Chapter

Graphene Based Nanocomposites for Supercapacitor Electrodes

Kefayat Ullah, Bakht Mand Khan, Amin ur Rashid and Won Chun Oh

Abstract

The demand for engineering and advancement of supercapacitor electrodes are increasing globally. To address the production and storage capacity of the supercapacitor electrodes, the development of new kind of composite materials are highly needful. To design materials with high surface area, excellent conductivity, porosity, and mechanical stability are the main critical points that need to be addressed. Various strategies have been utilized to fabricate excellent composite materials for supercapacitor electrodes. The effect of many composite materials was found to enhance the cyclability and storage capacities of the supercapacitor electrodes. In a class of materials, graphene-based nanocomposites and their derivatives were found to be the most excellent and suitable candidates to design and fabricate supercapacitor electrodes. The alliance of several active materials when analyzed with graphene and its derivatives was found to improve further the performance and stability of supercapacitor electrodes.

Keywords: graphene, nanocomposites, supercapacitor, electrodes, metal oxides

1. Introduction

Supercapacitor is an attractive electrochemical device that fulfills the requirement of all advanced electronic and electrical devices [1]. Supercapacitors have gained a lot of attention and have been employed in various fields, including various electronic devices, power supplies, and electric vehicles due to their high-power densities, rapid charge/discharge rates, and exceptional cycling stability [2–5]. Supercapacitors are divided into two categories depending on their charge storage capacity: 1) electrical double-layer capacitors (EDLCs) made of various carbon-based materials, while 2) pseudocapacitors made of transition metal oxides and other conductive polymers as active materials [6–9]. Ions are arranged on the interface of the electrode and electrolytes in EDLC charge storage. In this mechanism, ions adsorb and desorb quickly at the electrolyte-electrode contact, resulting in high power density. Furthermore, no chemical reactions are involved in this charge storage process; simply the transport and adjustment of ions occur during the process [10]. The energy storage of pseudocapacitors, on the other hand, is caused by the fast redox reactions or faradaic mechanisms of the electrochemically active materials in the electrode [11].

When EDLCs and pseudocapacitors are merged into a single device, a new subcategory known as hybrid capacitors is constructed [12]. The most important components of supercapacitors are the electrode materials that are used in cathodes and anodes [13]. The essential component of a supercapacitor is the electrode material, which directly influences the electrochemical performance [14]. As a result, the development and application of innovative electrode materials are critical for improving supercapacitor performance.

Graphene-based composite electrodes are regarded as one of the most effective electrode materials because of their impressive chemical, mechanical, and physical properties, such as excellent electrical conductivity, electrochemically active surface area, thermal conductivity, good mechanical strength, and optical transmittance [15–20]. Graphene can be combined with different metals to make its composites for supercapacitor electrodes. In this chapter, we mainly focus on different graphene-based composite electrode materials for supercapacitor applications.

2. Graphene based nanocomposites for supercapacitors electrodes

Graphene and its composites are the most attractive choices for increasing the functionality of supercapacitors through improving electrode conduction characteristics. Graphene has been evaluated for high-performance supercapacitor electrodes, whether as a single layer or as a beneficial component to make its nanocomposite for electrodes [21]. Composite materials are materials that combine two or even more materials with different characteristics to generate a final product consisting of remarkable properties. As previously stated, graphene has a variety of different attributions, any number of which might be exploited to create excellent composites. The presence of graphene allows for the creation of composites with exceptional properties, which ultimately improves the conductivity and mechanical strength of bulk material [22]. To make high-quality composites, graphene may be combined with polymers metals, ceramics, and some other active materials. Graphene composites have such a broad range of applications, and much research is being conducted to develop novel and fascinating materials.

2.1 Graphene/manganese dioxide composite

MnO_2 is regarded as a significant electrode option because of its significant specific capacity of about 1370 F g^{-1}, relatively inexpensive, and nontoxicity [4, 23–25]. Unfortunately, the conductivity of MnO_2 is low, and the practical specific capacitance is substantially lower than the theoretical value-specific capacitance [26]. Graphene a 2D material has the ability to enhance the electrical conductivity of MnO_2-based electrodes [27]. The large surface area and outstanding electrical conductivity of graphene enhance the interconnectivity of conductive paths for MnO_2, and the subsequent MnO_2/graphene nanocomposites demonstrated better electrochemical capacitive performance and increases the performance of energy production and storage devices.

