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A review on the different types of electrode materials for aqueous supercapacitor applications

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Abstract

The recent advancements in living standards impose massive pressure on existing energy resources such as fossil fuels. Also, the increasing number of inhabitants arises the need to develop eco-friendly and sustainable energy storage systems. In this regard, a large number of researchers have paid increasing attention to the different methods for sustainable energy like the use of solar cells, LEDs, energy-efficient electronic devices, and supercapacitor technology. Since supercapacitors belong to the class of energy storage systems that provides high capacitive performance and charging-discharging stability during long cycles. They also offer higher power density than batteries and higher energy density than capacitors. Since the selection of electrode material and its electrochemical performance is the most determined parameter for supercapacitor performance. The present review focuses on the different types of aqueous electrolyte based electrode material which is differentiated based on energy storage mechanisms for aqueous supercapacitors. Furthermore, the latest nanocomposites reported have been reviewed and differentiated based on their electrochemical performance for aqueous supercapacitors. Their future implications have also been discussed.

Keywords: graphene, energy storage, supercapacitors, nanocomposites, electrode materials Classification numbers: 2.00, 4.00, 5.11, 5.15

1. Introduction

In the past few decades, the speedy advancements in industrialisation and urbanisation have resulted in deteriorated global effects such as the greenhouse effect and global warming. These consequences in combination with the worldwide increase in human population have resulted in exaggerated demands for energy which further led to put a significant strain on the prevailing power infrastructure and cause serious implications for the long run of humanity. Until now, fossil fuels such as coal and petroleum are primarily used for meeting the energy requirements of society. However, with restricted fossil fuel resources, there is a necessity for developing alternate energy storage systems. In recent decades, there has been an increasing interest in developing new technologies to handle the present energy challenges. In this context, an appreciable effort has been placed into researching and developing more economical energy storage devices and systems. An example of such an energy storage device is the supercapacitor, additionally known as the ultracapacitor. Supercapacitor technology has undergone considerable analysis and development in recent years because of its potential to permit the advancement in energy storage technology [1].

Supercapacitors are energy storage systems that offer high capacitance and low internal resistance. Also, they are capable of preserving and transmitting energy at a comparatively faster rate than batteries. The experimental set-up of the supercapacitor consists of two electrodes, an electrolyte, and a separator. The performance of supercapacitor can be defined broadly in terms of two parameters i.e. capacitance achieved and charging-discharging cyclic stability. Thus, supercapacitors with large values of capacitance and cyclic stability can be identified as a high-performance supercapacitor. However, these two above mentioned parameters strongly rely on the efficiency of the selected electrode material. Therefore, the wise selection of electrode material for supercapacitors is one of the key factors in evaluating its performance [2].

Like other energy storage systems, supercapacitors also suffer from some limitations such as lower energy density than batteries and fuel cells, high fabrication cost, self-discharging, and low potential stability [3]. Since one of the considerable factors in determining the performance of supercapacitor is the properties of electrode materials as discussed above. Thus, the major investigation focuses on developing electrode materials that will eradicate the abovementioned limitations of supercapacitors. Based on the energy storage mechanisms, different types of electrode materials are categorised broadly into two; (a) carbon-based materials that undergo one type of energy storage mechanism and (b) conducting polymers and metal oxides which undergo another type of mechanisms. Also, there is another type where composite materials are employed for energy storage. Each of these materials has its pros and cons which can be utilised and compensated respectively on combining one type of electrode material with another [3].

Therefore, in the present review article, the prime emphasis is on the emerging electrode materials, their properties, advantages, and disadvantages. Nanocomposites of these electrode materials have also been discussed and compared based on capacitance and cyclic stability achieved. Although different types of electrolytes have been optimised for supercapacitor applications, we focussed on aqueous electrolyte based electrode materials in the present review article. Also, the high-performance nanocomposite reports were indexed in the literature survey table, and based on the literature survey conclusions have been drawn along with the future aspects to achieve high capacitance and cyclic stability of the different electrode materials for aqueous supercapacitor. The electrochemical performance of different energy storage systems in terms of energy and power densities is mentioned in the Ragone plot as shown in figure 1 [4].

1.1. What are supercapacitors?

Supercapacitors are an emerging technology in the field of energy storage systems that offers high values of capacitance and long charging-discharging stability in a wide thermal operating range. Hence, the electrochemical performance of supercapacitors can be examined based on, (i) the capacitance achieved per unit gram; (ii) the number of cycles; and (iii) fast charging-discharging. A typical supercapacitor is primarily composed of two electrodes, electrolyte, separator, and binder. The properties of electrode materials play a key factor in determining the overall performance of supercapacitors. Therefore, the wise selection of electrode material is of utmost importance. The separator isolates the two electrodes electrically. The electrolyte provides the flow of ions for the conduction of current between the electrodes while the binder helps in binding the active material over the substrate [5].



Figure 1. Ragone plot for different energy storage systems [Redrawn with permission from [4]. Copyright 2017, American Institute of Physics].

Supercapacitors offer several advantages such as ease of handling, lightweight, flexibility, and environmental friendliness that make it suitable for meeting energy requirements in future generations [5]. Furthermore, to comprehend their promise, the potential of supercapacitors must be properly utilised. An efficient method to address this is to develop advanced and efficient electrode materials that offer high capacitance and long charging-discharging cycles. Recent years have seen huge interest in the analysis of various materials and strategies for their synthesis for applications in supercapacitor electrode technology.

1.2. Need & importance of supercapacitors

Among the energy storage systems, batteries have higher energy density (of the order of 10 to 10^3 Wh Kg⁻¹) but lower power density (of the order of 10^2 to 10^3 W Kg⁻¹) while the capacitors offer higher power density (of the order of 10^4 to 10^7 W Kg⁻¹) but lower energy density (of the order of 10^{-2} to 10 W Kg⁻¹). Thus, supercapacitors have emerged to bridge the gap between batteries and capacitors that is, it offers higher power density than batteries and higher energy density than conventional capacitors. Also, supercapacitors have benefits over typical energy storage devices in terms of large numbers of charging-discharging cycles, high power capability, and a strong thermal operating range [6]. The important electrochemical parameters are shown to compare batteries, capacitors, and supercapacitors as shown in figure 2 [7].

The performance of supercapacitors mainly depends upon the (i) electrochemical properties of the electrode material (such as surface area, electrical conductivity, wettability, etc); (ii) selection of electrolyte; (iii) operating voltage window and (iv) low internal resistance. The ideal supercapacitor structural organisation facilitates effective ion transportation





Figure 3. Applications of supercapacitors.

and diffusion of the electrode materials to store the charge. Therefore, it can be said that the overall performance of supercapacitors can be increased by modifying the properties of the electrode materials [8].

However, the energy density of supercapacitors is less than that of batteries and fuel cells. This necessitates coupling with batteries or alternative power sources for applications requiring energy for longer periods. Therefore, there is a growing interest in increasing the energy density in supercapacitors to a level similar to batteries. This is one of the key reasons for the recent vital interest in the analysis and development of diverse materials and synthesis methods in supercapacitor technology.

1.3. Applications of supercapacitors

The selection of the appropriate energy storage system relies on two factors, namely (i) the requirement of power and (ii) the storage process efficiency. Therefore, based on the power requirement and storage process mechanism, the energy storage system can be properly selected. Owing to high capacitance and long cycling stability, supercapacitors have now emerged as a power solution to a large variety of applications wherever higher power bursts are needed for shorter durations like in hybrid electrical vehicles, elevators, aeroplanes, fork truck, overhead crane, and lots of others [9]. The different applications of supercapacitors are shown in figure 3. Furthermore, the high power density and fast chargingdischarging cycles of supercapacitors make it liable for applications requiring higher power output such as in computer chips, sensitive mechanization, and conveyable electronic devices. However, due to limited energy density, it cannot be used for energy backup applications. Supercapacitors in combination with batteries or fuel cells work as temporary energy storage devices providing high power capability to store energy from braking [7].

Apart from having many applications, supercapacitors still suffer from low energy density, self-discharging, high fabrication cost, and low operating voltage. Therefore, nowadays research has focussed mainly on synthesizing electrode materials with high energy density without affecting power density, capacitance, and cyclic stability.

