Carbon materials have attracted intense interests as electrode materials for electrochemical capacitors, because of their high surface area, electrical conductivity, chemical stability and low cost. Activated carbons produced by different activation processes from various precursors are the most widely used electrodes. Recently, with the rapid growth of nanotechnology, nanostructured electrode materials, such as carbon nanotubes and template-synthesized porous carbons have been developed. Their unique electrical properties and well controlled pore sizes and structures facilitate fast ion and electron transportation. In order to further improve the power and energy densities of the capacitors, carbon-based composites combining electrical double layer capacitors (EDLC)-capacitance and pseudo-capacitance have been explored. They show not only enhanced capacitance, but as well good cyclability. In this review, recent progresses on carbon-based electrode materials are summarized, including activated carbons, carbon nanotubes, and template-synthesized porous carbons, in particular mesoporous carbons. Their advantages and disadvantages as electrochemical capacitors are discussed. At the end of this review, the future trends of electrochemical capacitors with high energy and power are proposed.

1. Introduction

The tremendous growth of portable electronic devices and hybrid electric vehicles has promoted the urgent and increasing demand for high-power energy resources. The most common electrical energy-storage device is the battery due to the large amount of energy stored in a relatively small volume and weight while providing suitable levels of power for many applications and requirements of everyday life. However, as illustrated in a Ragone plot (Figure 1) for the most important energy storage systems, batteries suffer from slow power delivery, even though high energy densities, on the order of 180 Wh kg\(^{-1}\), can be obtained. The widespread use of batteries is thus restricted, especially in energy-storage systems where fast storage coupled with high power is required, such as pulse batteries. Electrochemical capacitors, also known as supercapacitors or ultracapacitors, can provide high specific power (10 kW kg\(^{-1}\)), a long cycle life (>10\(^5\)), and fast charge/discharge processes (within seconds), and therefore stimulate extensive interests as an alternative or supplement to batteries in the energy storage field.\(^{[1,2]}\) Currently, electrochemical capacitors are widely used in consumer electronics, memory back-up systems, industrial power and energy management.\(^{[3]}\) One of the major advantages is their ability to provide the energy necessary to accelerate a vehicle at its startup.\(^{[4]}\) This alleviates one shortcoming of batteries, i.e., slow energy discharge, by the ability to serve as an intermediate power source to propel a vehicle from stop to moving where fast discharge with high power output is required thus allowing the battery to carry the load at cruising speed reducing the stresses on the battery.

The mechanism by which electrochemical capacitors store energy has been discussed in detail.\(^{[1,2,5]}\) In principle, capacitive behavior can be classified into two categories: the electrical double layer capacitance arising from pure electrostatic attraction between ions and the charged surface of an electrode, such as carbon materials\(^{[5b,6]}\), and pseudo-capacitance associated with fast and reversible oxidation/reduction (redox) or Faradaic charge transfer reactions of the electro-active species on the surface of the electrode, for example, transition metal oxides\(^{[7]}\) and conducting polymers.\(^{[8]}\) As schematically represented in Figure 2, during the charging process the positive surface of electrical double layer capacitors (EDLCs) attracts the anions of electrolytes, whereas cations are accumulated on the surface of the negative electrode.\(^{[9]}\) The electrolyte ions approach the electrode material, but do not react with it or are not absorbed into it. The capacitance is dependent on the specific surface area of the electrode, the type of electrolyte and the effective thickness of the double layer (the Debye length), according to the formula:
the effective thickness of the double layer, and $A$ is the electrode surface area. Only the surface that is accessible to electrolyte ions can contribute to charge storage; therefore, optimization of pore size, pore structure, surface properties and conductivity of the electrode materials is required. This storage mechanism allows for very fast energy uptake and delivery and a high stability of EDLCs during millions of charge/discharge cycles.

In contrast to EDLCs, pseudo-capacitors involve Faradaic (i.e., redox) reactions between the solid electrode materials and electrolyte. In this case, charges accumulated in the capacitor are strongly related to the electrode potential, as

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \tag{1}$$

where $C$ is the capacitance of the EDLC, $\varepsilon_r$ is the electrolyte dielectric constant, $\varepsilon_0$ is the dielectric constant of the vacuum, $d$ is the effective thickness of the double layer, and $A$ is the electrode surface area. Only the surface that is accessible to electrolyte ions can contribute to charge storage; therefore, optimization of pore size, pore structure, surface properties and conductivity of the electrode materials is required. This storage mechanism allows for very fast energy uptake and delivery and a high stability of EDLCs during millions of charge/discharge cycles. In contrast to EDLCs, pseudo-capacitors involve Faradaic (i.e., redox) reactions between the solid electrode materials and electrolyte. In this case, charges accumulated in the capacitor are strongly related to the electrode potential, as

$$C = \frac{d Q}{d V} \tag{2}$$

where $C$ is the capacitance of the pseudo-capacitor, $Q$ is the quantity of charge, and $V$ is the potential. Pseudo-capacitors typically show much higher capacitance than that of EDLCs, but often suffer from low power density and lack of stability due to poor electrical conductivity and framework swelling during cycling.

Figure 1. Ragone plot showing the specific power against specific energy for various electrical energy storage systems. If a supercapacitor is used in an electric vehicle, the specific power shows how fast one can go, and the specific energy shows how far one can go on a single charge. Times shown are the time constants of the devices, obtained by dividing the energy density by the power. Reproduced with permission from [1]. Copyright 2008, Macmillan.

Figure 2. Scheme of an electrochemical double layer capacitor based on porous electrode materials. Reproduced with permission from [5d]. Copyright 2006, Elsevier B.V.
Further development of electrochemical capacitors is dependent on the discovery of new electrode materials and an improved understanding of ion behavior in small pores. Since the first discovery of the carbon-based electrochemical capacitor by Becker in 1957, numerous active materials with various components and structures have been designed and prepared. Among them, carbon materials have attracted more interest than other materials due to the high electrical conductivity, low cost and versatile forms such as powders, fibers, composites, monoliths, and tubes. More importantly, broad chemical stability in different solutions (from strongly acidic to basic) with the ability to perform in a wide range of temperatures increases the allure of carbon materials. Current well-established chemical and physical methods of activation allow the production of porous carbons with high surface areas (up to 3000 m² g⁻¹), that provide an extensively large electrode/electrolyte interface for charge storage. Until now, activated carbons produced by different activation processes from various precursors (e.g., wood, coal, nutshell) are the most common electrode materials. Recently, as more is understood about carbon materials, the ability to manipulate the nanoscale structure of the materials is being obtained which enables the proper control over the surface area, pore size, pore structure and surface properties of electrochemical capacitors, hence increasing the interest in nanostructured electrodes.

While carbon nanotubes (CNTs) exhibit properties amenable to capacitive energy storage with unique tubular porous structures and superior electrical properties, fast ion and electron transportation, the production costs limit their widespread use. Template synthesized porous carbons with a tailorable two- or three-dimensional (3D) structure and controllable micro-, meso- and macro-pore sizes, however, hold a great promise as supercapacitors due to a high specific capacitance of carbon-based electrode materials, approx. 100–300 F g⁻¹ in aqueous medium and 50–150 F g⁻¹ in organic medium.

Comparatively, metal oxides exhibit much higher specific capacitance, for example, the capacitance of ruthenium oxide (RuO₂) is reported more than 600 F g⁻¹ in an aqueous electrolyte. Furthermore, hydrous RuO₂ (RuO₂·xH₂O) has been reported to exhibit a capacitance as high as 1300 F g⁻¹. However, the high cost of precious metals such as ruthenium (Ru) is a major disadvantage for commercial production of RuO₂-based supercapacitors. Alternatives such as the oxides of iron, vanadium, nickel, manganese and cobalt have been tested, with manganese oxides, especially manganese dioxide (MnO₂), receiving tremendous attention due to the low cost and large potential window compared to most other metal oxides. The specific capacitance of manganese oxides generally range between 150 and 250 F g⁻¹. Prasad and Miura reported a 400 F g⁻¹ capacitance from amorphous nanostructured hydrated manganese dioxide deposited on stainless steel. However, it is still far from the theoretical value, ca. 1000 F g⁻¹, calculated in an MnO₂ alkaline battery due to its low surface area and poor electrical conductivity. Another disadvantage for manganese oxide supercapacitors is their instability in strong acidic and basic media; however, use under neutral conditions is possible.

Another promising material for high performance electrochemical capacitors are conducting polymers, e.g., polyaniline (PANI), polypyrrole, polythiophene and their derivatives. The conducting polymers can be positively (p-doping) or negatively (n-doping) charged with ion insertion in the matrix to balance the injected charge. The charge-discharge capacitance of conventional conducting polymers can reach 450 F g⁻¹ in organic electrolytes at approx. 3.0 V operating voltages. However, when being used as bulk materials, conducting polymers suffer from limited stability associated with swelling and shrinking during cycling.

In order to improve the electrochemical properties, multi-component electrode materials combining energy storage of electrostatic attraction and faradic reaction have been explored. Several carbon-based composites are developed, such as metal oxide/carbon and conducting polymer/carbon composites. Active materials, viz. metal oxides and conducting polymers can enhance the capacitance remarkably; meanwhile, carbon as a support, not only increases the effective utilization of active materials, but also improves the latter’s electrical conductivity and mechanical strength of the composite electrodes.

