J Solid State Electrochem (2011) 15:1563–1578
DOI 10.1007/s10008-011-1411-y

REVIEW

The electrochemistry of activated carbonaceous materials: past, present, and future

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Received: 3 February 2011 / Revised: 28 February 2011 / Accepted: 3 March 2011 / Published online: 4 May 2011

Abstract Carbonaceous materials are widely used in electrochemistry. All allotropic forms of carbons—graphite, glassy carbon, amorphous carbon, fullerenes, nanotubes, and doped diamond—are used as important electrode materials in all fields of modern electrochemistry. Examples include graphite and amorphous carbons as anode materials in high-energy density rechargeable Li batteries, porous carbon electrodes in sensors and fuel cells, nano-amorphous carbon as a conducting agent in many kinds of composite electrodes (e.g., cathodes based on intercalation inorganic host materials for batteries), glassy carbon and doped diamond as stable robust and high stability electrode materials for all aspects of basic electrochemical studies, and more. Amorphous carbons can be activated to form very high specific surface area (yet stable) electrode materials which can be used for electrostatic energy storage and conversion [electrical double-layer capacitors (EDLC)] and separation techniques based on electro-adsorption, such as water desalination by capacitive de-ionization (CDI). Apart from the many practical aspects of activated carbon electrodes, there are many highly interesting and important basic aspects related to their study, including transport phenomena, molecular sieving behavior, correlation between electrochemical behavior and surface chemistry, and more. In this article, we review several important aspects related to these electrode materials, in a time perspective

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(past, present, and future), with the emphasis on their importance to EDLC devices and CDI processes.

Keywords Carbon electrodes · Activated carbons · EDLC · CDI · Adsorption phenomena

Introduction

Carbon, the sixth most abundant element in the universe, has been known since ancient times. The three naturally occurring allotropes of carbon known to exist are amorphous carbon (coal), graphite, and diamond. Beyond the critical importance of carbon in organic chemistry, throughout human history and especially in modern times, carbon is highly important and is widely used as an element in its various allotropic forms. Carbon is the source of the highest strength fibers, one of the best lubricants (graphite), the strongest crystal and hardest material (diamond), an essentially noncrystalline product (vitreous carbon), one of the best gas absorbers (activated charcoal), and one of the best helium gas barriers (vitreous carbon) [1, 2]. A great deal is yet to be learned, and more recently discovered forms of carbon, such as the fullerene molecules [3], the hexagonal polytypes of diamond [4], carbon nanotubes [5], and graphene [6], are being studied extensively. Some of the structures of various carbon allotropes are presented in Fig. 1.

All the allotropic forms of carbons—graphite, glassy carbon, amorphous carbon, fullerenes, nanotubes, and doped diamond—are used as important electrode materials in all fields of modern electrochemistry. Examples include graphite and amorphous carbons as anode materials in high energy-density rechargeable Li batteries porous carbon electrodes in sensors and fuel cells [7], nano-amorphous carbon as a conducting agent in many kinds of composite electrodes (e.g., cathodes based on intercalation inorganic host materials for batteries), glassy carbon and doped diamond as stable robust and high stability electrode materials for all aspects of basic electrochemical studies, and many more. The unique stability of carbon in various electrolyte solutions under a wide range of potentials and temperatures, despite their exposure to various reactive gases and ions in those extremely reactive/corrosive conditions, enables the utilization of conductive carbon materials (e.g., amorphous carbon and graphite) for various electrochemical systems and devices [7].

Amorphous carbon is highly abundant in the earth's crust as coal. It was probably formed by the metamorphosis of organic materials (mostly plants) in the course of old geological thermal processes. Most organic materials can be carbonized by anaerobic heat treatments. In fact, the majority of carbon materials used today are derived from carbon-rich organic precursors treated in inert atmospheres at elevated temperatures (a process referred to as carbonization). The ultimate properties of these carbons depend on a number of critical factors, e.g., the carbon precursor, its dominant aggregation phase during carbonization (i.e., solid, liquid, or gas), processing conditions, and the structural and textural features of the products. During carbonization, a thermal decomposition of the carbon precursors occurs. This pyrolisis eliminates all the volatile materials including the heteroatoms, and therefore, the majority of atoms left are carbon. The increasing proportion of conjugated carbon atoms in the sp^2 state during carbonization progressively increases the conductivity of

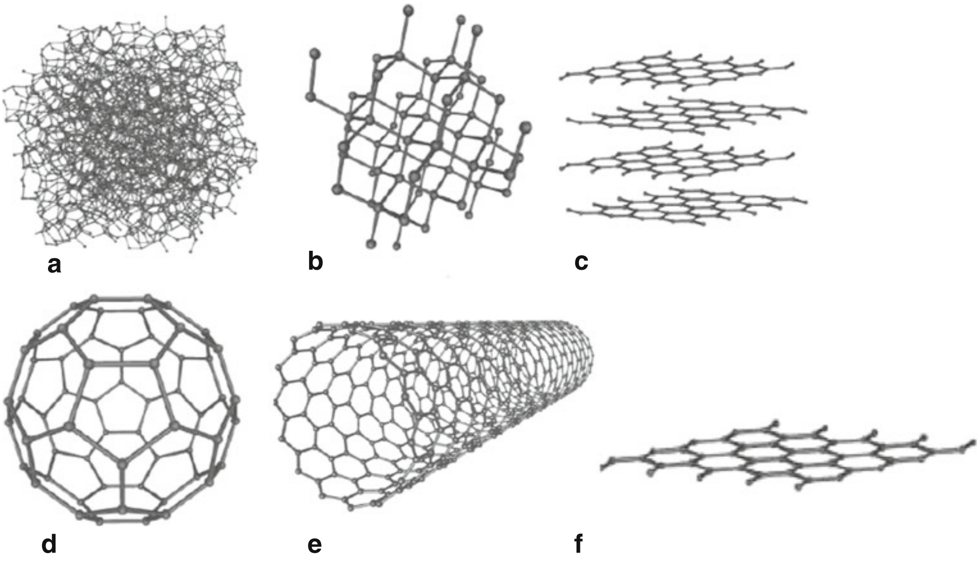

Fig. 1 Some of the structures of various carbon allotropes. **a** Amorphous carbon. **b** Diamond. **c** Graphite. **d** Fullerene. **e** CNT. **f** Graphene

the starting material as electrons associated with π-bonds are delocalized and become available as charge carriers. It is possible to design properties of carbonaceous materials for electrochemical applications, by a judicious choice of organic precursors (e.g., polymers, aromatic molecules, organic molecules containing heteroatoms such as nitrogen) and the carbonization parameters.

At the next stage, it is possible by mild oxidation to form highly porous carbon (with specific surface area >2,000 m^2/g) with adjustable porosity in terms of pore size and pore morphology (as discussed below). Activated carbons can be used together with more novel forms of carbon, nanotubes, or graphene sheets to form very interesting and important composite electrodes. Thus, highly porous, activated carbons can be considered among the most important electrode materials in modern electrochemistry and therefore constitute the main focus of this review.

Activated carbon electrodes: past and present

General description and discussion

The recent widespread use of conductive carbon materials for electrochemical systems started in the nineteenth century as replacement electrodes for copper in Volta batteries [7], and platinum in Grove cells [8]. A significant milestone in the history of carbonaceous material as candidates for electrochemical systems is the manufacture of artificial graphite by E.G. Acheson at the end of the nineteenth century [9]. Since then, there has been rapid growth in the use of carbons in electrochemical systems. Amorphous carbons are unique electrically and thermally conductive solids with adequate corrosion resistance, low thermal expansion coefficients, low densities, low elasticity, and low cost and can readily be obtained at high purities. These properties put amorphous carbon at the top of the list for electrochemical electrodes and conductive additives. In addition, carbon material can be produced in a variety of structures such as fibers, hollow fibers, thin films, powders, large blocks, etc., from various precursors.

