Review

Electrode Materials for Supercapacitors in Hybrid Electric Vehicles: Challenges and Current Progress

Sivakumar Rajagopal [1], Rameez Pulapparambil Vallikkattil [2], M. Mohamed Ibrahim [2,*] and Dimiter Georgiev Velev [3]

1   School of Electronics Engineering, Vellore Institute of Technology, Vellore 632014, India; rsivakumar@vit.ac.in
2   Automotive Research Centre, School of Mechanical Engineering, Vellore Institute of Technology, Vellore 632014, India; rameez.pv2020@vitstudent.ac.in
3   Department of Information Technology and Communications, University of National and World Economy, 1700 Sofia, Bulgaria; dgvelev@unwe.bg
*   Correspondence: ibrahim.m@vit.ac.in

Abstract: For hybrid electric vehicles, supercapacitors are an attractive technology which, when used in conjunction with the batteries as a hybrid system, could solve the shortcomings of the battery. Supercapacitors would allow hybrid electric vehicles to achieve high efficiency and better power control. Supercapacitors possess very good power density. Besides this, their charge-discharge cycling stability and comparatively reasonable cost make them an incredible energy-storing device. The manufacturing strategy and the major parts like electrodes, current collector, binder, separator, and electrolyte define the performance of a supercapacitor. Among these, electrode materials play an important role when it comes to the performance of supercapacitors. They resolve the charge storage in the device and thus decide the capacitance. Porous carbon, conductive polymers, metal hydroxide, and metal oxides, which are some of the usual materials used for the electrodes in the supercapacitors, have some limits when it comes to energy density and stability. Major research in supercapacitors has focused on the design of stable, highly efficient electrodes with low cost. In this review, the most recent electrode materials used in supercapacitors are discussed. The challenges, current progress, and future development of supercapacitors are discussed as well. This study clearly shows that the performance of supercapacitors has increased considerably over the years and this has made them a promising alternative in the energy sector.

Keywords: supercapacitors; hybrid capacitors; electrode materials: hybrid electric vehicles; energy storage devices

1. Introduction

The importance of finding an alternative fuel source that can eliminate the usage of fossil fuels is increasing day by day because of the alarming increase in the pollution level, global warming, and other geopolitical concerns across the world. Developing storage technologies is as important as developing alternative energy sources and that is why recently much attention has been given to the development of high power and high energy density storage systems. Among the clean energy portfolio, it is undeniably true that electrochemical energy is one of the most important parts of it. Fuel cells, batteries, and supercapacitors are the major devices working on the electrochemical energy conversion principle.

High specific capacitance, high power density, long life cycle, and very little maintenance have gained supercapacitors much attention as an energy storage device like a battery, and its ability to function as a bridge between capacitor and batteries has made the scientific community focus on the research and development of supercapacitors. One of the major attractive aspects of supercapacitors is that both charging and discharging can be done within a short period of time. Since both battery and capacitor collect and release

energy, they may seem similar, but the vital difference between battery and capacitor is how they work contrarily on set-up applications. While batteries deliver better energy density for storage, capacitors provide more speedy charge and discharge capabilities. Table 1 shows the comparison between batteries and supercapacitors [1].Batteries are preferred for applications where high energy density is required but with limited power output and requiring long term use of energy. When energy is required to be delivered at high power, capacitors are preferred.

Table 1. Comparison between batteries and supercapacitor [1].

Comparison Parameter	Battery	Supercapacitor
Storage mechanism	Chemical	Physical
Power limitations	Reaction kinetics, mass transport	Electrolyte conductivity
Charge rate	Kinetically limited	High
Energy storage	High	Limited
Cycle life limitations	Mechanical stability, chemical reversibility	Side reactions

The utilization of electrode materials with more surface area and very slim dielectrics makes supercapacitors accomplish better capacitance and that makes them different from the conventional capacitors. The higher power capabilities and long cycle life compared to batteries makes supercapacitors attractive technology and provide a promising technology to manufacture superior energy storage systems [2].

The electrode-electrolyte mechanism is the basis of the energy storage in supercapacitors [3] and even though it has similarities to conventional capacitors in basic principle, the process of charge/discharge is much quicker than a conventional capacitor. The charge storage range is between 100–1000 F for supercapacitors while it is only micro or millifarads for conventional capacitors [4].

Supercapacitors can manage high power rates, which, when compared with batteries, is high, but even though they provide very high power in the same volume compared to batteries [1], the inability to store a similar quantity of charge as batteries are capable of (three to thirty times lower) is their biggest disadvantage. This is why supercapacitors are used for applications where large energy storage capacity is not required but only high-power bursts are needed. In battery-based energy storage systems, supercapacitors can also be included to decouple the energy and power characteristics of the energy storage systems. This could improve the sizing and lifetime of the system while at the same time attaining the demands in power and energy.

In the case of an electric or hybrid electric vehicle, the efficiency can be increased by converting the excess kinetic energy produced whenever the automobile reduces the speed or stops into electrical energy. This technology is already in place with low power scale batteries, but if the efficiency is to be improved, very high amounts of power will be needed for which one possible way is with the help of other energy storage technologies like supercapacitors. For hybrid electric vehicles, supercapacitors are an attractive technology which, when used in conjunction with the batteries as a hybrid system, could solve the shortcomings of the battery. Usually, because of the unpredictable traffic conditions, mainly in urban driving scenarios, the vehicles powered by electricity require a time-varying and stochastic load power, since the proper response to these driving conditions is important. This makes the batteries supply swift power demand during the acceleration and deceleration, which means, for quickly responding to these variations, the batteries should possess the high-rate capability. Even though higher rate batteries are attainable, they will be costlier and bulkier and, more importantly, the frequent charge-discharge operations could reduce the life of the battery. This is where the idea of hybridization of supercapacitors and batteries looks promising. Hybridization of these two systems could overcome their respective limitations and accomplish an overall improved performance [5,6]. The super-

capacitors can be used to supply the high power density required for rapid acceleration in hybrid electric vehicles along with recovery of energy during breaking and protecting the batteries from high frequency fast charge-discharge process. They would allow hybrid electric vehicles to achieve high efficiency and better power control. The better power density, cycling stability of discharging and charging, and comparatively reasonable cost make them an incredible energy-storing device. In hybrid capacitors, when the output power of the battery is insufficient, the supercapacitors can be used for the peak power demand for a short period and since the energy density of the supercapacitors is very low, the batteries are used to store the energy. The supercapacitors here are a power buffer between the battery and the load. This type of dual technology system is not as simple as it seems but the performance improvement is too appealing to ignore [7].

The manufacturing strategy and the components like electrodes, current collector, binder, separator, and electrolyte define the performance of a supercapacitor. Among these, electrode materials play an important role when it comes to the performance of supercapacitors. They resolve the charge storage in the device and thus decide the capacitance. Porous carbon, conductive polymers, metal hydroxide, and metal oxides, which are some of the materials commonly used for the electrodes in the supercapacitors, have some limits when it comes to energy density and stability [8].

Major research in supercapacitors has been focused on the design of stable, highly efficient electrodes with low cost. In this review, the most recent electrode materials used in supercapacitors like metal-organic frameworks, graphene-based materials, ceramic materials, activated carbon-based materials, etc. are discussed. This review aims to provide a basic idea about different electrode materials used in supercapacitors and also the future studies required to improve their performance.

2. Electrode Materials

Supercapacitors are divided generally into different types mainly according to the charge storage mechanism. Figure 1 shows the general classification of the supercapacitors. One is electric double-layer capacitors (EDLCs) and the other is pseudo capacitors (PCs). EDLCs are sometimes also called electrostatic capacitors. The charge storage in EDLCs takes place at the electrode/electrolyte interface through the electrostatic charge absorption mechanism. The most attractive materials for EDLCs have been carbon-based materials, mainly due to their abundance in nature and the high surface area; on the downside, the relatively low specific capacitance is a disadvantage [9].
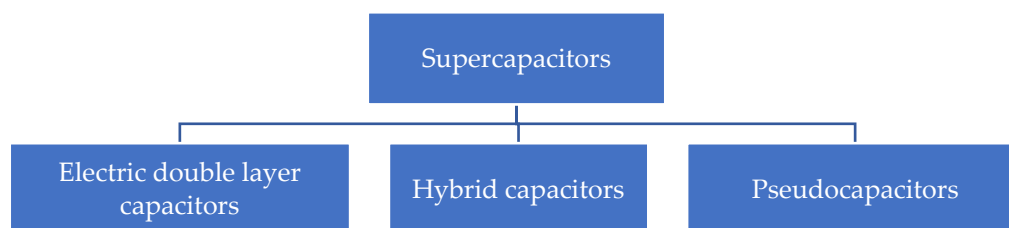

Figure 1. Classification of supercapacitors.

The Electric Double Layer Capacitor (EDLC) materials stock up charge mainly in an electrochemical double layer formed on the surface of the electrode but not in its bulk. Therefore, the capacitance mainly depends on the surface area of electrode, which can be accessed by the electrolyte ions. The important factors controlling the electrochemical activity of electrodes are the specific surface area, pore size distribution, pore shape, morphology, conductivity, and surface functionality. Among these, the pore size of electrode materials should be very close to the ion size of the electrolyte to yield maximum double layer capacitance. Meanwhile, if the sizes do not match, it leads to capacitance drop. On the other hand, pseudocapacitors store charges mainly via fast and reversible faradic reactions occurring on metal oxides or conducting polymers. Normally, pseudocapacitors can

generate the capacitance value of one order of magnitude higher than EDLCs. However, limited cyclability always exists because of the nature of redox reactions. Therefore, hybrid systems offer an alternative to conventional pseudocapacitors or EDLCs. In this case, materials for pseudocapacitors (battery like, energy source) and EDLCs (capacitor like, power source) are hybridized on one electrode substrate. By designing electrolytes with the most advantageous performance and by using such hybrid capacitance composition, the enormous demand for high-voltage operation with high stability and long-term cyclability can be accomplished. In a pseudocapacitor, the reversible redox reaction near the surface of the electrode materials helps them in attaining pseudocapacitance [10]. This makes pseudocapacitors (PCs) achieve a very high energy density compared to EDLCs [11]. The positive electrode of supercapacitor is usually made up of high-energy battery-type or pseudocapacitive materials and their composites. The energy density of the electrode mainly depends on the capacitance of the electrode, so utilization of its full theoretical capacitance of the materials is critical. Therefore, it is essential to study the various parameters, which are directly related to the capacitance of the material. The battery electrodes store the charges through reversible Faradaic reaction, which mainly depends on surface area, short diffusion path for electron and ions, and higher electrical conductivity with multiple oxidation states. The Faradaic reaction occurs in both pseudocapacitor and battery electrode but the electrochemical behavior like CV, GCD are different due to phase change in battery-type material [12].

The electrode of a supercapacitor must possess some characteristics like better conductivity, good temperature stability, large specific surface area, resistance to corrosion, less cost, and environmental friendliness. The overall specific capacitance (Cs) of the material is improved based on the ability of the electrode material to carry out the faradaic charge transfer efficiently. This means that if the material has small pores, the specific capacitance and in turn the energy density (Ed) will be higher. However, the problem with small pores is that the equivalent series resistance (ESR) will increase which will result in a reduced power density (Pd). So, the electrode material pore size varies as per the requirement for the application of supercapacitors. When it comes to high performance supercapacitors, if the porosity is larger, it will yield better surface area. The better surface area of a porous material will enable it to provide added active sites for desorption or adsorption reactions as well as for the transfer of electrons and ions. In general, the specific energy and capacitance will be higher when the pore size of the electrode is small. However, this small pore size will result in increasing the equivalent series resistance and at the same time reducing the specific power. This indicates that when the application demands high peak currents, larger pores will be required; meanwhile, when there is a need for higher specific energy, pores with smaller size will be preferred [13,14].

This section summarizes different electrode materials which have been studied and considered to be promising materials for the future developments of supercapacitors as energy storage devices.

2.1. Carbonaceous Materials

As discussed earlier, carbon-based materials are the most commonly used material for various applications in supercapacitors, thanks to their high availability and robust production processes in the industry, which in turn result in the reduced cost [15]. Among the applications, electrodes based on carbon materials are highly popular. They can be produced in various forms like fibers, nanotubes, and foams from 1D to the 3D structure. Usually, the electrode surface area, manufactured with carbon, is directly proportional to the specific capacitance, but this is not always the case. Some types of carbon will have higher specific capacitance even when they have a lower surface area compared to the electrode with a high specific area [16].

One of the most common types of electrode material based on carbon is activated carbon (AC). Already many kinds of research have been conducted which focused on these types of materials. In activated carbon, the carbon has undergone a chemical and

physical process to increase its adsorptive and porous qualities. They are used as conductive agents in most of the energy storage devices because of their comparably good electrical conductivity, porous structure, cost effectiveness, and ease of availability of material. In a similar way, AC was used as a positive/negative electrode for supercapacitor devices and carbon backbone for growing a hierarchical nanostructure. Further, it can be used to make a composite with metal oxides and with conducting polymers, to improve the energy density of the composite materials through Faradaic reaction, and can provide a good conducting path for electrons [12]. Recently the focus has been shifted from AC to other carbon-based materials which showed better performance than AC. While activated carbon-based materials are dispersed and suspended uniformly throughout a solution, the new materials mainly used colloidal methods of preparation. The below section briefly discusses some common types of carbon-based electrodes and some of the latest developments.

2.1.1. Graphene and Graphene Nanocomposites

Graphene is a single atom thick sheet constructed by sp^2 bonded carbon atoms in a poly aromatic honey comb crystal lattice [16–20]. The excellent physiochemical properties, better capacity, and cycle capability make them apt for high-performance energy storage systems [21]. The advantages of this material include the large surface area, better electrical conductivity, good flexibility, and favorable thermal and chemical stability [21]. Due to its extraordinary properties, it is highly utilized for different energy conversion and storage applications. Various methods are adopted for the synthesis of graphene or reduced graphene oxides such as chemical, thermal, and hydrothermal methods. Researchers reported supercapacitors based on graphene with a specific capacitance of 75 Fg^{-1} and energy density of 31.9 $Whkg^{-1}$ in ionic liquid electrolytes, 135 Fg^{-1} specific capacitance in aqueous electrolyte, and a specific capacitance of 99 Fg^{-1} in organic electrolytes [22,23]. For reduced graphene with low agglomeration, Wang Y et al. achieved a maximum specific capacitance of 205 Fg^{-1} in an aqueous electrolyte with an energy density of 28.5 $Whkg^{-1}$ [24]. Since graphene shows a tendency to re-stack, the determination of the intrinsic capacitance is difficult. One study reported 21 $\mu F\ cm^{-1}$ of intrinsic capacitance for the electric double layer in graphene [25]. The interfacial capacitance on the other hand depends on the amount of layers and from the surface area this calculation can be done.

Permanent capacity loss because of the re-stacking of graphene sheets is the major disadvantage of this material. The coulombic efficiency is also reduced because of this problem. The van der Waals interaction between the sheets is the reason for the re stacking and this reduces the surface area which in turn decreases the energy density [17].

Graphene and metal oxide composite seems to be a good solution to overcome the re-stacking of graphene sheet since metal oxides restrict graphene from this and as per the studies conducted in this area, this is advantageous for graphene as well as metal oxides because of the synergistic effect of the materials and this also increases the surface area. The purpose of combining graphene and metal oxide is to eradicate the problems faced by these materials individually. In graphene/metal oxide composite, the compatibility and chemical functionality to permit the smooth processing of metal oxides will be enhanced by graphene, while the better capacity will be provided by metal oxide. Combining metal oxides with graphene will efficiently synergize the electric double layer capacitance and pseudocapacitance. Here the graphene will act as a conductive channel for charge transfer and this will enhance the overall conductivity and at the same time pseudocapacitance will arise from the metal oxides. The metal oxide, besides improving the properties of graphene, will function as a stabilizer in preventing the accumulation of the sheets of graphene, which happens because of the van der Waals interactions among the graphene layers. The composite of graphene and metal oxide will result in distinctive structures like anchored, encapsulated, layered, sandwich, or wrapped. These unique structures help in substantially enhancing the electrochemical properties of the composite of graphene/metal oxide, like better capacity, improved rate capability, and exceptional cycling stability. Furthermore, these unique structured metal oxides on graphene nanosheets prevent the

agglomeration and re stacking of the graphene nanosheets while improving the surface area. This will result in high electrochemical activity. Meanwhile, the graphene will help in enhancing the growth and formation of micro or nanostructures of the metal oxides on the surface of graphene with even distribution and controlled morphology [17,26,27]. The capacitance of the graphene-metal oxide composites was found to be higher than the individually calculated capacitance of each material and, also, because of the integrated 3D structure, the performance is improved. This performance improvement was also detected in non-metal oxide materials like graphene nanosheet/polyaniline, graphene/$Co(OH)_2$, graphene/$Ni(OH)_2$, etc. [28–36]. It is important to note that the composite formed by graphene and metal oxide is not just a sum of the two components, but it can be termed as a new material with distinctive properties and functionalities. There are many other graphene-based composites that are studied and researched across the globe for their suitable applications in supercapacitors. Some of them are graphene/conductive polymers (e.g., polyaniline [37], polypyrrole [38], polythiophene [39]), graphene/metal oxides (e.g., Mn_3O_4 [40], Co_3O_4 [41], SnO_2 [42]), graphene/metal nitrides (e.g., VN [43], Ni_3N [44]), graphene/sulfides (e.g., FeS_2 [45], MoS_2 [46]), graphene/hydroxides (e.g., MnNi-LDH [47], NiCo-LDH [48]), and graphene/MXenes [49,50].

Graphene has gained great attention from different areas of science and engineering from the time of its discovery in 2004 until now [51]. Several methods like hetero atom doping and construction of 3D frameworks have been tried to eliminate issues like re-stacking or agglomeration [19,52–58]. Sindhuja Manoharan and her team manufactured and studied a graphene supercapacitor with excellent performance metrics and studied the application of the supercapacitor in electric vehicles as a supplementary source of power and how the addition of the supercapacitor enhances the storage of energy from regenerative breaking. The electrode material synthesized showed capacitance of 35.96 Fg^{-1} along with better energy density and power density (44.95 $Whkg^{-1}$ and 18,750 $Whkg^{-1}$ resepectively). Along with these properties, the low self-discharge of the supercapacitor depicted the applicability of supercapacitors in future hybrid electric vehicles [59].

2.1.2. Renewable Materials Based Activated Carbon

A brief explanation has already been given about activated carbon in the first section. The cost has always been one of the major barriers when it comes to the implementation of the super capacitor on a larger scale. Even though there are many high performing electrode materials, they are way too expensive at the moment for practical applications [60]. Cost-effective materials have been one of the major research focuses in the case of supercapacitors. Multiple studies can be seen where the prospect of activating and utilizing carbon from farming waste as electrode materials in SCs has been researched, like cassava peels [61] or apricot seeds [62]. The rice milling industry produces rice husks as a byproduct, which is one of the major wastes in the world, which has also been studied for the possibility of making AC electrodes. The study showed that the activated carbon, named rice husk activated carbon in electrolyte (6 M potassium hydroxide, KOH), showed a high specific capacitance of 367 Fg^{-1}. RHAC also exhibited 174 Fg^{-1} in organic electrolytes [63].