Xia Li et al. used the electrostatic self-assembly technique to synthesize HG/MnO_2 composites. A holey approach for graphene opens up additional ion channels, improving rate capability in supercapacitors. Furthermore, the electrostatic self-assembly of holey graphene and MnO_2 nanosheets significantly improves electron transport channels, leading to a high value of specific capacitance. Furthermore, the electrostatic self-assembly technique has the ability to regulate the mass ratio of graphene and MnO_2 throughout the final composite. At 0.5 A/g, the obtained HG/MnO_2 composite electrode containing a 14.8% holey graphene composition shows a specific capacitance of about 219.3 F g^{-1}, and also at 10 A/g, it shows good capacity retention of more than 61.4%. [28].

M. Zhang et al. [29] Developed a simple alcohol-improvement methodology based on electrodeposition to synthesize MnO_2 and MnO_2/RGO composite electrode materials. Following alcohol treatment, the accumulated MnO_2 on the substrate has even more homogeneous thickness as well as looser dispersion, whereas RGO has a broader depositing area having a higher compact distribution. Furthermore, the rate of capability, cycle performance, specific energy, and specific power have all been significantly enhanced. At 1 A/g, the prepared MnO_2 electrode shows a large value of specific capacitance about 270 F/g having a retention of a capacity was approximately 83.9% and also the MnO_2/RGO electrode exhibits a good specific capacity of about 467 F/g at 1/g having 93.1% capacity retention was achieved after 2500 cycles.

M. Zhang et al [30]. used a solution-based ultrasonic-assisted technique to prepare graphene-MnO2 composite. The porous MnO_2 microspheres coated in graphene nanosheets with such a large specific surface area, allowing for rapid ion diffusion/transport. At 0.5 A/g the graphene-MnO_2 composite electrode shows an excellent electrochemical performance having a specific capacity of about 1227 F/g and keeping capacity retention at approximately 90% of its first cycle. Furthermore, the asymmetric supercapacitor depending mostly on graphene-MnO_2 composite exhibits a large energy density of about 19.6 Wh kg^{-1} at even a power density of about 351 W kg^{-1}, indicating a strong prospective as an electrode material supercapacitor.

2.2 Iron oxide-graphene composite

Iron oxides (FeOx) are attractive electrodes among transition metal oxides due to their large capacitance, low price, varied oxidation states, and environment friendly nature [31–34]. While the poor conductivity of iron oxide has hindered its super capacitive applicability, combining Fe_3O_4 with graphene can be regarded as a viable solution technique. [35]. Graphene has the ability to improve the performance of iron oxide-based electrodes.

Siyu Su et al. [36] prepared Fe_3O_4/NG composite by using a simple one-step green and scalable dry technique. The generation of C-O-Fe bond shows that Fe_3O_4 nanoparticles are closely linked with the layers of graphene, resulting in good stability and electrical conductivity. The obtained Fe_3O_4/NG composite exhibits remarkable electrochemical capabilities, including a large value of specific capacitance of about 740 F/g even at 1 A/g, exceptional cycle stability, and significant rate capability.

A.J. Khan et al. [37] effectively manufactured nanodisc-shaped Fe_3O_4/rGO composites using a quick and simple hydrothermal technique and a brief annealing procedure. The electrochemical characteristics of a Fe_3O_4/rGO composite have been improved for use as electrode material for supercapacitor applications. The prepared Fe_3O_4/rGO composite outperforms the Fe_3O_4 nanodiscs in terms of electrochemical operation, achieving a high specific capacitance of about 1149 F/g at 1.5 A/g. Furthermore, after conducting consecutive 10,000 cycles at 10 A/g, the obtained Fe3O4/rGO composite demonstrates good cyclic stability of 97.53% and amazing rate capability of 87%. **Figure 1** shows the FESEM and TEM images of the Fe_3O_4/rGO composite.