The porosity and morphology of amorphous carbon can be shaped via mild burn-off processes using oxidants. This procedure, usually called activation, forms highly porous materials whose surface area is in the range of several hundreds to more than 2,000 m^2/g. These pores may occupy a large portion (30–80%) of the total volume of the activated carbon material. Due to their associated large internal surface area and high pore volume, the adsorption capacitance of activated carbon materials is substantial, more than 20 mol/kg, thus enabling the use of activated carbons in separation and purification processes for gaseous and liquid phases. Porous carbon materials with various pore sizes and pore structures can be produced via several different synthetic routes [10–17].

The pores in activated carbons are divided into three groups: micropores with diameters less than 2 nm, mesopores with diameters between 2 and 50 nm, and macropores with diameters greater than 50 nm [18]. Microporous activated carbons can be synthesized through the activation process, usually consisting of a partial burn-off of the amorphous carbon under mild oxidation conditions (e.g., CO_2 or KOH under elevated temperatures, or nitric acid in ambient conditions). Ordered microporous carbon materials can be produced using microporous zeolites as templates for polymerization followed by carbonization and etching of the aluminosilicate from the surface using HF [19–26]. Mesoporous carbons with a disordered pore structure can be obtained by various methods, including catalytic activation using metal species [27–30], carbonization of carbonize-able polymer/pyrolize-able polymer blends or copolymer [31–33] (e.g., PAN/PMMA or PAN/Hexamine), carbonization of organic aerogels (e.g., resorcinol-formaldehyde), or template synthesis using silica nanoparticles. Ordered mesoporous carbons with various pore structures have been synthesized using mesoporous silica materials as templates. Non-graphitizing carbons (e.g., carbons which cannot be converted to graphite by further high temperature treatment) are produced from materials such as biomass (e.g., wood, nut shells, etc.), non-fusing coals, and/or different thermosetting polymers (e.g., polyvinylidene chloride, PVDC, etc.). These carbon precursors remain in the solid phase during carbonization, and the resulting limited mobility of the formed crystallites leads to the formation of a rigid amorphous structure that consists of randomly oriented graphene layers. The loss of volatile compounds and the retention of a rigid, complex molecular structure during the carbonization of many non-graphitizable carbons can lead to a highly porous structure without the need for further activation. Fractal porous morphology can be obtained by multistage carbon treatment based on a sequence of several of the above-mentioned synthesis routes.

An important consideration related to activated carbons (ACs) as adsorption materials is the difference between their average pore size and the size of the species whose adsorption is required: pores that are smaller than a critical molecule or ion size cannot adsorb these species [34–38].

Thus, controlling the size of the pores in ACs is essential for achieving specific adsorption by molecular sieving. Unlike molecular sieves based on zeolites which are highly porous crystalline materials characterized by a three-dimensional pore network with pores of precisely defined dimensions [39, 40], the carbon molecular sieves are amorphous solids with a pore-size distribution that needs to be characterized before they can be used for separation. Among the porous solids, the selectivity achieved by zeolites and carbon adsorbents is the best reported, even among molecular probes of similar size. An interesting development in carbon molecular sieves is their application as stereoselective membranes for gas separation. Unlike zeolite molecular sieve membranes, carbon membranes for gas separation could be produced free of defects. Therefore, the motivation for developing these carbon allotropes as membranes has intensified [10, 41].

Many efforts have been made, using sophisticated, sometimes multistage, techniques, to adjust the pore size to fall between the sizes of the molecules that have to be separated. Pore-size calibrated carbon molecular sieves can be made by controlled activation [42, 43] or controlled closure, using carbon chemical vapor deposition [14, 15]. The calibration of molecular sieving carbon electrodes was carried out by monitoring adsorption kinetics in the gaseous phase of probe molecules having a known dimension. These calibrated carbon molecular sieves have been demonstrated as tools for estimating the effective dimensions of different ionic species in solutions. The molecular sieving effect of CMS is also used in the field of water purification, separation from organic pollutants, and separation by means of the selective adsorption of organic molecules in aqueous and non-aqueous solutions. In general, selectivity in the adsorption of different species originates from one or more of the following factors:

1. Differences in the solvation energy of the adsorbates in the fluid can relate to a difference in their ease of adsorption.
2. Adsorption stereoselectivity: the size of the pores is adjusted by different techniques to be close to the size of the adsorbed species. Therefore, only species that are smaller than the pores can be adsorbed and sized.
3. Adsorption of planar or flat-shaped molecules: these are selectively adsorbed into slit-shaped pores as long as the planar molecule is thinner than the slit-shaped pore.
4. Different functional groups on the AC surface can also induce specific adsorption. Hence, the most common methods to achieve adsorption stereoselectivity involve the control of the pore size and structure and the surface properties of the carbons.

The techniques used for developing ACs with sharp pore-size distribution functions may include control of the activation procedure of the carbons, formation of surface functional groups on the activated carbon, template carbon synthesis, extraction of metals from carbides, dehydrohalogenation of halogen-containing polymers, carbonization of copolymer, and chemical vapor deposition (CVD) of surface layers.

Generally speaking, electrochemical processes may be divided into two main categories: Faradaic (red-ox) processes in which charge transfer across interfaces occurs, and capacitive processes (adsorption/desorption phenomena), which occur within the EDL of a surface. Electrode red-ox processes can occur only when the applied potential exceeds a certain barrier beyond which an electrochemical reaction becomes thermodynamically favorable. Depending on the electro-active species present, each electrochemical system has a potential range between the cathodic and anodic potential barriers (for reduction and oxidation processes, respectively) in which only *capacitive* processes can take place. This potential range is termed the electrochemical window, or the EDL region of the system. Most of the efforts in electrochemistry have been devoted over the years to the study of red-ox reactions, their exploitation, e.g., for the storage of energy, or their prevention, e.g., when corrosion phenomena are involved. However, in the last years, many efforts have also been devoted to understanding and utilizing the non-Faradaic, electrostatic electrochemistry, which is so relevant to highly porous electrodes.

It is well established that the interface between electronically conducting solid surfaces and electrolyte solutions can be described by the EDL phenomenon. The configuration of this interfacial double layer includes either electron surface excess or deficiency at the electrode's side of the interface, leading to an accumulation of ions of opposite charge (to that of the electrode), and depletion of ions of the same charge sign at the solution side of the interface. Altogether, the interface between electrodes and electrolyte solutions may be considered as a parallel plate capacitor in which a layer of adsorbed solvent molecules are the dielectric separator between the plates [44]. In Helmholtz's view of the double-layer region, the attracted ions are assumed to approach the electrode surface at a distance limited by the size of the solvated ion: the overall result is two layers of charge and a linear potential drop that is confined to this region only. In a later model put forward by Gouy and Chapman, it was [45, 46] suggested that the electrostatic interactions near the interface are perturbed by the Brownian motion of the solution species, thereby leading to a charge distribution in a solution layer that may be a few nanometers thick (known as the diffuse layer). Hence, the potential drop at the solution side is not linear but rather exponential along the diffuse layer. A further understanding of the complicated situation at electrified interfaces lead to the presentation of the famous Stern model, which describes the EDL in terms of two capacitive components: the inner layer (which behaves like the Helmholtz model), which is in contact with the electrode, includes ions that are adsorbed onto the electrode surface due to high electrostatic interactions, and the outer, diffuse double layer, which behaves according to the Gouy–Chapman model.

The classical EDL theory presented above was developed for planar surfaces. Significant modifications of this theory are necessary to account for the *diffuse layer* formed in a meso- and micropores interface between a solid porous electrode, and the electrolyte solution.

Extensive work has been devoted over the years to EDL phenomena related to porous electrodes. Evidence was found that EDLs exist within the porous carbon as long as the pores are sufficiently large enough to accommodate hydrated ions [41, 47–49].