1.4. Types of supercapacitors

Since the process of storing charge is very crucial for the functioning of supercapacitors. Therefore, based on charge storage mechanisms, as shown in figure 4 [10], super-capacitors have been broadly classified into three categories which are given below:

1.4.1. Electrical double-layer capacitors. Electrical doublelayer capacitors or EDLCs are the class of supercapacitors where a charge is stored electrostatically. The oppositely charged double layers are accumulated at the junction of the



Figure 4. (a) EDLC mechanism; (b) Pseudocapacitance mechanism for supercapacitors. [Redrawn with permission from [10]. Copyright 2017, Molecular Diversity Preservation International].

electrode and electrolyte as a result of a reversible accumulation of electrolyte ions onto the surface of active electrodes. The storage mechanism is non-faradaic i.e. no charge is transferred between the electrodes chemically. Since EDLC is a surface storage process, therefore the surface properties of electrode materials such as surface area and porosity determine the optimum performance of this type of supercapacitor [9].

Carbon-based active materials such as activated carbon (AC), carbon quantum dots (CQDs), graphene, graphene oxide (GO), reduced graphene oxide (rGO), carbon nanotubes (CNTs), etc follow this kind of charge storage mechanisms. The high electrochemical stability, conductivity, porosity, and high surface area of carbon-based materials play a key role in achieving high capacitance in EDLCs. Since it was observed that higher capacitance values can be obtained from mesoporous carbon structures containing a large number of small micropores due to the partial desolvation of ions [11].

EDLCs have longer cycle life than its counterpart like pseudocapacitors due to the physical transportation of charges between the electrodes. Also, the surface charge storage mechanism facilitates fast energy input and throughput, which results in high power density but lower energy density.

1.4.2. Pseudocapacitors. Pseudocapacitors belong to that type of supercapacitors where a charge is stored electrochemically through the reversible redox reactions of electroactive species of electrode materials at the surface of active material. The charge storage mechanism is faradaic i.e. charge is transferred between the electrodes. Metal oxides (such as zinc oxide, manganese oxide, ruthenium oxide, nickel oxide, titanium oxide, etc) and conducting polymers (namely polyaniline, polypyrrole, polythionine) undergo pseudocapacitance mechanism to store the charge. The redox reactions of transition metal oxides and doping/ dedoping of CPs initiate the charge storing process in pseudocapacitors.

The performance of pseudocapacitors relies on many factors intrinsically and extrinsically. Intrinsically, it depends on the size of the particle and the architect of electrode materials. While extrinsically, pseudocapacitance depends on the accessibility of the electrode surface area. The fast redox reactions of metal oxides and conducting polymers result in the high capacitance of pseudocapacitors in comparison with EDLCs [1]. But due to the redox reactions, pseudocapacitors suffer from a lack of stability during the long chargingdischarging cycles because the possibilities of swelling and shrinking of polymeric long chains resulted in lower cyclic stability and power density of pseudocapacitors than EDLCs [5].

1.4.3. Hybrid supercapacitors. Since the value of energy density depends mainly on two factors, which are capacitance and voltage (according to the formula, $E = 1/2CV^2$). Therefore, an alternative approach is to combine the EDLC electrode with the pseudocapacitance electrode to develop a hybrid supercapacitor to give high capacitance and a wide operating range for increasing the cell total voltage. Thus, hybrid supercapacitors belong to that class of supercapacitors where simultaneous incorporation of both EDLC and pseudocapacitance mechanisms takes place. In other words, in hybrid supercapacitors, the charge is stored both electrostatically and electrochemically.

Hybrid capacitors are further divided into three categories, (i) asymmetric pseudotype electrodes in which both the electrodes are coated with completely different active materials, for example one electrode is coated with carbon material while the another with either metal oxide or conducting polymer; (ii) composite type electrodes in which carbon-based material combines with metal oxide/conducting polymers, thus enabling a single electrode to have both electrostatic and electrochemical charge storage mechanisms, both the electrodes are coated with the same active material and (iii) rechargeable battery type electrodes in which battery type electrode combines with supercapacitor electrode. In general, the faradaic electrode of the hybrid supercapacitors will result in increased energy density at the cost of low cyclic stability. Therefore, current research has been carried onto the above-mentioned types of hybrid supercapacitors to give high energy and power density with high cyclic stability.

1.5. Components of supercapacitor

The assembly of supercapacitors consists of various components, namely (i) electrode material; (ii) electrolyte; (iii) current collector; (iv) separator and (v) binder. Each of the components plays a key role in the overall functioning of supercapacitors as discussed in the given sections below.

2. Electrolyte

Electrolytes are among one of the main components that determine the efficiency of supercapacitors. Many electrolyte properties such as ion size, type, concentration, conductivity, electrochemical stability, thermal stability, internal resistance, cycle lifetime, viscosity, toxicity, melting point, freezing point, and boiling point have a profound influence on the functioning of supercapacitors.

As the energy density of supercapacitors depends mainly on the potential and capacitance. Therefore, it is more beneficial to raise the operating voltage of electrolytes in comparison to capacitance as energy density varies directly with the square of the voltage. The electrolyte's voltage here referred to its electrochemical stable potential window. The stronger the interaction between electrolyte ions and active material ions, the wider the potential window [12].

Thus, an ideal electrolyte should have certain features, namely: (i) wide operating cell voltage; (ii) high electrochemical & thermal stability; (iii) high conductivity; (iv) inertness to electrode material; (v) low combustibility; (vi) economy and (vii) eco-friendliness. However, a single electrolyte cannot have all the above-mentioned characteristics. Therefore, research has been going on to discover high-performance electrolytes for supercapacitors [6].

Based on the recent developments electrolytes have been broadly categorised into aqueous electrolytes, ionic liquid electrolytes, organic electrolytes, redox electrolytes, and solid-state electrolytes. Different types of electrolytes offer different operating voltage ranges. For instance, aqueous electrolytes have an operating potential window of 1.1-1.3 V in general but with the use of neutral aqueous electrolytes, it can be stretched up to 2 V. Also, ionic liquid and organic electrolytes offer a potential window of 3.5-4 V and 2.5-2.7 V respectively [13]. However, the present review article mainly focussed on aqueous supercapacitors as already mentioned. Thus, out of all types of electrolytes, the aqueous electrolytes are further discussed in the below section.

2.1. Aqueous electrolytes

These are primary electrolytes for supercapacitors for the reason of their durable cost and easy handling without any special need, which results in simplified congregation and fabrication of supercapacitors in comparison to organic and ionic liquid electrolytes which require a complex purification process. Also, aqueous electrolytes have higher ionic conductivity due to which they have low internal resistance as compared to organic and ionic liquid electrolytes. However, the narrow operating potential window of these electrolytes limits their use in commercial supercapacitors. The efficiency of aqueous electrolytes mainly relies on the motility of ions and size of hydrated ions as these factors directly affect the capacitance values. These electrolytes could be sub-divided into acid, alkaline, and neutral aqueous electrolytes. Examples of commonly used aqueous electrolytes are H2SO4, KOH, NaOH, NaCl, KCl, etc [12].

Based on the high ionic conductivity of H_2SO_4 i.e., 0.8 S cm^{-1} at 25 °C, it has been considered as the most primarily employed acidic electrolyte for aqueous supercapacitors. Likewise, KOH, owing to its high ionic conductivity of 0.6 S cm^{-1} for 6 M at 25 °C, has been mostly used as basic electrolyte for aqueous supercapacitors. Furthermore, neutral electrolytes offer longer voltage ranges, corrosion resistance, and safety than acidic and basic electrolytes. Sodium sulphate (Na₂SO₄) is an extensively employed neutral electrolyte in aqueous supercapacitors [14].

3. Electrode materials

The two important parameters for estimating the performance of supercapacitors, (i) high capacitance (ii) high cyclic stability, rely wholly on the properties of the electrode material. Therefore, on the basis of charge storage mechanisms, electrode materials are categorised as discussed in the previous section. In the research work so far, many active electrode materials have been reported which gave rise to high-performance aqueous supercapacitors [15].

