Express Polymer Letters Vol.18, No.10 (2024) 1023–1038
Available online at www.expresspolymlett.com
https://doi.org/10.3144/expresspolymlett.2024.78

Review article

Multifunctional energy storage polymer composites: The role of nanoparticles in the performance of structural supercapacitors

Péter Csvila[1], *Tibor Czigány*[1,2*]

[1]Budapest University of Technology and Economics, Faculty of Mechanical Engineering, Department of Polymer Engineering, Műegyetem rkp. 3., H-1111 Budapest, Hungary
[2]HUN-REN-BME Research Group of Composite Science and Technology, Műegyetem rkp. 3., H-1111 Budapest, Hungary

Received 2 June 2024; accepted in revised form 15 July 2024

Abstract. The article gives an overview of energy storage composites, their materials, manufacturing processes, and applications. Carbon- and metal-based nanoparticles and their relevant properties are presented. We focus on multifunctional structural supercapacitors and their components. Thus, we describe the main structural electrolytes and elements of the structural electrodes. We show that the nanoparticles significantly influence the electrochemical properties of the electrode. For example, carbon-based nanoparticles can achieve low energy density but high power density, while the opposite is true for metal-based nanoparticles. We show that when carbon- and metal-based nanoparticles are used together, a positive synergy is created between them, promoting the development of favorable electrochemical properties in the electrodes. Furthermore, we present structural supercapacitors and possible ways to introduce nanoparticles into the system. Finally, we present a summary of the progress achieved so far and the advancements expected in the future, as well as potential areas where structural supercapacitors could be used.

Keywords: *structural supercapacitor, electric double layer capacitor, carbon-based nanoparticle, metal-based nanoparticle, structural electrode, solid electrolyte*

1. Introduction

Polymer matrix composite materials – thanks to their excellent specific properties – play a significant role in applications where the low weight and low volume of components are essential, such as the automotive and energy industries. The anisotropic properties of composites can be exploited to produce more specific, consciously designed components with higher performance and lower weight. Polymer composite materials also offer excellent specific mechanical properties and other advantageous functionalities. These are so-called multifunctional composite materials. With them, we can produce machines with even better efficiency. These functionalities include, for example, targeted thermal conductivity, load-carrying capacity, deformation, or even the conduction of electric current [1, 2].

Today's technology (Industry 4.0 and Industry 5.0) is based on electricity and its necessity. Thus, there are great efforts to develop energy storage devices with the best possible energy density and power density, which can quickly and efficiently serve electric machines. For example, a vital issue in the current rise of electric vehicles is the range and performance that engineers will have to improve in the near future. The solution to this problem may be supercapacitors,

*Corresponding author, e-mail: czigany@eik.bme.hu

which emerged at the beginning of the 21st century, combining the favorable energy density of batteries with the excellent power density of capacitors. These supercapacitors also have excellent charge-discharge times and generally longer lives than batteries. A key role in the development of supercapacitors is to discover various nanoparticles, understand their properties, and apply them in a targeted manner [3–5].

According to their operating characteristics, supercapacitors are divided into three categories: electrochemical double-layer capacitors, pseudocapacitors, and hybrid capacitors. In electrochemical double-layer capacitors (EDLC), energy is stored electrostatically at the electrode–electrolyte interface (Figure 1a). This process is rapid, because there are no chemical reactions in the capacitor, so there is no morphological or volumetric change in the material. In pseudocapacitors, redox reactions are used to store energy. Charges flow between the electrodes and the electrolyte (Figure 1b), resulting in a greater energy density but with a significantly slower process. Hybrid capacitors take advantage of the positive properties of EDLCs and pseudocapacitors (Figure 1c), where energy can be stored both by electrostatically and by redox reactions [5, 6].

In addition to the excellent energy storage and energy delivery properties of supercapacitors, they also have great potential for future development. They can be made from solid or near-solid materials, which makes them able to resist static and dynamic loads. Therefore, they can be used as both load-bearing and energy-storing elements. For example, they could be used as body panels for electric cars, where they could be used to store extra energy thanks to their multifunctionality. For multifunctional solutions, EDLCs would be particularly suitable, where energy storage does not involve any chemical process, so as a structural element, its material properties are not affected by energy storage. The specific energy of EDLCs is far lower than that of batteries, but they are not designed to replace them. Batteries are characterized by high energy density at low power density, whereas capacitors have the opposite properties. However, several supercapacitors can already approach the energy density of some batteries. Figure 2 shows that while the energy density of EDLCs is lower than that of most batteries, they can approach the energy density of some batteries. Furthermore, a combination of EDLCs with batteries could yield both high power and high energy density. EDLCs make use of double-layer capacitance. When an electrode and an electrolyte come into contact, two layers of electric charges form. One layer in the electrode, and one layer in the electrolyte. Only a single layer of solvent (electrolyte) molecules separates the two layers. This single layer behaves like a dielectric in a conventional capacitor [3]. The energy of a capacitor is the Equation (1):

$$E = \frac{1}{2}CU^2 \tag{1}$$

where E is energy [J], C is capacitance [F], and U is voltage [V]. In supercapacitors, capacitance is increased, the voltage is relatively low. The capacitance of a conventional plate capacitor is Equation (2):

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \tag{2}$$

where ε_0 is the permittivity of vacuum, ε_r is relative permittivity, characteristic of the dielectric material

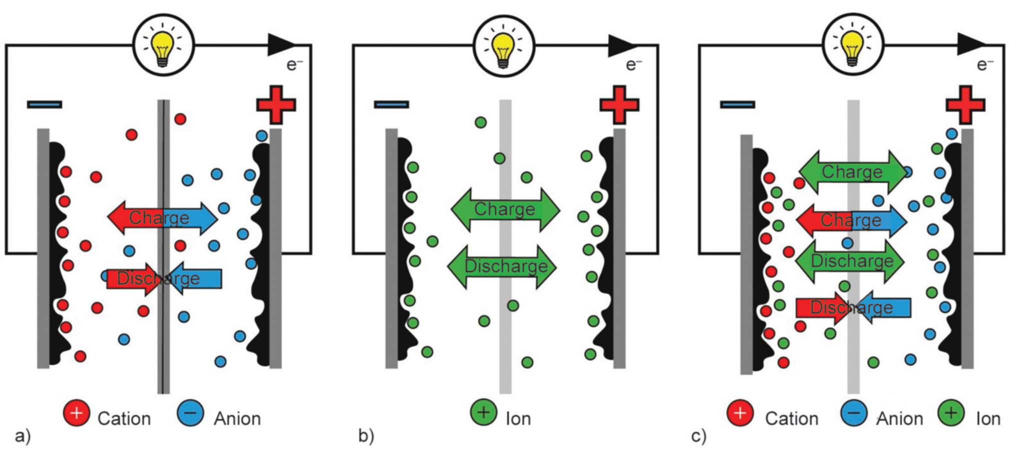

Figure 1. Electrostatic charging of EDLC (a) the charging method of a pseudocapacitor through redox reactions (b) and the charging method of a hybrid capacitor (c) (based on [5]).

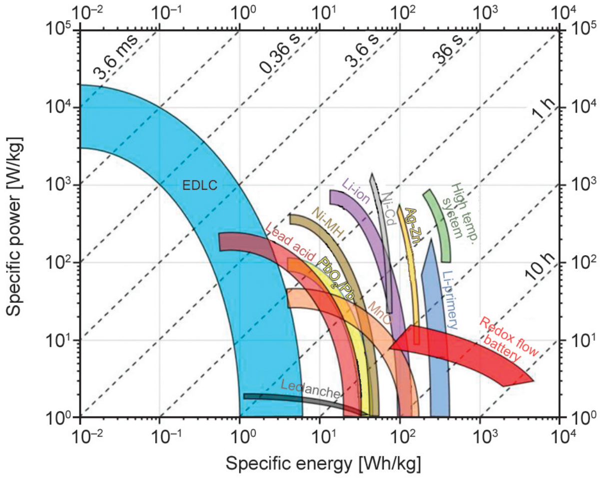

Figure 2. Ragone plot: various energy storage devices (EDLC and a few battery types) compared in terms of specific power and specific energy [5].

between the plates, A is the area of the plates and d is their distance. The formula also applies to EDLCs, where d is extremely small, far smaller than in a conventional capacitor. The use of nanomaterials can considerably increase A (see Table 1). Capacity can increase further if the solvent's relative permittivity is also high and facilitates a faster ion transfer. As a result of these factors, the capacity of EDLCs is far higher than that of conventional capacitors, therefore they deserve the name 'supercapacitor' [5].

Our goal is to present multifunctional structural composites for energy storage. In particular, their components (electrode, electrolyte) are described along with the applied nanoparticles. The article also presents the advancements in structural supercapacitors that have been published in the last five years, with special emphasis on the role of nanoparticles, which will help readers choose materials for designing supercapacitors. Supercapacitors are attracting increasing attention (the number of articles in this field has increased significantly in the last ten years), due to their ability to better manage electrical energy, complementing batteries. They are also very important from the point of view of energy storage, as they make it possible to store temporarily available energy from renewable resources, which is essential for more sustainable energy management.

