Table of content

10.	Supercapacitors (electrochemical capacitors).....	2
10.1.	Introduction	3
10.2.	Basic principles of electrochemical capacitors.....	5
10.3.	From biomass to capacitor electrode material.....	12
10.3.1.	Step 1: pre-treatment of the biomass crude	13
10.3.2.	Step 2: thermal treatment.....	15
10.3.3.	Step 3: activation	19
10.3.4.	Doping of the biomass-derived carbons	24
10.4.	Electrical double-layer capacitors.....	29
10.5.	Carbon-based capacitors with pseudocapacitive effects	35
10.6.	Asymmetric and hybrid capacitors.....	38
10.7.	Conclusions and prospects.....	44

10. Supercapacitors (electrochemical capacitors)

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10.1. Introduction

Energy storage is recently one of the most emerging issues attracting the scientific attention. In fact, several forms of energy might be produced/harvested/converted (e.g. from sun, wind, natural gas, geothermal sources, coal, nuclear processes, etc.), but then that energy needs to be stored for the later use; an immediate exploitation of the energy produced is a very seldom case. Therefore, the systems designed for accumulation of the energy and providing it “on demand” are required¹.

Rapid development of the technologies based on the electric energy in the last decades stimulated an intensive research on efficient power sources. The main concept of electrochemical energy storage exploits the chemical reactions (accompanied by the electron/charge transfer) as energy reservoirs. These processes might occur reversibly or irreversibly, hence, primary and secondary batteries might be distinguished. Of course, for a great majority of applications, reversible storage is much more convenient. Batteries exploited recently, mainly based on Li-ion technology, might reach more than 1 000 cycles of charging/discharging loops but still these numbers are not satisfactory as far as large-scale applications with difficult access for maintenance are considered²⁻³.

Fortunately, electrochemical energy conversion and storage systems are based not only on faradaic (charge transfer) mechanisms. Electrostatic attraction of ions at the electrode/electrolyte interface might be an interesting solution for the applications requiring moderate energy density, high power rates and long cycle life⁴.

Electrochemical capacitors, called often electric double-layer capacitors (EDLCs) or supercapacitors (not recommended), are energy storage devices exploiting charge accumulation in the electric double-layer. This phenomenon is based on the weak, electrostatic interaction of ions from the electrolyte bulk with the electrode surface⁵. Unlike batteries, EDLCs store the charge on the physical manner, hence, their energy density is moderate if compared to battery technology. At the same time, the lack of electrochemical reactions ensures very high power (with the response time up to 1 s) and the cyclability of 1 000 000 cycles. That characteristics places the electrochemical capacitors

as a functional link between conventional dielectric capacitors (high power) and batteries (high energy).

Figure 1 (Left) Ragone plot for various energy storage systems and (right) more detailed comparison of various electrochemical capacitors⁶. Reprinted with the permission from Nature and The Royal Society of Chemistry.

Ragone plot (Figure 1) reflects the application niches for all electrochemical systems. Definitely, electrochemical capacitors cannot compete with batteries in terms of the energy density (or specific energy) but their advantages appear in high power density and cyclability. In this place it is worth mentioning that these technologies are not competitive (at all) since their applications are usually different^{4, 7}. Furthermore, they perfectly complement each other once merged in one system; electrochemical capacitors usually play the protective role for batteries since they are much more resistant for high current loads, being extremely harmful for the batteries.

The application of electrochemical capacitors might be found in every system requiring fast charge delivery, quite often on repetitive manner. Therefore, in electric (EV) or hybrid vehicles (HEV) they could provide the power for starting the engine or acceleration, in lifts or cranes they could serve during the loading up-take⁸. Fast re-charging possibility allows them to be considered also in regenerative braking or for energy restoration. For small electronics, they can be applied in cameras and laptops for power-peak demands^{2, 9}.

In this place, it is worth mentioning that electrochemical capacitors are recently a growing family of electrochemical systems. Typical classification distinguishes electrical double-layer capacitors with purely capacitive charge storage mechanism and hybrid capacitors, merging capacitive charge storage with the faradaic one; the latter includes quite often asymmetric capacitors and the Li-ion capacitors, combining the advantages of fast capacitive storage in terms of power with faradaic one (based on the intercalation processes) in terms of energy. This classification is certainly not exhaustive ¹⁰.

