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Pseudocapacitors

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Abstract

World energy consumption has grown at a rate of knots. Economic growth, increasing prosperity and urbanization, the rise in per capita consumption, and the spread of energy access are the factors likely to considerably increase the total energy demand. In order to meet both the environmental and economic challenges, society realizes the necessity for harvesting the renewable resources, their storage, and recovery. To achieve accelerating clean energy innovation, cost reduction, and deployment of many clean energy technologies, it is important to formulating policies and their implementation, programmes for the development of new and renewable energy apart from coordinating and intensifying R&D in the sector. At present, aggravating energy and environmental issues, such as fossil fuel depletion, pollution problems, and global warming are ringing alarm bells to humans. Thus, there is an urgent need for enhanced energy security along with reducing greenhouse gas emissions. In this direction, renewable energy is one of the environmentally friendly sources of energy and effectiveness of growing economy of the whole world in general. The development of environmentally friendly materials is one of the key issues today.

Keywords: Energy Density, Cycling Stability, Faradaic, Conductivity

1. Introduction

Energy storage devices have received great interest in many emerging modern electronics such as electronic papers, collapsible displays, and other personal multimedia devices. They require highly efficient active materials with good electrochemical properties, high mechanical integrity upon bending, or folding and lightweight property. Renewable energies will not have an anticipated impact unless we find an efficient way to store and use the electricity produced by them [1]. There are various electrochemical energy storage/conversion systems including Capacitors, Supercapacitors (EDLCs, Pseudo-capacitors, Hybrid capacitors), Batteries (Li-ion batteries, Na-ion batteries, Mg-ion batteries), and Fuel cells [2]. Energy storage systems are much required to solve the issues of climate change and storing energy from renewable resources like solar, wind, and biomass. Therefore, energy storage devices have become crucial task for the research community to develop a highly efficient, inexpensive, and eco-friendly energy storage system. Batteries can explore high energy density and deliver low power density that results in the bursts of power requires like the automobiles industry [3]. Supercapacitors, on the other hand, complement batteries and are emerging as highly relevant devices for myriad electronic devices and systems on account of their less charging times (high power density) and exhibit long cycling stability. Hence, they applicable in numerous applications like renewable energy storage, grid leveling, and power conditioning [4, 5].

Nanomaterials are having a very important role in the energy storage systems due to their high aspect ratio followed by the enhanced surface area. Energy conversion and storage involve physical and chemical interaction to the surface of the materials. Hence, the surface energy, surface chemistry, and the specific surface area are the key points for these systems [6, 7]. The smaller dimensions of nanomaterials may also offer more favorable mass, heat, and charge transfer, as well as accommodate dimensional changes associated with some chemical reactions and phase transitions [8, 9].

Nanostructured materials deliver extensive surface to volume ratios, commendable transport properties, adjustable physical properties, and confinement effects resulting from the nanoscale dimensions, and have been enormously analyzed for the energy storage applications [10–13]. Metal oxides have always been salient materials that are extensively applicable in different fields, like catalysis, energy storage and conversion, biomedicine, and sensors [14, 15]. Nanostructured metal oxides have attracted tremendous interest in recent years because of their unique physical and chemical properties while the morphological and structural size became down to the nanoscale level [16]. There are lot of metal oxide nanostructures, ranging from nanoparticles, nanowires, nanotubes, and nanoporous structures.

Composite electrodes consist of carbon-based electrode with the combination of metal oxide or conducting polymer in a single electrode. It holds the charge storage mechanisms due to its extensive physical and chemical properties [17, 18]. Through Faradaic reaction, pseudocapacitive material increases the capacitance in the composite electrode [7, 19]. Two types of composite materials are available viz., binary and ternary. Binary composites contain two different electrode materials, whereas in the case of ternary, it comprises three different electrode materials to form a single electrode. In this chapter, the details about pseudocapacitors, the materials involved, and their energy storage performance have been briefly discussed.

