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Review

Recent Developments in Supercapacitor Electrodes: A Mini Review

Sumedha Harike Nagarajarao [1], Apurva Nandagudi [2], Ramarao Viswanatha [3], Basavanakote Mahadevappa Basavaraja [2], Mysore Sridhar Santosh [4,5,*], Beekanahalli Mokshanatha Praveen [1,*] and Anup Pandith [6,*]

1 Department of Chemistry, College of Engineering and Technology, Srinivas University, Mukka, Mangalore 574146, India; hnsumedha@gmail.com
2 Department of Chemistry, PES University, 100 Ft. Ring Road, BSK 3rd Stage, Bengaluru 560085, India; apurvagudi@gmail.com (A.N.); bmbasavaraja@pes.edu (B.M.B.)
3 Centre for Incubation, Innovation, Research and Consultancy (CIIRC) and Department of Chemistry, Jyothy Institute of Technology, Thataguni, Bengaluru 560082, India; vishwahosur@gmail.com
4 Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India
5 Coal to Hydrogen Energy for Sustainable Solutions (CHESS) Division, CSIR—Central Institute of Mining and Fuel Research (CIMFR), Digwadih Campus, Dhanbad 828108, India
6 Department of Chemistry, School of Natural Sciences, Kyung Hee University, Seoul 02447, Korea
* Correspondence: santoshms@cimfr.nic.in (M.S.S.); bm.praveen@yahoo.co.in (B.M.P.); anuppandith@khu.ac.kr (A.P.)

Abstract: The use of nonrenewable fossil fuels for energy has increased in recent decades, posing a serious threat to human life. As a result, it is critical to build environmentally friendly and low-cost reliable and renewable energy storage solutions. The supercapacitor is a future energy device because of its higher power density and outstanding cyclic stability with a quick charge and discharge process. Supercapacitors, on the other hand, have a lower energy density than regular batteries. It is well known that the electrochemical characteristic of supercapacitors is strongly dependent on electrode materials. The current review highlights advance in the TMOs for supercapacitor electrodes. In addition, the newly discovered hybrid/pseudo-supercapacitors have been discussed. Metal oxides that are employed as electrode materials are the focus of this study. The discovery of nanostructured electrode materials continues to be a major focus of supercapacitor research. To create high-performance electrode materials from a morphological standpoint, various efforts have been attempted. Lastly, we analyze the supercapacitor's evolving trend and our perspective for the future generations of supercapacitors.

Keywords: supercapacitors; metal oxides; hybrid supercapacitors; electrode pseudocapacitors; energy density; future trend; power density; redox mechanism

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1. Introduction

The challenges of global environmental pollution with climate change are expanding to substantial levels as a result of the fast growth of the global economy, which is speeding the consumption of fossil fuels, such as natural gas and coal fuel. Developing tidal, wind, solar and other forms of renewable energy is one strategy to address existing energy and pollution issues [1]. However, environmental concerns severely limit the use of renewable clean energy sources, and electricity production is inconsistent. As a result, developing effective and dependable energy storage systems is critical and urgent [2]. There may be an imbalance between supply and demand of electricity, not only for renewable energy sources but also for the grid system, opening spatial and temporal gaps between the availability of the energy and its consumption by end users. In this case, energy storage systems are also needed [3]. Supercapacitors have gained more interest in recent years as a new form of storage devices because of their high-power density, fast charge/discharge rate, and very

long cycle life. Portable electronic devices, hybrid power automobiles and renewable energy systems all have a lot of potential for supercapacitors. Supercapacitors (SCs) are sources of energy that sit between batteries and capacitors. They could hold greater energy and deliver it at larger power units than capacitors. SCs are attractive devices for energy storage because of these characteristics, as well as their excellent cyclability and long-term stability. SCs are still being used in a variety of applications, either in conjunction with other energy storage devices (most notably batteries) or as self-contained energy sources [4]. Electrical double-layer capacitors (EDLCs) and pseudocapacitors are two types of supercapacitors [5]. The charge accumulated on the interface between the electrolyte and electrode stores energy in EDLCs, whereas the energy is stored in pseudocapacitors via a quick and reversible faradaic redox process [6]. The low energy density of supercapacitors is still the hurdle. The formula of energy density is $\frac{1}{2} * C * V^2$, where energy density is represented by E, capacitance is C, andthe potential window is denoted by V. The energy density is dependent on both capacitive and operative voltages, and it can be improved by raising the potential window and choosing a high capacitance electrode material. The performance in electrochemical activity of supercapacitors is almost dependent on synthesis methods and design of materials. In other words, the electrode materials used in supercapacitors have a significant impact on their performance. Transition metal oxides (TMOs), conductive polymers, and carbon materials are the three types of electrode materials. For EDLCs, carbon materials are commonly employed as electrode materials [7,8]. They feature a pore size distribution, high specific surface area that may be adjusted, and great electrical conductivity. Carbon compounds can give high power density but poor energy density due to the storing method in EDLCs, which restricts overall results [9]. Carbon nanotubes, graphene, and carbon nanofibers have all been explored extensively as electrode materials. Further, the carbon materials Csp has affected the EDLCs capacity, and the usage of these types of carbon materials is limited because of their high cost. The pseudocapacitive and conductive properties of the polymer are good but, again, it has gained very little stability. On comparing all, TMOs have a higher energy density, specific capacity (100–2000 F/g) and better chemical stability than conductive polymers [10,11]. Many transition metal oxides are being studied in order to achieve extraordinary capacitance; ZnO, Co_3O_4, and MnO_2 have been extensively studied because of their easy availability and good capacity. Metal oxides such as the AB_2O_4 (A/B-Co, Mn, Ni, Mo) type show less electrical conductivity because of the presence of other metal ions' and elements' synergistic effect [12]. Furthermore, metal molybdates ($AMoO_4$) and spinel cobaltates (XCo_2O_4; X = Cu, Mn, Ni, etc.) have piqued researchers' interest due to their low cost, improved electrochemical activity, and easy availability [13].

