

Carbon nanotube (CNT) Based Electrodes in Supercapacitors: A Review

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Abstract: In today's world, quest for energy storage has gained significant momentum and many innovative energy storage solutions have turned up due to global efforts in power generation. One of the possible energy storage solutions is the use of supercapacitors that has turned out to be a significant development owing to its high charging-discharging speed, enhanced power density with long-term cycling stability when compared to customary batteries. The current review focusses on the use of one of the carbon materials viz. CNTs as supercapacitor electrode material, another refined material that can be used in making sustainable and highly efficient energy storage devices. The use of CNTs increases the surface area and the electrodes show high electrical conductivity.

Keywords: Supercapacitors, Electrodes, CNTs

1. INTRODUCTION

Past several decades have witnessed an urban sprawl leading to continuous perversion of natural resources leading to greater energy demands. Also, increasing human population globally has further put a challenge for meeting up the required energy demands. In keeping view of the above discussed factors, the current power infrastructure is unable to cope up with the ongoing trends and is thus a threat for a sustainable future. So far, the requisite needs of power have been largely catered through the use of fossil fuels. The large-scale exploitation of fossil fuels has contributed to rising environmental changes like global warming, an increased pollution, question on fuel economy and accountability of various other impactful geographical factors. Thus, focus of many researchers and academicians has been shifted to finding ways so as to reduce our dependence on fossil fuels. Further, acknowledging alternate renewable energy sources can bring into account more effective, efficient and high-performance energy storage devices and systems [1].

Therefore, there was much of dependence on conventional energy storage technologies like capacitors, fuel cells and batteries to name a few [2-5]. Recently a significant work has been carried out in the field of advanced energy storage technology using "supercapacitors". Supercapacitor or electrochemical capacitor or ultracapacitor have surpassed the use of traditional devices like batteries, cells etc owing to their unique high-power density ($>10 \text{ kW kg}^{-1}$), prolonged life cycle ($>10^5$), sufficient peak power, high power efficiency and providing inherently safe and environmentally clean, friendly energy storage systems solutions. and efficient storage devices.

An impressive combination of its high-power delivery and long cycle-life has extensively shown its popularity whether it be automobile industry or portable electronics or in memory backup systems. Discrete features of supercapacitors viz. high surface area electrodes and thinner dielectrics have made them exceptionally remarkable with maximum capacitance [6-10] when compared to traditional capacitors. A close comparison to the batteries reveals the fact that the supercapacitors possess high orders of power density magnitude and specific energy making them a viable candidate for an alternative energy storage system [11]. Their ability to store and release energy is one thousand times more than the batteries and thus make them suitable in many device applications where power delivery is a requisite; charge accumulation however is around 3-30 times low when compared to batteries. Fig.1 [12] below represents a plot showing fuel cells with highest energy in contrast to supercapacitors with greatest power. However, in case of batteries it possesses intermediary power and energies.

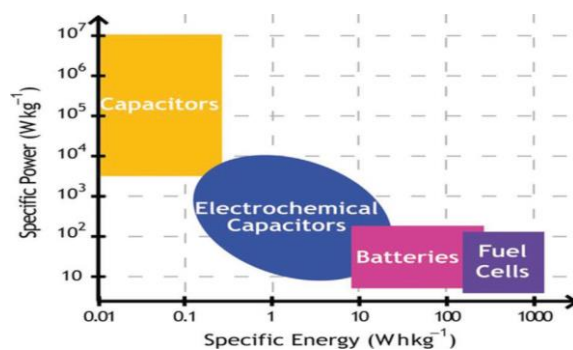


Fig. 1 Specific power density plotted against specific energy density for different types of energy storage devices. Reproduced with permission [2] Copyright 2004, American Chemical Society.

Supercapacitors thus stands suitable for energy storage applications meeting all the desired requirements be in terms of energy density or maximum power, their compact size, initial cost, weight or long life span or power to energy ratio. Energy is the main concern globally thus, development of these high energy systems like supercapacitors is the need of the hour.