The associated large surface area of porous carbon materials, together with their good electrical conductivity, enables the use of amorphous carbon *electro-adsorption*, namely the potential-induced adsorption/desorption of ions at the EDL within the pores. Figure 2 represents the EDL formation, its equivalent electrical circuit analog, and the potential profile on a porous carbon electrode in an electrolyte solution. Due to the high internal surface area, very high specific capacitance can be realized (<100 Fg^{-1} carbon depending on the level of porosity and the nature of the electrolyte solution) [50]. This high specific capacity can be exploited for energy storage in EDL capacitors, as discussed below, and for the removal of ions from saline water, i.e., water desalination by capacitive deionization (CDI).

Both the energy storage density and the water desalting capacity related to activated carbon electrodes increase with increase in their specific surface area. Hence, there is strong incentive to develop smaller and more extensive pores [51]. However, the reduction of the pore size is limited by the size of the adsorbate (i.e., it must be larger). Also, decreasing the pore size slows down the kinetics of the electro-adsorption. Therefore, the optimization of the pore system of adsorbing carbons entails a tradeoff between capacity and kinetics. Another inherent tradeoff between the parameters of the processes of electro-adsorption is the extent of burn-off (activation) which increases the surface area at the expense of the structural integrity, mechanical stability, and electrical conductivity of the carbon electrode.

In addition to the use of amorphous carbon materials for electro-adsorption applications, three additional graphitic allotropes of carbon have been investigated more recently, namely carbon nanotubes (CNT) [52, 53], fullerenes, and graphenes [54]. These forms can be utilized as the sole active electrode material, or incorporated as additives to the formulation of the active material of electro-adsorption electrodes.

Due to their unique morphology and extended graphitic layers [52–55], CNTs and graphene have both been

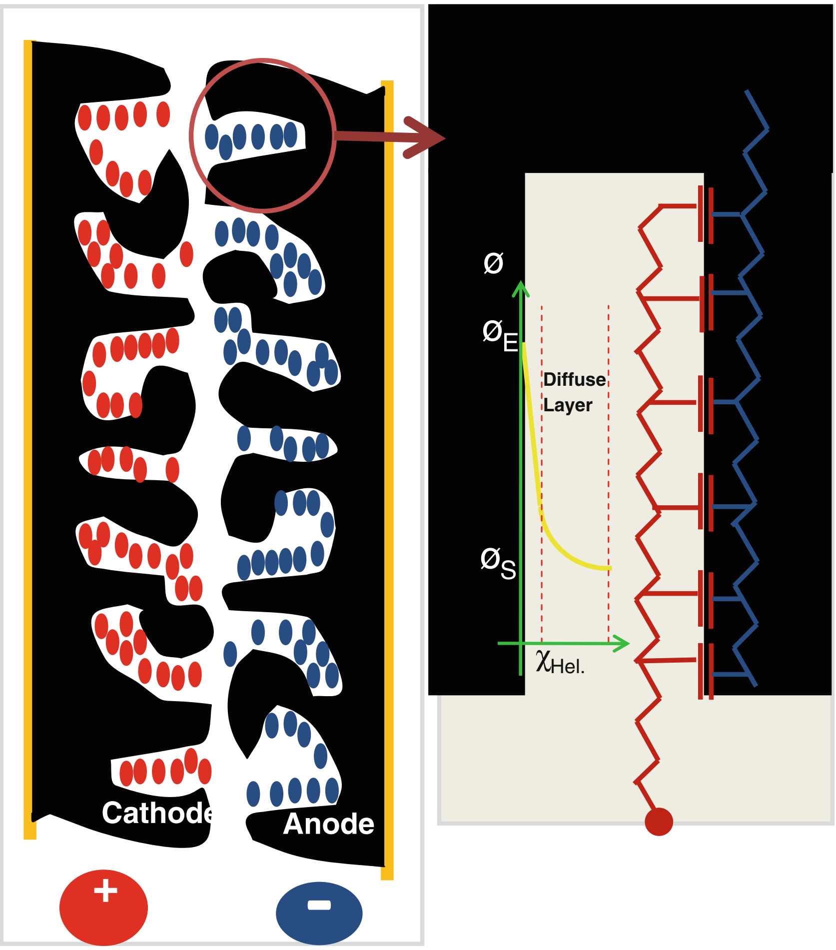

Fig. 2 Cartoon representation of the EDL formation, its equivalent electrical circuit analog, and the potential profile on a porous carbon electrode in an electrolyte solution

explored as candidate electrode materials which may overcome the drawbacks of conventional carbon materials (e.g., hindered electrical conductivity and mechanical strength). CNTs (especially multiwall) may be characterized by exceptional conduction and mechanical properties which allow them to be used directly as three-dimensional supports for active materials. Additionally, it was demonstrated that the open mesoporous network formed by the entanglement of nanotubes allows the ions to diffuse easily to the active surface of the composite components. The two latter properties (high conductivity and mesoporous structure) may be useful in lowering the equivalent series resistance (ESR) and consequently increasing the power of the device.

The surface area of a single graphene sheet is 2,630 m^2/g [56], substantially higher than values derived from BET surface area measurements of activated carbons used in current EDL capacitors. The surface accessibility of adsorbates to individual graphene sheets does not depend on the distribution of pores in a solid matrix in order to reach large surface area (as is the case for activated carbons); rather, every graphene sheet can be utilized for electro-adsorption of ions (to both sides) in various electrolyte solutions. Hence, electrodes comprising graphene sheets may enable the full utilization of their high surface area for capacitive interactions or red-ox reactions, while benefiting from the good electrical conductivity and excellent mechanical strength.

Surface groups on carbonaceous materials

Elementary carbon after alkali and alkaline earth metals is probably one of the strongest reducing agents in chemistry [1–3, 7]. At ambient temperatures, its oxidation is kinetically hindered; therefore, it is apparently chemically stable. However, at high temperatures, i.e., above 400 °C, its reducing ability becomes very effective. For instance, most of metals (except alkaline, alkaline earth, Al, B, and precious metals) are produced from their ores by high-temperature reduction processes with coal. Interestingly, even prior to total burn-off of carbon to CO and CO_2, oxygen is chemibound to the surface of carbonaceous materials, thus forming surface oxygen groups (SOG). The adsorption properties of activated carbons may be highly influenced by the presence of surface groups and their nature [57]. Their immediate influence is the existence of surface dipoles whose negative poles are facing the solution side. Such surface dipoles shift the PZC of the electrodes to more positive potentials, so that cation electro-adsorption becomes preferable to anion electro-adsorption within the electrochemical window of the EDL [7, 57]. Practically, all of these carbon–oxygen surface groups can be removed upon heating the carbon in anaerobic (or vacuum) conditions to 1,000 °C. It is noteworthy that an opposite effect exists when an activated carbon is treated with a reducing agent such as hydrogen above 550 °C (creating C–H groups with the positive poles facing the solution side). Such surface groups (C–H) shift the PZC to more negative values. The oxygen-containing surface groups on activated carbons can be divided into three types, depending on the nature of the C–O bonds:

1. Chemically fixed groups (e.g., carbonyl) which are degassed as CO, only upon heating the carbon to above 800 °C. These groups are electrochemically inactive, and their main effect is a shift of the PZC.
2. Carboxylic type groups which provide surface acidity. These are degassed at above 400 °C mostly as CO_2.
3. Surface groups with electrochemical red-ox activity such as quinone/hydroquinone moieties [7]. Such surface groups are easily recognized by the electrochemical response of the carbon electrodes (e.g., a couple of reversible peaks in voltammetric measurements). It should be noted that these red-ox sites are active only under acidic conditions (solutions of low pH).

Electro-adsorption into porous carbon electrodes

The quantification and characterization of the electro-adsorption capabilities of porous carbon electrodes, in either separation processes or in energy storage devices, should be divided into both thermodynamic and kinetics aspects. The capacitance of electro-adsorption devices is reported either per weight or per volume, depending on the particular application being considered. Such capacitance values represent the possible energy density relevant to a device from a thermodynamic point of view. However, for many applications, the power density should also be taken into account, as it relates to the kinetics of the electro-adsorption processes.