Not only agricultural waste but other innovative methods have also been tried by researchers, such as the production of AC with Coca-Cola. The high sugar content and the easy availability helped the researchers to study the possibility of producing heteroatom-doped AC. They efficaciously produced AC using hydrothermal carbonization and by activation of KOH and $ZnCl_2$. The AC showed 352 Fg^{-1} specific capacitance at 1 Ag^{-1}. The collection of Coca-Cola from expired bottles and unfinished drinks made this production in the renewable category. The production of AC from the renewable process is appealing and seems to be an appropriate and viable choice in the future of storage of energy [64].

Comparatively small cost and better specific surface area (1000–2000 $m^2\,g^{-1}$) [11,65,66] made activated carbon one of the most commonly used electrode materials for supercapacitors. Carbonization of carbon-rich organic precursors like coconut shells, wood pitch, coal, or polymers in an inter atmosphere followed by oxidation in water vapor, KOH, or CO_2 to

increase the specific surface area and pore volume is the method for obtaining AC. Initial studies were focused on refining the ACs activation process to increase the pore volume by specific surface area, but the change in capacitance was very little, which, even for the most porous samples, was not appreciable. Different ACs with various sizes of pore and in different electrolytes showed a relation between capacitance and specific surface area which is not linear in nature [67–69].

The high specific surface area of AC is attained because of its porous structure. The porous structure of activated carbon is mainly categorized into micropores (<2 nm), meso-pores (2–50 nm), and macropores (<50 nm) [70,71]. A dispersal of pore size around of 2–5 nm is found to be suitable to achieve better energy density and power capability as many of the preliminary investigations found that it is more apt since it is bigger than the size of two solvated ions [16,70,72,73]. The research shows that micropores (<2 nm) show better performance than mesopores (2–50 nm) even when mesopores are fine-tuned carbon. The partial desolvation by accessing the less than 2 nm pores of the micropores can help in better capacitance [74]. As the ions from the large electrolyte will struggle to enter into the small micropores of activated carbon, they will not contribute to the storage of charge, and the specific surface area is not fully utilized in the case of activated carbon.

Many types of research are still ongoing to determine the best suitable pore size for a given ion size and also the proper distribution of pore size in the fabrication process. Some studies show that, for aqueous electrolytes, a pore size between 0.4 and 0.7 nm is more appropriate and 0.8 nm is suitable in the case of organic electrolyte [75,76].

- Biomass-derived carbon

Even though it comes under renewable materials, biomass-derived materials for supercapacitors require a separate paper not only due to the large number of studies conducted in that area but also because of the importance of these materials. These electrode materials are considered a promising model of green chemistry. Some of the materials which have shown really promising properties in this field for high-performance supercapacitors include biomass-derived free-standing electrode materials, cellulose derived free-standing carbon materials, lignin-derived free-standing carbon materials, silk derived free-standing carbon materials, and carbohydrate derived free-standing carbon materials. Major research has been conducted with bacterial cellulose (BC) and lignin in biomass-based electrode material manufacturing process [77–80]. Bacterial cellulose has a 3D porous interconnected nanofibrous network as it contains abundant surface hydroxyl groups and nanofibers with random orientation. They also possess very good tensile strength which is more than 2GPa [81]. Another advantage of bacterial cellulose is that BC favors the diffusion of aqueous electrolytes because of their better hydrophilicity. Lignin has also gained wider attention in supercapacitor electrode manufacturing research, as it also is abundant in nature and is a byproduct of pulping and paper industries. Within its polymeric framework, lignin does not possess a consistent structure like cellulose-containing single monomeric linkages and as a typical polymer that is abundant in nature, lots of studies have been conducted with lignin [82–84].

The fabrication of electrodes for supercapacitors using renewable resource-based materials has been one of the major research areas because of the lesser impact it would create in the destruction of the environment, very low cost, and abundance in nature. Parts of the plants like shaddock peel, bamboo, petals, etc.; raw materials from animals like silk, crab shell, and honeycomb; and products from metabolisms like starch and cellulose are used in the synthesis of this material. All of these are easily available in our daily lives and this makes them attractive materials for electrodes [85–94].

2.1.3. Carbide Derived Carbons (CDC)

Carbides serving as precursors are used to produce CDCs. They are synthesized by extracting metals at high temperature from carbides. The production methods include chlorination at high temperature [76,95] and vacuum decomposition [96]. Since fine-tuning of the pore networks is possible through the carbide precursors, CDC has been seen as a

promising material for supercapacitors [97,98]. Improved control over surface functional groups, when compared with ACs, is also an advantage of CDCs [99]. The disposal of diverse atom distribution of carbon in carbides and changing the synthesis temperature can help in controlling or personalizing the pore network in CDCs as per the requirement.

An assessment between Ti carbide-derived carbons and Si carbide-derived carbons showed that for the same manufacturing temperature (1200 °C), distribution of pore size of the SiC-CDC was narrower and also exhibited a smaller average pore size [99]. Some studies also showed that as the synthesis temperature increased, it resulted in increasing the pore size and this common trend was independent of the precursor used for the study [97,100]. Post-treatment, like treatment with hydrogen, helps in improving the properties of CDC. Comparison of titanium CDC and SiC-CDC showed that the titanium CDC possesses the highest gravimetric capacitance of 220 Fg^{-1} in KOH and 120 Fg^{-1} in organic electrolyte compared to 126 F cm^3 and 72 F cm^3 volumetric capacitance of SiC-carbide derived carbon in organic and KOH electrolyte respectively. This explains that the capacitance mainly depends on the structure of CDC and the rate of performance depends on the starting carbide [96]. A study where the effect of pore size was investigated by preparing the CDC between 600 °C and 1200 °C with tailored porosity proposed that pores with 2 nm or less in size have a better effect on capacitance when compared with larger pore size, even when they had higher surface area [97,101]. Studies also showed that as the synthesis temperature increased, a decrease in capacitance happened even when the specific surface area and pore volume increased, which further confirms that the pore size controls the capacitance value.

2.1.4. Carbon Nanotubes (CNT)

Carbon nanotubes (CNTs) are one of the promising materials for electrochemical energy storage applications due to their higher electrical conductivity because of their one-dimensional structure and higher active surface area. The CNT electrode showed a higher specific capacitance of ~100–400 F g^{-1}, which is better than conventional carbon-based electrodes due to their high electrical conductivity, fast charge transportation, higher surface-to-volume ratio, and tremendous electrolyte accessibility. Similar to activated carbon materials, CNT is also hybridized with metal oxides (e.g., manganese oxide) or conductive polymers (e.g., polyaniline) for improving the energy density [12]. Catalytic decomposition of some kind of hydrocarbons has been used for the production of carbon nanotubes [102,103]. Their crystalline order can be controlled by manipulating various parameters and this will help in attaining more than one type of nano structured formation [102]. Carbon nanotubes as an intertwined mat are used as CNT electrodes in supercapacitors. The electrodes are developed with an open and accessible network of mesopores that are interconnected. This helps in forming a continuous distribution, which in turn helps in utilizing the specific surface area more efficiently [104]. The equivalent series resistance of carbon nano tube electrodes is lower than activated carbon because of the easy penetration of ions into the mesoporous network [68]. The morphology as well as the purity of the material greatly affect the specific capacitance of the carbon nanotubes and the surface of the electrode is largely mesoporous, linked to the tube's outer face [102].

Since it is possible to grow CNTs without the requirement of a binder in a substrate which is conductive, the minimization of the contact resistance between the current collector and the active material is achieved and this, in turn, simplifies the electrode fabrication [105,106]. The specific capacitance of carbon nanotubes which is between 20 to 80 Fg^{-1} [102,107] can be increased up to 130 Fg^{-1} with subsequent oxidative processes and this results in the modification of the surface structure and, eventually, an additional surface functionality is introduced which can contribute to pseudo capacitance [16,108,109].

Single-walled carbon nanotubes and multi-walled carbon nanotubes (SWCNT, MWCNT respectively) as shown in Figure 2 can be produced based on the synthesis parameters. Both SWCNT and MWCNT will have an external surface area which can be accessed completely and very large electrical conductivity [102,103]. The study on SWCNT (single-walled CNT) supercapacitor showed that the size of the ions and the accessibility

of electrolyte/electrode are the major aspects on which the performance depends. When SWCNT had a theoretical specific surface area of 1315 m^2 g^{-1}, SSA of MWCNT was lower than AC because the mesoporous of MWCNT allows easy flow of ions through the electrode/electrolyte [110]. The solvent molecules expose partly when the size of the pore becomes comparable to the ion and this eventually results in high ionic packing density. However, because of the significant change in volume caused by the repetitive intercalation and depletion, their mechanical stability decreases [91].
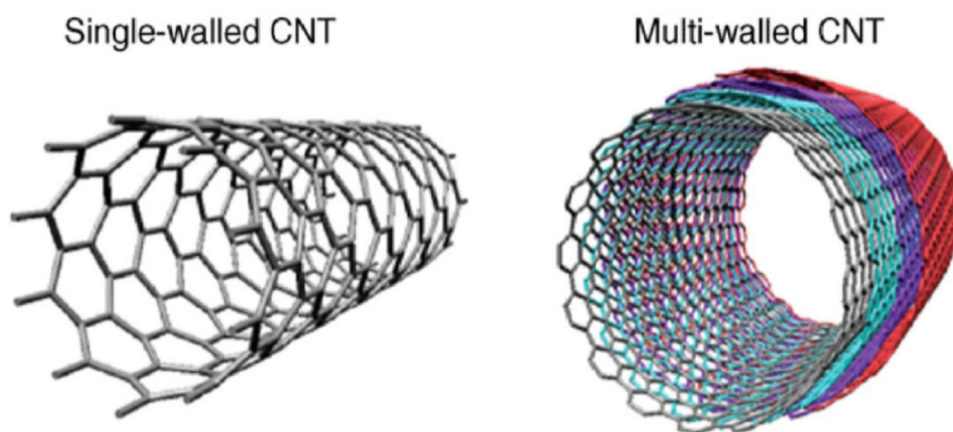

Figure 2. Single-walled carbon nanotube and multi-walled carbon nanotube [111].

MWCNT with a specific capacitance of 50 Fg^{-1} has been reported by Peng et al. [112], while through an easy carbonization method, HPCNTs (hierarchical porous carbon microtubes) with willow catkins have been prepared by Xie et al. [15] with a specific surface area of 1775.7 m^2 g^{-1}, 292 Fg^{-1} of specific capacitance at 1 Ag^{-1} and with an 83 percentage C_s retention with decent rate capability at 10 Ag^{-1} for HPCNT-800.

2.1.5. Carbon Aerogel

They are also known as frozen smoke. Carbon aerogel can bond chemically with the current collector and hence the requirement of a binding agent is eliminated. This highly porous, ultra-light synthetic material is constructed with mixed mesopores of a continuous network of carbon nanoparticles. These properties enable them to have a low ESR (equivalent series resistance) which in turn provides high P_d [113]. Pyrolysis of resorcinol-formaldehyde aerogels is used to prepare an electrode which is found to be a far better conductor than AC. They also provide mechanical and vibrational constancy for supercapacitors used in the high vibrational environment as the electrodes are thin and firm [114].

2.2. Metal-Organic Framework (MOF) Based Electrode Materials

The attention metal-organic framework is receiving as a template for the synthesis of nanocomposites of porous carbon, metal/metal oxides, and porous MOs has gathered momentum recently. In general, pristine MOFs are being used as positive electrodes for supercapacitor devices, whereas MOF-derived carbon is being used as a negative one. Compared to pure carbon-based materials, these MOF-derived carbon materials deliver excellent electrochemical performance owing to their favorable natures like high porosity, high specific surface area, etc. Annealing of MOFs at high temperature under inert atmosphere converts them into carbon, retaining the original MOF template [115,116]. The preparation of MOFs has been done by combining the organic and inorganic units through solid chemical bonds. Metal containing units is combined with polyvalent organic carboxylates produced 3D structures with high specific surface area (between 1000 to 10,000 m^2 g^{-1}) and well-defined pore size distributions. MOFs are developed using alkaline earth metals like Ba and Sr; p-block elements; transition metals like Co, Fe, Zn, and Ni; and mixed

metals [117]. The composition, pore size, and specific surface area of MOF derived oxides can be regulated by the annealing time and also by varying the temperature. Their electrochemical performance can be improved by combining them with various carbon-based materials like CNTs, graphene, etc. $Co_3O_4/NiCo_2O_4$, $CuO/Cu_2O@TiO_2$, $Fe_2O_3@TiO_2$, and $Co_3O_4/ZnFe_2O_4$ are some of the mixed metal oxides (MOs) and their composites that can be synthesized from MOFs. Zinc oxide, nickel oxide, cobalt oxide, and magnesium oxide are some of the porous TMOs acquired from metal-organic frameworks [118].

MOFs derived materials can be used for producing supercapacitor electrodes be-cause of the many advantages they possess such as high specific surface area, high porosity, etc. Still, studies are required on these materials to make them more suitable for supercapacitor applications. For example, even though some of the MOF derived materials show good electrical conductivity, most of them struggle with poor electrical conductivity at a large charge/discharge rate. More research in improving the electrical conductivity of such materials is required so that the application of MOF derived materials in supercapacitors can be enhanced. Some other drawbacks of these materials include the reduced cycle life at higher rates and inadequacies in the diffusion distance of the electrolyte within the porous metal oxides because of the high crystallinity [119]. There are many methods to improve the performance of MOF derived MOs. For example, to increase the specific surface area, heating the precursors of metal organic framework under a nitrogen atmosphere before heating them in the air is a method. This helps in stopping the rapid release of volatile gases which otherwise could have led to the failure of the frameworks. The chemical conductivity can be boosted by mixing the metal organic framework derived metal oxides with conductive carbon materials (graphene, CNTs etc.) together with a second metal oxide. The entering of the ions into the pores of MOs can be made easy by matching the heating conditions of the electrode and electrolyte and thus optimizing the pore size of the materials with the ion size of the electrolyte. Reducing the crystallinity of the material will help in attaining this [120].

Higher E_d and P_d values can be obtained with the help of three-dimensional materials which can provide many reaction sites in their networks. Polyhedral ZIF-8 and graphene-MOF composite on TiO_2/FTO substrate quantum dot MOF nanocomposite showed enhanced values of cycling life, P_d, and E_d. The one dimensional and two-dimensional materials can enable easy pathways for ion deintercalation and intercalation [115,121]. For practical applications, considering mechanical, chemical, and thermal stability is very important. Organic linkers and different types of clusters/metal ions have been used to attain remarkable stability for MOFs [122]. Poor chemical and mechanical stability and low intrinsic electrical conductivity limit the conventional MOFs large scale applications in supercapacitors. So far, most of the composite materials of MOFs have been produced and, in some cases, to attain long cycling stability, they have been used as precursors to manufacture metal oxides or carbon-based materials [123–125]. Many studies are still ongoing in MOFs, and MOFs have been considered as one of the promising electrode materials [126]. Still, only a few methods exhibit proper control over the dimensions of the metal oxides and this shows the importance of the metal organic framework derived materials. This also shows that, to attain an improved electrochemical performance, it is essential to have a clear and deep knowledge about the discharge and charge process of the metal organic framework derived metal oxides. Some of the promising MOFs are briefly explained in the coming sections.

2.2.1. Pristine MOFs

Studies on high-performance electrode materials have been gaining momentum recently and one of the materials involved in these studies has been pristine MOFs. MOF nanocrystals termed as nMOFs have been synthesized by Yaghi et al. and their electrochemical performance has been evaluated by employing them as electrodes in super-capacitors [127]. The researchers manufactured 23 nMOFs and they overcame the low electrical conductivity by mixing MOF nanocrystals with graphene in the film physi-

cally. One of the materials, nMOF-867 (zirconium MOF), showed 726 Fg^{-1} which is a very high capacitance and over 10,000 charge/discharge cycles. These outputs are far better than the currently available graphene and AC. Qu et al. used the solvothermal method and synthesized a nickel-based pillared MOF. As the pillar linker, they used DABCO (1,4-diazabicyclo [2.2.2] octane) and ADC (9,10 anthracenedicarboxylic) as the carboxylate linker. This electrode when used directly in the supercapacitor displayed a property of pseudocapacitive charge storage with 552 F/g specific capacitance at a current density of 1 Ag^{-1}. They also showed current capacitance retention of over 98 percent after 16,000 test cycles at 10 A/g. Through ligand functionalization, the material showed better kinetic stability and because of the large surface area of this structure, a reduction in electrode polarization has been detected [128]. The pristine MOFs still struggle with poor electrical conductivity and this is still a major hurdle that prevents them from attaining better cycling stability and specific capacitance [117].

2.2.2. MOFs Composite Materials

In some cases, MOFs are composited with materials like AC, conductive polymers, and graphene to eliminate the bad conductivity. This type of MOF composite material improves the overall multifunctionality of the material and also provides new physical and chemical properties [129].

Electrodeposition of PANI (polyaniline) on the cobalt-based metal organic framework to synthesize PANI-ZIF-67 has been studied by Wang et al. PANI-ZIF-67-CC synthesized this method when used as an electrode exhibited 35 mF cm^{-2} area capacitance at a current density of 0.05 mA cm^{-2} and after 2000 cycles showed more than 80 percent capacitive retention [130]. Using smear and electrodeposition method, zeolitic-imidazolate-framework (ZIF-67) and PPy as a composite material, coated on the carbon cloth (CC), has been synthesized, and efficient reduction in resistance during electron transportation has been found due to the nano stick like morphologies of PPy arrays. This also resulted in the acceleration of the zeolitic-imidazolate-framework charge transfer. The polypyrrole (PPy) arrays worked as a conductive link between the zeolitic-imidazolate-framework particles. After 40,000 cycles, the electrode exhibited very high capacitance retention of 100.7 percent and 284.3 F/g a specific capacitance at a current density of 1 mA/cm^2 [131].

2.2.3. MOF-Derived Materials

The well-organized pore structures, diverse structural topologies, large surface areas, and ample organic components make MOFs an ideal template for the manufacturing of nanostructured materials using high-temperature pyrolysis. These materials do not just strengthen the mechanical and chemical stabilities but also inherit the qualities of their parent MOFs. They are coordination polymers formed via the strong bonding between central metal ions and organic linkers. Intrinsic properties like high porosity, surface area, and appreciable aspect ratio of MOFs make them very useful for the application of supercapacitors. Some of the examples of MOF-derived nanostructures are metal carbides, chalcogenides, phosphides, metal oxides, and carbon-based materials. They also become multi-functional [132].

One of the main reasons the hollow nanostructures receive large attention is because this structure offers adequate contact area between electrolytes and active sites which in turn lessens the diffusion pathways of the ion and electron [133]. Yolk-shell structured ZIF-67/Ni-Co (ZIF-67/layered double hydroxide) nanosheets composite has been prepared by employing an etching coupled with deposition method by Hu and his team. They then formed the double-shell nanocage of Co_3O_4/$NiCo_2O_4$(DSNCs) by heat treatment (annealing) of the precursor [134]. The advanced structural stability of the DSNCs displayed an extraordinary capacitance of 92.5 percent after 12,000 cycles at 10 Ag^{-1} current density. They also exhibited a proper pore size distribution and attained 972 Fg^{-1} at 5 Ag^{-1} current density which is a very good capacitance. Hierarchically porous carbon film (HPCF) synthesized by using HKUST-1 as carbon source and CNTs as a template when used as an

electrode material showed more than 95 percent capacitive retention after 10,000 cycles at 10 Ag^{-1} [135].