2. Nanoparticle-based composites for structural supercapacitors

The development of supercapacitors has been strongly helped by the conscious use of nanoparticles. Nanoparticles can be used to upgrade ordinary capacitors (with a few microfarads) into supercapacitors (with multifarad capacitance). Nanoparticles are essential components of supercapacitors as they improve energy storage capability, conduction and reliability. They have a high specific surface area, which allows for greater charge accumulation at the electrode–electrolyte interface. Furthermore, their ability to conduct electric current promotes faster electron transport. It reduces internal resistance, enabling supercapacitors to operate with shorter charging and discharging times at high power densities. Another essential property is their good chemical and cyclic stability, which allows the production of reliable energy storage devices over the long term. In many cases, their porosity, capacitance and in some cases, their ability to undergo redox processes (especially for pseudocapacitors) are also important. In addition, if we want to achieve good mechanical properties, their strength and Young's modulus are also important, as well as their compatibility with the matrix. Based on these, mainly carbon-based and metal oxide–based nanoparticles are used in the fabrication of structural supercapacitors [1, 3, 4].

2.1. Carbon-based nanoparticles

Carbon-based nanoparticles, which are also very popular in polymer technology, are used in significant quantities in supercapacitors due to their excellent mechanical, conductive, and chemical properties. One of the most commonly used particles is graphene (Gr). Graphene is practically two-dimensional nanoparticle with a single atomic plane containing only carbon atoms. It has a theoretical specific surface area of 2630 m^2/g, but in practice an average specific surface area of 800–1000 m^2/g can be achieved due to various defects and manufacturing imprecision [7]. It has a theoretical tensile strength of 130 GPa and a Young's modulus above 1 TPa. Graphene is difficult to produce, so graphene oxide (GO), is often used, which is easier to produce. However, the properties of GO are inferior to those of Gr. Also worthy of mention is the increasing use of reduced graphene oxide (rGO), where the properties of GO are enhanced by various chemical processes [8, 9].

The other widely used carbon-based nanoparticle is the carbon nanotube (CNT). Among the two main types (single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT)), the single-walled carbon nanotube has the best electrical properties [10]. Its electrical conductivity is in the order of 10^6–10^7 S/m [11]. Its tensile strength is 100–200 GPa [12], and its theoretical elastic modulus is 1 TPa [12, 13].

Another commonly used carbon-based nanomaterial is activated carbon (AC). It can be produced with a variety of processes, therefore its electrical and mechanical properties are highly variable depending on the manufacturing parameters [14, 15]. AC may have an extremely high specific surface area of up to 1000 m^2/g [16], due to its surface pores, which are excellent for electron attachment [17, 18].

2.2. Metal-based nanoparticles

In addition to/instead of carbon-based nanomaterials, various metal-based nanoparticles are often used in structural supercapacitors. These materials can also improve the supercapacitor's energy and power density. As they are chemically stable materials, they increase the lifetime and reliability of capacitors, in addition to their high specific surface area and electrical properties to provide the necessary electrostatic charge.

Metal oxide–based nanoparticles include ruthenium dioxide (RuO_2), manganese dioxide (MnO_2), and titanium dioxide (TiO_2). Such nanoparticles generally have a high specific surface area but lower than the 40–400 m^2/g of carbon-based nanoparticles. Their main positive feature is that they have a very high specific capacitance (150–700 F/g), which allows the production of high–capacitance capacitors. The electrical properties of purely metal-based nanoparticles are excellent, but the electrical properties of the more commonly used metal oxides are poor in practice. Their mechanical properties cannot match those of carbon-based materials, but they still have a tensile strength of 224–300 MPa and an elastic modulus of 200–250 GPa [19–24].

Furthermore, in the field of metal-based nanomaterials, the transition metal dichalcogenides (TMDs), and various disulfides, such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), deserve mention. They can be generally fabricated as 2D nanopellets and have received much attention in the last few years due to their good mechanical and electrical properties. Also worth mentioning are MXenes, which have received much attention in recent years. They can also be produced as two-dimensional pellets by layering metals and chalcogenides. In general, they have excellent electrical properties, excellent mechanical strength, and good chemical stability, which are essential for producing high-performance supercapacitor electrodes [25–27].

2.3. Properties of nanomaterials for supercapacitors

We have seen that both carbon-based and metal-based nanoparticles can meet the requirements of supercapacitors. They have a high specific surface area for good capacitance, in many cases significant electron mobility, good conductivity, and in many cases, excellent mechanical properties. The most relevant characteristics of nanoparticles are summarised in Table 1.

3. The components of supercapacitors

Supercapacitors have two main components, which largely determine their electrochemical properties: the electrodes and the electrolyte between them. They are different from conventional capacitors, which do not have an electrolyte; although electrolytic

Table 1. Nanoparticles and their properties used in structural supercapacitors.

Material	Specific surface area [m^2/g]	Specific capacitance achieved with the following nanoparticles [F/g]	Electron mobility [$cm^2/(V·s)$]	Electrical conductivity [S/m]	Tensile strength [MPa]	Young's modulus [GPa]	References
Gr	1005 Theoretical: 2630	130–250	200 000	$1.46·10^6$–10^8	130 000	~1000	[7–10, 28]
CNT	600 Theoretical: 1315	2–64	80 000	10^6–10^7	100 000–200 000	~1000	[10–12, 29, 30]
AC	700–1031	56–400	48	$5.33·10^{-10}$–$1.22·10^1$	70–500	4–80	[14–18, 31, 32]
RuO_2	42	700	0.01–10	10–800	224	232	[19, 20, 33, 34]
MnO_2	118–337	163–477	~10^{-13}	10^{-5}–10^{-6}	–	225	[21, 22, 35–37]
TiO_2	280	385	0.1	$2.41·10^5$–$6.54·10^6$	367	230	[23, 24, 38–41]

The table shows that carbon-based particles have a relatively high specific surface area, while metal-based nanoparticles have a rather high specific capacitance (Figure 3).

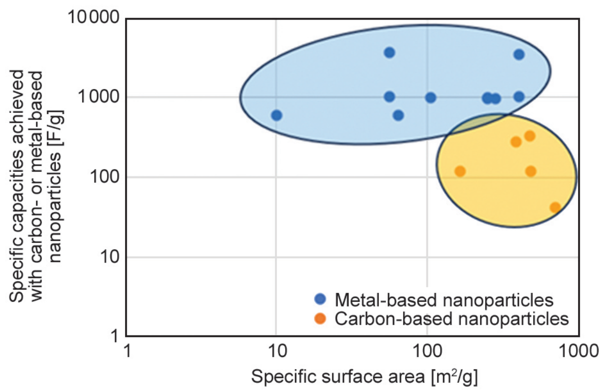

Figure 3. The specific surface area and specific capacitance of carbon- and metal-based nanoparticles [based on 7–24, 28–41].

capacitors have an electrolyte, it is the cathode itself. In supercapacitors, the electrolyte is not an electrode. In addition to these elements, supercapacitors have a separator between the electrodes and two current collectors, one on each electrode (Figure 4). The separator prevents the electrodes from being physically connected and the system from being short-circuited. In many cases, glass fiber fabrics are used as separators for structural supercapacitors due to their good mechanical and electrical properties [42, 43].
The current collectors also play an essential role in supercapacitors, enabling them to mobilize and release their charges and transfer them into the devices. Carbon-based materials such as carbon foils [44], ribbons, carbon fibers, and other carbon-based sheets can be used as current collectors. Another solution is metal-based current collectors made of nickel, copper, aluminum [45], gold, or silver [46]. These are mainly incorporated in the form of a foam, foil, or mesh. The performance of supercapacitors is also largely determined by the materials used for the current collector elements [47]. However, the electrochemical properties of a supercapacitor depend to

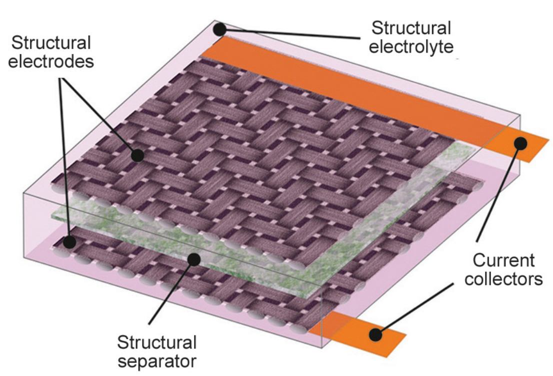

Figure 4. Schematic architecture of a structural supercapacitor with electrodes, electrolyte, separator, and current collectors [43].

the greatest extent on the electrolyte, the electrodes, and the connection between them.

