Promising Electrode Materials in Micro-Supercapacitor Printing

Subjects: Chemistry, Inorganic & Nuclear

Contributor: Tatiana L. Simonenko, Nikolay P. Simonenko, Philipp Yu. Gorobtsov, Elizaveta P. Simonenko, Nikolay T. Kuznetsov

The development of scientific and technological foundations for the creation of high-performance energy storage devices is becoming increasingly important due to the rapid development of microelectronics, including flexible and wearable microelectronics. Supercapacitors are indispensable devices for the power supply of systems requiring high power, high charging-discharging rates, cyclic stability, and long service life and a wide range of operating temperatures (from −40 to 70 °C). The use of printing technologies gives an opportunity to move the production of such devices to a new level due to the possibility of the automated formation of micro-supercapacitors (including flexible, stretchable, wearable) with the required type of geometric implementation, to reduce time and labour costs for their creation, and to expand the prospects of their commercialization and widespread use.

Keywords: carbon-based materials ; transition metal oxides ; polymers ; transition metal hydroxides ; metal sulphides ; MXenes ; electrodes ; printing technologies ; micro-supercapacitors

1. Introduction

The creation of efficient and environmentally friendly energy storage systems is currently one of the most important tasks of material science in the field of global energy, becoming more and more important due to the annually growing level of energy consumption and anthropogenic impact on the environment. In this context, the special attention of scientists and engineers is drawn to supercapacitors, also called ionistors or electrochemical capacitors, which occupy an intermediate position between traditional (electrolytic) capacitors and lithium-ion batteries, demonstrating higher values of energy density in comparison with the first type of devices and higher values of specific power in relation to the second type of devices. In addition, other advantages of supercapacitors over lithium-ion batteries include higher Coulombic efficiency (85–98% vs. 75–90% for lithium-ion batteries) and charge–discharge rate (from a few seconds to a few minutes vs. 0.3–3 h in rechargeable batteries), longer service life (more than 500,000 operating cycles versus about 1000 cycles in rechargeable batteries), and a wider range of operating temperatures (from −50 to 50 °C while Li-ion batteries lose about 50% of their capacity already at −20 °C) [1][2].

Based on the type of charge storage mechanism, supercapacitors can be divided into double-layer and pseudo-capacitors. Devices of the first type store charge in the double electric layer arising on the electrode–electrolyte boundary by means of reversible physical processes of ion adsorption in this area, whereas in pseudocapacitors, the process of charge accumulation occurs both due to the work of the double electric layer and due to the phenomenon of pseudocapacitance, namely the course of reversible redox chemical reactions in the near-surface (at a depth of a few nanometers) layers of electrodes. The described effect results in higher capacitive characteristics as well as power density values of pseudocapacitors compared to double-layer supercapacitors [3][4].

One of the main application areas of supercapacitors is microelectronics, which is currently striving for a paradigm shift as part of the transition from rigid to flexible printed circuit boards, functional and structural elements, and their miniaturization. The development of flexible, compact, portable microelectronics devices, including wearable devices, requires the creation of flexible electrical energy storage systems, including those based on supercapacitors, while maintaining their mechanical strength and high values of performance characteristics (specific capacity and power, charge-discharge rate, cyclic stability, number of operation cycles) [5][6]. To date, the search for different variants of geometric design of supercapacitors is underway in order to achieve the flexibility and compactness of their assembly. One of the most common types of configurations of these devices are the so-called sandwich structures, in which the electrolyte layer is located between two layers of electrodes. This type of assembly is widespread in the creation of volume-type supercapacitors due to the simplicity of design, low cost of its manufacture, and wide scaling possibilities. However, with this multilayer configuration, the electric current flows perpendicular to the entire assembly, resulting in a

significant resistance between the different layers as well as an increase in the ion diffusion path length, all of which leads to lower specific capacitance and power density values of the final device [7].

The formation of flexible planar micro-supercapacitors (MSCs) with complex geometries requires advanced high-tech methods and approaches. Thus, photolithography, vacuum sputtering, and laser engraving methods are used to solve this problem [8][9][10][11][12][13], but the complexity, high cost, and limited scalability of these approaches impede their wide application. Recently, in the formation of various electronics and alternative energy devices, including supercapacitors, the trend towards the use of additive technologies (3D printing [14], ink-jet printing [15], aerosol printing [16], pen plotter printing [17][18], microplotter printing [19], microextrusion printing [20], roll-to-roll printing [21], transfer printing [22], and screen printing [23]) is observed, which allow for the automated formation of structures of different (including complex) geometries with a high degree of reproducibility, dosing accuracy, and targeted material application as well as the provision of an opportunity to effectively scale the process while maintaining the microstructural and functional characteristics of manufactured devices.

The choice of substrate material is an important task in the formation of flexible planar type supercapacitors using printed technologies. In the context of these methods, parameters, such as the flexibility, thickness, roughness of the substrate as well as its density and thermal resistance, must be considered. The substrate wettability is an important parameter because it has a significant influence on the microstructure of the formed coatings during printing [24].

The set of functional elements of planar type supercapacitors with interdigital electrodes is similar to that for sandwich-type supercapacitors: current collectors, working electrodes, and the electrolyte layer. As a rule, materials with high electrical conductivity are used as current collectors: metals (stainless steel, silver, gold, etc.), conductive polymers (e.g., poly-3,4-ethylenedioxythiophene:polystyrene sulfonate—PEDOT:PSS), and various carbon materials (graphite, carbon nanotubes, reduced graphene oxide, etc.) [25][26][27]. It should be noted that carbon materials of current collectors, in addition to high electrical conductivity, environmental friendliness, and availability, are also characterized by a high specific surface area, which in turn provides better contact and charge transfer at the “current collector—working electrode” interphase boundaries [7].

2. The Most Common Electrode Components of Printed Micro-Supercapacitors

2.1. Carbon Materials

Carbon and its allotropic modifications are currently one of the most important elements in the development of advanced microelectronics [28][29], biosensors [30][31][32], and alternative energy applications [33][34]. In the development of energy storage devices, carbon materials, due to their high specific surface area, high electrical conductivity, and chemical stability, are more and more actively used for the development of electrodes that store charge via electrical double layer mechanism. Among the most widely explored varieties of carbon materials in terms of printing electrode structures for micro-supercapacitors are onion-like carbons, carbon nanotubes, graphene, carbon aerogels, and activated carbon [35].

In the study by Zeiger et al. [36], it is proposed to apply the concept of onion-like carbons (OLC) only to those carbon particles that have at least four shells (by analogy with multi-walled carbon nanotubes) are characterized by a size less than 100 nm, have a spherical or polyhedral shape and partially defective structure (amorphous domains or islands of sp^3-hybridized carbon are present). This category of materials includes both hollow onion-like carbons and those whose core consists of metal clusters or fragments of nanodiamonds left inside the carbon onions as a result of their incomplete transformation. When referring to onion-like carbons less than 10 nm in size, the term “carbon nano-onions” (CNO) may be used [36][37]. There are several approaches to the synthesis of these materials, but the most effective one is considered to be the thermal treatment of detonation nanodiamonds, which allows us to achieve a high practical yield of particles smaller than 10 nm with a high degree of carbon ordering, the value of the specific surface area for which can reach 600 m^2/g. Basic electrodes based on CNO and OLC, as a rule, demonstrate rather low values of specific capacitance (less than 100 F/g) [38] and specific energy, but are characterized by high conductivity (up to 4 S/cm) and charge/discharge rate. In connection with this, various attempts are made to physically and chemically activate these materials as well as to decorate them with redox-active substances in order to further optimize their electrochemical characteristics [38].

Carbon nanotubes (CNT) due to their high electrical conductivity (5×10^5 S/m [39]), mechanical strength, and relatively high specific surface area (the theoretical value of this parameter can reach 1315 m^2/g for single-walled CNTs [40]) are also of considerable interest in the context of electrode materials for supercapacitors. It is reported [41] that the specific capacitance of electrodes based on unmodified single- and multi-walled CNT does not exceed 45 and 80 F/g,

respectively. In order to achieve more impressive functional characteristics (specific capacitance, energy density, and charge/discharge rate), strategies such as functionalization of CNT with various conductive materials (graphene, metal nanoparticles, transition metal oxides, MXenes) as well as their deposition on thin metallic films are employed [42]. Fibers [43] and fabrics made of intertwined nanotubes [44] are actively used in the creation of flexible and wearable supercapacitors. Approaches, such as 3D printing [45], ink-jet printing [46], screen printing [47], and direct ink writing (DIW) [48], have been used to print CNT-based supercapacitors.

Graphene and materials based on it (graphene oxide and its reduced form) do not lose their popularity in the field of electrode formation of electrochemical energy storage devices. It is known that graphene is characterized by outstanding values of specific surface area (up to 2630 m^2/g) and charge carrier mobility (carrier mobility of up to 2×10^5 $cm^2 \cdot V^{-1} \cdot cm^{-2}$), as well as a fairly high specific capacitance compared to other carbon materials (about 550 F/g). Currently known varieties of graphene microstructures include wrinkled graphene, porous graphene, graphene nanomeshes, honeycomb-like graphene, graphene hydrogels, and 3D porous graphene [49]. Additionally, in order to improve its electrochemical characteristics, the approach of combining it with other materials to create hybrid electrodes (CNT, conducting polymers, transition metal oxides, and hydroxides) is being actively used [50][51].