2. Supercapacitor

A supercapacitor is a device that stores electrical energy in the electrical double layer that forms at the interface between an electrolyte solution and an electronic conductor [20]. Supercapacitors are one of the energy storage devices that have excessive power density, long cyclic stability, and can be charged and discharged rapidly. They can store more orders of energy than ordinary capacitors. They are friendly to the environment, much safer and can withstand in high temperatures. They have received considerable attention from both academic and industrial arenas because they meet the needs for a wide range of energy storage applications requiring short loading cycles with safety and stability such as power backup systems, portable devices, and electric vehicles. It can be made use of alone or with the combination of fuel cells and batteries. The major advantages of supercapacitors are in hybrid electric vehicles, wearable and flexible electronic gadgets, backup power systems, voltage stabilizer, and power sources for laptops.

Supercapacitors have the same principles as ordinary capacitors (**Figure 1**). However, they must have the electrodes with higher surface areas 'A' and much thinner dielectrics that decrease the distance 'D' between the electrodes [21]. A supercapacitor consists of two electrodes, an electrolyte, and a separator that electrically isolates the two electrodes. These are the essential components that decide the enhanced performance and should be taken into consideration when designing a supercapacitor device. The most important component in a supercapacitor is the electrode material. In general, the supercapacitor electrodes are fabricated from nanoscale materials that have a high surface area and high porosity. The charges are

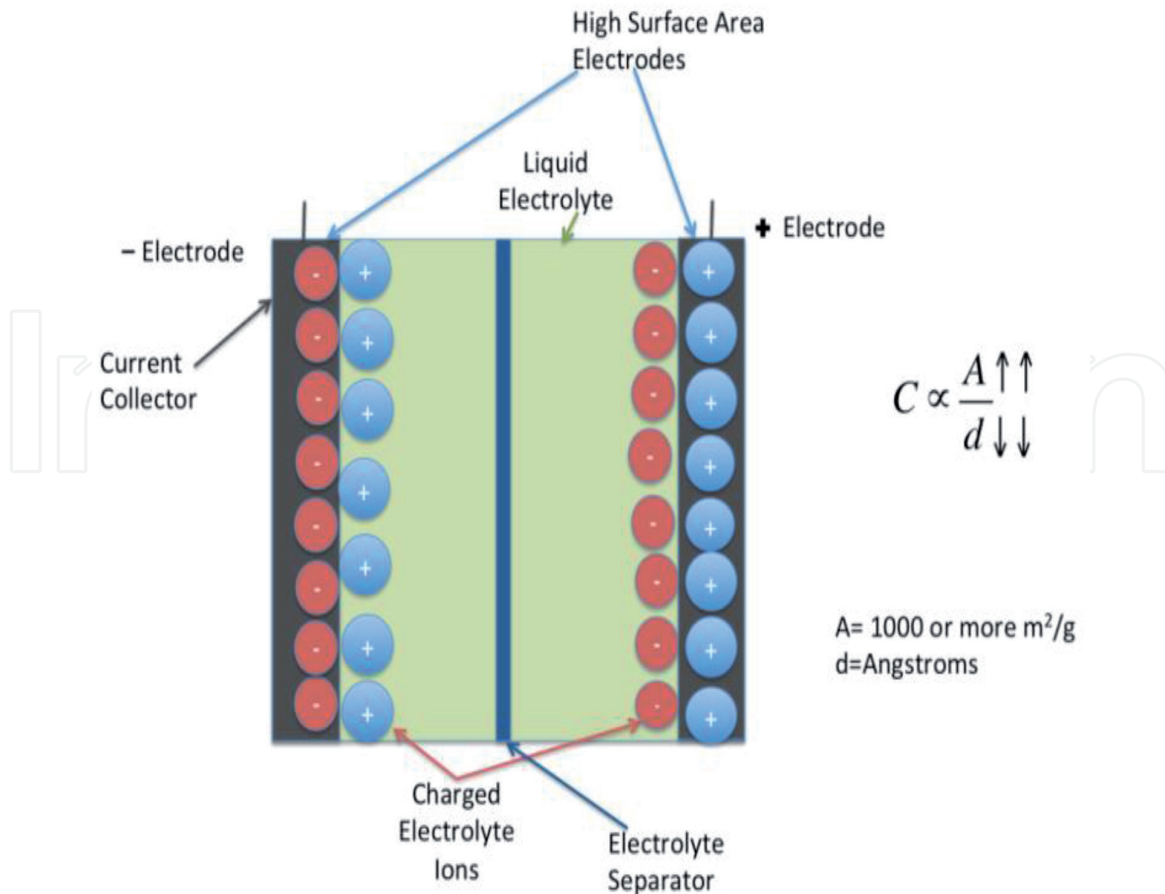


Figure 1.
 Schematic of a supercapacitor.

stored and separated at the interface between the conductive solid particles (such as carbon particles or metal oxide particles) and the electrolyte [22]. **Figure 1** explains the schematic of the supercapacitor device [23].