Definitely, activated carbons with their versatile properties (like specific surface area, well-developed and suitable porosity, heteroatoms in the graphene matrix) are the most popular materials in electrochemical capacitor application. It has been claimed by many authors that the textural and structural properties of the electrode material play the decisive role in the final performance of the electrochemical capacitor.

This chapter provides a comprehensive overview of the materials recently developed, with special attention devoted to the materials obtained by the biomass carbonization. Electrochemical properties demonstrated by such carbons are discussed in respect to their physicochemical characteristics.

10.2. Basic principles of electrochemical capacitors

As already stated, charge storage mechanisms in electrochemical capacitors is attributed to electrical double-layer (EDL) charging, formed at the electrode/electrolyte interface¹¹. The first EDL model has been proposed by Helmholtz and considered a simple organization of ions at charged surface with linear potential decrease along the distance from the electrode surface (Figure 2). Then, Gouy-Chapman model developed that concept by including so called diffuse layer with non-linear potential decrease and solvent presence at the proximity of the electrode. Stern model, updated later by Graham, is widely accepted today, merges both concepts and reflects most likely the situation at the electrode/electrolyte interface in the real device.

Figure 2 Schematic representation of the electric double-layer at positively charged electrode with various models: (a) the Helmholtz model; (b) the Gouy–Chapman model and (c) the Stern model, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). Reprinted from reference ¹² with the permission from The Royal Society of Chemistry.

The capacitance of that interface is directly proportional to the electrochemically accessible surface area (A), electrical permittivity of free space (often assigned as of vacuum) ϵ_0 , dielectric constant ϵ_r and inversely to the thickness of the double layer (d)¹³⁻¹⁵:

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad \text{Equation 1}$$

For that reason, the capacitance (C) increase is most often realized either by the development of the electrochemically accessible surface area of the electrode material or adjusting the ion size, impacting on the electrical double-layer thickness (d)¹⁶. It has to be stated that the parameter A cannot be considered as specific surface area of the electrode determined from the gas adsorption (N_2 , CO_2 , Ar) although these estimations are essential for the evaluation of the electrode materials in terms of their exploitation for electrochemical capacitors. Briefly, the interface should be considered as the surface in contact with the electrolyte and accessible for ions; this depends on many factors, at least on pore size/diameter, surface functionalities and the kind/size of the electrolyte. There is no direct dependence between the specific surface area determined by various models like BET equation, NLDFT or QSDFT ¹⁷⁻²⁰, however, the pore size and pore volumes seem to correlate much better ^{18, 21-26}. This reflects the typical interfacial character of charge accumulation as these electrode

features are intimately connected with the electrolyte properties. This issue will be discussed in more details in the next paragraphs.

More generally, the capacitance of the electrode is described as the charge (Q) accumulated within given potential range (U):

$$C = \frac{Q}{U} \quad \text{Equation 2}$$

Determination of the capacitance values might be realized with various electrochemical techniques. For typical quantitative purposes, galvanostatic charging/discharging is the first choice. Then, the capacitance is calculated from the following formula:

$$C = \frac{I \cdot t}{U} \quad \text{Equation 3}$$

Where I is the applied current (mA or A), t is the discharge time and U is the voltage range. For qualitative purposes only, cyclic voltammetry with given scanning rate dU/dt is a perfect choice. The capacitance calculation is then based on the formula:

$$dC = \frac{I dt}{dU} \quad \text{Equation 4}$$

Electrochemical impedance spectroscopy allows the capacitance values to be determined at narrow voltage amplitudes

$$C = \frac{1}{2\pi f Z} \quad \text{Equation 5}$$

where f is the alternating current frequency (Hz) and Z is the imaginary part of the impedance (Ohm).

In this place is worth stating that all techniques, although varying with electrochemical measurement origin, should reflect similar capacitance values. Usually, the highest values are reflected either by cyclic voltammetry or electrochemical impedance spectroscopy, since these are typical kinetic methods. For real applications, constant current load techniques seem to be the most reliable; for some applications, these techniques might be supported by constant power charging/discharging.