Widely commercially available materials for the manufacture of supercapacitors on an industrial scale are activated carbon, obtained by physical or chemical activation of carbon-containing materials, such as bamboo, willow peat, wood, plant biomass (fibers, husks, shells), fossil coal, and petroleum pitch. Physical activation involves carbonization in an inert environment (at <1000 K) followed by heat treatment (>1150 K) of the resulting coal in an environment of activating gaseous agents (CO_2, water vapor, air, or a combination thereof). Chemical activation is a one-stage process of carbonization of initial carbon-containing materials (700–1200 K) in the presence of activating agents (hydroxides of alkali and alkaline-earth metals, acids, and some salts) [52].

2.2. Transition Metal Oxides

Nowadays, transition metal oxides in the context of electrode components of energy storage devices are represented very widely. This class of materials is characterized by high electrochemical activity: its representatives can participate in reversible redox reactions (Faraday processes), providing additional (besides the work of the double electric layer) energy storage (pseudo-capacitive effect) due to the presence of metals with several oxidation degrees in their composition [53]. Ruthenium oxide stands out among transition metal oxides due to its high capacitive characteristics (the value of theoretical specific capacitance is 1400–2000 F/g), but the known problems of this material, such as is its high cost and high tendency to agglomeration in the process of long-term operation, significantly reduce its prospects for widespread use. In this connection, various options for creating RuO_2-based composites are currently being considered in order to “dilute” it with cheaper components while maintaining high electrochemical characteristics. In particular, the characteristics of ruthenium oxide composites with carbon materials, polymers, and other transition metals are being investigated [54].

Other materials that attract the increased attention of researchers in the context of the formation of electrode nanostructures are oxides of manganese [55], iron [56], nickel [57], and cobalt [58]. Thus, manganese is capable of forming a wide range of MnO_x oxides (MnO, Mn_2O_3, Mn_3O_4, Mn_5O_8, MnO_2) with different crystal structures, which are of interest not only in the field of electrochemical energy, but also in catalysis as well as optics and sensorics [17]. Manganese oxides both in individual form (e.g., δ-MnO_2 [59], MnO_2 [60]) and in the form of composites with carbon [61][62] and other [63] materials are actively used as component in functional inks for printing MSCs electrodes.

A considerable number of works have been devoted to the study of the possibilities of using iron oxides (FeO_x) as electrode materials for energy storage devices [64][65]. These materials have the advantages of high redox activity, high theoretical capacity, commercial availability, and low environmental impact. Despite their high energy and power density, they have several disadvantages, specifically low conductivity and a short lifetime due to low structural stability during cyclic volume changes occurring upon charge and discharge of the supercapacitor [56]. In a number of works [66][67], in order to eliminate the indicated problems of iron oxides, a combination with carbon materials is proposed, as was in the case of manganese oxides.

A further step towards the development of supercapacitor electrodes based on transition metal oxides was the use of oxides of complex composition, combining the advantages of individual oxides. Materials with spinel-type structure based on cobaltites, ferrites, and metal manganites are being especially actively investigated (e.g., $NiCo_2O_4$, $NiFe_2O_4$, $ZnCo_2O_4$, $MgCo_2O_4$, $CuCo_2O_4$, $ZnMn_2O_4$, and $CoMn_2O_4$) [68][69][70][71].

2.3. Polymers

Polymers are a particularly attractive class of materials for advanced supercapacitors, especially flexible and wearable supercapacitors, where there are special requirements for mechanical material properties while maintaining basic device functionality. The advantages of polymers include properties such as viscoelasticity and high resilience to various types of deformation. In addition, the possibility of modification of polymer chains, for example, by grafting various functional groups, and also the combination of polymeric material with materials of other types allows us to obtain new polymeric materials and composites on their basis, characterized by the required level of such important properties for modern supercapacitors as self-healability, electrical conductivity, electrochemical activity, and mechanical strength [72]. Due to these features, different types of polymers are now actively used in the creation of supercapacitors as substrates, various binding additives in the manufacture of functional inks, electrolytes, sealing coatings, and the active material of electrodes [7][73][74].

Polymers used as substrates (e.g., polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide (PI), polydimethylsiloxane (PDMS), etc.) are characterized by chemical resistance, bending strength (up to 180° while maintaining high capacity), water resistance, and different degrees of transparency, which is often important for the development of microelectronics devices [27]. However, it should be taken into account that the above materials are non-conductive, which requires the application of conductive layers of current collectors; in addition, some polymeric substrates (e.g., PDMS) may have problems with wettability by aqueous inks, which leads to inhomogeneity of the coatings formed on their surface as well as their poor adhesion [7].

The use of polymer binders (polyvinylidene fluoride (PVDF), cellulose, chitosan, lignin, poly-3,4-ethylenedioxythiophene (PEDOT), polyaniline (PANI), etc.) in the formation of micro-supercapacitors can help to significantly adjust such parameters of the formed functional coatings as adhesion to the substrate; improved contact between solid phase particles, which contributes to increased electrical conductivity of the final planar structures, homogeneity, and (often) flexibility and mechanical strength of formed films; and increased capacitive and cyclic characteristics of electrode structures [75][76][77][78].

Polymer-based electrolytes can be divided into three groups: (a) solid-state electrolytes (e.g., based on Nafion [79], polyaryletherketone [80]); (b) polymer gel electrolytes, which are further divided into hydrogel electrolytes (water as the solvent), e.g., systems based on polyvinyl alcohol (PVA), polyacrylamide (PAM), biopolymers (chitosan, agarose) [81], and organogel electrolytes (organic solvent is used, e.g., systems based on poly(acrylic acid-co-vinylimidazole) in ethylene glycol [82] and poly(vinylidene fluoride-co-hexafluoropropylene) in acetone [83]); and (c) polymer-ionic liquid electrolyte, which are melts (melting point below 100 °C) of organic salts consisting of highly asymmetric anions and cations distributed in a polymer matrix [84][85]. When developing polymer-based electrolytes, it is necessary to consider not only the value of their ionic conductivity, but also the degree of ion selectivity.

Polymers used as active electrode material can be categorized into conducting polymers (polypyrrole (PPy), PANI, polythiophene and its derivatives, redox conducting polymers) [72][86], composites based on conducting polymers (polymer–polymer: PEDOT:PSS [87], PEDOT:PSS/poly(ethylene glycol) diacrylate (PEGDA) [88], etc.; polymer–carbon material: PANI/C-MWCNTs [89], PANI/fullerene [90], PEDOT:PSS/CNT [91], etc.; polymer–metal oxide: PEDOT:TREN:MnO_2@$MnCO_3$ [92], Zn/PPy [93], etc.), and non-conductive polymers (elastomers: PDMS, polyurethane (PU), etc. [94][95]; and non-elastomers: materials based on natural polymers, such as cellulose [5][96]). It can be noted that electrodes based on conducting polymers and their composites demonstrate a pseudo-capacitive mechanism of charge accumulation. Currently, active research is underway to develop technological approaches to create miniaturized flexible/carrier supercapacitors based on polymer materials using inkjet printing, screen printing, and 3D printing.

2.4. Metal Hydroxides

Transition metal hydroxides are also a fairly widespread class of materials for supercapacitor electrodes. Due to its good pseudocapacitive performance and environmentally benign nature, one of the most common in this context is nickel hydroxide [97][98][99]. Thus, $Ni(OH)_2$ has a high value of theoretical specific capacitance (2082 F/g in a potential window of 0.5 V). However, the rather low electrical conductivity of this material and small specific surface area usually do not allow to achieve high real pseudocapacitive characteristics. For the formation of flexible supercapacitors containing nanoscale $Ni(OH)_2$ structures as an electrode component, printing technologies are also applied, which contributes to the homogeneity of the material and reproducibility of the characteristics of the obtained devices. For example, the authors of the study [100] studied the formation of electrodes based on $Ni(OH)_2$ nanoflakes using inkjet printing. The obtained asymmetric supercapacitor exhibited high energy density and power density per unit power (64.8 W·h/kg at 800 W/kg and 30.7 W·h/kg at 16,000 W/kg). In the fabrication of flexible electrodes by screen printing, $Ni(OH)_2$ nanoplates were used in

[101] while the authors of [102] formed a nickel hydroxide shell on the surface of carbon fibers for further fabrication of micro-supercapacitor electrodes by 3D printing. As can be seen, many researchers are striving to achieve a more developed surface of $Ni(OH)_2$ nanostructures, which contributes to the improvement of their electrochemical characteristics and partially compensates for the relatively low electrical conductivity. Much rarer are works that utilize cobalt hydroxide as a component of supercapacitor electrodes [103]. In particular, the authors of [104] studied the fabrication process of β-$Co(OH)_2$-based thin-film supercapacitor electrodes using screen printing. The synthesis of cobalt (II) hydroxide in this case was carried out by the hydrothermal method: monoethanolamine was added to an aqueous solution of cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), hexamethylenetetramine (HMT), and cetyltrimethylammonium bromide (CTAB), after which the reaction system was transferred to a steel autoclave with Teflon insert and subjected to heat treatment at 100 °C for 24 h. The formed solid phase was further dried at 80 °C in air. Based on the β-$Co(OH)_2$ powder thus obtained, an asymmetric supercapacitor was fabricated by screen printing, showing a specific capacitance of about 170 F/g at a current density of 0.5 mA. An aqueous KOH solution (3 mol/L) was used as the electrolyte in this case, and after 600 charge-discharge cycles, a capacity retention of 99.69% was observed. Recently, in order to improve the functional characteristics of hydroxide-based supercapacitor electrodes, a tendency to use materials of more complex composition has arisen, including those characterized by a layered structure. Thus, much attention in this context is paid today to the layered hydroxides (LH), which have a unique structure where charge-balancing anions are located in the interlayer space of metal hydroxides [105]. Layered double hydroxides (LDH), which have much higher electrical conductivity compared to individual hydroxides, attract the most attention. A very popular representative of LDHs is nickel-cobalt hydroxide (NiCo-LDH), which is actively used in the fabrication of electrodes of miniature supercapacitors, including printed technologies [106].

