MoS_2 nanosheets as a result of the redox reaction between ammonium tetrathiomolybdate and pyrrole. The conductivity of MoS_2 was effectively increased by using PPy and rGO, and MoS_2/PPy (MP) nanohybride gives MoS_2 low crystallinity, and PPy amorphousness. The MP-rGO electrode has a **high specific capacity of 1942 F/g** (215.8 mAh/g) at a current density of 1 A/g and satisfactory cycling stability. An asymmetric MP-rGO/AC supercapacitor was assembled, which has a **high energy density of 39.1 Wh/kg** with a specific power of 0.70 kW/kg, which confirms its potential use in energy storage. Fig. 10 shows the dependences of the specific capacitance on the specific current for the samples developed in [106].

Cobalt pentlandite (CoS) has lately become a promising electrode material for energy storage devices. A hybrid of CoS and graphene was synthesized by the hydrothermal method [107]. Small-sized CoS flakes are thinly deposited on the surface of the graphene sheet, and an interconnected CoS/graphene structure is obtained. The results of electrochemical tests showed that the CoS/graphene electrode provides a high charging capacity of **540 C/g** for 1 minute and retains 74.5% of the capacity for 14 seconds. The hybrid supercapacitor assembly with an electrode including CoS provides a high energy density of **37 Wh/kg** at a power density of 170 W/kg, and 15.3 Wh/kg can be maintained even at a high power density of **12 kW/kg**. The very high electrochemical characteristics should be explained by the large number of active centers, improved charge transfer characteristics, and the maximum capacitive contribution of the CoS/graphene electrode.

Nickel selenide and its nanocomposites (nickel graphene selenide; NiSe/G, graphene doped with nitrogen and boron, designated as NiSe/NG and NiSe/BG, respectively) were obtained using the hydrothermal method, and these materials were used for energy storage [108]. These materials were examined using various analytical and morphological methods such as X-ray diffractometry and FESEM analysis. Further, the prepared materials were examined by electrochemical methods such as voltammetry and a controlled potentiostatic test to calculate the capacitance, energy and power density of the manufactured electrode. The electrochemical behavior of graphene nanocomposites of nickel selenide was studied in KOH electrolyte. It was found that NiSe/NG showed a specific capacity of 99.03 F/g at a power density of 0.55 W/kg. The results proved that graphene doping has a synergistic effect.

In [109], a lightweight template method was developed for producing porous hollow copper-cobalt selenide microspheres wrapped in conductive networks of reduced graphene oxide (rGO-CCSe). The synthesized electrode is able to provide significant capacity retention at 91.5% after 6,000 charge cycles due to a well-thought-out structural design and the use of advantages of bimetallic synergy at the atomic level, with a very high specific capacity of **724 C/g at 2 A/g**. In addition, an asymmetric cell was manufactured using an rGO-CCSe hollow microspherical electrode to achieve very high energy densities **(57.8 Wh/kg)**. Graphene conductive carrier together with CCSe cubes of battery type create a synergistic effect, which explains such high electrochemical characteristics (Fig. 11*a*). Fig. 11*b* shows that pseudo-capacity makes a significant contribution to the capacity of rGO-CCSe and CCSe. Fig. 11*c* shows that there is a slight decrease in capacitance during cycling of the rGO-CCSe electrode for 6000 cycles [109].

[110] reports on the production of $NiSe_2$ nanoparticles by nitrogen doping of reduced graphene oxide (N-rGO/$NiSe_2$) using a simple two-stage method that includes hydrothermal production of $Ni(OH)_2$ precursor and then solvothermal synthesis of N-rGO/$NiSe_2$ composites with different N-rGO content. The newly prepared N-rGO/$NiSe_2$ composites have been characterized by X-ray diffraction, Raman spectroscopy, high-resolution X-ray photoelectron spectroscopy, autoemission scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, and BET. The results show that N-rGO acts as a protector of $NiSe_2$ nanoparticles, preventing their aggregation, which leads to an increase in the specific surface area and electrical conductivity of the material. The optimized N-rGO/$NiSe_2$ composite can provide a **very high specific capacitance of 2451.4 F/g at a current density of 1 A/g** (Fig. 12). Using activated carbon (AC) as the negative electrode and an optimized N-rGO/$NiSe_2$ composite as the positive electrode, an asymmetric supercapacitor was created. It operated stably in a potential window of 0–1.6 V and provided a high maximum energy density of **40.5 Wh/kg** at a power density of 841.5 W/kg. In addition, the asymmetric N-rGO/$NiSe_2$//AC supercapacitor demonstrated good cyclic stability (Fig. 12).

