Carbon-Based Electrochemical Capacitors

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Dependence of specific capacitance on pore size and BET surface area

Dependence of specific capacitance on micropore and mesopore volume
1. Introduction

Natural energy production and its storage have been hot issues for the last decade. The current and future demands for green energy production and proper storage systems are higher than ever for environmental protection and the replacement of fossil fuels. When solar cells, windmills, or hydroelectric turbines are considered as the best available sources of alternative energies, transmittance of energy and, more importantly, storage systems such as supercapacitors and batteries have to be taken into account.\(^\text{[1]}\) For instance, solar cells can produce sufficient energy and improved efficiency during the daytime, but energy needs to be stored for use at night. Hydroelectric power plants, windmills, and even, for better sunlight, solar cell panels are located in remote areas, which require the use of immediate storage systems. Storage systems with high energy and power densities are in strong demand for most mobile systems, such as cellular phones, laptop computers,\(^\text{[2]}\) iPads, and automobiles.\(^\text{[3]}\) We prefer to obtain higher energy density, that is, to store the maximum possible amount of energy within a specified mass or volume of storage material. This stored energy should be released smoothly and delivered with high current whenever necessary, which is possible only with a high power density device. For instance, in the case of electric cars, energy-storage devices with high energy densities are required for long-distance travel.\(^\text{[4]}\) High power density is also required to achieve enough acceleration whenever required at the start or on a slope.

In general, conventional batteries outperform conventional capacitors in terms of energy density, but they are poor in power density. Conversely, conventional capacitors have a much higher power density than batteries and can deliver a much higher current.\(^\text{[1,2]}\) Thus, no conventional capacitors or batteries could provide high energy density and high power density simultaneously. This situation demands a new type of storage device with the capability to obtain higher values in both energy and power density.\(^\text{[5]}\) Supercapacitors seem to be the best possible candidate to meet this requirement because supercapacitors possess power densities much higher than conventional batteries and much higher energy densities than conventional capacitors.\(^\text{[6]}\) A typical supercapacitor shows an energy density in the range of 5–10 Wh kg\(^{-1}\), which is much higher than those of conventional capacitors, but this is still significantly lower than those of conventional batteries. Conventional batteries have energy density values such as 20–35 Wh kg\(^{-1}\) for lead-acid, 40–100 Wh kg\(^{-1}\) for nickel metal hydride, and 120–170 Wh kg\(^{-1}\) for lithium ion cells. Therefore, the most important issue for supercapacitor research is to enhance energy density.\(^\text{[7]}\)

The performance of a supercapacitor depends upon several parameters, for instance, the active material used as the electrode, the nature of electrolyte, and the interface between electrode and electrolyte.\(^\text{[8]}\) Unfortunately, sometimes the effects of these parameters are interlinked and revealed in combination. Therefore, proper understanding of capacitor performance is necessary. Typical pore sizes of active materials need to be complemented by similar ion sizes. In other words, the size of the pores should be larger than those of the (hydrated) ion size of the electrolyte. Therefore, the choice of electrolyte is very important in addition to pore size control. Another important criterion in choosing an electrolyte is the operation voltage and related stability. Organic electrolytes can be used for an operating voltage of 2.5–3.0 V, whereas an aqueous electrolyte is limited to up to 1.0 V.\(^\text{[9]}\)

Carbons in different forms, such as powders, fibers, and sheets, along with their versatile availability, have been realized as the most promising and user friendly electrode materials. Carbons are appropriate for the fabrication of supercapacitor electrodes. Low cost, easy availability, nontoxic nature, environmental friendliness, and stability make carbons the most preferable materials to date.\(^\text{[10]}\) The charge-storage mechanism in a supercapacitor is mainly controlled by two principle mechanisms: one is based on electrostatic interactions, known as electric double-layer capacitance (EDLC) and the other involves...
chemical reactions, namely, pseudocapacitance. Whereas pure nonreactive carbon materials store charges electrostatically,\cite{11,12} carbon composites and carbons embedded with foreign reactive atoms take part in chemical reactions. For EDLC, activated carbons (ACs) received special recognition compared to other carbon materials because they have high surface areas along with controllable pore size distributions. Although high surface areas provide more sites for the EDLC in principle, different pores can adapt to different ion sizes.\cite{13,14}

Pure single-walled carbon nanotubes (SWCNTs),\cite{15} multiwalled carbon nanotubes (MWCNTs),\cite{16} and pure graphene\cite{17} have shown high EDLC performances. On the other hand, composites of ACs,\cite{18} CNTs,\cite{19} and graphene oxides (GOs),\cite{20} have been successfully applied to chemically reactive charge-storage phenomena or pseudocapacitance. Transition-metal oxides have been successfully tested by many research groups as potential candidates for pseudocapacitance. Their composites with porous carbon materials are one of the most popular electrode materials.\cite{21} This type of electrode can store charges both electrostatically and chemically. All of these different types of pure carbons and their composites have been explored based on their capability to store charges as EDLC and/or pseudocapacitance.

2. Theoretical Background for Supercapacitors

2.1. Supercapacitor performance

A capacitor is a device that stores energy in the form of electrical charge and can deliver the stored charge on demand in the form of an electric current. They have a typical structure consisting of two parallel plates, known as positive and negative electrodes, separated by a dielectric material. The total capacitance (C) of such a capacitor can be expressed by means of Equation (1):

\[ C = \frac{\varepsilon A}{d} \]  

in which A is the total area of the electrode plates, d is the separation distance between the two electrodes, and \( \varepsilon \) is the dielectric constant. These electrodes can be charged on the application of some external potential, and thus, the energy is stored. A capacitor of capacitance C can store a maximum energy (E) as expressed by Equation (2), in which V is the charging potential:

\[ E = \frac{1}{2} CV^2 \]  

When these two plates are connected through a load, the stored energy is released through discharge of the capacitance and it delivers power. The power released (P) can be expressed by Equation (3), in which R is the resistance of the capacitor:

\[ P = \frac{V^2}{4R} \]  

The capacitance can be expressed in terms of per unit mass or per unit volume of the electrode material, known as specific gravimetric capacitance or specific volumetric capacitance, respectively. These two terms have their own importance in practice when they are used as energy-storage systems.

Supercapacitors have almost the same basic structures as conventional capacitors. Electrolytes and separators are used instead of a dielectric material in the supercapacitors. In conventional capacitors, the dielectric material is polarized during charging, which helps to hold the charges on the electrodes. A higher dielectric constant yields enhanced charge-storage performance. In the case of supercapacitors, polarization occurs only at the interfacial surface between electrode and electrolyte. Electrolyte ions move towards the electrodes during charging and sit on the external surface of the electrode. These ions help to hold charges (supplied by external power sources) electrostatically at the inner wall of the electrode surface, and thus, form a double layer consisting of those charges and electrolyte ions. Here, no charge transfer takes place between the ions and electrode material. This purely electrostatic phenomenon is known as an EDLC. Electrolyte ions hold these charges electrostatically purely by columbic interactions, and thus, help to charge the capacitors. This storage mechanism is a pure surface phenomenon. If the sur-
face area of the electrode is increased, more ions can be accommodated and, as a consequence, more charges can be held to obtain higher capacitance. Conversely, when we have a chemically reactive environment between the electrode material and the electrolyte, charge transfers are involved between them at the interface, that is, faradaic interactions take place. These charge transfers provoke chemical changes (oxidation-state change) in the electrode materials, and thus, charges are stored chemically at some oxidation states. During discharge, this chemical reaction takes place in reverse, and the electrode materials are restored to the previous oxidation states and the stored charges are released. This faradaic charge-storage phenomenon is known as pseudocapacitance, which gives rise to another category of capacitors known as pseudocapacitors. From the above description, it is clear that both EDLCs and pseudocapacitors are surface phenomena and their dependence on surface area is similar. In both cases, a larger surface area is better for a higher capacitance. Porous electrodes are preferable for both types of capacitors because porosity increases the effective surface area and also provides entry to the inside of the bulk electrode material. Therefore, the fabrication of suitable porous electrodes is one of the most important areas of research.