Currently, electrochemical capacitors can store hundreds or thousands of times more charge than the conventional capacitors, however, they still have a low energy density compared with batteries. The discharge time of electrochemical capacitor is always less than a minute, whereas many applications clearly need more. Therefore, one of the most critical aspects in the development of electrochemical capacitors is to enhance their energy density while retaining their intrinsic high specific power. In order to meet such a demand, capacitor materials are expected to have high surface area and/or pseudo-active species for high charge storage, proper pore size and pore structure for electrolyte diffusion, and high electrical conductivity for fast charge transport. In this review, a brief summary of recent research progress on carbon-based electrode materials is provided. The effects of synthetic parameters on the material structures and further the performance as electrochemical capacitors are presented.

### 2. Carbon Materials and Sources

Prior to discussing the carbon source, it is important to discuss the types of carbon materials obtained. Carbon materials generally fall into three classes based as dictated by the carbon precursor: graphitic, diamond-like and amorphous. Graphitic carbons have been extensively sought and tremendous efforts put into the development of materials with the graphite structure due to its high electrical conductivity. Graphite is formed by 2D sheets of sp² hybridized carbon atoms with hexagonal lattice. Each graphene sheet is oriented to its adjacent sheets by 180° rotations generating in an ideal structure, a repeating ABA stacking sequence. The latter is known as the 3D crystal of graphite. The edges of its planes have terminations with carbon atoms arranged with either zigzag, or armchair configurations. Graphite is found in nature in coal mines and also produced from various sources. For the preparation of carbon with graphitic structure, the sources can in general be classified as soft and as hard carbons. Soft carbons are referred to as graphitized carbons due to the ease of graphitization, typically at temperatures below 2000 °C. Typical soft carbon precursors are...
pitch-based chemicals (coal tar, petrol pitch and organic polymers). Hard carbons, however, are non-graphitizeable carbon materials, even after thermal treatments at temperatures as high as 3000 °C. Phenolic resins, carbohydrates, and biomass (fruit stones, trees, etc.) are examples of hard carbon precursors. Soft and hard carbons have domains of microcrystalline graphite that are randomly stacked with a turbostratic structure. The latter largely resembles the graphite structure, but with large numbers of defect sites such as broken and dangling bonds, unpaired electrons and oxidized carbon sites. Most importantly, the term turbostratic relates to the lack of 3D stacking ordering found in graphite.

2.1. The Carbon Source and Porosity Conundrum

Porosity characteristics are either inherent or directed through various templates or activation methods. Materials properties largely depend on the presence of accessible pores and on pore size. Pores are classified according to the IUPAC as micropores, mesopores and macropores. Microporous materials contain pores which are predominately below 2 nm; mesoporous materials contain pores with diameters between 2 nm and 50 nm, whereas macroporous materials have pores with diameters larger than 50 nm. For pores exceeding several hundreds of nanometers, materials are most often classified as nonporous. Current state of the art energy storage and conversion technologies demand precise control over the type of porosity present in materials. A bimodal porosity containing micropores and either meso- or macro-pores is currently believed to be ideal due to the actual energy storage occurring predominately in the smaller micropores where the bulk of the surface area lies while the larger pores provide fast mass-transport of electrolytes to and from the micropores. Narrow distributions of pores are favored due to the increases in surface area of regular pore distributions vs. broad distributions of pores. Therefore, some control is required in porosity development to enable control in the energy storage capabilities of the carbon. To prepare carbon materials with narrow distributions of mesopores and even uniform macropores, different types of templates have been investigated.

Templates can be classified into two classes: hard and soft. Soft templates are organic molecules, such as micelles of ionic and nonionic surfactants with a side alkyl chain and a head group capable of interacting with species forming a framework of a given material, as well as block copolymers and other organic compounds forming liquid crystalline phases, or vesicles. Unlike most hard templates, the soft-templates are thermally unstable, thus being removed from the starting nanocomposites, while the precursors selected to form a porous framework could further consolidate during thermal treatments. This orchestrated process can result in a framework with micro, meso, or macropores, as well as hierarchical pore structures. Hard templates are materials with inherited porosity, viz. zeolites and ordered mesoporous silicates, or that assemble to form a porous network, such as colloidal silica spheres. After infiltrating the templates with a carbon precursor, followed by carbonization and etching of the template using sodium hydroxide (NaOH) or hydrofluoric acid (HF) solutions, porous carbons are formed with the pore size and structure being an inverse replica of that from the original template. In general, most porous hard templates are prepared from soft-templates; hence most hard-templating procedures, i.e., those using mesoporous silicates, imply additional synthesis steps compared to the one-pot soft-templating method. The latter method further requires the use of toxic reagents such as NaOH and HF for the etching of siliceous templates, imposing environmental issues to the development of carbons for “green” technologies to solve our present energy problems.

Other than porous template, activation is often used to increase the surface area of the material through the introduction of large amounts of micropores. Common activating agents are base (KOH, NaOH), zinc chloride (ZnCl2), phosphoric acid (H3PO4), CO2 and steam. Activation involves the high temperature treatment of the materials in an activation agent. The agent etches the carbon walls at high temperature leaving microporous fissures. Steam is the most benign of the activating agents as it requires no post-treatment to remove byproducts. However, surface oxygen functionalities can be formed which can decrease the electrical conductivity of the carbon material. Base activation, however, requires an additional step of neutralization and washing the excess base and salt out of the pores of the carbon, making the steam process more advantageous and environmentally friendly. Inorganic salts such as ZnCl2 have been used to produce high surface area carbon materials but it too requires post-activation washing in acid to remove residual zinc. Phosphoric acid is utilized especially with biomass such as fruit stones but can leave acidic phosphate functionalities on the carbon surface. Activation then becomes a balance of conductivity vs. surface functionality, while simultaneously providing a way to tailor the carbon surface for applications beyond energy storage, such as catalysis.

Development and control over the porosity of a material, is not only dictated by the type of templates used, but also the carbon precursor selected. Very important for energy storage applications, the selection of the carbon precursors also depends on the precursor availability, cost, on the presence of heteroatoms such as N, B and P that could dope the final carbons and on the extent to which it can be graphitized. The search for new, available and economically viable carbon sources that result in a porous carbon material has intensified, with focus on synthetic carbon sources that can combine all aforementioned properties. The most common chemical precursors to carbon materials have biomass and oil origins, including alcohols, carbohydrates, polysaccharides, lignocellulose sources pitches, phenolic resins and organic polymers. As more carbon sources are explored, a greater understanding of the surface chemistry involved will allow for the design of enhanced materials that will permit scientists to overcome existing barriers set by the present energy storage and conversion technologies.

2.2. Biomass Sources

Biomass sources are becoming increasingly important due to the large availability and to the environmental and cost implications.
of utilizing petrol-based resources for carbon materials. Many commercial carbons are cellulose and lignin-based from trees and agricultural wastes. The Norit Group and MeadWestvaco Corporation are two companies currently supplying tree-based biomass derived activated carbon materials. Therein lies a distinction with most biomass-derived carbon materials, i.e., during production the carbons are activated to introduce porosity. Steam is a common activating process used for biomass materials due to the inexpensive cost and lack of post-activation work-up. Microporosity is prevalent in the carbon materials; however, a broad distribution of mesopores can also be obtained.

Other lignocellulosic forms of carbon, such as fruit stones and coconut hulls are also used to produce activated carbon.[28] Here the biomass is often mixed with phosphoric acid prior to carbonization or treated with steam at a high temperature.[29] The phosphoric acid treatment is common and results in acidic phosphate sites on the carbon surface.[28] Microporous carbon is the predominant porosity present in this type of biomass materials with some pores encroaching on the mesopore domain.

Carbohydrate dehydration[10a,10b] to form porous carbon materials has received tremendous attention due to the variety of production methods including mild methods such as hydrothermal carbonization.[10a] A common carbohydrate used is sucrose. Carbohydrates can be impregnated in hard-templates as ordered mesoporous silica[22d,29] and treated with strong acids, such as sulfuric acid, to dehydrate the sugar forming a coating on the hard template. Successive impregnations and dehydrations occur to completely fill the pores of the hard templates used. Following carbonization, the hard template is removed yielding the carbon material.[22d,29] Sucrose, xylose, maltose, amylopectin, starch and biomass derivatives such as hydroxymethylfurfural (HMF) and furfural can also be hydrothermally dehydrated to form micrometer sized carbon spheres with diameters determined by the reaction conditions, the use of stabilizers and precursor concentration.[10b] Other polysaccharides such as starch have received great deal of attention lately due to the possibility to obtain carbons with large mesopores without templating methods and with pore volumes comparable to hard-templated carbons.[10b] The appeal of sucrose and starch is the renewable source aspect coupled with inexpensive precursor materials.