3.1. Carbon-based materials

Carbon-based materials are primarily used electrode materials for aqueous supercapacitor applications as they possess large surface area, thermal and electrochemical stability, reasonable conductivity, porous structure, ease of electrolyte accessibility, ease of availability in various morphologies from different precursors, environmental friendliness, and low cost. These materials undergo an EDLC charge storage mechanism in which accumulation of doubly charged layer takes place at the interface of electrode and electrolyte. Thus, the cyclic voltammetry (CV) curves of these materials are rectangularshaped indicating the significant capacitive performance of carbon-based aqueous supercapacitors. Also, galvanostatic charge-discharge (GCD) curves are triangular symmetrically indicating the same [16]. Since, EDLC is a surface phenomenon, therefore surface properties such as specific surface area, surface functionalisation, pore's size, structure, and shape plays a determinant role in achieving the higher capacitance value. Thus, the larger the surface area is available to electrolyte ions for the accumulation of charge, the larger the capacitance will be. The control over the porosity and diffusion rate of carbonbased materials offers a large specific surface area which leads to large adsorption of ions resulting in high capacitance. Therefore, carbon materials with a large and approachable surface area and good conductivity are highly preferable [17].

The carbon materials with a high surface area include activated carbon (AC), carbon nanotubes (CNT), carbon nanospheres (CNS), and carbon nanofibers (CNF). There is no direct correlation between the surface area and capacitance achieved due to the lack of accessibility of all electrolyte ions to the micropores of the electrode material while the low capacitance problem can be rectified by the introduction of functional groups consisting of heteroatoms such as oxygen, nitrogen, boron, etc on the surface of carbon materials. But the functionalisation further gives rise to the difficulties such as internal resistance owing to the high reactivity of heteroatoms and perishing of electrolyte ions due to the presence of active functional groups on the surface [18].

Therefore, carbon-based aqueous supercapacitors become important to develop carbon-based electrodes with a large surface area, appropriate pore size distribution, and surface modification property. The primarily used carbonbased electrode materials for aqueous supercapacitors are discussed below.

3.1.1. Activated carbon (AC). Activated carbon is one of the most used carbon-based electrode materials for aqueous supercapacitors due to their low cost and large surface area due to porous structure. AC can be prepared from various natural carbon precursors such as wood, coconut shell, coal, sugarcane bagasse, corn grain, coffee ground, etc either by the process of activation (physically or chemically) in the controlled oxidative atmosphere. Physical activation refers to the heating of carbon precursors at high temperatures (700 °C-1200 °C) in the atmosphere of CO₂ and H₂O while chemical activation refers to heating amorphous carbon at low temperatures (400 °C-700 °C) in combination with chemicals such as chlorides, alkalis, oxyacids, etc. The process of activation results in the formation of amorphous and porous carbon in large amounts with a high surface area. Furthermore, the obtained AC structure can be divided based on pore size as follows: (i) micropores (less than 2 nm); (ii) mesopores (2 to 50 nm) and (iii) macropores (greater than 50 nm) [19].

However, the activation for longer durations deteriorates the density of electrode material, thus leads to a lower power delivery rate. Therefore, research focusses on using AC in combination with different MOs, CPs, binders, and electrolytes so that all of the surface areas can be utilised to determine the capacitance. One of the many approaches to fabricate a high-performance asymmetric supercapacitor is to choose electrode materials with different potential windows for both the electrodes. AC, because of its ability to form a doubly charged layer efficiently to facilitate the transport of ions for storing charge owing to its significant electrical conductivity and high surface area, is employed as a negative electrode in combination with MO or CP as a positive electrode. An asymmetric nanocomposite using GO/PPY hybrid nanocomposite as positive and AC as a negative electrode was fabricated. The device yields a maximum energy density of 21.4 Wh kg⁻¹ and power density of 453.9 W kg⁻¹ with cyclic stability during 5000 long cycles [20]. Also, an asymmetric supercapacitor of MnO₂/carbon nanofiber hybrid composite and activated carbon nanofibers as positive and negative electrodes was also developed. The device exhibits good long cyclic stability with high retention of 94% of its initial capacitance after 5000 long cycles [21].

3.1.2. Carbon nanotubes (CNTs). The wrapping-up of graphene sheets in which carbon atoms are sp² hybridised covalently connected leads to the formation of CNTs. These nanotubes based on graphene layers are further classified as single-walled CNTs or SWCNTs and multi-walled CNTs or MWCNTs. CNTs offer high electrical ($\approx 5000 \text{ S cm}^{-1}$) and mechanical conductivity along with high thermal stability, unique porosity due to which electrolyte ions diffuse easily and contribute to low internal resistance and large surface area $(SWCNT > 1600 \text{ m}^2 \text{ g}^{-1}, \text{ MWCNT} > 430 \text{ m}^2 \text{ g}^{-1}).$ Also, CNTs are low-cost, easy to handle, and abundantly available. These superior properties enable CNTs to be a potent electrode material candidate for aqueous supercapacitor applications [22]. CNTs generally provide high power density owing to high electrical conductivity but lower energy density as compared to AC due to the low specific surface area of the former comparatively. Furthermore, it is not easy to hold on to the innate properties of individual CNT on a visual scale. Therefore, compositing CNTs with other materials and synthesising CNTs in different morphologies resulted in the enhanced performance of CNTs for supercapacitors [23].

Since AC offers a higher surface area than CNTs, therefore a composite of CNT with AC was reported in which initially a CNT and polymer composite was prepared, and then in the controlled oxidative environment, carbonisation was formed. The AC matrix over which the charge storage process occurred was strongly supported by the CNT mechanically and electrically. The enhanced performance of the prepared nanocomposite was analysed during the 50,000 long charging-discharging cycles in comparison to 30,000 cycles performed without CNT [24]. Also, combining CNT with either conducting polymers (such as PPY, PANI) or metal oxides resulted in the formation of hybrid composites with high capacitance and cyclic stability. In these hybrid composites, the high specific capacitance of CPs or MOs contributes to the overall high capacitance of nanocomposites while CNT due to its high conductivity provides a solid backbone to the charge storage mechanisms. In a comparison of randomly tangled CNTs, vertically aligned counterparts proved to be more advantageous in terms of accessibility of electrolyte ions which results in improved charge storage and delivery rates for supercapacitors [25, 26].

3.1.3. Carbon quantum dots (CQDs). CQDs are carbon nanomaterials with zero dimensions with a size of less than 10 nm. CQDs have high aqueous, chemical, and biological stability, ease of functionalisation, less toxicity, and fine electrical conductivity. Also, CQDs show the property of fluorescence and have high inherent capacitance due to superior electronic properties. These characteristics indicate the strong ability of CQDs to act as an electrode material for energy storage applications. However, CQDs have some limitations such as low productivity, costly instrumentation, and complex synthesis procedures. Thus, the need for an economical and highly productive synthesis method for CQDs has attracted the researcher's attention to preparing CQDs from a natural source. Several research works were reported in which CQDs were prepared from chitosan; fruit and vegetable peels such as watermelon and capsicum; and plant and grass leaves via a variety of synthesis methods such microwave-assisted, hydrothermal, as pyrolysis, electrochemical oxidation, annealing, and carbonisation [27].

Compositing CQDs with either MOs or CPs results in the formation of hybrid nanocomposites with improved electrochemical properties such as high capacitance and cyclic stability. A hybrid nanocomposite of Fe₃O₄ and CQD was prepared via cost-effective hydrothermal and green solvothermal methods. The achieved capacitance of the CQDs decorated Fe_3O_4 composite was 208 F g⁻¹ with 200 long cycles [28]. Also, combining CQDs with both EDLC and pseudo material resulted in the increased interaction which leads to effective charge transportation between the components and thus a high value of capacitance. In this regard, a ternary nanocomposite of CQDs with PPY and GO was prepared by the *in-situ* polymerisation method. Here, CQDs intermediated the PPY and GO and reduced the internal resistance, thus promoted the effective electron transfer between PPY and GO for storing charge. A high capacitance of 576 F g^{-1} was obtained with the 5000 long cyclic stability for the prepared nanocomposite [29].

3.1.4. Graphene. Graphene is a single layer 2D honeycomb lattice arrangement of sp² hybridised carbon atoms. Graphene possesses high mechanical strength (\approx 1TPa), thermal conductivity (2000–5000 Wm K⁻¹), electrical conductivity (electron mobility 2.5 × 10⁵ cm² V⁻¹ s⁻¹), and specific surface area (2620 m² g⁻¹). Also, it offers a tunable bandgap and low cost. These excellent electrical, mechanical, and chemical properties enable graphene for applications including energy generation as well as a storage [30]. Furthermore, it can enhance the overall performance of resulting nanocomposites on combining with different nanomaterials. Graphene acts as the conductive matrix for different MOs and CPs onto which the charge transport mechanism occurs [31]. These hybrid nanocomposites utilise the synergistic effect of EDLC and pseudocapacitance

electrode materials in such a way that dispersion of nanoparticles of MOs and CPs takes place over the conductive network of graphene resulting in the high capacitance achieved with long cyclic stability of hybrid nanocomposites [32].