Pseudocapacitance is distinctly different from EDLC. Because EDLCs follow purely electrostatic phenomena, their charge storage is completely reversible, that is, all stored charges are released during discharge, but this is certainly not true for pseudocapacitors. Chemical reactions are not 100% reversible even for the best possible reversible combination of electrode material and electrolyte. There are always some residual electrode materials that cannot take part in the reversible chemical reaction process, even after complete discharge. This is an unavoidable loss of active material, which reduces the value of maximum specific capacitance with increasing cycle numbers and affects the cyclic stability of the pseudocapacitors, whereas EDLCs show excellent cyclic stability. Compared to pseudocapacitors, EDLCs have a much faster response to any electrical potential changes. In the case of pseudocapacitance, we have the highest charge-transfer rate at a particular potential. Some time delay is required to overcome this potential barrier, and this time is responsible for the delayed response of pseudocapacitors relative to EDLCs, which have instantaneous electrostatic responses. Despite these cyclic-stability and response-time issues, pseudocapacitors are still appealing due to their impressive ability to boost the charge storing current to a significantly higher value because of electronic exchange in the chemical reaction; this results in an enhanced capacitive behavior. Thus, finding solutions to the above-mentioned problems have been the topic of scientific investigation in recent years. Recently, approaches to combine EDLCs and pseudocapacitance have been made to achieve optimized performance, which has led to the study of many new materials with both EDLC performance and pseudocapacitance.

In supercapacitors, charges must move quickly and smoothly, which requires a low internal resistance of the capacitor. Several sources contribute to the total internal resistance of capacitors. They are collectively known as the equivalent series resistance (ESR) of the capacitor. The ESR mainly comprises 1) electrode resistance, 2) interfacial resistance between the electrode and current collector, 3) ionic diffusion resistance through the pores, 4) resistance of ions while moving through separators, and 5) electrolyte resistance. Therefore, the conductivity of the electrode should be very high to lower the overall internal resistance of the capacitor. To reduce the diffusion resistance of ions through the pores, proper pore size distribution is required. Enhanced connectivity between several pores is very important to provide a smooth pathway for the movement of charges within the electrode. This reduces the diffusion resistance of ions. Proper choice of an electrolyte with a low solution resistance is important and one with good ion mobility is preferable.

2.2. Response to alternating current

When an alternating current (ac) is applied to an electrode, the electrode has a transient response in each half cycle, and the responses are opposite in nature for the positive and negative half cycles. This response is repeated with time, and the electrode possesses a time-invariant quasi-steady state as a whole. If an ac current \( I_{ac} = I_{ac0}\sin\omega t \) (\( I_{ac0} = \text{amplitude and } \omega = \text{angular frequency} \)) is applied to the electrode, the corresponding potential change \( \Delta E_{ac} \) (amplitude \( \Delta E_{ac0} \)) takes place. A purely resistive (ohmic) electrode should follow \( \Delta E_{ac0}/I_{ac0} = \Delta E_{dc}/I_{dc} \). However, no real electrode follows this behavior because a capacitive component is always found with a resistive part, and there is always a phase difference, \( \alpha \), between current and potential. Thus, instead of resistance, impedance \( Z \) is used to explain the response, in which the modulus of impedance is \( |Z| = \Delta E_{ac0}/I_{ac0} \) with a phase shift of \( \alpha \). The reciprocal of impedance \( Y = 1/Z \), which is known as admittance or ac conductance. The simplest model for a circuit with an ac response can be represented by a combination of resistors and capacitors in series and parallel (RC circuit), as shown in Figure 1a and b, respective.
tively. To demonstrate the ac response, either of these circuits can be used to crudely represent the capacitor.\(^1\)

To begin with, let us consider the parallel equivalent circuit (Figure 1 b), for which the overall impedance is a function of frequency \(\omega\). The components of impedance are \(Z'\) (the resistive part) and \(Z''\) (the capacitive part) and they can be expressed as Equations (4) and (5), respectively:

\[
Z' = R \\
Z'' = \frac{1}{j\omega C}
\]  

The overall impedance is given by Equation (6):

\[
Z = \frac{Z' + j \omega C}{1 + j \omega C}
\]  

Rationalizing Equation (6), \(Z\) can be expressed as shown in Equation (7):\(^2\)

\[
Z = \frac{j\omega R C - R}{\omega^2 R C^2 + 1} = \frac{j\omega R C}{\omega^2 C^2 + 1} + \frac{R}{\omega^2 R C^2 + 1}
\]

After rearranging Equations (4)–(7), we can obtain the expression given by Equation (8):

\[
(Z')^2 + (Z'' - R/2)^2 = (R/2)^2
\]

Equation (8) corresponds to a circle when \(Z'\) and \(Z''\) are considered to be the abscissa (x axis) and ordinate (y axis), respectively, of a coordinate system (i.e., the conventional plot of the imaginary part of the cell impedance on the y axis against its real part on the x axis). This circle has a radius of \(R/2\) and two intercepts on the \(Z'\) axis for \(Z'' = 0\), with values 0 and \(R\). The impedance behavior in this case is, therefore, represented by a semicircle.

In most systems of practical significance, another series resistor, \(R_s\) (representing the ohmic resistance of the solution and the separator), is included in the series of the above-mentioned circuit shown in Figure 1 a, and the resulting equivalent circuit is shown in Figure 1 c. When \(R_s\) is considered, the semicircle is displaced along the \(Z'\) axis by \(R_s\); the two intercepts of the semicircle are at \(Z' = R_s\) and \(Z'' = R + R_s\) (Figure 1 e).

The electrochemical reactions can be either kinetically or diffusion controlled, depending upon the frequency applied. For high-frequency signals, the kinetically controlled reaction is dominant and with decreasing frequency the diffusion-controlled reaction becomes more important. The impedance in the high-frequency region can be expressed by Equation (9):

\[
\omega \to \infty, Z = Z'' \to \frac{1}{j\omega C}
\]

that is, \(Z''\) is small and \(Z\) is determined by \(C\) only, which provides the main pathway for the ac current. For low-frequency values, we have \(\omega \to 0, Z'' \to \infty\), and the only pathway for the ac current is through \(R\) and \(Z' = Z\). Therefore, for the low-frequency region, the impedance plot generally shows almost linear behavior, as shown in Figure 1 e. These linear responses have different slopes, depending upon the phase difference. The phase difference exists because of the dependence of the electrode potential on the reactant concentration. The electrode potential, according to the Nernst equation, is determined by the reactant concentration at the electrode surface. The applied ac signal periodically changes the surface concentration, which introduces a phase shift between electrode potential and applied ac voltage. In Figure 1 e, curves “B” and “C” have different slopes. Here, the steeper slope (e.g., response, curve “C”) indicates that double-layer charge-storage phenomena are more dominant, whereas the shallower slope (e.g., response, curve “B”) accounts for a more faradaic capacitative behavior. If the periodic change in the surface concentration of the reactants is small, then the change in electrode potential has a phase shift of 45° with respect to the applied ac signal.\(^3\) When the phase shift is 45°, \(Z'' = Z'\). The obtained modulus of impedance is \(|Z| = \sqrt{R^2 + R_s^2}\), which is known as the Warburg impedance \((Z_w)\), and \(R_a\) and \(C_a\) are the corresponding components.\(^4\)

When both pseudocapacitance and EDLC contributions are considered, a different equivalent circuit has to be drawn (Figure 1 d). Here, \(C_a\) and \(C_p\) represent the double-layer capacitance and pseudocapacitance, respectively, and \(R_e\) and \(R_d\) represent the faradaic and desorption resistance, respectively. The impedance response of this equivalent circuit is shown in Figure 1 f. Here, two semicircles can be observed in the complex plane because relaxation processes involve \(C_a\) and \(C_p\) coupled with ohmic elements. These two semicircles intersect the \(Z'\) axis at three points: \(Z = R_e\), \(R_e + R_a\), and \(R_a + R_s + R_e\). The radii of the two semicircles are determined by the resistances \(R_e\) and \(R_s\), respectively.