In this study, metal oxides like MnO_2, Co_3O_4, ZnO, spinel cobaltates, NiO, CuO, XCo_2O_4 (X = Ni, Mn, Cu), and metal molybdates ($AMoO_4$; A = Ni, Co, Zn, Mn) are effectively studied and their problems in practical applications are discussed [14,15]. This study also includes synthesis methods, nano scale preparation of materials, oxygen vacancies, quantum dot modification, and battery-type material. In detail, we particularly discussed the most recent materials for supercapacitor applications and their future developments [16,17].

2. Transition Metal Oxide Electrode Materials

2.1. Co_3O_4

The Cobalt oxide belongs to the spinel family, and theoretical capacity of Co_3O_4 is found to be 3560 F/g [18]. Moreover, it is a cheap and environmentally friendly compound with excellent durability and stability. However, the capacitance is varied a lot in many applications from theoretical capacitance value. The lower conductivity, high volume expansion and contraction, slow kinetics, and particle aggregation are the reasons behind this variation in capacitance [19,20].

2.2. Co_3O_4 Nanoparticles

The big surface area and large active sites are the two major advantages of nanoparticles/nanomaterials. The ion diffusion path is one of the favorable conditions, as diffusion is easy due to the very short pathway. Morphology and dimension are important factors behind the maximum capacitance of nanomaterials. Different types of Co_3O_4 materials were reported so far, such as nanofibers, nanosheets, nanowires, and nanoparticles. Yue et al. synthesized Co_3O_4/rGO composite by a simple, environmentally friendly hydrothermal method [21]. A 3D structure of a small Co_3O_4 material is allowed to disperse on rGO flakes to show better electrochemical activity than Co_3O_4 nanowires. Indira-Priyadarshini et al. prepared Co_3O_4/rGO-120-12 and achieved capacitance of 1152 F/g at 1 A/g of current rate [22]. By using PVDF (polyvinylidene fluoride), carbon, and Co_3O_4 nanoparticle in the ratio of 1:1:8, a slurry was made and coated on nickel foam to get capacitance of 761 F/g at 11 mA/cm^2 [23]. Here, adding PVDF hinders the capacitance of the material because it causes a decrease in the interaction between the active material and collector, which tends to result in a lower number of active sites and, hence, a lower charge transfer rate. On the other hand, growing Co_3O_4 NPs directly on the metal foam, carbon sheets and carbon cloth can eliminate the need for binders and conducting materials [24,25]. Moreover, Ag-Co_3O_4 nanosheets grown on Ni foam exhibit the excellent capacitance of 1323 F/g at 10 A/g current rate and show retention of 104% of initial capacitance at 2000 cycles. The Co_3O_4/Nickel foam material prepared by Wang and Yang et al. shows an excellent capacitance of 1606 and 883 F/g at 1 A/g current density, respectively [26].

2.3. Synthesis of Co_3O_4 Nanomaterials

The metal organic frameworks (MOFs) type of materials have gained popularity in recent years in applications such as electrocatalysis, adsorption of gas, degradation of pollutants, energy devices, and so on. MOFs are also regarded to be an excellent template for the creation of Co_3O_4 nanoparticles because of their tunable porosity structure, variable pore size distribution, and large surface area [27,28]. The Zeolitic Imidazolate Frameworks 67 acts as a precursor to synthesize Co_3O_4 NPs, and Co_3O_4 material is converted by the calcination method to gain a good capacity of 190 F/g at 5 A/g. The composite α-Co/Ni$(OH)_2$@Co_3O_4-70 prepared by Bao et al. exhibits a large number of reactive sites, including good charge diffusion channels. Because of this, it shows an excellent capacity of 1000 F/g at 1 A/g current rate [18]. The addition of active carbon to α-Co/Ni$(OH)_2$ increases the capacity retention to 72.3% at current density of 10 A/g. In addition, it delivers 0.075 kW/kg and 23.88 Wh/kg of power and energy density, respectively [29]. In another way, Wei et al. developed a process where thermal treatment converts ZIF-67 into ultrathin Co_3O_4 nanoparticles. A very good result in oxygen evolution reactions of 2D-Co_3O_4 ultrathin nanomaterials is because of its Tafel slope value of 74 mV/dec and potential of 230 mV. The 3D porous carbon developed by Li et al. shows low specific capacitance of 423 F/g at current rate of 1 A/g. The low capacitance of material is due to the usage of 3D graphene/Co-metal organic framework (MOF) as a precursor, which slows down the transportation of electrons between electrolyte and active material [29].

The binders were used to lower the interparticle resistance offered by materials by Hans group, and they proved the increased activity of Co_3O_4@$CoNi_2S_4$ arrays on carbon cloth. Moreover, the synergistic effect of the Co_3O_4 compound is used to improve the electrochemical activity of $CoNi_2S_4$ and obtained 244 mAh/g of capacity at 1 A/g. Here, capacity retention of 86% is achieved even after 10,000 cycles [30]. On other hand, Co_3O_4@$CoNi_2S_4$/AC material shows 884 W/kg and 55 Wh/kg of energy and power density, respectively. The electrode of Co_3O_4@ graphene sheets prepared by Liao et al. exhibits outstanding specific capacity of 3840 F/g, and, moreover, it can bend at 0–150° with no loss in capacitance.

2.4. MnO_2

MnO_2 has been thoroughly investigated as the highly efficient TMO due to its abundant natural occurrence, lack of environmental pollution, and higher theoretical specific capacitance (1380 F/g) [31]. The MnO_2 material is limited in supercapacitor applications; this is because of a much lower charge transfer rate [32].

2.5. Carbon@MnO_2

The huge surface area and great electrical conductivity are the key factors behind the large use of carbonaceous materials like graphene, carbon nanofibers, carbon nanotubes, and carbon nanowires. In order to achieve a good capacity of material, there should be very little path difference between the electrolyte and electrode surface, which can be seen in carbon materials [33]. The N-doped hollow HNC@MnO_2 3D cores shell synthesized by Cai and coworkers exhibits specific capacitance of 247 F/g at 0.5 A/g current rate [34]. Long and coworkers prepared δ-MnO_2 on carbon cloth, which exhibited excellent power and energy density (asymmetric device) of 1198 W/kg and 49 Wh/kg, respectively. Lei et al. developed MnO_2nanosheet@CNTframework through the chemical vapor deposition method.