2.5. Sulfides

Recently, in the search for new more efficient supercapacitor electrodes, many researchers have increasingly turned their attention to metal sulfides, which often show improved functional characteristics compared to the corresponding oxides. For example, when replacing oxygen in such a highly popular and demanded oxide as $NiCo_2O_4$ with sulfur, the resulting sulfide of $NiCo_2S_4$ composition demonstrates even more outstanding properties [107]. In particular, in this case, there is an increase in the length of chemical bonds leading to easier electron transport, which may contribute to improved electrochemical performance. As a result, two orders of magnitude increase in electrical conductivity is observed for $NiCo_2S_4$ sulfide compared to $NiCo_2O_4$ oxide, and higher electrochemical activity and specific capacitance are observed. Due to the mentioned features of nickel–cobalt sulfide, this material is one of the most demanded sulfides as a component of supercapacitor electrodes [108][109]. In addition, researchers are also interested in a sulfide with the opposite ratio of metals of the composition $CoNi_2S_4$, which also shows high electrochemical properties as an electrode of supercapacitors [110][111]. One of the most popular pseudocapacitance sulfide materials in this context is also MoS_2, which is characterized by a graphene-like two-dimensional layered structure and sandwich-structured S-Mo-S atoms held together by weak van der Waals forces [112]. Due to the peculiarities of the structure, materials based on molybdenum disulfide can reach high values of a specific surface area, which promotes charge storage of EDLCs and also provides the possibility of Faraday redox reactions on molybdenum atoms with different oxidation degree (from +2 to +6). Thus, semiconducting molybdenum disulfide can be considered as one of the most promising materials for supercapacitor electrodes, which has a high theoretical specific capacitance (1000 F/g).

It should be noted that there are also works devoted to studying the properties of $CuCo_2S_4$ sulfide as a new electrode material for supercapacitors. Thus, replacement of nickel in the previously mentioned $NiCo_2S_4$ sulfide with more common copper can contribute to the reduction of material cost while maintaining competitive electrochemical characteristics [113]. Authors of [114] used this sulfide as a component of supercapacitor electrodes in their fabrication by 3D printing. The synthesis of the material in this case was carried out by hydrothermal process in the presence of reduced graphene oxide using copper and cobalt chlorides and thiourea. Heat treatment of the reaction system was carried out in an autoclave at 200 °C for 12 h. 3D printing of the supercapacitor electrode in this case was carried out with gel freezing, which, according to the authors, contributed not only to the formation of porous material, but also to the suppression of agglomeration of solid phase particles to improve charge transport. Electrochemical measurements allowed for establishing that the printed electrode has a high specific capacity (C_{sp} = 1123 F/g), and after 20,000 charge-discharge cycles at high current density (125 A/g), the value of this parameter remained at the level of 91.2%. It was also shown that the investigated electrode has low internal resistance, low ion exchange resistance, and high electric double layer capacitance.

Significant attention in the manufacture of supercapacitor electrodes is also paid to the sulfide $MnCo_2S_4$. In particular, the authors of [115] studied the process of forming the corresponding electrodes using 3D printing. The synthesis of manganese–cobalt sulfide was carried out by a thermal decomposition method with 1-dodecanethiol, which plays the role of both sulfur source and surfactant. For this purpose, manganese and cobalt chlorides in the required ratios were placed

in a three-neck flask containing 1-octadecene and vacuumized at room temperature for 30 min. Then, the reaction system was heated to 140 °C, dodecanethiol was quickly introduced, and the temperature was raised to 290 °C and kept for 1 h, with system being stirred. According to the electrochemical measurements of the obtained electrode, the specific capacitance values were 3812.5 F/g (at 2 A/g) and 1780.8 F/g (at 50 A/g). The results of the electrode cyclic stability study showed a capacity retention of 92% after 22,000 charge–discharge cycles (at 50 A/g).

2.6. MXenes

It is well known that MXenes are a rather new and extensive class of 2D nanomaterials with the general formula $M_{n+1}X_nT_x$, where M is the transition metal (most commonly, Ti, V, Nb, Mo, Cr, etc.), X is C or N, and T is the surface functional groups, most commonly F, OH, Cl [116][117]. Due to their layered structure, high electrical conductivity, and huge variation in composition (which allows its optimization for a specific task), MXenes are recognized as very promising component base for various modern devices, e.g., in sensorics [118][119][120][121][122], catalysis [123][124], industrial water purification [125][126], and the creation of electrodes that often retain high energy density at high current densities [127]. However, they are of the greatest interest as components of energy generation and storage devices—lithium/sodium-ion batteries and supercapacitors [128][129][130][131][132]—especially owing to the possibility of intercalation of various ions into the interlayer space and high hydrophilicity of surface groups. An attractive aspect for the development of portable and implantable devices (similar to e-textile or electronic-tattoo) based on MXene is their antibacterial activity and mechanical elasticity of the layers, as established in several studies [133][134]. The development of printing technologies has most significantly affected the issue of MXene-based supercapacitor and micro-supercapacitor electrodes [27][135][136][137].

Many scientific publications indicate that the history of MXene preparation (etching technique of initial MAX phases, reagents used, temperature, duration, delamination conditions) is crucial for the observed electrochemical characteristics as it significantly affects the composition of surface functional groups, the size and shape of formed 2D-particles, the interaction between individual MXene flakes, the interlayer distance, and the possibility of ionic and molecular intercalation. The number of layers in the MXene aggregates formed after etching and delamination can affect not only the electrochemical behavior of the applied coatings, but also the viscosity of the initial ink [138] (which is due to the significantly higher ζ-potential and strong long-range interactions for monolayer MXene compared to multilayer ones). As a result, this parameter can also determine the additive technology used to form the electrode layers: 2D printing (inkjet, extrusion, etc.) or 3D printing/screen printing.

Analyzing the features of MXene-based functional inks, it should be noted that usually, in addition to the electrochemically active component (in this case, MXene), they contain other components that provide the necessary viscosity, binding of particles to each other in the final coating, or surface-active components (to improve wetting of the so-called “pigment” by the dispersion medium). These additives significantly worsen the electrophysical properties, reduce the active surface area and complicate the fabrication process, and their removal most often requires high-temperature treatment (preferably pulsed and localized to prevent degradation of the main components). Due to the high chemical activity of MXenes, great attention is paid to minimizing the content of such additives.

Switching to non-aqueous solvents (most often polar solvents such as DMSO, N-methyl-2-pyrrolidone, ethanol, etc.) also allows us to increase the utilization time of dispersions compared to aqueous solvents. Notably, for dispersions in the above solvents, it was found in a study [139] that their viscosity is generally lower than when water is used as the dispersion medium; however, it may also be due to the higher concentration of MXene that is achievable in the aqueous medium.

A more complex composition modifying MXene $Ti_3C_2T_x$ is described in the study by Wang et al. [140]: the used sodium alginate in addition to protecting against oxidation serves to build three-dimensional framework structures (and levels the problem of aggregation of low-layer MXenes) and the introduction of Fe^{2+} salt structures of the pore space. With improved dispersion stability, it is characterized by a viscosity suitable for inkjet printing (1619.9 mPa/s). The micro-supercapacitor printed by this method on paper substrate with electrode spacing of 310 μm has a large number of active sites for ion storage and a network with high conductivity for electron transfer, resulting in good performance (capacitance 123. 8 mF/cm^2 at 5 mV/s, energy density 8.44 $\mu W{\cdot}h/cm^2$ with a power density of 33.70 $\mu W/cm^2$) with 91.4% capacitance retention after 10,000 cycles and 90% capacitance retention after 10,000 bending cycles.

Doping MXene with nitrogen and sulfur atoms is also considered promising for improving its environmental stability [141] and also helps to improve its electrochemical properties. Thus, using $Ti_3C_2T_x$, modified with sulfur and nitrogen, planar micro-supercapacitors with electrode spacing of 300 μm were formed with the direct inkjet printing method created by Sun et al., for which a high bulk capacitance of 710 F/cm^3 and an energy density of 8.9 $mW{\cdot}h/cm^3$ at a power density of 411 mW/cm^3 was observed. Long-term cyclic stability was also recorded for it (up to 94.6% after 10,000 cycles).