As discussed above, pseudocapacitance and EDLC depend on several interconnected parameters, such as total surface area of the electrodes, pore sizes, electrode interfaces, and the nature of the electrolytes. In the following, we try to explain all of these related parameters and their mutual dependence. The related difficulties are discussed and relevant research works have been addressed. Discussions related to EDLCs include surface area and porosity control of pure carbon materials. At the same time, composite carbon materials, functionalized carbon materials, and related issues are addressed to realize pseudocapacitance.

3. Electrolytes

Electrolytes are a central element of capacitors. Two electrodes are interconnected by an electrolyte that determines charge transport. In general, there are three types of electrolytes: 1) aqueous electrolytes, 2) organic electrolytes, and 3) ionic liquids (ILs). All three types of electrolytes have their own advantages and disadvantages when used in capacitors. Aqueous electrolytes have smaller solvated ions and higher dielectric constants, both of which promote capacitance. Whereas higher dielectric values promote storage, at the same time smaller solvated ions provide access to different pores. Aque-
uous electrolytes have higher conductivities than those of organic electrolytes, which results in a better power delivery. Conversely, aqueous electrolytes are limited to operations below 1.2 V because water molecules start to decompose above this voltage. The energy density is proportional to the square of the voltage, giving rise to a lower energy density. Due to this, organic electrolytes with higher operating voltages up to 2.5–3.0 V have been used, which gives rise to energy densities six to nine times that of the aqueous solution. However, the solvated ion size is supposedly larger than that of protons and generally leads to a smaller capacitance. Thus, control of the pore sizes of the electrodes is a key factor for achieving a high capacitance. Another drawback is the poor stability of organic electrolytes in air. Whereas aqueous solutions are free of environmental constraints, most organic electrolytes are hygroscopic, which means that they are sensitive to moisture, and, in particular, lithium-containing electrolytes are flammable when exposed to air. A further increase in operating voltage can be realized with the use of an IL; a potential window of 4.0 V has been obtained when using an IL along with a very high specific energy density of nearly 90 Wh kg$^{-1}$.[23] Although a wider potential window can be obtained, ILs suffer from their highly viscous nature. High viscosity provides good wettability of the electrode material, but at the same time it prevents smooth ion transfer. Proper temperature control could be key to overcoming the viscosity of ILs.[23]

4. Materials for EDLCs

4.1. Activated carbon

A typical example of an EDLC material is AC. A full understanding of the charge-storage mechanism in AC electrodes is very important due to the complexity of its pore structures. The capacity depends on several mutually interlinked parameters, that is, total specific surface area, normally referred to as the Brunauer–Emmet–Teller (BET) surface area; the nature of the porosity of the electrode; the pore size distribution; and the conductivity of the electrode material. ACs have highly porous surface areas consisting of different types of pores. Porous electrodes can be divided into three main categories based on the dimension of their diameters: 1) micro-$\langle$2 nm), 2) meso-(2–50 nm), and 3) macropores ($\geq$50 nm).[1] An electrode, in general, consists of these three types of pores. Because different types of pores interact with ions in electrolytes in different ways,[24] the capacitance performance of an electrode is affected by the relative amount of pores with different sizes present in the electrode.

The BET surface area plays an important role in the case of electrical double layer (EDL) charge storage. For high surface areas, more sites are available for ions to be accumulated by electrostatic interactions, and thus, an improved capacitance can be obtained. However, this proportionality between BET surface area and total charge-storage capacity deviates when the pore size of the electrode material is taken into account.[25] The development of surface areas with small pores that are inaccessible for ions does not improve capacitance performance.[24] Despite similar BET surface areas, electrodes with different pore sizes exhibit different capacitive behavior. Micropores were more efficient than mesopores.[26] An increased micropore volume in comparison to the mesopore volume enhanced the specific capacitance for a carbide-derived carbon electrode in aqueous solutions. During the electrochemical process, ions in the electrolyte are adsorbed onto the inner wall of the pores. In general, mesopores are larger than the ion sizes. In an aqueous medium, the effective ionic dimension of the cations, such as Cs$^+$, K$^+$, Na$^+$, and Li$^+$, is less than 0.42 nm and that of the anions, such as NO$$_3$$^-$, Cl$^-$, F$^-$, Br$^-$, and ClO$$_4$$^-$, is less than 0.51 nm.[27] Thus, electroadsorption in mesopores (2–50 nm) is not as efficient as that in micropores from the viewpoint of maximum utilization of the porous surface area. On the other hand, micropores are important because they are closer to the dimension of ions: a micropore that is larger than the ion can be accessed easily. Conversely, access to smaller pores may be difficult due to a sieving effect.[27] Therefore, a suitable micropore size is a key factor to obtain a maximum charge-storage performance. To obtain an intuitive idea of the preferable pore size for optimum performance, we present a 3D graphical representation of collated data[24,25,28–35] (Figure 2) and try to determine the dependence of the specific capacitance ($z$ axis) on pore size distribution ($x$ axis) and BET surface area ($y$ axis). Specific capacitances were obtained from different types of carbon samples with various pore sizes and different BET surface areas in aqueous electrolytes. When we look at the results, there are two important observations. If we focus on the capacitive behavior along a straight line parallel to the $y$ axis, that is, if we take the pore diameter as a fixed parameter, it can then be easily observed that larger BET surface areas result in higher specific capacitance values. This behavior is true regardless of pore diameter. On the other hand, for a fixed BET surface area value, higher capacitances are observed for smaller micropores. Micropores with diameters less than 1 nm and highest surface areas exhibit the best capacitive performance.

Figure 2. 3D graphical representation of the dependence of specific capacitance on pore diameter and BET surface area.
It has been reported that pore sizes very close to those of the ion size lead to an enhancement of the double-layer capacitance compared to larger pores.\[36, 37\] These observations are very interesting because they challenge the well-known axioms that the essential requirement for forming a double layer is to have pores larger than the solvated ion.\[36, 37\] These results showed that for pore sizes that matched the solvated ion sizes, the solvation shell became highly distorted as the ion was squeezed through the pore, in much the same way as a balloon. Such distortion allowed the ions to become adsorbed into the pores and provided a closer approach of the ion center to the electrode surface, which led to improved capacitance.\[37\] This distortion can sometimes remove the hydration sheath around ions and lead to adsorption.\[39\]

A similar interesting result is reported in Figure 3 a, which represents the maximum capacitance performance for a pore size of about 0.7 nm for the case of the IL 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([EMI][TFSI]). The ion sizes of the [EMI][TFSI] electrolyte were of the order of around 0.75 nm, as shown in Figure 3 a. For this perfect match of ion and pore size, the capacitance was enhanced because the average distance \(d\) between the pore wall and the center of the ion was minimized and capacitance was according to Equation (1). Therefore, for higher \(d\), in the case of 0.7–1.1 nm pore sizes, lower capacitances were obtained as pores smaller than 0.7 nm could not be accessed by the electrolytes.\[36\]

Conversely, removal of the hydration sheath is not easy for a bivalent ion, and a clear sieving effect for smaller pores was shown for bivalent ions in Figure 3 b. In a related study, the shape of cyclic voltammetry (CV) curves was affected by pore sizes.\[27\] When the pore sizes of the electrode material were significantly larger than those of the ion sizes, typical rectangular CV curves were obtained. Conversely, smaller pores resulted in a triangular-shaped CV curve. This was attributed to the mismatch in the stored charges during double-layer formation. Smaller ions were successfully incorporated into the pores at one side of the potential of zero charge (pzc). Incorporation of ions was significantly reduced in the case of electroadsorption of larger bivalent ions. These ions with hydration sheaths failed to be adsorbed into the smaller pores. A comparative study with MgCl\(_2\) and Li\(_2\)SO\(_4\) is presented in Figure 3 b. A triangular-shaped CV curve was obtained for the MgCl\(_2\) electrolyte.\[27\]

However, it is tricky to obtain a high surface area and suitable pore size distribution simultaneously. The mutual dependence of these parameters and the related complexity can be visualized from a study based on carbide-derived carbon (CDC; TiC- and ZrC-derived carbon), as shown in Figure 4.\[26\] Although an increased synthesis temperature produced larger BET surface areas (Figure 4 a), the gravimetric capacitance decreased (Figure 4 c) in the high-temperature region. This degradation in capacitance was attributed to the increased size of the micropores (Figure 4 b) and the reduced micropore surface area with increasing temperature. Again, a high synthesis temperature reduced the ESR for both samples, which was desirable for a better capacitance performance (Figure 4 d and e). Thus, high
BET surface area and improved conductivity were obtained at high temperature. Conversely, high-temperature treatment reduced the micropore contribution, and hence, the capacitance was reduced. At the same time, if the porosity was too high, it led to poor electrical conductivity and low volumetric capacitance. Therefore, an intelligent tradeoff of these parameters is needed, which can be controlled during the synthesis of ACs.