A hybrid nanocomposite of graphene with CoNi₂S₄ synthesised via physical processes of centrifugation and ultrasonication was reported. The exceptional electrochemical performance of this nanocomposite was analysed as the capacitance achieved was 2009.1 Fg^{-1} during 2000 long cycles [33]. Graphene-based ternary nanocomposites also showed superior electrochemical performance such that a hybrid ternary nanocomposite of graphene, PPY, and Cu₂O-Cu(OH)₂ was prepared by the economic electrodeposition technique. The electrochemical contributions of each of these three composites resulted in the large value of capacitance (i.e., 997 F g^{-1} and cyclic stability of 2000 long cycles). Similarly, a nanocomposite of graphene CNT and PPY was also prepared in which pyrrole was electropolymerised in the presence of CNT and PPY. The capacitance of the ternary nanocomposite achieved was 453 Fg^{-1} [34].

3.1.5. Graphene oxide (GO). As mentioned in the previous section, graphene exhibits excellent and flexible electronic, mechanical, and optical properties which make graphene an efficient building block for carbon-based electrode materials in energy storage applications. Graphene can be synthesised by a variety of techniques. Chemical oxidation followed by reduction is one of the most suitable techniques which results in the mass production of graphene at a durable cost. The process of chemical oxidation results in the formation of graphene oxide (GO) which can be further reduced to graphene and used for aqueous supercapacitors. GO is the single-layered derivative of graphene which can be synthesised in bulk directly from the oxidation of graphite or exfoliation of graphite oxide at low cost. Based on the synthesis method, different oxygen-containing functional groups such as hydroxyl, carboxyl, and epoxy are present around the edges of graphene sheets. Generally, the structure of GO consists of epoxy and epoxide groups at the basal plane while the ionisable carboxyl groups are present on the edges. The presence of ionisable groups in GO enhanced the dispersibility of GO in an aqueous medium via weak Vander Waals and dipole interactions [35].

GO exhibits a large surface area, high mechanical strength, and better electrolytic ion facilitation owing to the presence of hydrophilic oxygen-containing functional groups. Also, the oxygen-containing functionalities impart the additional pseudocapacitance to GO which results in higher capacitance and cyclic stability as compared to graphene [36]. Furthermore, GO on combining with MOs or CPs enhanced the electrochemical performance of these pseudocapacitance electrode materials by acting as a conducting platform for them such that hybrid nanocomposite of GO and PANI was prepared by the electrochemical process of co-deposition method. The SEM results indicated that PANI nanofibers were intercalated into the GO sheets. The higher capacitance

achieved is 1136.4 F g⁻¹ with 1000 long cycles in comparison to 484.5 F g⁻¹ capacitance obtained for PANI [37]. Similarly, 728 F g⁻¹ capacitance was achieved for GO/PPY nanocomposite prepared via chemical polymerisation method [20].

3.1.6. Reduced graphene oxide (rGO). As discussed in the previous section about GO, the partial reduction of GO leads to the formation of rGO. Like GO, rGO also serves as the porous and conducting platform with a large surface area for carrying out the effective electron transportation mechanism for storing charge. However, the partial reduction of GO leads to the formation of structural defects such as reduced conjugation, the formation of holes, and the presence of heteroatoms in rGO. The one and most prominent way to compensate for these structural defects are to combine this carbon material with pseudocapacitance electrode materials such as CPs or MOs. The resulting hybrid composites utilise the synergistic effect of these two types of materials (i.e., carbon-based and either CPs or MOs) which leads to the enhanced electrochemical activity of nanocomposites [38].

A hybrid nanocomposite of rGO with PANI was synthesised via diffusion-driven layer by layer assembly in which rGO acts as a scaffold onto which the nanoparticles of PANI were electropolymerised. The highest capacitance achieved was 438.8 F g⁻¹ with the 2000 long cycles [39]. A ternary nanocomposite of rGO, PANI, and PPY was also prepared by the physical process of blending. The π - π stacking of aromatic moieties of both rGO and CPs leads to improved electron transportation for storing charge and the highest capacitance obtained for nanocomposite was 317.5 F g⁻¹ with 4000 long cycles [40]. Furthermore, rGO, CNT, and Co₃O₄ based ternary nanocomposite was synthesised hydrothermally. The maximum capacitance achieved was 790 F g⁻¹ and 1000 cycle stability [41].

The above-discussed section indicated that each of the carbon-based electrode materials has its advantages and disadvantages. Furthermore, their properties can be tuned by combining these materials with another type of electrode materials in which carbon-based materials act as a conductive platform with a large surface area over which redox reactions via EDLC mechanism for storing charge will take place.

3.2. Metal oxides

Transition metal oxides offer high specific capacitances owing to the fast and reversible transportation of ions in the bulk electrodes and electrode-electrolyte interface giving rise to pseudocapacitance mechanism for storing charge. The efficiency of metal oxides as electrode material depends mainly upon the following factors: (i) electronic conductivity of metal oxide; (ii) various oxidation states of metal and (iii) redox ability of metal oxides. Metal oxide-based electrode materials possess higher energy densities and faster redox reaction ability in comparison to carbon-based electrode materials due to high specific capacitance and less resistance of metal oxides [42, 43]. The mainly used metal oxides for aqueous supercapacitors are discussed below. *3.2.1. Zinc oxide (ZnO).* Among metal oxides, ZnO is the wide bandgap (3.37 eV) semiconducting metal oxide with high binding energy (60 meV). It acts as a suitable electrode material for aqueous supercapacitor applications due to its good electrochemical activity, low cost, easy processing, non-toxicity, and environment-friendly nature. Furthermore, ZnO nanostructures have different morphologies such as nanoparticles, nanorods, nanotubes, nanospheres, nanowires, and its morphology plays a crucial role in determining its properties. However, it lacks cyclic stability and shows slow redox kinetics. This can be overpowered by combining ZnO with carbon-based materials that have high cyclic stability to form hybrid nanocomposites [44, 45].

The nanocomposites of rGO and ZnO were prepared in four different molar ratios using a one-step thermal reaction method. The resulting nanocomposite consisted of rGO as a conductive matrix onto which ZnO nanorods were decorated and the highest capacitance achieved for 1:2 molar ratios of rGO and ZnO respectively was 472 Fg^{-1} with 750 long cyclic stability indicating the high conductivity of ZnO [46]. In addition, a hybrid nanocomposite of rGO, ZnO and Cu nanoparticles was also synthesised using one-pot synthesis technique. The prepared nanocomposite interpreted the homogeneous distribution of ZnO nanorods and Cu nanoparticles over the conductive platform of rGO and the capacitance achieved was 365.5 Fg^{-1} with high cyclic stability of 3000 long cycles [47].

3.2.2. Manganese oxide (MnO). Apart from ZnO, MnO is also one among the widely studied metal oxides as electrode material for aqueous supercapacitor applications owing to its low cost, ease of availability, high capacitive performance $(1370 \,\mathrm{F}\,\mathrm{g}^{-1})$ and eco-friendliness. The high pseudocapacitance of MnO resulted from its reversible redox reactions between Mn^{+3}/Mn^{+2} , Mn^{+4}/Mn^{+3} and Mn⁺⁶/Mn⁺⁴. Like ZnO, MnO also exists in different morphologies such as nanorods, nanobundles, nanowires, nanoblets, flower like microspheres and nanowhiskers. Apart from many advantages, MnO suffers from some drawbacks such as limited surface area, low electronic conductivity and partial dissolution of MnO₂ in the electrolyte during chargingdischarging which lead to reduction in capacitance [43].

However, these limitations can be combated by compositing these oxides with carbon materials with high surface area. A sandwich type hybrid nanocomposite of MnO_2 nanospheres and rGO nanosheets was synthesised by filtration-directed self-assembly method. It was observed that MnO_2 nanospheres were uniformly embedded in the rGO matrix. The highest capacitance achieved is 446 F g⁻¹ during 1000 long cycles [48]. A ternary hybrid nanocomposite of MnO_2 was prepared with NiO and nitrogen-doped GO hydrothermally. The prepared nanocomposite exhibited a high capacitance of 1490 Fg^{-1} with 2000 long cycle stability [49].