Interesting from the economic and technological points of view is the approach of the authors of the article [142], who proposed to use not monolayer MXene obtained by delamination in DMSO and ultrasonic action and transferred by centrifugation (3500 rpm, 1 h) to the supernatant, but a precipitate containing more multilayer MXene and residues of the MAX-phase Ti_3AlC_2 for the fabrication of functional $Ti_3C_2T_x$ inks. This concentrated dispersed system with a solid phase content of 72.4 wt.% has the required rheological characteristics (viscosity 468 Pa/s at a shear rate of 10^{-1} s^{-1}) and exhibits the properties of a non-Newtonian fluid, which is required for extrusion printing.

2.7. Composites

As follows from the previous sections, in most cases, supercapacitor electrodes are formed by combining materials of different types, and the composites created in this way unite the properties of the corresponding components, which makes it possible to achieve optimal mechanical and electrochemical characteristics. Thus, there is a large number of works that consider approaches to obtaining composite electrodes based on all the materials (carbon structures, polymers, oxides, hydroxides and metal sulfides, and MXenes). In the fabrication of micro-supercapacitor electrodes using printing technologies, composites based on various polymers and carbon nanostructures, in particular fullerenes, are studied [143]. Thus, with the combination of polyaniline and fullerenes, the composite electrode is characterized by the specific capacitance value of 2201 F/g at a current density of 2 A/g (rate capability of about 73% at 10 A/g) [90]. As noted above, a good result in the context of electrochemical characteristics can be achieved using composites based on MXenes (including $Ti_3C_2T_x$ composition) and layered double hydroxides (in particular, CoAl-LDH): high energy density (8.84 μW·h/cm^2), flexibility, and cycling stability (capacitance remains at the level of 92% after 10,000 cycles).

The obtained material demonstrated improved electrochemical characteristics (good mechanical strength, specific capacitance of 103 mF/cm^2, promising areal energy density of 14.3 μW·h/cm^2, and capacitance retention at the level of 94% after 8000 charge-discharge cycles). In [144], the results of successful combination of MoS_2 and PEDOT:PSS in the electrode composition of a flexible supercapacitor are presented. In this case, due to the addition of the above polymer to the material composition, its electrostatic interaction with molybdenum disulfide particles occurred, leading to the formation of a hybrid hydrogel, which can be used as a functional ink in extrusion 3D printing of flexible supercapacitors, including miniature ones. The electrodes thus fabricated showed good mechanical and electrochemical performance in the environment of various electrolytes. As a result, it was found that composite materials are probably the most common and promising as electrodes for micro-supercapacitors formed using classical methods and different types of printing technologies.

3. Conclusions

Supercapacitors, as energy storage devices, will undoubtedly play an important role in the sustainable development of modern energy. Technologies for their creation are being improved for many years already; serious efforts are made to develop functional components of supercapacitors with improved electrochemical characteristics, the search for optimal methods of their automated manufacturing is underway, and more and more effective approaches to miniaturization and planarization of these devices are offered.

Thus, in the case of carbon materials, it is necessary to note insufficiently high values of specific capacitance. Although there are attempts to improve this parameter by increasing the specific surface area and adjusting the pore structure, these measures have had limited effect. Significant improvements in the capacitive performance of carbon materials can be achieved when they are combined with pseudo-capacitive materials. However, the power density and cyclic stability of the final materials may suffer in this case. Polymer electrode materials in turn can also suffer from low cyclic stability, mechanical strength, and insufficiently high conductivity. The latter parameter also requires correction for transition metal oxides and hydroxides. When working with metal sulfides, attempts should be made to increase their interlayer space to facilitate charge transfer. In addition, in aqueous electrolyte environments, this type of material cannot function in a wide potential window, whereas degradation is observed in ionic liquids. MXenes, which represent a new class of layered materials, despite their extremely attractive electrochemical properties, require the use of rather complex synthetic approaches, and improvements in oxidative stability during long-term storage as well as operation in aqueous electrolytes are need to be made.

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.

2. Pandolfo, A.G.; Hollenkamp, A.F. Carbon Properties and Their Role in Supercapacitors. J. Power Sources 2006, 157, 11–27.
3. 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.
4. Wu, C.; Lu, X.; Peng, L.; Xu, K.; Peng, X.; Huang, J.; Yu, G.; Xie, Y. Two-Dimensional Vanadyl Phosphate Ultrathin Nanosheets for High Energy Density and Flexible Pseudocapacitors. Nat. Commun. 2013, 4, 2431.
5. Ko, Y.; Kwon, M.; Bae, W.K.; Lee, B.; Lee, S.W.; Cho, J. Flexible Supercapacitor Electrodes Based on Real Metal-like Cellulose Papers. Nat. Commun. 2017, 8, 536.
6. Hu, L.; Cui, Y. Energy and Environmental Nanotechnology in Conductive Paper and Textiles. Energy Environ. Sci. 2012, 5, 6423–6435.
7. Zhang, Y.-Z.; Wang, Y.; Cheng, T.; Yao, L.-Q.; Li, X.; Lai, W.-Y.; Huang, W. Printed Supercapacitors: Materials, Printing and Applications. Chem. Soc. Rev. 2019, 48, 3229–3264.
8. Liu, W.; Lu, C.; Wang, X.; Tay, R.Y.; Tay, B.K. High-Performance Microsupercapacitors Based on Two-Dimensional Graphene/Manganese Dioxide/Silver Nanowire Ternary Hybrid Film. ACS Nano 2015, 9, 1528–1542.
9. Wu, Z.; Parvez, K.; Feng, X.; Müllen, K. Graphene-Based in-Plane Micro-Supercapacitors with High Power and Energy Densities. Nat. Commun. 2013, 4, 2487.
10. Beidaghi, M.; Wang, C. Micro-Supercapacitors Based on Interdigital Electrodes of Reduced Graphene Oxide and Carbon Nanotube Composites with Ultrahigh Power Handling Performance. Adv. Funct. Mater. 2012, 22, 4501–4510.
11. Cai, J.; Lv, C.; Watanabe, A. Laser Direct Writing of High-Performance Flexible All-Solid-State Carbon Micro-Supercapacitors for an on-Chip Self-Powered Photodetection System. Nano Energy 2016, 30, 790–800.
12. Wang, Y.-F.; Bian, S.W. Flexible Textile-Based Electrode Materials for Supercapacitors. Mater. Today Proc. 2019, 16, 1448–1455.
13. Li, R.-Z.; Peng, R.; Kihm, K.D.; Bai, S.; Bridges, D.; Tumuluri, U.; Wu, Z.; Zhang, T.; Compagnini, G.; Feng, Z.; et al. High-Rate in-Plane Micro-Supercapacitors Scribed onto Photo Paper Using in Situ Femtolaser-Reduced Graphene Oxide/Au Nanoparticle Microelectrodes. Energy Environ. Sci. 2016, 9, 1458–1467.
14. Zhu, C.; Liu, T.; Qian, F.; Han, T.Y.-J.; Duoss, E.B.; Kuntz, J.D.; Spadaccini, C.M.; Worsley, M.A.; Li, Y. Supercapacitors Based on Three-Dimensional Hierarchical Graphene Aerogels with Periodic Macropores. Nano Lett. 2016, 16, 3448–3456.
15. Sundriyal, P.; Bhattacharya, S. Scalable Micro-Fabrication of Flexible, Solid-State, Inexpensive, and High-Performance Planar Micro-Supercapacitors through Inkjet Printing. ACS Appl. Energy Mater. 2019, 2, 1876–1890.
16. Volkov, I.A.; Simonenko, N.P.; Efimov, A.A.; Simonenko, T.L.; Vlasov, I.S.; Borisov, V.I.; Arsenov, P.V.; Lebedinskii, Y.Y.; Markeev, A.M.; Lizunova, A.A.; et al. Platinum Based Nanoparticles Produced by a Pulsed Spark Discharge as a Promising Material for Gas Sensors. Appl. Sci. 2021, 11, 526.
17. Simonenko, T.L.; Simonenko, N.P.; Gorobtsov, P.Y.; Pozharnitskaya, V.M.; Simonenko, E.P.; Glumov, O.V.; Melnikova, N.A.; Sevastyanov, V.G.; Kuznetsov, N.T. Pen Plotter Printing of MnOx Thin Films Using Manganese Alkoxoacetylacetonate. Russ. J. Inorg. Chem. 2021, 66, 1416–1424.
18. Simonenko, T.L.; Simonenko, N.P.; Gorobtsov, P.Y.; Mokrushin, A.S.; Solovey, V.R.; Pozharnitskaya, V.M.; Simonenko, E.P.; Glumov, O.V.; Melnikova, N.A.; Lizunova, A.A.; et al. Pen Plotter Printing of Co3O4 Thin Films: Features of the Microstructure, Optical, Electrophysical and Gas-Sensing Properties. J. Alloys Compd. 2020, 832, 154957.
19. Simonenko, T.L.; Simonenko, N.P.; Gorobtsov, P.Y.; Vlasov, I.S.; Solovey, V.R.; Shelaev, A.V.; Simonenko, E.P.; Glumov, O.V.; Melnikova, N.A.; Kozodaev, M.G.; et al. Microplotter Printing of Planar Solid Electrolytes in the CeO2–Y2O3 System. J. Colloid Interface Sci. 2021, 588, 209–220.
20. Simonenko, N.P.; Kadyrov, N.S.; Simonenko, T.L.; Simonenko, E.P.; Sevastyanov, V.G.; Kuznetsov, N.T. Preparation of ZnS Nanopowders and Their Use in the Additive Production of Thick-Film Structures. Russ. J. Inorg. Chem. 2021, 66, 1283–1288.
21. Bae, S.; Kim, H.; Lee, Y.; Xu, X.; Park, J.-S.; Zheng, Y.; Balakrishnan, J.; Lei, T.; Ri Kim, H.; Song, Y.I.; et al. Roll-to-Roll Production of 30-Inch Graphene Films for Transparent Electrodes. Nat. Nanotechnol. 2010, 5, 574–578.
22. Zhang, C.J.; Kremer, M.P.; Seral-Ascaso, A.; Park, S.-H.; McEvoy, N.; Anasori, B.; Gogotsi, Y.; Nicolosi, V. Stamping of Flexible, Coplanar Micro-Supercapacitors Using MXene Inks. Adv. Funct. Mater. 2018, 28, 1705506.
23. Jost, K.; Stenger, D.; Perez, C.R.; McDonough, J.K.; Lian, K.; Gogotsi, Y.; Dion, G. Knitted and Screen Printed Carbon-Fiber Supercapacitors for Applications in Wearable Electronics. Energy Environ. Sci. 2013, 6, 2698–2705.