For the AC materials, the initial raw material has a significant impact on the formation mechanism and specific surface area of the final material. Raw materials such as coal-based carbon, resin-based carbon, and CDC have been widely used. AC materials, which originated from coconut shells, phenolic resins, and coal, were produced by steam activation and exhibited specific surface areas of 1860–2120 m² g⁻¹, depending on activation time. In some other works, similar raw materials, such as shells, olive-seed waste residues, and banana fibers, were also used as carbon sources to prepare ACs for EDLCs. The porosity of the AC strongly depends on the activation process and conditions. ACs with different pore sizes were prepared by using different physical and chemical activation methods. Activation processes with KOH, CO₂, and steam have been used by several groups. Physical activation with CO₂ can be better than steam activation. During physical activation with steam, the reaction increased the amount of mesopores (pore diameter > 2 nm) as the activation temperature increased. To obtain an adequate porous texture, the activation temperature must be kept low, which in turn leads to poor conductive materials. As a consequence, such materials have limited applicability for high-power-density devices. In contrast, it is known that physical activation with CO₂ results in a more homogeneous development of porosity within the carbon fibers than that with steam.

Although micropores can perform better than mesopores, having only micropores is not desirable because this prevents smooth transfer of ions in the electrolyte into the deeper region of the electrodes, that is, into the bulk of the active material. Conversely, mesopores provide entry for ions into the bulk of the material to access the micropores. Enhanced capacitance can be observed in the presence of mesopores on the surface.

A collated data set is given as a 3D graphical representation in Figure 5 to analyze the dependence of specific capacitance (z axis) on the relative amount of microporous volume (x axis) and mesoporous volume (y axis). Capacitance performance was observed in different aqueous electrolytes. A large capacitance value was obtained for a higher micropore volume. Along a straight line parallel to the x axis, that is, if we take a fixed mesopore volume, it is observed that the capacitance performance deteriorates with decreasing micropore volumes. High mesopore volumes result in poor capacitance performance. In Figure 5, the maximum specific capacitance was observed with a very high micropore volume (≈ 1.2 m³ g⁻¹) and moderate mesopore volume (≈ 0.42 m³ g⁻¹). The combination of high micropore and low mesopore volumes is suitable for certain ion sizes particularly in organic electrolytes. Developing micropores may sometimes have several negative aspects. During activation, the yield of micropores in the electrode material is sometimes even below 50%. Furthermore, the density of the electrodes is very low, which results in poor volumetric capacitance and poor electrical conductivity.

The performance of mesoporous electrodes is significantly enhanced when the pores are in a regular pattern or in the form of an interconnected 3D network. A 3D interconnected mesoporous electrode was prepared from isotropic pitch without activation. When the pitch was precipitated in water, microporous carbon nanospheres (MCNSs) were formed and aggregated together to form a 3D network. MCNSs were composed of nanospheres distributed from 100 to 300 nm in diameter. Nanocarbon spheres and micropores were bridged by mesopores. These structural features enabled MCNSs to have specific capacitances as high as 154 F g⁻¹ despite a moderate specific surface area of 245 m² g⁻¹. Recent work focused on mixing two pore sizes together and compared micro- and mesoporous capacitive behavior by means of CV and galvanostatic charge–discharge tests. Mesoporous carbons are good at high scan rates, whereas microporous carbons possess high capacitances at low scan rates.

Mesoporous structures, when ordered or in a pattern, can outperform microporous structures at energy storage. These ordered mesoporous carbons (OMCs) offer great potential in EDLCs, particularly for applications for which a high power output and improved high-frequency capacitive performances are required. OMCs are generally prepared by using different types of templates. Many nanoporous carbon materials with variable pore sizes and pore structures have been synthesized by using different carbon sources and different types of designed nanostructured silica materials as a template. These nanoporous carbon materials exhibit high surface areas, large pore volumes, and uniform mesopores, and showed good supercapacitor performances. Inverse replicas of mesostructured silica templates were used to obtain mesoporous carbons of different pore sizes and BET surface areas. Two types of mesoporous carbons, one with a pore size of 3 nm and a BET surface area of 1550 m² g⁻¹ and the other with pore sizes between 3 and 16 nm with a BET surface area of 1730 m² g⁻¹, were obtained with a narrow pore size distribu-
These OMCs exhibited enhanced capacitive behavior, better power output characteristics, and high-frequency performances.\cite{69} The relatively poor performance of ACs is believed to be due to their disordered pore structures.\cite{70} In Figure 6a–k, we can see a comparative study of three kinds of OMC structures with a disordered pore structure (Maxsorb). The small-angle diffraction pattern of the Maxsorb sample showed a very broad band. This is the signature of disordered and randomly connected pores. The corresponding 2D and 3D models are shown in Figure 6i and j. All three patterns for the three different kinds of ordered structures (OMC-1, OMC-2, and OMC-3) had distinct peaks, representing the highly ordered periodic structures; these three different structures consisted of 3D cubic symmetry (OMC-1; TEM image in Figure 6g and 3D model in Figure 6h), an ordered arrangement of carbon nanorods (OMC-2; TEM image in Figure 6d and e, 3D model in Figure 6f), and pipelike mesoporous carbon (OMC-3; TEM image in Figure 6a and b, 3D model in Figure 6c). For the disordered and random small porous structures, ionic diffusion was very slow. The ordered structures showed much better diffusive performance. In Figure 6k, the ordered electrode retained its capacitance performance much better than the disordered structure at higher scan rates. Disordered pore structures could not utilize the available surface area at higher scan rates, where faster ion movement was involved. OMCs were effective at higher scan rates because of their high periodicity.\cite{70} To optimize rapid ion diffusion in mesoporous structures, efforts have been devoted to construct the correct amount of secondary larger pores as a mass transport pathway (MTP).\cite{71,72} MTPs were constructed in wormhole-like mesoporous carbon (WMCs) and played an important role in improving the ion diffusion performance of the WMCs.\cite{73} Figures 6m and n show TEM images of WMC structures without and with the MTP layer, respectively; the schematics of which are shown in Figure 6o and p. The sample with the MTP layer exhibited a much lower ESR (Figure 6l) and a steeper slope in the linear region of the impedance spectrum than the sample without MTP layers. This suggested an accelerated movement of ions inside the nanopores and better pore accessibility in the WMC with an MTP.\cite{73} Therefore, proper modification of the OMC structures can improve the capacitance performance significantly.
Carbon aerogels are another type of very effective electrode material due to special pore properties and they have received considerable interest in several studies. They are highly porous and highly conductive with conductivities up to 100 S cm\(^{-1}\), controllable pore structures, low mass densities, and high surface areas up to 1100 m\(^2\) g\(^{-1}\). [74–77] These monolithic porous carbon aerogels are suitable for supercapacitor applications. Carbon aerogels were prepared in the resorcinol–formaldehyde (RF) system in several studies. [78, 79] The structures and properties of aerogels are generally affected by the amount of reactant and catalyst. The structures, pore sizes, and particle sizes can be controlled by operating a sol–gel process. [80] The radii and morphologies of the primary particles constituting the RF hydrogel determined the pore characteristics. [81] Sol–gel microspheres with diameters ranging from about 30–1000 μm were obtained by means of inverse phase suspension of RF, and a high specific capacitance of 215 F g\(^{-1}\) was reported. [82]

Transportation of electrolyte ions through a 3D electrode material is controlled by several parameters, that is, the curved nature of the ion transport path; the shapes and sizes of the pores, that is, whether they are micro-, meso-, or macroporous; the conductivity of the electrodes; the connectivity between the pores and solid–liquid interfacial properties; their wettability; and so forth. Easier ion transport results in better charge storage and power performance of an electrode material. Easier charge transport requires short diffusion pathways for the ions and low values of electrode resistance, [83–85] otherwise a significant electrode-potential drop (IR drop) and low ion-accessible surface area at large current values are expected, which severely reduces the performance of the capacitor. [86] OMCs provide shorter diffusion pathways (0.5–1.0 μm) and lower transport resistances than those of microporous carbons with comparatively long diffusion routes (> 5 μm) and high ion transport resistances. All of these important parameters rank OMCs ahead of microporous carbons in terms of electrochemical capacitance performance.