Advanced capacitor testing includes several other parameters like self-discharge, leakage currents and cyclability. Self-discharge of the capacitors is measured usually for 24 hours as Open Circuit Voltage (OCV) when no polarization is applied to the device. This measurement quite often follows

the leakage current measurement where the system is hold at the certain voltage for a given time (1-12 hours) and the current response is recorded. Both measurements complement each other, although the leakage current is only one of the components causing capacitor self-discharge²⁷⁻³³.

Cycling stability of the capacitors is usually measured on two ways – either by continuous constant current charging/discharging or by keeping the system at elevated voltages for a given time. It is widely accepted that end-of-life of the capacitor is reached once 20% of initial capacitance or 100% increase of internal resistance is observed. Again, both techniques are extremely useful in description of the capacitor long-term performance but there is no point in the discussion about the advantageous character of one of them. The ageing mechanisms imposed by these techniques are different, even if they lead to the same effect, i.e. performance fade³⁴⁻³⁷.

For activated carbons with well-developed surface area, the specific capacitance is of ca. 100 F/g or 20-50 $\mu\text{F}/\text{cm}^2$ or 70 F/cm^3 and varies slightly with the nature of carbon and applied electrolyte⁹. By definition, the capacitance is independent on the potential/voltage range. Definitely, this is always true, but in practice, for planar, non-porous electrodes only; in real conditions and on porous electrodes, faradaic contributions to charge accumulation might influence the final result. Furthermore, the amount of charge received will depend on the current load applied too, since the porosity of the electrode will impact the transport of ions from electrolyte bulk to the electrode surface. This dependence is called as rate capability and reflects the amount of the charge provided/received under conditions applied rather than the changes of the capacitance itself.

Although the capacitance is one of the most important parameters for capacitor evaluation, the energy density (Wh/L) or specific energy (Wh/kg) seems to be more useful for final applications^{11, 38-43}. For electrochemical capacitors, the amount of energy stored is directly proportional to the capacitance (C) and squared voltage (U):

$$E = \frac{1}{2} C_{\text{device}} U^2 \quad \text{Equation 6}$$

This equation should be used for energy calculation with special care and full understanding of electrochemical systems. Namely, it must be used for the capacitance and voltage determined in

real, two-electrode configuration; it must not be used for the capacitance values obtained in three-electrode configurations for two reasons. Firstly, three-electrode set-up is perfect for fundamental characterization of the electrodes but usually the metrics obtained from these experiments are far from practical ones (oversized counter-electrodes, excess of the electrolyte, etc.). Furthermore, three-electrode experiments reflect the performance of one electrode which cannot – itself – store the energy; the energy can be stored in full electrochemical system, hence, reporting the energy for the electrode is simply pointless. The second aspect comes with the principles of capacitive charge storage and the final capacitance of the system. Namely, two-electrode device is composed of two capacitors connected in series, hence, the final capacitance is expressed by the following formula:

$$\frac{1}{C} = \frac{1}{C_+} + \frac{1}{C_-} \quad \text{Equation 7}$$

This indicates that the final capacitance (in F) of symmetric device (with identical electrodes) is two times less than for single electrode. Furthermore, once the gravimetric capacitance (in F/g) is considered, the final gravimetric capacitance will be four times lower than for individual electrodes. Therefore, for calculating the energy for symmetric devices from single electrode capacitance, one should correct the fraction in the Equation 6 by 4:

$$E = \frac{1}{8} C_{electrode} U^2 \quad \text{Equation 8}$$

However, it is strongly advised to calculate the energy from the capacitance of the full device.

The energy stored in the capacitor, as indicated by Equation 6, depends on the capacitance and the squared voltage. The capacitance-related issues of the carbon-based electrodes will be discussed in the next paragraphs, however, the issues related to the electrolyte cannot be neglected.

The maximum voltage of the capacitor is governed by the nature of the electrolyte applied. Initially, aqueous (protic) and organic (aprotic) electrolytes were distinguished⁴⁴. Recently, tremendous development of ionic liquids resulted in considering them as a third class of the electrolytes for electrochemical capacitors^{11, 45-46}. Apart from electrolytes in the liquid state, one might find so-called solid-state-electrolytes, (hydro)gels or polyelectrolytes⁴⁷.