A few important parameters related to the electrodes' physiochemical properties eventually determine the power and energy density of devices comprising them.

The ratio between pore and ion size

In the case of volume-based optimization, the goal is to attain as large a surface area per volume as possible. This requires as great a subdivision of the solid as possible, resulting in smaller pores. In other words, an increasingly larger surface area can be packed into a unit volume of a porous electrode as the pores are smaller. It is important to emphasize that the relationship between the electrode pore size and the ionic dimension of the solution species is very important for electro-adsorption performances of activated carbon electrodes [58]. It has been demonstrated by many studies that upon charging the EDL of porous electrodes, the ions enter into pores whose size conforms to the hydrated state of the ions (this may be denoted as the effective ion size). In the case of pores that are significantly larger than the effective ion size, the specific EDL differential capacity of the porous electrodes (Fg^{-1} or F/cc) is proportional to the overall pore surface.

As stated earlier, there is a lower limit to the desirable size of the pores, which corresponds to their accessibility by the ions from the solution bulk outside the pores. As the average pore size approaches the size of the ion, the electro-adsorption kinetics becomes hindered. When the average pore size is smaller than the smallest ions size in solution, no ion electro-adsorption into the pores can take place. As is the case with adsorption from the gas phase, an ideal situation can be attained when the average electrode pore size is slightly larger than the ion size, enabling ion interactions with the pore walls. Thus, an optimal capacity can be achieved with no adverse effects on the electro-adsorption and desorption kinetics.

The effective ion size plays a most important role in determining transport phenomena in both bulk electrolyte solutions and in the course of electro-adsorption processes. In fact, consideration of the effective ion size goes back to the early corrections for finite-size charge carriers in the Debye–Huckel theory for point charge electrolytes. Many studies have been carried out to determine optimal porous structures of activated carbon electrodes in order to achieve optimal electro-adsorption performances. Gogotsi et al. [59] demonstrated an anomalous increase in EDLC using new, sophisticated carbon materials with well-tuned porous morphologies and tuning the pores to be slightly smaller than the solvated ion, hence enabling distortion of the hydration shell.

In order to understand the tradeoff between kinetics and thermodynamics, we recently reported on a comparison among various carbon materials with different porous morphologies, indicating the feasibility and beneficial use of hierarchical, fractal morphologies of porous structures within activated carbon electrode [me rate]. We also recently demonstrated an effective utilization of in situ electrochemical quartz crystal microbalance (EQCM) measurements as a new tool for investigating electro-adsorption phenomena. These studies revealed the nature of ionic fluxes during electro-adsorption and desorption processes and how they are affected by the electrode micro/mesoporous structural parameters and by unique ion–pore interactions [60].

Efforts have been devoted to understanding the impedance behavior of activated carbon electrodes in electro-adsorption processes. It was demonstrated that the shape, size, and volume of the pores, as well as the pore size distribution, all have serious effects on the impedance of these systems, and therefore on the kinetics of electro-adsorption [50, 61, 62]. Additionally, it was demonstrated that the presence of heteroatoms (such as nitrogen atoms) in carbon electrodes' structure may have significant influence on the nature of electro-adsorption processes. The presence of surface groups on carbon electrodes also has a pronounced influence on their electro-adsorption processes [50].

The electron conductivity of porous activated carbon electrodes

Upon discussing and analyzing electro-adsorption processes into activated carbon electrodes, most attention is focused on the solution side and on the transport phenomena related to ions. Although amorphous carbons are very good electron-conducting materials, as they are more activated (i.e., more porous), their electrical conductivity may become worse because the cross sections for electron transfer in their bulk structure become narrower [50]. The correlation between activation and electrical conductivity of porous carbons and the impact of electro-adsorption on the electrical conductivity of activated carbon electrodes has been studied and reported [7, 63]. For instance, it was found that annealing processes of activated carbon at high temperatures under inert atmosphere increase their electronic conductivity remarkably, not at the expense of the capacity of electro-adsorption processes into them [7, 50]. Also, when highly porous active mass have to be used (in order to obtain maximal capacity), whose porosity is at the expense of electronic conductivity, it is possible to use composite electrodes that contain in addition to the active mass, additives such as graphite, carbon black, or CNTs (maybe even graphene sheets) that maintain good enough electrical integrity for the entire composite electrode. The advantage of CNTs and graphene sheets as conductive additive relies on the fact that these materials have high electrical conductivity, very good electrochemical stability, high intrinsic surface area, and high aspect ratios, which enables good electrical contact with particulate active mass. Recently, it was demonstrated that CNTs or graphene sheets can be incorporated into a carbon precursor (e.g., a polymer) for activated carbon electrodes [64–68]. Then, carbonization and further activation of the amorphous carbon matrix so formed, leaving the CNT or graphene components unaffected. This results in the formation of highly robust and electronically conducting activated carbon electrodes with improved mechanical and electrical properties (despite the highly porous structure). In recent years, we see more and more publications reporting on the use of CNTs and graphene sheets as stand-alone active electrode materials for EDLC applications.

On the relation between EDL charging and the electronic conductivity of activated carbon electrodes

The EDL charging of activated carbon electrodes may affect their electrical conductivity over wide potential ranges [63, 68, 69] (see for instance Figs. 10 and 16 in [70]). Normally, in the absence of sieving effects, the electrical conductivity of activated carbon electrodes shows a parabolic dependence on the electrode potential with a minimum at the PZC. This is because electro-adsorption intensifies accumulation of charge carriers with the opposite sign, at the electrode (solid) side of the EDL. The minimum in electrical conductivity measured usually at electrodes' PZC is because at that potential electro-adsorption (and hence its effect on the electrode side of the EDL) is minimal. Hence, electrical conductivity measurements of activated carbon electrodes as a function of potential, during electro-adsorption processes can serve as a method for determining their PZC. See further detailed discussions on these phenomena in [63].

EDL applications

The high EDL capacitance of activated carbon electrodes has led to the successful development of commercial carbon-based electrical double-layer capacitors (EDLCs). These capacitors are electrochemical energy storage devices that have higher energy densities than electrolytic capacitors and higher power densities than rechargeable batteries. Because only electrostatic interactions exist between the electrodes and the solution species, with no involvement of red-ox reactions, the electro-adsorption/desorption cycles of EDLC systems are highly reversible, with practically no capacity fading. Typical voltammetric and the chronopotentiometric responses of activated carbon electrodes in electrolyte solutions are presented in Fig. 3a, b.

The electro-adsorption of ions from salt-containing aqueous solutions onto activated carbon electrodes is also the basis of water desalination by capacitive deionization (CDI) processes. In fact, impressive electro-adsorption capacities (1–2.5 mE/g), comparable to the capacity of ion exchangers, can be achieved in CDI processes. Short historical descriptions of these applications, the state-of-the-art (present) devices and developments, and some future insights are presented below.

EDLC (called also super- or ultracapacitors), past and present

The most common and important electrochemical devices for energy storage and conversion devices are batteries. In fact, batteries can be considered as the most important application (and success) of modern electrochemistry. Especially impressive in this respect is Li ion battery technology that conquers more and more markets and is currently at the focus of R&D into electric vehicles (EV). EV applications expose the limitations of rechargeable batteries in terms of cycle life, safety features, and power density (all resulting from the fact that batteries involve complicated red-ox reactions, in which three bulks (electrodes and electrolyte solution) and two interfaces have to work simultaneously with no side reactions).