24. Dubal, D.P.; Kim, J.G.; Kim, Y.; Holze, R.; Lokhande, C.D.; Kim, W.B. Supercapacitors Based on Flexible Substrates: An Overview. Energy Technol. 2014, 2, 325–341.

25. Xu, J.-L.; Liu, Y.-H.; Gao, X.; Sun, Y.; Shen, S.; Cai, X.; Chen, L.; Wang, S.-D. Embedded Ag Grid Electrodes as Current Collector for Ultraflexible Transparent Solid-State Supercapacitor. ACS Appl. Mater. Interfaces 2017, 9, 27649–27656.

26. Liu, C.; Yan, X.; Hu, F.; Gao, G.; Wu, G.; Yang, X. Toward Superior Capacitive Energy Storage: Recent Advances in Pore Engineering for Dense Electrodes. Adv. Mater. 2018, 30, 1705713.

27. Liang, J.; Jiang, C.; Wu, W. Printed Flexible Supercapacitor: Ink Formulation, Printable Electrode Materials and Applications. Appl. Phys. Rev. 2021, 8, 021319.

28. Kamran, U.; Heo, Y.-J.; Lee, J.W.; Park, S.-J. Functionalized Carbon Materials for Electronic Devices: A Review. Micromachines 2019, 10, 234.

29. Jariwala, D.; Sangwan, V.K.; Lauhon, L.J.; Marks, T.J.; Hersam, M.C. Carbon Nanomaterials for Electronics, Optoelectronics, Photovoltaics, and Sensing. Chem. Soc. Rev. 2013, 42, 2824–2860.

30. Mohanraj, J.; Durgalakshmi, D.; Rakkesh, R.A.; Balakumar, S.; Rajendran, S.; Karimi-Maleh, H. Facile Synthesis of Paper Based Graphene Electrodes for Point of Care Devices: A Double Stranded DNA (DsDNA) Biosensor. J. Colloid Interface Sci. 2020, 566, 463–472.

31. Laghlimi, C.; Ziat, Y.; Moutcine, A.; Hammi, M.; Zarhri, Z.; Maallah, R.; Ifguis, O.; Chtaini, A. Analysis of Pb(II), Cu(II) and Co(II) in Drinking Water by a New Carbon Paste Electrode Modified with an Organic Molecule. Chem. Data Collect. 2020, 29, 100496.

32. Laghlimi, C.; Moutcine, A.; Chtaini, A.; Isaad, J.; Soufi, A.; Ziat, Y.; Amhamdi, H.; Belkhanchi, H. Recent Advances in Electrochemical Sensors and Biosensors for Monitoring Drugs and Metabolites in Pharmaceutical and Biological Samples. ADMET DMPK 2023, 11, 151–173.

33. Yuan, S.; Gao, Q.; Ke, C.; Zuo, T.; Hou, J.; Zhang, J. Mesoporous Carbon Materials for Electrochemical Energy Storage and Conversion. ChemElectroChem 2022, 9, e202101182.

34. New Carbon Based Materials for Electrochemical Energy Storage Systems: Batteries, Supercapacitors and Fuel Cells; Barsukov, I.V.; Johnson, C.S.; Doninger, J.E.; Barsukov, V.Z. (Eds.) NATO Science Series II: Mathematics, Physics and Chemistry; Springer: Dordrecht, The Netherlands, 2006; Volume 229, ISBN 978-1-4020-4810-4.

35. Zhai, Z.; Zhang, L.; Du, T.; Ren, B.; Xu, Y.; Wang, S.; Miao, J.; Liu, Z. A Review of Carbon Materials for Supercapacitors. Mater. Des. 2022, 221, 111017.

36. Zeiger, M.; Jäckel, N.; Mochalin, V.N.; Presser, V. Review: Carbon Onions for Electrochemical Energy Storage. J. Mater. Chem. A 2016, 4, 3172–3196.

37. Siemiaszko, G.; Breczko, J.; Hryniewicka, A.; Ilnicka, A.; Markiewicz, K.H.; Terzyk, A.P.; Plonska-Brzezinska, M.E. Composites Containing Resins and Carbon Nano-Onions as Efficient Porous Carbon Materials for Supercapacitors. Sci. Rep. 2023, 13, 6606.

38. Plonska-Brzezinska, M.E.; Echegoyen, L. Carbon Nano-Onions for Supercapacitor Electrodes: Recent Developments and Applications. J. Mater. Chem. A 2013, 1, 13703–13714.

39. Ryan, S.; Browne, M.P.; Zhussupbekova, A.; Spurling, D.; McKeown, L.; Douglas-Henry, D.; Prendeville, L.; Vaesen, S.; Schmitt, W.; Shvets, I.; et al. Single Walled Carbon Nanotube Functionalisation in Printed Supercapacitor Devices and Shielding Effect of Tin(II) Oxide. Electrochim. Acta 2023, 448, 142168.

40. Peigney, A.; Laurent, C.; Flahaut, E.; Bacsa, R.R.; Rousset, A. Specific Surface Area of Carbon Nanotubes and Bundles of Carbon Nanotubes. Carbon 2001, 39, 507–514.

41. Grądzka, E.; Winkler, K. Recent Progress on Electrochemical Capacitors Based on Carbon Nanotubes. In Carbon Nanotubes–Recent Progress; InTech: London, UK, 2018.

42. Han, Y.; Ha, H.; Choi, C.; Yoon, H.; Matteini, P.; Cheong, J.Y.; Hwang, B. Review of Flexible Supercapacitors Using Carbon Nanotube-Based Electrodes. Appl. Sci. 2023, 13, 3290.

43. Joseph, K.; Kasparian, H.; Shanov, V. Carbon Nanotube Fiber-Based Wearable Supercapacitors—A Review on Recent Advances. Energies 2022, 15, 6506.

44. Liang, Y.; Luo, X.; Weng, W.; Hu, Z.; Zhang, Y.; Xu, W.; Bi, Z.; Zhu, M. Activated Carbon Nanotube Fiber Fabric as a High-Performance Flexible Electrode for Solid-State Supercapacitors. ACS Appl. Mater. Interfaces 2021, 13, 28433–28441.

45. Yu, W.; Zhou, H.; Li, B.Q.; Ding, S. 3D Printing of Carbon Nanotubes-Based Microsupercapacitors. ACS Appl. Mater. Interfaces 2017, 9, 4597–4604.