For a two-electrode supercapacitor cell, the two working electrodes are placed across a separator, and the voltage variation in between the electrodes is observed and managed. Each electrode/electrolyte interface represents a capacitor and a resistance. Therefore, the total specific capacitance (C), which is the capacitance per unit mass for the cell, is calculated from the following equation in which C_1 and C_2 are the specific capacitances of the two electrodes, respectively [24].

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1)$$

The supercapacitors consist of anode, cathode, separator, and electrolyte. The *anode* denotes the negative terminal of a supercapacitor cell associated with the oxidative chemical reactions that expose the electrons into the external circuit. The *cathode* indicates the positive electrode of a cell associated with reductive chemical reactions that observe the electrons from the external circuit. An *electrolyte* is a material that provides pure ionic conductivity between the positive and negative electrodes of a cell. A *separator* is a physical barrier between the positive and negative electrodes that is used to prevent the electrical shorting during the electrochemical reactions. The separator can be a gelled electrolyte or a microporous plastic film, or other porous inert material filled with electrolyte. Separators must be permeable to the ions and inert in the battery environment. The schematic of the pseudocapacitors is explained in **Figure 2** [25].

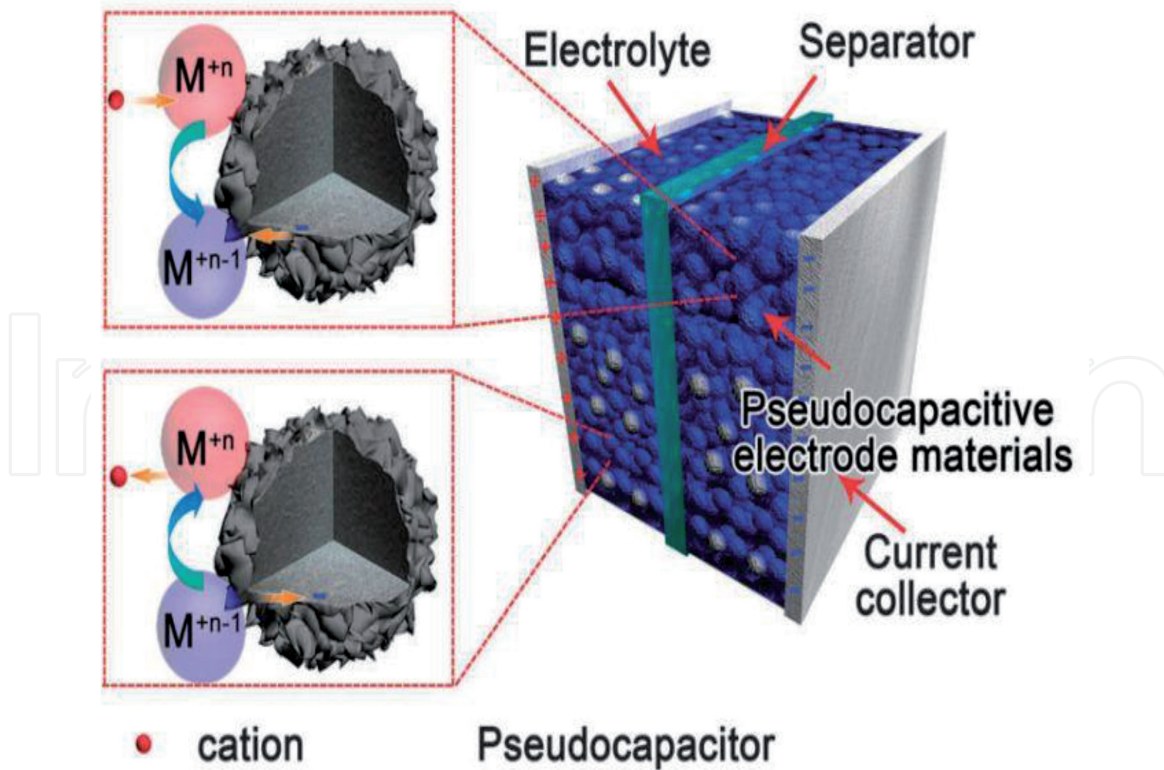


Figure 2.
Schematic of pseudocapacitors.