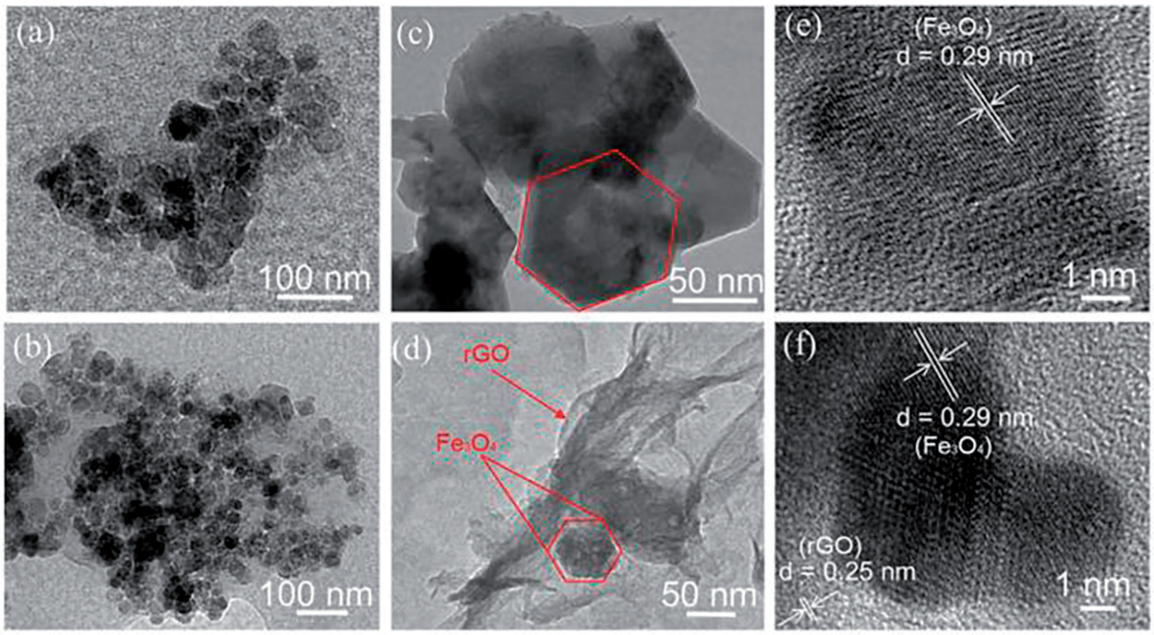

Figure 1.
(a, b) FESEM pictures of Fe_3O_4/rGO nanodiscs electrode composite at various resolutions; (c, d) TEM picture of Fe_3O_4/rGO composite; and (e, f) HRTEM pictures of $Fe3O_4$ nanodiscs and Fe_3O_4/rGO nanodiscs. Reprinted with permission from ref [37] Elsevier Copyright @ 2020.

Siyu Su et al. [38] used an effective and sustainable pyrolysis knowledge to produce nitrogen-loaded porous graphene decorated with Fe_3O_4 nanoparticles (NPGF). The NPGF nanohybrids have an equally dispersed pore architecture and a very pure content that is free of contaminants, according to structural and compositional evaluation. Furthermore, electrochemical characterization confirms the excellent electrochemical efficiency, which includes specific capacitance of about 713 F g^{-1} even at 1 A g^{-1}, remarkable capability rate having retention of capacity of about 77.3% and also shows best capacity retention of approximately 67.9% whenever the current density is rapidly increased from 1–10 and 20 A g^{-1}, as well as exceptional cycling stability (after 3000 it shows a capacitance retention about 94.3% .

By using a chemical reduction-high-temperature process, Zhang et al. [39] created graphene/Fe3O4 (GN/Fe_3O_4) nanocomposites as the electrode of supercapacitors. The surface of graphene is routinely decorated with Fe_3O_4 particles of equal size. At 0.5 A/g, the obtained GN/Fe_3O_4 composite electrode delivers a good specific capacitance about 265.6 F/g. Ultimately, the button supercapacitors were built using the produced composite materials as electrodes. After 100 consecutive charging / discharging cycles, the nanocomposites demonstrate constant capacitance efficiency. After 500 charging/discharging cycles, the capacitance efficiency remains above 80%, suggesting that the nanocomposite has outstanding cycle stability.