The performance of OMCs can be further improved by facilitating a faradaic pseudocapacitance. [87–90] Further activation to enhance electrolyte accessibility to the microporous area. This electrode had an excellent frequency response and outstanding capacitance retention at high current densities. [95] A direct comparison between aligned CNTs were used as polarizable electrodes in EDLCs, and an energy density in the range from 7–6.5 Wh kg\(^{-1}\). [96] Heat treatment of SWCNTs modified the pore formation significantly. High temperature increased the capacitance and reduced the SWCNT electrode resistance. The increased capacitance was explained by enhancement of the specific surface area and abundant pore distributions at lower pore sizes of 3–5 nm. [103] Electrodes prepared from catalytically grown MWCNTs with a surface area of 430 m\(^2\) g\(^{-1}\) showed a maximum specific capacitance of 113 F g\(^{-1}\) and a power density of 8 kW kg\(^{-1}\) at an energy density of 0.56 Wh kg\(^{-1}\). [104]

Various forms of CNTs have been tested as electrode materials, that is, directly grown, porous tablets, aligned CNTs, entangled CNTs, and assembled structures of CNTs. CNTs 50 nm in diameter directly grown on graphite foil exhibited EDLC behavior, and a specific capacitance of 115.7 F g\(^{-1}\) was obtained. Direct growth minimized the contact resistance between the active materials and the current collector. [100] Porous tablets of CNTs were used as polarizable electrodes in EDLCs, and an energy density up to 20 Wh kg\(^{-1}\) using a 10 mA discharge current was obtained. [101] A direct comparison between aligned
and entangled CNTs was also reported and established that aligned electrodes were better than entangled CNTs. Lower ESR and better reaction rate capability was obtained in the aligned CNTs because of larger pore sizes, more regular pore structures, and conductive pathways of aligned CNT electrodes.

Flexible CNTs have found potential applications in a compact electrode design. This compact electrode was rolled together with separators by using large-scaled, free standing, and flexible SWCNT films and used as both anode and cathode. High energy and power densities of 43.7 Wh kg$^{-1}$ and 197.3 kW kg$^{-1}$, respectively, were reported for the prepared SWCNT film-based compact-designed supercapacitors with small ESRs. The specific capacitance obtained was about 35 F g$^{-1}$ with an organic electrolyte.[108]

Supercapacitor electrodes prepared from as-grown SWCNTs with a SWCNT selectivity (>99%) delivered an energy density of 94 Wh kg$^{-1}$ and a power density of 210 kW kg$^{-1}$ when 1 m Et$_4$NBF$_4$/propylene carbonate was used as an electrolyte. A specific capacitance of 160 F g$^{-1}$ was obtained with a higher operation voltage of 4 V, which was beneficial for obtaining a higher energy density.[104]

One interesting property of CNTs is the relationship between BET surface area and capacitance. The BET surface area of the annealed SWCNTs was 360 m$^2$ g$^{-1}$, which is smaller than that of ACs. We can estimate a theoretical capacity by considering a planar electrode capacity of 20–50 μF cm$^{-2}$.[11] For typical ACs of MSC30 with a BET surface area of 3000 m$^2$ g$^{-1}$, the estimated capacity is 20–50 μF cm$^{-2}$ × 3000 m$^2$ g$^{-1}$ = 600–1500 F g$^{-1}$. Similarly, for SWCNTs with a BET surface area of 360 m$^2$ g$^{-1}$, the estimated capacity is 72–180 F g$^{-1}$. This strongly implies that all of the pores contribute to the capacity in SWCNTs, whereas a major portion of the large surface area in ACs does not contribute to the capacity. This again confirms an appropriate match of pore sizes and distributions to the sizes of the ions in the electrolyte.

5. Materials for Pseudocapacitors

5.1. Carbon embedded with redox agents

5.1.1. Functionalized carbon nanotubes

When both sides of a graphene sheet are considered, the surface area has a high theoretical limit of 2630 m$^2$ g$^{-1}$.[105] However, when these sheets are rolled up to form CNTs, accessible surface areas are reduced drastically to values in the order of 240–1250 m$^2$ g$^{-1}$. Typical closed structures of CNTs, that is, closed-cap structures at the end of CNTs or defect-free continuous honeycomb lattices, leave no effective entry point for the electrolyte ions. Thus, the inner surface of the CNTs remains inaccessible to the electrolyte. Another obstacle is tightly bundled CNTs, which prevent electrolyte access to inner volume, and thus, results in only limited outer-surface accessibility. For similar reasons, MWCNTs have even lower accessible surface areas.[106] Because of these typical properties of CNTs, special surface treatments are needed, which help to develop some defects or pores or increases the separation distance between the CNTs in the bundle. To address this issue, several attempts have been made by several research groups.

An effort to create open edges on the closed surface of the SWCNTs through oxidation was reported; this resulted in a structure composed of aligned and closely packed open SWCNTs with a very high surface area of over 2200 m$^2$ g$^{-1}$.[107] Windows were opened on the sidewalls of the CNTs by controlled slow oxidation to gain access to the inner surface. In Figure 7 a–c, a comparison between open and as-grown SWNT bundles (with closed surfaces) is shown. TEM images of as-grown SWNTs and open SWNTs are shown in Figure 7 b and c, respectively, in which open surfaces can be clearly observed. Nitrogen adsorption–desorption isotherms at 77 K for as-grown (blue) and open SWNTs (red), and purified HiPco (black) exhibited maximum surface areas for open samples (Figure 7 a) and thus high energy (24.7 Wh kg$^{-1}$) and power densities (98.9 kW kg$^{-1}$).[107] Similarly, the porosity of the SWCNTs was increased by opening the nanotube tips and damaging the sidewalls through electrochemical treatment using KOH. Figure 7 d shows a high resolution HRTEM image of chemically modified SWCNTs with an etched surface area. These modified SWCNTs exhibited better nitrogen adsorption (Figure 7 e), which indicated better porosity than that of the as-grown sample. Modified SWCNTs had a considerably improved capacity performance compared to that of as-grown CNTs (Figure 7 f).[108]

The specific surface area has been also engineered by fluorination of SWCNTs. Despite similar specific surface areas of pristine and fluorinated SWCNTs, the electrochemical reactions were significantly different from each other. Although the initial specific capacitance of the fluorinated SWCNTs was lower than that of the pristine sample (Figure 8 a and b), the fluorinated sample gave a larger specific capacitance than the pristine sample after heat treatment (Figure 8 c and d). This indicates the importance of proper functionalization and post-treatment of the functionalized sample.[109]

By using surface functionalization techniques, CNTs can be converted from hydrophobic to hydrophilic in nature. By introducing surface carboxyl and hydroxyl groups, the wettability was improved, and a larger capacitance was created due to the increased hydrophilicity of the MWCNTs in aqueous electrolytes. Conversely, the introduction of alkyl groups resulted in a marked decrease in capacitance. The capacitance even disappeared for samples functionalized with alkyl groups longer than octyl, indicating increased hydrophobicity.[110] Pyrrole-treated functionalized SWCNTs showed high capacitance (350 F g$^{-1}$).[111]

5.1.2. Functional redox agents in porous carbon

The presence of functional redox agents, such as nitrogen and oxygen, can significantly enhance capacitance performance. The presence of nitrogen can enhance the capacitive behavior of carbon materials in several ways. Incorporated nitrogen atoms modify the space charge distribution of porous carbon materials, and thus, the enhanced pseudocapacitive interaction between protons and electron donor nitrogen atoms results in an enhanced charge storage performance.[46] Nitrogen-en-
Riched carbon matrices, MWCNTs, mesoporous carbon spheres, and nitrogen-doped microporous templated carbons are typical routes for the preparation of high-capacitance electrode materials.