The Specific capacitance of the supercapacitor cell can be calculated from the charge–discharge measurements using the formula:

$$C = (I.t) / (\Delta V.m) \quad (2)$$

where C is the specific capacitance of the electrode material, I is the constant discharge current, t is the discharge time, m is the mass loading of the active material and ΔV is the potential window during discharge. *Energy density* is the amount of energy stored by a supercapacitor.

$$E_s = \frac{1}{2} C \Delta V^2 \quad (3)$$

where ' E_s ' is the energy density, ' C ' is the specific capacitance of the material and ' ΔV ' is the potential window (Volt).

Power density is the amount of power that a supercapacitor can deliver when connected to an external load.

$$P_s = \frac{E_s}{t} \quad (4)$$

where ' P_s ' is the power density, ' E_s ' is the energy density and ' t ' is the discharge time.

3. Energy storage mechanism in supercapacitors

The performance of the supercapacitor is subjected to the energy storage, the insertion and exertion of ions between the surface of the electrodes, and the

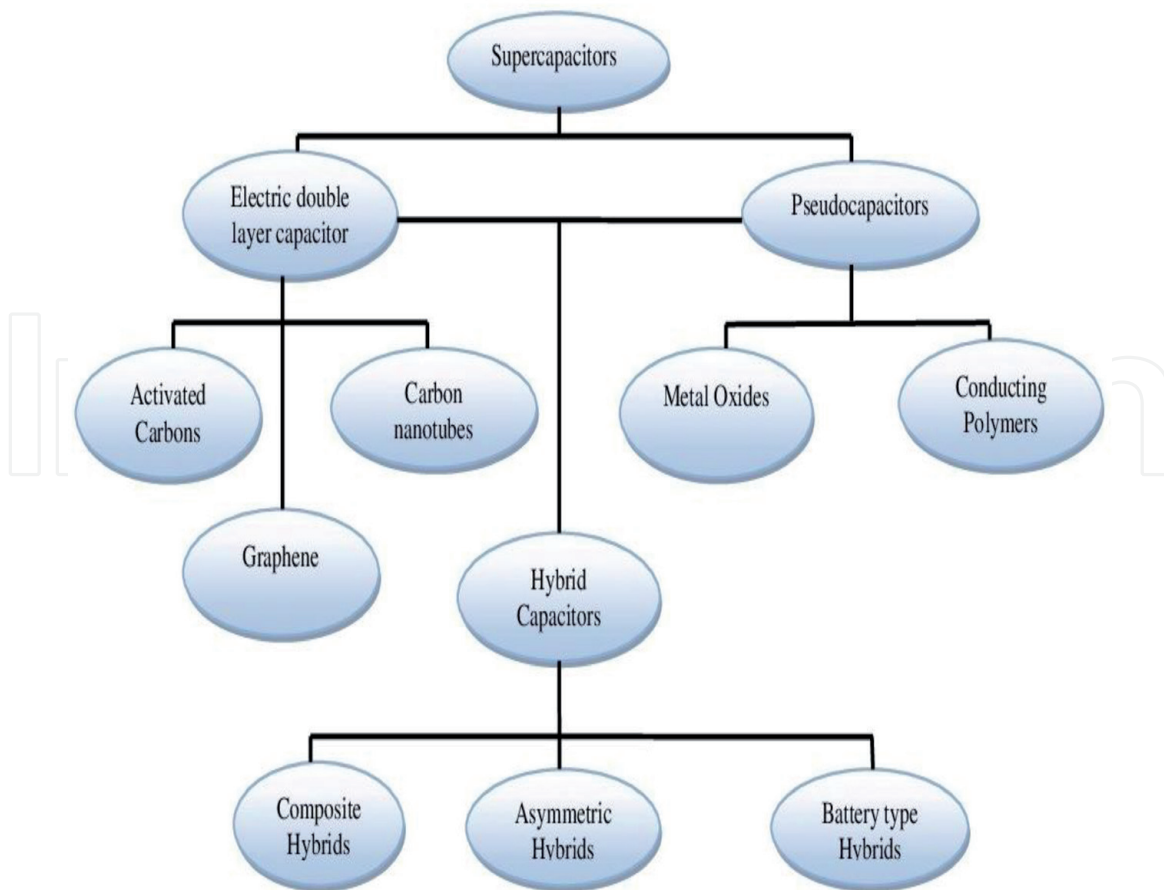


Figure 3.
Taxonomy of supercapacitors.