2. OVERVIEW: CONVENTIONAL CAPACITORS Vs SUPERCAPACITORS

Traditional supercapacitors comprise mainly a non-conducting insulator or dielectric substance/medium placed in between two conducting electrodes. When voltage is applied, positive and negative charge accumulation takes place on the electrodes separated by the dielectric thereby resulting in the production of electric field so that energy storage can take place in capacitors.

Capacitance C is defined as the amount of charge Q stored on the electrodes to the applied potential difference V across the electrodes i.e.

$$C = \frac{Q}{V} \quad (1)$$

The capacitance for a capacitor can be calculated using the primary relation:

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (2)$$

where ϵ_0 : dielectric constant or permittivity of free space; ϵ_r : dielectric constant of the insulating material or the dielectric used between the electrodes, A : surface area of each electrode, d : separation gap/distance between the two electrodes. Eq. (2) shows direct relation of the capacitance of the capacitor with the area A of each electrode and dielectric constant of the material but an inverse relation with the distance d between the electrodes.

The direct relationship between the capacitance of the capacitor and its stored energy E is given as:

$$E = \frac{1}{2} CV^2 \quad (3)$$

Other important factors that need lot of attention is the energy density of a capacitor i.e. how much of the energy can be stored by a capacitor per unit volume and its power density i.e. the rate at which the capacitor can absorb or deliver energy per unit volume. Power for a capacitor can be understood by knowing how much is the energy converted per unit time. Power determination in a circuit for a capacitor requires a capacitor and external load resistance R in series. Ideally a capacitor has an infinite capacitance but the assembly of various constituents like electrodes, current collectors, and dielectric material of the capacitors etc offers some cumulative resistance known as Equivalent Series Resistance (ESR). The efficiency of any capacitor for storing and releasing energy depends largely on ESR. Once it is calculated some restriction is imposed on the maximum power ($P_{\max}$) delivered by the capacitor [6-7,10] using the following Eq. 4 as:

$$P_{\max} = \frac{V^2}{4 \times \text{ESR}} \quad (4)$$

While batteries and fuel cells can store more of energy due to high energy densities and less power delivery due to low power densities supercapacitors show a contrast to this. They can unleash their stored energy inside them by delivering immense power. Eqs. (2)-(3) above clearly indicates that high storage capacity in a supercapacitor depends on the high capacitance [16]. This can be accomplished by maximising surface area of the electrodes and minimising dielectric gap(d) between them.

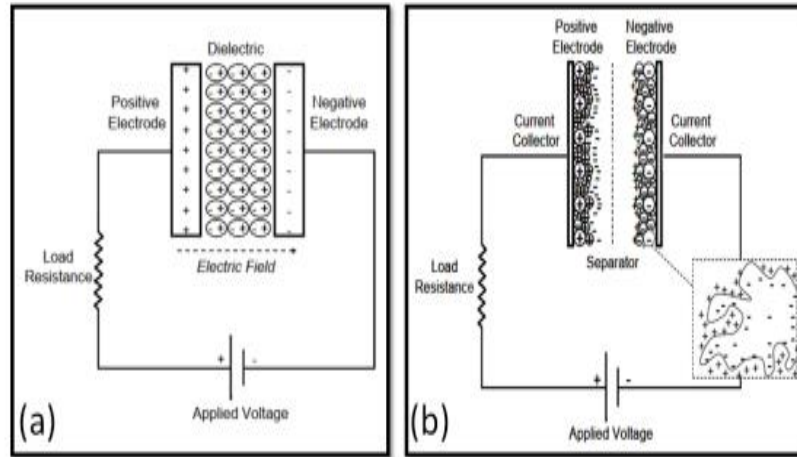


Fig. 2 a) Conventional Capacitor, b) Supercapacitor Source: reproduced with permission from [16]

3. SUPERCAPACITORS: CLASSIFICATION ON THE BASIS OF ENERGY STORAGE MECHANISM

Highly efficient storage system for a supercapacitor depends on: large surface area of electrodes, electrolyte for ionic conduction, separation of charges followed by accumulation of charges on the electrodes forming an electrically double layer.