Commercial carbon compounds, on the other hand, are prohibitively expensive and difficult to prepare on a largescale due to their high cost and complicated preparation process. As a result, developing low-cost and renewable materials is critical in order to meet rising demand [35]. Biomass is a renewable resource with a large value of usage. Yang et al. prepared MnO_2/biomass-based porous carbon via hydrothermal approach by using banana peel as a carbon source, which shows 139 F/g of specific capacitance at 300 mAh/g of current density and 70 F/g at current rate of 10 A/g [36,37].

2.6. Nickel Oxide

Nickel oxide (NiO) has gained a huge amount of value in recent years because of its unique properties in terms of heat, light, electricity, sound, catalysis, and magnetism properties [38]. As a result of their environmental friendliness and huge availability, they are often employed in the areas of supercapacitors. Because it has two or more oxidation states, it promotes rapid redox reactions, which contributes to storage techniques that are in charge. At 0.5 V potential window, nickel oxide exhibits theoretical capacitance of 2584 F/g [39]. Unfortunately, due to NiO_2's low electrical conductivity of 0.01 to 0.32 Sm^{-1} [40], the experimental findings never achieve the theoretical capacitance because it can expand, which leads to destroying the active materials and causing electrical contact damage [41]. As of now, the SC values for NiO-type electrodes, including nanostructure and SSA, have been 50 to 1776 F/g [42]. The link between NiO and NiOOH is described using two primary hypotheses. The energy storage mechanism occurs between NiO and NiOOH in one model, whereas in the other, NiO converted to $Ni(OH)_2$ in the influence of an alkaline medium, resulting from $Ni(OH)_2$ and NiOOH reactions, like those given below [43,44].

$$NiO + OH^- \leftrightarrow 2NiOOH + e^-$$

$$NiO + H_2O \leftrightarrow NiOOH + H^+ + e^-$$

For example, at 2.0 A/g, mesoporous amorphous carbon-coated core shell NiO had a specific capacitance of 931 F/g. Similarly, Liu and coworkers used heat techniques and hydrothermal methods to produce 3D core–shell architecture (Ni/RGO/NiO), which consisted of a NiO shell and Ni NP core and reduced graphene oxide (RGO) conductivity layer [45]. Three components exist in the HRTEM image taken from the edge of the NiO/Ni/RGO sample [46]. The existence of Gr produces the core shell semi-coated NiO/Ni structure, as seen in Figure 1. Furthermore, it has an unusually high Csp (2048.3 F/g at 1.0 A/g), as well as exceptional cyclic stability (77.8%) and retention in capacity after 10,000 cycles at a current rate of 50 A/g [47].

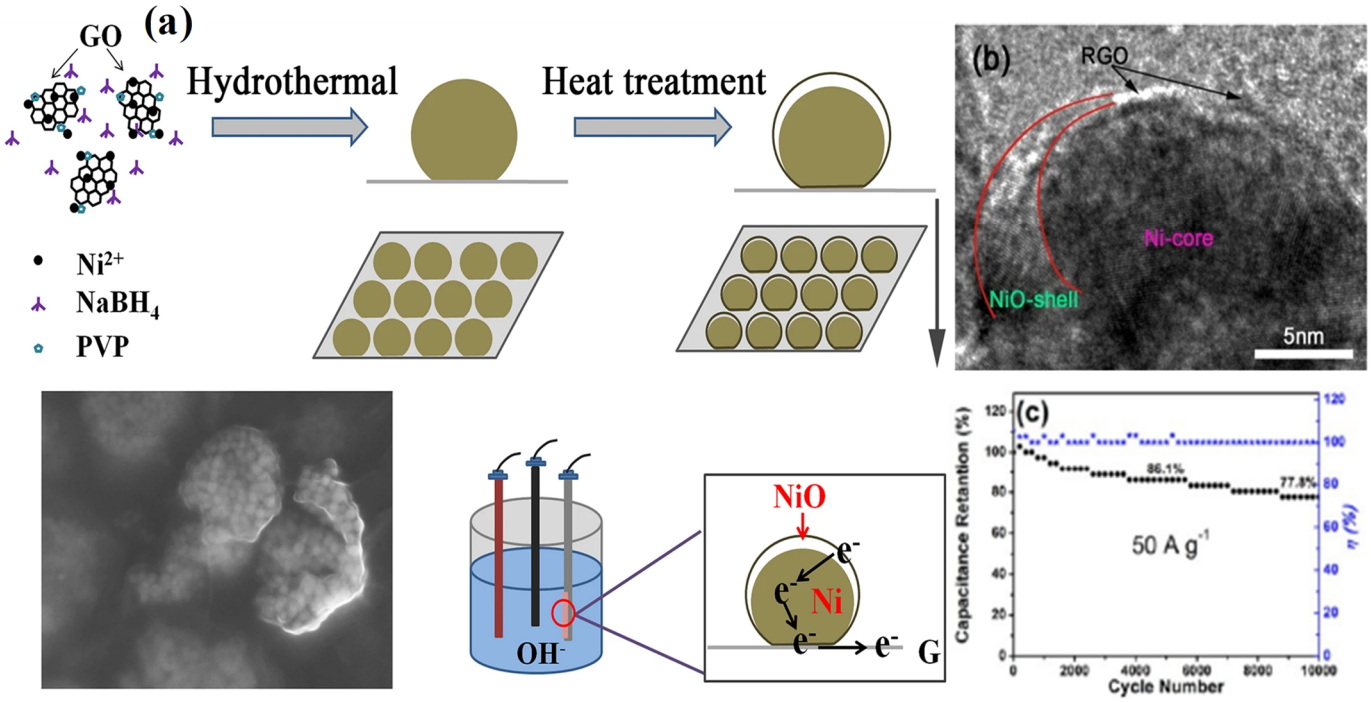

Figure 1. (**a**) Schematic representation of Conducive mechanism of material. (**b**) HRTEM micrographs of NiO/Ni/RGO. (**c**) Columbic efficiency at current rate of 50 A/g. Figure reprinted from ref. [46]. The Author(s) licensed under CC BY 4.0.