2.3. Bimetallic Metal-Organic Framework (BMOF)

To enhance the intrinsic properties of MOFs, bimetals are combined with MOF structure as they can favorably introduce high porosity and defects due to the combinational effects between the various types of metals. This enables BMOFs to be used in various applications like electrodes of supercapacitors. Producing heterojunctions with the help of bimetallic metal organic frameworks is going to provide a new way to study the effects between the mixed metal atoms and this is believed to eliminate many limitations faced during the current practical applications of electrode materials. Enhancing the performance of metal organic framework based supercapacitors by combining another metal ion into the framework has been proposed [136]. The electron's electrical conductivity between electrolyte surfaces and electrodes is improved considerably as the second metal node is doped in a MOF, which could effectively endorse electronic coupling between the metal node [137]. Even though BMOF is manufactured from MOF, its morphology is different, but still in most of the cases it holds the crystal structure of the pristine MOF [136–140]. As the BMOF possesses improved surface area, porosity, lesser particle size, and better conductivity in comparison to MOF supercapacitors, its capacitance can be elevated. Multiple valance states of the metal species are present in BMOFs inducing higher redox sites, which makes them an interesting material in the supercapacitor electrode research studies [141].

When carbonaceous compounds like CNT and graphene are incorporated in BMOFs, they form composites that increase the conductivity, and this also seems like an attractive thing about BMFOs [142,143]. BMOF carbon composite has also been produced with the help of organic wastes like humate and rice husk by taking into consideration the environmental benefits it has to offer [144]. Another research focus has been manufacturing BMOFs at room temperature without losing the structural stability of the material [145]. Because of the exceptional physiochemical feature, BMOFs have been considered as a promising option for positive electrodes in supercapacitors. Some of the BMOF based materials used for the synthesize of electrodes are bimetallic-organic framework, BMOF-derived metal-carbon composite, BMOF-derived metal oxides, BMOF-derived metal sulfur composite, and hybrid materials from pristine bimetallic metal organic frameworks and their derivatives as supercapacitor electrodes.

2.3.1. Bimetallic-Organic Framework

Zinc doped Ni-MOF was the first BMOF implemented as an electrode in supercapacitors. This material when used in a tri electrode pseudocapacitive supercapacitor attained comparatively high capacitance (1620 Fg^{-1}) at 0.25 Ag^{-1} current density and as the current density increased the capacitance reduced and it was 854 Fg^{-1} at 10 Ag^{-1} current density. The stability of cycling was stronger for this material than that of nickel metal organic framework [146]. Even though many studies have been conducted on the application of pristine BMOFs as electrode materials in supercapacitors, they still have not improved drastically due to the poor electrical conductivity [147]. Synthesis of hybrid electrodes by using BMOFs as precursors could increase the cyclic stability, capacitive retention, and electrical conductivity is another area where much research is ongoing [138]. Mainly a combination of nickel and cobalt have been used as the base for the BMOF derived materials [138,139,148,149] but sulfide-based electrodes of zinc/cobalt have also been studied [150]. To effectively use BMOFs as supercapacitor electrodes, many improvements and studies are still required to overcome the major limitations of the material like complex synthesis, problems for mass production like large cost in manufacturing precursors of bimetallic metal organic frameworks, and also the corrosive effects which could cause a decrease in cycling stability [147].

2.3.2. BMOF-Derived Metal-Carbon Composite

When compared with conventionally prepared carbonaceous materials, because of the microstructures, surface volumes, pore sizes, and tunable morphologies of BMOF derived carbon materials, they possess very good capacitance performance and increased energy density [120]. Direct and indirect carbonization has been used for the synthesis of BMOF derived carbonaceous materials.

2.3.3. Bimetallic Metal Organic Framework Derived Metal Oxides

Mixed metal oxides as bimetallic metal organic framework derived metal compounds with their attributes exhibits enhanced specific capacitance as the ionic species transport is swift across the surfaces of electrodes and through electrolytes since they can easily penetrate electrolytes. Hollow Mn_2NiO_4 flowers as electrodes exhibited 531.5 Fg^{-1} specific capacitance at 1 Ag^{-1} current density [151] and, when the morphology of the MN_2-NiO_4 altered, exceptional improvements in the performance of capacitance have been found [152].

2.3.4. BMOF-Derived Metal Sulphur Composite

The electrical conductivity and capacitance performance of BMOF derivatives have been boosted when sulfur is integrated into the mixed-metal materials, mainly because of the effective redox reversibility [153]. The bimetallic sulfides contain different metal ions which can improve the transfer of charge in electrolyte among various ions. The charge transfer is also improved in surfaces of electrodes. Because of this they produce richer electrochemical reactions compared to the monometallic sulfides. $NiCo_2$-S_4 hollow capsules, spheres, nanotubes, ball-in-ball hollow spheres, nanosheets, and nano boxes are some of the bimetallic sulfides manufactured as electrode material for supercapacitors [139,154,155]. When sulfurization of NiCo-MOF is used to synthesize NiCo-S composite, it shows a spherical geometry compared to the flower-like geometry of NiCo-metal organic framework and the performance is improved, with 1377.5 Fg^{-1} specific capacitance compared to NiCo-MOF specific capacitance of 1220.2 Fg^{-1} at 1 Ag^{-1}. The cyclic stability was also enhanced by 93.7 percentage after 3000 cycles [139].

2.3.5. BMOF-Derived Metal-Phosphorous Composite

One of the widely employed supercapacitor electrodes has been mono-metal phosphide and mixed metal phosphides. Unique electrode materials with high capacitance have been synthesized when in an inert atmosphere, and phosphorization of BMOFs has been conducted [156].

2.3.6. Hybrid Materials from Pristine Bimetallic Metal Organic Frameworks and Their Derivatives as Electrodes of Supercapacitors

The better surface area and porosity of bimetallic metal organic frameworks made them a favorite in the study of electrode materials for high performance supercapacitors. The electroactive redox sites are also a very big advantage of BMOFs when it comes to their application as electrode materials. However, there are many hurdles which restrict their applications in a supercapacitor. The bad electrical conductivity is one of the major disadvantages of BMOF. Very high agglomeration is another drawback which limits the application of BMOFs. Synthesizing a novel bimetallic metal organic framework with better electrical conductivity or combining it with materials like aerogel, graphene, acetylene black, activated carbon, nickel foam, polypyrrole, etc. can be adapted to overcome these issues [157].

2.4. Conducting Polymers

Conducting polymers (CPs) enables the faradaic redox reactions and thus helps improve the specific capacitance of the supercapacitors. They are usually seen in composite materials used for the synthesis of supercapacitor electrodes. An improved pseudocapacitance is resultant due to the faradaic redox reactions. The charging of conducting

polymers takes place all over the material, whereas only surface is involved for plain carbon electrodes. For the redox reaction, the ions from the electrolyte transfer into the polymer and out of it which results in an improved capacitance and also exhibits reduced cyclability [158]. Polyaniline (PANI) is one of the examples of this type of polymer which has undergone many studies. Its low cost, better conductivity, and comparatively easier production methods made them an attractive material.

When CNT, nanosheets of graphene, and polyaniline were studied in different blends for the application as electrode materials in supercapacitors, they exhibited better performance. The experiments were conducted in a three-electrode setup and the maximum specific capacitance attained at 1 mVs^{-1} for CNT/PANI, GNS/CNT/PANI, GNS/PANI, and pure PANI were 780,1035,1046 and 115 Fg^{-1} correspondingly. Even though the specific capacitance of graphene nanosheets/PANI/carbon nanotube is narrowly smaller than graphene nanosheets/PANI, they exhibited 94 percent capacitance retention after 1000 cycles with higher stability whereas the value was only 48% for GNS/PANI [159]. The reduced graphene/polyaniline (rGO/PANI) synthesized by Zhang and his team also exhibited really good capacitance (1182 Fg^{-1} at 1 Ag^{-1}). They tested the material in a three-electrode system. For a symmetrical two-electrode system, rGO/PANI showed capacitance of 808 F/g at 1 A/g current density [160]. The material acquired an energy density of 28.06 Wh/kg at 250 W/kg power density. It is evident from the research articles related to conducting polymer-based supercapacitors that almost all of them have used PANI and performed the studies. This may be due to the vast number of favorable properties of the material apart from the electrochemical performance in supercapacitors. For example, polyaniline is more suitable because of its capability to distribute efficiently in some type of solvents under specific conditions, whereas some other CPs like polyacetylene lack the structural integrity for broader applications.

2.5. Transition Metal Oxides

Most of the research based on transition metals for supercapacitors has mainly studied the oxides of transition metals, since pseudocapacitance was discovered in 1971 [62]. The studies on transition metal dichalcogenides (TMDC) has begun only recently. TMDC also contains oxides like RuO_2. However, as chalcogen is in the 16th group of the periodic table, transition metal dichalcogenides are not metal oxides in reality and that is why the two are labelled separately in most cases. TMDC includes oxides of metals like titanium, molybdenum, sulfides of metals like tungsten, etc. [161–168]. Figure 3 shows some of the most studied transition metal oxides.

For pseudocapacitor applications, mostly RuO_2-based electrode material is used due to its good proton conductivity, high specific capacitance, high rate capacity, wide potential window (up to 1.2 V), higher reversible surface redox reactions, and long cycle life. The nanotubular arrayed hydrous RuO_2 electrode showed a maximum specific capacitance of 1300 F g^{-1} with good cycle stability.

Even though it has higher specific capacitance and good cycle stability, the real-time application is challenging due to its higher cost and toxicity to the environment [12]. Ideal capacitive performance, considerably less cost, and environmental friendliness of transition metal oxides made them an attractive material for supercapacitors. Their charge storage mechanism follows pseudocapacitive behavior. The significant inherent stability and the challengeable valence, which permits the intercalation of electrons and ions into the lattice of metallic compounds, are the main characteristics of TMO [169–172]. Some of the well-known materials which have been studied for the application in supercapacitors as electrode materials are MnO_2, NiCo LDH, Fe_2O_3, ZnO, CoAl LDH, and their composites. Some of them are briefly discussed in the following sections.
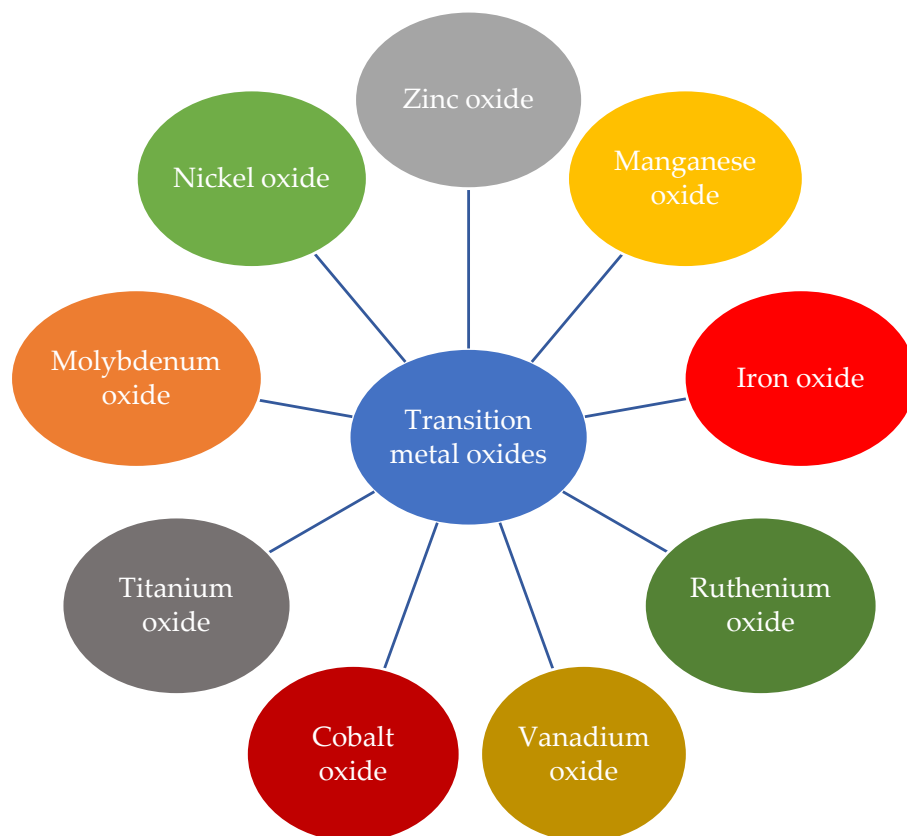
Figure 3. Examples of transition metal oxides.

2.5.1. Nickel-Based Supercapacitor Electrodes

The excellent theoretical capacitance of nickel-based electrode materials has been gaining attention recently. Their high chemical stability, easy availability, low cost, better theoretical capacitance, and non-toxic nature make them a promising material in the application for high-performance supercapacitors [173–176]. Methods like electrodeposition, hydrothermal, solvothermal, etc. have been used for the synthesis of high surface area nickel-based electrodes. Preparation with these methods helped in a reduced ion diffusion length and also improved the electrolyte penetration. Some of the major nickel-based electrodes used in the applications of supercapacitors are briefly summarized in the coming sections.

- Nanoparticles based on nickel

Nanoparticles based on nickel have been studied for their application as electrodes in high-performance supercapacitors. They can be synthesized by an easy and economical solvothermal process. NiO nanoparticles synthesized by solvothermal process showcased an outstanding 1385 F/g capacitance at 1 A/g on NF (nickel foam) based electrodes. The homogenous nanoparticle morphology attained during the synthesis and also the strong chemical bonding of nickel oxide on nickel foam which reduced the diffusion of ion path and helped the transfer of charge at the contact interfaces during the electrochemical process helped in achieving these excellent electrochemical properties [177]. Nickel nanoparticles-based composites and core-shell nanostructures have also received attention recently for their applications in high-performance supercapacitors as electrode materials [178,179].

- Nickel-based nanowires

Nanowires are an important electrode material used in the application of supercapacitors. Nickel-based nanowires are superior to other types of nanowires in many areas when it comes to electrode materials. Nickel-based nanowires produced by electrospinning of

an aqueous polymeric solution encompassing nickel onto NF substrate resulted in closely packed cuboidal grains of diameter between 50 to 70 nm and with relatively fewer crystal imperfections [180]. $NiMoO_4$ nano wires on NF was manufactured by hydrothermal method. They are utilized as a binder-free electrode in supercapacitor applications. This electrode material showcases advantages like rapid electron transportation because of the strong adhesion of nanowires on NF, which eliminates the use of polymer binders, and easy diffusion of electrolyte into the inner region of the electrode as the nanowires possess open spaces between them. This reduces the electrolyte diffusion resistance. Additionally, the cyclic stability has been improved due to the remarkable morphological stability of the nanowire-based electrodes. All these properties of the electrode material resulted in exhibiting an excellent 3.12 F cm^2 specific capacitance at 40 mA cm^2 [181]. The core-shell morphology also received attraction in the area of nanowires because of the better electrochemical properties they exhibit. One example of this type of material as a supercapacitor electrode is three dimensional porous zinc-nickel-cobalt oxide (ZNCO)@$NiMoO_4$ nanowire-nanosheet arrays (NWNSAs) on nickel foam [182].

- Nickel-based thin films

Supercapacitor electrode material based on thin-film morphology is another area that has been gaining attention recently. One such example for the nickel-based thin film is $Ni(OH)_2$ on a glass substrate. It has been synthesized from an electrolyte having nickel ions and ammonia through chemical methods. At 333 K, thermal decomposition of ammonia with nickel ions is the deposition method used for the synthesis of this material. The thin films after the synthesis undergo an annealing process for 2 h at 623 k. This is done to remove the hydroxide part [183].

- Nickel-based nanofibers

Nickel-based nanofibers are another supercapacitor electrode material. One example of such nanofiber-based electrode material is $NiMoO_4$/g-C_3N_4 nanofiber which has been synthesized through the hydrothermal method [184].

- Spherical structured materials based on nickel

The nickel-based spherical structured materials have been studied for their application as positive electrodes in high-performance supercapacitors. One example of this type of material is nickel oxide-carbon hollow sphere nanocomposite which can be synthesized by semi sacrificial hydrothermal method, which is template assisted along with calcination. NiO/C-HS manufactured by this method exhibited excellent electrochemical performance. It not only showcased the better capacitance of nickel oxide but also had the better stability and outstanding conductivity of C. The material displayed a capacitance of 686 F/g at 1 A/g. The capacitive retention was 72%, which was better than the 65% capacitive retention of NiO-HS [185].

- Nickel-based nanosheets

Nickel-based nanosheet materials which have adequate electroactive sites, high porosity, and a self-supported three-dimensional network are other promising electrode materials that can be used for the application of high-performance supercapacitors. Examples of this type of electrode material are NiCoS nanosheets arrays on carbon cloth (CC) [186] and 3D NiFeP@$NiCo_2S_4$ nanosheet arrays on CC [187].

2.5.2. Zinc Oxide

ZnO is widely used in many applications because of the good electrical and optical properties it possesses. Many studies conducted on ZnO concluded that it can be used in the application of supercapacitors as it has a very high energy density (650 Ag^{-1}) [188–190].

Manufacturing of a sandwich of rGO/ZnO and nanorods/rGO through deposition of chemical vapor on graphene film/polyethene terephthalate substrate as an electrode for supercapacitors displayed a specific capacitance of 51.6 F/g at 10 mV/s. Figure 4 shows

synthesis of a sandwich ZnO/rGO/ZnO paper by sol-gel dip coating method. Due to the existence of zinc oxide nanorods in the electrodes, the formation of porous structure improved. The study showed the promising application of the material in supercapacitors [191].
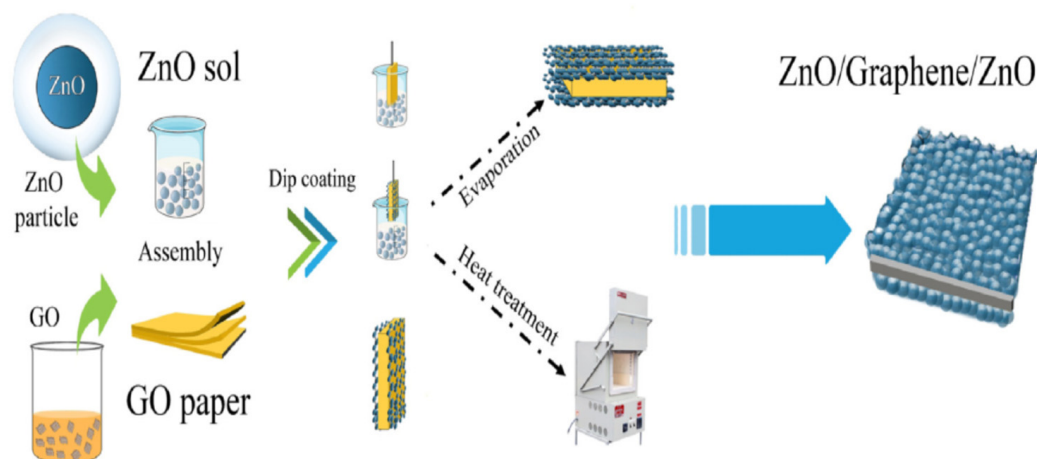

Figure 4. Schematic representation of synthesis of sandwich ZnO/rGO/ZnO paper by sol-gel dip coating method [192].

2.5.3. Titanium Oxide

Comparatively reduced cost, less toxicity, and environmental friendliness of titanium oxide made it an upcoming material for the anode of lithium-ion batteries [193]. TiO_2 nanoparticles with conductive activated carbon nanopores help in manufacturing a high-performance TiO_2 Li-HSCs (hybrid supercapacitor) [194]. The method included vacuum infiltration, calcination, and hydrothermal processing that permits precursor-like titanium butoxide to decompose and crystalize into TiO_2 with activated carbon nanopores. The large surface area and high porosity of the titanium oxide/activated carbon composite particles enable quick ion transportation through a liquid electrolyte.