The main feature of the electrolyte impacting the amount of the energy stored in the capacitors is the electrochemical stability window. For organic electrolytes, this value reaches 2.7 – 2.8 V for acetonitrile or propylene carbonate-based formulations⁴⁸. Other solvents, like ethylene carbonate, dimethyl carbonate, butylene carbonate, gamma-butyrolactone, gamma-valerolactone, propionitrile, glutaronitrile have been proposed as promising alternatives, but their low conductivity aggravates the final power rate of the device. Apart from the solvent, the salt as the ion source should be briefly commented. Tetraethylammonium tetrafluoroborate (TEABF₄) is the most often applied salt in commercial capacitors. However, TEABF₄ is highly soluble in acetonitrile while its solubility in propylene carbonate is limited (up to 1 mol/L) and results in high internal resistance of the device. It has been stated that the conductivity of the salts in organic electrolytes depends on the cation and anion in the following order: TEA⁺ > Pr₄N⁺ > Bu₄N⁺ > Li⁺ > Me₄N⁺ for cations and BF₄⁻ > PF₆⁻ > ClO₄⁻ > CF₃SO₃⁻ for anions. Therefore, TEABF₄ appears again to be the best candidate as salt for the organic electrolyte⁴⁸⁻⁵².

Ionic liquids (ILs) are electrolytes built entirely from ions. An enormous number of organic compounds which might be designed prior to requirements initiated a wide research on ionic liquids as tentative electrolytes for electrochemical capacitors^{46, 53-56}. General classification distinguishes three types of ILs: protic (substituted with all-organic R^x substituents), aprotic (with a labile proton in the structure) and zwitterionic (with merged, usually polymeric structure). Imidazolium, pyrrolidinium, ammonium, sulfonium or phosphonium-based cations together with BF₄⁻, PF₆⁻, bis(trifluoromethanesulfonyl)imide (TFSI⁻), bis(fluorosulfonyl)imide (FSI⁻) and dicyanamide (DCA⁻) anions are the most often reported in electrochemical application^{11, 16, 45-46, 57-60}. Although the three-electrode investigations on non-porous electrodes demonstrated extremely high stability windows (up to 6 V), these values have never been confirmed in two-electrode configurations on porous carbon electrodes. It seems that 3 V is the practical limit as far as the porous electrodes are considered. Undoubtedly, ionic liquids offer wide range of features promising in electrochemical capacitors application, essentially in terms of user safety – contrarily to conventional non-aqueous

electrolytes, these electrolytes demonstrate negligible vapor pressures, limited toxicity and non-flammable character. However, their decomposition chemistry and long-term impact on the environment still needs to be verified.

Finally, aqueous electrolytes seem to be promising, eco-friendly alternative to organic solvents and ionic liquids⁶¹⁻⁶⁵. On one hand, their conductivities are incomparably higher than for non-aqueous systems (usually above 80 mS/cm, reaching even 600 mS/cm for concentrated KOH) resulting in excellent power rates. Furthermore, assembling the capacitors with water-based electrolytes does not require thorough and expensive drying of the electrode material and an inert atmosphere (oxygen- and moisture-free). Apart from strongly acidic electrolytes, neutral and alkaline electrolytes might be applied to the systems with stainless steel current collectors which positively impacts the final price of the device. On the other hand, electrochemical stability of aqueous electrolytes is limited by the water decomposition voltage (theoretically at 1.23 V) and this is the major obstacle on the way to wide commercialization of these systems. Nonetheless, for systems operating with neutral electrolytes (with pH around 7) such as 0.5-2 mol/L solutions of Li-, Na-, K₂SO₄ or 1-5 mol/L Li-, Na-, KNO₃ effective operating voltages up to 1.9 V have been reported ^{34, 39, 66-72}.

The electrolytic solution might play a prominent role not only for maximum voltage. Incorporation of redox species introduces the pseudocapacitance to the system and boosts the capacitance values. Pseudocapacitance has been primary reported for RuO₂ ⁷³⁻⁷⁴ and then translated to various transition metal oxides, but recently, it is widely accepted that apart from RuO₂, only MnO₂ can be accepted as typical pseudocapacitive material. Detailed explanation and elaboration on the pseudocapacitance phenomenon is presented elsewhere ^{14, 73, 75-80}.