2.7. Copper Oxide

Copper oxides, like CuO and Cu_2O-based SCs, have gained a lot of attention because of their abundance, low cost, nontoxicity, and ease of synthesis of diverse nanostructures [48]. Further, the capacity (loading storage) was diminished by much less electrical and cyclic abilities [49]. For example, Zhang et al. reported the fabrication of flower-like CuO in a KOH electrolyte, yielding a specific capacitance of 133.6 F/g [50,51], whereas Li and coworkers focused on developing CuO nanostructures immediately onto Cu foam surfaces, yielding a capacitance of 212 F/gin the same electrolyte [21,52]. To achieve a higher Csp of 569 F/g^{-1}, Wang et al. constructed CuO nanosheet arrays on Ni foam surface; yet, the synthesis approach is a pretty tricky approach with a very low yield [53–55].

2.8. Battery Type MOs (Metal Oxides)

Incorporating battery-type MOs with MnO_2-type electrodes has been regarded to be an important technique to boost the energy density and capacity of supercapacitors [56,57], according to Nie's work. Synergistic effect, redox reactions, and battery metal oxides are the main reasons to improve the capacitance of supercapacitors. In addition to that, MnO_2@NiO exhibits very high capacitance of 1277 F/g at 10 A/g with retention of 76% even after 10,000 cycles [58,59]. The Co_3O_4 on MnO_2 shows extraordinary performance by exhibiting 616 F/g at 2 A/g current rates, and, moreover, it achieved 83% of capacity retention after 10,000 cycles. On the other hand, AS electrode of Co_3O_4@ MnO_2CC90 exhibits energy density and power density of 54 Wh/kg and 1 kW/kg, respectively [60].

2.9. ZnO

The specific capacity, stability, and all other aspects of supercapacitors are controlled by choosing a good and capable material as an electrode. As a result, researchers have been investigating electrode materials that perform well electrochemically [61]. Because of their good theoretical capacitance, strong redox activity, and affordable prices, TMOs have earned a lot of interest. ZnO has the features of environment friendly, wide availability, and constant capacitance [62]. Dhivya Angelin and coworkers modify the ZnO by doping

it with Zirconium. An appreciable capacitance of 518 F/g at 1 A/g was achieved in 9 wt% Zr-Zno nanoparticle, and capacity retention of 94%, even after 5000 cycles, was achieved. Zno nanomembranes exhibit different capacities in different electrolytes, like 846 F/g in 6 M KOH, 465 F/g in 1 M KCl, and65 F/g in 6 M Na_2SO_4, each at 1 A/g of current densities [63].

2.10. ZnO Composites

Various types of ZnO composites are synthesized as supercapacitor electrodes, such as metal oxide, polymer, and carbon, to find out the most suitable material for electrochemical studies [64]. Graphene nanocapsules (GNCs) show excellent capacitance of 194 F/g at 20 A/g current rate, and, moreover, only 2.6% of capacity loss is found even after 15,000 cycles [65]. Chebrolu et al. synthesized ZnO/NiO electrode, which exhibits extraordinary capacitance of 1248 F/g at 8 mA/cm^2, greater than that of ZnO/PbO, ZnO/FeO, and ZnO/CuO electrode materials. The reason behind this is the uniform surface area of nanosheets, including good electrical conductivity. To avoid the distraction of the ZnO framework, Di's team synthesized ZnO with a small quantity of Al_2O_3. The specific capacitance of 463 F/g with excellent stability of 96% was achieved. Later, all studies proved that multicomponent compounds along with ZnO could increase the capacity and stability. The CoO3-CuO-ZnO@GO nanocomposite prepared by Obodo et al. delivered excellent Csp of 1950 F/g at 10 mV/s current density.

2.11. XCo_2O_4 (X-Cu, Ni, Mn)

The spinel structure exhibits good electrochemical activity and conductivity, so these ternary transition materials were used extensively for supercapacitor studies [66,67]. The $MnCo_2O_4$ electrode synthesized by Shanmugavadivel et al. by the combustion method showed an excellent capacitance of 270 F/g. Moreover, the electrodeposition method followed to prepare the same material showed increased Csp of 585 F/g at 0.2 mA/cm^2 current rate [68]. Later, by the electrodeposition method, $NiCo_2O_4$ was coated on nickel wire and exhibited good capacitance of 315 C/g at 1 A/g with loss of 8.4% capacity after 50,000 cycles [69,70]. $CuCo_2O_4$wasdeveloped by Pawar et al. by the electrodeposition and annealing process [71]. An appreciable capacity of 1473 F/g even after 5000 cycles was achieved at 1 A/g current density [72]. The Csp of 1933 F/g at current rate of 1 A/g was achieved by Wang's group by synthesizing $MnCo_2O_4$ electrode material [73]. The $NiCo_2O_4$@MnO_2 synthesized by Xu and coworkers exhibited a good specific capacitance of 1.23 F/cm^{-2} at 50 mA/cm^{-2} after 8000 cycles. By using the as-prepared material, an asymmetric device was developed with potential window of 1.5 V and specific capacitance of 112 F/g at 1 mA/cm^{-2} and the material exhibited superior energy density of 35 Wh/kg. The three-dimensional $CuCo_2O_4$@Ni $(OH)_2$ with very good surface area showed extraordinary electrochemical applications and delivered 2160 F/g at 1 A/g of current density with good capacity retention of 82% [74].

2.12. Transition Metal Molybdates

Due to a redox mechanism on the material's surface, pseudocapacitive materials such as organic conductive materials and metal oxides show larger specific capacitances than carbon materials [75]. Furthermore, due to the large number of active sites, quick redox reactions ternary metal oxide could be the potential material to replace RuO_2. The transition metal molybdates have receiveda lot of interest as the main choiceof mixed transition metal oxides because of their features such as abundant availability, higher specific, theoreticalcapacitance, and low prices [76,77]. The morphology and structure of supercapacitor electrode materials play a big role in their performance. As a result, it is critical to create electrode materials with distinct spatial structural features. The large specific surface area leads to the improved interfacial conductivity and increase in the number of active sites and porous structure; the Ag Quantum Dots/$NiMoO_4$nanoparticles

showed excellent specific capacitance of 3342 F/g at voltage of 1 mV/sand 2074 F/g at current density of 1 A/g, as shown in Figure 2 [78].