### 2.3. Pitch Based Carbon Fibers and Foams

Pitch-based carbon sources have the advantage of being soft-carbon materials that can be graphitized and has been used to obtain carbon fibers and nanocomposites of enhanced conductivity compared to those based on hard-carbons.[26] Pitch is a viscoelastic polymer composed of highly aromatic hydrocarbons obtained from petrol or coal sources, also referred to as bitumen. Pitches can also originate from plants, which are typically known as resins. Pitch has been commercially made from pyrolysis of polyvinyl chloride (PVC) for the preparation of carbon fibers.[26] Upon pitch pyrolysis between 350 and 450 °C, condensation and aromatization of isotropic pitch occurs.[26] The isotropic liquid phase then converts into anisotropic liquid-crystalline phases, in which optically anisotropic spherical particles are visible.[26] Such phases are known as mesophase pitch and do not have well defined melting points, being thus characterized by their softening points. Furthermore, anisotropic spherical particles in the mesogenic phase then grow larger and coalesce upon further heating. Coalescence of spherical particles then results in a continuous phase, which upon solidification results in semicokes at temperatures as low as 500 °C.[26]

In general, the preparation of carbon fibers may be hindered by the softening point of pitches. Stabilization in air at temperatures below 300 °C is usually required prior to carbonization and graphitization.[26,40] By blending pitches from tar and coal with polymers such as polyacrylonitrile (PAN), the structures of final fibers could be tailored in order to increase either the conductivity, or the mechanical strength of the fibers by changing the molecular orientations with the PAN addition.[31] By varying the spinning and flow conditions during fiber preparation, different textures for the cross-sections perpendicular to the length of the fibers can be obtained. These textures form radial, onion-skin, flat-layer, random, etc, and influence the ability to graphitize the fibers, as well as their final electrical and mechanical properties.[31,32] For instance, it has been shown that fibers with radial textures favored lithium intercalation in batteries compared to fibers with onion-skin textures over several charge-discharge cycles.[32] Graphitized fibers with radial textures were demonstrated to exhibit longer life cycles, larger capacities, higher rate capabilities and reversibility than graphite anodes.[33] Despite the excellent properties of pitch based carbon fibers as anodes in lithium-ion batteries, their use in supercapacitors are limited to their low textural porosity and low specific surface areas. Pitch based carbons have thus been activated with potassium hydroxide (KOH) to obtain materials with high surface areas and specific capacitances of 130 F g⁻¹ in aqueous electrolytes[34] and 35 F g⁻¹ in tetraethylammonium tetrafluoroborate ([Et₄N][BF₄]) in an organic solvent [propylene carbonate (PC)].[10b] The addition to fibers, foaming of polymers and various pitches have led to the development of carbon foams with high mechanical modulus and thermal conductivity.[35] In general, carbon foams have micrometer size macropores and low surface areas. As support materials, it has been demonstrated that only composites with conductive polymers such as PANI exhibited capacitive behavior in contrast to bare nonporous carbon foams.[36] Most processing conditions available for making mesoporous foams however, are costly and as aforementioned, produce exclusively nonporous materials due to the extremely large diameter of these macropores.

In order to obtain foams and fibers with small pores, pitches have been thermally treated with magnesium oxide nanocrystals formed in situ in order to generate small pores and improve the electrochemical properties. The reported surface areas were as large as 1400 m² g⁻¹ and specific capacitances were in the range of 230–290 F g⁻¹.[37] Another interesting synthetic approach combining pre-oxidizing a mesophase pitch in alkaline conditions and vesicles formed by ionic surfactants in solutions was attempted.[38] In this, mesoporous carbon foams were obtained after thermal treatments to remove the surfactant. In a different approach, two immiscible polymers and with different thermal stabilities were used to prepare porous foam-like fibers with small macropores. These blends were prepared by mixing solutions of PAN, which formed the carbon walls during...
thermal treatments, with solutions of poly(methyl methacrylate) (PMMA) which left macropores by undergoing thermal decomposition.\[^{[39]}\] Despite the fact that the use of surfactants and mixtures of polymers resulted in carbons with broad distributions of pores and relatively low specific surface areas, these procedures paved the way for additional developments in the synthesis of mesoporous carbons with enhanced adsorption and structural properties.

### 3. Nanostructured and Nanoporous Carbon Materials

#### 3.1. Graphene and Graphene Oxide

The unique electronic and mechanical properties of graphene (Gr) have brought great interest to this material.\[^{[40b]}\] Single-layer Gr is a 2D material composed by an atom-thick hexagonal carbon lattice with delocalized \(\pi\)-electrons. In general, single layer suspensions can contain up to five layers, denoted as few layers graphene (FLG).\[^{[40b]}\] Its properties can be greatly affected by the number of layers, their stacking sequence and by the degree of surface reduction or oxidation.\[^{[40b]}\] For instance, while single layer Gr exhibits quantum electronic properties,\[^{[40a, 41]}\] multilayer structures behave as semi-metals only if sheets exhibit a regular ABA stacking similar to graphite. Otherwise, multilayer Gr may behave as single layer Gr as a result of lattice mismatches that increase interlayer distances.\[^{[40f]}\] Furthermore, graphene in its reduced and oxidized forms, graphite\[^{[42]}\] and graphite oxide (GO),\[^{[43]}\] respectively, behave as insulators as a result of the disruption of long-range aromatic structure of Gr.

FLG has been originally prepared by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG).\[^{[44]}\] Other methods for production of FLG include epitaxial growth onto SiC wafers\[^{[45]}\] and chemical vapor deposition (CVD) on single-crystal metal surfaces\[^{[45]}\] or arc discharge of graphite\[^{[46]}\] and use of metal intercalated multi-layered graphene as starting material.\[^{[47]}\] Solution-based methods for the large scale processing of graphene have been developed using selected solvents,\[^{[48]}\] ionic liquids\[^{[49]}\] and stabilizers\[^{[50]}\] to disperse graphene based on matching the surface energy of Gr sheets or more often of a GO intermediate.\[^{[51]}\]

GO has been most commonly prepared in large quantities from graphite by the Hummers method using potassium permanganate and sulfuric acid.\[^{[43]}\] The obtained GO colloids have been subsequently stabilized with surface charges,\[^{[51a]}\] or with ionic surfactants\[^{[50b]}\] and ionic liquid\[^{[51b]}\] followed by reduction with hydrazine solution\[^{[53]}\] or by thermal treatments in hydrogen-rich atmospheres.\[^{[51e]}\] The latter methods are lengthy and utilize highly toxic oxidizing and reducing reagents. In addition, the chemical oxidation and covalent functionalization of Gr significantly affects its conductivity due to local disruptions of the aromatic system within the basal planes or may decrease its water solubility. After several reduction steps the electronic conductivity of Gr is only partially restored.\[^{[51b]}\] As an alternative to the covalent functionalization, GO has been dispersed by non-covalent interactions using selected polymers and surfactants\[^{[50a, 50b, 51b, 51d, 52]}\] and liquid (IL) and IL polymers.\[^{[53]}\]

Both Gr and GO materials and their nanocomposites have been extensively studied as electrodes for supercapacitors.\[^{[56]}\] Among the various materials reported in recent years, the gravimetric capacitance for graphene\[^{[57]}\] and reduced graphene\[^{[58]}\] electrodes has been in the order 117 and 150 F g\(^{-1}\), respectively. Whereas the capacitance values for graphene nanocomposites with conductive polymers such as PANI were considerably higher. For instance, GO-coated PANI fibers composites exhibited capacitances of 531 F g\(^{-1}\)\[^{[59]}\] about twice higher than that of pure PANI (216 F g\(^{-1}\)), to Gr-PANI paper nanocomposites (233 F g\(^{-1}\))\[^{[60]}\] and to Gr-PANI fibers (210 F g\(^{-1}\)).\[^{[61]}\] However, for in situ polymerized PANI nanoparticles with average size of 2 nm on Gr sheets,\[^{[62]}\] gravimetric capacitance reached 1046 F g\(^{-1}\), much higher than pure PANI sample investigated under similar conditions (115 F g\(^{-1}\)). Furthermore, the interfacial capacitance of graphene materials largely increases with increasing number of stacked layers.\[^{[63]}\] Even more promising, for capacitor types of nanotubes, the network of metal current collectors and with AC line filters,\[^{[64]}\] the RC time constants found were as fast as 200 \(\mu\)s. It has been proposed that devices could be miniaturized to sizes smaller than the low voltage aluminum electrolytic capacitors currently used in semiconductors.\[^{[64]}\]

#### 3.2. Carbon Nanotubes, “Nanohorns” and “Nano-ions”

Carbon nanotubes (CNTs) are a class of tubular carbon materials with a graphitic structure.\[^{[65]}\] Two types of CNTs are available, single-walled (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs have walls that are one atom layer thick whereas MWNTs have many layers of graphitic carbon in the wall. The former can be seen as a single graphene sheet rolled on itself to form a tube. The final nanotubes can be metallic, or semiconductors depending on the direction of the sheets that the tubes are rolled, resulting in zigzag, armchair and chiral configurations, and also on the tube diameter.\[^{[66]}\] In both single and multi-walled nanotubes, the electronic transport occurs ballistically, i.e., over long tube ranges without electronic scattering. This property allows nanotubes to carry high densities of currents without energy dissipation by heating.\[^{[67]}\] Because of their enhanced electronic conductivity, CNTs and nanocomposites have been tested as materials for supercapacitors and lithium batteries.

While in lithium batteries the CNTs have shown over 30% irreversible capacity, and careful ball-milling processing is required to reduce such losses,\[^{[68]}\] thus limiting their uses as battery anodes. The well developed network of open pores however, have made them successful candidates for supercapacitors electrodes.\[^{[66]}\] In addition to the internal micro/mesopores of the various types of nanotubes, the network of large external mesopores and small macropores formed by the entanglement of CNTs allows for fast solvated ion diffusion during charge and discharge processes.\[^{[66]}\]

Moreover, high capacitance values have been reported for CNT-polypyrrole nanocomposites.\[^{[66]}\] In cases where large diameter MWNTs (100–200 nm pores) exhibited low surface areas (50 m\(^2\) g\(^{-1}\)) and 5 F g\(^{-1}\) capacitance, the final nanocomposites with uniform 5 nm thick polypyrrole coatings showed
capacity of nearly 130 F g\(^{-1}\). In the latter case, both internal and external surfaces of the MWNTs were coated during the electrochemical polymerization of pyrroles. In addition, polypyrrole provided additional contributions from pseudofaradaic processes to the final capacitance of the nanocomposites, making the latter promising materials for electrochemical capacitors. Also, for CNTs with narrow diameters centered at 8 nm and large surface areas, maximum capacitance values close to 113 F g\(^{-1}\) have been reported for frequencies below 1 Hz. It has also been shown that large SWNTs, with diameters of 10–20 nm, the composites with poly(vinylene chloride) could achieve 180 F g\(^{-1}\) of specific capacitance at 20 kW kg\(^{-1}\) of power density and 6.5 Wh kg\(^{-1}\) of energy density after carbonization at 1000\(^\circ\)C. In the latter case, the polymer binder yielded carbon residue with a pore diameter below 5 nm, further increasing the specific surface areas of the final composites and their electrical conductivity while lowering the electrical series resistance.