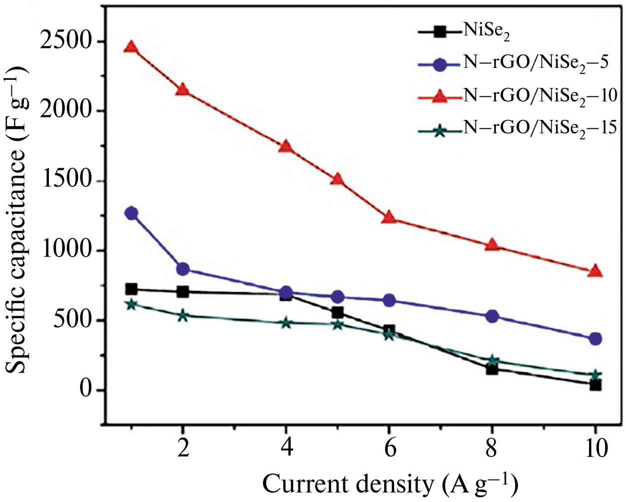

Fig. 12. Dependences of the specific capacitance of the N-rGO/NiSe2 EHSC on the specific current [121].

Thus, it has been shown that supercapacitors using graphene-selenide composites have high electrochemical characteristics.

2.3. Composites with metal particles

High efficiency in supercapacitors was demonstrated by electrodes based on composites doped with metal particles. In [122], in order to increase the stored energy, defective graphene was doped with Ni nanoparticles. During the first charge cycle in an aqueous electrolyte (3.5 M KOH), it was found that Ni attached to graphene is easily converted into Ni(OH) at the nanoscale. Such a reversible Faraday mechanism led to an increase in the specific capacitance of the electrodes by an order of magnitude, reaching a very high value of **1900 F/g** at 2 mV/s in 3.5 M KOH. An asymmetric supercapacitor was manufactured by coupling a negative electrode made of pure graphene with a positive graphene electrode decorated with nickel. Such a supercapacitor was successfully cycled in the voltage range 0–1.5 V, reaching a maximum specific energy of **37 Wh/kg and a maximum specific power of 5 kW/kg**. The supercapacitor has shown good reversibility and conservation of 72% of specific energy over 10,000 cycles.

In [123], an electrode was made by producing paper with silver-modified fibers and graphene oxide-modified (GO) fibers, followed by GO reduction. Ag- and GO-modified fibers were obtained by *in situ* growing Ag nanoparticles and self-assembling GO sheets on cellulose fibers, respectively. The Ag-modified fibers act as a flexible current receiver with numerous three-dimensional interconnected electron transport pathways, allowing the recovered GO-modified fibers to be used as electrode materials to achieve high conductivity and high performance. Simple drying can reduce the weight of the supercapacitor by 40% to facilitate transportation and storage, and capacity efficiency can be restored by wetting if necessary.

In [124], an efficient textile-based electrode was successfully obtained by introducing silver nanoparticles (AgNPs) onto the surface of cotton fabric (CF) with reduced graphene oxide (rGO). The CF electrode with Ag/rGO coating showed a high specific capacity of **426±10 F/g** in 0.5M NaOH. Symmetrical supercapacitor cells based on the Ag/rGO/CF composite had a very long service life (126% retention of the initial specific capacity after 1000 charge-discharge cycles) and good speed characteristics. The rGO coating layer gives the electrode excellent electrical conductivity, high power consumption and high DES capacity. At the same time, the chemical coating with silver improves the capacitive properties by increasing conductivity and induces pseudo-capacitance effects. Thus, the favorable synergistic effects of rGO, AgNPs, and the 3D hierarchical CF structure lead to high electrochemical performance. A fully solid-state flexible symmetrical supercapacitor was assembled using this composite fabric. It demonstrated high electrochemical stability under mechanical bending (89% of the initial capacity is retained after 1000 bending cycles) and provided a **high energy density of up to 34.6 Wh/kg** (at a power density of 125 W/kg).

3. COMPOSITES WITH CONDUCTIVE POLYMERS (CPS)

One of the achievements of electrochemistry in the last 25–30 years has been the development of the (CPs). The electronic conductivity of the (CPs) is displayed in the process of its doping with counterions due to the formation of delocalized π-electrons or holes and their transfer under the influence of an electric field through a system of polyconjugated double bonds, which any CP possesses. CP includes: polyacetylene (PAc), polyaniline (PANi), poly- (p-phenylene) (PPh), polythiophene (PT), polypyrrole (PPy), polyporphine (PP) and their derivatives. Since quasi-reversible electrochemical charge-discharge processes can occur in many electronic devices, they are widely used in ECSC [125–150]. CP adds a pseudo-high Faraday capacitance to the total capacity of the composites.