Mustafa Aghazadeh et al. [40] used a simple one-step electrochemical approach to create 3D N-combined porous graphene/magnetite nanoparticles hybrids on nickel foam (Fe_3O_4/3D-NPG/NF electrode). Three-dimensional nitrogen combined with porous graphene are electrophoretically synthesized on Ni foam in this process, while magnetite particles are electrochemically deposited on the surface of 3D-NPG layers. In contrast, clean Fe_3O_4/NF and 3D-NPG/NF composite electrodes was produced by depositing Fe_3O_4 particles and N-doped graphene individually over Ni foam. At 2 A/g, after 5000 GCD cycles, the obtained Fe_3O_4/3D-NPG composite electrode shows good specific capacity value about 715 F/g and also delivers cycle life about 94.3%.

2.3 Cobalt oxide—graphene composites

Co_3O_4 is one of the extensively investigated transition metal oxides for supercapacitor applications because of its long-term cycle performance, wide surface area, high conductivity, superior corrosion resistance, and natural availability [41–45]. However, Co_3O_4 has weaker electronic conductivity dramatically reduces its practical applicability. To address this issue, through a growth mechanism, Co_3O_4 is mixed with electrically conductive carbon-based materials to produce a hybrid nanocomposite [46, 47]. Because of its large surface area and exceptional electrical conductivity, graphene is the most suitable candidate to combine with Co_3O_4 to enhance the electrochemical characteristics of the Co_3O_4 electrode.

Venkatachalam et al. [48] used a hydrothermal technique to produce a 1D/2D Co_3O_4/rGO composite. The Co_3O_4/rGO composite electrode demonstrated greater specific capacitance and improved cycle stability than the conventional Co_3O_4 electrode. At 0.5 A g^{-1}, the composite material provided an exceptional supercapacitance of about 916.6 F g^{-1}.

S. Sagadevan et al. [49] used a straightforward hydrothermal method to synthesize a Co_3O_4/rGO nanocomposite that was then used as an appropriate electrode in supercapacitors. The addition of rGO in Co_3O_4 improved the electrochemical performance of the produced Co_3O_4/rGO nanocomposite. The Co_3O_4/rGO composite-based supercapacitor obtained a maximum specific capacitance of about 754 Fg1 as well as outstanding stability, holding 96% capacity after 1000 consecutive cycles. The reduction in surface area of graphene sheets is responsible for the stability, rise in specific capacity, wettability, and stability of electrode materials. As a result, the electrochemical behavior of Co_3O_4/rGO nanocomposite makes it an obvious option for a high-performance supercapacitor. **Figure 2** shows SEM pictures of graphene oxide, Co_3O_4, and Co_3O_4/rGO composite.

M. Yun et al. [50] used a one-step hydrothermal assembly procedure to make a high-capacitive Co_3O_4/HG composite electrode. Holey graphene offers a suitable framework for high electrical conductivity in the prepared electrode; the numerous holes in holey graphene give a shorter ion channel, and the Co_3O_4 nanoparticles encapsulated in the holey graphene network give high capacitance. As a consequence, the Co_3O_4/HG composite electrode shows excellent performance as compared to the pure Co_3O_4 electrode. At 1 A/g, the Co_3O_4/HG composite-based supercapacitor provided a high value of specific capacity of about 825 F g^{-1} at 1 A g^{-1} with higher rate capacity after further refining mass ratio of Co_3O_4 to holey graphene.

Y. Jiang et al. [51] used a simple and cost-effective method for the preparation of graphene/Co_3O_4 composite through one-pot ball-milling of graphite, $Co(CH_3COO)_2$ and $(NH_4)_2CO_3$ (**Figure 3**). Graphite was inserted by $(NH_4)_2CO_3$ and simultaneously separated into a few layers of graphene sheets having consisted of functional groups during the process. Mechanochemical interactions involving $(NH_4)_2CO_3$ and $Co(CH_3COO)_2$ were then used to generate Co_3O_4 nanocrystals on the interface of graphene sheets. The two components' synergistic effects increase electron/ion conduction and capacitive responses, resulting in outstanding rate performance and a large value of specific capacitance for graphene/Co_3O_4 composite electrodes.