Based on various mechanisms involved in energy storage of supercapacitors, they can be categorised as: Electrochemical double-layer capacitors (EDLCs), pseudo capacitors, and hybrid supercapacitors.

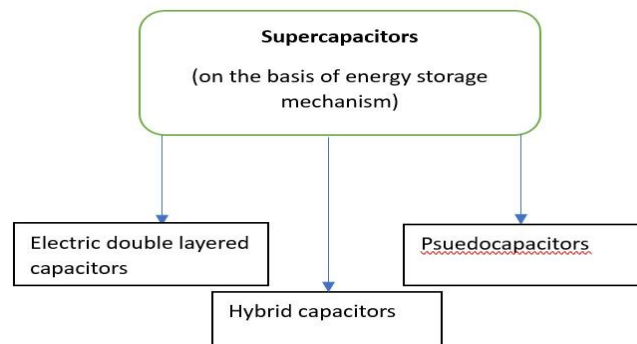


Fig.3 Classification of Supercapacitors (based on energy storage mechanisms)

3.1 EDLCs:

EDLCs involves three important elements:

- (i) **Electrodes:** These are generally made of combination of two carbon-based materials having high surface area essential for high energy storage capacity.
- (ii) **An Electrolyte:** Either an aqueous or an organic conductive liquid is chosen so that an ionic flow is maintained throughout in between the electrodes during charging or discharging.
- (iii) **Separator:** In between the electrodes, a thin insulating ion-permeable membrane exist preventing short circuit while still allowing the flow of ions through the circuit.

The charge storage in EDLCs can be either: electrostatically or by a non-faradic process. The latter avoids any chemical changes but involves only the physical separation of charges i.e. non electron transference between the electrodes and the electrolyte [12-14] resulting in a non-faradic redox reaction [15]. Thus, energy storage in case of EDLC's depends on the formation of electrochemical double layer. A significant potential difference can be observed after applying voltage that leads to accumulation of charges on large electrode surface area. Diffusion of ions from electrolyte takes place to the oppositely charged electrodes. Formation of double layer of charges at electrode leads to non-recombination of ions. All the factors including double layer formation, high surface area and minimising the separating distance between the electrodes contributes to the higher energy density [16] in EDLC's.

Thus, EDLC's show high capacitance and high-power density when compared with conventional capacitors. This very fact allows for a high charging and discharging. Since a non-faradic process causes no chemical change, there is no material degradation or a volume change in any active material which in contrast is shown by the batteries during the charging and discharging process.

3.2 Pseudocapacitors:

The principle involved in case of pseudocapacitors for the storage of charges is Faradic process wherein the charges are transferred between electrode and electrolyte [17] highlighting reversible redox reactions or intercalations [18]. After applying potential, oxidation-reduction reaction occurs at electrodes. Thus, electron transfer between electrode and ions generates faradic current thereby enhancing specific capacitance and energy densities in pseudocapacitors in contrast to EDLCs. However, the redox reactions are responsible for an instability during cycling resulting in low power density [19-21].

3.3 Hybrid SCs:

These aims at combining the advantages of both batteries and capacitors. Two different electrodes based on two distinct mechanisms of electrical charge storage exist: one battery-type Faradic providing high power density and other capacitive [22]. A proper selection of electrode material can lead to high performance of SCs with an increased cell voltage and enhanced energy and power densities. However, it is seen that in case of hybrid devices, electrode material degradation takes place over time due to faradic processes that ultimately decreases the charge storage and its release ability decreasing its capacitance and thus a failure as a high-power supercapacitor in long run. Based on the electrode configuration, one can categorize hybrid supercapacitors into three different types: symmetric, asymmetric supercapacitors (ASCs), and battery-type.