An oxygen-enriched carbon network showed results similar to a nitrogen-enriched one. Despite low porosity, the electrode performed well as a capacitor because of the increased oxygen content. Oxygen atoms participated in faradaic charge-transfer reactions to give an improved capacitance. In addition, the incorporated oxygen might provoke a potential shift of both electrodes, allowing the operating voltage to be enhanced, thus resulting in a high energy density. Therefore, functionalization of the carbon surface is an effective way to improve capacitive performance. This process is sometimes more preferable than highly porous structures because highly porous structures can be detrimental to the conductivity of the electrodes.

5.2. Graphene oxide and its composites

Graphene is a 2D carbon allotrope, that is, a sheet of carbon atoms arranged in a hexagonal lattice. As mentioned, a 2D graphene sheet has a theoretical surface area of 2630 m² g⁻¹, which is excellent for capacitance applications. The intrinsic capacitance of graphene was reported to be 21 mF cm⁻². With this high surface area and outstanding conductivity (200–3000 S cm⁻¹), graphene possesses great potential to be an excellent candidate for supercapacitor applications. However, in reality, making a proper electrode from graphene suffers from problems such as restacking of the graphene layers. Electrolytes need to access large surface areas of electrode materials to obtain high specific capacitances, but restacking of the graphene layers prevents charge storage and reduces the accessible volume and surface area, which in turn reduces the charge-storage capability.

To achieve separated graphene layers, an effective approach is exfoliation of GO followed by reduction to give the final product, reduced graphite oxide (RGO). Because GO is electrically insulating, this reduction process is very important to restore the conjugated network and electrical conductivity of graphene. A stable colloidal solution of GO was obtained by simple sonication of GO in aqueous media. Large-scale dispersed GO in organic solution is highly desirable. GO dispersed in N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and ethylene glycol (EG) was obtained through exfoliation of GO. A dispersion of GO was obtained in other organic media, including chloro-
centrated solution of KOH, and this modification resulted in enhanced performance.[141]

Graphene electrodes with other carbon materials have been tested: graphene/CNT hybrid films and graphene/carbon black composite electrodes.[142, 143] Graphene composites with MnO2 have been studied by several groups, and high capacitance performances were obtained in different electrolytes, such as Na2SO4, KCl, and KOH.[144–147] Other metal oxides (MOs), such as ZnO, SnO2, Ni(OH)2, RuO2, Co3O4, and Bi2O3, were also tested for the preparation of composite electrodes with graphene.[148–154] Poly(aniline) (PANI) was used to prepare composite electrodes with hydrazine-reduced GO, chemically converted graphene, and microwave-treated GO.[155–157] An in situ polymerization method was used to prepare a PANI film on graphene paper, a graphene nanosheet/PANI composite, and other PANI composites.[158–161] PANI nanowires were aligned vertically on GO substrate, and a high capacitance of 555 F g–1 was obtained in an H2SO4 electrolyte.[162] Composites of GO with other polymers exhibited good results. Poly(pyrrrole) (Ppy) composites with GO and graphene nanosheets exhibited high capacitances of 500 and 482 F g–1, respectively.[163, 164] A poly(sodium 4-styrene sulfonate) (PSS)–GO composite showed enhanced capacitance in organic electrolytes.[165] A composite electrode of GO/RF resin showed a capacitance of 397 F g–1 in a 6 M KOH electrolyte.[166] Recently, hydrogen-exfoliated graphene was used as a supercapacitor electrode. The functionalization of graphene provided anchoring sites for decoration of MO nanoparticles and conducting polymers.[167]

5.3. Composites of CNTs

In composite forms, CNTs can be used as excellent 3D host materials to support other active materials with good pseudocapacitance properties, that is, electronically conducting polymers (ECP) and MOs.[19, 168–171] In addition, CNTs play a crucial role as conducting additives for the electrodes.[172, 173] The ESR can be decreased significantly, and a highly conducting electrode can be obtained, which results in high power density.[174] The addition of CNTs also improves the mechanical and electrochemical properties of the electrode material significantly.[175, 176] Due to the excellent mechanical properties of CNTs, they can adapt to any volume change during electrochemical performance, which leads to excellent cycling performance.[175]

CNTs were introduced as a conductive additive to amorphous manganese dioxide (a-MnO2·nH2O) prepared by chemical coprecipitation of manganese(VII) and manganese(II). CNTs enhanced the capacitance and improved the electrochemical properties more than carbon black. This enhancement was due to the high entanglement of CNTs, which formed a network of open mesopores, thus allowing bulk MnO2 to be easily accessible for the ions.[172]

When MWCNTs were embedded in polyacrylonitrile (PAN) nanofibers by means of an electrospinning process, the conductivity was enhanced, and a large anisotropy was observed. The electrical conductivity of the carbonized nanofiber paper along the spinning direction was about three times larger than that along the normal to the spinning direction. This result

form[119] and propylene carbonate.[120] By means of thermal exfoliation of GO, functionalized graphene sheets (FGSSs) were prepared by several groups.[121–125] One simple way to obtain FGSSs is to use thermal exfoliation at low temperatures of around 300 °C. This is advantageous in comparison to high-temperature explosion methods because the sample can be extracted easily in high yield. In addition, microwave-irradiated GO[126] and a directly heated suspension of GO[120] have been successfully used to prepare GO. Thermally exfoliated FGSS was further annealed at high temperature (1900 °C) and under high vacuum conditions (0.133 mPa).[127]

Hydrazine, hydroquinone, and NaBH4 have been widely used as reducing agents for GO.[128–135] GO platelets have also been extracted easily in high yield. In addition, microwave-treated GO. Thermally exfoliated FGSS was further annealed at high temperature (1900 °C) and under high vacuum conditions (0.133 mPa).[127]

Figure 8. A comparison of the specific capacitance of raw and fluorinated samples a, b) before and c, d) after heat treatment. Reproduced from Ref. [109] with permission.

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was in contrast to the observation that carbonized PAN nanofiber paper without CNTs did not have an anisotropy in electrical conductivity.[177]

But excessive addition of CNTs can decrease the capacitance per unit mass. Figure 9 shows the variance in capacitance performance with different amounts of CNTs and the dependence of ESR on the amount of added CNTs. Galvanostatic measurements showed that a CNT content higher than 15% led to a significant decrease in the ESR of the electrode (Figure 9b). This improved conductivity led to enhanced power performance. However, at the same time, a significant decrease in specific capacitance was observed (Figure 9a). Higher CNT content led to poor capacitance performance. A CNT content of 15% in the electrode was the best compromise between charge-storage capability and conductivity of the electrode.[174]

The TEM image of a strip of Mn$_3$O$_4$/CNT array (CNTA) composites is shown in Figure 10a. Mn$_3$O$_4$ nanoparticles were found to coat the walls of the CNTAs. This composite material (loaded with 33 or 84 wt% Mn$_3$O$_4$) exhibited superior capacitance performance in comparison to the CNTA-only sample, as observed from CV data (Figure 10b). The capacitance obtained per unit mass was higher in the case of the 33 wt% loaded sample than in the case of the 84 wt% loaded one (Figure 10c) because of larger oxide particle sizes and aggregation.[178] The synthesis of RuO$_2$-xH$_2$O nanodots on the surfaces of PSS-functionalized (PMWCNTs resulted in good surface distribution and nanodot coverage, which provided an enhanced capacitance performance.[179] A direct approach to grow RuO$_2$ nanoparticles on CNTs resulted in well-dispersed RuO$_2$ nanoparticles (with diameters less than 2 nm) on the outer surface of CNTs, and a high specific capacitance of 953 F g$^{-1}$ was obtained.[180] An inkjet-printed hybrid RuO$_2$ nanowire/SWCNT nanostructured thin-film electrode displayed enhanced device performance in terms of a coulombic efficiency of > 99%; a specific capacitance of 138 F g$^{-1}$, with a power density of 96 kW kg$^{-1}$; and an energy density of 18.8 Wh kg$^{-1}$.[181] The RuO$_2$/CNT com-

![Figure 9](image1.png)

**Figure 9.** Variation of a) specific capacitance and b) ESR with different CNT content in the active material. Reproduced from Ref. [174] with permission.