Initially, the iodide/iodine and bromide/bromine redox couples present in the electrolyte have been introduced as a source of enormous capacitance ⁸¹⁻⁸⁵. Redox-active electrolyte concept has been widely developed and several other species have been proposed to date: hydroquinone (HQ) with isomers ⁸⁶⁻⁸⁹, methylene blue (MB) ⁹⁰, indigo carmine (IC) ⁸⁹, p-phenylenediamine (PPD) ⁹¹, m-phenylenediamine⁹²⁻⁹³, lignosulfonates ⁹⁴, sulfonated polyaniline (SPANI) ⁹⁵ and humic acids ⁹⁶.

However, the performance of the capacitors operating with redox-active electrolytes is closer to the high-power batteries, hence, one should take a special care for reporting the correct metrics, essentially for capacitance estimation^{75, 97}.

Decisive role of the electrolyte on the final electrochemical performance is always accompanied by the properties of the carbon electrodes. As already stated, great variety of precursors and adjustable synthesis conditions impacting the final features definitely play an important role for further development of these systems and must be discussed in more details.

10.3. From biomass to capacitor electrode material

Ever since the late 80s, when Nippon Electric Corporation launched the first electrochemical double-layer capacitor (EDLC) on the market, activated carbons (ACs) became the inherent part of this energy storage system, playing almost the first fiddle. Although for a long time these materials were considered as “golden goose”, recently they are more and more often seen as weak links limiting further progress of high-performance capacitors. This is mainly because of the expensive and often hazardous synthetic routes of ACs as well as scarcely tunable pore structure dominated by micropores restricting the diffusion of the electrolyte ions⁹⁸⁻¹⁰⁰. Optimizing the pore structure of these materials is never an easy task and requires well-thought-out choice of both carbon precursor and its processing conditions. Besides the optimal pore size and geometry, the ideal candidate for the electrochemical capacitor (EC) electrode materials should have a relatively high specific surface area (SSA), high electronic and ionic conductivities, and sufficient mechanical and chemical stability¹⁰¹ (Scheme 1), the interplay of which will be the focus of this chapter.

Scheme 1 Illustration summarizing the concept of the chapter, namely the interplay between the properties of the electrode material and those related to the performance of the capacitor.

In addition, it is arranged such that the subsequent parts constitute a guideline for the preparation of the biomass-derived carbon materials for different types of ECs, from classical EDLCs to their asymmetric and hybrid counterparts. Not only does it lead through the process of preparation and optimization of the biomass-derived carbon for this specific application but also highlights the key parameters of the resultant chars/carbons used to quantify their promise as cost-effective high-performance robust electroactive materials for capacitor application.

10.3.1. Step 1: pre-treatment of the biomass crude

On one hand, coconut shells¹⁰², olives pits¹⁰³, pine cones¹⁰⁴, sunflower seed shell¹⁰⁵, and other plant-based carbon-rich resources are all mainly composed of cellulose, lignin and hemicellulose – a starting point for capacitor electrode material. On the other hand, bovine, porcine and other animal bones are a source of apatite¹⁰⁶, a phosphate mineral which can also act as the seed of macro-mesoporous carbon. While the source of the biomass predestines the morphology (shape, particle size, and porosity) of the end-annealing products (Figure 3), the primary chemical composition, in particular the presence of impurities, has a big share in defining other physico-chemical properties.

Inorganic elements, e.g. calcium¹⁰⁷, potassium¹⁰⁷, silica¹⁰⁸, sodium¹⁰⁷, and oxides, e.g. SiO₂¹⁰⁹, present in the plant-based biomass are often considered as undesired because their presence in to-be-annealed biomass may i) significantly reduce the overall char yield and promote secondary reactions¹¹⁰, ii) impede the formation of pores¹⁰⁸ and the surface chemistry of the resulting char (formation of fusions, inclusions, and glassy melt phases)¹⁰⁷ and iii) lead to a partial blocking of the micropores and, thus, restricted diffusion of the electrolyte ions therein¹¹¹.

Figure 3 SEM images of hydrochars derived from different pollens. Reproduced from reference ¹¹² with permission from John Wiley and Sons.