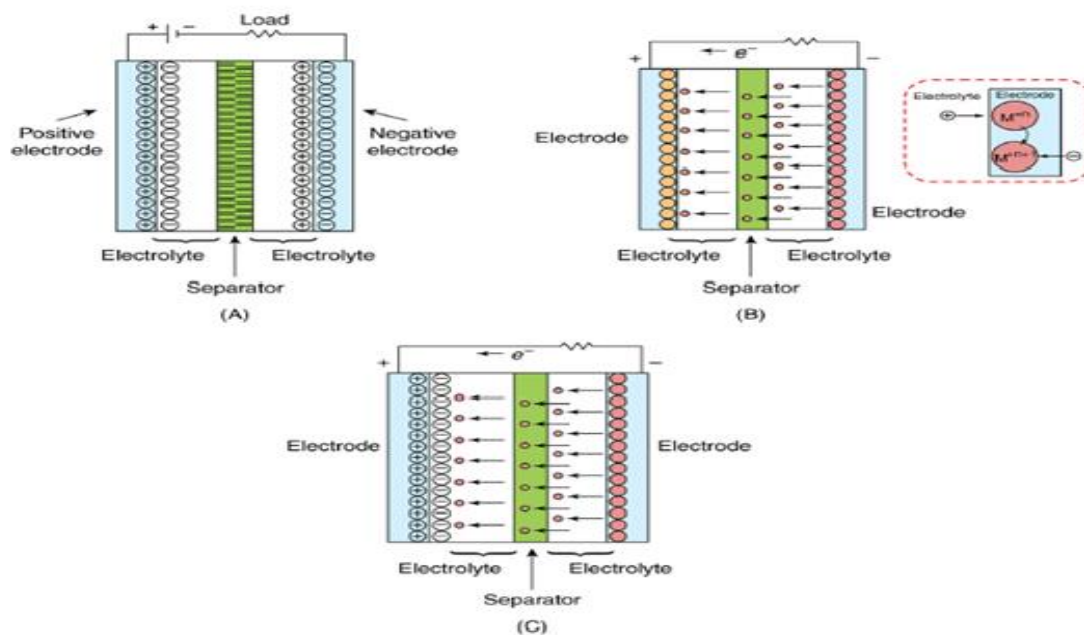


Fig. 4 Supercapacitor types: A) EDLC, B) pseudocapacitor, C) hybrid capacitor Source: reproduced with permission from Ref. [1]

Unlike symmetric supercapacitors, which use identical materials for both electrodes, asymmetric supercapacitors employ two distinct materials for the positive and negative electrodes. This setup allows for the integration of electrode materials with contrasting charge storage mechanisms, or even the utilization of the same electrochemical double-layer capacitor (EDLC) material as positive and negative electrodes but with varying surface functional groups [22].

Asymmetric configurations exhibit significant advantages over symmetric configurations, notably the ability to operate within broader and more consistent voltage ranges. Most of the symmetric supercapacitors are restricted to function below 1.0 V, constrained by the thermodynamic limit of water molecule decomposition when using aqueous electrolytes. Conversely, asymmetric supercapacitors allow for higher operational voltages, facilitating them to attain higher energy densities (E_d) by effectively utilizing increased operating voltages (V) [22,23].