The growing development of flexible and wearable supercapacitors has stimulated the smart electronics industry. Conductive polymer hydrogels are considered the most promising and viable sources for manufacturing flexible supercapacitors, as well as for powering flexible miniature electronic devices. As reported in [127], conductive polymer hydrogels can be synthesized using numerous physical and chemical bonding methods. Conductive polymer hydrogels as electrodes have a combination of high electrical conductivity, outstanding electrochemical characteristics, and unique three-dimensional porous morphology with swelling characteristics, ideal electrolyte interaction, environmental friendliness, strength, and mechanical flexibility. These features make them ideal options for flexible supercapacitors. Conductive polymers such as polypyrrole, polyaniline, and poly (3,4-ethylenedioxythiophene): polystyrene sulfate (PEDOT: PSS) are effective electrode materials for supercapacitors with the aforementioned important properties. These conductive polymers in a composite hybrid with graphene hydrogel are used as electrode materials in highly efficient and stable flexible supercapacitors. Subsequently, these highly efficient flexible supercapacitors will contribute to the development of wearable electronics, as well as environmentally friendly transportation.

Conductive polymers (CPs) have the potential to become next-generation ECSC electrodes due to their low cost, easy synthesis methods, and high pseudo-capacity. Graphene/CP-based composites demonstrate sufficiently high electrochemical characteristics when used as electrode materials for ECSC. Synthesis methods and electrochemical characteristics of graphene/CP composites for ECSC are summarized in [128]. In addition, a method for synthesizing electrode materials to improve electrochemical characteristics is discussed.

In [129], a durable, highly efficient graphene electrode modified with polyaniline was successfully used to assemble the supercapacitor. Graphene is covalently bonded to doped polyaniline (SPANi) and is therefore used in supercapacitors. Layered graphene modified with 4-aminobenzoic acid (ABF-G) was first attached to aniline functional groups. Aniline, the monomer of o-aminobenzenesulfonic acid, and an oxidizer were then added to the aqueous dispersion of ABF-G to achieve polymerization on the surface of ABF-G. This covalently bonded thin-film electrode material ABF-G (SPANi-ABF-G), modified by SPANi, was then used to manufacture supercapacitors. The supercapacitor with the proposed SPANi-ABF-G electrodes has a **high specific capacity of 642.6 F/g at a current density of 1 A/g**. After testing for a service life of 5,000 cycles, this supercapacitor demonstrated the retention of charging and discharging capacity of 100% and 98.13% at current densities of 1 and 2 A/g, respectively. These capacity retention rates are higher than those of supercapacitors with conductive polymer electrodes. The results obtained prove that electrode materials prepared using covalently bonded graphene and PANi can significantly improve the performance of supercapacitors.

In [130], a graphene-based film (CNT@PANi/rGO/TA) was made from biomass using electroactive tannin (TA), which serves as an adhesive bonding carbon nanotubes to a composite (CNT@PANi) and for bonding with reduced graphene oxide (rGO). Thanks to the thin PANi layer on CNT@PANi, the nanowires intercalate into the intermediate layers of rGO, thereby binding the nanolayers and forming a well-defined porous multilayer structure. The resulting CNT@PANi/rGO/TA film has high mechanical strength (174.6 MPa) and impact strength (9.17 MJ m^3). Meanwhile, the fully solid-state flexible supercapacitor assembly with CNT@PANi/rGO/TA demonstrates a **high capacity of 548.6 F/cm**^{3} and a very high performance of 70.5% from 1 to 50 A/g. Even at –40 °C, the specific capacity of the supercapacitor is up to 454.9 F cm^{-3}, i.e. approximately 83% of the capacity produced at room temperature.

The review article [131] presents the latest achievements in the field of synthesis, fabrication, and characterization of PANi@r-GO hybrid nanocomposites for supercapacitors. Market data for such ECSCs is also presented.