3.2.3. Ruthenium oxide (RuO_2). Among all the transition metal oxides, RuO_2 is the most widely studied

electrode

pseudocapacitive

material for aqueous 3.3. Conducting polymers supercapacitors due to its numerous advantages. These

include high capacitance ($\approx 1000 \,\mathrm{F \,g^{-1}}$), high cyclic stability, high redox reaction ability, high metallic conductivity, high thermal stability, and wide potential window (1.2 V). Despite these advantages, the high cost of RuO₂ limits its applications. Therefore, various approaches have been used to compensate for its high costs such as synthesis of mixed oxide composites and synthesis of ruthenium-based composites with low-cost materials such as carbon materials and CPs [9, 50].

A binary nanocomposite of RuO2 and PANI was prepared in which RuO₂ nanoparticles were embedded onto the PANI layer electrochemically deposited on a tantalum sheet. The highest capacitance achieved is 474 F g^{-1} with 1000 long cycle stability [51]. Furthermore, the same composition (i.e., PANI / RuO₂) was also reported where composite thin films were prepared using chemical bath deposition technique and the maximum capacitance achieved is quite high (830 F g^{-1}) [52].

3.2.4. Nickel oxide (NiO). NiO is also one of the promising metal oxide electrode materials that can be used for aqueous supercapacitors as it offers a simplified synthesis procedure, low cost, non-toxicity, and high capacitance ($\approx 3750 \text{ Fg}^{-1}$). The electrochemical activity of NiO relies strongly on its crystal structure which depends on the synthesis temperature. During synthesis, the calcination temperature affects the crystallinity of NiO and thus changes the capacitance value. Like other metal oxides, NiO also has some drawbacks such as low cyclic stability and low electrical conductivity. These sufferings can be overcome by combining NiO with conductive and high surface area carbon-based materials such that the conductive network of carbon materials enhances the electrical conductivity of NiO and the high surface area provides the more active sites for redox reactions of NiO to take place [5, 8].

A binary hybrid nanocomposite of NiO with rGO was synthesised using an eco-friendly hydrogen reduction method. The zest of this prepared nanocomposite is that apart from acting as an additive, NiO also facilitates the reduction by acting as a catalyst. The capacitance achieved is 428 Fg^{-1} and the cyclic stability is analysed through 5000 long cycles [53]. A hybrid supercapacitor using NiO/ Graphene nanocomposite was fabricated. The NiO nanoflakes were grown in-situ using the chemical bath deposition technique on a graphene scaffold supported on Ni foam. The highest capacitance achieved for the nanocomposite is 425 Fg^{-1} and the cycle life was analysed during 2000 long cycles [54].

The above-discussed section interpreted that each of the metal oxides has its own merits and demerits. While their merits can be availed and demerits can be eradicated by combining these metal oxides with carbon-based materials where the redox reactions will be performed by metal oxides for achieving high capacitance values via pseudocapacitance mechanism for storing charge.

The high flexibility, tunable morphology and conductivity, bulk production, low cost, and doping/dedoping or reduction/oxidation ability to conduct polymers make them potent electrode materials for aqueous supercapacitors. In a comparison with bulk counterparts, CPs nanostructures have additional advantages which are as follows: (i) high electrical conductivity; (ii) large specific surface area; (iii) ease of handling due to low weight and (iv) effective transportation of ions due to short path length. Thus, CPs store charge through the reversible electrochemical process of doping-dedoping via pseudocapacitance mechanism. However, the inherent swelling-shrinkage property of CPs limits their use during long charging-discharging cycles which can be overcome by combining with carbon-based materials. These materials improved the structural orientation of long polymeric chains and also promoted the delocalisation of electrons resulting in high conductivity. In addition, nowadays research has focussed on modifying the morphologies of CPs and hybridising the CPs [55, 56]. The primarily used CPs for aqueous supercapacitors are given in the below section.

3.3.1. Polyaniline (PANI). Among all the CPs, PANI is the most promising electrode material for aqueous supercapacitor applications owing to its better electrical conductivity, bulk production, low cost, ease of synthesis, and redox ability. Furthermore, PANI exhibits three interconvertible oxidation states; (a) Leucoemaraldine salt (O.S. = +1) is the complete reduced state and on oxidation get converted to (b) emaraldine salt (O.S.= +0.5) which further oxidised to (c) pernigraniline salt (O.S.=0) which is the fully oxidised state. PANI is the p-doped CP owing to the lower n-doping potential in comparison to the reduction potential of the electrolytic solution. A protic solvent is generally preferred to PANI due to the requirement of proton for charging and discharging [57, 58].

PANI has some limitations also. During the long cycles of charging-discharging, it is highly susceptible to degradation due to the swelling-shrinkage property of the polymeric chain and has limited available surface area also. These limitations can be overcome by combining PANI with high surface area carbon-based materials which result in high capacitance with an improved electrochemical performance of PANI, for example a binary hybrid composite of PANI with rGO was prepared and the highest capacitance achieved is 715 Fg^{-1} in the 1:6 ratios of rGO and PANI respectively [59]. Also, a hybrid nanocomposite of PANI with binary nanocomposite of nickel hydroxide Ni(OH)₂ and iron oxide (FeO) doped rGO was synthesised by the process of in-situ oxidative polymerisation. The maximum capacitance achieved for this nanocomposite was quite high 2714 Fg^{-1} and cyclic stability of 2000 long cycles [60].

3.3.2. Polypyrrole (PPY). Apart from PANI, PPY is also among the promising CP based electrode material candidate for energy storage applications. PPY possesses fast reversible faradaic redox reaction ability, high energy density, wide operating thermal range, high conductivity, and reasonable cost. Its monomer, pyrrole is water-soluble and can be easily oxidised making PPY the fast-developing CP of all. Furthermore, the appropriate use of aromatic dopants enhances the electron transportation property of PPY resulting in high values of pseudocapacitance. However, sometimes the use of anionic dopants destabilises its polymeric structure which leads to the deteriorated electrochemical performance of PPY. The prime advantages of PPY as an electrode material for aqueous supercapacitor include its fast charging-discharging ability and high energy density [6, 8].

Owing to fast redox reaction capability, PPY on combining with carbon-based materials gives high pseudocapacitance, for example a hybrid ternary nanocomposite of rGO, PPY, and Cu₂O-Cu(OH)₂ was prepared by the low-cost electrodeposition method. This hybrid nanocomposite utilises the synergistic effect of both EDLC and pseudocapacitance electrode materials as the highest capacitance achieved for nanocomposite is 997 Fg^{-1} in comparison to binary GO/ PPY (500 Fg^{-1}) and rGO/PPY (685.5 Fg^{-1}) . The cyclic stability of the nanocomposite was analysed via 2000 long cycles [61]. Similarly, a hybrid ternary nanocomposite of PPY was also synthesised with graphene and CNT via in-situ polymerisation [25]. The capacitance achieved for this nanocomposite was not that much (i.e., 453 Fg^{-1}) due to the pseudocapacitance contribution of only one component (i.e., PPY) in comparison to the previous reference where there are two pseudocapacitance components (PPY and $Cu_2O-Cu(OH)_2).$

3.3.3. Polythiophene (PTh). Like PANI and PPY, PTh is also one of the CP that offers high charge carrier mobility, oxidative stability, tunable doping/dedoping ability, tunable electrochemical activity, ease of synthesis, and economy. PTh can be easily prepared by a variety of synthesis methods such as chemical, photochemical, electrochemical, templateassisted, and ultrasonic-assisted methods. However, it suffers from a sudden decrease in capacitance due to the structural degradation during long charging-discharging cycles. This demerit can be overcome somehow by forming the hybrid composites of PTh with carbon materials as these carbon materials offer a large surface area for carrying out the redox reactions of PTh [62, 63].

A binary hybrid nanocomposite of PTh and MWCNT was prepared by the electropolymerisation method and the capacitance achieved for this nanocomposite was $110 \,\mathrm{Fg}^{-1}$ with the cyclic stability of 1000 long cycles [64]. A binary nanocomposite of PTh was also prepared with different ratios of TiO2 to analyse the performance of PTh after the incorporation of TiO₂ via oxidative polymerisation method. The maximum capacitance achieved was 250 Fg^{-1} with 10:2 ratios of PTh and TiO₂ respectively [65].