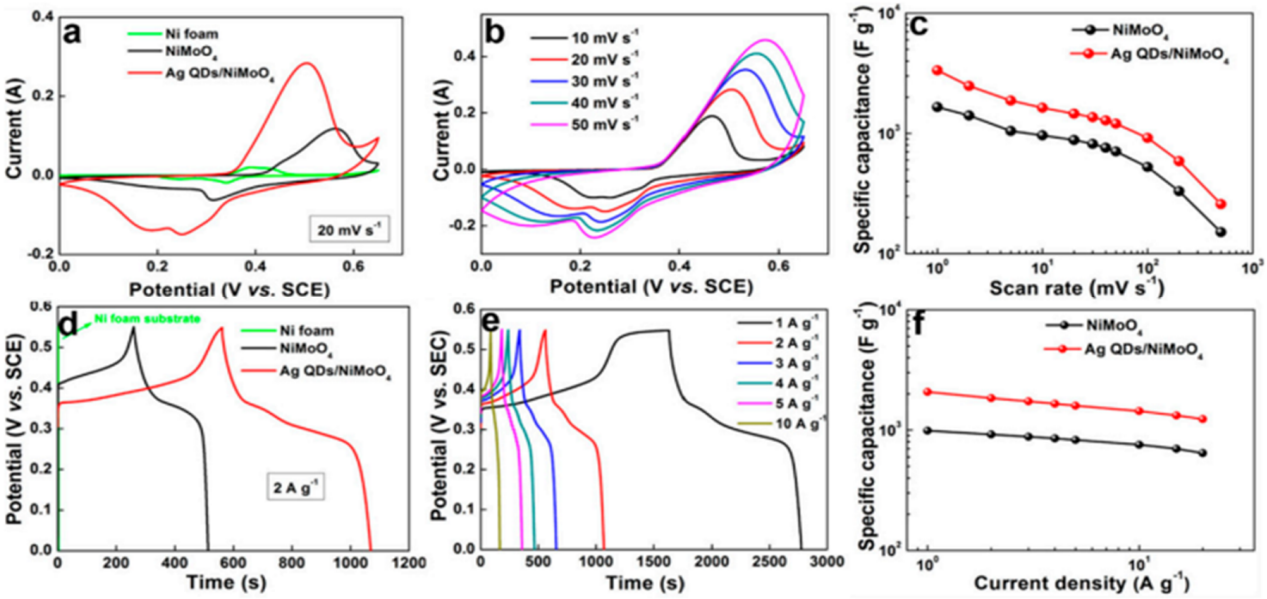

Figure 2. The three-electrode system showing Ag QDs/$NiMoO_4$ and $NiMoO_4$ materials CV and GCD measurements (**a**) CV curves at 20 mV/s; (**b**) CV curves of Ag Quantum Dots/$NiMoO_4$ electrode; (**c**) specific capacitances Vs scan rate measurements; (**d**) GCD curves at 2 A/g; (**e**) rate capabilities of electrodes and (**f**) specific capacitances Vs current densities. Reproduced with permission from ref. [78]. Copyright 2020 Elsevier.

2.13. Design of Transition Metal Oxides

The construction of hetero-type composites has proven to be a promising technique to execute the electrochemical characteristics of TMOs, as per Yi's research [77]. Heterostructures include core–shell structures. The core shell configuration can provide a lot of surface area with a lot of porosity. Likewise, core materials enhance electron transmission, while shell materials provide electrochemical redox active sites. Furthermore, each material's synergistic effect is used to boost the electrochemical behavior of the electrode. A 3D hierarchical core–shell ($CoMoO_4$@CoS) was successively developed by Xuan and team; here, they took rGO/Ni foam for the preparation. Figure 3 displays different magnifications of SEM images of CoS, $CoMoO_4$, and $CoMoO_4$@CoS materials [79]. The synergistic impact, unique material structure, and superior conductivity of rGO help to boost the electrochemical active sites and raise the capacitance, so this composite exhibit capacity of 3380 F/g at 1 A/g current rate (Table 1).