46. Wang, S.; Liu, N.; Tao, J.; Yang, C.; Liu, W.; Shi, Y.; Wang, Y.; Su, J.; Li, L.; Gao, Y. Inkjet Printing of Conductive Patterns and Supercapacitors Using a Multi-Walled Carbon Nanotube/Ag Nanoparticle Based Ink. J. Mater. Chem. A 2015, 3, 2407–2413.
47. Jiang, L.; Hong, H.; Hu, J.; Yan, X. Fabrication and Seamless Integration of Insensitive-Bending Fully Printed All-in-One Fabric-Based Supercapacitors Based on Cost-Effective MWCNT Electrodes. ACS Appl. Mater. Interfaces 2022, 14, 12214–12222.
48. Chen, B.; Jiang, Y.; Tang, X.; Pan, Y.; Hu, S. Fully Packaged Carbon Nanotube Supercapacitors by Direct Ink Writing on Flexible Substrates. ACS Appl. Mater. Interfaces 2017, 9, 28433–28440.
49. Sang Tran, T.; Dutta, N.; Roy Choudhury, N. Graphene-Based Inks for Printing of Planar Micro-Supercapacitors: A Review. Materials 2019, 12, 978.
50. Yang, C. Review of Graphene Supercapacitors and Different Modified Graphene Electrodes. Smart Grid Renew. Energy 2021, 12, 1–15.
51. Yao, Y.; Yu, Y.; Wan, L.; Du, C.; Zhang, Y.; Chen, J.; Xie, M. Structurally-Stable Mg-Co-Ni LDH Grown on Reduced Graphene by Ball-Milling and Ion-Exchange for Highly-Stable Asymmetric Supercapacitor. J. Colloid Interface Sci. 2023, 649, 519–527.
52. Heidarinejad, Z.; Dehghani, M.H.; Heidari, M.; Javedan, G.; Ali, I.; Sillanpää, M. Methods for Preparation and Activation of Activated Carbon: A Review. Environ. Chem. Lett. 2020, 18, 393–415.
53. Delbari, S.A.; Ghadimi, L.S.; Hadi, R.; Farhoudian, S.; Nedaei, M.; Babapoor, A.; Sabahi Namini, A.; Van Le, Q.; Shokouhimehr, M.; Shahedi Asl, M.; et al. Transition Metal Oxide-Based Electrode Materials for Flexible Supercapacitors: A Review. J. Alloys Compd. 2021, 857, 158281.
54. Majumdar, D.; Maiyalagan, T.; Jiang, Z. Recent Progress in Ruthenium Oxide-Based Composites for Supercapacitor Applications. ChemElectroChem 2019, 6, 4343–4372.
55. Zhang, S.W.; Chen, G.Z. Manganese Oxide Based Materials for Supercapacitors. Energy Mater. 2008, 3, 186–200.
56. Gaire, M.; Khatoon, N.; Subedi, B.; Chrisey, D. Flexible Iron Oxide Supercapacitor Electrodes by Photonic Processing. J. Mater. Res. 2021, 36, 4536–4546.
57. Simonenko, T.L.; Simonenko, N.P.; Gorobtsov, P.Y.; Simonenko, E.P.; Kuznetsov, N.T. Hydrothermal Synthesis of a Cellular NiO Film on Carbon Paper as a Promising Way to Obtain a Hierarchically Organized Electrode for a Flexible Supercapacitor. Materials 2023, 16, 5208.
58. Lu, Y.; Deng, B.; Liu, Y.; Wang, J.; Tu, Z.; Lu, J.; Xiao, X.; Xu, G. Nanostructured Co3O4 for Achieving High-Performance Supercapacitor. Mater. Lett. 2021, 285, 129101.
59. Wang, Y.; Zhang, Y.-Z.; Dubbink, D.; ten Elshof, J.E. Inkjet Printing of δ-MnO2 Nanosheets for Flexible Solid-State Micro-Supercapacitor. Nano Energy 2018, 49, 481–488.
60. Yao, B.; Chandrasekaran, S.; Zhang, J.; Xiao, W.; Qian, F.; Zhu, C.; Duoss, E.B.; Spadaccini, C.M.; Worsley, M.A.; Li, Y. Efficient 3D Printed Pseudocapacitive Electrodes with Ultrahigh MnO2 Loading. Joule 2019, 3, 459–470.
61. Liu, B.; Cao, Z.; Yang, Z.; Qi, W.; He, J.; Pan, P.; Li, H.; Zhang, P. Flexible Micro-Supercapacitors Fabricated from MnO2 Nanosheet/Graphene Composites with Black Phosphorus Additive. Prog. Nat. Sci. Mater. Int. 2022, 32, 10–19.
62. Mokhtarnejad, M.; Ribeiro, E.L.; Mukherjee, D.; Khomami, B. 3D Printed Interdigitated Supercapacitor Using Reduced Graphene Oxide-MnOx/Mn3O4 Based Electrodes. RSC Adv. 2022, 12, 17321–17329.
63. Lu, Q.; Liu, L.; Yang, S.; Liu, J.; Tian, Q.; Yao, W.; Xue, Q.; Li, M.; Wu, W. Facile Synthesis of Amorphous FeOOH/MnO2 Composites as Screen-Printed Electrode Materials for All-Printed Solid-State Flexible Supercapacitors. J. Power Sources 2017, 361, 31–38.
64. Xu, B.; Zheng, M.; Tang, H.; Chen, Z.; Chi, Y.; Wang, L.; Zhang, L.; Chen, Y.; Pang, H. Iron Oxide-Based Nanomaterials for Supercapacitors. Nanotechnology 2019, 30, 204002.
65. Lv, L.; Peng, M.; Wu, L.; Dong, Y.; You, G.; Duan, Y.; Yang, W.; He, L.; Liu, X. Progress in Iron Oxides Based Nanostructures for Applications in Energy Storage. Nanoscale Res. Lett. 2021, 16, 138.
66. Xu, C.-H.; Shen, P.-Y.; Chiu, Y.-F.; Yeh, P.-W.; Chen, C.-C.; Chen, L.-C.; Hsu, C.-C.; Cheng, I.-C.; Chen, J.-Z. Atmospheric Pressure Plasma Jet Processed Nanoporous Fe2O3/CNT Composites for Supercapacitor Application. J. Alloys Compd. 2016, 676, 469–473.
67. Zhang, X.; Pei, Y.; Tian, B.; Wu, Y.; Tang, G.; Liu, Q.; Liang, J.; Wu, W. Soft Fully-Printed RGO/Fe2O3-Based Supercapacitors for Wearable Electronics. J. Energy Storage 2022, 56, 106136.
68. Aparna, M.L.; Grace, A.N.; Sathyanarayanan, P.; Sahu, N.K. A Comparative Study on the Supercapacitive Behaviour of Solvothermally Prepared Metal Ferrite (MFe2O4, M = Fe, Co, Ni, Mn, Cu, Zn) Nanoassemblies. J. Alloys Compd. 2018,

745, 385–395.

69. Simonenko, T.L.; Simonenko, N.P.; Gorobtsov, P.Y.; Simonenko, E.P.; Kuznetsov, N.T. Microplotter Printing of a Miniature Flexible Supercapacitor Electrode Based on Hierarchically Organized NiCo2O4 Nanostructures. Materials 2023, 16, 4202.
70. Simonenko, T.L.; Simonenko, N.P.; Simonenko, E.P.; Vlasov, I.S.; Volkov, I.A.; Kuznetsov, N.T. Microplotter Printing of Hierarchically Organized Planar NiCo2O4 Nanostructures. Russ. J. Inorg. Chem. 2022, 67, 1848–1854.
71. Jose, V.; Jose, V.; Freeda Christy, C.E.; Nesaraj, A.S. Spinel-Based Electrode Materials for Application in Electrochemical Supercapacitors–Present Status and Future Prospects. Inorg. Nano-Metal Chem. 2022, 52, 1449–1462.
72. Wang, Z.; Zhu, M.; Pei, Z.; Xue, Q.; Li, H.; Huang, Y.; Zhi, C. Polymers for Supercapacitors: Boosting the Development of the Flexible and Wearable Energy Storage. Mater. Sci. Eng. R Rep. 2020, 139, 100520.
73. Bora, M.; Bhattacharjya, D.; Saikia, B.K. Coal-Derived Activated Carbon for Electrochemical Energy Storage: Status on Supercapacitor, Li-Ion Battery, and Li–S Battery Applications. Energy Fuels 2021, 35, 18285–18307.
74. Wolf, M.P.; Salieb-Beugelaar, G.B.; Hunziker, P. PDMS with Designer Functionalities—Properties, Modifications Strategies, and Applications. Prog. Polym. Sci. 2018, 83, 97–134.
75. Arunkumar, M.; Paul, A. Importance of Electrode Preparation Methodologies in Supercapacitor Applications. ACS Omega 2017, 2, 8039–8050.
76. Landi, G.; La Notte, L.; Palma, A.L.; Sorrentino, A.; Maglione, M.G.; Puglisi, G. A Comparative Evaluation of Sustainable Binders for Environmentally Friendly Carbon-Based Supercapacitors. Nanomaterials 2021, 12, 46.
77. Ruschhaupt, P.; Varzi, A.; Passerini, S. Natural Polymers as Green Binders for High-Loading Supercapacitor Electrodes. ChemSusChem 2020, 13, 763–770.
78. Song, B.; Wu, F.; Zhu, Y.; Hou, Z.; Moon, K.; Wong, C.-P. Effect of Polymer Binders on Graphene-Based Free-Standing Electrodes for Supercapacitors. Electrochim. Acta 2018, 267, 213–221.
79. Huang, C.; Zhang, J.; Young, N.P.; Snaith, H.J.; Grant, P.S. Solid-State Supercapacitors with Rationally Designed Heterogeneous Electrodes Fabricated by Large Area Spray Processing for Wearable Energy Storage Applications. Sci. Rep. 2016, 6, 25684.
80. Ainiya, L. The Recent Advances on Potential Solid Electrolytes for All-Solid-State Supercapacitors: A Short Review. J. Phys. Conf. Ser. 2019, 1417, 012031.
81. Salleh, N.A.; Kheawhom, S.; Hamid, N.A.A.; Rahiman, W.; Mohamad, A.A. Electrode Polymer Binders for Supercapacitor Applications: A Review. J. Mater. Res. Technol. 2023, 23, 3470–3491.
82. Wang, Y.; Auad, M.L.; Beckingham, B.S. 3D Printing Flexible Supercapacitors Based on Crosslinked Poly (Acrylic Acid-co-vinylimidazole). Eng. Rep. 2023, e12650.
83. Zhu, J.-J.; Martinez-Soria, L.; Gomez-Romero, P. Coherent Integration of Organic Gel Polymer Electrolyte and Ambipolar Polyoxometalate Hybrid Nanocomposite Electrode in a Compact High-Performance Supercapacitor. Nanomaterials 2022, 12, 514.
84. Yu, L.; Chen, G.Z. Ionic Liquid-Based Electrolytes for Supercapacitor and Supercapattery. Front. Chem. 2019, 7, 272.
85. Novakov, C.; Kalinova, R.; Veleva, S.; Ublekov, F.; Dimitrov, I.; Stoyanova, A. Flexible Polymer-Ionic Liquid Films for Supercapacitor Applications. Gels 2023, 9, 338.
86. Pan, L.; Yu, G.; Zhai, D.; Lee, H.R.; Zhao, W.; Liu, N.; Wang, H.; Tee, B.C.-K.; Shi, Y.; Cui, Y.; et al. Hierarchical Nanostructured Conducting Polymer Hydrogel with High Electrochemical Activity. Proc. Natl. Acad. Sci. USA 2012, 109, 9287–9292.
87. Manjakkal, L.; Pullanchiyodan, A.; Yogeswaran, N.; Hosseini, E.S.; Dahiya, R. A Wearable Supercapacitor Based on Conductive PEDOT:PSS-Coated Cloth and a Sweat Electrolyte. Adv. Mater. 2020, 32, 1907254.
88. Bertana, V.; Scordo, G.; Camilli, E.; Ge, L.; Zaccagnini, P.; Lamberti, A.; Marasso, S.L.; Scaltrito, L. 3D Printed Supercapacitor Exploiting PEDOT-Based Resin and Polymer Gel Electrolyte. Polymers 2023, 15, 2657.
89. Chu, X.; Zhu, Z.; Huang, H.; Xie, Y.; Xu, Z.; Wang, Y.; Yan, C.; Jin, L.; Wang, Y.; Zhang, H.; et al. Conducting Polymer Ink for Flexible and Printable Micro-Supercapacitors with Greatly-Enhanced Rate Capability. J. Power Sources 2021, 513, 230555.
90. Ramadan, A.; Anas, M.; Ebrahim, S.; Soliman, M.; Abou-Aly, A.I. Polyaniline/Fullerene Derivative Nanocomposite for Highly Efficient Supercapacitor Electrode. Int. J. Hydrog. Energy 2020, 45, 16254–16265.