The hybrid capacitor showed very high-rate capabilities with a specific capacity of 140 mAh g^{-1} at slow charge and 60 mAh g^{-1} at a 3.5 s fast charge. This material looks promising for the applications of hybrid supercapacitors in many areas.

2.5.4. Cobalt Oxide

Cobalt oxide (Co_3O_4) is an attractive material that can replace the use of environmentally hazardous ruthenium oxide. This is mainly due to the fine redox characteristic, the high specific capacitance of 3560 Fg^{-1}, and easy synthesis of the material. The electrochemical characteristics of Co_3O_4 depend on the material morphology and the electronic state of the material and due to this, different forms of cobalt oxide can be developed to attain a better charge storage performance [195,196].

2.5.5. Iron Oxide

The high specific capacity of 1005 mAhg^{-1}, natural abundance, low cost, and environmental friendliness have made iron oxide (Fe_2O_3) another important candidate in the supercapacitor applications; however, the poor conductive nature and high agglomeration of the iron oxide during the charge-discharge process could lead to rapid loss capacity, which is a major problem [25,197].

One of the important considerations to be taken into account during the fabrication of a supercapacitor is its properties like flexibility and reduced weight. Using stainless steel mesh, which is low in cost, with very little weight can be used to overcome this obstacle. SS mesh also provides an additional advantage of high surface area compared to flat steel sheets [198].

2.5.6. Molybdenum Oxide

Molybdenum oxide possesses the better theoretical specific capacitance of 1256 F/g amid other materials of this type because of the two-dimensional structure and various oxidation states the material possess [199]. Still, intrinsic redox reaction and low conductivity are the major disadvantages of this material as they could lead to poor cyclic performance.

2.5.7. Manganese Oxide

Manganese oxide is one of the most studied super capacitor electrode materials, thanks to its excellent power density and better cycle life when applied as electrodes. Reduced cost, very low toxicity, and also its environmental safety aspects when compared to some other electrode materials show the importance of conducting more research into manganese oxide based super capacitor electrodes. The theoretical capacitance of MnO_2 can go up to 1100–1300 Fg^{-1} [200–203].

Some other promising transition metal oxides for the applications in supercapacitors include binary nickel cobaltite oxide [204,205], vanadium oxide [206], and ruthenium oxide [207–211].

2.6. Transition Metal Nitrides

The exceptional chemical bonding and intrinsic structures of transition metal nitrides allow them to exhibit outstanding conductivity and physiochemical properties and this has gained them great attention for supercapacitor applications. The poor stability in cycling and low conductivity are major hurdles when it comes to the application of metal oxides and conducting polymers as pseudocapacitive materials. This is where metal nitrides come into the picture as a promising alternative. The metal nitrogen bond formation decides the properties of the material. Very good ionic conductivity has been shown by group 1 and group 2 based nitrides whereas nitrides formed from group III and IV, because of their intrinsic covalent bonding, exhibit stiffness and tolerance against high temperatures [212].

TMN bonding is a combination of metallic, ionic, and covalent bonding. Additionally, the lattices of transition metal nitrides are metallic structures occupied by nitrogen atoms which are disoriented in nature at the interstitial sites [213]. All these unique characteristics provide them with exceptional properties such as multiple crystal structures and valence states, better electrical conductivity than the transition metal oxides, and also better redox chemistry which in turn results in good electrochemical activities [214–216]. Since the demonstration of titanium metal nitride applications in supercapacitors began when molybdenum nitride films were studied to use as a substitute in electrodes of ruthenium oxide [217], they have become one of the most important materials studied and considered to be promising in energy-related research and there have already been made commendable achievements both in practical and theoretical developments. Figure 5 shows some of the promising transition metal nitrides studied for application in high-performance supercapacitors and they are briefly discussed in below sections.
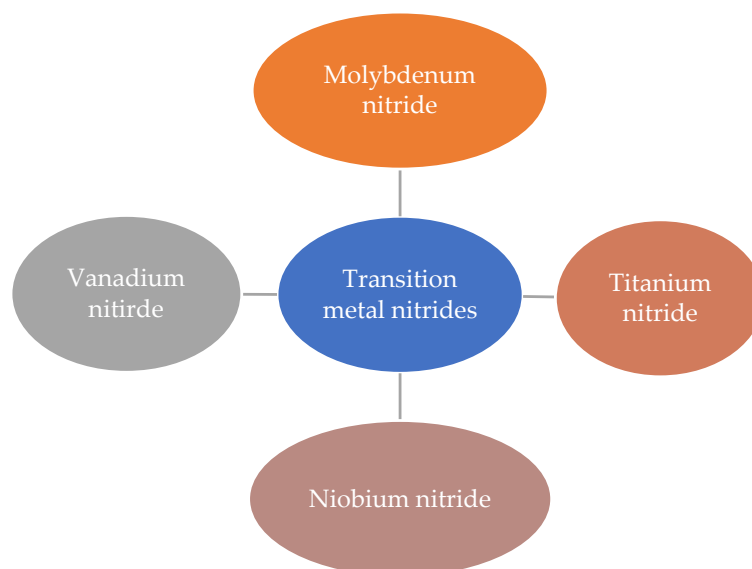
Figure 5. Examples of transition metal nitrides.

2.6.1. Vanadium Nitrides

The exceptional electrical conductivity approximately of 1.67×10^6 S m^{-1} and reduced cost make vanadium nitrides (VN) one of the important materials among titanium metal nitrides [218]. The negative voltage window of vanadium nitrides makes them suitable to be utilized as a negative electrode material for supercapacitors with large energy density and also for supercapacitors with high capacitance. The charge storage mechanism of the vanadium nitride has been studied in the various mechanism by conducting electrochemical tests of vanadium nitride crystallines in alkaline, neutral, and acidic electrolytes [219]. Vanadium nitride exhibited a higher capacitance of 273 Fg^{-1} and an operating potential of -1.1 to 0 (vs. Hg/HgO) in KOH electrolytes. Even though vanadium nitride exhibits a high specific capacitance of 1340 Fg^{-1}, its rate performance is very poor [218]. Vanadium nitride seems to be the most suitable titanium metal nitride as electrode material for supercapacitors. However, many more studies are required to optimize the performance of this material. Some of the methods to improve the electrochemical performance of these materials are the selection of suitable precursors like VCl_4 and NH_4VO_3, improving the specific surface area, and combining materials based on carbon which possess high electrical conductivity and better surface area with vanadium nitrides which could increase the cycle performance.

2.6.2. Titanium Nitride

Electrical conductivity between 4000–55,500 S cm^{-1} of titanium nitride is the main attractive point when it comes to the application of the material as electrodes in supercapacitors. Additionally, the thermal stability, comparatively low cost, and good mechanical properties make it a promising electrode material [220,221]. However, many studies reported that the generation of pseudocapacitance is more difficult in titanium nitride when compared with vanadium nitride. The capacitance can be improved by modifying titanium nitride with pseudocapacitive materials and also some of the new technologies for engineering the surface chemistry like surface oxidation and promoting external diffusion of nitrogen. More research is required to improve the performance of the material.

2.6.3. Molybdenum Nitride

Molybdenum nitride was initially used as a substitute electrode material for RuO_2 in supercapacitors [217]. Its outstanding corrosion resistance [222] and high conductivity [223] has gained popularity among researchers in the area of electrochemical capacitors. The electrochemical performance of molybdenum nitride depends on the nature of the electrolyte

and the phase of the material. Studies indicated that they showed outstanding cycling stability in acidic mediums [224–226]. The most studied objects among the molybdenum nitride family are γ-Mo$_2$N and δ-Mo$_2$N. They are further divided into three structures known as δ_1, δ_2, and δ_3 [227].

The limitations of existing molybdenum nitride such as capacitive behavior, cycle performance, and rate capacity can be eliminated by hybridizing with other materials. Some examples for such materials are γ-Mo$_2$N/Co$_3$Mo$_3$N, MoNx/TiN [228], and amorphous Ta$_2$O$_5$ modified with γ-Mo$_2$N [229].

2.6.4. Niobium Nitride

The outstanding electrical conductivity [230–232], good capacitive behavior, and continuous creation of faradaic process due to the nitrogen-rich intermetallics like Nb$_5$N$_6$ and Nb$_4$N$_5$, which contain high-valence Nb ions [233], and the excellent volumetric energy density attained because of the intrinsic high molar density of niobium nitride [214,234] make it an attractive capacitive material.

Some other examples of metal nitrides that can be used in high-performance supercapacitor applications are MnN, LaN, Fe$_2$N, RuN, CrN, WN, HfN, and NiXN [235–242].

2.7. *Mesoporous Cobalt Silicate Nanosheets (Co$_2$SiO$_4$ NSs)*

The small diameter and a specific area of 114 m^2 g^{-1} of mesoporous cobalt silicate nanosheets can provide ample reactive spots where the electrochemical reaction take place and this can improve the mass transfer and attain good performance in electrochemical process. They were initially manufactured by the sacrificial template stÖber SiO$_2$ spheres [243]. The specific capacitance of Co$_2$SiO$_4$ nano sheets is 638 F/g at 0.5 A/g current density and they exhibited 82 percentage capacitance stability after 10,000 cycles. When a hybrid supercapacitor of Co$_2$SiO$_4$/activated carbon is synthesized, they attained a specific capacitance of 571 mF cm^{-2} at 1 mA cm^{-2} and after 10,000 cycles exhibited capacitance retention of 92 percent. The energy density of the Co$_2$SiO$_4$//activated carbon HSC was 1.55 Wh/m at 1.75 Wm^{-3} power density. Even though the application of cobalt silicate for batteries has been widely explored, fewer studies are conducted in the area of supercapacitors, and this limits the potential use of cobalt silicate in supercapacitors [244–248].

The morphology structure of cobalt silicate which is divided into spherical shaped and belt-shaped morphologies influences the actual performance of the material greatly [249,250]. A hollow sphere structure represents the spherical shaped morphologies of cobalt silicate. Cobalt nickel silicate hollow spheres displayed 144 F/g at 1 A/g [251] whereas cobalt silicate hollow spheres exhibited 452.8 Fg^{-1} at 0.5 A/g [250]. The spherical cobalt silicate hollow sphere is characterized by its higher volume with more than 200 nm in diameter [251]. On the other hand, the belt-shaped cobalt silicate has structure which has a great effect on the capacitive performance. Cobalt silicate nanobelts achieved 244 Fg^{-1} at 0.5 Ag^{-1} [249] whereas amorphous Co$_2$SiO$_4$ nanobelts@MnSiO$_3$ exhibited the electrochemical characteristics with 309 Fg^{-1} at 0.5 A g^{-1} [252].

However, both the spherical and belt-shaped structures of mesoporous cobalt silicate nanosheets are unable to meet the requirements for porous and high SSA of supercapacitor electrodes and this limits them from achieving the required electrochemical properties. More studies are required to understand cobalt silicate with other structures so that it can be fully utilized for the applications of supercapacitors [88].

2.8. *CuCo$_2$O$_4$-Based Electrode Materials*

The advantages of CuCo$_2$O$_4$ like increased theoretical capacity, low cost, abundance in nature, and environmental friendliness have recently made them an attractive material in the research for high-performance supercapacitor electrodes. CuCo$_2$O$_4$ still requires many more studies and experiments to overcome its limitations such as low cyclic durability, reduced conductivity, and comparatively small specific capacity for the applications of the material in supercapacitors. CuCo$_2$O$_4$ possess two types of crystal structures, namely

normal spinel structure ($Cu[Co]_2O_4$) and inverse spinel structure($Co[CuCo]O_4$). The normal spinel structure can be changed into an inverse spinel structure when X in the equation $Cu_xCo_{3-x}O_4$ is higher than 0.2 [253].

Many scientists and engineers are still working to synthesize an advanced $CuCo_2O_4$ electrode material that possesses superior performance and unique structure. There are many methods adapted for the synthesize of $CuCo_2O_4$ electrode materials with different structures. Some of the most used and effective techniques are solvothermal, electrodeposition, hydrothermal, electrospinning, and template-assisted methods [254].

Hydrothermal method: In hydrothermal methods, the solvent is pure water and the temperature of reaction is more than 100 °C and they require a sterilizer. There are many advantages for hydrothermal methods, for example the size and structure of the materials can be regulated. Since this is a very simple and cost-effective operation, it is the most commonly used method for the synthesis of the material. Many shapes of $CuCo_2O_4$ have been prepared with this process and after the process, the post-annealing process is done. $CuCo_2O_4$ nanoparticles with the help of oxalic acid and sodium hydroxide as precipitate agents are an example. This hydrothermally synthesized material showed a very big specific surface area of 133 m^2/g and a specific capacity of 229.5 c/g at 2 Ag^{-1}. They also produced good cyclic performance (95 percentage capacity retention after 2000 cycles) [255].

Solvothermal method: This is almost similar to the hydrothermal method. The main difference is that pure water is not used as a solvent; this method uses mixed solvent or organic solvent and most of the time the temperature of reaction is greater than the boiling point of the solvent. For example, methanol was used as a solvent in the synthesis of copper-cobalt hybrid oxide (CuCoO-H) micro flowers which include $CuCo_2O_4$, CoO, and Cu_2O components. The precursor underwent heat treatment in argon atmosphere in this two-step growth annealing approach [256].

Electro-deposition synthesis: Another commonly used method for the synthesis of $CuCo_2O_4$ is the electro-deposition method. In this method, in a solution which contains cobalt and copper salts, the products are placed on the conductive substrates. This method is generally used for the preparation of two-dimensional nanosheet structures. These ultrathin nanosheets increase the SSA and electroactivity and also help the diffusion of electrolytes to reduce the ion diffusion distance [254].

Template-assisted method: In this method, the selective removal of the inner templates through etching or thermal decomposition and coating of the desired material's shell on the removable templates is the main process. The removable templates include soft types like surfactant micelles and silica templates which are hard in nature and also carbon templates. One example is the synthesis of the highly ordered mesoporous $CuCo_2O_4$ nanowires with the help of silica SBA-15 as the hard template [257].

2.9. Redox Polymers

Redox polymers are another promising material that can be used as electrodes in the manufacturing of a sustainable, affordable, and high-performance supercapacitor. Their mechanical flexibility, better processability, small cost, molecular diversity, and good electrochemical activity has made them an attractive material. These properties make them a better candidate for the practical application of supercapacitors than conventional inorganic materials like metal oxides or carbons [258]. The supercapacitors based on this material not only generate pseudocapacitance from the reversible redox reaction of electrode materials but also accumulate charge at the electrical double layer. Because of this, a much better specific capacitance and energy density than EDLCs is exhibited by the supercapacitor [259].

Mainly conventional conducting polymers like polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), and their derivatives have been the commonly used redox polymers so far due to their electrochemical activity, good conductivity, better theoretical capacitance, and easy synthesis. Lack of research in this area still limits their applications because of the incomplete doping, poor life cycle due to their volume change during the

electrochemical process, and sloping voltage [260]. Some studies developed redox polymers with better stable structures to overcome these limitations and promote the practical application of organic supercapacitor technologies. The organic electrode materials possess better properties when compared to inorganic electrode materials such as excellent mechanical flexibility, reduced cost, and environmental friendliness. Some examples where redox polymers as active electrode materials have been used are all-solid-state flexible supercapacitors [261,262] and paper-based flexible supercapacitors [263].

When it comes to high-performance supercapacitors, the best alternative to inorganic electrode materials is organic redox polymers because of their excellent electrochemical activity, reduced cost, natural abundance, better processability, and versatility in structure. Additionally, the softer mechanical properties and the chemical diversity of the materials helps them in the manufacturing of stretchable or flexible electrodes for supercapacitors. Despite the promising nature of redox polymers for the application of high-performance supercapacitors, one major hurdle which should be eliminated is their intrinsically poor electrical conductivity. This low electrical conductivity might result in reduced utilization of active sites which in turn leads to poor rate performance. Studies are still performed by many researchers to overcome this barrier and some of the promising studies showed that this low electrical conductivity problem can be reduced with the help of ingeniously molecular design [264].

3. Conclusions

The rising pollution and other environmental concerns from the automotive sector have increased the popularity of electric vehicles and hybrid electric vehicles. Even though they have improved significantly in recent years, the electrochemical energy storage system is still far behind and this is the major disadvantage of the HEV and EV compared with conventional fuel-based vehicles. This is where the integration of supercapacitors along with the battery system comes into play. This combined system, usually termed hybrid capacitors, shows promising results in energy storage technologies and has received wide attention recently. In this setup, the supercapacitors can supply the energy rapidly for a short period when the battery is unable to do so and then when a steady energy flow is required, the battery can again supply the required energy. This hybrid system helps the batteries to achieve better performance and improve their lifecycle and is going to be in great demand in the future applications of the energy sector. Hybrid electric vehicle systems with hybrid capacitors which use both battery and supercapacitors is an area that requires more studies and a breakthrough in this research could help in tackling the limitations of the hybrid-electric automotive industry. Even though much research has been conducted in this area, high-performance supercapacitors are still in the early stages. More studies are required, especially in energy storage mechanisms and proper design of the electrodes to improve the performance of supercapacitors. One of the major areas in supercapacitors that require more studies are the electrode materials and, in this review, we briefly discussed various electrode materials, summarized their performance in supercapacitors, and their advantages and disadvantages.

This review focused not just on the most commonly used materials like carbon-based materials, MOs and their composites, and CPs, but also on the latest materials like MOFs, COFs, and metal nitrides. One of the important types of materials which should receive more focus is the nano-dimensional materials, as they possess the ability to improve the capacitive performance of the high-performance supercapacitors and still maintain the high cycle life and the outstanding kinetic reversibility. Nanocomposite materials are one of the most promising materials which can be used for the manufacturing of high-performance supercapacitor electrodes and more research should be focused on these materials. Renewable materials as supercapacitor electrodes have also gained attention because of the environmentally friendly aspects they provide and their abundance in nature. Carbonaceous electrode materials like activated carbon, graphene, and carbon nanotubes were also considered in this review even though they are the most commonly used materials

because they still seem to be promising since they can be used in combination with other materials like metal oxides or conducting polymers which can form a composite or hybrid supercapacitors which seems to be an interesting alternative as reported by some authors. More studies in this area could make an impact in energy-related applications. It is clear from this study that the performance of supercapacitors has increased considerably over the years. The energy density and specific capacitance have significantly improved in recent years, and this has made supercapacitors a promising alternative in the energy sector. However, the growing energy demands make it necessary that continuous study is still required in electrode materials for their application in high-performance supercapacitors which can provide high capacitance, better cyclic stability, and exceptional rate. The research should also focus on the manufacturing parameters and properties of the materials to synthesize the most suitable electrode material which could help in improving the supercapacitors and meet the energy demands.

Many manufactures have already started investing more in supercapacitor technology as their requirement in the automotive sector as well as in other industries is increasing. This review clearly shows that supercapacitors are becoming an emerging energy storage technology as the improvements in electrode materials have been outstanding lately, which in turn has enhanced the performance of supercapacitors significantly, and they are going to have an important part in the future of energy storage systems.