4. Choice of CNTs as Electrode materials in Supercapacitors

The increased energy density [24] of any supercapacitor depends largely on the choice of electrolytes that can hold a high-voltage window as there is a direct relationship between the energy density of supercapacitors and square of the working voltage. While using such kind of electrolytes which work with large working voltages, the functional groups holding oxygen in them viz. COOH, OH, or C = O etc, must be avoided so as to get rid of any breakdown of these groups at high voltages [25] that can lead to lower capacitor stability. Instead, a better choice between two sp^2 carbon nanomaterials viz. carbon nanotubes (CNTs) or graphene that are independent of any surface-dangling bonds stands best suited. Both of these can be used widely as electrode materials due to synergism between the chemical stability and extraordinarily high surface area ($\sim 1300 \text{ m}^2/\text{g}$ and $\sim 2630 \text{ m}^2/\text{g}$ for CNTs and graphene respectively) realising a large electrolyte-electrode interface, ideal for double-layer capacitance. In between carbon atoms, the presence of covalent sp^2 bonds facilitates a large movement of electrons that increases the electrical conductivity thereby reducing the overall resistance of the system. These materials act as basic building blocks in the development of novel 3D architectural structures along with graphene nanofibers (GNFs), CNT foam, etc. [26-31]. Whether it be graphene or CNTs, each of these carbon materials contributes uniquely to the performance and efficiency of EDLCs, highlighting the versatility and potential of carbon-based technologies in energy storage applications. Ega et al. [32] demonstrated the performance of PANI//AC asymmetric cell, where activated carbon material has a high BET specific surface area of $860 \text{ m}^2/\text{g}$ and a large total pore volume of 199 cm^3 . PANI//AC exhibits a high specific capacitance of 157 F/g @ 5 mA/cm^2 and cycle life stability over 5000 cycles with a coulombic efficiency of 93% @ 10 mA/cm^2 . Habib et al. [33] showed reduced graphene oxide (rGO), conducting polymer polyaniline and Tellurium composite (rGO/PANI/Te₅₀) symmetric electrode cell attained its maximum specific capacitance of 895 F/g @ 10 mV/s . The sample exhibits high coulombic efficiency $\sim 92\%$ alongside impressive energy and power densities of 41 Whkg^{-1} and 3679 Wkg^{-1} and cyclic stability of $\sim 91\%$ after 5000 charge-discharge cycles. Additionally, the rGO/PANI/Te₅₀ showed electrical conductivity of 86.2 S/m .

In a study conducted by Wang et al. [34], covalently modified graphene (DMFrGO180) has been found to possess outstanding supercapacitive properties. Specifically, when tested using a PVA/KOH gel as the electrolyte, DMFrGO180 exhibit specific capacitance of 193.5 Fg^{-1} @ 1 Ag^{-1} and 86.9 Fg^{-1} @ 50 Ag^{-1} along with high energy density 11.35 Whkg^{-1} and 5.09 Whkg^{-1} at power density of 649.7 W/kg and 32.4 KW/kg respectively.

As, the right choice of electrode material [35-38] depends on an extensive large surface area, high electrical conductivity, and large electrolyte accessibility, CNTs can be taken up as excellent candidate for building up new electrode materials. As electrodes and electrolyte are key elements for a CNT SC, an extensive research work has been carried out to evolve out with variety of CNT electrode materials and studying further their combinations with various electrolytes. Further both SWCNTs and MWCNTs [39] can be fruitful in making electrochemical supercapacitor electrodes as they exhibit unique structures, nanometre range size distribution, high surface area, reduced resistivity with enhanced cycling stability. Cyclic stability refers to the ability of a supercapacitor to retain its performance characteristics, such as energy storage capacity and power delivery, over numerous charge-discharge cycles. The cyclic behavior depends on different factors, such as the cyclical operations of both the positive and negative electrodes, the durability of the membrane, and the properties of the electrolyte [40]. Mu et al. [41] showed that electrode based on CNT/rGO/MnMoO₄ achieved a remarkable specific capacitance of 2374.9 F/g @ 2 mV/s and displayed impressive durability over time, retaining 97.1% of their initial specific capacitance even after undergoing 3000 charge-discharge cycles. Zhang et al. [42] synthesized a novel MWCNTs/PANI/MoS₂ via a facile in situ polymerization and hydrothermal method which exhibits impressive rate capabilities, with a capacity retention of 62.5% at a high current density of 10 A/g . Furthermore, the composite exhibited outstanding cycling stability, retaining 73.71% of its capacitance over the course of 3000 cycles.