3.1. Solid electrolytes

Although gel-phase polymer electrolytes are also available for structural supercapacitors with significant mechanical load-bearing capacity, it is preferable to use solid-state electrolytes. This ensures that the reinforcing material is protected from external effects and provides sufficient strength. In general, the electrolyte material must perform two functions: mechanical and electrochemical. In addition to these functions, the lifetime of the supercapacitor, its discharge and charging times, resistance, and thermal stability depend mainly on the electrolyte material [48].
Materials used in polymer technology, such as vinyl ester resin, epoxy resin, polyvinyl alcohol (PVA), and polyethylene oxide (PEO), which have good mechanical properties, are often used as a base material for solid electrolytes. In addition, various ion-conducting materials (*e.g.*, lithium salts, potassium hydroxide (KOH), polyethylene glycol (PEG)) are introduced into the matrix to improve the efficiency of supercapacitors. This solution improves the electrochemical efficiency of the capacitor/electrolyte but degrades its mechanical properties [4, 49].
A theoretical dichotomy was described by Asp [50] for solid polymer electrolytes (SPE). The author described that in the case of bifunctional polymers, improvement of one function can only occur due to significant deterioration of the other. Zhang *et al.* [51] investigated this property–feature relationship in a biphasic solid electrolyte context. They dispersed different concentrations of lithium salts (bis(trifluoromethane)sulfonamide lithium (LiTFSI)+1-ethyl-3-methylimidazolium-bis(trifluoromethanesulfonyl) imide (EMIm-TFSI)) in epoxy resin. They found that as the concentration of lithium salts increased, the toughness of the epoxy resin increased while its tensile and flexural strength decreased significantly. Furthermore, they observed that lithium salts increased ionic conductivity in contrast to strength, but at concentrations lower than 45%, no coherent ionic conducting phase formed, so ionic mobility between molecular chains was not significant (Figure 5).
A solution to this problem can be found in dual-function single-phase polymers, which can perform mechanical and ion-conducting functions without degrading properties. Joyal *et al.* [52], tried to eliminate the problem of degrading mechanical properties

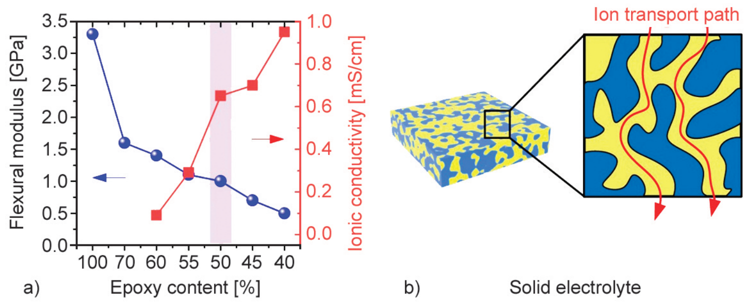

Figure 5. Schematic diagram of ionic conductivity versus mechanical properties in solid polymer electrolytes (a) ion transport paths in solid polymer electrolyte (b) [5].

associated with improving ionic conductivity. Instead of a biphasic polymer electrolyte, they created a solid electrolyte that can perform both mechanical and electrochemical functions. They prepared a new structural electrolyte consisting of poly(ethylene terephthalate) (PET) and lithium perchlorate trihydrate ($LiClO_4$–$3H_2O$) with different weight ratios. The best-performing solid electrolyte had a modulus of 2.1 GPa, an ionic conductivity of 1.05 µS/cm, and a capacitance of 199 µF/cm^2. Their results indicate that single-phase polymer electrolytes can have better multifunctional properties and thus produce better structural supercapacitors.

3.2. Nanoparticles in supercapacitor electrodes

In the case of structural supercapacitors, carbon fibers or other carbon-based materials are most commonly used as electrode materials. Still, other reinforcing materials, such as aramid fibers, can also be used. For example, such solutions have been investigated by Yang *et al*. [53], who fabricated structural electrodes by combining $Ti_3C_2T_x$ metal-based nanoparticles with aramid nanofibers. Using the electrodes, they produced a supercapacitor with an energy density of 11.8 W·h/kg and a power density of 105 W/kg (calculated with the mass of the fully assembled device), which had a tensile strength of 153 MPa.

The advantage of carbon-based structural electrodes is that carbon is a very versatile material. In addition to its excellent mechanical properties, it has good electrical conductivity, and manufacturing processes can significantly vary its properties. Nanoparticle-free structural capacitors based only on carbon fiber electrodes can be fabricated. Shirshova *et al*. [42] used untreated and activated woven carbon fiber fabric as the electrode, glass cloth as the separator, and then impregnated this layered arrangement with matrix materials of various lithium salts, such as polyacrylonitrile (PAN) and polyethylene glycol diglycidyl ether (PEDGE). They achieved power densities ranging from 0.05 to 90.4 W/kg and energy densities ranging from 3.2 µW·h/kg to 10.54 mW·h/kg. The structural capacitor with the best energy and power density was obtained with activated carbon fabric and a PAN matrix doped with propylene carbonate/ethylene carbonate (PC/EC) + 0.1 M LiTFSI. It had a power density of 71.63 W/kg and an energy density of 10.54 mW·h/kg. The study also showed that electrochemical properties could vary greatly depending on the matrix material (Figure 6).

Supercapacitor electrodes can be produced from other carbon-based materials and nanomaterials with or without carbon fiber. Examples include carbon nanotubes, graphene, graphite, carbon nanofibers, and various porous carbon foams. They can be used to increase the electrode–electrolyte interface of supercapacitors, allowing improved electrochemical properties to be achieved without a significant deterioration in mechanical properties. Carbon-based structural supercapacitors are characterized by excellent mechanical properties combined with better power and energy density than structural supercapacitors containing only carbon fiber [54–58]. Melkiyur *et al*. [54], presented several EDLCs produced with carbon-based materials. Of the carbon-based materials used, they analyzed porous carbon foam, reduced graphene oxide, nanotubes, and nanofibers. The supercapacitors they reviewed varied in power density from 228 to 48 000 W/kg and energy density from 2.8 to 21.9 W·h/kg. Several researchers have developed carbon fiber–based and carbon nanotube–based electrodes for supercapacitors [55, 56]. For example, Li *et al*. [55] describe electrodes fabricated from carbon nanotubes and carbon foam or carbon fabric. Carbon fabric with CNTs had a power density of 44 W/kg and an energy density of 5.73 W·h/kg (calculated with the mass of the complete device).

Carbon foam with CNTs, on the other hand, had a significantly higher power density (3700 W/kg) and energy density (28 W·h/kg), due to its more porous structure. Carbon nanotubes are often created by chemical vapor deposition (CVD) on the carbon substrate for better multifunctional properties. Felhősi *et al*. [56] also used this technique to produce supercapacitors. They created CNTs on a non-activated woven carbon fabric. The resulting supercapacitor had an energy density of 1.5 W·h/kg and a maximum power density of 20 000 W/kg (calculated with the mass of the electrodes). In addition to CNTs, graphene nanoparticles and their derivatives, graphene oxide (GO) and reduced graphene oxide (rGO), are also commonly used to produce supercapacitor electrodes [57, 58]. For example, Jiang *et al*. [57] fabricated an electrode using reduced graphene and carbon fiber and the supercapacitor with this electrode had a power density of 2200 W/kg and an energy density of 19.6 W·h/kg. Frequently, activated carbon-based materials are used to achieve better electrochemical properties, because carbon-based materials generally increase specific surface area. Such materials could be, for example, activated carbon fiber or even activated graphene. Skrypnychuk *et al.* [58] fabricated an electrode using activated graphene and carbon nanotubes to achieve a high specific surface area. Their supercapacitor reached a power density of 42 200 W/kg and an energy density of 35.6 W·h/kg (calculated with the mass of the electrodes). The electrodes presented show that the electrochemical properties of supercapacitor electrodes can be significantly improved with the use of carbon nanoparticles and other carbon-based materials with a high specific surface area (Figure 6).

Metal-based nanoparticles are also often used. They can increase the energy density of capacitors, as they are capable of redox processes during energy storage. In supercapacitors, numerous metal nanoparticles (*e.g*., copper (Cu), titanium nitride (TiN)) and metal oxides (*e.g*., RuO_2, MnO_2) are used. Metals are good electrical conductors but less suitable for charge storage, unlike metal oxides, which, in addition to being conductors of electric current, are also capable of storing electrons and participating in electrochemical processes. Such capacitors have been produced, for example, by Muhommad *et al*. [59], who used morphologically oriented copper cobalt boron (Cu–Co–B) alloy-based nanosheets to fabricate a supercapacitor electrode, with which they produced a supercapacitor with a power density of 4626.6 W/kg and an energy density of 90.2 W·h/kg. Yi *et al*. [60] investigated the advantages of metal oxides and nitrides in pseudocapacitors. They investigated TiN-based electrodes and the supercapacitor had a power density of 150–3000 W/kg and an energy density of 12.3-45 W·h/kg and RuO_2-based electrodes with which the supercapacitor had a power density of 1500 W/kg and an energy density of 41.6 W·h/kg. Liu *et al.* [61] investigated MnO_2/Ti_3C_2-based electrodes – the supercapacitor had a power density of 221.33 W/kg and an energy density of 8.3 W·h/kg (calculated with the mass of the electrodes). Melkiyur *et al*. [54] described several pseudocapacitors with electrodes containing only metal-based nanoparticles. The capacitors with metal-based particles had a lower power density than supercapacitors with only carbon-based electrodes. However, they had better energy density due to their ability to take part in redox processes. The power density of the described supercapacitors varied from 2 to 125 W/kg, and their energy density from 15.6 to 41.5 W·h/kg (Figure 6).