electrolyte. Based on the energy storage mechanism as well as the active materials used, supercapacitors are classified into three categories: electrochemical double-layer capacitors, pseudocapacitors, and hybrid supercapacitors as shown in **Figure 3**.

Pseudocapacitors store energy through faradaic reaction. They store charge electrostatically in which the transfer of charge between electrode and electrolyte [25]. When a voltage is subjected to a pseudocapacitor, both reduction, and oxidation take place on the electrode material. It involves the passage of charge across the double layer, resulting in faradic current passing through the supercapacitor electrode material. The faradic process employed in pseudocapacitors enhances the electrochemical reactions that result to achieve greater specific capacitance and energy densities compared to EDLCs.

4. Material for pseudocapacitors

4.1 Transition metal oxides (TMO)

Transition-metal oxides, a type of pseudocapacitive material, exhibit fast and reversible redox reactions at the surface of the electrode materials. It exhibits high specific capacitance and low resistance that makes an easy way to construct supercapacitors with high energy and power.

The commonly used metal oxides are RuO_2 , MnO_2 , Co_2O_3 , NiO , SnO_2 , Fe_3O_4 , IrO_2 , V_2O_5 , and MoO as supercapacitor electrodes. Among the various metal oxide electrode materials for supercapacitor applications, RuO_2 is considered as the most promising electrode material because its high specific capacitance (720 F g^{-1}) and

high electrical conductivity [26]. However, the high cost, as well as the non-availability of Ru on the earth has limited its application in practical usage. By considering these issues, the identification of the low cost pseudocapacitance materials is essential and where the research community is looking into. TMOs exhibit various oxidation states at different potentials and possess crystalline structures that allow high conductivity which enables charges to propagate within their lattice. As faradaic materials, in the same phases, TMOs exhibit two or more oxidation states. When charging and discharging take place, TMOs are able to change their oxidation states, and protons can insert into and extract from the oxide lattice during reduction and oxidation surface reactions.

4.2 Conducting polymers

Conducting polymers (CPs) are the second group of candidate materials for redox pseudocapacitors due to their fast and reversible oxidation/reduction processes, good electrical conductivity, and relatively low cost. The most commonly used conducting polymers include Polyaniline (PANI), Polypyrrole (PPy), Poly (3,4-ethylenedioxythiophene) (PEDOT), Polythiophene (PTh), and Poly (p-phenylene vinylene) (PPV). They are typically synthesized either through chemical or electrochemical oxidation of the monomer and rendered conductive through a conjugated bond system along the polymer backbone [27, 28]. Conducting polymers exposed the enhanced conductivity, capacitance, and reduced equivalent series resistance when compared with carbon-based electrode materials. The ions are observed/drifted from the electrolyte to the polymers and released to the electrolyte while oxidation and reduction take place correspondingly. Because of no phase transition occurs, the conductive polymers exhibit highly reversible reactions that lead to the enhanced cycling stability. They are positively or negatively charged by the redox reactions that induce the enhanced conductivity.