These limitations have focused attention on EDLCs as complementary devices for energy storage and conversion [63–69]. The most effective way to judge and compare energy storage and conversion devices is by the so-called Ragone charts, in which the power density of various devices is plotted as a function of energy density (see an example in Fig. 4). As demonstrated in Fig. 4, EDLCs may have much lower energy density (by orders of magnitudes) than advanced rechargeable batteries due to the lower energy that can be involved in capacitive, electrostatic interactions, compared to red-ox reactions. However, the power density of EDLCs is generally much higher than that of advanced batteries, and in addition, their cycle-ability is much longer as well, because electrostatic interactions are very fast and are not supposed to affect the electrodes' structure at all. Hence, there are many designs of power sources, coupling batteries and EDLCs, in which the energy should be provided by the battery and high power by the capacitor. Consequently, we see in recent years accelerated R&D related to EDLCs and their components and also emergence of commercial EDLCs.

ECs have been studied for many years. The first patents date back to 1957, in which a capacitor based on high surface area carbon was described by Becker [71]. In 1969, the first attempts to market such devices were undertaken by SOHIO. However, it was only in the 1990s that EDLCs became important in the context of hybrid electric vehicles. A first DOE (US) EDLC development program was initiated in 1989. In parallel, many research groups around the world have struggled to develop novel carbon electrode materials for EDLCs with optimized physicochemical properties from a variety of carbon precursors using various carbonization and activation procedures. Matching optimized electrolyte solutions to EDLCs is also highly important [70, 72–76]. In aqueous solutions, it was possible to obtain very high capacity in electro-adsorption processes into activated carbon electrodes (up to 350 F/g, corresponding to 80–90 mAh/g, in acidic solutions). However, since the energy density of EDLC is proportional to E^2 (the cell voltage), there is a strong incentive to develop non-aqueous EDLCs to which potential up to 3 V can be applied and even EDLCs with ionic liquids, whose electrochemical window may reach 4 V (see further discussion below). Using non-aqueous solutions means one can achieve a much lower EDL capacity (e.g., up to 150 F/g compared to >300 F/g obtainable in aqueous solutions) and also slower kinetics. However, in cases where the energy density of the EDLCs is important, non-aqueous systems are better due to the high voltage, despite the lower EDL capacity.

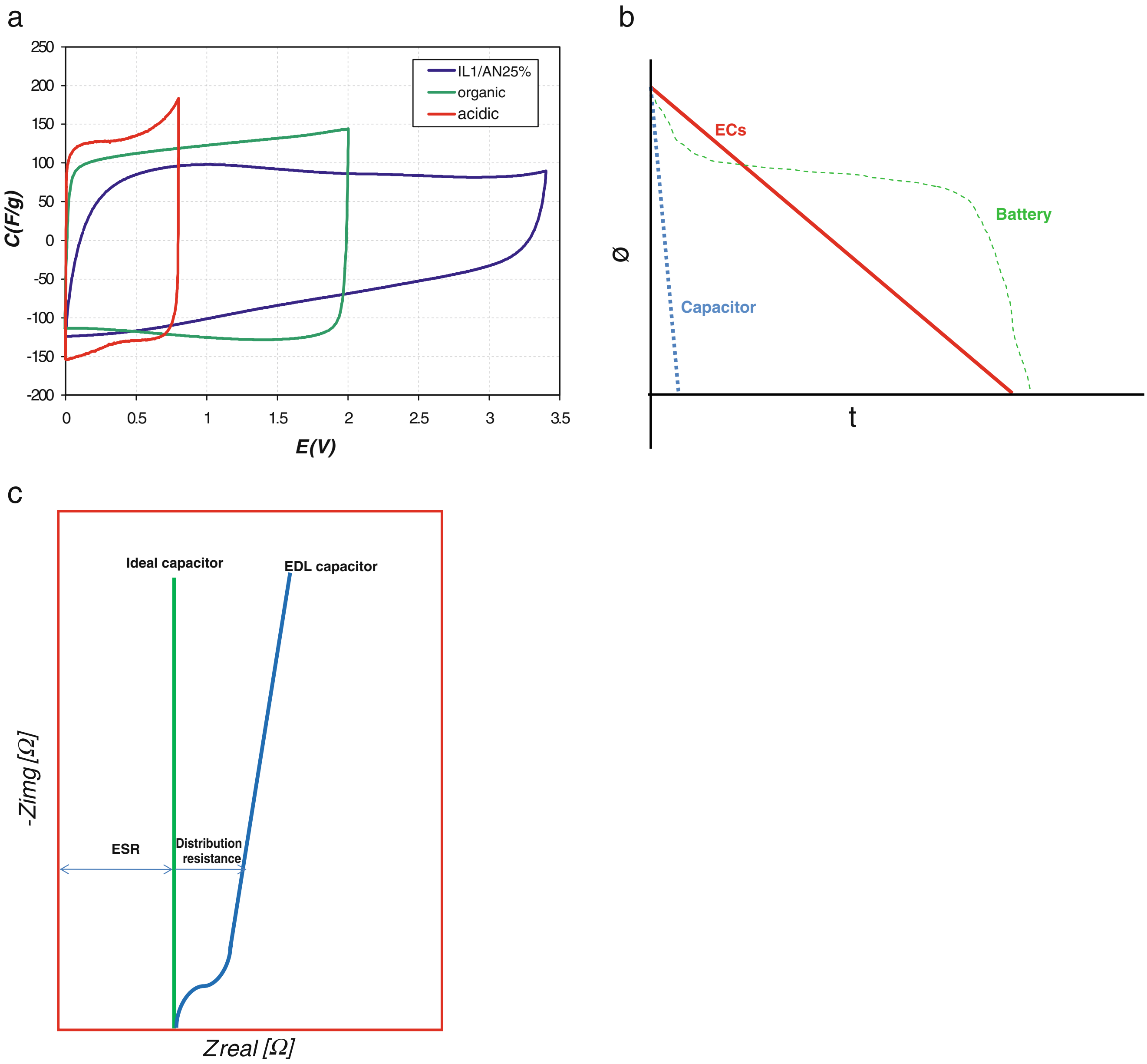

Fig. 3 Typical responses to electrochemical measurements. **a** Cyclic voltammetric in aqueous, organic, and ionic liquids electrolyte solutions Reused with permission from Elzbieta Frackowiak, Grzegorz Lota, and Juliusz Pernak, Applied Physics Letters, 2005, 86, 164104. Copyright 2005, American Institute of Physics. **b** Chrono-potentiometric discharge profile of different devices. **c** Electrochemical impedance spectroscopy responses (Nyquist plot) of activated carbon electrodes in electrolyte solution

Hence, the tradeoff between the energy density and the electro-adsorption time constants of the device (e.g., higher specific surface area means higher capacitance, but lower electrode conductivity, non-aqueous solutions means higher voltage but lower adsorption kinetics) is an important design consideration. The electrochemical stability of carbon electrodes is unique. Theoretically, activated carbon electrodes may reach electrochemical windows wider than 5 V (slightly affected the presence of surface groups) limited only by the stability of the electrolytic medium. Although the electrochemical window of water is 1.23 V, the practical operational voltage of aqueous EDLCs should be below 1 V, in order to avoid parasitic reactions, especially at elevated temperatures. Non-aqueous solutions for EDLC applications should possess high ionic conductivity in order to maintain a reasonable rate capability for these devices (always lower compared to aqueous systems). Relevant solvents are alkyl carbonates, esters, and acetonitrile (ACN). Since in the presence of metallic cations these solvents are reduced to form insoluble species that can precipitate and block the electrodes pores, tetra-alkyl ammonium-based electrolytes are used (e.g., tetraethyl