For the development of highly efficient supercapacitors in [132], the initial PANi and PANi nanocomposites with highly conductive two-dimensional graphene were successfully produced by chemical method. The electrochemical properties of ready-made solid-state supercapacitors, established for initial polyaniline composites (PANi/PVA/PANi) and nanocomposites based on polyaniline/graphene (PANi-graphene/PVA/PANi-graphene), were studied using CVA, galvanostatics, and electrochemical impedance spectroscopy. The electrochemical device based on PANi electrodes has a capacity of ~160F/g while retaining ~64% of the capacity. This capacity of polyaniline electrodes was significantly increased to **~1,412 F/g** with ~89% of the capacity remaining after 10,000 charge-discharge cycles, at a content of 8 wt.% of graphene nanolayers in PANi electrodes. A supercapacitor based on a polyaniline nanocomposite with a content of 8 wt.% graphene also had **very high values of energy density (~1382 Wh/kg) and power (~49786 W/kg)**.

Nanocomposites of graphene materials and conductive polymers have been widely studied as promising materials for supercapacitor electrodes. In [133], the heterostructure of the graphene/PANi composite, consisting of a monolayer of graphene and polyaniline, and its electrochemical operation in a supercapacitor were investigated. The synthesis is based on the functionalization of graphene by phenylene sulfone groups and the oxidative polymerization of aniline by ammonium persulfate under reaction conditions that do not produce bulk polyaniline. Scanning electron microscopy, atomic force microscopy, and Raman spectroscopy have shown the selective formation of polyaniline on graphene. *In situ* Raman spectroscopy and cyclic voltammetry (both in a microdroplet setup) confirmed the reversibility of polyaniline redox transitions and electrochemical doping of graphene. After an increase during the initial 200 cycles due to the formation of benzoquinone-hydroquinone defects in polyaniline, the specific surface capacity was maintained for 2400 cycles with a retention of ±1% at 21.2 μF cm^{-2}; this is an order of magnitude higher than the capacity of the original graphene.

[134] demonstrates a simple synthetic method for covalent grafting of aniline tetramer (TANI), the main building block of PANi, to 3D graphene networks with perfluorophenylazide to create a hybrid electrode material for supercapacitors with an ultra-long service life. The design, which replaces long-chain PANi with short-chain TANI and introduces covalent bonds between TANI and 3D graphene, significantly increases the cyclic charge-discharge stability of PANi-based supercapacitors. The electrode material, as well as the symmetrical fully solid-state supercapacitors manufactured, demonstrate an unusually long service life (retaining a capacity of >85% after 30,000 charge-discharge cycles). The capacity can be further increased by rapid and reversible redox reactions on the electrode surface using a redox electrolyte while maintaining excellent cycle stability (retaining 82% capacity after **100,000 cycles** for a symmetrical fully solid-state device). Despite the fact that conductive polymers

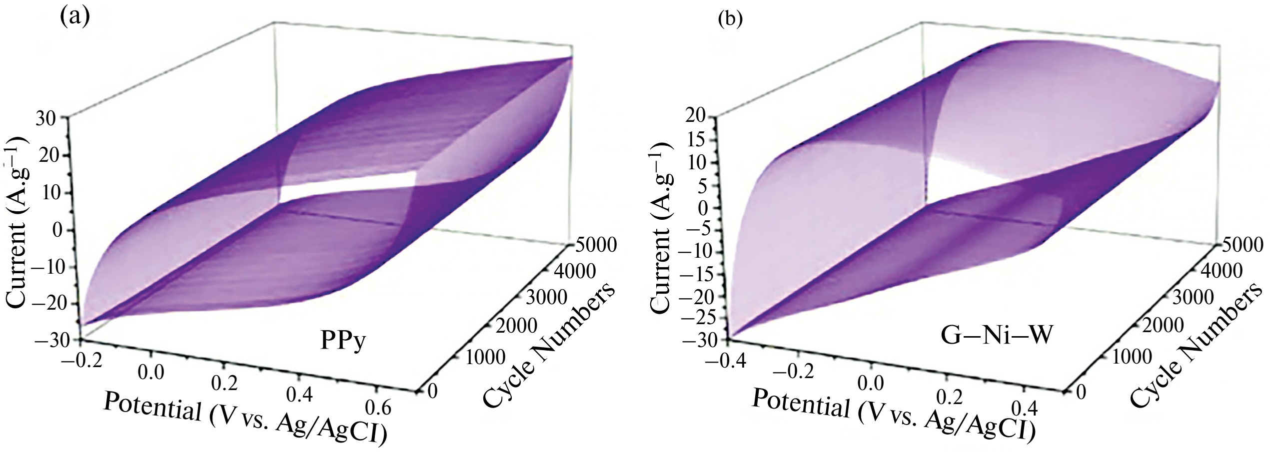

Fig. 13. Three-dimensional demonstration of cyclic stability of a three-electrode supercapacitor system based on (a) PPy, (b) G-Ni–W [138].

are known to be limited by their low cyclic stability, this work offers an effective strategy to achieve an extended service life of supercapacitors.