References

1. González, A.; Goikolea, E.; Barrena, J.A.; Mysyk, R. Review on supercapacitors: Technologies and materials. *Renew. Sustain. Energy Rev.* **2016**, *58*, 1189–1206. [CrossRef]
2. Abdel Maksoud, M.I.A.; Fahim, R.A.; Shalan, A.E.; Abd Elkodous, M.; Olojede, S.O.; Osman, A.I.; Farrell, C.; Al-Muhtaseb, A.H.; Awed, A.S.; Ashour, A.H.; et al. *Advanced Materials and Technologies for Supercapacitors Used in Energy Conversion and Storage: A Review*; Springer International Publishing: Berlin/Heidelberg, Germany, 2021; Volume 19, ISBN 0123456789.
3. Zhang, Y.; Mei, H.X.; Cao, Y.; Yan, X.H.; Yan, J.; Gao, H.L.; Luo, H.W.; Wang, S.W.; Jia, X.D.; Kachalova, L.; et al. Recent advances and challenges of electrode materials for flexible supercapacitors. *Coord. Chem. Rev.* **2021**, *438*, 213910. [CrossRef]
4. Sharma, K.; Arora, A.; Tripathi, S.K. Review of supercapacitors: Materials and devices. *J. Energy Storage* **2019**, *21*, 801–825. [CrossRef]
5. Kouchachvili, L.; Yaïci, W.; Entchev, E. Hybrid battery/supercapacitor energy storage system for the electric vehicles. *J. Power Sources* **2018**, *374*, 237–248. [CrossRef]
6. Wang, C.; Song, Z.; Shi, P.; Lv, L.; Wan, H.; Tao, L.; Zhang, J.; Wang, H.; Wang, H. High-rate transition metal-based cathode materials for battery-supercapacitor hybrid devices. *Nanoscale Adv.* **2021**, *3*, 5222–5239. [CrossRef]
7. Afif, A.; Rahman, S.M.; Tasfiah Azad, A.; Zaini, J.; Islam, M.A.; Azad, A.K. Advanced materials and technologies for hybrid supercapacitors for energy storage—A review. *J. Energy Storage* **2019**, *25*, 100852. [CrossRef]
8. Miller, E.E.; Hua, Y.; Tezel, F.H. Materials for energy storage: Review of electrode materials and methods of increasing capacitance for supercapacitors. *J. Energy Storage* **2018**, *20*, 30–40. [CrossRef]
9. Raj, B.; Padhy, A.K.; Basu, S.; Mohapatra, M. Review—Futuristic Direction for R&D Challenges to Develop 2D Advanced Materials Based Supercapacitors. *J. Electrochem. Soc.* **2020**, *167*, 136501. [CrossRef]
10. Xu, Y.; Shi, G.; Duan, X. Self-Assembled Three-Dimensional Graphene Macrostructures: Synthesis and Applications in Supercapacitors. *Acc. Chem. Res.* **2015**, *48*, 1666–1675. [CrossRef] [PubMed]
11. Brousse, T.; Bélanger, D.; Chiba, K.; Egashira, M.; Favier, F.; Long, J.; Miller, J.R.; Morita, M.; Naoi, K.; Simon, P.; et al. Materials for electrochemical capacitors. In *Springer Handbook of Electrochemical Energy*; Springer: Berlin/Heidelberg, Germany, 2017; pp. 495–561. [CrossRef]
12. Balasubramaniam, S.; Mohanty, A.; Balasingam, S.K.; Kim, S.J.; Ramadoss, A. Comprehensive Insight into the Mechanism, Material Selection and Performance Evaluation of Supercapatteries. *Nano-Micro Lett.* **2020**, *12*, 85. [CrossRef]

13. Largeot, C.; Portet, C.; Chmiola, J.; Taberna, P.L.; Gogotsi, Y.; Simon, P. Relation between the ion size and pore size for an electric double-layer capacitor. *J. Am. Chem. Soc.* **2008**, *130*, 2730–2731. [CrossRef]
14. Wang, G.; Zhang, L.; Zhang, J. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* **2012**, *41*, 797–828. [CrossRef]
15. Xie, L.; Sun, G.; Su, F.; Guo, X.; Kong, Q.; Li, X.; Huang, X.; Wan, L.; Song, W.; Li, K.; et al. Hierarchical porous carbon microtubes derived from willow catkins for supercapacitor applications. *J. Mater. Chem. A* **2016**, *4*, 1637–1646. [CrossRef]
16. Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and electrolytes for advanced supercapacitors. *Adv. Mater.* **2014**, *26*, 2219–2251. [CrossRef] [PubMed]
17. Yang, Z.; Tian, J.; Yin, Z.; Cui, C.; Qian, W.; Wei, F. Carbon nanotube- and graphene-based nanomaterials and applications in high-voltage supercapacitor: A review. *Carbon N. Y.* **2019**, *141*, 467–480. [CrossRef]
18. Wu, Z.S.; Zhou, G.; Yin, L.C.; Ren, W.; Li, F.; Cheng, H.M. Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy* **2012**, *1*, 107–131. [CrossRef]
19. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric field in atomically thin carbon films. *Science* **2004**, *306*, 666–669. [CrossRef]
20. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Katsnelson, M.I.; Grigorieva, I.V.; Dubonos, S.V.; Firsov, A.A. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **2005**, *438*, 197–200. [CrossRef]
21. Geim, A.K. Graphene: Status and prospects. *Science* **2009**, *324*, 1530–1534. [CrossRef]
22. Chen, H.; Müller, M.B.; Gilmore, K.J.; Wallace, G.G.; Li, D. Mechanically strong, electrically conductive, and biocompatible graphene paper. *Adv. Mater.* **2008**, *20*, 3557–3561. [CrossRef]
23. Pumera, M. Graphene-based nanomaterials and their electrochemistry. *Chem. Soc. Rev.* **2010**, *39*, 4146–4157. [CrossRef]
24. Kakaei, K.; Esrafili, M.D.; Ehsani, A. Graphene-Based Electrochemical Supercapacitors. *Interface Sci. Technol.* **2019**, *27*, 339–386. [CrossRef]
25. Zhu, X.; Zhu, Y.; Murali, S.; Stoller, M.D.; Ruoff, R.S. Nanostructured reduced graphene oxide/Fe_2O_3 composite as a high-performance anode material for lithium ion batteries. *ACS Nano* **2011**, *5*, 3333–3338. [CrossRef] [PubMed]
26. Khan, M.; Tahir, M.N.; Adil, S.F.; Khan, H.U.; Siddiqui, M.R.H.; Al-warthan, A.A.; Tremel, W. Graphene based metal and metal oxide nanocomposites: Synthesis, properties and their applications. *J. Mater. Chem. A* **2015**, *3*, 18753–18808. [CrossRef]
27. Ke, Q.; Wang, J. Graphene-based materials for supercapacitor electrodes—A review. *J. Mater.* **2016**, *2*, 37–54. [CrossRef]
28. Wang, Y.; Shi, Z.; Huang, Y.; Ma, Y.; Wang, C.; Chen, M.; Chen, Y. Supercapacitor Devices Based on Graphene Materials.pdf. *J. Phys. Chem. C* **2009**, *113*, 13103–13107. [CrossRef]
29. Xia, J.; Chen, F.; Li, J.; Tao, N. Measurement of the quantum capacitance of graphene. *Nat. Nanotechnol.* **2009**, *4*, 505–509. [CrossRef]
30. Wang, D.W.; Li, F.; Zhao, J.; Ren, W.; Chen, Z.G.; Tan, J.; Wu, Z.S.; Gentle, I.; Lu, G.Q.; Cheng, H.M. Fabrication of graphene/polyaniline composite paper via in situ anodic electropolymerization for high-performance flexible electrode. *ACS Nano* **2009**, *3*, 1745–1752. [CrossRef]
31. Xu, J.; Wang, K.; Zu, S.; Han, B.; Wei, Z. Hierarchical nanocomposites of polyaniline nanowire arrays on graphene oxide sheets with synergistic effect for energy storage. *ACS Nano* **2010**, *4*, 5019–5026. [CrossRef]
32. He, Y.S.; Bai, D.W.; Yang, X.; Chen, J.; Liao, X.Z.; Ma, Z.F. A $Co(OH)_2$-graphene nanosheets composite as a high performance anode material for rechargeable lithium batteries. *Electrochem. Commun.* **2010**, *12*, 570–573. [CrossRef]
33. Wang, H.; Casalongue, H.S.; Liang, Y.; Dai, H. $Ni(OH)_2$ nanoplates grown on graphene as advanced electrochemical pseudocapacitor materials. *J. Am. Chem. Soc.* **2010**, *132*, 7472–7477. [CrossRef] [PubMed]
34. Fan, Z.; Yan, J.; Zhi, L.; Zhang, Q.; Wei, T.; Feng, J.; Zhang, M.; Qian, W.; Wei, F. A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors. *Adv. Mater.* **2010**, *22*, 3723–3728. [CrossRef] [PubMed]
35. Jeong, H.K.; Jin, M.; Ra, E.J.; Sheem, K.Y.; Han, G.H.; Arepalli, S.; Lee, Y.H. Enhanced electric double layer capacitance of graphite oxide intercalated by poly(sodium 4-styrensulfonate) with high cycle stability. *ACS Nano* **2010**, *4*, 1162–1166. [CrossRef] [PubMed]
36. Wang, H.; Robinson, J.T.; Diankov, G.; Dai, H. Supporting Information Nanocrystal Growth on Graphene with Various Degrees of Oxidation. *J. Am. Chem. Soc.* **2010**, *132*, 3270–3271. [CrossRef] [PubMed]
37. Zhang, K.; Zhang, L.L.; Zhao, X.S.; Wu, J. Graphene/Polyaniline Nanofiber Composites as Supercapacitor Electrodes. *Chem. Mater.* **2010**, *22*, 1392–1401. [CrossRef]
38. Zhao, Y.; Liu, J.; Hu, Y.; Cheng, H.; Hu, C.; Jiang, C.; Jiang, L.; Cao, A.; Qu, L. Highly Compression-Tolerant Supercapacitor Based on Polypyrrole-mediated Graphene Foam Electrodes. *Adv. Mater.* **2013**, *25*, 591–595. [CrossRef] [PubMed]
39. Alabadi, A.; Razzaque, S.; Dong, Z.; Wang, W.; Tan, B. Graphene oxide-polythiophene derivative hybrid nanosheet for enhancing performance of supercapacitor. *J. Power Sources* **2016**, *306*, 241–247. [CrossRef]
40. Chen, S.; Wang, L.; Huang, M.; Kang, L.; Lei, Z.; Xu, H.; Shi, F.; Liu, Z.-H. Reduced graphene oxide/Mn_3O_4 nanocrystals hybrid fiber for flexible all-solid-state supercapacitor with excellent volumetric energy density. *Electrochim. Acta* **2017**, *242*, 10–18. [CrossRef]
41. Liao, Q.; Li, N.; Jin, S.; Yang, G.; Wang, C. All-Solid-State Symmetric Supercapacitor Based on Co_3O_4 Nanoparticles on Vertically Aligned Graphene. *ACS Nano* **2015**, *9*, 5310–5317. [CrossRef]
42. Velmurugan, V.; Srinivasarao, U.; Ramachandran, R.; Saranya, M.; Grace, A.N. Synthesis of tin oxide/graphene (SnO_2/G) nanocomposite and its electrochemical properties for supercapacitor applications. *Mater. Res. Bull.* **2016**, *84*, 145–151. [CrossRef]

43. Balamurugan, J.; Karthikeyan, G.; Thanh, T.D.; Kim, N.H.; Lee, J.H. Facile synthesis of vanadium nitride/nitrogen-doped graphene composite as stable high performance anode materials for supercapacitors. *J. Power Sources* **2016**, *308*, 149–157. [CrossRef]

44. Yu, Y.; Gao, W.; Shen, Z.; Zheng, Q.; Wu, H.; Wang, X.; Song, W.; Ding, K. A novel Ni_3N/graphene nanocomposite as supercapacitor electrode material with high capacitance and energy density. *J. Mater. Chem. A* **2015**, *3*, 16633–16641. [CrossRef]

45. Venkateshalu, S.; Goban Kumar, P.; Kollu, P.; Jeong, S.K.; Grace, A.N. Solvothermal synthesis and electrochemical properties of phase pure pyrite FeS_2 for supercapacitor applications. *Electrochim. Acta* **2018**, *290*, 378–389. [CrossRef]

46. Zhou, R.; Han, C.; Wang, X. Hierarchical MoS_2-coated three-dimensional graphene network for enhanced supercapacitor performances. *J. Power Sources* **2017**, *352*, 99–110. [CrossRef]

47. Lee, I.; Jeong, G.H.; An, S.; Kim, S.-W.; Yoon, S. Facile synthesis of 3D MnNi-layered double hydroxides (LDH)/graphene composites from directly graphites for pseudocapacitor and their electrochemical analysis. *Appl. Surf. Sci.* **2018**, *429*, 196–202. [CrossRef]

48. Qin, K.; Wang, L.; Wen, S.; Diao, L.; Liu, P.; Li, J.; Ma, L.; Shi, C.; Zhong, C.; Hu, W.; et al. Designed synthesis of NiCo-LDH and derived sulfide on heteroatom-doped edge-enriched 3D rivet graphene films for high-performance asymmetric supercapacitor and efficient OER. *J. Mater. Chem. A* **2018**, *6*, 8109–8119. [CrossRef]

49. Couly, C.; Alhabeb, M.; Van Aken, K.L.; Kurra, N.; Gomes, L.; Navarro-Suárez, A.M.; Anasori, B.; Alshareef, H.N.; Gogotsi, Y. Asymmetric Flexible MXene-Reduced Graphene Oxide Micro-Supercapacitor. *Adv. Electron. Mater.* **2018**, *4*, 1700339. [CrossRef]

50. Fan, Z.; Wang, Y.; Xie, Z.; Wang, D.; Yuan, Y.; Kang, H.; Su, B.; Cheng, Z.; Liu, Y. Modified MXene/Holey Graphene Films for Advanced Supercapacitor Electrodes with Superior Energy Storage. *Adv. Sci.* **2018**, *5*, 1800750. [CrossRef] [PubMed]

51. Yan, J.; Wei, T.; Shao, B.; Ma, F.; Fan, Z.; Zhang, M.; Zheng, C.; Shang, Y.; Qian, W.; Wei, F. Electrochemical properties of graphene nanosheet/carbon black composites as electrodes for supercapacitors. *Carbon N. Y.* **2010**, *48*, 1731–1737. [CrossRef]

52. Lee, J.K.; Smith, K.B.; Hayner, C.M.; Kung, H.H. Silicon nanoparticles-graphene paper composites for Li ion battery anodes. *Chem. Commun.* **2010**, *46*, 2025–2027. [CrossRef]

53. Chen, P.; Yang, J.J.; Li, S.S.; Wang, Z.; Xiao, T.Y.; Qian, Y.H.; Yu, S.H. Hydrothermal synthesis of macroscopic nitrogen-doped graphene hydrogels for ultrafast supercapacitor. *Nano Energy* **2013**, *2*, 249–256. [CrossRef]

54. Śliwak, A.; Grzyb, B.; Díez, N.; Gryglewicz, G. Nitrogen-doped reduced graphene oxide as electrode material for high rate supercapacitors. *Appl. Surf. Sci.* **2017**, *399*, 265–271. [CrossRef]

55. Wu, Z.S.; Winter, A.; Chen, L.; Sun, Y.; Turchanin, A.; Feng, X.; Müllen, K. Three-dimensional nitrogen and boron co-doped graphene for high-performance all-solid-state supercapacitors. *Adv. Mater.* **2012**, *24*, 5130–5135. [CrossRef] [PubMed]

56. Xing, L.B.; Hou, S.F.; Zhang, J.L.; Zhou, J.; Li, Z.; Si, W.; Zhuo, S. A facile preparation of three dimensional N, S co-doped graphene hydrogels with thiocarbohydrazide for electrode materials in supercapacitor. *Mater. Lett.* **2015**, *147*, 97–100. [CrossRef]

57. An, H.; Li, Y.; Long, P.; Gao, Y.; Qin, C.; Cao, C.; Feng, Y.; Feng, W. Hydrothermal preparation of fluorinated graphene hydrogel for high-performance supercapacitors. *J. Power Sources* **2016**, *312*, 146–155. [CrossRef]

58. Ates, M.; Cinar, D.; Caliskan, S.; Gecgel, U.; Uner, O.; Bayrak, Y.; Candan, I. Active carbon/graphene hydrogel nanocomposites as a symmetric device for supercapacitors. *Fuller. Nanotub. Carbon Nanostructures* **2016**, *24*, 427–434. [CrossRef]

59. Manoharan, S.; Krishnamoorthy, K.; Sathyaseelan, A.; Kim, S.-J. High-power graphene supercapacitors for the effective storage of regenerative energy during the braking and deceleration process in electric vehicles. *Mater. Chem. Front.* **2021**, *5*, 6200–6211. [CrossRef]

60. Zhang, Y.; Wen, G.; Gao, P.; Bi, S.; Tang, X.; Wang, D. High-performance supercapacitor of macroscopic graphene hydrogels by partial reduction and nitrogen doping of graphene oxide. *Electrochim. Acta* **2016**, *221*, 167–176. [CrossRef]

61. Ni, L.; Zhang, W.; Wu, Z.; Sun, C.; Cai, Y.; Yang, G.; Chen, M.; Piao, Y.; Diao, G. Supramolecular assembled three-dimensional graphene hybrids: Synthesis and applications in supercapacitors. *Appl. Surf. Sci.* **2017**, *396*, 412–420. [CrossRef]

62. Augustyn, V.; Simon, P.; Dunn, B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy Environ. Sci.* **2014**, *7*, 1597–1614. [CrossRef]

63. Ismanto, A.E.; Wang, S.; Soetaredjo, F.E.; Ismadji, S. Preparation of capacitor's electrode from cassava peel waste. *Bioresour. Technol.* **2010**, *101*, 3534–3540. [CrossRef] [PubMed]

64. Rachiy, B.I.; Nykoliuk, M.O.; Budzulyak, I.M.; Kachmar, A.I. Ultrasonic modification of carbon materials for electrochemical capacitors. *Nanoscale Res. Lett.* **2017**, *12*, 1–5. [CrossRef]

65. Gao, Y.; Li, L.; Jin, Y.; Wang, Y.; Yuan, C.; Wei, Y.; Chen, G.; Ge, J.; Lu, H. Porous carbon made from rice husk as electrode material for electrochemical double layer capacitor. *Appl. Energy* **2015**, *153*, 41–47. [CrossRef]

66. Boyjoo, Y.; Cheng, Y.; Zhong, H.; Tian, H.; Pan, J.; Pareek, V.K.; Jiang, S.P.; Lamonier, J.F.; Jaroniec, M.; Liu, J. From waste Coca Cola®to activated carbons with impressive capabilities for CO_2 adsorption and supercapacitors. *Carbon N. Y.* **2017**, *116*, 490–499. [CrossRef]

67. Zhang, L.; Zhao, X.S. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* **2009**, *38*, 2520–2531. [CrossRef]

68. Simon, P.; Burke, A. Nanostructured carbons: Double-layer capacitance and more. *Electrochem. Soc. Interface* **2008**, *17*, 38–43. [CrossRef]

69. Gamby, J.; Taberna, P.L.; Simon, P.; Fauvarque, J.F.; Chesneau, M. Studies and characterisations of various activated carbons used for carbon/carbon supercapacitors. *J. Power Sources* **2001**, *101*, 109–116. [CrossRef]