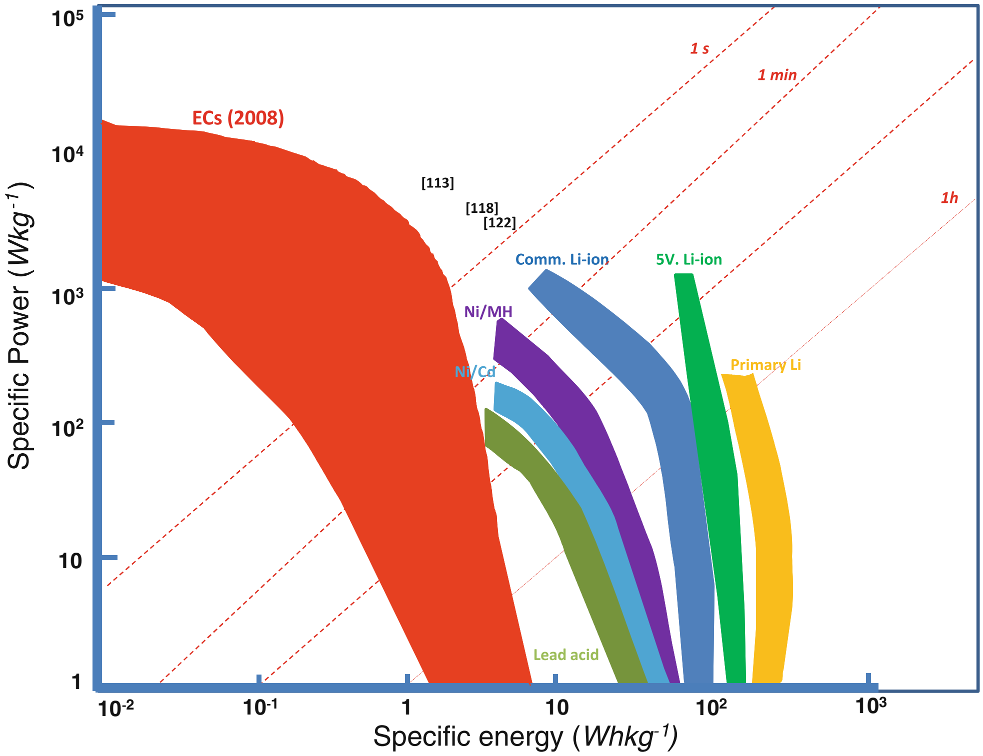

Fig. 4 Ragone charts, in which the power density of various devices is plotted as a function of energy density; *inserted numbers* are for remarkable results reported for ECs (*numbers* are in correlation with the references)

ammonium tetrafluoroborate, $TEABF_4$) [70, 73–76]. EDLCs loaded with alkyl carbonates or ACN and electrolyte such as $TEABF_4$ can work in a practical potential domain up to 2.5 V. The voltammetric response presented in Fig. 3. shows a comparison between the electrochemical window of activated carbon electrodes in various electrolyte solutions.

A further increase in EDLC voltage range can be achieved using ionic liquids (ILs) [72]. ILs based on derivatives of imidazolium, piperidinium, and pyrrolidinium cations (with anions such as BF_4^-, $(CF_3SO_2)_2N^-$) may demonstrate electrochemical windows wider than 5 V. They have high thermal stability and negligible vapor pressure which implies good safety features [77–79]. However, they are often characterized by a high viscosity which complicates the wetting of the carbon materials, especially those with a highly developed microporosity (which means relatively low rate capability). The conductivity of ILs is also lower than common non-aqueous electrolyte solutions. Hence, since the ions in non-aqueous systems are more voluminous than those in aqueous systems, the porosity of activated carbon electrodes for non-aqueous EDLCs has to be designed and adjusted accordingly.

Carbon materials for EDLCs, past and present

Starting with carbon black (CB), this is a group of materials with nearly spherical particles of sub-micrometric and even nano-metric size [7]. The main stages of carbon black formation in the thermal decomposition or partial oxidation of their hydrocarbon precursors are the formation of polyaromatic macromolecules in the vapor phase, followed by their nucleation into droplets and final conversion into carbon particles. The key properties of carbon black are considered to be fineness (primary particle size), structure (aggregate size/shape), porosity, and surface chemistry. The morphology and physiochemical properties of those particles\particle agglomerates vary with feedstock and manufacturing conditions, and they are usually classified according to their method of preparation or intended application. The surface-area (BET) of carbon blacks covers a wide range, i.e., from <10 to greater than 1,500 m^2/g [7, 80]. The porous net of this material is generally considered to be more accessible than other forms of high surface-area carbon. EDLC electrodes have been produced from high surface-area carbon black (using a chemical binder such as polyvinyl difluoride, PVdF) with specific capacitances of up to 250 F/g, corresponding to double-layer capacitances in the range of 10–16 $\mu F\ cm^{-2}$. The main drawback of CB as an active mass in EDLC electrodes is their [2, 81, 82] relatively small particle size, which requires the use of a large amount of binder in order to compose mechanically stable electrodes. Such electrodes may suffer from low electrical conductivity and volumetric capacitance.

Pekala et al. synthesized carbon aerogels from the carbonization of organic aerogels based on a resorcinol–formaldehyde gel [83–85]. Later studies presented the synthesis of carbon aerogel from various other organic aerogels (e.g., phenol-furfural, phenol-resorcinol-formaldehyde, melamine-formaldehyde, polyurethanes, polyureas, and polyvinyl chloride) according to the same procedures [83–93]. Generally, the porous organic aerogel is prepared via polymerization of the monomers into cross-linked polymer clusters forming wet gels. These gels are then dried under conditions that prevent the collapse of the porous structure (e.g., CO_2 supercritical drying, solvent exchange and controlled evaporation). The aerogels are then carbonized at elevated temperatures. Carbon aerogels can be prepared in the form of monoliths, powders, microspheres, and thin film composites.

Electrochemical studies on carbon aerogels have reported that their specific capacity is correlated with their true mesoporous surface-area rather than with their total BET surface-area. The corresponding double-layer charge storage capacity of carbon aerogels is typically 18 $\mu F\ cm^{-2}$. Their surface area can be increased by activation of the carbon aerogel, thus forming activated carbon electrodes with fractal porous structures composed both of meso- and micropores [94].

Glassy carbon (GC), also referred to as vitreous carbon, is a typically hard solid material [7]. Its production consists of the thermal degradation of selected organic polymers similar to those used for the carbon aerogel [7, 95]. The resin is treated in three stages and cured very slowly, then carbonized and heated to elevated temperatures (typically 1,800 °C). Glassy carbon has a very low electrical resistivity ($3–8\times10^{-4}$ Ωcm) [96] and is therefore particularly suitable for high-power EDLCs that require a low internal resistance [7, 97]. Another attractive feature of glassy carbon is the possibility to produce it as free-standing films, thin sheets, or powders. During the special carbonization processes that form glassy carbons, some internal, isolated porosity can be developed within the carbon. Such pores in GC can be opened by thermal oxidation processes (activation) to produce a material with a high specific surface area that is well suited for use as an EDLC electrode material. Volumetric surface areas of ~800 $m^2\ cm^{-3}$ and double-layer capacitances of ~20 $\mu F\ cm^{-2}$ have been achieved for thermally oxidized glassy carbons [97–101].

Templated porous carbon material can also be utilized for electroadsorption applications [102, 103]. The general template synthetic procedure for porous carbons includes the following steps: (1) preparation of the carbon precursor/inorganic template composite, (2) carbonization, and (3) etching out the inorganic template. Various inorganic materials, including silica nanoparticles (silica sol), zeolites, anodic alumina membranes, and mesoporous silica materials have been used as templates [102–107]. The carbonization and subsequent removal of the templates generate porous carbons with interconnected pore structures and relatively uniform pore sizes. Various carbon structures with well-controlled micropores, mesopores, and/or macropores produced from different types of templates and various template carbons have been studied for EDLC applications. A functionalized microporous carbon material was obtained by using zeolite Y as a template, and the resulting carbon material possessed a high gravimetric capacitance of about 340 F/g in aqueous electrolyte with good cyclability (over 10,000 cycles) [108]. Yamada's group has also synthesized ordered porous carbons containing meso/macro/micropores with large surface areas using a colloidal-crystal templating technique. A high EDL capacitance of 200–350 F/g was achieved in an acidic electrolyte solution [109].