Like metal oxides, CPs also suffer from pros and cons which can be utilised and compensated on combining CPs with carbon-based materials to form composites where CPs due to their tendency to show variable oxidation states S Chaudhary et al

undergo faster redox reactions through pseudocapacitance mechanism for energy storage.

3.4. MXenes

MXenes are the new class of 2D layered inorganic materials derived from a bulk crystal named MAX. These materials are in the form of molecular sheets made from the carbides, nitrides, and carbo nitrides of transition metals (such as molybdenum or titanium). MXenes possess two types of structures: (i) Mono transition metal MXenes with the one transition metal site and general formula $M_{n+1}AX_n$ (example, Mo_2Ga_2C) where M = transition metal, A = group 13 or 14 elements, X = C and/or N and n = (1-4) and (ii) Double transition metal MXenes with two transition metal sites and the general formulas $M'_2M'C_2$, $M'_2M'_2C_3$, or $M'_4M'C_4$ (examples, Mo₂TiC₂, Mo₂Ti₂C₃, Cr₂TiC₂, and Mo₄VC₄) where M' and M' are different transition metals. MXenes possess high metallic conductivity and volumetric capacitance inherently due to the presence of transition metals.

Also, owing to their layered structure, these materials undergo curling and peeling during contortion. This gives rise to the novel combination of properties such as brittleness, elastically stiffness, and heat tolerance. Furthermore, MXenes are resistant to oxidation, chemicals, and thermal damages. These materials can be prepared by the process of exfoliation of layered MAX phases to separate two MXenes sheets which are few atoms thick. Furthermore, the unique properties of these materials are utilised via intercalation. Owing to all these properties, these materials are effectively used as electrode material in aqueous supercapacitors for energy storage. Like MOs and CPs, MXenes undergo a pseudocapacitance mechanism for storing charge. For example, Ti₃C₂ MXene clay has achieved a volumetric capacitance of $900 \,\mathrm{F \, cm^{-3}}$ with the cyclic stability of 10,000 long cycles [66].

The redox mechanisms of individual electrode materials can be very different. It is the synergistic effect of the charge storage mechanism of the individual electrode material in the nanocomposite which leads to the high performance of the resulting composite as electrode material for aqueous supercapacitor applications. Patil et al have reported gold (Au) nanoparticle decorated hybrid nanocomposite of rGO and ZnCo₂O₄ utilising synergistic properties of Au nanoparticles and rGO [67]. The charge storage mechanisms involved diffusion and capacitive controlled kinetic reactions. The high cyclic stability (5000 long cycles) can be ascribed to the inclusion of Au nanoparticles and rGO in nanocomposite to make the electron transportation easier through the electrochemically active sites. Nitrides also speed up the electron storage process for storing the charge. Nongthomban et al synthesised nanocomposites of gallium nitride (GaN) with rGO with varying concentrations of GaN from 1% to 20% using a one-step chemical reduction process [68]. The hybrid mechanism proposed for the above nanocomposites has been described in such a way that the introduction of GaN nanoparticles increased the surface pores of rGO resulting in the enhanced capacitive performance (454 F g^{-1}) of the nanocomposite.

A novel composition of Cu₂O/MoS₂/rGO was also reported by Selvamani et al and synthesised via economic microwave technique [69]. The morphological and topographical studies depicted that spherically shaped Cu nanoparticles were coated with both MoS₂ and rGO thin layers. The combination of two redox materials (Cu_2O and MoS_2) with one carbon material (rGO) resulted in the high capacitance retention of 95.6% over 3000 long charging-discharging cycles. One more rGO based composition of cobalt ferrite (CoFe₂O₄) with rGO was also presented by Rani et al in which glycol functionalised CoFe₂O₄ nanoparticles were composited with rGO [70]. It was further observed that glycol functionalised CoFe₂O₄/rGO nanocomposite gives superior electrochemical performance of 551 F g⁻¹ with 98% capacitive retention after 2000 long cycles compared to bare $CoFe_2O_4/rGO$ nanocomposite.

4. Synthesis of nanocomposites

The synthesis conditions such as the temperature, pressure, amount of solvent, melting, and boiling point, etc play a role in determining the physical and chemical properties of the resulting nanocomposite. Therefore, due care must be taken in selecting the synthesis method for nanocomposites. Some of the primarily used synthesis techniques for nanocomposites that are economic, feasible, and highly productive have been discussed in the section given below.

4.1. Blending method

The blending technique is one of the typical methods used for the synthesis of composites. The prime advantage of this technique is that the ratios of individual components can be easily tuned in the resulting composite and additionally, the desired morphology can be obtained. Furthermore, the blending method is simple, low cost, and an effective way to get composites with desired properties supported by other synthesis processes [60]. For instance, the sonication-assisted blending method improves the dispersion properties and promotes the uniform distribution of individual components in the resulting composites especially polymer-based composites. A hybrid nanocomposite of MWCNTs was prepared with polystyrene matrix in which solvent blending assisted ultrasonication technique was used to increase the dispersibility of MWCNTs in polystyrene matrix [61].

4.2. Hydrothermal method

The term 'hydrothermal' basically refers to the heterogeneous reaction in an aqueous medium under the conditions of high temperature and high pressure. The hydrothermal technique is also one of the preferable technique for preparing nanocomposites due to its tunable morphology, homogeneity, and growth. This technique is especially useful for preparing composites of those substances which are insoluble in ordinary temperature and pressure (i.e., <100 °C, <1 atm). Furthermore, hydrothermal synthesis gives good quality composites in large amounts without disturbing the composition. In addition, it can be easily hybridised with other techniques such as microwave, ultrasonication, and electrochemistry to enhance the overall efficiency of the hydrothermal method. However, it has some demerits also such as expensive instrumentation (autoclaves are also known as a hydrothermal bomb) and the inability to observe the growing crystals [71].

A wide range of different morphologies has been obtained using the hydrothermal method. A hybrid nanocomposite of PANI nanostructures was prepared with graphene sheets in different morphologies via a hydrothermal assisted oxidative polymerisation method. The ultrathin layers of PANI were composited with graphene nanosheets while PANI nanofibers/graphene nanocomposite was obtained by the direct hydrothermal process [72].

4.3. One-pot synthesis method

One-pot synthesis techniques refer to those classes of techniques in which sequential chemical reactions are carried out in a single reactor (in series) to obtain the required product without isolating and purifying the intermediates during sequential chemical reactions. Thus, one-pot synthesis techniques are economic as it makes uses of little chemicals and solvents in a single reaction flask. Furthermore, it does not involve isolation and purification steps, thus, there will be no loss of material. In addition, it saves time and simplifies the synthesis process also. However, it has some disadvantages, for example compatibility of various solvents and chemicals should be ensured initially, otherwise this technique will be a failure. There are also chances that intermediate obtained in the previous step may act as an impurity for the next step. Therefore, it is a mandate to check whether the compatibility of chemicals and solvents with every single step is a clean chemical reaction.

One-pot synthesis strategy can be employed for various synthesis methods such as one-pot thermal reduction, one-pot hydrothermal, etc. A hybrid nanocomposite of Mn_3O_4 nanoparticles and graphene sheets was prepared using a one-pot hydrothermal method. The growth of Mn_3O_4 nanoparticles and reduction of graphene oxide occurred simultaneously in the one-pot. It was observed that hexagonal-shaped Mn_3O_4 nanoparticles were well dispersed on graphene sheets [73].

4.4. Oxidative polymerisation method

Oxidative polymerisation technique is one of the primarily used techniques for preparing aromatic amines, aromatic hydrocarbons, phenols, and thiophenols such as PANI and PPY. Oxidative polymerisation refers to the reaction which results in covalent bond formation between two monomer molecules at the expense of loss of two hydrogens in the presence of an oxidising agent while the monomers should have high electron-donating or oxidation tendency. This technique is quite simple, economic, and results in the bulk production of polymers. However, the amount of oxidising agent and the concentration of the aqueous medium should be properly optimised for the efficient working of this method.

A ternary nanocomposite of PANI was prepared with MWCNTs and molybdenum disulphide (MoS₂) by an *in-situ* oxidative polymerisation method. Initially, PANI/MWCNT nanocomposite was prepared via oxidative polymerisation and then oxidative polymerisation of PANI with an *in-situ* approach of ammonium persulfate (APS), MWCNT, and MoS₂ was used to prepare PANI/ MWCNT/MoS₂ nano-composite [74].