The paper [135] presents the production of hydrophilic graphene oxide nanolayers by liquid-shear peeling. Graphene oxide nanolayers were used to synthesize three-dimensional graphene/polyaniline composites, which were used directly as supercapacitor electrodes. Composites have better electrochemical properties (gravimetric capacity **483 F/g at 1 A g)** compared to materials made from a mixture of graphene, graphene oxide and polyaniline as precursors. In addition, a symmetrical supercapacitor made of composites demonstrated a high energy density of **17.9 Wh/kg** at a power density of 500 W/kg.

In [9], during polymerization to obtain PANi, the time of electrochemical polymerization was controlled, which led to the formation of graphene-coated paper (PANi-Graphene). The newly prepared electrode showed a high surface capacity of 176 mF/cm^2 in a three-electrode cell at a current density of 0.2 mA/cm^2, which is about 10 times higher than that of pure graphene paper due to the pseudo-capacitance behavior of PANi. More importantly, a fully solid-state symmetrical capacitor assembled with two PANi-Graphene electrodes with a polymer electrolyte had a surface capacity of 123 mF/cm^2, which corresponds to a surface energy density of 17.1 MWh/cm^2 and a surface power density of 0.25 MW/cm^2. The symmetrical capacitor retained 74.8% of its capacity after 500 bending tests from 0 to 120°, indicating good flexibility and mechanical stability.

In [136], the synthesis of stable, conductive, and highly active polythiophene enriched in graphene nanoplatelets (GNPL) by chemical polymerization *in situ* was investigated. X-ray diffraction studies have confirmed the formation of finished nanomaterials. Morphological studies have shown that polythiophene is successfully fixed on the surface of GNPL during polymerization. Elemental mapping has shown the presence of carbon, oxygen, and sulfur in the GNPLs/PTh electrode. Cyclic voltammetry (CV) measurements have shown that the GNPLs/PTh electrode has a maximum specific capacity of **960.71 F/g** at a scanning speed of 10 mV/s. The gravimetric capacity of the manufactured electrodes reached 673 F/g at a current density of 0.25 A/g, which corresponds to an energy density of 2.25 Wh/kg. A cyclic stability study has shown that a GNPLs/PTh-based supercapacitor can retain 84.9% of its initial capacity after 1,500 consecutive CV cycles, indicating excellent cyclic stability of the material.

In the study [137], composite films of reduced graphene oxide (rGO) and poly (3,4-ethylenedioxythiophene) polystyrene sulfate (PEDOT: PSS) were prepared by solvent evaporation using PEDOT: PSS as a binder for fixing oriented graphene in order to ensure its good conductivity and strong π-π-packing interactions with graphene layers. Analyses using scanning electron microscopy (SEM), nitrogen adsorption-desorption, and small-angle X-ray scattering showed that graphene layers were well aligned when a magnetic field was applied, although they were randomly oriented without a magnetic field. As a capacitor electrode material, the composite oriented RGO and (PEDOT: PSS) demonstrated a specific capacitance of 169/g while maintaining about 70% of the capacitance at a current density of 50 A/g, and its CV curves retain a rectangular shape at a voltage scanning rate of 2 V/s.

In [138], a highly active 2D nanostructure consisting of reinforced conductive polypyrrole (PPy) with decorated rGO and a hybrid complex of Ni/W metal oxides (PPy-G-Ni-W) was developed for use in supercapacitors. The hybrid 2D platform showed remarkable specific capacitance of **597 and 557 F/g** when measuring CV and galvanostatic analysis, respectively, using a three-electrode system. The developed supercapacitor has demonstrated very high stability, retaining 98.2% of its overall performance after 5,000 charge-discharge cycles. Similarly, studies in a two-electrode electrochemical cell consisting of PPy-G-Ni-W//PPy-G-Ni-W showed specific capacitances of 361 and 342 F/g at a scanning speed and current density of 2 mV/s and 0.5 A/g using CV and galvanostatic methods, respectively. At the same time, a high energy density of 14.4 Wh/kg was obtained with a power density of 275 W/kg. More importantly, the device retained 96.4% of its total specific capacity after 5,000 charge-discharge cycles (Fig. 13), which highlights the high capacity, mobility, and superstability of the developed ECSC in relation to real-world energy applications.