70.　Qu, D. Studies of the activated mesocarbon microbeads used in double-layer supercapacitors. *J. Power Sources* **2002**, *109*, 403–411. [CrossRef]

71.　Shi, H. Activated carbons and double layer capacitance. *Electrochim. Acta* **1996**, *41*, 1633–1639. [CrossRef]

72.　Kim, Y.J.; Horie, Y.; Ozaki, S.; Matsuzawa, Y.; Suezaki, H.; Kim, C.; Miyashita, N.; Endo, M. Correlation between the pore and solvated ion size on capacitance uptake of PVDC-based carbons. *Carbon N. Y.* **2004**, *42*, 1491–1500. [CrossRef]

73.　Arbizzani, C.; Mastragostino, M.; Soavi, F. New trends in electrochemical supercapacitors. *J. Power Sources* **2001**, *100*, 164–170. [CrossRef]

74.　Jurewicz, K.; Vix-Guterl, C.; Frackowiak, E.; Saadallah, S.; Reda, M.; Parmentier, J.; Patarin, J.; Béguin, F. Capacitance properties of ordered porous carbon materials prepared by a templating procedure. *J. Phys. Chem. Solids* **2004**, *65*, 287–293. [CrossRef]

75.　Fernández, J.A.; Morishita, T.; Toyoda, M.; Inagaki, M.; Stoeckli, F.; Centeno, T.A. Performance of mesoporous carbons derived from poly(vinyl alcohol) in electrochemical capacitors. *J. Power Sources* **2008**, *175*, 675–679. [CrossRef]

76.　Salitra, G.; Soffer, A.; Eliad, L.; Cohen, Y.; Aurbach, D. Carbon Electrodes for Double-Layer Capacitors I. Relations Between Ion and Pore Dimensions. *J. Electrochem. Soc.* **2000**, *147*, 2486. [CrossRef]

77.　Pérez-Madrigal, M.M.; Edo, M.G.; Alemán, C. Powering the future: Application of cellulose-based materials for supercapacitors. *Green Chem.* **2016**, *18*, 5930–5956. [CrossRef]

78.　He, S.; Hu, C.; Hou, H.; Chen, W. Ultrathin MnO_2 nanosheets supported on cellulose based carbon papers for high-power supercapacitors. *J. Power Sources* **2014**, *246*, 754–761. [CrossRef]

79.　Zheng, C.; Yue, Y.; Gan, L.; Xu, X.; Mei, C.; Han, J. Highly stretchable and self-healing strain sensors based on nanocellulose-supported graphene dispersed in electro-conductive hydrogels. *Nanomaterials* **2019**, *9*, 937. [CrossRef] [PubMed]

80.　Yue, Y.; Wang, X.; Han, J.; Yu, L.; Chen, J.; Wu, Q.; Jiang, J. Effects of nanocellulose on sodium alginate/polyacrylamide hydrogel: Mechanical properties and adsorption-desorption capacities. *Carbohydr. Polym.* **2019**, *206*, 289–301. [CrossRef] [PubMed]

81.　Zuo, L.; Fan, W.; Zhang, Y.; Huang, Y.; Gao, W.; Liu, T. Bacterial cellulose-based sheet-like carbon aerogels for the in situ growth of nickel sulfide as high performance electrode materials for asymmetric supercapacitors. *Nanoscale* **2017**, *9*, 4445–4455. [CrossRef] [PubMed]

82.　Park, J.H.; Rana, H.H.; Lee, J.Y.; Park, H.S. Renewable flexible supercapacitors based on all-lignin-based hydrogel electrolytes and nanofiber electrodes. *J. Mater. Chem. A* **2019**, *7*, 16962–16968. [CrossRef]

83.　Herou, S.; Ribadeneyra, M.C.; Madhu, R.; Araullo-Peters, V.; Jensen, A.; Schlee, P.; Titirici, M. Ordered mesoporous carbons from lignin: A new class of biobased electrodes for supercapacitors. *Green Chem.* **2019**, *21*, 550–559. [CrossRef]

84.　Leguizamon, S.; Díaz-Orellana, K.P.; Velez, J.; Thies, M.C.; Roberts, M.E. High charge-capacity polymer electrodes comprising alkali lignin from the Kraft process. *J. Mater. Chem. A* **2015**, *3*, 11330–11339. [CrossRef]

85.　Zhang, Y.; Feng, H.; Wu, X.; Wang, L.; Zhang, A.; Xia, T.; Dong, H.; Li, X.; Zhang, L. Progress of electrochemical capacitor electrode materials: A review. *Int. J. Hydrogen Energy* **2009**, *34*, 4889–4899. [CrossRef]

86.　Fic, K.; Platek, A.; Piwek, J.; Frackowiak, E. Sustainable materials for electrochemical capacitors. *Mater. Today* **2018**, *21*, 437–454. [CrossRef]

87.　Rolison, D.R.; Long, J.W.; Lytle, J.C.; Fischer, A.E.; Rhodes, C.P.; Mc Evoy, T.M.; Bourg, M.E.; Lubers, A.M. Multifunctional 3D nanoarchitectures for energy storage and conversion. *Chem. Soc. Rev.* **2009**, *38*, 226–252. [CrossRef]

88.　Yu, Z.; Tetard, L.; Zhai, L.; Thomas, J. Supercapacitor electrode materials: Nanostructures from 0 to 3 dimensions. *Energy Environ. Sci.* **2015**, *8*, 702–730. [CrossRef]

89.　Gao, S.; Tang, G.; Hua, D.; Xiong, R.; Han, J.; Jiang, S.; Zhang, Q.; Huang, C. Stimuli-responsive bio-based polymeric systems and their applications. *J. Mater. Chem. B* **2019**, *7*, 709–729. [CrossRef]

90.　Lv, D.; Zhu, M.; Jiang, Z.; Jiang, S.; Zhang, Q.; Xiong, R.; Huang, C. Green Electrospun Nanofibers and Their Application in Air Filtration. *Macromol. Mater. Eng.* **2018**, *303*, 1–18. [CrossRef]

91.　Lv, D.; Wang, R.; Tang, G.; Mou, Z.; Lei, J.; Han, J.; De Smedt, S.; Xiong, R.; Huang, C. Ecofriendly Electrospun Membranes Loaded with Visible-Light-Responding Nanoparticles for Multifunctional Usages: Highly Efficient Air Filtration, Dye Scavenging, and Bactericidal Activity. *ACS Appl. Mater. Interfaces* **2019**, *11*, 12880–12889. [CrossRef]

92.　Tang, G.; Xiong, R.; Lv, D.; Xu, R.X.; Braeckmans, K.; Huang, C.; De Smedt, S.C. Gas-Shearing Fabrication of Multicompartmental Microspheres: A One-Step and Oil-Free Approach. *Adv. Sci.* **2019**, *6*. [CrossRef]

93.　Guo, Z.; Tang, G.; Zhou, Y.; Shuwu, L.; Hou, H.; Chen, Z.; Chen, J.; Hu, C.; Wang, F.; De Smedt, S.C.; et al. Fabrication of Sustained-release CA-PU Coaxial Electrospun Fiber Membranes for Plant Grafting Application. *Carbohydr. Polym.* **2017**, *169*, 198–205. [CrossRef] [PubMed]

94.　Zhu, M.; Xiong, R.; Huang, C. Bio-based and photocrosslinked electrospun antibacterial nanofibrous membranes for air filtration. *Carbohydr. Polym.* **2019**, *205*, 55–62. [CrossRef] [PubMed]

95.　Raymundo-Piñero, E.; Kierzek, K.; Machnikowski, J.; Béguin, F. Relationship between the nanoporous texture of activated carbons and their capacitance properties in different electrolytes. *Carbon N. Y.* **2006**, *44*, 2498–2507. [CrossRef]

96.　Ersoy, D.A.; McNallan, M.J.; Gogotsi, Y. Carbon coatings produced by high temperature chlorination of silicon carbide ceramics. *Mater. Res. Innov.* **2001**, *5*, 55–62. [CrossRef]

97.　Gogotsi, Y.G.; Jeon, I.D.; McNallan, M.J. Carbon coatings on silicon carbide by reaction with chlorine-containing gases. *J. Mater. Chem.* **1997**, *7*, 1841–1848. [CrossRef]

98. Cambaz, Z.G.; Yushin, G.N.; Gogotsi, Y.; Vyshnyakova, K.L.; Pereselentseva, L.N. Formation of carbide-derived carbon on β-silicon carbide whiskers. *J. Am. Ceram. Soc.* **2006**, *89*, 509–514. [CrossRef]

99. Chmiola, J. Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer. *Science* **2014**, *313*, 1760–1763. [CrossRef]

100. Gogotsi, Y.; Nikitin, A.; Ye, H.; Zhou, W.; Fischer, J.E.; Yi, B.; Foley, H.C.; Barsoum, M.W. Nanoporous carbide-derived carbon with tunable pore size. *Nat. Mater.* **2003**, *2*, 591–594. [CrossRef]

101. Dash, R.; Chmiola, J.; Yushin, G.; Gogotsi, Y.; Laudisio, G.; Singer, J.; Fischer, J.; Kucheyev, S. Titanium carbide derived nanoporous carbon for energy-related applications. *Carbon N. Y.* **2006**, *44*, 2489–2497. [CrossRef]

102. Erdemir, A.; Kovalchenko, A.; McNallan, M.J.; Welz, S.; Lee, A.; Gogotsi, Y.; Carroll, B. Effects of high-temperature hydrogenation treatment on sliding friction and wear behavior of carbide-derived carbon films. *Surf. Coatings Technol.* **2004**, *188–189*, 588–593. [CrossRef]

103. Chmiola, J.; Yushin, G.; Dash, R.; Gogotsi, Y. Effect of pore size and surface area of carbide derived carbons on specific capacitance. *J. Power Sources* **2006**, *158*, 765–772. [CrossRef]

104. Pandolfo, A.G.; Hollenkamp, A.F. Carbon properties and their role in supercapacitors. *J. Power Sources* **2006**, *157*, 11–27. [CrossRef]

105. Frackowiak, E.; Metenier, K.; Bertagna, V.; Beguin, F. Supercapacitor electrodes from multiwalled carbon nanotubes. *Appl. Phys. Lett.* **2000**, *77*, 2421–2423. [CrossRef]

106. An, K.H.; Kim, W.S.; Park, Y.S.; Moon, J.M.; Bae, D.J.; Lim, S.C.; Lee, Y.S.; Lee, Y.H. Electrochemical properties of high-power supercapacitors using single-walled carbon nanotube electrodes. *Adv. Funtional Mater.* **2001**, *11*, 387–392. [CrossRef]

107. Emmenegger, C.; Mauron, P.; Züttel, A.; Nützenadel, C.; Schneuwly, A.; Gallay, R.; Schlapbach, L. Carbon nanotube synthesized on metallic substrates. *Appl. Surf. Sci.* **2000**, *162*, 452–456. [CrossRef]

108. Chen, J.H.; Li, W.Z.; Wang, D.Z.; Yang, S.X.; Wen, J.G.; Ren, Z.F. Electrochemical characterization of carbon nanotubes as electrode in electrochemical double-layer capacitors. *Carbon N. Y.* **2002**, *40*, 1193–1197. [CrossRef]

109. Talapatra, S.; Kar, S.; Pal, S.K.; Vajti, R.; Ci, L.; Victor, P.; Shaijumon, M.M.; Kaur, S.; Nalamasu, O.; Ajayan, P.M. Direct growth of aligned carbon nanotubes on bulk metals. *Nat. Nanotechnol.* **2006**, *1*, 112–116. [CrossRef] [PubMed]

110. Frackowiak, E.; Delpeux, S.; Jurewicz, K.; Szostak, K.; Cazorla-Amoros, D.; Béguin, F. Enhanced capacitance of carbon nanotubes through chemical activation. *Chem. Phys. Lett.* **2002**, *361*, 35–41. [CrossRef]

111. Zhang, Y.; Bai, Y.; Yan, B. Functionalized carbon nanotubes for potential medicinal applications. *Drug Discov. Today* **2010**, *15*, 428–435. [CrossRef]

112. Peng, C.; Jin, J.; Chen, G.Z. A comparative study on electrochemical co-deposition and capacitance of composite films of conducting polymers and carbon nanotubes. *Electrochim. Acta* **2007**, *53*, 525–537. [CrossRef]

113. Aricò, A.S.; Bruce, P.; Scrosati, B.; Tarascon, J.-M.; van Schalkwijk, W. Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mater.* **2005**, *4*, 366–377. [CrossRef]

114. Chien, H.C.; Cheng, W.Y.; Wang, Y.H.; Lu, S.Y. Ultrahigh specific capacitances for supercapacitors achieved by nickel cobaltite/carbon aerogel composites. *Adv. Funct. Mater.* **2012**, *22*, 5038–5043. [CrossRef]

115. Wang, R.; Jin, D.; Zhang, Y.; Wang, S.; Lang, J.; Yan, X.; Zhang, L. Engineering metal organic framework derived 3D nanostructures for high performance hybrid supercapacitors. *J. Mater. Chem. A* **2017**, *5*, 292–302. [CrossRef]

116. Wang, L.; Han, Y.; Feng, X.; Zhou, J.; Qi, P.; Wang, B. Metal-organic frameworks for energy storage: Batteries and supercapacitors. *Coord. Chem. Rev.* **2016**, *307*, 361–381. [CrossRef]

117. Zhao, Y.; Song, Z.; Li, X.; Sun, Q.; Cheng, N.; Lawes, S.; Sun, X. Metal organic frameworks for energy storage and conversion. *Energy Storage Mater.* **2016**, *2*, 35–62. [CrossRef]

118. Zhao, Y.; Li, X.; Yan, B.; Li, D.; Lawes, S.; Sun, X. Significant impact of 2D graphene nanosheets on large volume change tin-based anodes in lithium-ion batteries: A review. *J. Power Sources* **2015**, *274*, 869–884. [CrossRef]

119. Xie, L.S.; Skorupskii, G.; Dincă, M. Electrically Conductive Metal–Organic Frameworks. *Chem. Rev.* **2020**, *120*, 8536–8580. [CrossRef] [PubMed]

120. Salunkhe, R.R.; Kaneti, Y.V.; Yamauchi, Y. Metal-Organic Framework-Derived Nanoporous Metal Oxides toward Supercapacitor Applications: Progress and Prospects. *ACS Nano* **2017**, *11*, 5293–5308. [CrossRef]

121. Kaur, R.; Rana, A.; Singh, R.K.; Chhabra, V.A.; Kim, K.H.; Deep, A. Efficient photocatalytic and photovoltaic applications with nanocomposites between CdTe QDs and an NTU-9 MOF. *RSC Adv.* **2017**, *7*, 29015–29024. [CrossRef]

122. Dai, S.; Zhao, B.; Qu, C.; Chen, D.; Dang, D.; Song, B.; deGlee, B.M.; Fu, J.; Hu, C.; Wong, C.P.; et al. Controlled synthesis of three-phase NixSy/rGO nanoflake electrodes for hybrid supercapacitors with high energy and power density. *Nano Energy* **2017**, *33*, 522–531. [CrossRef]

123. Wang, C.; Kim, J.; Tang, J.; Kim, M.; Lim, H.; Malgras, V.; You, J.; Xu, Q.; Li, J.; Yamauchi, Y. New Strategies for Novel MOF-Derived Carbon Materials Based on Nanoarchitectures. *Chem* **2020**, *6*, 19–40. [CrossRef]

124. Meng, F.; Fang, Z.; Li, Z.; Xu, W.; Wang, M.; Liu, Y.; Zhang, J.; Wang, W.; Zhao, D.; Guo, X. Porous Co_3O_4 materials prepared by solid-state thermolysis of a novel Co-MOF crystal and their superior energy storage performances for supercapacitors. *J. Mater. Chem. A* **2013**, *1*, 7235–7241. [CrossRef]

125. Meng, W.; Chen, W.; Zhao, L.; Huang, Y.; Zhu, M.; Huang, Y.; Fu, Y.; Geng, F.; Yu, J.; Chen, X.; et al. Porous Fe_3O_4/carbon composite electrode material prepared from metal-organic framework template and effect of temperature on its capacitance. *Nano Energy* **2014**, *8*, 133–140. [CrossRef]

126. Du, W.; Bai, Y.L.; Xu, J.; Zhao, H.; Zhang, L.; Li, X.; Zhang, J. Advanced metal-organic frameworks (MOFs) and their derived electrode materials for supercapacitors. *J. Power Sources* **2018**, *402*, 281–295. [CrossRef]

127. Choi, K.M.; Jeong, H.M.; Park, J.H.; Zhang, Y.B.; Kang, J.K.; Yaghi, O.M. Supercapacitors of nanocrystalline metal-organic frameworks. *ACS Nano* **2014**, *8*, 7451–7457. [CrossRef] [PubMed]

128. Qu, C.; Jiao, Y.; Zhao, B.; Chen, D.; Zou, R.; Walton, K.S.; Liu, M. Nickel-based pillared MOFs for high-performance supercapacitors: Design, synthesis and stability study. *Nano Energy* **2016**, *26*, 66–73. [CrossRef]

129. Wang, H.; Zhu, Q.L.; Zou, R.; Xu, Q. Metal-Organic Frameworks for Energy Applications. *Chem* **2017**, *2*, 52–80. [CrossRef]

130. Wang, L.; Feng, X.; Ren, L.; Piao, Q.; Zhong, J.; Wang, Y.; Li, H.; Chen, Y.; Wang, B. Flexible solid-state supercapacitor based on a metal-organic framework interwoven by electrochemically-deposited PANI. *J. Am. Chem. Soc.* **2015**, *137*, 4920–4923. [CrossRef]

131. Liu, Y.; Xu, N.; Chen, W.; Wang, X.; Sun, C.; Su, Z. Supercapacitor with high cycling stability through electrochemical deposition of metal-organic frameworks/polypyrrole positive electrode. *Dalt. Trans.* **2018**, *47*, 13472–13478. [CrossRef]

132. Dang, S.; Zhu, Q.L.; Xu, Q. Nanomaterials derived from metal-organic frameworks. *Nat. Rev. Mater.* **2017**, *3*. [CrossRef]

133. Nai, J.; Lou, X.W. Hollow Structures Based on Prussian Blue and Its Analogs for Electrochemical Energy Storage and Conversion. *Adv. Mater.* **2019**, *31*, 1–20. [CrossRef] [PubMed]

134. Hu, H.; Guan, B.; Xia, B.; Lou, X.W. (David) Designed Formation of Co_3O_4/$NiCo_2O_4$ Double-Shelled Nanocages with Enhanced Pseudocapacitive and Electrocatalytic Properties. *J. Am. Chem. Soc.* **2015**, *137*, 5590–5595. [CrossRef]

135. Liu, Y.; Li, G.; Guo, Y.; Ying, Y.; Peng, X. Flexible and Binder-Free Hierarchical Porous Carbon Film for Supercapacitor Electrodes Derived from MOFs/CNT. *ACS Appl. Mater. Interfaces* **2017**, *9*, 14043–14050. [CrossRef]

136. Qu, C.; Zhao, B.; Jiao, Y.; Chen, D.; Dai, S.; deglee, B.M.; Chen, Y.; Walton, K.S.; Zou, R.; Liu, M. Functionalized Bimetallic Hydroxides Derived from Metal–Organic Frameworks for High-Performance Hybrid Supercapacitor with Exceptional Cycling Stability. *ACS Energy Lett.* **2017**, *2*, 1263–1269. [CrossRef]