4.5. Electrodeposition method

The electrodeposition method is one of the conventional surface modification methods in which *in-situ* metallic coatings will be obtained on a conductive substrate in the solution of deposited metal salt under the influence of an electric current. This method utilised the material fully with a suitable and stable electrolyte. This method offers controllable grain size, crystallinity, and coverage area. Furthermore, electrodeposition is an economic, low temperature, and one-step process for preparing crystalline metals, alloys, and their nanocomposites in large production. It is one of the major techniques employed for preparing protective metal coatings in industries for corrosion resistance and decorative appearance. However, some precautions need to be kept in consideration during electrodeposition such as uniformity of coating and disposal of electroplating solution [75].

A hybrid nanocomposite of rGO and MnO_2 was prepared by the process of *in-situ* electrodeposition method by using GO solution and different volumes of 0.01 M manganese acetate solution. Furthermore, the electrodeposition green method was used to synthesise rGO/MnO₂-glucose carbon nanocomposite with the differently concentrated solutions of glucose [76].

Microwave-assisted method

Like other synthesis strategies, the microwave-assisted technique is the novel and facile technique in which the processing of materials is carried out quickly, systematically, and renewably. In addition, particle size, shape, and solubility can be easily tuned in microwave-assisted synthesis. Initially, microwaves react with molecules of the material and then thermal reaction or heating starts uniformly from the surface to the bulk of the material which results in thermal conductivity in fast periods. Furthermore, it is an eco-friendly method for preparing different structural arrangements such as nanostructures, film coatings, and agglomerates [77].

Like other methods, the microwave method was also used in combination with other methods such as the hydrothermal method, for instance, the microwave-assisted hydrothermal approach was utilised to synthesise Mn_3O_4 nanocrystals and rGO based composite in which crystal size, phase, and composition of Mn_3O_4 nanocrystals can be controlled and anchored on rGO [78].

5. Literature survey

The different combinations of electrode materials reported with the capacitance and cyclic stability using different synthesis methods and electrolytes are mentioned in table 1 given below for aqueous supercapacitors.

The latest literature survey (summarised in table 1) depicted that theoretical capacitances of most electrode materials are very high, thus, current studies on the improvement of the performance of aqueous supercapacitors focus on optimising the geometric structure and composition of materials and electrolytes. In this regard, the latest literature survey (summarised in table 1) reveals that majorly spinel (AB2X4) closely packed type structure based composites give high capacitance values (900 F g⁻¹) owing to their richer redox ability, high electrochemical activity, high electronic conductivity and have low cost. For instance, the highest capacitance reported so far is 2009.1 F g^{-1} with 2000 cycles for CoNi₂S₄/graphene nanocomposite. However, spinels also have some limitations such as complex synthesis procedures, poor conductivity of ferrites, impurities, defects and limited stability of spinels in acidic and neutral medium. Owing to these limitations, synthesis of pure and defect free spinels with high chemical stability is still a challenge [33].

Likewise, metal sulfide based composites also achieved higher capacitance values ($^{8}800 \text{ F g}^{-1}$) with high cyclic stability. Metal sulfides especially nickel disulfide (Ni₃S₂) and molybdenum disulfide (MoS₂) are employed as electrode materials for high performance supercapacitors as they offer high redox activity, high capacitance, high electronic conductivity and high theoretical capacity. Apart from these advantages, these sulfides have limited electrical conductivity due to non-uniformity in grain size that inhibits fast electron transportation and limited cyclic stability, which results in limited applications [69, 97].

6. Summary

The present review gives an overview of the basics of supercapacitor (its need, importance, applications, types, components). Furthermore, the components (electrode materials and electrolytes) were discussed in detail. Also, synthesis methods used primarily for nanocomposites were explained. At last, the latest literature survey enlisting all the recent combination of the electrode materials as composites with the experimental and charge storage mechanisms involved details (in table 1) for aqueous supercapacitors. Thus, it can be concluded that both the spinels and metal sulfides as an electrode material give a high performance as clearly depicted from the latest literature survey table. However, like carbonbased materials, metal oxides, and conducting polymers (as discussed in the present review article), they have some drawbacks also as mentioned above. Therefore, to achieve high capacitive performance using these electrode materials (spinels and metal sulfides) for aqueous supercapacitor applications, an efficient and facile route is to synthesise their nanocomposites with carbon-based electrode materials.

S. No.	Composite	Synthesis method	Electrolyte used	Capacitance achieved	Cycle life	Potential window	Year
1.	(RGO-PANi)	In situ polymerisation	_	361 F g ⁻¹	1000	-0.1	2012
	(RGO-PPy)			$248 \ {\rm F} \ {\rm g}^{-1}$		to 0.8 V -0.6	[79]
	(RGO-PEDOT)			108 F g^{-1}		to 0.4 V -0.4	
2.	Nitrogen enriched reduced graphene oxide and graphene oxide quantum dots based (NrGO/GQDs) nanocomposite	Combination of	6 M KOH	344 F g ⁻¹	3000	to 0.6 V 0 to 1 V	2017
		photoreduction and	1 M Li ₂ SO ₄				[<mark>80</mark>]
3.	Graphene oxide, carbon dots and poly-pyrrole based (GO/CDs/PPy) nanocomposite	NH ₃ gas Hydrothermal assisted	1 M LiCl	576 F g ⁻¹	5000	-0.2	2017
4	$Mn\Omega_{n}$ nanorods intervalating	in-situ polymerisation	1 M	512 $F g^{-1}$	5000	to 0.8 V 0 to 1 V	[<mark>81</mark>] 2014
т.	MilO ₂ nationous increating	assisted with ultra- sonication and self- assembly method	Na ₂ SO ₄	512 F g	5000	0101 V	[82]
5.	graphene oxide/polyaniline based graphene oxide/ polyaniline/MnO2 (GOPM) ternary nanocomposite p-toluenesulfonic doped polypyrrole and reduced graphene oxide based (PPy/RGO) nanocomposite	Oxidative poly-	3 M HCl	$280.3 \ {\rm F} \ {\rm g}^{-1}$	10000	-1 to 1 V	2015
6.	Polyaniline nanofibers and carbon nanotubes based (PANI-CNT) nanocomposite	Electrospinning	1 M H ₂ SO ₄	$385 \ {\rm F} \ {\rm g}^{-1}$	1000	-0.2	2016
7. composite with gra- phene	Novel PANI derivative poly (2-methyl thioaniline) coated MWCNT (PMTA@CNT) and its In-situ chemical oxidative polymerisation	6 M KOH	616 F g^{-1}	1000	-0.3 to	2016 [85]	[04]
RGO)				ac	0.7 v		
8.	RGO sheets and PPY nanowires based (RGO-PPy) nanocomposite	In-situ reduction and self-assembly method	2 M KCI	284 F g ·	5000	0 to 0.8 V	2013 [86]
9.	Zinc oxide nanoparticles decorated reduced graphene oxide sheets based (ZnO/RGO) nanocomposite	Supercritical CO ₂ assisted <i>in-situ</i> method	2 M KOH	314 F g ⁻¹	1000	-0.5 to 0.5 V	2014 [87]
10.	Diffusion driven layer by layer assembly of reduced graphene oxide/polyaniline hybrid film based (rGO/PANI) nanocomposite	Diffusion driven layer by layer assembly and bydrothermal method	1 M H ₂ SO ₄	438.8 F/g	2000	0 to 0.8 V	2017 [39]
11.	Polyaniline nanowire arrays on reduced graphene oxide sheets based (PANI-frGO) nanocomposite	In-situ polymerization	$2 \text{ M H}_2\text{SO}_4$	$590 \ {\rm F} \ {\rm g}^{-1}$	1000	-0.2	2013
12.	$\rm Fe_2O_3$ nanoparticles, PPY nanoparticles and graphene nanosheets based polypyrrole/Fe_2O_3/reduced graphene oxide (PFG)	Hydrothermal assisted oxidative polymerisation	1 M Na2SO4	$140 \ {\rm F \ g}^{-1}$	5000	-1 to 0 V	2016 [89]
13.	ternary composite Nitrogenated reduced graphene oxide nanosheets and polyaniline nanoparticles based (NRGO-PANI) in the ratio (1:1) nanocomposite	Oxidative	2 M H ₂ SO ₄	$561 \ {\rm F} \ {\rm g}^{-1}$	500	-0.2	2014
14.	PANI grafted	polymerisation Oxidation poly- merisation method	1 M H ₂ SO ₄	1045.51 F/g	1000	to 0.8 V -0.2 to 0.8 V	[59] 2014 [90]
15	reduced graphene oxide based (PANI/rGO) hybrid nanocomposite Reduced	Electrochemical dis-	0.5 M	997 F σ ⁻¹	2000	-0.8	2017
	graphene oxide/polypyrrole/Cu ₂ O-Cu(OH) ₂	position method	Na ₂ SO ₄			to 0 V	[34]
16.	BiFeO ₃ nanowire and reduced graphene oxide (BFO-RGO) nanocomposite	Hydrothermal	3 М КОН	928.43 F g^{-1}	1000	0 to 0.42 V	2018 [91]
17.	Co ₃ O ₄ nanosheets	method Hydrothermal	6 M KOH	$894 \ {\rm F} \ {\rm g}^{-1}$	3000	-0.1 to 0.4 V	2016
18.	anchored on reduced graphene oxide (Co ₃ O ₄ @RGO) nanocomposite CoNi ₂ S ₄ nanoparticles and graphene nanosheets based	method Simple physical pro- cess (ultrasonication & centrifugation)	3 М КОН	2009.1 F g ⁻¹	2000	0 to 0.5 V	2014 [33]
19.	$CoNi_2S_4/graphene \ nanocomposite \\ NiO/MnO_2@nitrogen-doped \ graphene \ oxide \ ternary \ hybrid \ composite$	Hydrothermal	6 M KOH	$1490 \ {\rm F} \ {\rm g}^{-1}$	2000	-0.34	2017
20.	NiO@MnO2/NGO nanocomposite NiCo2O4/MWCNT nanocomposite	method Supercritical CO ₂ drving method	2 M KOH	$1010 \ {\rm F} \ {\rm g}^{-1}$	1000	-0.1	2017
21.	aerogels NiS nanoparticles were	Hydrothermal method followed by super-	6 M KOH	$852 \ {\rm F} \ {\rm g}^{-1}$		-0.1 to 0.5 V	2015 [94]
	successfully incorporated into the 3D conductive graphene framework OVE DECO	critical drying					