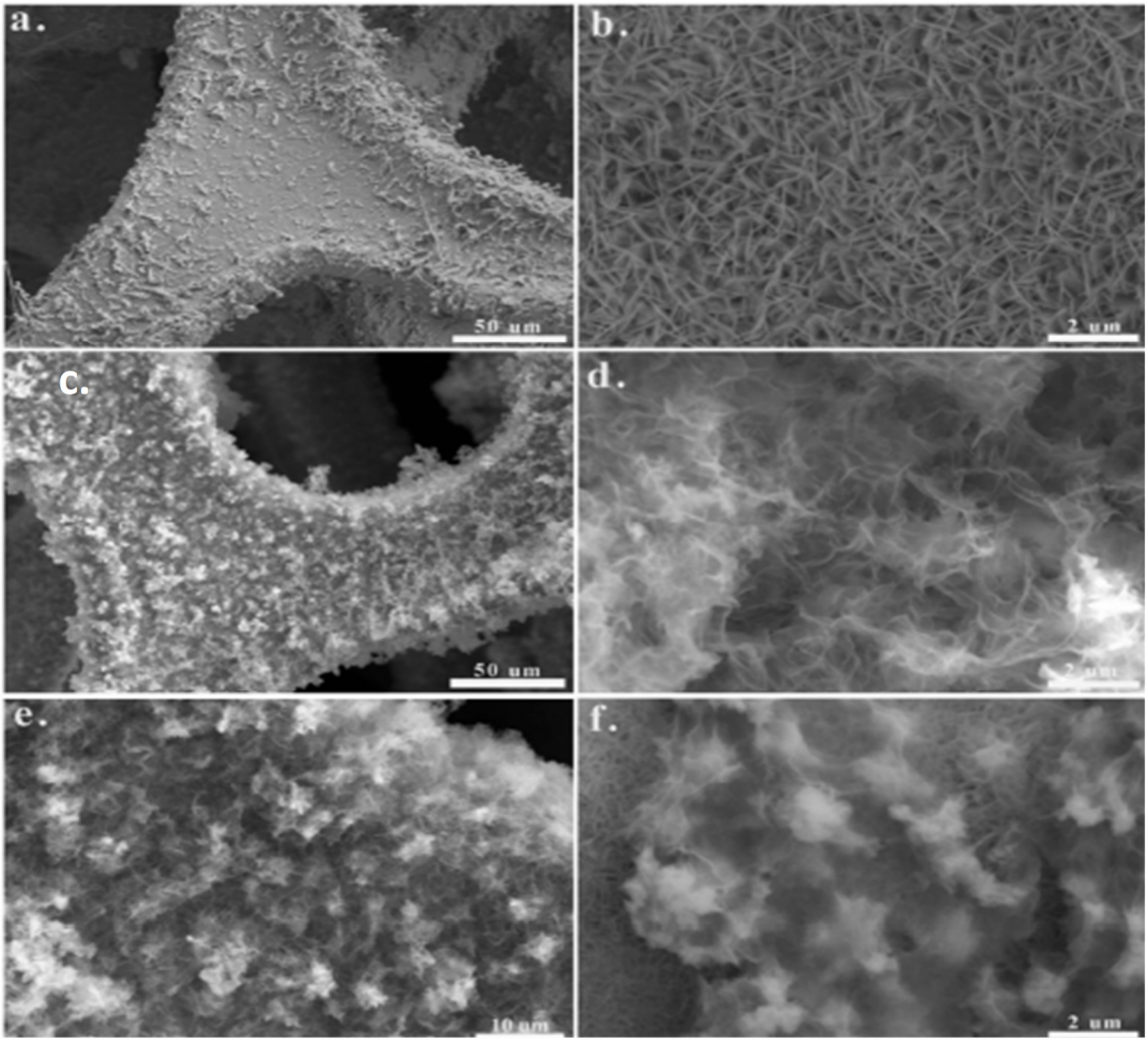

Figure 3. (**a**,**b**) Different magnification micrographs of $CoMoO_4$; (**c**,**d**) SEM micrographs at two magnifications of CoS; (**e**,**f**) SEM micrographs of $CoMoO_4$@CoS with different magnification. Reproduces with permission from ref. [79]. Copyright 2020 Elsevier.

Table 1. Performance of different type of electrodes.

Maaterials	Elecctrolyte	Specific Capacitance	Cycles	References
Co_3O_4	2 M KOH	282 C/g	4000 (90.1%)	[76]
Ag-Co_3O_4/NF	3 M KOH	1425 F/g	5000 (96.4%)	[80]
NiO@Co_3O_4	3 M KOH	1242 C/g	12,000 (95.5%)	[81]
Co_3O_4/MnO_2	1 M Na_2SO_4	616 F/g	10,000 (83.1%)	[82]
NiO@MnO_2	-	1219 F/g	10,000 (76.7%)	[83]
ZnO/CeO_2	0.2 M $K_4[Fe(CN)_6]$ in 3 M KOH	495 F/g	2000 (95%)	[84]
ZnO/Mo-C graphene QD/$MnCo_2O_{4.5}$	2 M KOH	1625 F/g	5000 (80%)	[85]
Co_3O_4@NiCo2S4/NF	3 M KOH	17 F/cm^{-2}	10,000 (114%)	[86]
Ag Quantum dots/$NiMoO_4$	3 M KOH	2074 F/g	1000 (81%)	[78]
Co_9S_8@$NiCo_2O_4$	3 M KOH	1966 F/g	5000 (92%)	[87]
$CoMoO_4$@$MoZn_{22}$	3 M KOH	923 C/g	7000 (92%)	[88]
$CuCo_2O_4$@$Ni(OH)_2$	2 M KOH	2160 F/g	5000 (92%)	[89]

3. Pseudocapacitors

The transfer of charge takes place between the electrode and electrolyte, and it undergoes redox reactions with the faradaic process [90]. They are prepared by various approaches, like redox, intercalation, and electrospinning methods. Compared to EDLCs (electrochemical double layer capacitors), pseudocapacitors exhibit higher energy; metal doped carbon, conductive polymers, and metal oxides are considered as the pseudocapacitor type of materials [91]. However, this type of material exhibits less power density and less cycle life because of redox reactions.

When compared to carbon-based EDLCs, the conducting polymer pseudocapacitors have a higher capacitance, a higher conductivity, and a lower cost. In addition, polythiophene, polypyrrole, and polyaniline are examples of materials that are considered to have high potential densities [92]. The cyclic stability of polymer electrodes is lower than that of carbon materials. Polymers can increase conductivity when doped, but they also change volume, producing swelling and an increase in electrode thickness, which is a safety concern for any device [93]. The schematic representation of three and two electrode systems are given in Figure 4 [94].