137. Bhardwaj, S.K.; Bhardwaj, N.; Kaur, R.; Mehta, J.; Sharma, A.L.; Kim, K.H.; Deep, A. An overview of different strategies to introduce conductivity in metal-organic frameworks and miscellaneous applications thereof. *J. Mater. Chem. A* **2018**, *6*, 14992–15009. [CrossRef]

138. Young, C.; Kim, J.; Kaneti, Y.V.; Yamauchi, Y. One-Step Synthetic Strategy of Hybrid Materials from Bimetallic Metal-Organic Frameworks for Supercapacitor Applications. *ACS Appl. Energy Mater.* **2018**, *1*, 2007–2015. [CrossRef]

139. Chen, C.; Wu, M.-K.; Tao, K.; Zhou, J.-J.; Li, Y.-L.; Han, X.; Han, L. Formation of bimetallic metal–organic framework nanosheets and their derived porous nickel–cobalt sulfides for supercapacitors. *Dalt. Trans.* **2018**, *47*, 5639–5645. [CrossRef] [PubMed]

140. Fu, D.; Chen, Z.; Yu, C.; Song, X.; Zhong, W. Bimetallic-organic coordination polymers to prepare N-doped hierarchical porous carbon for high performance supercapacitors. *Prog. Nat. Sci. Mater. Int.* **2019**, *29*, 495–503. [CrossRef]

141. Shinde, P.A.; Khan, M.F.; Rehman, M.A.; Jung, E.; Pham, Q.N.; Won, Y.; Jun, S.C. Nitrogen-doped carbon integrated nickel–cobalt metal phosphide marigold flowers as a high capacity electrode for hybrid supercapacitors. *CrystEngComm* **2020**, *22*, 6360–6370. [CrossRef]

142. Huang, S.; Shi, X.R.; Sun, C.; Duan, Z.; Ma, P.; Xu, S. The application of metal–organic frameworks and their derivatives for supercapacitors. *Nanomaterials* **2020**, *10*, 2268. [CrossRef]

143. Tan, L.; Guo, D.; Chu, D.; Yu, J.; Zhang, L.; Yu, J.; Wang, J. Metal organic frameworks template-directed fabrication of hollow nickel cobalt selenides with pentagonal structure for high-performance supercapacitors. *J. Electroanal. Chem.* **2019**, *851*, 113469. [CrossRef]

144. Wang, X.; Yang, N.; Li, Q.; He, F.; Yang, Y.; Cong, S.; Li, K.; Xiong, S.; Zhou, A. Hydrothermal Synthesis of Humate-Layer-Based Bimetal Organic Framework Composites as High Rate-Capability and Enery-Density Electrode Materials for Supercapacitors. *ChemistrySelect* **2020**, *5*, 2794–2804. [CrossRef]

145. Rajak, R.; Saraf, M.; Mobin, S.M. Robust heterostructures of a bimetallic sodium-zinc metal-organic framework and reduced graphene oxide for high-performance supercapacitors. *J. Mater. Chem. A* **2019**, *7*, 1725–1736. [CrossRef]

146. Yang, J.; Zheng, C.; Xiong, P.; Li, Y.; Wei, M. Zn-doped Ni-MOF material with a high supercapacitive performance. *J. Mater. Chem. A* **2014**, *2*, 19005–19010. [CrossRef]

147. Liu, Y.; Xu, X.; Shao, Z.; Jiang, S.P. Metal-organic frameworks derived porous carbon, metal oxides and metal sulfides-based compounds for supercapacitors application. *Energy Storage Mater.* **2020**, *26*, 1–22. [CrossRef]

148. Gholipour-Ranjbar, H.; Soleimani, M.; Naderi, H.R. Application of Ni/Co-based metal-organic frameworks (MOFs) as an advanced electrode material for supercapacitors. *New J. Chem.* **2016**, *40*, 9187–9193. [CrossRef]

149. Liu, X.; Zang, W.; Guan, C.; Zhang, L.; Qian, Y.; Elshahawy, A.M.; Zhao, D.; Pennycook, S.J.; Wang, J. Ni-Doped Cobalt-Cobalt Nitride Heterostructure Arrays for High-Power Supercapacitors. *ACS Energy Lett.* **2018**, *3*, 2462–2469. [CrossRef]

150. Tao, K.; Han, X.; Cheng, Q.; Yang, Y.; Yang, Z.; Ma, Q.; Han, L. A Zinc Cobalt Sulfide Nanosheet Array Derived from a 2D Bimetallic Metal–Organic Frameworks for High-Performance Supercapacitors. *Chem.-A Eur. J.* **2018**, *24*, 12584–12591. [CrossRef] [PubMed]

151. Chu, D.; Li, F.; Song, X.; Ma, H.; Tan, L.; Pang, H.; Wang, X.; Guo, D.; Xiao, B. A novel dual-tasking hollow cube $NiFe_2O_4$-NiCo-LDH@rGO hierarchical material for high preformance supercapacitor and glucose sensor. *J. Colloid Interface Sci.* **2020**, *568*, 130–138. [CrossRef]

152. Wei, H.; Wang, J.; Yu, L.; Zhang, Y.; Hou, D.; Li, T. Facile synthesis of $NiMn_2O_4$ nanosheet arrays grown on nickel foam as novel electrode materials for high-performance supercapacitors. *Ceram. Int.* **2016**, *42*, 14963–14969. [CrossRef]

153. Gao, Y.; Mi, L.; Wei, W.; Cui, S.; Zheng, Z.; Hou, H.; Chen, W. Double metal ions synergistic effect in hierarchical multiple sulfide microflowers for enhanced supercapacitor performance. *ACS Appl. Mater. Interfaces* **2015**, *7*, 4311–4319. [CrossRef] [PubMed]

154. Hou, L.; Hua, H.; Bao, R.; Chen, Z.; Yang, C.; Zhu, S.; Pang, G.; Tong, L.; Yuan, C.; Zhang, X. Anion-Exchange Formation of Hollow NiCo$_2$S$_4$ Nanoboxes from Mesocrystalline Nickel Cobalt Carbonate Nanocubes towards Enhanced Pseudocapacitive Properties. *Chempluschem* **2016**, *81*, 557–563. [CrossRef]

155. Pan, Q.; Yang, X.; Yang, X.; Duan, L.; Zhao, L. Synthesis of a MnS/NixSy composite with nanoparticles coated on hexagonal sheet structures as an advanced electrode material for asymmetric supercapacitors. *RSC Adv.* **2018**, *8*, 17754–17763. [CrossRef]

156. Hou, S.; Xu, X.; Wang, M.; Xu, Y.; Lu, T.; Yao, Y.; Pan, L. Carbon-incorporated Janus-type Ni2P/Ni hollow spheres for high performance hybrid supercapacitors. *J. Mater. Chem. A* **2017**, *5*, 19054–19061. [CrossRef]

157. Liu, Y.; Wang, Y.; Wang, H.; Zhao, P.; Hou, H.; Guo, L. Acetylene black enhancing the electrochemical performance of NiCo-MOF nanosheets for supercapacitor electrodes. *Appl. Surf. Sci.* **2019**, *492*, 455–463. [CrossRef]

158. Ates, M. Graphene and its nanocomposites used as an active materials for supercapacitors. *J. Solid State Electrochem.* **2016**, *20*, 1509–1526. [CrossRef]

159. Yan, J.; Wei, T.; Fan, Z.; Qian, W.; Zhang, M.; Shen, X.; Wei, F. Preparation of graphene nanosheet/carbon nanotube/polyaniline composite as electrode material for supercapacitors. *J. Power Sources* **2010**, *195*, 3041–3045. [CrossRef]

160. Zhang, L.; Huang, D.; Hu, N.; Yang, C.; Li, M.; Wei, H.; Yang, Z.; Su, Y.; Zhang, Y. Three-dimensional structures of graphene/polyaniline hybrid films constructed by steamed water for high-performance supercapacitors. *J. Power Sources* **2017**, *342*, 1–8. [CrossRef]

161. Liu, Y.; Cai, X.; Jiang, J.; Yan, M.; Shi, W. Nitrogen and carbon co-doped Ni-TiO$_2$ spindles for high performance electrochemical capacitor electrodes. *Appl. Surf. Sci.* **2017**, *396*, 774–779. [CrossRef]

162. Jung, M.-J.; Kim, Y.; Lee, Y.-S. Enhancement of the electrochemical capacitance of TiOF$_2$ obtained via control of the crystal structure. *J. Ind. Eng. Chem.* **2016**, *47*. [CrossRef]

163. Zhang, T.; Kong, L.B.; Liu, M.C.; Dai, Y.H.; Yan, K.; Hu, B.; Luo, Y.C.; Kang, L. Design and preparation of MoO$_2$/MoS$_2$ as negative electrode materials for supercapacitors. *Mater. Des.* **2016**, *112*, 88–96. [CrossRef]

164. Gigot, A.; Fontana, M.; Serrapede, M.; Castellino, M.; Bianco, S.; Armandi, M.; Bonelli, B.; Pirri, C.F.; Tresso, E.; Rivolo, P. Mixed 1T-2H Phase MoS$_2$/Reduced Graphene Oxide as Active Electrode for Enhanced Supercapacitive Performance. *ACS Appl. Mater. Interfaces* **2016**, *8*, 32842–32852. [CrossRef]

165. Tu, C.C.; Lin, L.Y.; Xiao, B.C.; Chen, Y.S. Highly efficient supercapacitor electrode with two-dimensional tungsten disulfide and reduced graphene oxide hybrid nanosheets. *J. Power Sources* **2016**, *320*, 78–85. [CrossRef]

166. Ratha, S.; Rout, C.S. Supercapacitor electrodes based on layered tungsten disulfide-reduced graphene oxide hybrids synthesized by a facile hydrothermal method. *ACS Appl. Mater. Interfaces* **2013**, *5*, 11427–11433. [CrossRef]

167. Hu, B.; Qin, X.; Asiri, A.M.; Alamry, K.A.; Al-Youbi, A.O.; Sun, X. WS2 nanoparticles-encapsulated amorphous carbon tubes: A novel electrode material for supercapacitors with a high rate capability. *Electrochem. Commun.* **2013**, *28*, 75–78. [CrossRef]

168. Mayorga-Martinez, C.C.; Moo, J.G.S.; Khezri, B.; Song, P.; Fisher, A.C.; Sofer, Z.; Pumera, M. Self-Propelled Supercapacitors for On-Demand Circuit Configuration Based on WS2 Nanoparticles Micromachines. *Adv. Funct. Mater.* **2016**, *26*, 6662–6667. [CrossRef]

169. Jing, C.; Song, X.; Li, K.; Zhang, Y.; Liu, X.; Dong, B.; Dong, F.; Zhao, S.; Yao, H.; Zhang, Y. Optimizing the rate capability of nickel cobalt phosphide nanowires on graphene oxide by the outer/inter-component synergistic effects. *J. Mater. Chem. A* **2020**, *8*, 1697–1708. [CrossRef]

170. Jing, C.; Liu, X.D.; Li, K.; Liu, X.; Dong, B.; Dong, F.; Zhang, Y. The pseudocapacitance mechanism of graphene/CoAl LDH and its derivatives: Are all the modifications beneficial? *J. Energy Chem.* **2021**, *52*, 218–227. [CrossRef]

171. Li, X.; Du, D.; Zhang, Y.; Xing, W.; Xue, Q.; Yan, Z. Layered double hydroxides toward high-performance supercapacitors. *J. Mater. Chem. A* **2017**, *5*, 15460–15485. [CrossRef]

172. Jing, C.; Dong, B.; Zhang, Y. Chemical Modifications of Layered Double Hydroxides in the Supercapacitor. *Energy Environ. Mater.* **2020**, *3*, 346–379. [CrossRef]

173. Verma, S.; Khosla, A.; Arya, S. Performance of Electrochemically Synthesized Nickel-Zinc and Nickel-Iron (Ni–Zn//Ni–Fe) Nanowires as Battery Type Supercapacitor. *J. Electrochem. Soc.* **2020**, *167*, 120527. [CrossRef]

174. Feng, M.; Gu, J.; Zhang, G.C.; Xu, M.; Yu, Y.; Liu, X. Homogeneous nickel bicarbonate nanocrystals as electrode materials for high-performance asymmetric supercapacitors. *J. Solid State Chem.* **2019**, *282*, 121084. [CrossRef]

175. Bivo, T.; Visible, E.; Photocatalytic, L.; Zhang, G.C.; Zhong, J.; Xu, M.; Yang, Y.; Li, Y.; Fang, Z.; Tang, S.; et al. Ternary BiVO4/NiS/Au Nanocomposites with Efficient Charge Separations for Enhanced Visible Light Photocatalytic Performance. *Chem. Eng. J.* **2019**, *375*, 122093. [CrossRef]

176. Natarajan, S.; Ulaganathan, M.; Aravindan, V. Building next-generation supercapacitors with battery type Ni(OH)$_2$. *J. Mater. Chem. A* **2021**, *9*, 15542–15585. [CrossRef]

177. Cai, G.; Wang, X.; Cui, M.; Darmawan, P.; Wang, J.; Eh, A.L.; See, P. Electrochromo-supercapacitor based on direct growth of NiO nanoparticles. *Nano Energy* **2015**, *12*, 258–267. [CrossRef]

178. Trung, N.B.; Van Tam, T.; Dang, D.K.; Babu, K.F.; Kim, E.J.; Kim, J.; Choi, W.M. Facile synthesis of three-dimensional graphene/nickel oxide nanoparticles composites for high performance supercapacitor electrodes. *Chem. Eng. J.* **2015**, *264*, 603–609. [CrossRef]

179. Su, Y.; Xiao, K.; Li, N.; Liu, Z.; Qiao, S. Amorphous Ni(OH)$_2$@ three-dimensional Ni core-shell nanostructures for high capacitance pseudocapacitors and asymmetric supercapacitors. *J. Mater. Chem. A Mater. energy Sustain.* **2014**, *2*, 13845–13853. [CrossRef]

180. Vidhyadharan, B.; Khayyriah, N.; Zain, M.; Misnon, I.I.; Aziz, R.A.; Ismail, J.; Yusoff, M.M.; Jose, R. High performance supercapacitor electrodes from electrospun nickel oxide nanowires. *J. Alloys Compd.* **2014**, *610*, 143–150. [CrossRef]

181. Guo, D.; Zhang, P.; Zhang, H.; Yu, X.; Zhu, J.; Li, Q.; Wang, T. NiMoO$_4$ nanowires supported on Ni foam as novel advanced electrodes for supercapacitors. *J. Mater. Chem. A* **2013**, *1*, 9024–9027. [CrossRef]

182. Bandyopadhyay, P.; Saeed, G.; Kim, N.H.; Hee, J. Zinc-nickel cobalt oxide@ NiMoO$_4$ core-shell nanowire/nanosheet arrays for solid state asymmetric supercapacitors. *Chem. Eng. J.* **2019**, *384*, 123357. [CrossRef]

183. Patil, U.M.; Salunkhe, R.R.; Gurav, K.V.; Lokhande, C.D. Chemically deposited nanocrystalline NiO thin films for supercapacitor application. *Appl. Surf. Sci.* **2008**, *255*, 2603–2607. [CrossRef]

184. Thiagarajan, K.; Bavani, T.; Arunachalam, P.; Lee, S.J.; Theerthagiri, J.; Madhavan, J.; Pollet, B.G.; Choi, M.Y. Nanofiber NiMoO 4/g-C$_3$N$_4$ Composite Electrode Materials for Redox Supercapacitor Applications. *Nanomaterials* **2020**, *10*, 392. [CrossRef] [PubMed]

185. Liu, T.; Zhang, L.; Cheng, B.; You, W.; Yu, J. Fabrication of a hierarchical NiO/C hollow sphere composite and its enhanced supercapacitor performance. *Chem. Commun.* **2018**, *54*, 3731–3734. [CrossRef] [PubMed]

186. Liu, T.; Liu, J.; Zhang, L.; Cheng, B.; Yu, J. Construction of nickel cobalt sulfide nanosheet arrays on carbon cloth for performance-enhanced supercapacitor. *J. Mater. Sci. Technol.* **2020**, *47*, 113–121. [CrossRef]

187. Wan, L.; He, C.; Chen, D.; Liu, J.; Zhang, Y.; Du, C.; Wan, L.; He, C.; Chen, D.; Liu, J.; et al. In situ grown NiFeP@NiCo$_2$S$_4$ nanosheet arrays on carbon cloth for asymmetric supercapacitors. *Chem. Eng. J.* **2020**, *399*, 125778. [CrossRef]

188. Sagadevan, S.; Pal, K.; Chowdhury, Z.Z.; Foley, M. Controllable synthesis of Graphene/ZnO-nanocomposite for novel switching. *J. Alloys Compd.* **2017**, *728*, 645–654. [CrossRef]

189. Fahimi, Z.; Moradlou, O. Fabrication of ZnO@C foam: A fl exible free-standing electrode for energy storage devices. *Mater. Des.* **2020**, *189*, 108525. [CrossRef]

190. Rong, P.; Ren, S.; Yu, Q. Fabrications and Applications of ZnO Nanomaterials in Flexible Functional Devices-A Review. *Crit. Rev. Anal. Chem.* **2019**, *49*, 336–349. [CrossRef]

191. Guo, G.; Huang, L.; Chang, Q.; Ji, L.; Liu, Y.; Xie, Y.; Shi, W.; Jia, N. Sandwiched nanoarchitecture of reduced graphene oxide/ZnO nanorods/reduced graphene oxide on flexible PET substrate for supercapacitor. *Appl. Phys. Lett.* **2011**, *99*, 2012–2015. [CrossRef]

192. Delbari, S.A.; Ghadimi, L.S.; Hadi, R.; Farhoudian, S.; Nedaei, M.; Babapoor, A.; Namini, A.S.; Van Le, Q.; Shokouhimehr, M.; Asl, M.S.; et al. Transition metal oxide-based electrode materials for flexible supercapacitors: A review. *J. Alloys Compd.* **2021**, *857*, 158281. [CrossRef]

193. Xian, K.; Nie, B.; Li, Z.; Gao, M.; Li, Z.; Shang, C.; Liu, Y.; Guo, Z.; Pan, H. TiO$_2$ decorated porous carbonaceous network structures offer confinement, catalysis and thermal conductivity for effective hydrogen storage of LiBH$_4$. *Chem. Eng. J.* **2021**, *407*, 127156. [CrossRef]

194. Fu, W.; Zhao, E.; Ma, R.; Sun, Z.; Yang, Y.; Sevilla, M.; Fuertes, A.B.; Magasinski, A.; Yushin, G. Anatase TiO$_2$ Confined in Carbon Nanopores for High-Energy Li-Ion Hybrid Supercapacitors Operating at High Rates and Subzero Temperatures. *Adv. Energy Mater.* **2020**, *10*, 1–8. [CrossRef]

195. Subramani, K.; Kowsik, S.; Sathish, M. Facile and Scalable Ultra–fine Cobalt Oxide/Reduced Graphene Oxide Nanocomposites for High Energy Asymmetric Supercapacitors†. *ChemistrySelect* **2016**, *1*, 3455–3467. [CrossRef]

196. Mohd Abdah, M.A.A.; Azman, N.H.N.; Kulandaivalu, S.; Sulaiman, Y. Review of the use of transition-metal-oxide and conducting polymer-based fibres for high-performance supercapacitors. *Mater. Des.* **2020**, *186*, 108199. [CrossRef]