13

S. No.	Composite	Synthesis method	Electrolyte used	Capacitance achieved	Cycle life	Potential window	Year
22.	Ultrathin CoMn ₂ O ₄ nanosheets supported on reduced graphene	Simple	6 M KOH	1089.3 F/g	5000	0 to 0.5 V	2015
	oxide (rGO)	coprecipitation method and post- annealing treatment					[<mark>95</mark>]
23.	(rGO@CoMn ₂ O ₄ NSs) Hierarchical flowerlike nickel sulfide	Hydrothermal method	2 M KOH	$880 \ {\rm F} \ {\rm g}^{-1}$	2000	0 to 0.65 V	2018
	nanostructure materials and their composite with carbon					10 0.05 V	[70]
24.	Vertically aligned Ni_3S_2 mesoporous nanosheets on three-dimensional	Electrodeposition	6 M KOH	$1886 \ {\rm F} \ {\rm g}^{-1}$	30000	-0.3	2017
	reduced graphene oxide (Ni ₃ S ₂ /3DrGO)	combined with a high-temperature postannealing processes					[27]
5.	Iron oxide decorated reduced graphene oxide (Fe3O4/rGO) nanocomposites	One-step chemical reduction method	1 M H ₂ SO ₄	416 F g^{-1}	1000	-0.4 to 0.6 V	2020
6.	FeCo ₂ O ₄ nanoparticles and rGO nanosheets based rGO/FeCo ₂ O ₄ nanocomposite	Hydrothermal method	1 M Na-SO4	$1710 \ {\rm F} \ {\rm g}^{-1}$	5000	-1 to -0.3 V	2018
	Binary metal oxide (Mn ₃ O ₄ -Fe ₂ O ₃ /Fe ₃ O ₄ nanoparticles) anchored reduced graphene oxide nanosheets (rGO NSs) based Mn ₃ O ₄ -Fe ₂ O ₃ /Fe ₃ O ₄ @rGO nanocomposite	Microwave assisted method	1 M KOH	590.7 F/g	1000	-0.05 to 0.6 V	2019 [100
8.	Mn ₃ O ₄ /rGO hybrid nanocomposite	Sol-gel based in-situ reduction method	1 M KOH	427 F g ⁻¹	3000	-0.5 to 1 V	2019 [101
Э.	Ag-Ni reduced graphene oxide nanocomposite	An <i>in-situ</i> coprecipi- tation method	3 M KOH	$897 \ {\rm F} \ {\rm g}^{-1}$	4000	-0.3 to 0.8 V	2019
).	Cobalt ferrite (CoF) and rGO based CoF-rGO nanocomposite	One-pot solvothermal method	2 M KOH	551 F g ⁻¹	2000	0.1 to 0.55 V	2020
	Co ₃ O ₄ nanoparticles and rGO based Co ₃ O ₄ /rGO nanocomposite	Hydrothermal method	3 M KOH	$754 \ {\rm F} \ {\rm g}^{-1}$	1000	-0.1 to 0.5 V	201
2.	Cobalt sulfide decorated reduced graphene oxide (CoS/rGO) nanocomposite	Hydrothermal method	6 M KOH	$813 \ {\rm F} \ {\rm g}^{-1}$	1000	-0.05	2019
3.	Cu ₂ O/MoS ₂ /rGO nanocomposite	Microwave assisted	6 M KOH	$388 \ {\rm F} \ {\rm g}^{-1}$	3000	-0.2	2020
4.	Hexgonal shaped CuS/rGO nanocomposite	Hydrothermal method	3 M KOH	$1604 \ {\rm F} \ {\rm g}^{-1}$	5000	0 to 0.5 V	2019
5.	Insitu generated Mn ₃ O ₄ -rGO nanocomposite	In-situ method	0.1 M KOH	$310 \ {\rm F} \ {\rm g}^{-1}$	10000	-0.8	2019
36.	rGO/ MWCNT Films	Sonication assisted annealing method	2 М КОН	$200 \ {\rm F} \ {\rm g}^{-1}$	15000	-1 to 0.2 V	2019 [107
			2 M LiOH 2 M NaOH				
7.	Polyaniline (PANI) nanofibers, rGO and cerium oxide nanorods (CNRs) based PANI/rGO/CNR nanocomposite	Spray drying method	$1 \text{ M H}_2\text{SO}_4$	684 F g^{-1}	6000	-0.2 to 0.8 V	2019 [108
8.	rGO/polypyrrole/ferrites nanocomposites	Hydrothermal method	1 M LiNO ₃	$261~\mathrm{F~g^{-1}}$	2500	0 to 0.7 V	2019
9.	rGO, RuO_2 and polyvinylcarbazole (PVK) based rGO/RuO_2/PVK nanocomposite	Microwave assisted	1 M H ₂ SO ₄	$2698 \ {\rm F} \ {\rm g}^{-1}$	1000	0 to 0.8 V	2019
0.	Reduced graphene oxide/tungsten oxide (rGO/WO ₃) nanocomposite	Nascent hydrogen reduction based	1 M H ₂ SO ₄	$287 \ {\rm F} \ {\rm g}^{-1}$	3000	-0.3 to 0.3 V	2019 [111
1.	Gold nanoparticles decorated rGO-ZnCo2O4 nanocomposite based Au@rGO-ZnCo2O4	Hydrothermal method	Aqueous KOH	288.5 mAh/g	5000	-0.3 to 0.5 V	202 [67
2.	Crystalline hexagonal ZnO	Chemical	2 M KOH	(specific capacity) 203 F g ⁻¹	10000	-0.9	201
3.	nanoflowers/RGO nanocomposite (ZnO-NFs/RGO NCs) Ruthenium (Ru)/reduced graphene oxide (RGO) nanocomposite	Liquid plasma-assis-	2 M H ₂ SO ₄	136.7 F/g	_	-0.6	201
.4.	Reduced graphene oxide/gallium nitride (RGO-GaN) nanocomposite	One-step	1 M H ₂ SO ₄	454 F/g	1000	-0.4	202
		chemical reduction method				to 1 V	[68]

S Chaudhary et al

Furthermore, the nanocomposites should be prepared in such a way that the advantages and limitations of both the electrode materials should be utilised and compensated, respectively.

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