Liang et al. [40] Ti₃C₂Tx-MWCNT//Ppy coated MWCNT asymmetric supercapacitor exhibited capacitance retention rates of 94% and 72% over about 1000 cycles when cycled within voltage windows of 0-1.6 V and 0-1.8 V, respectively. Ryan et al. [43] demonstrated that incorporating a small amount of SnO into SWCNTs significantly improves cycling stability. Specifically, under a current density of 10 A/g , this enhancement allows the system to maintain 95% of its initial capacity after undergoing 7,500 cycles. Additionally, in a setup involving an asymmetric device with MXene, a similar level of improvement was observed, with the device retaining 90% of its initial capacity over the same number of cycles. In their research titled "High-performance wearable supercapacitors based on PANI/N-CNT@CNT fiber with a designed hierarchical core-sheath structure," Tian et al. [44] found that the capacitance of PANI/N-CNT@CNT fiber could be preserved at 95.5% even after being subjected to repeated bending tests for up to 10,000 cycles. Other researchers like Zhang et al [45] have investigated Fe₂O₃/CNTs composite having shell-core hierarchy architecture and fabricated them using microwave-assisted Fenton's reagent technique. The conductivity is improved tremendously when CNT is introduced into Fe₂O₃ at current density of 0.5 A/g . A high capacitance of about 204 F/g is observed, however with 1 kW/kg power density, 28.3 Wh/kg energy density is observed. The Fe₂O₃/CNTs composite thus results in an increased capacitance, high cycling

stability and enhanced energy density. $\text{Fe}_2\text{O}_3/\text{CNTs}$ composite stands as one of the best electrode materials for SC's. Large scale fabrication of $\text{Fe}_2\text{O}_3/\text{CNTs}$ composite can be taken up using microwave-assisted Fenton's reagent technique. Yang et al. [46] have successfully deposited binder-free Ti_3C_2 MXene/carbon nanotubes ($\text{Ti}_3\text{C}_2/\text{CNTs}$) on graphite substrate using electrophoretic deposition (EPD) technique for supercapacitor electrodes. When compared to pristine Ti_3C_2 and CNTs films, the as-grown $\text{Ti}_3\text{C}_2/\text{CNTs}$ electrode showed an increased specific capacitance. $\text{Ti}_3\text{C}_2/\text{CNTs}$ electrode exhibits remarkable cycling stability even at 5 A g^{-1} without any loss of capacitance over 10,000 cycles. CNTs in the hybrid film act as interlayer spacers for Ti_3C_2 providing non-stoppable charge transportation thereby preventing restacking of Ti_3C_2 nanosheets and magnified electrochemical performance. Yue et al [47] in their present work fabricated $\text{CoFe}_2\text{O}_4/\text{CNTs}$ composite using simple hydrothermal method. CoFe_2O_4 nanoparticles are spread on the CNT surface externally. The $\text{CoFe}_2\text{O}_4/\text{CNTs}$ composite is then used as an electrode material exhibiting high specific capacitance of 1240 F/g at 0.5 A/g . Retention of around 75.8% capacitance i.e. 941 F/g took place even when the current density increased to 10 A/g i.e. around 20 times from the earlier figure using traditional three-electrode system. They also achieved energy density as high as 30.4 W h/kg and power density as high as 400 W/kg for an asymmetric supercapacitor (ASC) fabricated with $\text{CoFe}_2\text{O}_4/\text{CNTs}$ composite and active carbon (AC) as the positive and negative electrode respectively. Even after 1000 charging-discharging cycles specific capacitance retention of around 86.5% could be observed at a current density of 2 A/g . These remarkable observations indicate $\text{CoFe}_2\text{O}_4/\text{CNTs}$ composite as suitable electrode materials for supercapacitors. Li et al [48] have explored in their recent study a high-performance electrode material, viz. a hierarchically hybrid composite of $\text{CuCo}_2\text{S}_4/\text{CNTs}$. This was synthesised using a simplistic process comprising both hydrothermal and sulfuration. A right proportion of CNTs in the CuCo_2S_4 composite may lead to an increased specific surface area. A low series and charge transfer resistance for $\text{CuCo}_2\text{S}_4/\text{CNTs}$ electrode indicates a higher specific capacitance (557.5 Fg^{-1}) with high cyclic stability for long term charging-discharging cycles if compared to pristine CuCo_2S_4 (373.4 Fg^{-1}) and $\text{Co}_3\text{O}_4/\text{CuO}/\text{CNTs}$ (356.5 Fg^{-1}) electrodes at a current density of 1 Ag^{-1} . When compared to earlier reported CuCo_2S_4 based ASC devices, $\text{CuCo}_2\text{S}_4/\text{CNTs}$ -3.2%//AC ASC devices were far better and improved even after 10,000 cycles with energy density $\sim 23.2 \text{ Whkg}^{-1}$ at a power density $\sim 402.7 \text{ Wkg}^{-1}$. It can be concluded that for supercapacitors though CuCo_2S_4 stands as one of the finest electrode materials, but limited conductivity and low cyclic stability has restricted its wide-range uses. The addition of CNTs into binary metal sulphides improvise largely high capacity and high-performance of energy storage devices with remarkable cycle stability. Below is a comparative table of different CNTs based electrodes.