Metal-based nanoparticles can be combined with carbon-based particles to produce supercapacitors with both good energy density and good power density. The carbon and metal-based particles have a synergistic effect, and together, they enhance the energy and power density of the supercapacitor. Tang *et al.* [62] investigated a supercapacitor consisting of a cathode based on CNT and MnO_2 particles and an anode based on CNT and polypyrrole (asymmetric). They achieved a power density of 519 000 W/kg and an energy density of 40 W·h/kg (calculated with the cell mass of the supercapacitor). Gupta and Kumar [63] fabricated supercapacitor electrodes using SWCNT buckypaper and MnO_2 metal oxide nanoparticles. The power densities of the fabricated supercapacitors were 1000 and 10 000 W/kg, and energy densities were 151 and 88 W·h/kg, respectively. Vinodhini and Xavier [64] fabricated electrodes using a combination of carbon-based CNT particles and two metal-based nanoparticles, MoS_2 and TiO_2. The supercapacitor with these electrodes had a power density of 4546.8 W/kg, an energy density of 757.8 W·h/kg, and excellent cycle stability – after 10 000 cycles with 98.83% capacity retention. Li *et al.* [55] describe several graphene and other particle-based electrodes. They report energy densities of 3.2 and 29 W·h/kg and power densities of 1280 and

1200 W/kg for graphene/MnO_2/CNT, and energy densities of 19.24 W·h/kg and power densities of 5398 W/kg (calculated with the mass of the complete device) with graphene/CNT/nickel foam–based electrodes. Yi *et al.* [60] investigated electrodes with carbon-based nanoparticles and RuO_2. With RuO_2/carbon nanofiber-based electrodes, power density was 17 545.5 W/kg and energy density was 21.5 W·h/kg, for RuO_2/carbon fiber, power density was 427.6 W/kg and energy density was 133.8 W·h/kg, and for RuO_2/CNT power density was 557.3 W/kg and energy density was 127.9 W·h/kg. Melkiyur *et al*. [54] and An *et al*. [65] also reported several hybrids, *i.e*., carbon and metal-based nanoparticle supercapacitor electrodes. Overall, these electrodes can have, on average, better electrochemical properties compared to supercapacitor electrodes with only metal and carbon-based nanoparticles, due to synergistic effects. The power density of the supercapacitors built from the mixed/hybrid nanoparticle electrodes described in this chapter varied from 850 to 28 000 W/kg, and their energy density ranged from 23 to 185 W·h/kg (Figure 6).

Overall, the specific electrode–electrolyte interface is significantly smaller for nanoparticle-free materials than for those containing nanoparticles, since the energy density and the power density are highly dependent on the size of the electrode–electrolyte interface. Nanoparticles can increase this interface to a large extent due to their high specific surface area. Carbon-based nanoparticles can increase power density due to their electrostatic charge storage, while metal-based nanoparticles can undergo redox processes, which can increase the energy density more. When applied together, both properties can be improved (Figure 6).

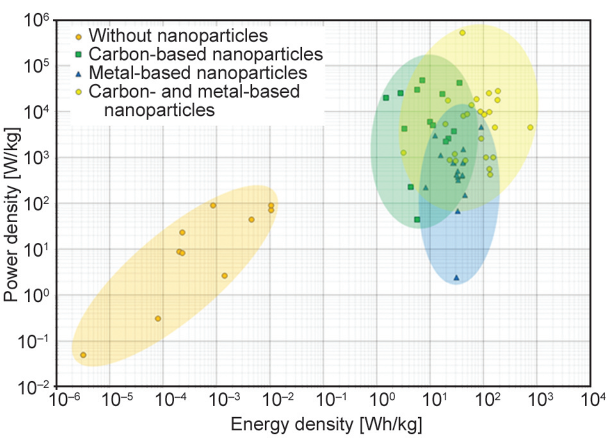

Figure 6. Different nanoparticle-based supercapacitors Ragone plot [42, 53–65].

4. Manufacturing methods

The previous chapter shows that nanoparticles play a significant role in improving the electrical properties of supercapacitors, and with them, energy and power density can be increased. The fabrication of structural supercapacitors requires a great deal of attention. Thus, in addition to the proper distribution of nanoparticles, adhesion between the elements that make up a structural supercapacitor is essential for good mechanical and electrochemical properties.

4.1. Nanoparticle dispersion in nanocomposites

One of the major challenges in fabricating structural supercapacitors is to disperse the nanoparticles properly in the polymer matrix. The main problem in the dispersion of nanoparticles is their tendency to aggregate due to their high specific surface area. Avoiding the formation of aggregates is critical in producing nanocomposites, as they act as defect sites, impairing mechanical properties. Furthermore, nanoparticles are used in composites to improve some properties or functions (*e.g.*, strength, thermal conductivity, electrical conductivity), where the dispersion of conductive nanoparticles mixed in the polymer matrix is critical. The dispersion of conductive nanoparticles has a significant impact on the electrical conductivity of the composite [66].

Various surface energy–reducing solvents or input energy (*e.g.*, shear forces, force fields) are often used to break up the aggregates. An appropriate solvent can successfully reduce the surface energy of the nanoparticles and the strength of the physical bonds between them [67]. However, some chemical treatment affect the properties of the nanoparticles, for example, they reduce their conductivity [68].

It is also common to use mixing by external forces for better dispersion, such as ultrasonic mixing, in addition to solvent dispersion. Mostovoy *et al*. [69] worked on a complex mixing procedure, where functionalized carbon nanotubes were dispersed in epoxy resin. To improve the quality of dispersion and disperse the aggregates, they stirred the suspension with an ultrasonic mixer for one hour, treated it in a vacuum degasser after the addition of the crosslinking component, and then prepared the nanocomposites for testing, procedures which reduced the aggregates, thus giving the nanocomposites better strength.

For structural capacitors, in addition to various mixing processes, so-called buckypaper can be used to introduce nanoparticles into a controlled system. Buckypaper is typically fabricated by creating a dispersion of nanoparticles, which are filtered in various ways to create a non-woven fabric that makes the nanoparticles easier to handle [70]. Gupta and Kumar [63] fabricated supercapacitor electrodes using SWCNT buckypaper and MnO_2. The supercapacitor thus prepared had a specific capacitance of 605 F/g compared to the reference supercapacitor with the MnO_2 and stainless steel electrode, which had a specific capacitance of 340 F/g. Furthermore, the supercapacitor produced with SWCNT buckypaper had the advantage of an excellent current rate capability. At 20 A/g, which is a very high specific current for a capacitor, only a 15% loss of capacitance was observed compared to the 50% loss of capacitance of the reference.

Furthermore, nanoparticle growth can be a good and efficient way to introduce nanoparticles into the system for structural supercapacitors. For example, an advantage of growing nanoparticles on carbon fibers is that direct contact between the carbon fiber and the nanoparticle can be established, thus providing better mechanical and conductive properties for the electrode. Such electrodes have been fabricated by Xiong *et al*. [71], who have grown reduced graphene oxide–carbon nanotube particles on carbon fiber using electrophoretic deposition (EPD) and chemical vapor deposition (CVD). Fabrication involved first dissolving graphene oxide in deionized water and then immersing the carbon fabric in the solution while passing a current through the carbon fabric (CF), varying between 2 and 5 V. The resulting CF-GO hybrid material was placed in a tube furnace with a carbon source/catalyst and then subjected to an argon and hydrogen flow at 750 °C for 35 min. During this time, the GO was converted into reduced graphene oxide, which served as a base for the growth of CNTs. The resulting CF-RGO-CNT hybrid material retained the flexibility of CF and had a specific capacitance of 203 F/g, which was four times higher than the specific capacitance of an electrode composed of plain CF.

4.2. Structural supercapacitor fabrication solutions

In producing structural supercapacitors, choosing the proper manufacturing process is important to ensure the best possible surface contact between the structural elements (electrodes, electrolyte, current collector, and separator). The precision of the production of supercapacitors has a major influence on their mechanical and electrochemical properties. Four significantly different designs of structural supercapacitors (integrated energy storage, structural fiber energy storage, laminated structural energy storage, enhanced/hybrid structural energy storage) are reported in the literature – the goal is multifunctionality, *i.e*. the combination of energy storage capability and favorable mechanical properties [43, 72].

In the first solution, a structure with energy storage capability is integrated into a basic composite system (packing non-structural elements in the composite). The advantage of such multifunctional composites is that they are simple to produce and do not require any unique materials (matrix material, reinforcing material) other than the basic composite. A battery or capacitor can be incorporated as an energy storage device. The energy storage capacity of the system depends only on the energy storage device incorporated but will deteriorate the mechanical properties of the base composite. The adhesion between the energy storage device and the composite will be less than the adhesion between the fiber and the matrix so the system will fail along the interface, and the built-in device will also significantly increase the mass of the base composite. Pattarakunnan *et al.* [73] incorporated a lithium-ion battery with an energy density of 185 W·h/kg and an enclosure size of 40×30×4 mm into an epoxy–carbon fiber composite. In their tests, they placed 1, 3, and 5 batteries in the tensile test specimens. In each case, the tensile strength of the energy storage composites was about forty percent of that of the reference energy storage–free specimen, regardless of the number of batteries. This type of multifunctional composite is of limited use due to its poorer mechanical properties. A solution could be to use them in composite sandwich structures when energy storage is needed in a component that is mainly subject to bending. Although the mechanical properties of the composite material are still inferior to those of a part without energy storage, embedding in a sandwich structure can reduce mechanical degradation. Similar to batteries, capacitors can be incorporated between composite layers. Sun *et al*. [74] fabricated structural capacitors by interposing Kevlar-epoxy prepregs. The energy density achieved was 0.169 W·h/kg, and the power density was 20 W/kg. The flexural strength of the multifunctional composite was 192 MPa, which was lower than the 295 MPa of the reference material without energy storage.