2.4 Nickel oxide- graphene composite

Nickel oxide (NiO) is considered to be one of the best electrode materials because of its affordable cost, non-toxicity, good chemical/thermal stability, easily accessible, and eco-friendly nature [52–58]. Oxides of Ni are highly fascinating because

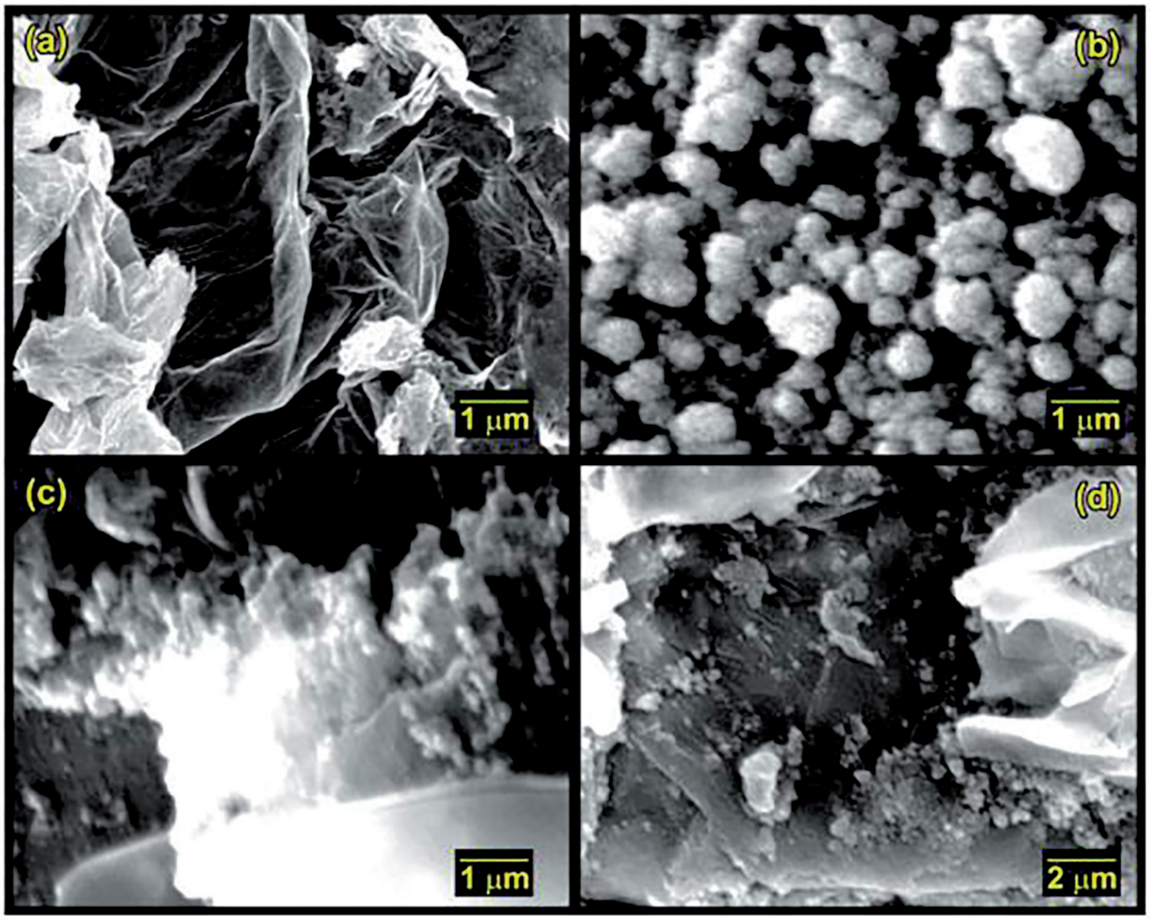

Figure 2.
SEM pictures of (a) Graphene oxide; (b) Co_3O_4; and (c & d) Co_3O_4/rGO nanocomposite. Reprinted with permission from ref [49] Elsevier Copyright @2020.