4. COMPOSITES WITH MXENES

MXenes are a class of two-dimensional inorganic compounds that consist of atomically thin layers of carbides, nitrides, or carbonitrides of transition metals. MXenes have various hydrophilic surface groups. MXenes was first reported in 2012, and their research is undergoing exponential growth. Since 2020, the number of patents on MXenes has exceeded the number of journal articles on MXenes, indicating that they are potentially commercially successful materials. In recent years, MXenes have been used in supercapacitors [5, 139–146].

The great popularity of portable smart electronics has intensively stimulated the development of energy storage devices and other advanced products such as displays and touchpads. Interactive devices such as smartphones, tablets, and other touchscreen devices require mechanically strong transparent conductive electrodes (TCE). The development of a transparent supercapacitor as a power source is essential for next-generation transparent electronics. Recently, graphene and MXene, two representatives of a large two-dimensional family, have shown excellent electronic conductivity and attracted a lot of attention from researchers in the field of energy storage. It is important to note that high-performance TCEs are necessary conditions for creating transparent supercapacitors. The reviews [139, 140] provide a comprehensive analysis of flexible TCEs based on graphene and MXene, covering detailed methods for manufacturing thin films, estimates, performance limitations, as well as approaches to overcome these limitations. Special attention is paid to the fundamental aspects of TCE, such as percolation and conduction.

The new 2D $Ti_3C_2T_x$MXene material (T_x – surface functional groups) is widely studied in the field of supercapacitors. However, the electrochemical characteristics of supercapacitors are reduced due to the presence of $Ti_3C_2T_x$. However, the $Ti_3C_2T_x$ flexible composite/composite membrane/graphene synthesized in [140] effectively eliminates this disadvantage. In contrast to the use of traditional reduced graphene oxide, the structural integrity and large flakes of graphene were synthesized in this work using anhydrous ferric chloride $FeCl_3$. The assembled symmetrical supercapacitor without binder showed a high energy density of 13.1 Wh/kg with a specific power of 75 W/kg. The article presents new perspectives on the analysis of the mechanism of inhibition of MXene self-storage.

Despite the fact that large capacities have been obtained using MXene electrodes in supercapacitors, the relatively high resistance limits the scope of application of these materials. [141] reports on an innovative simple method for manufacturing MXene wrapped in graphene in combination with plasma exfoliation. This method includes two key aspects: 1) incorporation of graphene oxide (GO) into MXene and 2) plasma exfoliation of GO-modified MXene. The resulting materials, referred to as MXene@rGO, have a layered structure with reduced graphene oxide on the surface of MXene. Fully solid-state flexible supercapacitors were manufactured from MXene@rGO materials. Compared to conventional MXenes, MXene@rGO supercapacitors have shown twice the specific capacity, as well as excellent cycling and mechanical stability.

In [142], an ultrahigh-capacity supercapacitor was manufactured using nanolayer MXene as an active electrode material, and nickel foil was used as a current collector. High-quality titanium for $Ti_3C_2T_x$, obtained from the filler fluid, significantly increases the specific capacity in the etching and washing processes. As another technique, graphene grown by chemical deposition from the gas phase was applied to the surface of nickel foil. Graphene grown directly on nickel foil is used as a current collector, forming the $Ti_3C_2T_x$/graphene/Ni electrode structure. It has been found that the capacity of graphene-based supercapacitors is more than 1/5 times higher than the capacity without graphene. A high specific capacity of **~542 F/g** is achieved at a scanning speed of 5 mV/s. In addition, the graphene-based supercapacitor exhibits a quasi-rectangular shape on cyclic voltammetric curves and symmetrical behavior on galvanostatic charge/discharge curves. Cyclic stability of up to 5000 cycles is confirmed by maintaining high capacity at a high scanning speed of 1000 mV/s.

It follows from the well-known formula for energy density [2] that expanding the voltage window and increasing the capacitance are effective ways to increase the energy density of supercapacitors. However, aqueous electrolyte-based devices usually have a voltage window of less than 1.2 V, taking into account water electrolysis, and chemically converted graphene provides mediocre capacity. According to [143], multielectron redox, structurally stable π-frameworks of indanthrone (IDT:(6,15-dihydrodinaphtho[2,3-a;2',3'-h] phenazine-5,9,14,18-tetraone) were effectively bound to reduced graphene oxide (rGO) to form the IDT@rGO molecular heterojunction. Such electrodes, which do not contain conductive agents and binders, provided a maximum capacity of up to 345 F/g in the potential range from –0.2 to 1.0 V. The $Ti_3C_2T_x$ MXene film partner electrode, operating in the negative potential range from –0.1 to –0.6 V, provided a capacity of up to 769 F/g. Thanks to the realized potentials of the IDT@rGO heterojunction positive electrode Ti3C2Tx MXene and the negative electrode polyvinyl alcohol/H2SO4, the flexible asymmetric supercapacitor based on hydrogel electrolyte provided an increased voltage window of 1.6 V and an impressive energy density of **17 Wh/kg** with a high specific power of **8 kW/kg**, as well as efficient high-speed capability and long service life (maintaining 90% capacity after 10,000 cycles), as well as exceptional flexibility.