Another important self-supporting carbon material is activated carbon fibers (ACFs). The initial processing steps of most carbon fibers involve stabilization (heating organic fiber precursors, e.g., polyacrylonitrile, Rayon, cellulose, phenolic resins, and pitch-based materials), in air to temperatures up to 300 °C to render the fibers thermosetting via cross-linking, followed by heating (inert atmosphere) to temperatures <1,000 °C to convert the stabilized fibers to carbon. ACFs with very high associated surface areas (up to 2,500 m^2/g) are now commercially available in many forms, such as tow (bundles), chopped fiber, mat, felt, cloth, and thread. The majority of the pores in ACFs are micropores [1–3, 110]; hence, some hindrance in the rates of electro-adsorption may be expected. This kinetic limitation is compensated, however, by the thin fiber dimensions, which means that the porosity of ACFs is largely situated at the surface of the fibers and thereby provides good accessibility of solution species to the active sites. Additionally, it was shown that both the pore diameter and pore length can be more readily controlled in ACFs, compared to regular activated carbon materials [1–3, 7, 111]. These features, together with the ease of preparation of electrodes comprising such fibers, make ACFs a very attractive electrode material (high adsorption capacities and rates). On the other hand, the cost of ACF products is generally higher than that of activated carbon powders.

Some non-graphitized carbons were also tested for EDLC applications. Among this group of carbons, however, few works with outstanding results were published, especially with carbonized PVDC [111, 112].

One of the most important features, unique to PVDC-based carbons, is that carbonization of this polymer produces carbons with high surface area, up to >800 m^2/g. Remarkable capacitance values of 350–400 F/g were obtained for those carbons, even without activation of the carbon [111, 112].

CNTs and nanofibers are also interesting and maybe promising candidates as electrode material for EDLC and other energy-storage devices. Single-walled (SWNT) and multi-walled nanotubes (MWNTs) have been studied as electrode materials in both aqueous and non-aqueous electrolyte solutions by many groups worldwide. Generally, the specific capacitance of unmodified CNTs has been shown to be highly dependent on their morphology and purity. The values of their specific capacitance vary typically from 15 to 80 F/g for pure CNTs without amorphous carbon as additive. Specific capacitance of CNTs can be increased to 130 F/g by subsequent oxidative treatment (e.g., with nitric acid) which modifies the surface texture of the CNTs and introduces additional surface functionality, which contributes to the capacitance via pseudo-capacitance behavior of the functionalized surface of the CNTs [95].

Kay Hyeok An et al. [113] have investigated the key factors determining the performance of EDLC using SWCNT electrodes. By heat treatment of SWCNT electrodes, they managed to reduce the CNT-electrode resistance, demonstrating a maximal specific capacitance of 180 F/g with a large power density of 20 kWkg^{-1} at an energy density of 6.5 Whkg^{-1} (1 in Fig. 4).

Niu et al. [114] produced catalytically grown MWNTs, subsequently treated with nitric acid and formed into electrodes that consisted of freestanding mats of entangled nanotubes with an increased surface-area of 430 $\text{m}^2\ \text{g}^{-1}$. The specific capacitance of the nanotube mat electrodes in sulfuric acid was determined to be 102 F/g (at 1 Hz), and this corresponds to a double-layer capacity of 24.2 $\mu\text{F cm}^{-2}$. The same cell also had an estimated power density of >8 kWkg^{-1}.

Chunsheng Du and coworkers, using an electrophoretic deposition technique, succeeded in fabricating CNT thin films. The supercapacitors built from such thin film electrodes have a very small equivalent series resistance and a high specific power density (over 20 kWkg^{-1}) [115].

By activation of MWCNTs with potassium hydroxide, Frackowiak et al. managed to increase the BET surface-area of MWNTs from an initial value of 430 to 1,035 $\text{m}^2\ \text{g}^{-1}$. While the product still maintained a high degree of mesoporosity, the activation process also introduced considerable microporosity to that active mass. The specific capacitance of the material was 90 F/g (8.7 $\mu\text{F cm}^{-2}$) in alkaline media [116].

Composite carbon material synthesized by the carbonization of polymer/CNTs composites are also addressed as active material for EDLC. An interesting CNT–aerogel composite material was synthesized by uniformly dispersing a carbon aerogel throughout the CNT host matrix without destroying the integrity or reducing the aspect ratio of the CNT. A high specific surface area of 1,059 $\text{m}^2\ \text{g}^{-1}$ and extremely high specific capacitance of 524 F/g were obtained, but at the expense of a tedious preparation pathway [117].

Activated polyacrylonitrile (PAN)/carbon nanotube (CNT) composite film-based electrodes have been prepared by chemical activation with potassium hydroxide for electrochemical capacitors. A maximum value of specific capacitance of 302 F/g was achieved for the samples activated at 800 °C. Energy density for PAN/CNT 80/20 sample when tested with ionic liquid/organic electrolyte system was as high as 22 Whkg^{-1} [118] (2 in Fig. 4).

A novel composite of single-walled carbon nanotubes (20 wt.%) as scaffolding for single-walled carbon nanohorns (80 wt.%) was recently presented as a supercapacitor electrode with a high maximum power rating (1 GW/kg, 396 kW/l) exceeding power performances of any other electrodes [119]. The high power capability of these electrodes was attributed to the unique meso–macropore structure of the material engineered. These novel composite electrodes also exhibited durable operation (6.5% decline in capacitance over 100,000 cycles) as a result of their monolithic chemical composition and mechanical stability.

CNTs directly grown on conductive substrates can also be considered as very interesting self-standing electrode materials for EDLC applications. Indeed, there are recent publications on CNTs grown on graphite and aluminum foils tested as monolithic electrodes for EDLC applications with promising performances [120, 121].

Graphene is the name given to a two-dimensional sheet of sp^2-hybridized carbon. Long-range π-conjugation in graphene sheets yields extraordinary thermal, mechanical, and electrical properties [6], which have long been the subject of many theoretical studies and more recently became an exciting area for experimentalists and various application including EDLC.

Rao et al. have fabricated graphenes, prepared by three different methods, as electrodes for electrochemical supercapacitors [122]. The samples prepared by exfoliation of graphitic oxide and by the transformation of nanodiamond exhibit high specific capacitance in aqeous H_2SO_4, with values reaching up to 117 F/g. Using IL-based electrolyte solution, it was possible to operate grapheme-based EDLC at 3.5 V demonstrating energy density close to 32 Whkg^{-1}.

There are other recent publications [123, 124] on graphene-based EDLC, and it seems that extensive work in this direction is in progress. In a recent pioneering work, chemically modified graphene (CMG) was also tested as active mass in electrodes for EDLCs [125].

Desalination by CDI, past and present

Currently, most of the electrochemical studies related to activated carbons are connected to the field of energy storage and conversion, mostly as EDLC electrodes but also for batteries and fuel cells electrodes (being the current collectors and support of the catalysts necessary to conduct effective oxygen electro-reduction and fuel electro-oxidation).

However, another potentially highly important use of activated carbon electrodes electro-adsorption capability is for water desalination (so-called capacitive deionization—CDI). A CDI cell is principally composed of two activated carbon electrodes between or through which the saline water flows. When the cell is charged, ions are removed by *electro-adsorption* onto the electrodes, resulting in a diluted aqueous solution as the product. Subsequent discharging (shorting) the cell regenerates the electrodes via *de*sorption of the ions, resulting in a flow of concentrated (waste) solution [126].