The second solution is fiber structural batteries. Unlike the energy storage elements integrated into the composite, energy is stored within the composite system, so the material is already multifunctional. A modified carbon fiber provides the anode and mechanical functions in structural fiber batteries, and the matrix material is the cathode. The carbon fiber is coated with a thin electrolyte layer, thus shortening the distance between the two electrodes. In the system, the electrolyte layer also performs an insulating function. Carlstedt *et al.* [75] modeled structural energy storage devices fabricated in such a way. In their model, the negative electrode was a carbon fiber coated with a polymer system in which the elastic and insulating properties were provided by ethylene oxide. The positive electrode was lithium metal oxides dispersed in a polymer matrix. The advantage of these solutions is that they allow the production of structural energy reservoirs in a fully solid state within a material and have more favorable mechanical properties. However, the cathode particles introduced into the matrix and the electrolyte introduced on the surface of the fiber impair adhesion, resulting in impaired mechanical properties compared to the base composite [72].

The third type of structural supercapacitors is laminated structural energy storing devices, which are structural energy storage devices similar to a capacitor. Thus, they are built up of electrodes, electrolytes, and an insulating material. Such a solution has been presented, for example, by Shirshova *et al.* [42], described in Section 3.2 (Nanoparticles in supercapacitor electrodes), where a glass fiber fabric with activated carbon fiber fabric electrodes and solid electrolyte was produced to withstand mechanical stresses. In such arrangements, different metal and carbon-based materials are used as electrodes, often with glass fiber as an insulator and the polymer matrix as an electrolyte. Such a device has the advantage that all its components are solid and have favorable mechanical properties thanks to the fibrous materials. The multifunctional composite can also perform energy storage and mechanical functions without extra materials. However, the disadvantage is that with a structural polymer electrolyte, an optimal ratio of the components has to be chosen for good mechanical and electric conduction functions at the same time [72].

It is also possible to combine the three approaches to achieve the best possible multifunctional properties. Senokos *et al.* [76] have combined these methods to produce structural energy storage devices. They first fabricated an EDLC with CNT electrodes, a polymer electrolyte membrane, and a lattice aluminum current collector, which was compacted by compression. After compression, the electrolyte-free supercapacitor was sandwiched between carbon fabrics and impregnated with an epoxy matrix (Figure 7). The resulting supercapacitor had an energy density of 37.5 W·h/kg, a power density of 30 W/kg, an elastic modulus of 60 GPa, and a tensile strength of 153 MPa.

Nguyen *et al*. [77] have developed a C-section beam for opening an aircraft door. In addition to performing its mechanical functions, the door opener can provide sufficient power for emergency door opening, so it can operate even in the event of an aircraft power failure. The multifunctional component allows for weight reduction, which is critical for aircraft. The fabricated beam consisted of carbon fiber-carbon aerogel (CF-CAG) electrodes, a polyester-ceramic insulator, and epoxy resin, on which an aluminum current collector was placed. The resulting capacitors had an energy density of 0.35 W·h/kg and a power density of 400 W/kg.

Literature data show that composites made with embedded batteries will achieve the best electrical energy-storing properties of structural energy storage composites. In this case, their electrochemical

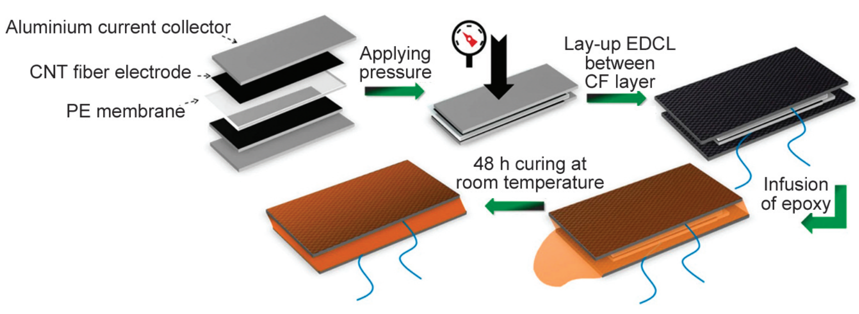

Figure 7. A possible way to manufacture a structural supercapacitor [76].

properties will only depend on the properties of the embedded energy storage device. However, this way, the battery will become a failure site in the system, thus weakening its mechanical properties. An even better solution is structural fiber capacitors. They have good electrochemical properties, but their mechanical properties are inferior to those of their single-function counterparts since the electrolyte layer applied to the surface of the fibers will weaken fiber–matrix adhesion. With laminated structural capacitors, significantly improved mechanical properties can be achieved, but their electrochemical properties can only be improved to the detriment of their mechanical properties. If we retain the favorable mechanical properties of this structure and improve their electrochemical properties (*e.g.*, by combining methods), we obtain improved structural capacitors. As a result, thanks to their sufficient electrochemical and mechanical functions, these can now be effectively used as multifunctional components. In the future, the aim is to improve the energy storage properties of these composites while retaining their mechanical properties – this could be greatly aided by applying nanoparticles or new types of solid electrolyte materials (Figure 8).

5. Conclusions and future perspectives/trends

As we have seen in Chapter 4.2., the energy storage and mechanical functions of structural supercapacitors can be used to create multifunctional elements,

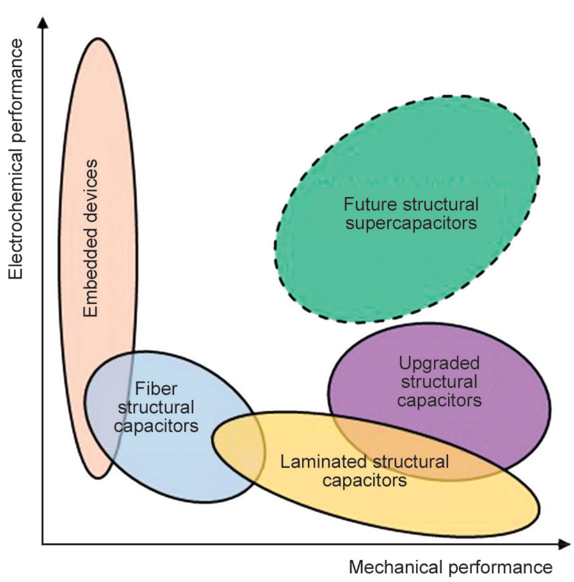

Figure 8. Schematic diagram of the performance of capacitors made with different manufacturing processes.

therefore structural supercapacitors is currently one of the most researched fields. Thus, reviewing their impact on our environment and examining their challenges is important. The use of nanoparticles, as we have seen, can significantly increase the efficiency of capacitors. They can increase the energy and power density of capacitors to the level where they are now called supercapacitors based on their performance and different structures. This means that significantly less material is needed for the same performance compared to typical capacitors. Furthermore, by using them as structural elements (multifunctional components), further weight and volume can be saved, which is highly desirable in vehicles from a sustainability point of view, as they allow lower energy consumption and lower emissions [43]. Another advantage of supercapacitors may be that they can be produced in a more environmentally friendly way from biopolymers/bio-based materials. For example, Mo *et al*. [78] produced graphene-like porous carbon (GPC) from cellulose sheets for supercapacitor electrodes (achieving a specific capacitance of 353 F/g and an energy density of 120.1 W·h/kg). Schlee *et al*. [79] produced nanofibers from eucalyptus lignin by electrospinning and carbonized them. Their electrodes had a specific capacity of 155 F/g, an energy density of 4 W·h/kg, and a power density of 52 000 W/kg. An additional environmental advantage of structural supercapacitors over conventional batteries is that they contain only solid material, thus avoiding the release of dangerous liquid chemicals into the environment in case of damage. Furthermore, a major advantage of supercapacitors compared to batteries is that they do not undergo any chemical process in the case of EDLCs, so their lifetime is theoretically infinite [43]. However, the careful handling of nanoparticles is important in manufacturing processes, as their health effects are still questionable due to their small size. A solution to this problem could be establishing and strictly enforcing standards and regulations for them [80].

Future developments in structural supercapacitors should aim to achieve higher efficiency, increase power density and energy density, and optimize manufacturing processes. In industry, structural supercapacitors with suitable safety features can be used in a wide range of applications (Figure 9). Thanks to their multifunctionality, they can be used in all areas where a combination of excellent mechanical and good energy storage functions are required.