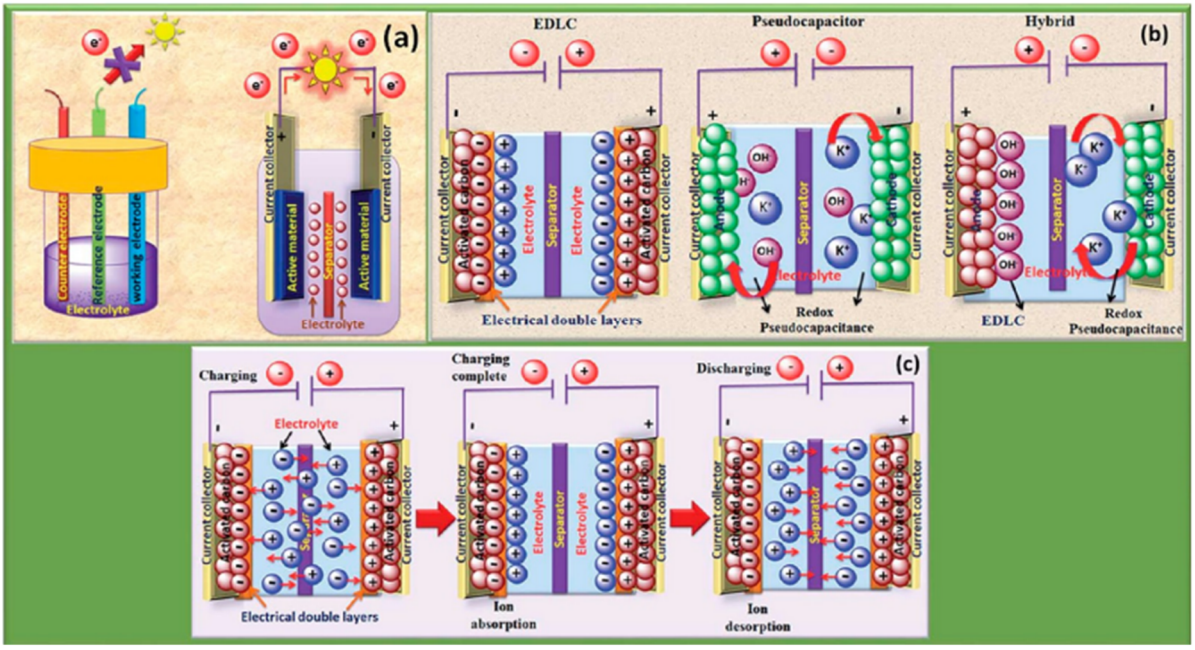

Figure 4. (**a**) Schematic representation of the two-electrode system and three-electrode system. (**b**) Supercapacitors types. (**c**) Mechanism during charge storing. Reprinted with permission from ref. [94]. Copyright 2019 Royal Society of Chemistry.

3.1. Metal Oxide-Pseudocapacitors

The conductivity of metal oxide pseudocapacitor materials is extremely high. RuO_2 is among the most studied metal oxides [95]. In addition, it features a low ESR and a high specific capacitance. However, its exorbitant cost in comparison to other TMOs has prompted researchers to look into other options [96]. Oxidative synthesis, sol-gel method, intercalation, hydrothermal method, insertion, etc. are some of the methods of fabrication. At the lowest current rate, metal oxides exhibit higher capacitance and higher energy densities [97]. Metal oxides, on the other hand, are reported to cause electrode cracking, resulting in short-term stability, because their pores cannot be adjusted or altered in any way [98]. Furthermore, carbon-based materials are commonly used as electrodes for developing pseudocapacitor electrodes, and their mixture with nanosized TMO materials, such as MnO_2, Co_3O_4, ZnO, and Fe_3O_4, has been shown to have the ability to reach very high specific capacitance values [99].

To store charges, hybrid capacitors use polarizable (carbon) and non-polarizable (conducting polymer or metal) electrodes, which include both faradaic and non-faradaic reactions. This type of capacitor has very good cyclic stability and is cheaper compared to EDLCs.

3.2. Asymmetric Supercapacitors

Because of its two different electrodes, this sort of supercapacitor stands out among others. Since one electrode operates as capacitive and one as faradaic, they are designed to function together to meet the power and energy density requirements [100]. The negative electrode is usually made of carbon-based materials, whereas the anode is made of metal or metal oxide. Metal electrodes have a large intrinsic volumetric capacity, which leads to higher energy densities [101]. In comparison to symmetric supercapacitors, these capacitors have the ability to have a better energy density and cyclic stability, which could be observed from carbon and MnO_2/NF electrodes. Capacitor self-discharge is a major problem with all capacitors. One solution is to include a basic rocking-chair mechanism inside an asymmetric capacitor. At zero current, this is where the greatest potential is secured [102]. The charge storage mechanism through EDLC [103] and pseudocapacitive mechanism is demonstrated in Figure 5 [104].

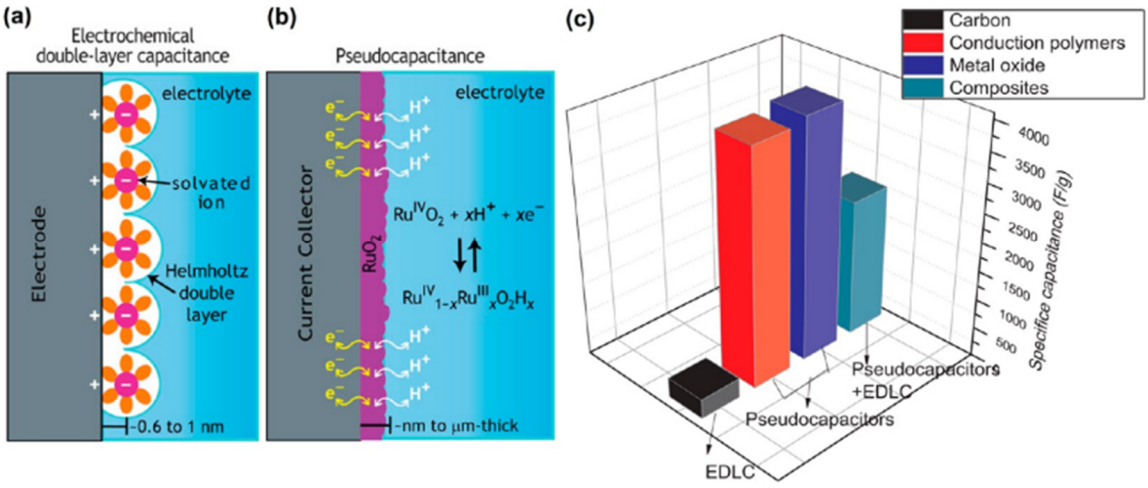

Figure 5. Charge storage mechanism through the process of (**a**) EDLC. (**b**) Pseudocapacitance Reprinted with permission from ref. [103]. Copyright 2011 Materials Research Society. (**c**) Difference between the latest SC application materials. Reprinted with permission from ref. [104]. Copyright 2018 Elsevier.