Another recent nanomaterials, carbon nanohorns (CNHs) prepared by CO\(_2\) laser vaporization of a graphite target, have attracted considerable attraction. These tubular structures with cone shaped endings are bundled up in flower shaped superstructures. Single-walled nanohorn (SWNH) nanocomposites with phenolic resins and polymers exhibit high electrical conductivities as a result of the addition of SWNHs. Composites of SWNHs and PANI nanobrushes also showed major improvement in capacitance values. For instance, the specific capacitance increased from 48 F g\(^{-1}\) from PANI brushes to 168 F g\(^{-1}\) in the SWNH-PANI nanocomposites.

Despite of the major improvements achieved with this type of materials, the synthesis of the CNTs requires sacrificial metal catalysts in methane or ethane gas flowing at high temperatures. Most synthetic procedures for CNTs and CNHs further require high energy input and purification procedures with a low yield. In case of SWNTs, precise control over electronic properties makes them cost prohibitive, especially when compared to other types of porous carbon materials. Recently, CNTs have received renewed interest due to the ability to “unzip” of SWNT to form graphene nanoribbons, thus making semiconducting materials with ballistic electron conductivity effects independently of the chirality and diameter of the parent SWNT.

Carbon onions prepared by vacuum annealing of nanodiamond (ND) powder at 1200 °C usually show a core-shell structure, namely, graphitized surfaces and diamond cores. The graphitic shells grow from the surface to the center and no diamond core could be observed after annealing at 1800 °C or above. It is noted that, carbon onions have almost no small sub-nanometer pores and all sites on the surface are nearly equal. The outer surface of carbon onions is fully accessible to electrolyte ions, leading to an increased ability to quickly deliver the stored energy. The carbon onion cells show a capacitance twice than the one obtained with MWNTs, while less than 10% capacitance losses occur for carbon onions produced above 1800 °C at high current densities of 800 mA cm\(^{-2}\). The time constant of ~1 s is around 10 times smaller for ND annealed at above 1800 °C than for activated carbons and is closely approaching the one for MWNTs. These properties make carbon onions as a potential material used in supercapacitors.

3.3. Templated Microporous Carbons

Microporous carbons prepared as inverse replicas of zeolites and from metal carbides have also been intensely investigated as supercapacitors electrodes. The former zeolite templated carbons (ZTCs) are prepared by filling the micropores of zeolites such as zeolite Y and X13 with a suitable carbon source, e.g., furfuryl alcohol, followed by carbonization of composites and dissolution of the siliceous framework. As a result of the well-defined crystal structure of the starting zeolite materials, ZTCs exhibit amorphous carbon walls having periodic microporous structures. The micropores of the ZTCs exhibit the same periodicity as the starting microporous templates in the range of 1.0 to 2.0 nm. As for carbide derived carbons (CDCs), these are prepared during high temperature chlorination of silicon and titanium carbides, for example, that etches the Si and Ti cations from crystal lattices of SiC and TiC, respectively, followed by an additional carbonization step. The removal of the metals as chloride vapors during this process results in microporous carbons with 50 to 80% open pore volume and specific surface areas as high as 2000 m\(^2\) g\(^{-1}\). The latter materials further exhibit disordered structures of micropores due to the collapse of the carbide lattices forming amorphous carbon walls. Despite of lacking structural ordering, CDCs allow for control over microporosities within 0.6 to 1.1 nm in size by properly selecting the starting carbide material, the chlorination and the carbonization temperatures.

The various ZTCs prepared as inverse replicas of zeolite X for example, exhibited gravimetric capacitances up to 300 F g\(^{-1}\) for H\(_2\)SO\(_4\) electrolyte at high sweep rates and 0.6 to 0.6 V. It has been shown that the reduction of the pore tortuosity, high pore connectivity, improved accessibility to microporous cages by chemical activation and increase in the specific surface areas are detrimental for the high capacitances and power densities. Furthermore, the capacitance for nitrogen-doped ZTCs was even higher, 340 F g\(^{-1}\) also for aqueous H\(_2\)SO\(_4\) electrolyte operating at a cell voltage of 1.2 V and 200 mA g\(^{-1}\) current density. Nitrogen-doping however did not improve the capacitance of ZTCs for [Et\(_4\)N][BF\(_4\)] solution in acetonitrile electrolytes (~146 F g\(^{-1}\) between zero and 2.3 V) at low current densities. Capacitance, however, was found to linearly increase with increasing surface areas.

The capacitance of CDCs has been systematically investigated and the capacitance found to increase with the reciprocal of the micropore diameter of the CDCs. Maximum capacitance values for both inorganic and organic electrolytes were found for carbons with micropores of approximately 0.7 nm in diameter. In H\(_2\)SO\(_4\) the capacitance for CDCs prepared from TiC at different temperatures reached 160 to 190 F g\(^{-1}\) with a sweep rate of 5 mV s\(^{-1}\) and ~0.5 to 0.5 V. While in acetonitrile solution of tetraethylammonium tetrafluoroborate, TiC-originated CDCs with pore size of 0.6 nm show a capacitance of 140 F g\(^{-1}\) and good ionic transport in the porous network where capacitance fading was found to be small even at 100 mA cm\(^{-2}\). According to this model, for solvated cations and anions of 1.3 and 1.16 nm in size, partial or complete removal of the solvation shell permitted the access of the ions inside the small micropores.

All the aforementioned carbons were exclusively microporous and particles excessively large. Hence the effect of...
downsizing the CDC particles to the nanometer scale, as well as introducing mesopores[76d] and macropores for maximum electrolyte diffusion and consequently optimum accessibility to the small micropores remains open for investigation. The advantages of making hierarchical microporous-mesoporous structures has been recently demonstrated for zeolites especially in catalytic reactions involving large molecules.[78] The presence of large mesopores greatly improves the diffusion of large molecules throughout micrometer size crystals and consequently increases the accessibility to the catalytically active sites.[78] Thus, similar rationale could be used to prepare electrodes especially designed for organic electrolytes for high diffusivity and maximum accessibility to the micropores.

3.4. Templated Mesoporous Carbons and Hierarchical Porous Carbons

The first ordered mesoporous carbons were fabricated by a hard-template nanocasting strategy,[22d,29b,29c,79] in which ordered mesoporous silica are often used as the hard templates. Variable carbon sources can be utilized in the synthesis, e.g., sucrose, furfuryl alcohol, phenolic resin, benzene, poly-vinyl chloride, pitches,acenaphthene, propylene, acetonitrile, etc.[29b,29c,80] However, the use of mesoporous silica as a sacrificial scaffold makes the process complicated, high-cost and time-consuming, and in turn, unsuitable for the large-scale production and industrial applications.

In 2004, Dai's group reported direct soft-template synthesis of ordered mesoporous carbon films by using resorcinol-formaldehyde as a carbon source and lab-prepared diblock copolymer polystyrene-block-poly(4-vinylpyridine) (PS-P4VP) as a soft template.[81] Resorcinol monomers can interact with the P4VP segment of the copolymer via hydrogen bonds. They were pre-organized into well-ordered mesostructured films with the assistance of amphiphilic PS-P4VP self-assembly through spin-coating and solvent annealing, and then in situ polymerized with formaldehyde vapor to form a carbon precursor. Upon carbonization under N₂ atmosphere, ordered mesoporous carbon films with a hexagonal structure and large pore size of ca. 34 nm were obtained (Figure 3). Because of

![Figure 3](image-url)

*Figure 3.* (a) Scheme presentation of ordered mesoporous carbon films obtained via organic-organic self-assembly of resorcinol-formaldehyde and block copolymer PS-P4VP. (b) High-resolution SEM image of the surface of the carbon film with uniform hexagonal-pore array. (c) SEM image of the film cross section. The inset is the FT of the cross section image. The scale bar is 100 nm for each image. Reproduced with permission from [81].
the commercial unavailability of PS-P4VP and the complicated preparation procedure, its use is limited to large-scale synthesis of ordered mesoporous carbons. Later, Tanaka et al. reported a successful synthesis of ordered mesoporous carbon films (COU-1) through a similar route, but using triblock copolymer Pluronic F127 as a template. The synthesis involves the use of triethyloctaoacetate (EOA) as co-carbon source in addition to resorcinol-formaldehyde resins. However, the ordered mesostructure may undergo partial collapse during the high-temperature carbonization process. [81]

Major advances have been made simultaneously by Zhao’s and Dai’s groups using all commercially available, low-cost raw materials, namely, phenolic resins and triblock copolymer PEO-PPO-PEO (PO: propylene oxide; EO: ethylene oxide), e.g., Pluronic F127, P123, F108, to prepare highly ordered mesoporous carbons. In the synthesis developed by the former group, low-molecular-weight and water-soluble phenolic resins (resols) which are polymerized from phenol and formaldehyde under an alkaline condition, first mixes with the Pluronic PEO-PPO-PEO in ethanol. The homogeneous solution is poured into dishes to evaporate the solvent. It induces the organic–organic self-assembly of resols with amphiphilic block copolymers by hydrogen-bonds to form ordered mesostructures. In the synthesis reported by the Dai’s group, phloroglucinol-glyoxal are polymerized in the presence of Pluronic triblock copolymers. The forming polymeric framework interacts with the structure directing agents by strong hydrogen bonds and where strong acidic conditions are used, also by electrostatic interactions. The in situ polymerization is followed by microphase separation of polymer nanocomposites, which are then dispersed in tetrahydrofuran-ethanol solvents and cast as films on different substrates. The drying steps involve similar structural organization mechanism to the method reported by Zhao’s group. Because of the different chemical and thermal stability between the resins and triblock copolymers, the templates can be removed either by calcination at 350 °C under inert atmosphere or by extraction with sulfuric acid solution, leaving ordered mesoporous polymers. Heating at a high temperature above 600 °C, polymers can transform to homologous carbon frameworks. Through simply varying the surfactant/resol ratio or choosing different block copolymers in Zhao’s synthesis, porous carbons with various mesostructures have been obtained. Figure 4 illustrates this solvent evaporation induced self-assembly (EISA) synthesis procedure. Following this concept, other PEO-containing block copolymers, including diblock copolymers, ABC triblock copolymers and reverse triblock copolymer, can also be used as templates to propagate the pore structures. While mesoporous carbons prepared following pre-polymerization of resins exhibit pore sizes in the range of 2–5 nm, those from in situ polymerization and microphase separation are typically larger, typically above 6 nm. The ability to prepare mesoporous carbon materials with different pore sizes makes both synthetic pathways complementary and offering a broader range of materials to be chosen based on the desired applications.