As demand for wearable electronic devices grows, so does interest in small, lightweight, and deformable energy storage devices. Among these devices, wire supercapacitors (WSC) are considered key components of wearable devices due to their geometric similarity to woven fiber. One of the potential methods for creating WSC devices is the layer-by-layer assembly (LbL) method, which is a bottom-up electrode manufacturing method. WSC stands for the conformal and adhesive coating of a functional material on a wire substrate, which is difficult to obtain using other processing methods such as vacuum filtration or spray coating. The LbL assembly technology allows for convenient and durable coatings that can be applied to various substrates and shapes, including wire. A study [144] reports on WSCs made using LbL assembly of alternating layers of positively charged reduced graphene oxide functionalized with poly(diallyldimethylammonium chloride) and negatively charged $Ti_3C_2T_x$ MXene nanolayers effectively deposited on activated carbon filaments. In this design, the added LbL film increases capacity, energy density, and power density by 240, 227, and 109%, respectively, compared to uncoated activated carbon yarn, providing high specific and volumetric capacity (**237 F/g**, 2193 F/cm^3). In addition, the WSC has good mechanical stability, maintaining 90% of its original performance after 200 bending cycles. This study demonstrates that LbL coatings based on carbon filaments are promising as energy storage devices for fiber electronics.

2D-MXene materials have attracted close attention in the field of energy storage. However, MXenes usually undergo major re-engineering to increase stability, which significantly hinders their continued commercial use. The article [145] demonstrates an effective and fast self-assembly method for obtaining a 3D porous MXene/graphene (PMG) composite resistant to oxidation to suppress oxidation and self-assembly of MXene. The self-organizing 3D porous architecture can effectively prevent oxidation of MXene layers without visible changes in electrical conductivity in air at room temperature, ensuring high electrical conductivity and a large number of electrochemical active sites accessible to electrolyte ions. The PMG electrode has a high specific capacity of **393 F/g** at 10V/s, excellent performance and outstanding cycling stability. In addition, the assembled asymmetric supercapacitor had a high energy density of 50.8 Wh/kg and remarkable cycle stability with a decrease in specific capacity of only 4.3% after 10,000 cycles. This work paves a new path for solving important issues with MXene in the future.

Two-dimensional (2D) materials are expected to be among the most efficient compounds for use in the energy industry. The ability to store energy in two two-dimensional materials, reduced graphene oxide (rGO) and NbCMXene due to the creation of hetero-assembly, was first realized in [146] by double doping with nitrogen on both lattices using the method of supercritical fluid treatment. As is well known, supercritical fluid synthesis of hetero-assembly based on 2D/2D MXene is unique and distinctive. The high charge storage capacity of N-(NbC/rGO) composites and the typical reaction kinetics contribute to very high electrochemical performance due to this unique synthetic technique. Thus, N-(NbC/rGO) exhibits exceptional electrochemical characteristics **with a high specific capacity of 816 F/g at a current density of 1 A/g and a remarkable energy density of 29 Wh/kg in an aqueous H_2SO_4 electrolyte and 33 Wh/kg in a non-aqueous $TEABF_4$/acetonitrile electrolyte**. In addition, after **100,000 cycles**, 100% of the initial capacity is retained in a quasi-solid electrolyte based on PVA/HSO_4.

5. QUANTUM DOTS

The Nobel Prize in Chemistry in 2023 was awarded to three scientists for one discovery. Moungi Bawendi, Louis Brus and Alexey Ekimov were awarded the highest scientific award for the discovery and synthesis of quantum dots, semiconductor nanocrystals with unique optical and electronic properties.

A quantum dot is a fragment of a conductor or semiconductor whose charge carriers are limited in space in all three dimensions. The size of a quantum dot should be so small that the quantum effects are significant.