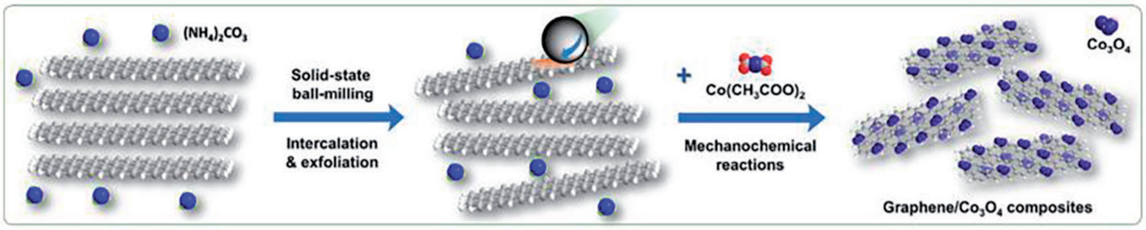

Figure 3.
Synthesis procedure of graphene/Co_3O_4 composites electrode by ball-milling technique. Reprinted with permission from ref [51] Elsevier Copyright @2020.

of numerous oxidation states exhibited by Ni [59]. Combining two-dimensional NiO nanosheets with graphene can increase electrical conductivity of the material, which has proven to be a very successful method of improving the electrochemical characteristics of NiO-based electrode materials [60].

Y. Zhang et al. [61] used an electrode-assisted plasma electrolysis technique to produce rGO/NiO composite electrodes. This approach is simple and quick, allowing for one-step production of rGO/NiO composites. At 1 A/g^{-1}, the obtained rGO/NiO composite exhibits a good value of specific capacitance of about 1093 F g^{-1}. It also has good cycle stability, as well as coulombic efficiency about 90.6% was retained after 5000 cycles. **Figure 4** shows the preparation procedure for rGO/NiO composite and HRTEM images of rGO/NiO composite.