At first glance, this operation looks simple, involving purely capacitive interactions of ions which are electro-adsorbed/desorbed into (and out of) the porous electrodes. However, CDI processes may be highly complicated due to the breakdown of the permselectivity of the electrodes: application of potentials leads to simultaneous adsorption of counter ions and desorption of co-ions [127]. The latter process may significantly reduce the charge efficiency of electrochemical desalination processes by CDI. The extent of this problem depends on the electrode structure and the potentials applied to the cells. For instance, it is possible to considerably increase the charge efficiency of CDI processes by discharging the CDI cells to certain low positive potentials but not to zero (i.e., avoid full shorting) [128].

Depending on impurities in solutions, functional groups on the electrodes (leading to shifts in their PZC), and the potential applied to CDI cells, they may behave asymmetrically even if their electrodes were initially identical [7]. Hence, there is a general challenge in R&D of CDI processes: increasing to maximum the charge efficiency of water desalination with a minimal compromise on the capacity of salt removal per cycle. Meeting this challenge requires appropriate electrode design (porosity, surface groups) and judicious application of potential on CDI cells.

The early studies of CDI date back to the electrochemical demineralization work of the Caudle and Johnson groups in the late 1960s and early 1970s [129]. The introduction of the concept of CDI and the use of porous carbon electrodes for water desalination were first performed by Caudle et al. [130]. Later, Johnson et al. studied CDI as a reversible process. Funds were dedicated to their work, for the theoretical understanding of the basis of CDI by parametric studies of the electro-adsorption from flowing solution on various carbon electrode materials. On the basis of this research, a comprehensive theoretical analysis of ion adsorption into porous electrodes was published by Johnson and Newman [129, 131]. Nevertheless, due to stability limitations of the relevant carbon electrodes, mainly the anode side (i.e., the positive electrodes), the research was postponed [132].

During the late 1970s and the early 1980s, only Soffer and Oren were investigating the field of CDI. They studied fundamental aspects of electro-adsorption phenomena on various electrodes, and also established and modeled new mode of solution flow inside CDI cells, which they referred to as electrochemical parametric pumping [126]. It was only in the mid 1990s that a new version of CDI device was established. Farmer and coworkers at Lawrence Livemore National Labs utilized new high surface area, high conductivity carbon conducting carbon formed as aerogel electrodes for water desalination by CDI [133]. A recent comprehensive review, with description of fundamental aspects regarding electro-adsorption processes, and various flow modes in CDI reactors, has been presented by Y. Oren [132]. It is beyond the scope of this article to describe all of these aspects. Our focus is mainly on the various porous carbon materials used in this field.

Since the early work of the Caudle and Johnson groups, substantial efforts have been made to develop new carbon materials, which will be suitable for effective electro-adsorption processes in CDI reactors. Although the main physical phenomenon in both CDI and EDLC is electro-adsorption; the conditions under which this process is involved in CDI cells are significantly more complex because the solution in the latter process is flowing through the cell. Thereby, contaminants such as dissolved oxygen, biological, and fouling agents are continuously introduced into the cell and affect the electrodes. Red-ox reactions of oxygen and water that may accidentally occur in CDI cells lead to corrosion of the activated carbon electrodes. The majority of current CDI electrode materials are high-surface carbons in a variety of forms. As for EDLC applications, the basic requirements of the electrodes are high available specific surface area, optimized electric conductivity, and high electrochemical stability. A simple electrode for the electro-adsorption of charged species from aqueous solutions in CDI reactors was fabricated using pressed activated carbon granules or ordered mesoporous carbon microbeads synthesized by a modified sol–gel process [128, 134].

Carbon aerogels were also used in CDI processes [135–138]. Other electrode materials include activated carbon cloth [139], carbon sheets, activated carbon cloth modified by titania, carbon felt, carbon black, sintered activated carbon, carbon nanotubes, and carbon nanofibers [132, 140].

Recent work demonstrated the feasibility of selective desalination using carbon molecular sieve electrodes, produced by CVD treatment of activated carbon cloth [94, 110]. We also struggled with possible limitations to the stability of activated carbon electrodes in prolonged periodic CDI processes and explored ways to stabilize them by pretreatments, judicious application of potential to CDI cells and maintenance of the electrodes which avoids the need for their replacement after long service periods [141].

Activated carbon electrodes: future and concluding remarks

Activated carbon electrodes, due to their high specific surface area, unique stability, and good electrical conductivity, can be utilized as electro-adsorption electrodes for electrostatic energy storage and conversion (e.g., EDLCs), and for separation processes by electroadsorption, such as water desalination by CDI.

In addition to their relevant physicochemical properties, carbon materials can be produced at very reasonable costs and can be obtained in various forms with reasonably adaptable porosity and surface functionality.

In the ongoing efforts for R&D of sustainable and renewable energy sources (e.g., solar, wind), we suffer from a lack of suitable technologies for energy storage (the so-called load leveling application). Here, the most important properties are not energy density but rather superb stability, very prolonged cycle life, and the use of safe and abundant materials (since large devices for storing huge amount of energy are needed). EDLC technology may be found to be very suitable for such applications due to the impressive cyclability, the abundance of carbonaceous materials on earth, and the fact that carbons are safe and non-toxic electrode materials (no adverse environmental aspects). The high power capabilities of EDLCs make them attractive also as elements in mobile power sources (e.g., for EV applications). However, EDLCs have much lower energy density than batteries, and their low energy density is in most cases the factor that determines the feasibility of their use for high power applications. A major future challenge related to EDLCs and to R&D of their components is to maximize the energy density of these devices, with a minimal compromise on power density. Some recent advances have involved the engineering of nanoporous carbons with tunable pore sizes to fit the size of ions in selected electrolytes solutions, incorporating and/or modifying carbon nanotubes and graphene sheets as critical components in EDLCs and the use of organic and IL-based electrolyte solutions for higher operating voltages.

Nano-architecture of electrodes can lead to further improvements in power delivery of EDLC devices. This is also an important future direction related to carbon electrochemistry. There are so many carbon-based active materials developed so far as well as so many electrolyte solutions available. Hence, we need to develop judicious and effective tools (theoretical and analytical) that will provide guidance for appropriate and effective selection of materials and fit them in an optimal way to the desired uses. It is important to intensify theoretical work related to porous electrodes and electro-adsorption processes. Remarkable progress was demonstrated recently in a better understanding of the intimate pore–ion interaction using EQCM. This direction deserves more effort, especially in taking into account viscoelastic effects by using this tool not just in its gravimetric mode but rather working also in the frequency domain (i.e., impedance-type measurements and analysis). In recent years, we see more and more attempts to develop composite electrodes that comprise both activated carbons and electro-active materials which possess surface red-ox behavior (e.g., nano particles of transition metal oxides or electronically conductive polymers). It is challenging to develop such composite electrodes that can close the gap between EDLC and battery technologies in terms of energy density, but NOT at the expense of superb cycle life and high power density which are the main advantages of EDLCs. In parallel, there is a great challenge in R&D of novel electrolyte solutions, especially ionic liquids and their blends that can provide the widest electrochemical window and yet posses better ionic conductivity and better wet porous structures than existing currently tested ILs. Improved electrochemical capacitors can be used in rechargeable power sources for many kinds of portable devices. They can be integrated into smart clothing, sensors, electronics, and drug delivery systems. In some instances, they will replace batteries, but in many cases, they will either complement batteries, increasing their efficiency and lifetime, or serve as energy solutions where an extremely large number of cycles, long lifetime, and high power uptake and delivery are required.

Another field in which activated carbon electrodes can be very important is separation processes. Electrochemical water desalination (by CDI processes) can be very suitable for brackish water. It is possible to develop highly selective water purification processes, in which special contaminants can be removed. There are future challenges in electrode design for water purification processes and the engineering of effective integral systems for such processes which include optimized cells, switching, sensing, and monitoring devices.

Finally, it is important to note that this review is devoted mostly to activated carbon electrodes with an emphasis on two main applications. However, the electrochemistry of carbonaceous materials is a much broader field that relates to batteries, fuel cells, sensors, electro-catalysis in general, electro-synthesis, and many more.

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