The inclusion of new functional components in a three-dimensional graphene (3DG) framework improves the performance of 3DG-based supercapacitors in electrodes by adapting the structure and properties of the framework. Recently, quantum dot materials have been used in supercapacitors [7, 32, 94, 113, 147–150]. In [147] graphene quantum dots (GQD) were incorporated into 3DG by single-stage hydrothermal treatment of GQD and graphene oxide (GO). By simply adjusting the GQDs/GO ratio by weight, various GQD/3DG composites were formed. The maximum ratio was 80%, while composites obtained with a GQDs/GO ratio of 40% for electrodes showed a maximum specific capacity of **242 F/g** for supercapacitors, which means an increase of 22% compared to pure 3DG electrodes (198F/g). This improvement in performance was mainly due to the higher electrical conductivity and larger surface area of GQD/3DG composites. The manufactured GQD/3DG composites as electrodes for supercapacitors have shown high electrochemical stability. Their capacity remained 93% of its original value after 10,000 charge-discharge cycles.

Despite the fact that activated carbons (AC) with a large surface area are widely used in supercapacitors, they usually have limited capacity and speed characteristics, primarily due to their low conductivity and slow electrochemical kinetics caused by their amorphous microporous structure. The article [148] suggests a simple strategy for improving the electrochemical characteristics of AC by embedding highly crystallized graphene quantum dots. Due to the formation of common conductive networks, the kinetics of charge transfer and ion migration in the battery is significantly improved, facilitating the transportation and storage of electrolyte ions in deep and branched micropores. As a result, graphene quantum dots are embedded in activated carbon, which has a microporous structure with a specific surface area of **2829 m^2/g**. This results in a high double-layer capacity of **388 F/g at 1 A/g**, as well as excellent speed characteristics while maintaining 60% of the capacity at 100 A/g in a two-electrode system. The capacitance and velocity characteristics are much higher than those of AC without graphene quantum dots, as well as most porous carbons reported in the literature. This strategy opens up new opportunities for the development of advanced porous carbon materials for high-performance energy storage.

The paper [149] reports on mathematical modeling to study the contribution of quantum dots to the total differential capacitance of functionalized graphene as a material for electrodes of water-based supercapacitors. The effects of nitrogen and oxygen inclusion in the quantum and double-layer capacitance of graphene in four different models of supercapacitors with Li_2SO_4 and LiTFSI aqueous electrolytes are considered. It was found that the total differential capacitance is limited by the double-layer capacitance. The best model of the electrode/electrolyte system was obtained for a symmetrical supercapacitor assembled from epoxy/hydroxyl-functionalized graphene electrodes impregnated with 1 M Li_2SO_4 aqueous electrolyte.

In [150], a simple hydrothermal method for the synthesis of CeO_2/Ce_2O_3 quantum dots fixed on layers of reduced graphene oxide (rGO) of various weight fractions is reported for use as a supercapacitor electrode. Of all the tested samples, a sample containing 7 wt.% rGO ($CrGO_3$), measured by thermogravimetry, demonstrated the highest specific capacity of **1027 F/g at 1 A/g** along with good cyclic stability. At a current density of 4 A/g, the $CrGO_3$ sample showed charge retention of 79% after 5,000 cycles, whereas at 20 A/g it showed charge retention of 85% after 3,000 cycles. The values obtained for the $CrGO_3$ electrode are higher than for all previous cerium and rGO-based electrodes, which suggests its potential use in supercapacitors. High-resolution transmission electron microscopy (HRTEM) clearly revealed crystalline CeO_2 nanoparticles (~5 nm) evenly distributed on the rGO layers, as well as several lattice planes indicating the presence of some amount of Ce_2O_3 mixed with CeO_2. X-ray photoelectron spectroscopy (XPS) revealed the presence of mixed oxides containing mainly CeO_2 with some phase Ce_2O_3 on the surface.

CONCLUSION

This review examines the literature, mainly for recent years, on the relevant subject of graphene applications in supercapacitors. The influence of the porous structure of graphenes, the effect of doping and irradiation of graphenes is considered. Methods for obtaining graphenes, graphene composites with metal oxides, sulfides and selenides, composites with metal particles, with electron-conducting polymers, with MXenes, as well as quantum dots are considered. Electrochemical characteristics are given for various types of graphenes and their composites.

Particularly high electrochemical characteristics were obtained for composites of graphene with polyaniline, with metal oxides, with selenides, with MXenes and with doping of graphene with boron.

The following maximum values of specific energy were obtained: 40.5 Wh/kg (for $NiSe_2$), 78.66 Wh/kg (for TiO_2), 79.5 Wh/kg (for boron doping), 1382 Wh/kg (polyaniline).

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CONFLICT OF INTEREST

The author declares that he has no conflict of interest.

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