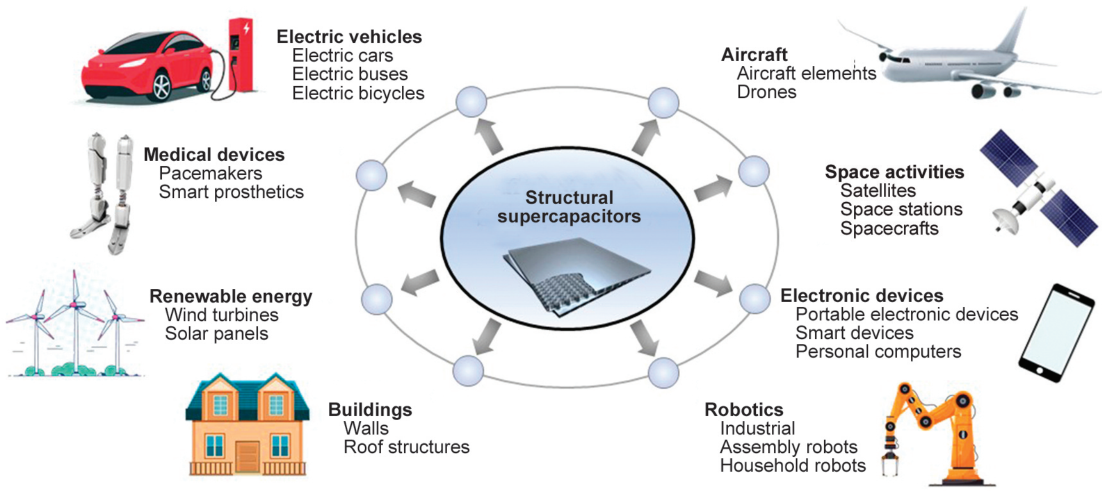

Figure 9. Potential applications of structural supercapacitors.

The most researched field for structural supercapacitors is currently electric vehicles, such as electric cars, public transport, or bicycles. They have the advantage of increasing the range, reliability, and acceleration of electric vehicles. Furthermore, they can also be used in other vehicles, for example, in structural components of aircraft or drones, where they can supplement the power supply reliably. They can also be used in space applications, for example, as structural components for satellites and spacecraft, reducing overall mass, which is critical in space applications. They could also be useful in the electronics industry, both in portable electrical devices and in smart devices and robots, which could benefit from a consistent and reliable supplementary power supply without the need for extra components [81]. There are also many opportunities for structural supercapacitors in the construction industry. In these areas, the many static structural elements (*e.g.*, walls and roof structures) could be supplemented with energy storage functions, a potential that several patents have already recognized [82]. They could also be used as energy storage devices for sustainable energy storage, for example, in wind parks or solar panels, where by adding energy storage functions to structural elements, a more balanced operation and energy supply can be achieved. Another application worth mentioning is in medical technology, where they could be used to smart prostheses, for example. However, despite their advantages, structural supercapacitors have not yet been able to spread in industry because they also have limitations. Firstly, they are multifunctional materials, so unlike batteries, for example, the production of a single component requires a specific, conscious choice of materials and design. Thus, the cost of producing such a component can be significantly higher than for a device with another kind of energy storage. Furthermore, there are difficulties in handling nanoparticles, where reproducibility of production can be a problem, which may also increase costs.

However, there are already prototypes where structural supercapacitors have been used (*e.g.*, drones, radio-controlled cars, Volvo project). The future goal is therefore to bring down the cost of structural supercapacitors and establish their safety regulation.

Acknowledgements

The research reported in this paper was supported by the National Research, Development and Innovation Office (NRDI, Hungary) through grants OTKA K 138472. Project no. TKP-6-6/PALY-2021 has been implemented with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme. Project no. 2022-2.1.1-NL-2022-00012 'National Laboratory for Cooperative Technologies' has been implemented with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the National Laboratories funding scheme. The project supported by the Doctoral Excellence Fellowship Programme (DCEP) is funded by the National Research Development and Innovation Fund of the Ministry of Culture and Innovation and the Budapest University of Technology and Economics, under a grant agreement with the National Research, Development and Innovation Office.

References

[1] Psarras G.: Polymer nanocomposites and transport (in their) properties. Express Polymer Letters, **17**, 563 (2023).
https://doi.org/10.3144/expresspolymlett.2023.41

[2] Anurangi J., Herath M., Galhena D. T. L., Epaarachchi J.: The use of fibre reinforced polymer composites for construction of structural supercapacitors: A review. Advanced Composite Materials, **32**, 942–986 (2023).
https://doi.org/10.1080/09243046.2023.2180792

[3] Xu Y., Lu W., Xu G., Chou T-W.: Structural supercapacitor composites: A review. Composites Science and Technology, **204**, 108636 (2021).
https://doi.org/10.1016/j.compscitech.2020.108636

[4] Chung D. D. L.: Development, design and applications of structural capacitors. Applied Energy, **231**, 89–101 (2018).
https://doi.org/10.1016/j.apenergy.2018.09.132

[5] Galek P., Mackowiak A., Bujewska P., Fic K.: Three-dimensional architectures in electrochemical capacitor applications – Insights, opinions, and perspectives. Fron-tiers in Energy Research, **8**, 139 (2020).
https://doi.org/10.3389/fenrg.2020.00139

[6] Jalal N. I., Ibrahim R. I., Oudah M. K.: A review on supercapacitors: Types and components. Journal of Physics: Conference Series, **1973**, 012015 (2021).
https://doi.org/10.1088/1742-6596/1973/1/012015

[7] Shubha B. V., Praveen B. M., Bhat V.: Graphene – Calculation of specific surface area. International Journal of Applied Engineering and Management Letters, **7**, 91–97 (2023).
https://doi.org/10.5281/zenodo.7657647

[8] Shen C., Oyadiji S. O.: The processing and analysis of graphene and the strength enhancement effect of graphene-based filler materials: A review. Materials Today Physics, **15**, 100257 (2020).
https://doi.org/10.1016/j.mtphys.2020.100257

[9] Ke Q., Wang J.: Graphene-based materials for supercapacitor electrodes – A review. Journal of Materiomics, **2**, 37–54 (2016).
https://doi.org/10.1016/j.jmat.2016.01.001

[10] Wang Y., Weng G. J.: Electrical conductivity of carbon nanotube- and graphene-based nanocomposites. in 'Micromechanics and nanomechanics of composite solids' (eds.: Meguid S. A., Weng G. J.) Springer, Cham, 123–156 (2018).
https://doi.org/10.1007/978-3-319-52794-9_4

[11] Takakura A., Beppu K., Nishihara T., Fukui A., Kozeki T., Namazu T., Miyauchi Y., Itami K.: Strength of carbon nanotubes depends on their chemical structures. Nature Communications, **10**, 3040 (2019).
https://doi.org/10.1038/s41467-019-10959-7

[12] Grądzka E., Winkler K.: Recent progress on electrochemical capacitors based on carbon nanotubes. in 'Carbon nanotubes-Recent progress' (eds.: Rahman M. M., Asiri A. M.) IntechOpen, London (2017).
https://doi.org/10.5772/intechopen.71687

[13] Sheikhpour M., Naghinejad M., Kasaeian A., Lohrasbi A., Shahraeini S. S., Zomorodbakhsh S.: The applications of carbon nanotubes in the diagnosis and treatment of lung cancer: A critical review. International Journal of Nanomedicine, **15**, 7063–7078 (2020).
https://doi.org/10.2147/IJN.S263238

[14] Zhang K., Sun J., Lei E., Ma C., Luo S., Wu Z., Li W., Liu S.: Effects of the pore structure of commercial activated carbon on the electrochemical performance of supercapacitors. Journal of Energy Storage, **45**, 103457 (2022).
https://doi.org/10.1016/j.est.2021.103457

[15] Adinaveen T., Vijaya J., Kennedy L.: Comparative study of electrical conductivity on activated carbons prepared from various cellulose materials. Arabian Journal for Science and Engineering, **41**, 55–65 (2016).
https://doi.org/10.1007/s13369-014-1516-6

[16] Li Y., Zhang M.: Mechanical properties of activated carbon fibers. in 'Activated carbon fiber and textiles' (eds.: Chen J. Y.) Woodhead, Sawston, 167–180 (2017).
https://doi.org/10.1016/B978-0-08-100660-3.00006-7

[17] Liang Y., Luo X., Weng W., Hu Z., Zhang Y., Xu W., Bi Z., Zhu M.: Activated carbon nanotube fiber fabric as a high-performance flexible electrode for solid-state supercapacitors. ACS Applied Materials and Interfaces, **13**, 28433–28441 (2021).
https://doi.org/10.1021/acsami.1c02758

[18] Cheng F., Yang X., Zhang S., Lu W.: Boosting the supercapacitor performances of activated carbon with carbon nanomaterials. Journal of Power Sources, **450**, 227678 (2020).
https://doi.org/10.1016/j.jpowsour.2019.227678

[19] Hong S-K., Kim H. J., Yang H-G.: Stress measurements of radio-frequency reactively sputtered RuO_2 thin films. Journal of Applied Physics, **80**, 822–826 (1996).
https://doi.org/10.1063/1.362891

[20] Zhu J., Yeap K. B., Zeng K., Lu L.: Nanomechanical characterization of sputtered RuO_2 thin film on silicon substrate for solid state electronic devices. Thin Solid Films, **519**, 1914–1922 (2011).
https://doi.org/10.1016/j.tsf.2010.10.014