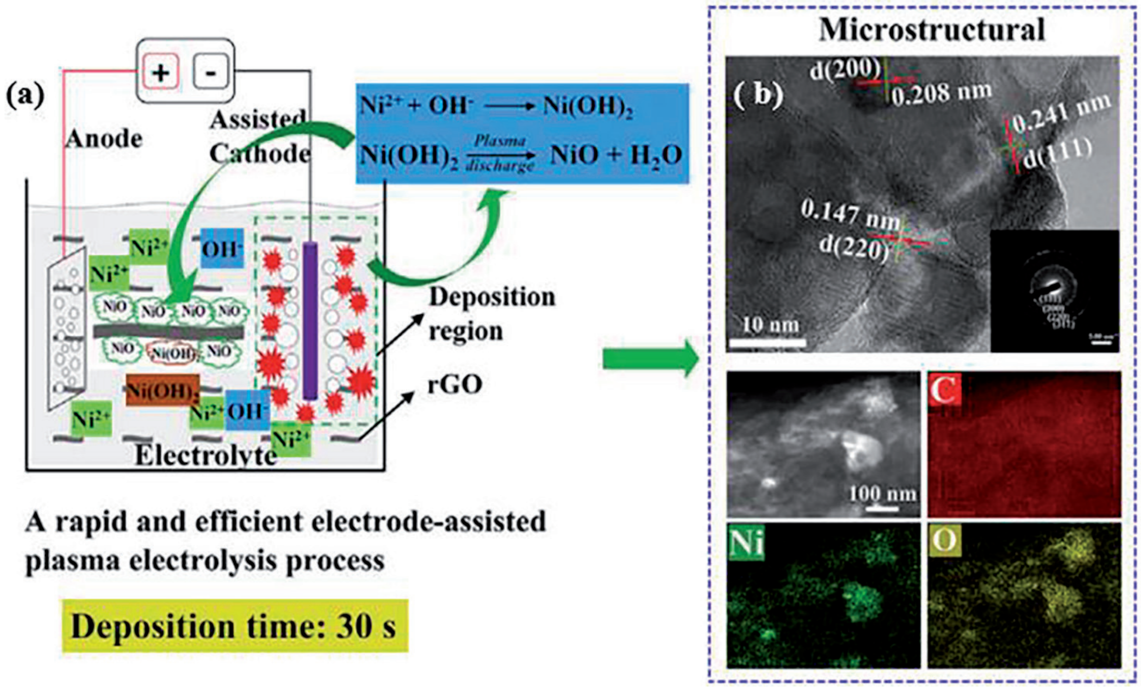

Figure 4.
(a) The electrode-assisted plasma electrolysis method equipment; (b) rGO/NiO composite electrode HRTEM image; and (c) The SAED profile of the prepared rGO/NiO composite electrode is shown in the inset. Images of rGO/NiO composite. Different EDS-elemental mapping: of C, Ni, and O elements. Reprinted with permission from ref [61] Elsevier Copyright @ 2020.

M. Sethi et al. [62] developed a solvothermal technique to easily synthesize porous graphene-NiO (PGNO) electrodes using a mixed solvent solution. When the PG is properly loaded onto the NiO nanoflakes, a stronger composite structure is formed, which contributes to resisting volumetric changes throughout electrochemical cycling. The obtained composite material shows an amazing specific capacitance of about 511.0 F g^{-1} for the one electrode at 5 mV s^{-1}, good power density, and excellent cycle stability. The excellent electrochemical performance of this composite is principally attributed to the synergistic effect of the constituent materials, which offered an effective ion reservoir as well as mechanical strength, allowing for continuous transfer of electrolyte ions during much of the electroactive material once confined to charge and discharge processes.

Shu-xia Yuan et al. [63] used heterogeneous self-assembly to create a GO/$Ni(HCO_3)_2$ composite, which was then thermally treated to produce rGO/NiO. The prepared rGO/NiO composite has a porous volume of about 0.26 cm^3 g^{-1} and a larger specific surface area (121.3 m^2 $g^{-1)}$ and porous volume of about 0.26 cm^3 g^{-1}. Because of the release of H_2O and CO_2, The hierarchical porosity dispersion of rGO/NiO composite is around 2–100 nm. Because of its porosity dispersion and large specific surface area, the rGO/NiO composite shows a larger value of specific capacitance of about 919 F g^{-1} at 0.5 A g^{-1}, and an enhanced rate capability of about 71% was achieved whenever the current density is increased from 0.5 to 5 A g^{-1}.

2.5 Zinc oxide- graphene composite

ZnO is a highly interesting electrode material due to its affordable cost, environmentally friendly nature, nontoxicity, availability, high specific energy, and excellent electrochemical stability [64–68]. Because of the synergistic interaction between the constituents, a novel nanocomposite made of ZnO, and graphene is predicted to have unique characteristics and capabilities. Many innovative techniques have been developed to produce graphene-based zinc oxide nanocomposites and their potentially advantageous properties [67]. Graphene-based ZnO composites electrode has the ability to improve the performance of supercapacitor. R Kumar et al. [69] used a simple and rapid microwave approach to synthesize ZnO NPs and bind them to rGO-NSs surfaces to produce ZnO/rGO nanocomposite for supercapacitor electrode application. At 30 mV/s, the electrode of ZnO/rGO nanocomposite displayed a good specific capacitance of about 102.4 F g^{-1}. After 3000 cycles, the capacitance stability was reattained at 82.5%.

M miah et al. [70] used a simple ex-situ wet chemical procedure to produce porous ZnO nanospheres implanted on rGO (ZnO/rGO composite). At 1 A g^{-1}, the ZnO/rGO composite electrodes deliver a good specific capacitance of about 949 F g^{-1}. The ZnO/rGO composite also has remarkable cyclic stability, retaining 91% of its original capacitance during 10000 cycles. The pseudocapacitive effect of very porous ZnO nanospheres and the EDLCs of reduced graphene oxide increase specific capacitance.