91. Yang, J.; Cao, Q.; Tang, X.; Du, J.; Yu, T.; Xu, X.; Cai, D.; Guan, C.; Huang, W. 3D-Printed Highly Stretchable Conducting Polymer Electrodes for Flexible Supercapacitors. J. Mater. Chem. A 2021, 9, 19649–19658.
92. Selvam, S.; Yim, J.-H. Effective Self-Charge Boosting Sweat Electrolyte Textile Supercapacitors Array from Bio-Compatible Polymer Metal Chelates. J. Power Sources 2023, 556, 232511.
93. Tian, W.; Li, Y.; Zhou, J.; Wang, T.; Zhang, R.; Cao, J.; Luo, M.; Li, N.; Zhang, N.; Gong, H.; et al. Implantable and Biodegradable Micro-Supercapacitor Based on a Superassembled Three-Dimensional Network Zn@PPy Hybrid Electrode. ACS Appl. Mater. Interfaces 2021, 13, 8285–8293.
94. Lu, Y.; Jiang, Y.; Lou, Z.; Shi, R.; Chen, D.; Shen, G. Wearable Supercapacitor Self-Charged by P(VDF-TrFE) Piezoelectric Separator. Prog. Nat. Sci. Mater. Int. 2020, 30, 174–179.
95. Jeong, H.T.; Du, J.F.; Kim, Y.R.; Raj, C.J.; Kim, B.C. Electrochemical Performances of Highly Stretchable Polyurethane (PU) Supercapacitors Based on Nanocarbon Materials Composites. J. Alloys Compd. 2019, 777, 67–72.
96. Nargatti, K.I.; Subhedar, A.R.; Ahankari, S.S.; Grace, A.N.; Dufresne, A. Nanocellulose-Based Aerogel Electrodes for Supercapacitors: A Review. Carbohydr. Polym. 2022, 297, 120039.
97. Min, S.; Zhao, C.; Zhang, Z.; Chen, G.; Qian, X.; Guo, Z. Synthesis of Ni(OH)2/RGO Pseudocomposite on Nickel Foam for Supercapacitors with Superior Performance. J. Mater. Chem. A 2015, 3, 3641–3650.
98. Dai, X.; Chen, D.; Fan, H.; Zhong, Y.; Chang, L.; Shao, H.; Wang, J.; Zhang, J.; Cao, C. Ni(OH)2/NiO/Ni Composite Nanotube Arrays for High-Performance Supercapacitors. Electrochim. Acta 2015, 154, 128–135.
99. Chen, S.; Duan, J.; Tang, Y.; Qiao, S.Z. Hybrid Hydrogels of Porous Graphene and Nickel Hydroxide as Advanced Supercapacitor Materials. Chem. Eur. J. 2013, 19, 7118–7124.
100. Li, X.; Chen, R.; Zhao, Y.; Liu, Q.; Liu, J.; Yu, J.; Li, J.; Liu, P.; Li, J.; Wang, J. Layer-by-Layer Inkjet Printing GO Film Anchored Ni(OH)2 Nanoflakes for High-Performance Supercapacitors. Chem. Eng. J. 2019, 375, 121988.
101. Wu, X.; Zeng, F.; Song, X.; Sha, X.; Zhou, H.; Zhang, X.; Liu, Z.; Yu, M.; Jiang, C. In-Situ Growth of Ni(OH)2 Nanoplates on Highly Oxidized Graphene for All-Solid-State Flexible Supercapacitors. Chem. Eng. J. 2023, 456, 140947.
102. Yu, W.; Yin, X.; Wang, J.; Ding, S. Carbon Nanotube@Nickel Hydroxide Nanosheets Core–Shell Nanostructures Enabling Thermally Assisted 3D-Printed Solid-State Microsupercapacitors. Adv. Eng. Mater. 2023, 25, 2201191.
103. Wang, R.; Yan, X.; Lang, J.; Zheng, Z.; Zhang, P. A Hybrid Supercapacitor Based on Flower-like Co(OH)2 and Urchin-like VN Electrode Materials. J. Mater. Chem. A 2014, 2, 12724–12732.
104. Ji, X.; Hallam, P.M.; Houssein, S.M.; Kadara, R.; Lang, L.; Banks, C.E. Printable Thin Film Supercapacitors Utilizing Single Crystal Cobalt Hydroxidenanosheets. RSC Adv. 2012, 2, 1508–1515.
105. Wang, X.; Yan, C.; Sumboja, A.; Yan, J.; Lee, P.S. Achieving High Rate Performance in Layered Hydroxide Supercapacitor Electrodes. Adv. Energy Mater. 2014, 4, 1301240.
106. Simonenko, T.L.; Simonenko, N.P.; Gorobtsov, P.Y.; Nikitin, A.S.; Muradova, A.G.; Tokunov, Y.M.; Kalinin, S.G.; Simonenko, E.P.; Kuznetsov, N.T. Synthesis and Printing Features of a Hierarchical Nanocomposite Based on Nickel–Cobalt LDH and Carbonate Hydroxide Hydrate as a Supercapacitor Electrode. Appl. Sci. 2023, 13, 5844.
107. Gao, Y.-P.; Huang, K.-J. NiCo2S4 Materials for Supercapacitor Applications. Chem. Asian J. 2017, 12, 1969–1984.
108. Peng, S.; Li, L.; Li, C.; Tan, H.; Cai, R.; Yu, H.; Mhaisalkar, S.; Srinivasan, M.; Ramakrishna, S.; Yan, Q. In Situ Growth of NiCo2S4 Nanosheets on Graphene for High-Performance Supercapacitors. Chem. Commun. 2013, 49, 10178–10180.
109. Guan, B.Y.; Yu, L.; Wang, X.; Song, S.; Lou, X.W.D. Formation of Onion-Like NiCo2S4 Particles via Sequential Ion-Exchange for Hybrid Supercapacitors. Adv. Mater. 2017, 29, 1605051.
110. Mei, L.; Yang, T.; Xu, C.; Zhang, M.; Chen, L.; Li, Q.; Wang, T. Hierarchical Mushroom-like CoNi2S4 Arrays as a Novel Electrode Material for Supercapacitors. Nano Energy 2014, 3, 36–45.
111. Du, W.; Zhu, Z.; Wang, Y.; Liu, J.; Yang, W.; Qian, X.; Pang, H. One-Step Synthesis of CoNi2S4 Nanoparticles for Supercapacitor Electrodes. RSC Adv. 2014, 4, 6998–7002.
112. Li, B.; Liang, X.; Li, G.; Shao, F.; Xia, T.; Xu, S.; Hu, N.; Su, Y.; Yang, Z.; Zhang, Y. Inkjet-Printed Ultrathin MoS2-Based Electrodes for Flexible In-Plane Microsupercapacitors. ACS Appl. Mater. Interfaces 2020, 12, 39444–39454.
113. Tang, J.; Ge, Y.; Shen, J.; Ye, M. Facile Synthesis of CuCo2S4 as a Novel Electrode Material for Ultrahigh Supercapacitor Performance. Chem. Commun. 2016, 52, 1509–1512.
114. Tung, D.T.; Tam, L.T.T.; Dung, H.T.; Dung, N.T.; Hong, P.N.; Nguyet, H.M.; Van-Quynh, N.; Van Chuc, N.; Trung, V.Q.; Lu, L.T.; et al. Freeze Gelation 3D Printing of RGO-CuCo2S4 Nanocomposite for High-Performance Supercapacitor

Electrodes. Electrochim. Acta 2021, 392, 138992.