[21] Li Y., Li L. H., Chu G. W., Zeng X. F., Chen J. F., Shao L.: Facile preparation of MnO_2 with large surface area in a rotor–stator reactor for supercapacitors. International Journal of Electrochemical Science, **11**, 9644–9655 (2016).
https://doi.org/10.20964/2016.11.48

[22] Yao W., Wang J., Li H., Lu Y.: Flexible α-MnO_2 paper formed by millimeter-long nanowires for supercapacitor electrodes. Journal of Power Sources, **247**, 824–830 (2014).
https://doi.org/10.1016/j.jpowsour.2013.09.039

[23] Maloth B., Srinivasulu N. V., Rajendra R.: Influence of titanium oxide fillers on the tensile and flexural properties of E-glass fabric/epoxy composites. Materials Today: Proceedings, **27**, 1073–1078 (2020).
https://doi.org/10.1016/j.matpr.2020.01.462

[24] Reddy D. A. K., Rajesh G., Anbuchezhiyan G., Ponshanmugakumar A., Ganesan R., Latha A., Satyanarayana Gupta M.: Investigating the mechanical properties of titanium dioxide reinforced magnesium composites. Materials Today: Proceedings, in press (2024).
https://doi.org/10.1016/j.matpr.2023.05.193

[25] Pisal K. B., Babar B. M., Mujawar S. H., Kadam L. D.: Overview of molybdenum disulfide based electrodes for supercapacitors: A short review. Journal of Energy Storage, **43**, 103297 (2021).
https://doi.org/10.1016/j.est.2021.103297

[26] Mohan V. V., Mohan M., Rakhi R. B.: High performance supercapacitors based on WS_2 nanoflower electrodes with commercial-level mass-loading. Surfaces and Interfaces, **42**, 103496 (2023).
https://doi.org/10.1016/j.surfin.2023.103496

[27] Chen Y., Yang H., Han Z., Bo Z., Yan J., Cen K., Ostrikov K. K.: MXene-based electrodes for supercapacitor energy storage. Energy Fuels, **36**, 2390–2406 (2022).
https://doi.org/10.1021/acs.energyfuels.1c04104

[28] Lim S., Park H., Yamamoto G., Lee C., Suk J. W.: Measurements of the electrical conductivity of monolayer graphene flakes using conductive atomic force microscopy. Nanomaterials, **11**, 2575 (2021).
https://doi.org/10.3390/nano11102575

[29] Birch M. E., Ruda-Eberenz T. A., Chai M., Andrews R., Hatfield R. L.: Properties that influence the specific surface areas of carbon nanotubes and nanofibers. The Annals of Occupational Hygiene, **57**, 1148–1166 (2013).
https://doi.org/10.1093/annhyg/met042

[30] Chae S. H., Lee Y. H.: Carbon nanotubes and graphene towards soft electronics. Nano Convergence, **1**, 15 (2014).
https://doi.org/10.1186/s40580-014-0015-5

[31] Shulga Y. M., Kabachkov E. N., Korepanov V. I., Khodos I. I., Kovalev D. Y., Melezhik A. V., Tkachev A. G., Gutsev G. L.: The concentration of $C(sp^3)$ atoms and properties of an activated carbon with over 3000 m^2/g BET surface area. Nanomaterials, **11**, 1324 (2021).
https://doi.org/10.3390/nano11051324

[32] Folaranmi G., Bechelany M., Sistat P., Cretin M., Zaviska F.: Activated carbon blended with reduced graphene oxide nanoflakes for capacitive deionization. Nanomaterials, **11**, 1090 (2021).
https://doi.org/10.3390/nano11051090

[33] Sugimoto W., Kizaki T., Yokoshima K., Murakami Y., Takasu Y.: Evaluation of the pseudocapacitance in RuO_2 with a RuO_2/GC thin film electrode. Electrochimica Acta, **49**, 313–320 (2004).
https://doi.org/10.1016/j.electacta.2003.08.013

[34] Osofsky M., Krowne C., Charipar K., Bussmann K., Chervin C., Pala I., Rolison D.: Disordered RuO_2 exhibits two dimensional, low-mobility transport and a metal–insulator transition. Scientific Reports, **6**, 21836 (2016).
https://doi.org/10.1038/srep21836

[35] Wang C., Bongard H-J., Weidenthaler C., Wu Y., Schüth F.: Design and application of a high-surface-area mesoporous δ-MnO_2 electrocatalyst for biomass oxidative valorization. Chemistry of Materials, **34**, 3123–3132 (2022).
https://doi.org/10.1021/acs.chemmater.1c04223

[36] Ma Z., Zhao J., Fan Y., Qin X., Shao G.: High surface area of crystalline/amorphous ultrathin MnO_2 nanosheets electrode for high-performance flexible micro-supercapacitors. Journal of Alloys and Compounds, **920**, 166012 (2022).
https://doi.org/10.1016/j.jallcom.2022.166012

[37] Wang J-G.: Engineering nanostructured MnO2 for high performance supercapacitors. in 'Supercapacitor design and applications' (ed.: Stevic Z.) IntechOpen, London, 43–65 (2016).
https://doi.org/10.5772/65008

[38] Lin Y., Qian Q., Chen Z., Dinh Tuan P., Feng D.: Fabrication of high specific surface area TiO_2 nanopowders by anodization of porous titanium. Electrochemistry Communications, **136**, 107234 (2022).
https://doi.org/10.1016/j.elecom.2022.107234

[39] Kang X., Liu S., Dai Z., He Y., Song X., Tan Z.: Titanium dioxide: From engineering to applications. Catalysts, **9**, 191 (2019).
https://doi.org/10.3390/catal9020191

[40] Bak T., Nowotny M. K., Sheppard L., Nowotny J.: Mobility of electronic charge carriers in titanium dioxide. The Journal of Physical Chemistry C, **112**, 12981–12987 (2008).
https://doi.org/10.1021/jp801028j

[41] Yildiz A., Lisesivdin S. B., Kasap M., Mardare D.: Electrical properties of TiO_2 thin films. Journal of Non-Crystalline Solids, **354**, 4944–4947 (2008).
https://doi.org/10.1016/j.jnoncrysol.2008.07.009

[42] Shirshova N., Qian H., Shaffer M. S. P., Steinke J. H. G., Greenhalgh E. S., Curtis P. T., Kucernak A., Bismarck A.: Structural composite supercapacitors. Composites Part A: Applied Science and Manufacturing, **46**, 96–107 (2013).
https://doi.org/10.1016/j.compositesa.2012.10.007

[43] Greenhalgh E. S., Nguyen S., Valkova M., Shirshova N., Shaffer M. S. P., Kucernak A. R. J.: A critical review of structural supercapacitors and outlook on future research challenges. Composites Science and Technology, **235**, 109968 (2023).
https://doi.org/10.1016/j.compscitech.2023.109968

[44] Luo P., Huang L.: Carbon paper as current collectors in graphene hydrogel electrodes for high-performance supercapacitors. Nanomaterials, **10**, 746 (2020).
https://doi.org/10.3390/nano10040746

[45] Wu H-C., Lin Y-P., Lee E., Lin W-T., Hu J-K., Chen H-C., Wu N-L.: High-performance carbon-based supercapacitors using Al current-collector with conformal carbon coating. Materials Chemistry and Physics, **117**, 294–300 (2009).
https://doi.org/10.1016/j.matchemphys.2009.06.001

[46] Xu J-L., Liu Y-H., Gao X., Sun Y., Shen S., Cai X., Chen L., Wang S-D.: Embedded Ag grid electrodes as current collector for ultraflexible transparent solid-state supercapacitor. ACS Applied Materials and Interfaces, **9**, 27649–27656 (2017).
https://doi.org/10.1021/acsami.7b06184

[47] Abdisattar A., Yeleuov M., Daulbayev C., Askaruly K., Tolynbekov A., Taurbekov A., Prikhodko N.: Recent advances and challenges of current collectors for supercapacitors. Electrochemistry Communications, **142**, 107373 (2022).
https://doi.org/10.1016/j.elecom.2022.107373

[48] Mendhe A., Panda H. S.: A review on electrolytes for supercapacitor device. Discover Materials, **3**, 29 (2023).
https://doi.org/10.1007/s43939-023-00065-3

[49] Bhat T. S., Patil P. S., Rakhi R. B.: Recent trends in electrolytes for supercapacitors. Journal of Energy Storage, **50**, 104222 (2022).
https://doi.org/10.1016/j.est.2022.104222

[50] Asp L. E.: Multifunctional composite materials for energy storage in structural load paths. Plastics, Rubber and Composites, **42**, 144–149 (2013).
https://doi.org/10.1179/1743289811Y.0000000043

[51] Zhang J., Yan J., Zhao Y., Zhou Q., Ma Y., Zi Y., Zhou A., Lin S., Liao L., Hu X., Bai H.: High-strength and machinable load-bearing integrated electrochemical capacitors based on polymeric solid electrolyte. Nature Communications, **14**, 64 (2023).
https://doi.org/10.1038/s41467-022-35737-w

[52] Joyal N., Chang Y-C., Shonar M., Chalivendra V., Shen C.: Solid polymer electrolytes with hydrates for structural supercapacitors. Journal of Energy Storage, **51**, 104459 (2022).
https://doi.org/10.1016/j.est.2022.104459