3.3. Composite Supercapacitor

These types of hybrid supercapacitors are designed to produce synergistic results in terms of high conductivity, specific capacitance, and cycling stability [105]. Carbon-supercapacitors, as shown in EDLCs, have high mechanical strength, large surface area, low resistance, and no Joule heating. Furthermore, when compared to commercially available lead acid and lithium-ion batteries, carbon has a low energy density, while metal oxides, which are being explored, get a low conductivity. Composite hybrid supercapacitors combine the features of carbon and metal oxides, resulting in the sought-after synergistic properties of specific capacitance, high conductivity, and cycling stability. Collectively, carbon and metal oxide could create a charge transport channel, while redox reactions would store charge, resulting in a high energy density and high specific capacitance.

3.4. Battery Type Rechargeable Hybrid Supercapacitor

The future of this type of supercapacitor resides in the effort to break through the Ragone plot's midway diagonal, which holds potential qualities such as better specific

capacitance, power density, and energy density that must still be achieved, as compared to current supercapacitors [106]. Because the production of electroactive nanoparticles led to rapid reactions with the electrolyte, undergoing redox with electroactive nanoparticles should also result in faster reactions. Furthermore, there is a problem because it is probable that it will also encounter false reactions with the electrolyte. Multiple obstacles exist while creating nanocomposite materials using metal oxides [107]. The material $LiMnPO_4$has a greater potential than its Fe analogue but is harder to coat with a carbon layer like $LiFePO_4$. However, a surprising, strategic way to solve this problem was to create a multi-layered carbon structure layered over Fe over Mn, which worked. Indeed, the paper claims that it functioned better than expected at greater speeds and with no direct contact between the oxidizing Mn metal oxide and the electrolyte [108]. Figure 6 shows the classification of hybrid supercapacitors [98].

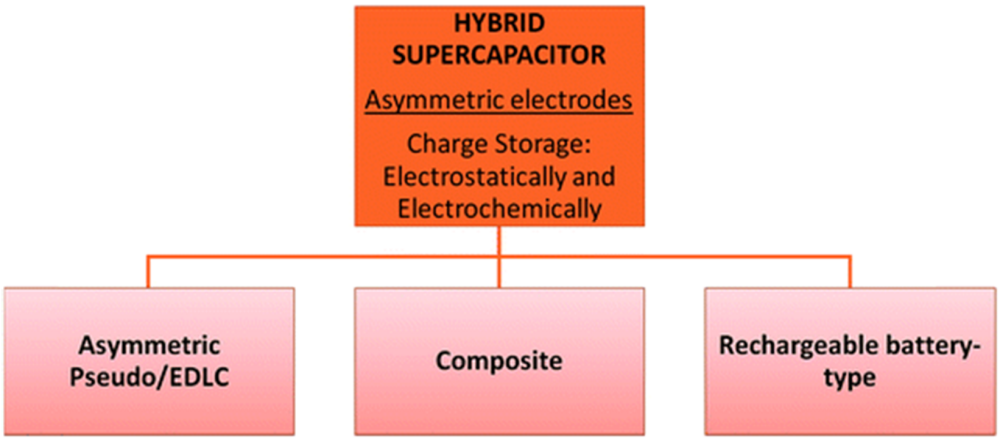

Figure 6. Hybrid supercapacitors are classified into three types based on their working and design. Reprinted with permission from ref. [98]. Copyright 2019 Royal Society of Chemistry.

The comparison table of supercapacitor and battery is given in Table 2.

Table 2. The comparison table of supercapacitor and battery.

	Supercapacitors	*Batteries*
Cost	Lower cost	Some material are higher cost
Heat build	Due to 95% of cycle efficiency, Low thermal energy releases	Charging of a cell causes serious damage, by producing enormous amount of heat
Charge protection	No danger if overcharged	Circuits are required to detect the overcharging
Environmental	No corrosive chemicals	Chemicals required to create and dispose of
Energy density	Stores only 10–20% of that of an electrochemical battery, but it has highest energy density of all capacitors	Stores about 10 times the capacity of supercapacitors
Power density	Very rapid discharge of energy, and voltage level is non usable for about 3/4th of the discharge cycle	Steady and linear discharge of energy and uses specific voltage for 95% of the batteries discharge cycle
Voltage range	Maximum voltage is low	Maximum voltage can reach double digits

4. Conclusions

The primary goal of supercapacitor development is to address the need for storing renewable energy. Higher power density, exceptional cyclic stability, and a quick charge and discharge process are all advantages of supercapacitors. This type of electrode has a big impact on supercapacitor performance. TMOs are preferred over carbon materials because they have a higher specific capacity and energy density, as well as superior

chemical stability over conductive polymers. We have covered current developments in TMO-based supercapacitor electrode materials, including fabrication, design, and electrochemical performance, in this review. RuO_2 is expected to be replaced by MnO_2, ZnO, and Co_3O_4. Issues such as low conductivity make them unsuitable for use in electrode materials. As a result, we have offered some ways for dealing with the issues. Among those, first is nanoscale material preparation. Because of the compact size, the contact surface is larger and the ion diffusion distance between electrolyte and materials is shorter. Second is synergistic effect. Taking advantage of the synergistic effect, it is critical that the synergistic impact between multiple components could be employed to increase electrochemical activity strongly using various mixtures of transition metal oxides, carbon materials, transition metal sulphides, and various materials. Third is, creating materials with a unique structure. Core–shell, porous, and hollow structures can increase surface area with abundant electrochemical active sites while lowering ion and electron transfer resistance, resulting in increased conductivity and redox reaction rate.

We have three suggestions for supercapacitor development: (i) Researchers should focus their efforts on finding low-cost, non-polluting electrode raw materials, and the usage of biomass carbon sources is a suitable example; (ii) Electronic devices should be developed that are easy to use, such as portable, wearable, and durable; thus, flexible supercapacitors will emerge easily; (iii) There are numerous publications on flexible and transparent electrode materials for solar batteries now available. Furthermore, battery-type supercapacitor electrodes have received a lot of attention. Hybrid supercapacitors, on the other hand, can bridge the gap between supercapacitors and traditional metal ion batteries. We are curious if supercapacitors will be able to charge from the sun in the future. If this miracle occurs, it will mark a tremendous step forward in the development of supercapacitors.

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