Usually washing the crude biomass only with water is sufficient to remove 90% of alkali metals unless they are present in high concentrations and bound to the organic structure¹¹⁰. In this case, the use of strong acids, e.g. HCl¹¹³⁻¹¹⁴ and HNO₃, instead of water is recommended as they hydrolyze cellulose and hemicellulose, therefore increasing the content of lignin (resistant to acid hydrolysis¹¹⁴) and, thus, the overall char yield. While it removes metal ions from the biomass, strong acid washing alters the native polymer structure of the crude (promotes the development of the pores) and causes non-negligible loss of mass¹¹⁵. In addition, the acid-washed biomass has to be thoroughly rinsed with water and subsequently dried to remove remaining chlorine and other acid ions and reduce the moisture content before further treatment¹¹⁰.

High moisture content might significantly decrease the efficiency of the “waste to wealth” conversion process because in some cases, mainly in pyrolysis, the presence of water in carbonized feedstock promotes the formation of liquid products (bio-oil), ultimately reducing already low char yield (10-35%)¹¹⁶. In addition, it also causes inhomogeneous heat transfer during charring, thereby adversely affecting the properties of the end solid products. That is why besides the drying in classical, as for

this type of materials, conditions, elevated temperature and reduced pressure, other possibilities are currently being considered. These include for example mechanical dewatering of the biomass or adding a surfactant to the washing solution¹¹⁰. In the latter case the surface-active “additive” not only reduces the amount of moisture kept by the biomass but also removes most of the inorganic impurities, thereby trimming the operational cost¹¹⁰.

10.3.2. Step 2: thermal treatment

The choice of the biomass and its extraction and/or pre-treatment commences the chains of consequences for the end-product, carbonaceous material. In addition, although there is no thermal treatment-memory effect, the properties of the resulting char are closely intertwined with the annealing and processing conditions. Most common biomass carbonization methods include hydrothermal carbonization (HTC) and pyrolysis. HTC, often referred to as pre-carbonization or wet torrefaction, is more and more often seen as “waste to wealth” conversion route for biomass¹⁰⁰. Carried out in presence of hot compressed water between 120 and 250°C⁹⁸, HTC mimics natural coal formation but in much shorter time¹¹⁷. This carbonization method is, however, not a single-reaction conversion of the crude to structured carbon but a collection of complex chemical reactions of the biomass basic building blocks – cellulose, hemicellulose and lignin, taking place at the interface of water and given biopolymer as well as in its bulk⁹⁸. These reactions include, among others, dehydration, hydrolysis, aromatization and polymerization¹¹⁸. Overall, the hydrochars produced through HTC are rich in oxygenated and other heteroatomic functional groups, and have low level of aromaticity, rendering them good precursors for activated carbons (ACs)¹¹⁸. The combination of the starting material (also later referred to as parent material) and other parameters, namely: i) annealing temperature, ii) dwell time (also referred to as residence time), iii) concentration of the reactants, and iv) the presence / absence of the catalyst, plays a substantial role in producing HTC-derived AC precursors with desired chemical and physical characteristics¹¹⁸. In particular, the choice of the annealing temperature comes to the fore when aiming at high-surface-area activated carbons

with well-developed pore structure. As shown by Jain *et al*¹¹⁹ on the example of coconut shell-derived hydrochars, there is a threshold value, after which further increase in the HTC temperature does not result in higher yield of the oxygenated functional groups but quite the opposite – it leads to their decomposition to carbon di- and monoxide, methane, hydrogen and others gaseous products¹²⁰⁻¹²¹. Among the advantages of the HTC are relatively low environmental impact and the carbon yield reaching the highest value of all biomass-based technologies, 95%¹²². Besides that, unlike other methods, HTC does not require pre-drying of biomass, which inevitably increases the cost of the entire conversion process. It falls short, however, in adding value to the crude rich in lignin because the presence of this non-polysaccharide during the thermal treatment causes so-called “shadowing effect” lowering the carbon content and the coalification degree of the hydrochar¹²³. In addition, high energy and water consumption always accompany this carbonization process taking place in saturated steam and at high pressure¹²⁴ thereby postponing its industrial implementation.

Figure 4 Schematics illustrating decomposition of the biomass basic building blocks as a function of temperature, a concept adapted from reference ¹²⁵.