EISA method, which relates with a liquid-deposition coating technique (such as dip-coating or spin-coating on an accessible and planar substrate), is a powerful route for preparing ordered mesoporous carbon materials. However, disordered or nonporous carbons are often produced if simply thickening the films above several hundred micrometers. Therefore, organic–organic self-assembly on the planar substrate is not an economical route for mass production due to the difficulties in forming vast accessible spaces. Recently, Xue et al. improved this EISA method by replacing planar substrate with bulk polyurethane (PU) foam. The PU foam scaffolds have a hydrophilic surface. Most important, its unique 3D interconnecting macroporous architecture provides large voids and interfaces for self-assembly of the ordered mesostructures. As presented in Figure 5, when the PU foam is impregnated into the dilute ethanol solution, the precursors, e.g., resols with/without silicate oligomers, and triblock copolymer F127, together with the ethanol solvent, are infused into the interconnecting 3D networks and large macropore voids by capillary and wetting driving forces. During the solvent evaporation, the precursors catalyzed by Pluronic F127 foams and form a uniform layer of ordered mesostructured composites on the PU foam skeleton. It is noted that triblock copolymer templates and more than 97% of PU foam can be removed during carbonization and the primitive macroporous architecture with the 3D interconnecting struts is retained to form a hierarchical macro/ mesoporous carbon-silica or carbon materials. Compared to the convenient EISA method carried out on the planar substrates, this approach expands the EISA technique into capacious space for saving area. Consequently, it is more suitable for mass production of ordered mesoporous carbons.

As the fast development of soft-templating synthesis of ordered mesoporous carbons, the exploration of their applications as electrochemical capacitors has been gradually carried out. In general, the research focuses on the following aspects: 1) increasing the surface area; 2) optimizing the pore size; 3) designing hierarchical pore structure; and 4) controlling carbon morphology.

3.4.1. Activation of the Ordered Mesoporous Carbons

As EDLCs utilize the electric double layer formed at the electrode/electrolyte interface for charge storage, a highly developed surface area is necessary for carbon electrodes to obtain high specific capacitance. Generally speaking, the process employed to increase surface area and porosity from a carbonized organic precursor is referred to as “activation.” So far, the most used agent to activate soft-template mesoporous carbons is potassium hydroxide. The activation is performed by heating a physical mixture of solid KOH and mesoporous carbons under N2 at a desired temperature (400–1000 °C). During this process, KOH dehydrates and transforms into potassium oxide (K2O) at about 400 °C and the latter is further reduced into metallic potassium by carbon at high temperature. Therefore, reaction of K2O with carbon and intercalation of metallic potassium into pseudo graphitic layers are considered to be the two major factors in the development of microporosity and increase in BET surface area of mesoporous carbons. The quantity of KOH and the activation temperature greatly affect the textural properties of the mesoporous carbons. Generally, the surface area, micropore volume and total pore volume increase with increasing the mass ratio of KOH/carbon. Enhancing activation
temperature has the similar effect as increasing KOH amount. It should be mentioned that, nearly 70% of the total surface area comes from micropore regardless of the KOH/carbon mass ratio and activation temperature. Besides affecting the surface area and pore volume, the carbon burn-off during activation is another important factor to be considered. High carbon burn-off increases cost and gas emissions, which are undesirable from both economic and environmental perspectives. More KOH and higher activation temperature can increase surface area of mesoporous carbons, but at the cost of increasing carbon burn-off, therefore, imposing a trade-off between desired materials properties and economic/environmental impacts. When using as EDLCs, activated mesoporous carbon with high surface area of 1940 m² g⁻¹ shows a gravimetric capacitance of 188 F g⁻¹ between -0.4 to 0.6 V with a sweep rate of 1 mV s⁻¹ in 0.1 M sodium chloride (NaCl) aqueous electrolyte. This value is much higher than the capacitance (71.3 F g⁻¹) of mesoporous carbons derived from the same phenolic resin precursors without activation treatment, which have a low surface area of 520 m² g⁻¹.\[91c\]

Carbon dioxide (CO₂) is another conventional agent to activate soft-template porous carbons through well-known basic reaction between CO₂ and carbon, which produces CO gas.\[91c,93\] Activation reaction of ordered mesoporous carbon FDU-15 under CO₂ occurs until the temperature reaches 700 °C, but over-activation is observed if it is above 800 °C.\[93c\] The BET surface area of FDU-15, increases from 655 to 1040 m² g⁻¹ with increasing activation temperature from 700 to 750 °C, but decreases to 899 m² g⁻¹ at 800 °C. Meanwhile, the mesostructural regularity is stable below 750 °C, but collapses at 800 °C caused by the severe etching of CO₂. Upon increasing treatment time from 1 to 10 h at 750 °C, the surface area of activated FDU-15 increases from 674 to 2750 m² g⁻¹. In comparison with KOH activation, which leads to a considerable development of microporosity, CO₂ activation maintains high fractions of mesopores and generates a slight increased mesopore size. A small fraction of (40–50%) of the total surface area is associated with micropores. This difference may be due to the large dimension of CO₂ molecule, which restricts the accessibility of CO₂ into micropores, leading to an “etching” of mesopores and a low microporosity.

Figure 4. Scheme for the preparation of the ordered mesoporous carbon via solvent evaporation induced self-assembly of phenolic resins and PEO-PPO-PEO block copolymers. Reproduced with permission from [84d]. Copyright 2006 American Chemical Society.
Recently, the activation performance of water vapor \(^{[93a,93c]}\) and ammonia (NH\(_3\)) \(^{[94]}\) has also been investigated. Water vapor can activate FDU-15 in the temperature range of 600 to 800 °C with the time from 1 to 7 h. Water vapor renders a development of micropores, which accounts for 45–62% of the total surface area. This value is higher than that for CO\(_2\)-activated mesoporous carbon, but still lower than one of KOH-activated carbons. Ammonia activation not only increases both BET surface area and pore volume, but also incorporates nitrogen atom into carbon framework in the forms of pyridinic-, pyrrolic-, quaternary-N, and N-oxides of pyridinic-N. \(^{[94]}\) Nitrogen doping can improve the wettability of mesoporous carbons to electrolyte solution, and in turn increase its electrochemical activity. However, the extremely toxic HCN gas is produced during the reaction and thus limits the application of NH\(_3\) activation.

### 3.4.2. Pore Size Control

Developed surface area is always desired for EDLCs, however, with few exceptions\(^{[76h]}\) there is no linear relationship between the area and capacitance, \(^{[10e,95]}\) mainly because the surface area is commonly measured by small N\(_2\) molecules. The small pores, which can be accessed by N\(_2\), may constrain the accessibility of electrolytes, especially the organic electrolytes with large ionic sizes. Therefore, the preparation of mesoporous carbons with continuously adjustable pore size, which can meet the requirements in different electrolytes, is much in demand.

Inspired from the pore size control of silica, initial researches on pore size regulation of mesoporous carbons synthesized from soft-template approach are mainly focused on selecting surfactants with various hydrophobic groups. Generally, larger hydrophobic segments occupy more space, and then can convert to larger mesopores. For example, the pore size of mesoporous carbon FDU-16 increases from 2.8 to 4.3 nm if replacing the triblock copolymer F108 template (EO\(_{132}\)PO\(_{50}\)EO\(_{132}\)) with F127 (EO\(_{106}\)PO\(_{70}\)EO\(_{106}\)), which contains longer hydrophobic PPO chains. \(^{[84d]}\) Diblock copolymers, such as PEO-b-PS and PEO-b-PMMA, are inclined to form a compact packing of globular micellar aggregation, and consequently favor large pore shaping in mesoporous carbons. By utilizing lab-made diblock copolymer PEO\(_{127}\)-b-PMMA\(_{124}\) and PEO\(_{127}\)-b-PS\(_{210}\), mesoporous carbons with pore sizes of 10.5 and 23.0 nm have been obtained. \(^{[84g,96]}\) Large pore mesoporous carbons can also be obtained under acidic conditions by using resorcinol-formaldehyde and blend templates of F127 and polyoxyethylene (20) cetyl ether (C\(_{156}\)H\(_{433}\)EO\(_{20}\), Brij 58), and polyoxyethylene (20) stearyl ether (C\(_{18}\)H\(_{416}\)EO\(_{20}\)-OH, Brij 78). \(^{[97]}\) By changing the ratios of Brij 58 and Brij 78 to F127, the mesopores could further be enlarged from 4 to 8 nm, as well as the average size and amounts of micropores. \(^{[97]}\)

Also, the temperature and pH for the in situ polymerization of phenol-formaldehyde and self-assembly with P123, in combination to their mass ratios used have been found to largely change the mesopore size and other adsorption parameters of disordered mesoporous carbons. \(^{[98]}\) For instance, mesopores were twice as large for the same mass ratios of carbon precursors to F127 when lowering the temperature from 55 or 40 °C down to 15 °C. At the lowest temperature investigated the mesopores of final carbons were as large as 16 nm. \(^{[98]}\)

Adding organic swelling agents has been demonstrated to be a significant way to expand pore sizes of mesoporous silica, but only a disordered mesostructure is observed when hydrocarbon molecules, e.g., 1,3,5-trimethylbenzene (TMB), heptane and hexane are added in the phenol-formaldehyde/copolymer P123, \(^{[84a]}\) or in the phenol-formaldehyde/copolymer...
P123 systems. The sole successful preparation of ordered ultra-large-mesopore carbons via a pore swelling approach was reported by Deng et al. They introduced homopolymer $h$-PS into the diblock copolymer PEO$_{125}$-b-PS$_{230}$ templated system. The pores of obtained mesoporous carbon can continuously increase from 22.9 to 37.4 nm.