115. Thanh Tam, L.T.; Tung, D.T.; Nguyet, H.M.; Ngoc Linh, N.T.; Dung, N.T.; Van Quynh, N.; Van Dang, N.; Vernardou, D.; Le, T.K.; Tuan, L.A.; et al. High Electrochemical Performance of Ink Solution Based on Manganese Cobalt Sulfide/Reduced Graphene Oxide Nano-Composites for Supercapacitor Electrode Materials. RSC Adv. 2022, 12, 20182–20190.
116. Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M.W. Two-Dimensional Transition Metal Carbides. ACS Nano 2012, 6, 1322–1331.
117. Naguib, M.; Mochalin, V.N.; Barsoum, M.W.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. Adv. Mater. 2014, 26, 992–1005.
118. Sinha, A.; Zhao, H.; Huang, Y.; Lu, X.; Chen, J.; Jain, R. MXene: An Emerging Material for Sensing and Biosensing. TrAC Trends Anal. Chem. 2018, 105, 424–435.
119. Simonenko, E.P.; Simonenko, N.P.; Mokrushin, A.S.; Simonenko, T.L.; Gorobtsov, P.Y.; Nagornov, I.A.; Korotcenkov, G.; Sysoev, V.V.; Kuznetsov, N.T. Application of Titanium Carbide MXenes in Chemiresistive Gas Sensors. Nanomaterials 2023, 13, 850.
120. Pei, Y.; Zhang, X.; Hui, Z.; Zhou, J.; Huang, X.; Sun, G.; Huang, W. Ti3C2TX MXene for Sensing Applications: Recent Progress, Design Principles, and Future Perspectives. ACS Nano 2021, 15, 3996–4017.
121. Simonenko, N.P.; Glukhova, O.E.; Plugin, I.A.; Kolosov, D.A.; Nagornov, I.A.; Simonenko, T.L.; Varezhnikov, A.S.; Simonenko, E.P.; Sysoev, V.V.; Kuznetsov, N.T. The Ti0.2V1.8C MXene Ink-Prepared Chemiresistor: From Theory to Tests with Humidity versus VOCs. Chemosensors 2022, 11, 7.
122. Pazniak, H.; Plugin, I.A.; Loes, M.J.; Inerbaev, T.M.; Burmistrov, I.N.; Gorshenkov, M.; Polcak, J.; Varezhnikov, A.S.; Sommer, M.; Kuznetsov, D.V.; et al. Partially Oxidized Ti3C2Tx MXenes for Fast and Selective Detection of Organic Vapors at Part-per-Million Concentrations. ACS Appl. Nano Mater. 2020, 3, 3195–3204.
123. Chen, Y.; Yao, H.; Kong, F.; Tian, H.; Meng, G.; Wang, S.; Mao, X.; Cui, X.; Hou, X.; Shi, J. V2C MXene Synergistically Coupling FeNi LDH Nanosheets for Boosting Oxygen Evolution Reaction. Appl. Catal. B Environ. 2021, 297, 120474.
124. Li, K.; Zhang, S.; Li, Y.; Fan, J.; Lv, K. MXenes as Noble-Metal-Alternative Co-Catalysts in Photocatalysis. Chin. J. Catal. 2021, 42, 3–14.
125. Rana, G.; Dhiman, P.; Kumar, A.; Sharma, G.; Verma, Y.; Chauhan, A. Functionalization of Two-Dimensional MXene-Based Nanomaterials for Water Purifications and Energy Conversion Applications: A Review. Mater. Sci. Semicond. Process. 2023, 165, 107645.
126. Malati, M.L.; Abrahams, A.; Chauke, V.; Seopela, M.P.; Dlamini, L.N. Monitoring and Optimizing the Biocatalytic Degradation of Efavirenz with Immobilized Trametes Versicolor Laccase on Ti2NTx MXene: A Lab-Scale Wastewater Treatment Plant Process. J. Environ. Chem. Eng. 2023, 11, 110420.
127. Guo, T.; Zhou, D.; Gao, M.; Deng, S.; Jafarpour, M.; Avaro, J.; Neels, A.; Hack, E.; Wang, J.; Heier, J.; et al. Large-Area Smooth Conductive Films Enabled by Scalable Slot-Die Coating of Ti3C2Tx MXene Aqueous Inks. Adv. Funct. Mater. 2023, 33, 2213183.
128. Anasori, B.; Lukatskaya, M.R.; Gogotsi, Y. 2D Metal Carbides and Nitrides (MXenes) for Energy Storage. Nat. Rev. Mater. 2017, 2, 16098.
129. Pang, Y.; Cao, Y.; Chu, Y.; Liu, M.; Snyder, K.; MacKenzie, D.; Cao, C. Additive Manufacturing of Batteries. Adv. Funct. Mater. 2020, 30, 1906244.
130. Zhong, Y.; Xia, X.; Shi, F.; Zhan, J.; Tu, J.; Fan, H.J. Transition Metal Carbides and Nitrides in Energy Storage and Conversion. Adv. Sci. 2016, 3, 1500286.
131. Kumar, K.S.; Choudhary, N.; Jung, Y.; Thomas, J. Recent Advances in Two-Dimensional Nanomaterials for Supercapacitor Electrode Applications. ACS Energy Lett. 2018, 3, 482–495.
132. Ji, C.; Cui, H.; Mi, H.; Yang, S. Applications of 2D MXenes for Electrochemical Energy Conversion and Storage. Energies 2021, 14, 8183.
133. Zheng, X.; Cao, W.; Hong, X.; Zou, L.; Liu, Z.; Wang, P.; Li, C. Versatile Electronic Textile Enabled by a Mixed-Dimensional Assembly Strategy. Small 2023, 19, 2208134.
134. Melianas, A.; Kang, M.; VahidMohammadi, A.; Quill, T.J.; Tian, W.; Gogotsi, Y.; Salleo, A.; Hamedi, M.M. High-Speed Ionic Synaptic Memory Based on 2D Titanium Carbide MXene. Adv. Funct. Mater. 2022, 32, 2109970.
135. Abdolhosseinzadeh, S.; Heier, J.; Zhang, C. Printing and Coating MXenes for Electrochemical Energy Storage Devices. J. Phys. Energy 2020, 2, 031004.

136. Li, B.; Yu, M.; Li, Z.; Yu, C.; Wang, H.; Li, Q. Constructing Flexible All-Solid-State Supercapacitors from 3D Nanosheets Active Bricks via 3D Manufacturing Technology: A Perspective Review. Adv. Funct. Mater. 2022, 32, 2201166.
137. Azadmanjiri, J.; Reddy, T.N.; Khezri, B.; Děkanovský, L.; Parameswaran, A.K.; Pal, B.; Ashtiani, S.; Wei, S.; Sofer, Z. Prospective Advances in MXene Inks: Screen Printable Sediments for Flexible Micro-Supercapacitor Applications. J. Mater. Chem. A 2022, 10, 4533–4557.
138. Akuzum, B.; Maleski, K.; Anasori, B.; Lelyukh, P.; Alvarez, N.J.; Kumbur, E.C.; Gogotsi, Y. Rheological Characteristics of 2D Titanium Carbide (MXene) Dispersions: A Guide for Processing MXenes. ACS Nano 2018, 12, 2685–2694.
139. Vural, M.; Pena-Francesch, A.; Bars-Pomes, J.; Jung, H.; Gudapati, H.; Hatter, C.B.; Allen, B.D.; Anasori, B.; Ozbolat, I.T.; Gogotsi, Y.; et al. Inkjet Printing of Self-Assembled 2D Titanium Carbide and Protein Electrodes for Stimuli-Responsive Electromagnetic Shielding. Adv. Funct. Mater. 2018, 28, 1801972.
140. Wang, G.; Zhang, R.; Zhang, H.; Cheng, K. Aqueous MXene Inks for Inkjet-Printing Microsupercapacitors with Ultrahigh Energy Densities. J. Colloid Interface Sci. 2023, 645, 359–370.
141. Sun, P.; Liu, J.; Liu, Q.; Yu, J.; Chen, R.; Zhu, J.; Sun, G.; Li, Y.; Liu, P.; Wang, J. Nitrogen and Sulfur Co-Doped MXene Ink without Additive for High-Performance Inkjet-Printing Micro-Supercapacitors. Chem. Eng. J. 2022, 450, 138372.
142. Yuan, M.; Wang, L.; Liu, X.; Du, X.; Zhang, G.; Chang, Y.; Xia, Q.; Hu, Q.; Zhou, A. 3D Printing Quasi-Solid-State Micro-Supercapacitors with Ultrahigh Areal Energy Density Based on High Concentration MXene Sediment. Chem. Eng. J. 2023, 451, 138686.
143. Kausar, A. Polymer/Fullerene Nanocomposite Coatings—Front Line Potential. Emergent Mater. 2022, 5, 29–40.
144. Chao, Y.; Ge, Y.; Chen, Z.; Cui, X.; Zhao, C.; Wang, C.; Wallace, G.G. One-Pot Hydrothermal Synthesis of Solution-Processable MoS2/PEDOT:PSS Composites for High-Performance Supercapacitors. ACS Appl. Mater. Interfaces 2021, 13, 7285–7296.