4.3 Composites of conducting polymers with metal oxides/hydroxides

The electrode materials of metal hydroxides/oxides have better energy densities than carbon materials and higher cyclic stability than conductive polymers [29]. Besides, the higher capacitances of metal hydroxides/oxides are due to the electrochemical process which occurs on the surface and bulk of the electrode materials [30]. The composites of metal hydroxides/oxides with conducting polymer perform remarkable cyclic stability and high specific capacitance that reduce the agglomeration and the restacking of metal hydroxide/oxide permitting uniform dispersion of metal hydroxides/oxides and the conducting polymer matrix [31–33]. Moreover, the association between the electrode and current collector increases the electroactive area in metal oxide/hydroxide-conducting polymer composites. The low cost and high theoretical capacitance of MnO_2 (1100 F g^{-1}) make it as a good alternative for expensive metal oxides and its composites with CPs have become one of the centre of attraction of many researchers. Sharma et al., synthesized nucleated MnO_2 nanoparticles over polypyrrole chains by electrochemical co-deposition in polished graphite surfaces. The embedded PPy chains of MnO_2 offer high surface area due to the special arrangement of MnO_2 nanoparticles and PPy in the composite. The nanocomposite showed better Faradaic redox reactions which in turn lead to significant supercapacitor performance with good conductivity and stability. The specific capacitance obtained was 620 F g^{-1} which is higher than its individual components MnO_2 (225 F g^{-1}) and PPy (250 F g^{-1}) [34]. Zhang et al. intercalated PANI- MnO_2 nanocomposite by exchange reaction with PANI and MnO_2 intercalated n-octadecyltrimethylammonium precursors using N-methyl-2-pyrrolidone as the

solvent. The nanocomposite exhibited the highest specific capacitance of 330 F g^{-1} with 94% of capacitance retention even after 1000 cycles. The composite exhibited outstanding performance than MnO_2 and PANI [35]. Liu et al., introduced the synthesis of nanocomposite $\text{MnO}_2/\text{PEDOT}$ by electro co-deposition of EDOT monomer (80 mM) and manganese acetate (10 mM) in a porous alumina template. The coaxial nanowires of the composite exhibited high specific capacitance (210 F g^{-1}) and high current density due to the fast ionic diffusion into the core MnO_2 of the coaxial nanowires [36]. Gan et al., synthesized MnO_2/PPy composite by in situ chemical synthesis method which improves the porosity and enhances specific surface area with fast intercalation/deintercalation of the electrolyte. The fabricated supercapacitor device showed the specific capacitance of 312 F g^{-1} at 10 mV s^{-1} with 93.2% cyclic stability over 1000 charge/discharge cycles [37]. Debelo et al., prepared single-phase electrodeposition on stainless steel using the aqueous solution of manganese nitrate and pyrrole. The $\text{Mn}(\text{OH})_2/\text{PPy}$ porous nanosheets exhibited the specific capacitance of 430 and 220 F g^{-1} for anodic and cathodic films [38]. Some of the MnO_2 and PPy composites are shown in **Figure 4** [37, 38].

Along with the CPs with MnO_2 , nickel hydroxide ($\text{Ni}(\text{OH})_2$) and nickel oxide (NiO) form composites with CPs as supercapacitor electrode material owing to the easy synthetic procedure, low cost, and redox reactions, and high theoretical specific capacitance (2584 F g^{-1} for NiO and 2081 F g^{-1} for $\text{Ni}(\text{OH})_2$) [39]. Sun et al., used binder free approach for the synthesis of NiO -PANI on nickel foam for the fabrication of supercapacitor. The composite showed 2565 F g^{-1} specific capacitance at 1 A g^{-1} and showed excellent cyclic stability with 100% retention of specific capacitance after 5000 cycles [40]. Yang et al., encapsulated porous $\text{NiO}/$