Pore size control of ordered mesoporous carbons based on templates and organic additives is so far very limited. It is caused by the molecule composition limitation of the soft templates and the enormous shrinkage of the phenolic resin frameworks during pyrolysis. The latter always leads to a serious decrease of pore size, for instance, the size of FDU-15 reduces from 7.1 to 4.3 nm along with increasing pyrolysis temperature from 350 to 800 °C. Consequently, attempts to lessen the framework shrinkage have been made. Liu et al. demonstrated a triconstituent co-assembly route to prepare well-ordered mesoporous carbon-silica nanocomposites. In their system, phenol-formaldehyde resol along with TEOS were used to co-assembly with triblock copolymer F127 via an EISA strategy. After triblock copolymer removal and carbonization, ordered mesoporous carbon-silica composites were yielded. The presence of rigid silicates that act as a “reinforcing-steel-bar” dramatically inhibits framework shrinkage during pyrolysis. The pore size of carbon-silica composites is ~6.7 nm, which is much larger than that (~2.9 nm) of ordered mesoporous carbon from similar synthetic process without silica addition. Mesoporous carbon was obtained by HF etching of silica in the carbon-silica composites. This process builds pores in the carbon pore walls, and the dimension can be simply adjusted by tuning hydrolysis and condensation degrees of silicates before co-assembly. The highly ordered mesoporous carbon has extremely large surface area (~2400 m$^2$ g$^{-1}$) and relatively large mesopores (~6.7 nm). When using as an EDLC electrode in the organic electrolyte [(C$_2$H$_5$)$_4$N][BF$_4$], it exhibits a high capacitance of 112 F g$^{-1}$ between 0 and 3 V at a scan rate of 200 mV s$^{-1}$, and a good cycling stability with capacitance retention of 88% over 1000 cycles.

Another recent example of reinforced nanocomposite materials was that for mesoporous carbon-graphitic carbon nano-composites prepared by a “brick and mortar” soft-templating method. These nanocomposites were prepared by systematically replacing the resorcinol-formaldehyde “mortar” in the synthesis gels of soft-templated carbons with graphitic nanostructures “bricks”, namely onion-like carbons (CO) and carbon black (CB). After carbonizations at 850 °C, carbons with larger mesopore volumes and widths were obtained with increasing brick/mortar ratios as shown by the N$_2$ adsorption isotherms and calculated pore size distributions, respectively. Most importantly, the resorcinol-based mesoporous carbon provided enough electronic conductivity for electronic percolation between the graphitized CO and CB particles. The latter feature highly improved the electronic conductivity of the mesoporous carbons without high temperature graphitization.

3.4.3. Hierarchical Pore Structure

Rate capability of EDLC is another important consideration for their practical application, especially under a high current density. A hierarchical porous structure can enhance the rate capability of EDLC by providing abundant access for electrolyte ions and reducing the diffusion distance of ions within the electrode materials. The mesoporous carbon-silica composites exhibit a high rate capability with a capacitance retention of over 60% at a scan rate of 3000 mV s$^{-1}$, and a good cycling stability with capacitance retention of 80% over 1000 cycles.
However, porous-carbon-based EDLCs are always known to suffer from electrolyte kinetic problems that are related to inner-pore ion-transport resistance and the long diffusion distance from electrolytic solution to the depths of pores. Hierarchically porous carbons, especially those possessing well-defined macropores and interconnected meso- and/or micro-pores, have attracted much attention because they combine the excellent performance of mass transport from macropores and the advantages of high surface areas from micro-/mesopores.

The hierarchical structure has typically been obtained by the impregnation of preformed macroporous structures with the carbon precursor sols, followed by precursor carbonization and macropore voids freeing. According to this strategy, Deng et al. reported hierarchically macro-/mesoporous carbons fabricated by combining a surfactant-templating organic resol self-assembly with a colloidal-crystal templating approach (Figure 8). Monodispersed silica colloidal crystals (240, 320, and 450 nm) are used for the generation of ordered fcc macropore arrays. The organic-organic self-assembly of the resins and triblock copolymers F127 results in the formation of the ordered mesostructure in the interstitial voids. The rigid silica spheres prevented the shrinkage of the mesostructure during the thermosetting and carbonization procedure, resulting in large mesopore sizes (~11 nm). Finally, silica spheres were etched by HF solution to yield hierarchically ordered macro-/mesoporous carbons with tunable macropore sizes of 230–430 nm and 3D interconnected windows of 30–65 nm.

This dual hard silica colloid/soft block copolymer templating approach was also adopted by Liang et al. to prepare ordered...
mesoporous carbons with interconnected channels. But differently, the SiO$_2$ colloids they used have small particle sizes of around 8 nm, and the mass ratio of SiO$_2$/phenol is as low as 7%. The hydrophilic SiO$_2$ nanoparticles and phenolic resol can co-assemble with Pluronic F127 to form the mesopore walls together as presented in Figure 9a. Because the diameters of the SiO$_2$ nanoparticles are larger than the thickness of the pore walls, neighboring channels of the 2D hexagonal mesostructure are interconnected after etching of the SiO$_2$. The obtained mesoporous carbons show surface areas of $\sim 750$ m$^2$ g$^{-1}$ and bimodal pores of $\sim 3.4$ and $\sim 7.6$ nm. Ion diffusion is accelerated through the much more diffusion routes, and thus, porous carbons have much lower impedances to ion transport inside the interconnected channels and within the micropores compared to that without mesotunnels in their pore walls. The capacitance of the hierarchically structured mesoporous carbons basically stays constant (136–143 F g$^{-1}$) at sweep rate range of 10–300 mV s$^{-1}$ in aqueous KOH electrolyte (Figure 9b). In contrast, the ordered mesoporous carbons without mesotunnels have a lower capacitance; with an increase of the sweep rate only 76% of its initial capacitance can be retained at 300 mV s$^{-1}$. In addition, when SiO$_2$ colloids with the size of 20 or 50 nm were used, bimodal distributions of mesopores were obtained after SiO$_2$ etching. The addition of TEOS to the previous synthesis gels afforded micropores after treatment with HF. Final carbons could be further activated with steam and CO$_2$ and carbons with pore volumes of $\sim 6$ cm$^3$ g$^{-1}$ and specific surface areas exceeding 2000 m$^2$ g$^{-1}$ were obtained.

Incorporation of “hard templates” into the system usually accompanies with an additional step to eliminate the templates, which undoubtedly complicates the preparation procedures. Recently, Dai’s group reported a polymerization-induced spinodal decomposition way to synthesize bimodal meso-/macroporous carbon monoliths. Pre-polymerized mixture of phloroglucinol-formaldehyde resol and copolymer F127 was dissolved in glycolic solvents and immediately transferred into a glass tube. Mesopores were formed by a soft-template approach in which the triblock copolymer formed a micelle structure with the phloroglucinol-formaldehyde resin through hydrogen bonding (Figure 10). As the polymerization of resin progressively developed by heating in air bath, it became more and more immiscible with glycolic solvent, and polymerization-induced phase separation occurred. As a result, macropores were evolved from the solvent-rich phase. The size of the macropores (1–3 μm) varied with reaction temperatures, prepolymerization times, and solvent compositions, whereas the mesopores ($\sim 8.0$ nm) tended to be independent of the spinodal decomposition process. Similar polymerization-induced phase separation was as well observed by Huang and co-worker. They used a blend of Pluronic F127 and P123...
as templates, and phenolic resols as carbon precursors. The synthesis was carried out under hydrothermal conditions, in an aqueous medium at 100 °C for 10 h. Fast polymerization under hydrothermal conditions causes the macro-domains to be divided into a phenolic resin/Pluronic-rich phase and a water-rich phase, where both phases are continuous and highly interconnected. After drying in air, the aqueous phase domains can turn to the interconnected macropore system. The resulted carbons show an ordered 2D hexagonal mesostructure with a uniform pore size (3 nm) and 3D irregular macroporous scaffolds with a size of ~3 μm.

A major advancement to the synthesis of hierarchical carbons with meso/macroporous structures was recently achieved by Mayes, et al. By replacing formaldehyde by glyoxal in the self-assembly synthesis with phloroglucinol and F127, ordered mesoporous carbons with additional macropores with average sizes of ~200 nm were obtained (Figure 11). Most importantly, this synthesis did not require hydrothermal synthesis step, or for secondary volatile solvents and mixtures of triblock copolymers, making it more attractive from environmental and economic perspectives.