Configuration	Electrode	Electrolyte	Operating voltage	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (kWkg ⁻¹)	Reference
Symmetric configuration	PANI/MWCNT (5:1)	0.5 M Na ₂ SO ₄	0-1 V	300	9.8	-	[49]
	FCNT-MOF	1M KOH	0-1 V	465 @ 2Ag ⁻¹	40.5	11.9	[50]
	Free standing electrode						
	Polyaniline/MWCNTs composite (8%)	PVA/H ₂ SO ₄	-0.2 to 0.8 V	446.89	248.29	16.86	[51]
	CNTs/GNFs			270 @ 1 Ag ⁻¹	72.2	686.	[52]
	Polyaniline/f-MWCNTs composite (PFC1)	0.1 M H ₂ SO ₄ +0.1 M Na ₂ SO ₄	0 - 0.8 V	865	77	801	[39]
	MWCNTs/NiS/graphitic carbon nitride // AC	2M KOH	0.8-1.6 V	206 @ 0.5 Ag ⁻¹	73.3	1.599	[53]
	Ti ₃ C ₂ T _x -MWCNT // Ppy coated MWCNT	Na ₂ SO ₄	0-1.6 V	0.94 Fcm ⁻²	-	-	[40]
	NiMOF/CNTs//AC	2M KOH	0-1.6V	320 @ 1 Ag ⁻¹	113.8	800	[54]
	SWCNT/SnO//MXene	H ₂ SO ₄	-0.4 to 1 V	-	6.6	51.5	[43]

Asymmetric configuration	Co ₃ O ₄ @CNTs@NF//AC@NF	-	-	1291 F g ⁻¹ at 5 mA/cm ²	57.6	273.4	[55]
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5. Limitations of carbon-based electrode for supercapacitors

The limitations of carbon-based materials includes low capacitance and energy density than pseudo-capacitive materials which may be due to several key factors low packaging density, hydrophobic nature of carbon-based materials impedes their compatibility with aqueous electrolytes, leading to suboptimal ion transport and overall performance in electrochemical system, low DOS in carbon materials that limits the charge storage capability per unit volume and chemical inertness that inhibits effective interaction with electrolytes, particularly impacting the ion intercalation process crucial for capacitor charging, thus affecting both capacitance and energy density [56,57].

6. CONCLUSION

The present review provides an overview on the contrasting features of supercapacitors and traditional batteries. Latest research on use of one of the carbon materials viz. CNTs as supercapacitor electrode material has been taken into account owing to its unique and distinctive property of high electrical conductivity, resistive to corrosion, low density, remarkable stability and high specific surface area. Addition of CNTs thus enhances the electrochemical performance of the devices. Still much of the research work is coming up to upgrade the energy storage devices by improving their energy and power density of devices.

7. FUTURE SCOPE

The improvisation in performance can pave the way to increased applications of CNTs as supercapacitor electrode material ranging across various sectors from portable electronics to large scalable energy storage solutions. The recent advancements in this field is a clear indicator of future prospects of CNT-based supercapacitors being understood more efficiently so as to provide renewable energy solutions globally. The future scope involves its integration with latest emerging technologies of IoT and smart grid to get sustainable energy solutions. Focus on better biomedical devices with biocompatibility is another area where its scope can be explored. Whether it be energy harvesting and storage or sensor integration sensing capabilities of CNT based supercapacitors can further be explored. Further many new hybrid or composite materials can be chosen so as to cut down the cost of CNT-based electrodes for their access in various applications.

8. ACKNOWLEDGEMENTS

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