197. Wang, B.; Chen, J.S.; Wu, H.B.; Wang, Z.; Lou, X.W. Quasiemulsion-templated formation of α-Fe$_2$O$_3$ hollow spheres with enhanced lithium storage properties. *J. Am. Chem. Soc.* **2011**, *133*, 17146–17148. [CrossRef] [PubMed]

198. Yu, Z.-J.; Dai, Y.; Chen, W. Electrochemical Deposited Nanoflakes Co(OH)$_2$ Porous Films for Electrochemical Capacitors. *J. Chinese Chem. Soc.* **2010**, *57*, 423–428. [CrossRef]

199. Yao, B.; Huang, L.; Zhang, J.; Gao, X.; Wu, J.; Cheng, Y.; Xiao, X.; Wang, B.; Li, Y.; Zhou, J. Flexible Transparent Molybdenum Trioxide Nanopaper for Energy Storage. *Adv. Mater.* **2016**, *28*, 6353–6358. [CrossRef]

200. Toupin, M.; Brousse, T.; Bélanger, D. Influence of Microsture on the Charge Storage Properties of Chemically Synthesized Manganese Dioxide. *Chem. Mater.* **2002**, *14*, 3946–3952. [CrossRef]

201. Toupin, M.; Brousse, T.; Bélanger, D. Charge Storage Mechanism of MnO$_2$ Electrode Used in Aqueous Electrochemical Capacitor. *Chem. Mater.* **2004**, *16*, 3184–3190. [CrossRef]

202. Chang, J.-K.; Lee, M.-T.; Tsai, W.-T. In situ Mn K-edge X-ray absorption spectroscopic studies of anodically deposited manganese oxide with relevance to supercapacitor applications. *J. Power Sources* **2007**, *166*, 590–594. [CrossRef]

203. Pang, S.-C.; Anderson, M.A.; Chapman, T.W. Novel Electrode Materials for Thin-Film Ultracapacitors: Comparison of Electrochemical Properties of Sol-Gel-Derived and Electrodeposited Manganese Dioxide. *J. Electrochem. Soc.* **2000**, *147*, 444. [CrossRef]

204. Wang, H.W.; Hu, Z.A.; Chang, Y.Q.; Chen, Y.L.; Wu, H.Y.; Zhang, Z.Y.; Yang, Y.Y. Design and synthesis of NiCo$_2$O$_4$-reduced graphene oxide composites for high performance supercapacitors. *J. Mater. Chem.* **2011**, *21*, 10504–10511. [CrossRef]

205. Jiang, H.; Ma, J.; Li, C. Hierarchical porous NiCo$_2$O$_4$ nanowires for high-rate supercapacitors. *Chem. Commun.* **2012**, *48*, 4465–4467. [CrossRef] [PubMed]

206. Wang, Z.; Ren, Z.; Jian, N.; Gao, M.; Hu, J.; Du, F.; Pan, H.; Liu, Y. Vanadium oxide nanoparticles supported on cubic carbon nanoboxes as highly active catalyst precursors for hydrogen storage in MgH$_2$. *J. Mater. Chem. A* **2018**, *6*, 16177–16185. [CrossRef]
207. Kate, R.S.; Khalate, S.A.; Deokate, R.J. Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for supercapacitors: A review. *J. Alloys Compd.* **2018**, *734*, 89–111. [CrossRef]
208. Yan, Y.; Li, B.; Guo, W.; Pang, H.; Xue, H. Vanadium based materials as electrode materials for high performance supercapacitors. *J. Power Sources* **2016**, *329*, 148–169. [CrossRef]
209. Zhang, Y.; Li, L.; Su, H.; Huang, W.; Dong, X. Binary metal oxide: Advanced energy storage materials in supercapacitors. *J. Mater. Chem. A* **2015**, *3*, 43–59. [CrossRef]
210. Kang, Y.J.; Kim, B.; Chung, H.; Kim, W. Fabrication and characterization of flexible and high capacitance supercapacitors based on MnO$_2$/CNT/papers. *Synth. Met.* **2010**, *160*, 2510–2514. [CrossRef]
211. Li, Z.; Mi, Y.; Liu, X.; Liu, S.; Yang, S.; Wang, J. Flexible graphene/MnO$_2$ composite papers for supercapacitor electrodes. *J. Mater. Chem.* **2011**, *21*, 14706–14711. [CrossRef]
212. Alpen, U.V.; Rabenau, A.; Talat, G.H. Ionic conductivity in Li$_3$N single crystals. *Appl. Phys. Lett.* **1977**, *30*, 621–623. [CrossRef]
213. Chen, J.G. Carbide and nitride overlayers on early transition metal surfaces: Preparation, characterization, and reactivities. *Chem. Rev.* **1996**, *96*, 1477–1498. [CrossRef]
214. Balogun, M.S.; Yu, M.; Li, C.; Zhai, T.; Liu, Y.; Lu, X.; Tong, Y. Facile synthesis of titanium nitride nanowires on carbon fabric for flexible and high-rate lithium ion batteries. *J. Mater. Chem. A* **2014**, *2*, 10825–10829. [CrossRef]
215. Gage, S.H.; Trewyn, B.G.; Ciobanu, C.V.; Pylypenko, S.; Richards, R.M. Synthetic advancements and catalytic applications of nickel nitride. *Catal. Sci. Technol.* **2016**, *6*, 4059–4076. [CrossRef]
216. Alexander, A.M.; Hargreaves, J.S.J. Alternative catalytic materials: Carbides, nitrides, phosphides and amorphous boron alloys. *Chem. Soc. Rev.* **2010**, *39*, 4388–4401. [CrossRef]
217. Liu, T.-C.; Pell, W.G.; Conway, B.E.; Roberson, S.L. Behavior of Molybdenum Nitrides as Materials for Electrochemical Capacitors: Comparison with Ruthenium Oxide. *J. Electrochem. Soc.* **1998**, *145*, 1882–1888. [CrossRef]
218. Choi, D.; Blomgren, G.E.; Kumta, P.N. Fast and reversible surface redox reaction in nanocrystalline vanadium nitride supercapacitors. *Adv. Mater.* **2006**, *18*, 1178–1182. [CrossRef]
219. Cheng, F.; He, C.; Shua, D.; Chen, H.; Zhang, J.; Tang, S.; Finlow, D.E. Preparation of nanocrystalline VN by the melamine reduction of V2O5 xerogel and its supercapacitive behavior. *Mater. Chem. Phys.* **2011**, *131*, 268–273. [CrossRef]
220. Jiang, Q.W.; Li, G.R.; Gao, X.P. Highly ordered TiN nanotube arrays as counter electrodes for dye-sensitized solar cells. *Chem. Commun.* **2009**, 6720–6722. [CrossRef]
221. Sun, P.; Lin, R.; Wang, Z.; Qiu, M.; Chai, Z.; Zhang, B.; Meng, H.; Tan, S.; Zhao, C.; Mai, W. Rational design of carbon shell endows TiN@C nanotube based fiber supercapacitors with significantly enhanced mechanical stability and electrochemical performance. *Nano Energy* **2017**, *31*, 432–440. [CrossRef]
222. Nagae, M.; Yoshio, T.; Takemoto, Y.; Takada, J. Microstructure of a Molybdenum Nitride Layer Formed by Nitriding Molybdenum Metal. *J. Am. Ceram. Soc.* **2001**, *84*, 1175–1177. [CrossRef]
223. Inumaru, K.; Nishikawa, T.; Nakamura, K.; Yamanaka, S. High-Pressure Synthesis of Superconducting Molybdenum Nitride δ-MoN by in Situ Nitridation. *Chem. Mater.* **2008**, *20*, 4756–4761. [CrossRef]
224. Zhang, W.-B.; Ma, X.-J.; Kong, L.-B.; Liu, M.-C.; Luo, Y.-C.; Kang, L. Electrochemical Performance of Pseudo-Capacitive Intermetallic Molybdenum Nitride in Acid. *J. Electrochem. Soc.* **2016**, *163*, A1300–A1305. [CrossRef]
225. Liu, J.; Huang, K.; Tang, H.L.; Lei, M. Porous and single-crystalline-like molybdenum nitride nanobelts as a non-noble electrocatalyst for alkaline fuel cells and electrode materials for supercapacitors. *Int. J. Hydrogen Energy* **2016**, *41*, 996–1001. [CrossRef]
226. Chen, L.; Liu, C.; Zhang, Z. Novel [111] oriented γ-Mo$_2$N thin films deposited by magnetron sputtering as an anode for aqueous micro-supercapacitors. *Electrochim. Acta* **2017**, *245*. [CrossRef]
227. Shah, S.I.U.; Hector, A.L.; Owen, J.R. Redox supercapacitor performance of nanocrystalline molybdenum nitrides obtained by ammonolysis of chloride- and amide-derived precursors. *J. Power Sources* **2014**, *266*, 456–463. [CrossRef]
228. Xie, Y.; Tian, F. Capacitive performance of molybdenum nitride/titanium nitride nanotube array for supercapacitor. *Mater. Sci. Eng. B* **2017**, *215*, 64–70. [CrossRef]
229. Deng, C.Z.; Pynenburg, R.A.J.; Tsai, K.C. Improved Porous Mixture of Molybdenum Nitride and Tantalum Oxide as a Charge Storage Material. *J. Electrochem. Soc.* **1998**, *145*. [CrossRef]
230. Hardy, G.F.; Hulm, J.K. The Superconductivity of Some Transition Metal Compounds. *Phys. Rev.* **1954**, *93*, 1004–1016. [CrossRef]
231. Meyer, O.; Friedland, E.; Scheerer, B. Superconductivity of niobium nitride single crystals after implantation of carbon and nitrogen. *Solid State Commun.* **1981**, *39*, 1217–1221. [CrossRef]
232. Radparvar, M. Superconducting niobium and niobium nitride processes for medium-scale integration applications. *Cryogenics (Guildf.)* **1995**, *35*, 535–540. [CrossRef]
233. Gao, B.; Xiao, X.; Su, J.; Zhang, X.; Peng, X.; Fu, J.; Chu, P.K. Synthesis of mesoporous niobium nitride nanobelt arrays and their capacitive properties. *Appl. Surf. Sci.* **2016**, *383*, 57–63. [CrossRef]
234. Cui, H.; Zhu, G.; Liu, X.; Liu, F.; Xie, Y.; Yang, C.; Lin, T.; Gu, H.; Huang, F. Niobium Nitride Nb$_4$N$_5$ as a New High-Performance Electrode Material for Supercapacitors. *Adv. Sci.* **2015**, *2*, 1500126. [CrossRef]
235. Zhang, W.-B.; Ma, X.-J.; Kong, L.-B.; Luo, Y.-C.; Kang, L. Capacitive Intermetallic Manganese Nitride with High Volumetric Energy Densities. *J. Electrochem. Soc.* **2016**, *163*, A2830–A2834. [CrossRef]

236. Zhang, W.-B.; Ma, X.-J.; Loh, A.; Li, X.; Walsh, F.C.; Kong, L.-B. High Volumetric Energy Density Capacitors Based on New Electrode Material Lanthanum Nitride. *ACS Energy Lett.* **2017**, *2*, 336–341. [CrossRef]
237. Śliwak, A.; Moyseowicz, A.; Gryglewicz, G. Hydrothermal-assisted synthesis of an iron nitride–carbon composite as a novel electrode material for supercapacitors. *J. Mater. Chem. A* **2017**, *5*, 5680–5684. [CrossRef]
238. Bouhtiyya, S.; Lucio Porto, R.; Laïk, B.; Boulet, P.; Capon, F.; Pereira-Ramos, J.P.; Brousse, T.; Pierson, J.F. Application of sputtered ruthenium nitride thin films as electrode material for energy-storage devices. *Scr. Mater.* **2013**, *68*, 659–662. [CrossRef]
239. Arif, M.; Sanger, A.; Singh, A. Sputter deposited chromium nitride thin electrodes for supercapacitor applications. *Mater. Lett.* **2018**, *220*, 213–217. [CrossRef]
240. Choi, D.; Kumta, P.N. Synthesis, Structure, and Electrochemical Characterization of Nanocrystalline Tantalum and Tungsten Nitrides. *J. Am. Ceram. Soc.* **2007**, *90*, 3113–3120. [CrossRef]
241. Gao, Z.; Wu, Z.; Zhao, S.; Zhang, T.F.; Wang, Q.M. Enhanced capacitive property of HfN film electrode by plasma etching for supercapacitors. *Mater. Lett.* **2019**, *235*, 148–152. [CrossRef]
242. Keraudy, J.; Athouël, L.; Hamon, J.; Girault, B.; Gloaguen, D.; Richard-Plouet, M.; Jouan, P.-Y. Electrochemical characteristics of NixN thin films deposited by DC and HiPIMS reactive magnetron sputtering. *Thin Solid Films* **2019**, *669*, 659–664. [CrossRef]
243. Dong, X.; Yu, Y.; Zhang, Y.; Xu, Z.; Jiang, H.; Meng, C.; Huang, C. Synthesis of cobalt silicate nanosheets with mesoporous structure and high surface area as the promising electrode for high-performing hybrid supercapacitor. *Electrochim. Acta* **2021**, *380*, 138225. [CrossRef]
244. Qiu, C.; Jiang, J.; Ai, L. When Layered Nickel—Cobalt Silicate Hydroxide Nanosheets Meet Carbon Nanotubes: A Synergetic Coaxial Nanocable Structure for Enhanced Electrocatalytic Water Oxidation. *ACS Appl Mater Interfaces* **2016**, *8*, 945–951. [CrossRef]
245. Mueller, F.; Bresser, D.; Minderjahn, N.; Menne, S.; Winter, M.; Passerini, S. Cobalt orthosilicate as a new electrode material for secondary lithium-ion batteries. *Dalton Trans.* **2014**, *43*, 15013–15021. [CrossRef]
246. Yang, J.; Guo, Y.; Zhang, Y.; Sun, C. Cobalt silicate hierarchical hollow spheres for lithium-ion batteries. *Nanotechnology* **2016**, *27*, 1–7. [CrossRef] [PubMed]
247. Cheng, W.; Rechberger, F.; Ilari, G.; Ma, H.; Lin, W.-I.; Niederberger, M. Amorphous cobalt silicate nanobelts@carbon composites as a stable anode material for lithium ion batteries. *Chem. Sci.* **2015**, *6*, 6908–6915. [CrossRef]
248. Treacher, J.C.; Wood, S.M.; Islam, M.S.; Kendrick, E. Na$_2$CoSiO$_4$ as a cathode material for sodium-ion batteries: Structure, electrochemistry and diffusion pathways. *Phys. Chem. Chem. Phys.* **2016**, *18*, 32744–32752. [CrossRef] [PubMed]
249. Cheng, Y.; Zhang, Y.; Jiang, H.; Dong, X.; Meng, C. Coupled cobalt silicate nanobelt-on-nanobelt hierarchy structure with reduced graphene oxide for enhanced supercapacitive performance. *J. Power Sources* **2020**, *448*, 227407. [CrossRef]
250. Wang, Q.; Zhang, Y.; Jiang, H.; Li, X.; Cheng, Y.; Meng, C. Designed Mesoporous Hollow Sphere Architecture Metal (Mn, Co, Ni) Silicate: A Potential Electrode Material for Flexible All Solid-State Asymmetric Supercapacitor. *Chem. Eng. J.* **2021**, *403*, 126285. [CrossRef]
251. Rong, Q.; Long, L.; Zhang, X.; Huang, Y.; Yu, H. Layered cobalt nickel silicate hollow spheres as a highly-stable supercapacitor material q. *Appl. Energy* **2015**, *153*, 63–69. [CrossRef]
252. Cheng, Y.; Zhang, Y.; Jiang, H.; Dong, X.; Zheng, J.; Meng, C. Synthesis of Amorphous Cobalt Silicate Nanobelts@Manganese Silicate Core-shell Structures as Enhanced Electrode for High-Performance Hybrid Supercapacitors. *J. Colloid Interface Sci.* **2019**, *561*, 762–771. [CrossRef] [PubMed]
253. Angelov, S.; Zhecheva, E.; Petrov, K.; Menandjiev, D. The properties of a spinel copper cobaltite prepared at low temperatures and normal pressure. *Mater. Res. Bull.* **1982**, *17*, 235–240. [CrossRef]
254. Sun, J.; Xu, C.; Chen, H. A review on the synthesis of CuCo$_2$O$_4$-based electrode materials and their applications in supercapacitors. *J. Mater.* **2020**, *7*, 98–126. [CrossRef]
255. Boopathiraja, R.; Parthibavarman, M.; Begum, A.N. Hydrothermal induced novel CuCo$_2$O$_4$ electrode for high performance supercapacitor applications. *Vacuum* **2019**, *165*, 96–104. [CrossRef]
256. Jin, C.; Cui, Y.; Zhang, G.; Luo, W.; Liu, Y.; Sun, Y.; Tian, Z.; Zheng, W. Synthesis of copper-cobalt hybrid oxide microflowers as electrode material for supercapacitors. *Chem. Eng. J.* **2018**, *343*, 331–339. [CrossRef]
257. Pendashteh, A.; Moosavifard, S.E.; Rahmanifar, M.S.; Wang, Y.; El-kady, M.F.; Kaner, R.B.; Mousavi, M.F. Highly Ordered Mesoporous CuCo$_2$O$_4$ Nanowires, a Promising Solution for High-Performance Supercapacitors Highly Ordered Mesoporous CuCo$_2$O$_4$ Nanowires, a Promising So- lution for High-Performance Supercapacitors. *Chem. Mater.* **2015**, *27*, 3919–3926. [CrossRef]
258. Larcher, D.; Tarascon, J. Towards greener and more sustainable batteries for electrical energy storage. *Nat. Publ. Gr.* **2014**, *7*, 19–29. [CrossRef]
259. Esser, B.; Dolhem, F.; Becuwe, M.; Poizot, P.; Vlad, A.; Brandell, D. A perspective on organic electrode materials and technologies for next generation batteries. *J. Power Sources* **2021**, *482*, 228814. [CrossRef]
260. Meng, Q.; Cai, K.; Chen, Y.; Chen, L. Research progress on conducting polymer based supercapacitor electrode materials. *Nano Energy* **2017**, *36*, 268–285. [CrossRef]
261. Zhang, Y.; Cheng, T.; Wang, Y.; Lai, W.; Pang, H.; Huang, W. A Simple Approach to Boost Capacitance: Flexible Supercapacitors Based on Manganese Oxides@MOFs via Chemically Induced In Situ Self-Transformation. *Adv. Mater.* **2016**, *28*, 5242–5258. [CrossRef] [PubMed]

262. Xu, X.; Tang, J.; Qian, H.; Hou, S.; Bando, Y.; Pan, L.; Yamauchi, Y. Three-Dimensional Networked Metal—Organic Frameworks with Conductive Polypyrrole Tubes for Flexible Supercapacitors. *ACS Appl. Mater. Interfaces* **2017**, *9*, 38737–38744. [CrossRef] [PubMed]

263. Zhang, Y.-Z.; Wang, Y.; Cheng, T.; Lai, W.-Y.; Pang, H.; Huang, W. Flexible supercapacitors based on paper substrates: A new paradigm for low-cost energy storage. *Chem. Soc. Rev.* **2015**, *44*, 5181–5199. [CrossRef] [PubMed]

264. Zhang, X.; Xiao, Z.; Liu, X.; Mei, P.; Yang, Y. Redox-active polymers as organic electrode materials for sustainable supercapacitors. *Renew. Sustain. Energy Rev.* **2021**, *147*, 111247. [CrossRef]