![Figure 10](image2.png)

**Figure 10.** a) TEM image of Mn$_3$O$_4$/CNTA (33 wt%); the inset shows an HRTEM image of the Mn$_3$O$_4$ nanoparticle. b) CV curves of Mn$_3$O$_4$/CNTA composite electrodes (33 and 84 wt%) and as-grown CNTA electrode at 50 mV s$^{-1}$. c) Specific capacitance for the Mn$_3$O$_4$/CNTA composite electrodes (● 33 and ● 84 wt%) at various scan rates. Reproduced from Ref. [176] with permission.
Composite was obtained by depositing Ru by means of magnetic sputtering. The capacitance of the MWCNT electrode significantly increased from 0.35 to 16.94 mC m⁻².[192] Several other MO and CNT composite electrodes were also tested, such as a layer-by-layer assembly of MnO₂ and CNTs[183,184] and intertwined CNT/V₂O₅ nanowire nanocomposites.[185] Electrochemically prepared RuO₂ on a CNT film substrate with a 3D nanoporous structure showed enhanced capacitive behavior.[186] Several groups have investigated the electrochemical deposition of MnO₂ on vertically aligned MWCNTs,[187] the chemical deposition of Ni(OH)₂ onto CNTs,[188,189] the in situ loading of Ni(OH)₂,[190] the direct formation of Ni–Co oxides from thermally decomposed nickel, and the deposition of Co(NO₃)₂ onto the surface of CNT/graphite electrodes.[191] Iron oxide and CNT composite electrodes were prepared by means of chemical co-precipitation of Fe²⁺ and Fe³⁺,[192] spray deposition,[193] and chemical methods.[194]

A chemically induced deposition method resulted in MoO₃/ SWCNT composite electrodes with a specific capacitance of 597 F g⁻¹.[195] Superaligned-CNTs (SACNTs) and MnO₂ composite electrodes were prepared through direct synthesis of MnO₂ on SACNT films.[196] CNTs were also tested with several other oxide materials, such as In₂O₃, Co₃O₄, Cr₂O₃, and TiO₂.[197–200] The electrostatic charge storage and faradaic reactions of oxide nanoparticles were affected by the surface functionality of the CNTs. Functionalized electrodes composed of RuO₂/MWCNTs showed increased hydrophilicity, which enabled easy access of the solvated ions to the electrode/electrolyte interface and increased the number of faradaic reaction sites, that is, RuO₂ nanoparticles. This resulted in the increase of the capacitance from 500 to 900 F g⁻¹ with respect to the mass of RuO₂ loaded.[201]

The presence of CNTs can also influence the deposition mechanism of oxides during electrode material preparation, and hence, electrochemical performance. For the codeposition of crystalline MnO₂ and MWCNT onto a graphite substrate, the nucleation mechanism of MnO₂ deposition was reported to be influenced significantly by the introduction of MWCNTs in the plating baths.[202]

Composite electrodes made from CNTs, polymers, and MOs have also been tested: MWCNT/PANI/MnO₂ ternary coaxial structures were fabricated as supercapacitor electrodes by using a simple wet-chemical method.[203] PSS-dispersed MWCNTs have been used as a support for Ppy/MnO₂ in a supercapacitor electrode. The MWCNT–PSS/Ppy–MnO₂ nanocomposite exhibited a specific capacitance of 268 F g⁻¹ at a scan rate of 5 mV s⁻¹ in CV.[204] One oxide material can influence the performance of another oxide material by engineering the electronic properties. The presence of SnO₂ enhanced the electronic properties of V₂O₅ and improved the capacitive behavior in an SnO₂–V₂O₅–CNT composite electrode.[205]

Electrodeposition has been applied successfully to deposit a very thin layer of MO on CNTs: an RuO₂ film with a thickness of 2.5 μm was deposited on CNTs and a high pseudocapacitance was obtained:[206] An MnO₂ thin layer was successfully formed on different types of CNTs by means of electrochemical anodization, electrochemical deposition, and direct redox reactions.[207,208]

Nanocomposite electrodes of SWCNTs and Ppy were fabricated to improve the specific capacitance of the supercapacitor by in situ chemical polymerization of pyrrole. The SWCNT–Ppy nanocomposite electrode showed much higher specific capacitance (265 F g⁻¹) than pure Ppy and as-grown SWCNT electrodes, due to uniformly coated Ppy on the SWNTs, which increased the active sites on the Ppy chains. The specific capacitance significantly increased with increasing the amount of conducting agent up to 15 wt%, then decreased at 20 wt%, again establishing the fact that, similar to that described in the previous section, a maximum limit for the addition of the conducting agent occurred.[209]

5.4. Composites of activated carbon materials

Composites of ACs have been prepared by using MOs and conducting polymers. These electrodes have a mixed response from both pseudocapacitance and EDLC. For example, whereas MO contributed to pseudocapacitance, the porosity of the carbon material contributed to EDLC.

A V₂O₅ ultra-thin film (3–18 nm thick) was coated throughout the outer surface of a PAN-based carbon nanofiber by using an electrodeposition method.[210] The porous carbon nanofiber mat served as a self-standing substrate that maintained the carrier transport layer. A TEM image of the electrodeposited (5 cycles of deposition) nanofiber mat is shown in Figure 11a with a corresponding vanadium mapping image obtained by means of energy-dispersive X-ray (EDX) spectroscopy (Figure 11d), which shows that vanadium was uniformly coated throughout the nanofiber surface. The magnified images for one nanofiber are presented in Figure 11c, e, and f. 

![Figure 11. TEM images of a) a fiber network and b) a single fiber of deposit- ed V₂O₅, and their mapped images for vanadium EDX in (d) and (e), respecti- vely. The oxide layer thickness after 5 and 20 cycles of deposition are shown in (c) and (f), respectively. g) Performance comparison of the total composite capacitance and effective oxide capacitance on different V₂O₅ wt% h⁻¹ values. h) Plot of conductance (multiplied by 1000) with differ- ent amounts of V₂O₅. Reproduced from Ref. [21] with permission.](image-url)
shown in Figure 11b with the corresponding vanadium mappings in Figure 11e. The thickness of electrodeposited oxide was very thin. The reported thicknesses were 3, 10, and 20 nm for 5, 20, and 40 cycles of deposition. The 3 and 10 nm thick layers are shown in Figure 11c and 11f, respectively. The thinnest layer, that is, the minimum weight percentage of deposited \( \text{V}_2\text{O}_5 \), to achieve the best performance was about 15 wt\% as shown in Figure 11g. This result suggested that the maximum electrochemical interaction was obtained for the thinnest layer of oxide because a thick layer prevents diffusion of ions to inner bulk region. A thick layer also increases the overall electrode resistance, as shown in Figure 11h.\(^{[21]}\)

A 3D ultraporous carbon structure was prepared by using amorphous \( \text{MnO}_2 \), and exhibited a high area-normalized capacitance (1.5 F cm\(^{-2}\)) and high volumetric capacitance (90 F cm\(^{-3}\)); this was a consequence of the facilitated high-rate electrochemical performance due to the 3D design of the electrode.\(^{[28]}\) Chemical precipitation was tested for the fabrication of composite electrodes by incorporating different MOs into carbon materials.\(^{[209, 210]}\) Other MO composites, such as hydrous \( \text{RuO}_2 \) and carbon black nanocomposites, carbon aerogel/Ru composites, \( \text{RuO}_2/\text{AC} \) composites, \( \text{Ni(OH)}_2/\text{AC} \) composites, and \( \text{MnO}_2/\text{AC} \) have been fabricated for capacitor applications.\(^{[221–226]}\) The electrodeposition technique was considered to be among the most useful techniques to deposit conducting polymers, such as PANI, on different carbon materials to fabricate different types of PANI/carbon composites.\(^{[217–221]}\)