PPO-PEO-PPO reverse triblock copolymers are an important family of commercial surfactants that have the hydrophilic PEO block located in the middle and the hydrophobic PPO blocks at either end of the polymer chain. It has been suggested that the reverse copolymers facilitate the formation of interconnected micelles in which the two outer PPO blocks of a chain participate in two different micelles or aggregation. Their unique micelle structures make them promising candidates to prepare porous carbons with hierarchical structure. For instance, upon using reverse triblock copolymer PO15EO22PO15 as a template and resol as a precursor, Huang et al. successfully synthesized ordered mesoporous carbon with a tunable bimodal architecture consisting of small (3.2–4.0 nm) and large (5.4–6.9 nm) mesopores. It induces the formation of a cubic Fd3m mesostructure with high curvature, which contains two caged mesopore systems with different pore sizes.

Lately, with a short chain reverse block copolymer PO15EO23PO15, monolithic carbon aerogels with macro- and micropores were reported. As shown in Figure 12, hydrolysis and condensation of resorcinol and formaldehyde resol were conducted in an acid water/ethanol mixed solution of PO15EO23PO15 block copolymer. A low water content resulted in the formation of a macroscopic rich polymer phase containing a certain amount of water in the form of nanodroplets. Resin colloids were formed at those nanodomains of high hydrophilicity, e.g., water nanodroplets. As continuous polymerization of the resin, some PO15EO23PO15 was trapped within growing colloids, which ultimately contributed to the major formation of microporosity. Further growth of resin colloids made them come into contact and partially sinters. Finally, thermal treatment at 800 °C in inert atmosphere resulted in further colloid sintering and carbonization. The elimination of the rich polymer phase formed by PO15EO23PO15 gave rise to the formation of the macropores while the elimination of the reverse copolymer entrapped within the growing colloids resulted in the formation of micropores. The carbon monoliths have specific BET surface and micropore area of 725 and 470 m² g⁻¹, and a trimodal macro- (2.4 μm and 100 nm) and microporous (below 2 nm) structure. This structure is demonstrated to be suitable for EDLCs, as a remarkable capacitance of 180–225 F g⁻¹ and 25–31 μF cm⁻² obtained in KOH or H₂SO₄ electrolytes. Moreover, the capacitance was also stable for increased current densities, keeping values of 120–130 F g⁻¹ even at 150 mA cm⁻².

3.4.4. Morphology Control

Practical applications always require various macroscopic morphologies, such as uniformly sized spheres for chromatography, films and membranes for sensor and separation, transparent monoliths and thin films for optics. As an EDLC electrode, certain morphologies, which can, for instance, reduce the resistance of the electrode, facilitate high-rate ion diffusion, etc. spark more and more interest.

One of these morphologies is monolith. It is known that, conventional carbon electrodes are composed by packed beds of carbon particles, and the electrical resistance is a function of both intra-particle resistance and the contact (or inter-particle) resistance. The latter is a major factor to the resistance of aggregated carbon powders. Carbon monoliths, because of the absence of grain boundaries between the powders, exhibit remarkably high conductivities. For instance, the carbon monolith prepared by the template PO15EO23PO15 block copolymer as described above, shows a conductivity of 2.5 S cm⁻¹. The
value decreases noticeably (e.g., up to 0.2 S cm$^{-1}$) after grinding the monolith into fine carbon powders and mixing them with a binder (polyvinylidene fluoride) to form compacted pellets.$^{[112]}$

3D ordered mesoporous carbon sphere arrays with short pore lengths and large interconnected window sizes between them also show their advantages as EDLCs.$^{[113]}$ As described in Figure 13, ordered macroporous silica were firstly prepared by using polystyrene sphere arrays as the sacrificial template, and then the sol containing Pluronic P123 and phenolic resol was soaked into the voids of the skeleton. Ordered mesoporous carbon spheres with face-centered cubic arrays, which inherited from colloidal crystal arrays of polystyrenes, were formed after the self-assembly of Pluronic P123 and resol, carbonization and silica removal. The carbon spheres with diameters of $\sim$250 nm, show pore sizes of around 4.0 nm, interconnected window sizes of $\sim$60 nm, and BET surface area of 601 m$^2$ g$^{-1}$. As an electrode material for supercapacitors, this carbon shows a capacitance of 14 $\mu$F cm$^{-2}$ between 0 and 3 V over a wide range of scan rates even as high as 200 mV s$^{-1}$, and exhibits a good cycling stability with retention of 93% over 5000 cycles. The excellent performance is possibly related to the short pore channels, large mesopore sizes and interconnected window sizes for high-rate ion transport, and better electrical conductivity than loosely aggregated powdery materials.

In addition, 1D nanostructures, such as nanofibers and nanotubes, with well-controlled dimensions are favorable for electrochemical application too. Besides the extra surface area derived from the 1D nanostructures, they provide a shortened path for the electron transportation. Meanwhile, the ordered mesostructures can facilitate the penetration of the electrolytes from the direction perpendicular to the longitudinal axis of the nanostructures. Thus, 1D mesoporous carbons are highly
desirable for the EDLCs with both high capacitance and high rate capability. Recently, mesoporous carbon nanofiber arrays were fabricated through a confined self-assembly of triblock copolymer F127 and resols within the pore channels of anodic alumina (AAO) membranes.[114] The diameter of the carbon nanofibers is approximately 200 nm (Figure 14a). The circular mesopore channels are concentrically coiled around the axis of the fibers and a lot of openings exist on the outside walls (Figure 14b). The mesopores show bimodal pore distributions at 3.4 nm and a relatively wide range from 5 to 8 nm. Their BET surface area is 1424 m² g⁻¹. Cyclic voltammetry (CV) measurements of the nanofibers (Figure 14c) shows that the capacitances of charge and discharge are kept at a constant value in the range of 90 – 152 F g⁻¹ in a wide sweep rates range from 3 to 50 mV s⁻¹, while the mesoporous carbon powders (Figure 14d) experience a dramatic decay in capacitances with the increase of sweep rates.

Instead of an AAO membrane, Xia’s group used a natural crab shell, which contains a number of relatively uniform ellipse-type macropores with dimensions of ca. 1 × 0.5 μm, as a confined space for Pluronic P123-templated self-assembly of phenolic resol (Figure 15).[115] The obtained mesoporous carbon nanofibers retain an interpenetrated ordered array that is replicated from the crab shell hard-template and all the carbon nanofibers are composed of ordered mesopores with closed to 2D hexagonal structure. Three types of pores are consisted in the materials, namely, 11 nm mesopores originated from Pluronic P123 template, 70 nm void pores formed between the nanofibers, and 1 μm macropores between nanofiber arrays. The multi-modal pores ensure the retention and immersion of electrolyte, as well as greatly reducing the resistance for the ions. Their BET surface area and total pore volume are 1270 m² g⁻¹ and 4.3 cm³ g⁻¹. The specific capacitance is estimated to be ~12 μF cm⁻² (~152 F g⁻¹) in 1.0 M [(C₂H₅)₄N][BF₄] electrolyte, and 95% of initial capacitance can be maintained even after 1000 cycles.

The research of soft-template synthesis of porous carbons is still in its early stages. To date, the carbon precursors are mostly centered on phenolic resins, which, as hard carbon precursors, are difficult to graphitize. Moreover, compared to the synthesis of ordered mesoporous silicas, the submicrometer pore size control of the mesoporous carbons is more complicated. Also post activation process is always necessary to get high surface areas comparable to ZTC and CDC materials. However, the soft-template method is one of the most suitable techniques to mass-scale preparation of ordered porous carbons with various pore diameters and structures. Furthermore, soft-templated carbons...
are also important reference materials providing information about the effect of pore size, morphology, channel structures and other parameters on the ion diffusion and charge storage in the nanoconfined system.

4. Pseudo-Capacitance

As the specific capacitance of carbon materials mainly derives from EDLC, pure carbon-based capacitors cannot meet the requirements in high energy storage field. An efficient method to enhance the capacitance is to incorporate additional contributions from pseudo-capacitance.

Transition metal oxides (MO$_x$), such as RuO$_2$, MnO$_2$, which possess high theoretical pseudo-capacitance, might be a promising alternative for enhanced energy storage capacity. However, most of the pseudo-capacitance comes from surface redox reactions and only the first few nanometers from the surface layer are utilized in the faradic processes. Consequently, the capacitance of MO$_x$ in bulk is much lower than the theoretical value. In addition, the poor electrical conductivity of MO$_x$ results in poor rate capability and thus limits their applications as electrode materials for high power supercapacitors. Because porous carbon materials show high surface area and good electrical conductivity, deposition of MO$_x$ onto carbon supports not only increases the effective utilization of the active materials, but also improves the electrical conductivity of the composites.

RuO$_2$ is the most promising electrode materials for supercapacitors due to its high specific capacitance, highly reversible redox reactions in a wide potential range and much long cycle life. Many studies have demonstrated that specific capacitance of carbons can be significantly enhanced with RuO$_2$ incorporation.$^{[18a,116]}$ For example, a specific capacitance up to 599 F g$^{-1}$ has been obtained for RuO$_2$/carbon composites with 80 wt% of RuO$_2$ loading.$^{[116]}$ However, the specific capacitance calculated based on the weight of RuO$_2$ decreases along with the increase in its content due to limited reaction of the large particles.$^{[18a,116a,116c]}$ Hence, the high dispersion of RuO$_2$ is a key factor to increase the capacitance of nanocomposites for supercapacitors.$^{[117]}$ Das et al.$^{[118]}$ reported the electro-deposition of RuO$_2$ onto high porous SWNT films. The maximum specific capacitance is as high as 1084 F g$^{-1}$. The specific capacitance based on the weight of RuO$_2$ is calculated to be 1715 F g$^{-1}$, which closely approaches the theoretical maximum capacitance (2000 F g$^{-1}$).