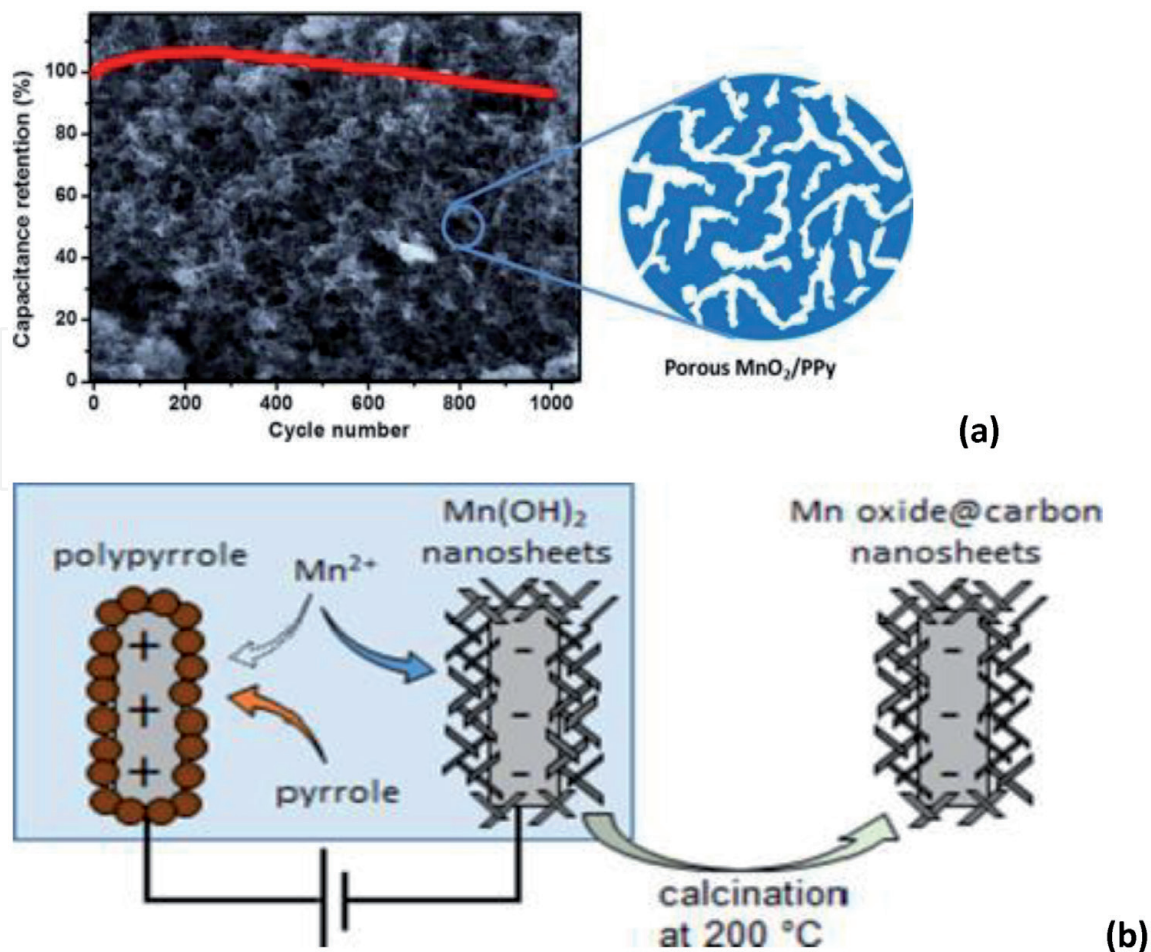


Figure 4.
 MnO_2 with PPy composites for supercapacitor (a and b).

Ni(OH)₂ with PEDOT on Cu-Ni alloy wires by facile and low cost electrochemical route. The protective layer of PEDOT on the surface of PNS enhances the electronic conductivity and stability. This hybrid electrode achieved a high specific capacitance of 404.1 mF cm⁻² at a current density of 4 mA cm⁻² with 82.2% capacitance retention even after 1000 cycles. The supercapacitor device delivered the power density of 0.33 mW cm⁻² and the energy density of 0.011 mWh cm⁻² with an output voltage of 1.5 V [41].

Vanadium oxide (V₂O₅), cobalt monoxide (CoO), and hematite (α -Fe₂O₃) have also been explored as supercapacitor electrode materials with CPs. The layered structure, different oxidation state, and redox reactions at the electrode surface make it as a good energy material [29]. Liu et al., synthesized V₂O₅-PANI composite by electro co-deposition method with a specific capacitance of 443 F g⁻¹ at the potential window 1.6 V. The composite film exhibited a power density of 720 W kg⁻¹ and an energy density of 69.2 Wh kg⁻¹ with excellent stability [42]. The same group electro-codeposited V₂O₅-PPy using an aqueous solution of vanadyl sulphate (VOSO₄) and pyrrole. The nanocomposite showed specific capacitance 412 F g⁻¹ at 4.5 mA cm⁻² owing to the synergistic effect of V₂O₅ and PPy.