Carbon nanofibers derived from PAN are potential candidates for electrode materials. A porous carbon nanofiber paper electrode without any binder or percolator was obtained by activation of PAN-based nanofiber paper at temperatures from 700 to 1000 °C in a \( \text{CO}_2 \) atmosphere. These carbons could withstand high current loads without a noticeable decrease in capacitance, and the normalized capacitance reached 67 \( \mu \)F cm\(^{-2}\). Activation at 1000 °C led to the development of subnanometer pores (\( S_\text{BET} = 705 \text{ m}^2 \text{ g}^{-1} \)). Despite moderate BET specific surface areas, the capacitance reached values higher than 100 F g\(^{-1}\) in organic electrolytes. At high power densities, the nanofiber paper obtained at 1000 °C outperformed the energy density retention of ACs in organic electrolytes.\(^{[212]}\) The porosity of the PAN fiber was controlled by introducing camphor, which is a pore former, and a micropore volume of > 90%, with a high surface area of 886 F g\(^{-1}\), was obtained.\(^{[223]}\) A high surface area of 1300 m\(^2\) g\(^{-1}\) with a capacitance of 290 F g\(^{-1}\) was obtained with the PAN-based nanofiber.\(^{[224]}\) AC fiber cloth electrodes were also fabricated based on PAN fabrics.\(^{[225]}\) KOH activation improved the performance because of improved porosity of the fiber.\(^{[226]}\) The advantage of using PAN as a precursor is the possibility of easily preparing nanofiber-based paper.\(^{[179]}\) In addition, high amounts of nitrogenated and oxygenated functionalities were retained after activation of PAN-based materials using \( \text{CO}_2 \).\(^{[227, 228]}\)

6. Asymmetric capacitors

A recent trend in supercapacitor research is to design asymmetric capacitors. The term asymmetric refers to asymmetry in the electrode materials. These new types of capacitors use two different types of electrode materials for positive and negative electrodes. Thus, the working principles of the positive and negative electrodes are different. These asymmetrically coupled electrodes operate reversibly in different potential ranges, and thus, the potential window can be increased. In general, one type of electrode material works based on a non-faradaic charge-storage mechanism and the other electrode is involved in faradaic interactions. For non-faradaic interactions, ACs are generally preferred.\(^{[14]}\) MOs have been widely used as pseudocapacitive electrodes. Because asymmetric capacitors can work in a higher potential window, they can give higher energy densities. A change in potential window from 1.0 to 1.5 V enhanced the capacitance of an asymmetric capacitor based on nickel oxide and HPC from 28 to 38 F g\(^{-1}\).\(^{[229]}\) Operating voltages of 1.8 and 2.0 V were obtained by using \( \text{Fe}_3\text{O}_4 \) and \( \text{MnO}_2 \) as the positive electrodes, respectively, in aqueous electrolytes.\(^{[230, 231]}\) Other MOs, such as \( \text{RuO}_2 \), \( \text{MnO}_2 \) iron oxide, and \( \text{V}_2\text{O}_5 \) have been investigated by several research groups as asymmetric capacitor electrodes.\(^{[232–238]}\) An asymmetric configuration based on \( \text{MnO}_2 \) and AC emphasized the importance of an optimum mass ratio between the positive and negative electrode.\(^{[239]}\) A spherically shaped \( \text{MnO}_2 \) and AC combination operated over a wide voltage range up to 3.0 V, and a specific energy density of 128 Wh kg\(^{-1}\) was reported.\(^{[240]}\) Alternative candidates to MOs are conducting polymers. Polymers such as PANI and polyp(3,4-ethylenedioxyxyphe) (PEDOT) have been coupled with carbon electrodes in asymmetric capacitance configurations.\(^{[241, 242]}\)

Li-ion supercapacitors are another type of asymmetric capacitor that integrates bulk Li-ion storage with non-faradaic charge storage to achieve optimized performances. Different Li-based compounds, such as spinel-structured \( \text{LiMn}_2\text{O}_4 \), \( \text{LiMn}_3\text{O}_8 \), \( \text{LiFeSiO}_4 \), and \( \text{Li}_4\text{Ti}_5\text{O}_{12} \), have been used as Li-ion storage electrodes with carbon-based non-faradaic counter electrodes.\(^{[245–247]}\) An asymmetric capacitor prepared from aligned \( \text{TiO}_2 \) nanotubes as the anode and mesoporous carbon as the cathode exhibited a high energy density of 25 Wh Kg\(^{-1}\) and a high power density of 3000 W Kg\(^{-1}\). The main issues with these new types of capacitors are cyclic performance and stability. Whereas MO electrodes suffer from poor cycle lives, polymer-based electrodes are unstable. Li-ion supercapacitors exhibit better cyclic stability and good safety reliability.

7. Summary and Outlook

Nanocarbons have been used as the main electrode material for supercapacitors. They have been widely utilized in the fabrication of electrodes both in pure and composite forms. In the pure form, with optimized BET surface areas and pore structures, they exhibited excellent EDLC performances. Microporous carbons showed better charge-storage capability than mesoporous carbons. Ultra-micropores, with sub-nanometer sizes, were the most efficient of the micropores particularly in aqueous solutions. Charge storage in mesopores was less efficient because the mesopores were too big relative to the ion sizes. Despite this fact, mesopores are important for providing
a smooth charge-transfer pathway for the ions in electrolytes. Mesopores provide gateways to micropores in the bulk. Therefore, the correct combination of interconnected meso- and micropores is the key for optimized performance. Improved power output characteristics and high frequency performance can be obtained from templated mesoporous and HPCs. An ordered distribution of pores facilitates charge transportation and optimizes accessibility to the active sites because these sites are arranged in a regular pattern compared to other carbon materials with randomly distributed pores. CNTs, both SWCNTs and MWCNTs, with their very high conductivity and moderate porosity have been used successfully for EDLC applications. Proper functionalization of CNTs and other ACs provide favorable surface-charge distributions, which promote more active sites for charge storage. Pseudocapacitive active materials, such as ECPs and MOs, decorated vast amounts of the surface of the carbon host material, such as ACs, CNTs, and other carbon nanofibers, and the effective surface area of active material increased; this resulted in maximum utilization of the active materials. Asymmetric configurations enabled improved energy density.

An electrode should have high porosity with a suitable arrangement of micro- and mesopores. An ideal electrode can be realized when a charge transportation pathway is obtained through the mesopores. These mesopores should channel ions in the electrolyte to the abundant number of micropores available throughout the surface of the mesoporous channels. Therefore, a possible ideal electrode can be a treelike, branched structure made of mesoporous channels with micropores around the different branches. The pore size distribution of these micropores can be optimized by suitable treatments and accordingly suitable electrolytes should be chosen to optimize ion adsorption. This type of structure can further be decorated by redox-active material for a combined EDLC and pseudocapacitive contribution. Ultra-thin layers of MOs or ECPs can be deposited throughout the surface of the mesoporous channels so that ionic access to the active material becomes smooth and fast, whereas the ultra-thin layer ensures less resistivity and optimum use of the active material. The amount of active materials loaded should be limited to ensure that the micropores of the host material are not blocked. Present research is focused on the fabrication of similar key structures to solve related problems. The choice of a suitable electrolyte remains an interesting research area for further investigation.

From an industrial point of view, the direct application of supercapacitors to some practical applications, such as electrical cars and mobile high power storage devices, is still limited due to low energy densities. Hybrid cars with an additional battery may be a short-term solution. An ultimate ideal solution could be asymmetric capacitors, which combine redox reactions in one electrode with EDLC in the other. To achieve this, nanocarbon materials could be the best materials: one redox-active electrode could be combined with MOs to enhance the redox reaction. Research should be focused on the design of nanocarbon materials and the optimization of both electrodes in terms of cyclability, stability, and charge transport.

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