Despite of the excellent performance of RuO$_2$, the high cost greatly restricts its commercial application. Recently, MnO$_2$ has been more investigated as a suitable alternative material due to its low-cost, rich redox behavior and good environmental compatibility. Gao et al.$^{[119]}$ have prepared homogenous MnO$_2$/MWNT composite via an in situ coating technique. The specific capacitance of the composite is 250.5 F g$^{-1}$, which is about eight times higher than that of the pure MWNT. Dong et al.$^{[120]}$ have prepared MnO$_2$/mesoporous carbon composites with different nanoparticle sizes embedded into the matrix through redox reaction between permanganate ions and carbons. They have found that the capacitance of the composites improved with increasing MnO$_2$ amount. A high capacitance up to 220 F g$^{-1}$ was obtained for the composite with the highest MnO$_2$ loading and 600 F g$^{-1}$ was calculated based on the MnO$_2$ content. Another ideal support is carbon nanotube array (CNTA) which is vertically grown on the current collector. By using this CNTA as a support, a binder-free MnO$_2$/CNTA electrode with hierarchical porous structure, high surface area and superior conductivity has been successfully fabricated.$^{[118]}$ This
MnO$_2$-CNTA composite showed excellent rate capability (50.8% capacity retention at 77 A g$^{-1}$), high capacitance (199 F g$^{-1}$ and 305 F cm$^{-3}$) and long cycle life (3% capacity loss after 20 000 charge/discharge cycles).

For soft-templated mesoporous carbons containing MnO$_2$, the capacitances differed for materials prepared by post-synthesis grafting of MnO$_2$\cite{121} to those made in one-pot synthesis method.\cite{120} For instance, materials modified with a 1 nm thick film of MnO$_2$ prepared by a post-synthesis method\cite{121} retained its capacitance at much higher scan rates than the mesoporous carbons containing MnO$_2$ nanocrystals in the mesopore walls (one-pot synthesis).\cite{122} The former materials exhibited twice as large mesopores (~8 nm), compared to the latter composites. This feature implied in lower electrolyte resistance and better diffusion in the materials with larger mesopores. Furthermore, similar oxide contents deposited on MWNT afforded thicker MnO$_2$ films (6 nm)\cite{119} than on the surface of mesoporous carbons, resulting in better conductivity in the latter case at 100 mV s$^{-1}$ scan rates.\cite{121} While for MnO$_2$/MWNT the gravimetric capacitance dropped from 350 F g$^{-1}$MnO$_2$ at 2 mV s$^{-1}$ down to 37 F g$^{-1}$MnO$_2$ at 100 mV s$^{-1}$, the capacitance approached 137 F g$^{-1}$MnO$_2$ at 100 mV s$^{-1}$ for the MnO$_2$ coated mesoporous carbon.

In addition to metal oxides, many kinds of conducting polymers have been tested as pseudo-capacitive materials as well, due to its low cost, easy synthesis and relatively high conductivity.\cite{86,122} PANI, as an important member in the family of conducting polymers, has been extensively investigated. However, it is well-known that contrary to porous carbons, PANI as a supercapacitor electrode has a main drawback of the poor cycling stability derived from the big volumetric change in the doping/de-doping process.\cite{123} Therefore, the compounding of porous carbon and PANI seems to be an effective method to fully utilize their respective advantages. Xia et al.\cite{124} has synthesized whisker-like PANI grown on the surface of ordered mesoporous carbon. The capacitance of this PANI/mesoporous carbon composite was measured to be up to 900 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$. The effect of compounding process on electrochemical capacitive properties of the composite has been studied by Li et al.\cite{125} and the results showed that the in situ synthesized composite exhibited the highest specific capacitance of 747 F g$^{-1}$ at a current density of 0.1 A g$^{-1}$ and excellent rate capability. Lately, a high-performance PANI electrode was prepared by potentiostatic deposition of aniline on a hierarchically macro/mesoporous carbon monolith.\cite{126} A capacitance value of 300 F g$^{-1}$ is observed. The active PANI shows high stability attributed to the backbone role of the porous carbon. The hierarchical pore structure favors kinetics at high power densities, thus, contributing to the increase of ionic conductivity and power density, as well as a good cyclability.

Another strategy to introduce pseudo-capacitance to carbon materials is to dope hetero-atoms which give the capacitance through Faradic reaction in the framework or as functional groups on the surface. The most commonly present hetero-atoms are nitrogen and oxygen. However, organic groups involved with oxygen and nitrogen are not stable during long cycling and a gradual decreasing of pseudo-capacitance is observed. In addition, in organic electrolyte, these hetero-atoms could cause decomposition of the electrolyte and thereby show negative affection to cycle life. Recently, Liu’s group has reported P-rich porous carbons prepared by phosphoric acid activation and the highest specific capacitance of 220 F g$^{-1}$ is obtained for the sample with specific BET surface area of 633 m$^2$ g$^{-1}$.\cite{126} Moreover, the voltage window of this sample is extended to 1.3 V in an aqueous solution, which is higher than conventional carbon materials as the decomposition potential of water is ca. 1.2 V. This is very vital in the enhancement in energy density (E) as E is proportional to the squared of V according to $E = 1/2 CV^2$. Most importantly, the P-containing porous carbons also show long cycle life performance. Therefore, this work provides a new way to improve specific capacitance of carbon materials with high stable performance. Also promising for pseudo-capacitor applications are heteroatom-doped soft-templated mesoporous carbons prepared from the co-condensation of phenolic resins with TEOS and organosilanes such as tris-(3-trimethoxysilylpropyl)isocyanurate (ICS) (in the presence of F127).\cite{127} Nitrogen-doped carbon-silica composites and silica-free carbons with mesopores (~8 nm in diameter, specific surface areas within 211–1208 m$^2$ g$^{-1}$ and N contents of 0.3–3.4 wt.% were obtained.\cite{127} These materials combine a hierarchical structure of micro- and mesopores with nitrogen doping that may be largely accessible for Faradic reactions. Similarly, different doping elements could also be introduced to the carbon frameworks by properly selecting the starting organosilanes.

In this direction, other promising carbon sources are ionic liquids\cite{128} and task specific ionic liquids\cite{129} for the synthesis of N, B and P-doped porous carbons and carbon-oxide nanocomposites. It has been known that despite of their extremely low vapor pressures, non-flammability and low toxicity, ionic liquids have no carbon yield resulting from the lack of cross-linkable intermediates during thermal decomposition. However, it has been demonstrated that the confinement of ionic liquids in a porous oxide matrix during thermal treatments results in the formation of a carbon-oxide nanocomposites.\cite{128} These nanocomposites were prepared as monoliths by non-hydrolytic sol-gel method and crack-free monoliths were obtained after thermal treatments. Upon removal of the oxide matrix, hierarchical porous carbons exhibiting micro and mesopores, high specific surface areas and doped with elements such as N from the ionic liquids used were obtained.\cite{128,129} Highly conducting N-doped ordered mesoporous carbon have also been prepared as inverse replicas of ordered mesoporous silica SBA-15 using ionic liquid precursors. While the growth of graphitic domains was favored at temperatures below 1000 °C, their N contents were near 8–10 wt% and exhibiting electrical conductivities comparable to graphite.\cite{128,129}

Furthermore, in case of task specific ionic liquids having anion groups capable of polymerizing during thermal treatments yield heteroatom doped carbons with high specific surface area without the need for an oxide matrix (Figure 16).\cite{129} More interesting, the latter studies revealed a templating effect by the cation of such task specific ionic liquids.\cite{128} For instance, by tailoring the size of the cations of such ionic liquids, not only micropores, but also mesopores were formed. Other carbon precursors recently reported include deep eutectic solvents.\cite{130} By using low temperature thermal treatments for
the polycondensation with formaldehyde followed by carbonization, macro-/meso porous carbon monoliths with mesopores in the range of 10 to 25 nm were obtained. It has been suggested that the deep eutectic solvents played a double role in this synthesis, acting as both carbon precursor and template for the micro and mesopores.[130] Further studies may reveal the ability to prepare heteroatom doped carbons using deep eutectic solvents, whereas the design of ionic liquids could further increase the number of sources available to make carbon electrodes for supercapacitors with all the aforementioned properties.

5. Conclusions

Carbon materials science has progressed tremendously from simply carbonizing cellulosic biomass or transforming coal precursors into porous materials. The ability to generate pore sizes that span the micropore to macropore range, while maintaining well-defined mesopores continuously motivates research on these materials. The advancements have come at opportune times to capitalize on the demand for alternative energy sources and storage platforms as the world looks away from petrol-based energy sources.

The continued study of mesoporous carbon materials is expected due to the requirement to optimize volumetric density with high-surface-area materials. The volumetric density relates specifically to the practicality of use where high storage capacity is needed in dense carbon materials resulting in low-volume, high-capacity cells. Furthermore, the ability to tailor pore sizes in the mesopore regime to facilitate fast mass-transport kinetics coupled with a tailored micropore size for optimized ion storage is needed for optimization of supercapacitor cells. These two factors are primary research topics that must be tackled prior to mass deployment of supercapacitors in the energy grid or transportation. These goals, albeit challenging, are not out of reach with the current level of research interest in porous carbon materials and the current ability to tailor the mesopore regime.

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