It exhibited the operating voltage window of 2 V with an energy density of 82 Wh kg⁻¹ [32]. Aamir et al., fabricated an electro-codeposition technique for the synthesis of V₂O₅-PANI composite on Ni foam which is a porous and conductive framework for pseudocapacitors. The synthesized composite showed the specific capacitance of 1115 F g⁻¹ due to the small charge transfer resistance [43]. α -Fe₂O₃ has also been investigated as the electrode material for supercapacitors because of its abundance, low cost, and good theoretical capacitance. The inclusion of α -Fe₂O₃ on CPs makes α -Fe₂O₃ as a promising material for supercapacitance properties with good cyclic stability. Lu et al., investigated the areal capacity of α -Fe₂O₃@PANI core shell synthesized by simple electrodeposition method. The electrochemical performance of the nanowires arrays offers enhancement of structure stability, fast movement, and transfer of ions, and large surface area. The designed material serves as the anode and PANI on carbon cloth as cathode and obtained good volumetric capacitance (2.02 mF cm⁻³). The fabricated asymmetric supercapacitor also experienced a high power density (120.51 mW cm⁻³) and energy density (0.35 mW cm⁻³) with excellent cyclic stability [44].

In order to address the capacitance and stability issues, CoO was also incorporated with CPs for pseudocapacitor. Liu et al., developed CoO@PPy nanowire on nickel foam to enhance the pseudocapacitor due to the synergistic effect of CoO and PPy. The well aligned asymmetric supercapacitor showed a high specific capacitance (2223 F g⁻¹) with capacitance retention of 99.8% after 2000 cycles [45]. Yang et al., fabricated a hybrid electrode with Co₃O₄ nanosheet on PPy by solvothermal route and electrodeposition. The combination of Co₃O₄ and PPy benefits the fast transfer of ions at the electrode-electrolyte interface exhibited high areal capacitance (2.11 F cm⁻²) at the current density of 2 mA cm⁻² with superior cyclic stability (after 5000 cycles) of 85.5% capacitance retention [46]. The high conductivity and electrochemical activity of nickel cobaltite (NiCo₂O₄) make outstanding specific capacitance (1400 F g⁻¹) in comparison with pure NiO and Co₃O₄ [47, 48].

4.4 Composites of metal sulfides with conducting polymers

Metal sulfides are cheap and abundant in nature undergo different valence states and redox reactions due to the presence of metal ions [49]. The metal sulfides of Mo, Cu, Ni, and Co with CPs have become the centre of attraction due to the high specific capacitance and outstanding reversible redox reactions [50]. Peng et al., developed CuS with PPy by solvothermal route in the absence of surfactant and

exhibited the specific capacitance of 427 F g^{-1} with outstanding cyclic stability due to the intertwined structural properties of CuS@PPy [51]. Wei et al., synthesized flexible electrode with $\text{PPy/NiS/bacterial cellulose}$ and obtained excellent supercapacitor properties with 713 F g^{-1} specific capacitance at 0.8 mA cm^{-2} [52]. MoS_2 is considered as one of the excellent metal sulfides with high electrochemical capacitive properties and variable oxidation state of Mo (+2 to +6) which is a promising material for pseudocapacitance behavior. Ren et al., used in situ oxidative polymerization method for the controllable synthesis of MoS_2/PANI hybrid material where PANI nanowires are aligned on the external and internal surface of MoS_2 . The porosity and excellent conductivity of the hybrid material provide fast ion diffusion between the electrode and the electrolyte. The capacity to withstand the volume change during cycling and the large surface area, make it as a smart material for the excellent specific capacitance of 552 F g^{-1} at 0.5 A g^{-1} and rate capability of 82% from 0.5 to 30 A g^{-1} [53]. Yang et al., synthesized carbon shell coated PANI grown on 1 T monolayers of MoS_2 ($\text{MoS}_2/\text{PANI@C}$). The composite exhibited outstanding specific capacitance of 678 F g^{-1} in 1 mV s^{-1} with excellent capacitance retention of 80% even after 10,000 cycles due to synergistic effect of PANI, 1 T MoS_2 , as well as the thin carbon shell [54].

5. Conclusion

The development of novel materials for energy applications has been identified as one of the priority areas of all the other countries. In order to meet both the environmental and economic challenges, the globe realizes the necessity for harvesting renewable resources, their storage, and recovery. We believe that this generation holds the key to transforming the future of sufficient energy for usage, which could be possible by making improvements in energy storage devices. By considering these issues, the energy storage mechanism of supercapacitors and the details about the advanced materials of pseudocapacitors with some recent literature works are briefly discussed in this chapter for the researchers to develop novel pseudocapacitors.

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