[53] Yang X., Li T., He X., Li Q., Sun J., Lei Z., Liu Z-H.: $Ti_3C_2T_x$/aramid film electrode with high capacitance and good mechanical strength and the assembled wide temperature all-solid-state symmetrical supercapacitor. Journal of Power Sources, **520**, 230899 (2022).
https://doi.org/10.1016/j.jpowsour.2021.230899

[54] Melkiyur I., Rathinam Y., Kumar P. S., Sankaiya A., Pitchaiya S., Ganesan R., Velauthapillai D.: A comprehensive review on novel quaternary metal oxide and sulphide electrode materials for supercapacitor: Origin, fundamentals, present perspectives and future aspects. Renewable and Sustainable Energy Reviews, **173**, 113106 (2023).
https://doi.org/10.1016/j.rser.2022.113106

[55] Li Z., Xu K., Pan Y.: Recent development of supercapacitor electrode based on carbon materials. Nanotechnology Reviews, **8**, 35–49 (2019).
https://doi.org/10.1515/ntrev-2019-0004

[56] Felhősi I., Keresztes Z., Marek T., Pajkossy T.: Properties of electrochemical double-layer capacitors with carbon-nanotubes-on-carbon-fiber-felt electrodes. Electrochimica Acta, **334**, 135548 (2020).
https://doi.org/10.1016/j.electacta.2019.135548

[57] Jiang X., Cao Y., Li P., Wei J., Wang K., Wu D., Zhu H.: Polyaniline/graphene/carbon fiber ternary composites as supercapacitor electrodes. Materials Letters, **140**, 43–47 (2015).
https://doi.org/10.1016/j.matlet.2014.10.162

[58] Skrypnychuk V., Boulanger N., Nordenström A., Talyzin A.: Aqueous activated graphene dispersions for deposition of high-surface area supercapacitor electrodes. The Journal of Physical Chemistry Letters, **11**, 3032–3038 (2020).
https://doi.org/10.1021/acs.jpclett.0c00272

[59] Muhommad J., Kumar L., Baruah P. K., Das M. R., Deka S.: All-solid-state flexible symmetric supercapacitor based on morphology oriented amorphous Cu–Co–B alloy nanosheets for energy storage. Batteries and Supercaps, **5**, e202100314 (2022).
https://doi.org/10.1002/batt.202100314

[60] Yi C-Q., Zou J-P., Yang H-Z., Leng X.: Recent advances in pseudocapacitor electrode materials: Transition metal oxides and nitrides. Transactions of Nonferrous Metals Society of China, **28**, 1980–2001 (2018).
https://doi.org/10.1016/S1003-6326(18)64843-5

[61] Liu W., Wang Z., Su Y., Li Q., Zhao Z., Geng F.: Molecularly stacking manganese dioxide/titanium carbide sheets to produce highly flexible and conductive film electrodes with improved pseudocapacitive performances. Advanced Energy Materials, **7**, 1602834 (2017).
https://doi.org/10.1002/aenm.201602834

[62] Tang Q., Chen M., Yang C., Wang W., Bao H., Wang G.: Enhancing the energy density of asymmetric stretchable supercapacitor based on wrinkled CNT@MnO_2 cathode and CNT@polypyrrole anode. ACS Applied Materials and Interfaces, **7**, 15303–15313 (2015).
https://doi.org/10.1021/acsami.5b03148

[63] Gupta V., Kumar S.: MnO_2/SWCNT buckypaper for high performance supercapacitors. Journal of Energy Storage, **26**, 100960 (2019).
https://doi.org/10.1016/j.est.2019.100960

[64] Vinodhini S. P., Xavier J. R.: Novel synthesis of layered MoS_2/TiO_2/CNT nanocomposite as a potential electrode for high performance supercapacitor applications. International Journal of Energy Research, **46**, 14088–14104 (2022).
https://doi.org/10.1002/er.8125

[65] An C., Zhang Y., Guo H., Wang Y.: Metal oxide-based supercapacitors: Progress and prospectives. Nanoscale Advances, **1**, 4644–4658 (2019).
https://doi.org/10.1039/C9NA00543A

[66] Feng Y., Zou H., Tian M., Zhang L., Mi J.: Relationship between dispersion and conductivity of polymer nanocomposites: A molecular dynamics study. The Journal of Physical Chemistry B, **116**, 13081–13088 (2012).
https://doi.org/10.1021/jp305815r

[67] Pan Y., Li L., Chan S. H., Zhao J.: Correlation between dispersion state and electrical conductivity of MWCNTs/PP composites prepared by melt blending. Composites Part A: Applied Science and Manufacturing, **41**, 419–426 (2010).
https://doi.org/10.1016/j.compositesa.2009.11.009

[68] Khan U., Ryan K., Blau W. J., Coleman J. N.: The effect of solvent choice on the mechanical properties of carbon nanotube–polymer composites. Composites Science and Technology, **67**, 3158–3167 (2007).
https://doi.org/10.1016/j.compscitech.2007.04.015

[69] Mostovoy A., Yakovlev A., Tseluikin V., Lopukhova M.: Epoxy nanocomposites reinforced with functionalized carbon nanotubes. Polymers, **12**, 1816 (2020).
https://doi.org/10.3390/polym12081816

[70] Kobashi K., Hirabayashi T., Ata S., Yamada T., Futaba D. N., Hata K.: Green, scalable, binderless fabrication of a single-walled carbon nanotube nonwoven fabric based on an ancient Japanese paper process. ACS Applied Materials and Interfaces, **5**, 12602–12608 (2013).
https://doi.org/10.1021/am403936n

[71] Xiong C., Li T., Zhao T., Dang A., Li H., Ji X., Jin W., Jiao S., Shang Y., Zhang Y.: Reduced graphene oxide-carbon nanotube grown on carbon fiber as binder-free electrode for flexible high-performance fiber supercapacitors. Composites Part B: Engineering, **116**, 7–15 (2017).
https://doi.org/10.1016/j.compositesb.2017.02.028

[72] Zhou H., Li H., Li L., Liu T., Chen G., Zhu Y., Zhou L., Huang H.: Structural composite energy storage devices– A review. Materials Today Energy, **24**, 100924 (2022).
https://doi.org/10.1016/j.mtener.2021.100924

[73] Pattarakunnan K., Galos J., Das R., Mouritz A. P.: Tensile properties of multifunctional composites embedded with lithium-ion polymer batteries. Composites Part A: Applied Science and Manufacturing, **136**, 105966 (2020).
https://doi.org/10.1016/j.compositesa.2020.105966

[74] Sun J., Gargitter V., Pei S., Wang T., Yan Y., Advani S. G., Wang L., Chou T-W.: Mechanical and electrochemical performance of hybrid laminated structural composites with carbon fiber/solid electrolyte supercapacitor interleaves. Composites Science and Technology, **196**, 108234 (2020).
https://doi.org/10.1016/j.compscitech.2020.108234

[75] Carlstedt D., Marklund E., Asp L. E.: Effects of state of charge on elastic properties of 3D structural battery composites. Composites Science and Technology, **169**, 26–33 (2019).
https://doi.org/10.1016/j.compscitech.2018.10.033

[76] Senokos E., Ou Y., Torres J., Sket F., González C., Marcilla R., Vilatela J.: Energy storage in structural composites by introducing CNT fiber/polymer electrolyte interleaves. Scientific Reports, **8**, 3407 (2018).
https://doi.org/10.1038/s41598-018-21829-5

[77] Nguyen S., Anthony D. B., Katafiasz T., Qi G., Razavi S., Senokos E., Greenhalgh E. S., Shaffer M. S. P., Kucernak A. R. J., Linde P.: Manufacture and characterisation of a structural supercapacitor demonstrator. Composites Science and Technology, **245**, 110339 (2024).
https://doi.org/10.1016/j.compscitech.2023.110339

[78] Mo R. J., Zhao Y., Zhao M. M., Wu M., Wang C., Li J. P., Kuga S., Huang Y.: Graphene-like porous carbon from sheet cellulose as electrodes for supercapacitors. Chemical Engineering Journal, **346**, 104–112 (2018).
https://doi.org/10.1016/j.cej.2018.04.010

[79] Schlee P., Hosseinaei O., Baker D., Landmér A., Tomani P., Mostazo-López M. J., Cazorla-Amorós D., Herou S., Titirici M. M.: From waste to wealth: From Kraft lignin to free-standing supercapacitors. Carbon, **145**, 470–480 (2019).
https://doi.org/10.1016/j.carbon.2019.01.035

[80] Ding X., Pu Y., Tang M., Zhang T.: Environmental and health effects of graphene-family nanomaterials: Potential release pathways, transformation, environmental fate and health risks. Nano Today, **42**, 101379 (2022).
https://doi.org/10.1016/j.nantod.2022.101379

[81] Motora K. G., Wu C-M., Rani G. M., Yen W-T.: Effect of ZnO particle size on piezoelectric nanogenerators and mechanical energy harvesting. Express Polymer Letters, **16**, 1208–1227 (2022).
https://doi.org/10.3144/expresspolymlett.2022.88

[82] Hucker M. J., Dunleavy M., Haq S.: Structural supercapacitor usable in a mechanical structure. WO2014020338A1, GB (2014).