Jianping Xu et al. [71] used a straightforward hydrothermal method to produce ZnO nanorods/NG composite electrodes. ZnO nanorods with length of 1–2 m and diameters 50–100nm was supported uniformly distributed on NG networks. The prepared ZnO/NG composite has good electrochemical performance, having a large value of specific capacity of about 237.18 F/g at 0.5 A/g, rate capability of about 150 F/g at 10 A/g, and after 2000 cycles it shows long-term stability of about 90.8%.

3. Optimization of graphene electrode-electrolyte for supercapacitors

Carbon materials with large surface areas for charge storage are now the most researched materials. Despite these huge precise surface areas, the charges substantially deposited on the carbon electrodes. The deposition is somehow restricted by many factors, such as volume expansion, layer formation on the surface, surface-to-volume ratio, etc. [72]. Therefore, an alternate electrode material is needed to enhance the performance of supercapacitor electrodes. Metal oxides and graphene is considered to be the exceptional electrode ingredients to enhance the performance of supercapacitors.

Electrolyte parameters, particularly specific capacitance and energy density are critical in determining the capacitive efficiency of electric double-layer capacitors (EDLCs). In particular, electrolytes with such a large electrochemical stability window (ESW) can provide superior specific capacitance as well as density, and that is why ionic liquid-based electrolytes have received a lot of attention. The quantity of ionic liquid (IL) is a significant parameter for controlling its viscosity, potential window, and ionic conductivity, which is represented in the EDLC working voltage and has yet to be well investigated [73]. A pseudocapacitor achieves charge aggregation by faradic reactions (redox reactions) of redox-active materials deposited on the electrodes or immersed in fluids. Because of their excellent redox characteristics, metal oxides have frequently been employed as cathodes for those deposited on the electrodes [74].

Graphene-based micro-supercapacitors on standard Xerox paper substrates were created in response to future demands for flexible, simple, and moderate energy storage devices. To enhance the overall performance of the device, the usage of redox-active species (iodine redox couple) was investigated. At 6.5 mA cm^{-3}, the smart printed device based on graphene composite had an amazing high volumetric capacitance of 29.6 mF cm^{-3} (volume of entire device). These electrodes contain redox-active potassium iodide. Surprisingly, the device demonstrated enhanced volumetric capacitance of 130 mF cm^{-3}. In an H_2 SO_4 solution, the maximal density for a graphene +K device was determined to be 0.026 mWh cm^{-3} [75].

Surjit Sahoo et al. [76] described a unique supercapacitor device that uses 2D graphene sheets as electrode material. The markedly high energy storage and a porosity PVDF electrolyte incorporating $TEABF_4$ as a solid-like piezo-polymer separator were used. When placed under stress, stresses ranging from 5 to 20 N, the porous PVDF film produced a voltage ranging from 4 to 11 V. The graphene polymer composite device had the highest particular device capacitance of 28.46 F g^{-1} (31.63 mF cm^{-2}) as well a specific energy of 35.58 Wh kg^{-1}, as well as a great power density of 7500 W kg^{-1}. The above discussion shows that the optimum composition of electrolyte, as well as electrode configuration, is very important to obtain high capacity as well as cyclability.

4. Conclusion

Regarding graphene's amazing and unique properties, it is one of the best-known materials that may be applied for a variety of purposes. Graphene can be applied as electrode material in energy storage devices including rechargeable batteries and supercapacitors to store, absorb, and release large amounts of energy. Moreover, graphene-based metal oxides have the ability to increase the energy density, capacity, and performance of supercapacitors. Metal oxides have been considered one of the best electrode materials for supercapacitor application due to their affordable cost, easy synthesis, high capacity, environment friendly nature, and non-toxicity. However, conventional metal oxides have many disadvantages which limit their practical application including weak cyclic stability, low electrical conductivity, low power, and energy density. Graphene a 2D has the ability to solve these problems. Graphene can be combined with these metal oxides to make its composites to improve the performance of supercapacitors. Moreover, much attention has been focused in recent years on structural architecture, material production, and device performance assessment. To achieve the predicted full-scale actual use, the electrode materials' efficiency, as well as reproducible quantity, must be increased in the near future.

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