The high energy consumption and the “shadowing effect” are not a concern for pyrolysis that starts to mature as a commercial technology¹²⁶. In combination with a physical or chemical activation

(Chapter 10.3.3) pyrolysis constitutes almost a classical synthesis route for converting majority of biowastes into value-added carbons for capacitors⁹⁸. Given the operating temperature range (500 and 1000°C)⁹⁸, this carbonization method is in particular suited for woody and herbaceous plants¹²⁷, and other lignin-rich biowastes difficult to carbonize otherwise (the thermal decomposition of lignin occurs between 100 and 900°C¹²⁸ (Figure 4)). Pyrolysis of lignocellulosic materials yields three different products, namely biochar, bio-oil and syn-gas, the relative ratio of which depends, among other, on the particle size of the starting material, processing temperature and heating rate. As shown by Demirbas *et al.*¹²⁹ on the example of olive husk, corncob and tea waste, large particle size in combination with low pyrolysis temperature and slow heating rate promotes formation of carbon¹³⁰, significantly increasing fuel-to-feed efficiency. The latter is also related to the chemical composition of to-be-pyrolyzed feedstock. The higher is the lignin content in there, the higher the char yield after the pyrolysis, which in the given example leads to the following order: olive husk > tea waste > corncob. The effect of pyrolysis temperature, dwell time, and heating rate on the biomass-derived carbon was also studied by Lua *et al.*¹³¹ on the example of oil-palm shells with a lignin content similar to that of olive husk (around 54 wt%)¹³². They confirmed that the three main textural properties of the ACs, that is, specific surface area (SSA) micropore area and volume, are already decided during the thermal treatment. Moreover, materials with the most favorable characteristics were also obtained at lower temperatures, between 400 and 600°C. Once 600°C was exceeded, further increase in temperature (up to 900°C) had an adverse effect on the forming char, causing softening and sintering of the high-molecular-weight volatiles. These, in turn, triggered the depolymerization of the melt and eventually led to an increase in char density. Consequently, ACs produced from these compact chars could not boast of well-developed micropores network and high SSA (Figure 5, left).

Figure 5 (Left) Effect of pyrolysis temperature on the BET surface area, micropore area and micropore volume of the activated carbons; (Right) Effect of pyrolysis hold time on the BET surface area, micropore area and micropore volume of the activated carbons. Reprinted from reference ¹³¹ with permission from Elsevier.

Besides pyrolysis temperature, residence time is a second most frequently changed parameter. As can be seen in Figure 5, right, it can also have its large share in defining the structure of the end-pyrolysis products. The longer the residence time, the higher the release of volatile components, and, thus, the larger the micropore volume, unless the heat treatment at the optimal as for this case temperature of 600°C last longer than 2 h. Once this threshold is exceeded, the micropore area and micropore volume drop steeply down, from almost 460 m²/g to 340 m²/g and from 0.22 cm³/g to less than 0.16 cm³/g, respectively, and the SSA decreases correspondingly.

In a pursuit of energy saving and cost reduction other carbonization method are currently being investigated. Among them, molten-salt carbonization, which can be considered as a derivative of HTC, continue gathering attention. In this very method, thermo-chemical decomposition of the biomass takes place in a bath of molten salt or their eutectics¹³³⁻¹³⁴, through which inert gas is passed at the temperature higher than 400°C. Alkali metal carbonates, halides, and nitrates are the essential ingredients of this bath. Not only do they act as catalysts accelerating gasification of the carbon with CO₂ and steam by cracking the links between cellulose, hemicellulose, and lignin (mainly glycosidic bonds) but also they play a role of heat carriers and suppliers, as well as reaction media. Molten salts are involved in different commercial and non-commercial gasification processes. They are known from kraft pulping as efficient converters of wood into paper pulp, and perhaps for this reason are

often employed for upgrading the biomass rich in cellulose. Lu *et al.*¹³⁵ reported a study of firewood-derived carbon prepared with and without the eutectic carbonate molten salt, Na_2CO_3 and K_2CO_3 , in to-be-pyrolyzed feedstock. For this, the wood blocks were first grounded and sieved to a length of 0.09 to 2 cm and subsequently they were carbonized at 850°C under continuous flow of argon. Although the yield of the carbon was significantly lower when molten salt was used for biomass conversion (11.6 *versus* 35.9%), the end-product had SSA and pore volume twice as big as SSA and pore volume of its reference pyrolyzed only under argon (818 *versus* 463 m^2/g , and 0.44 *versus* 0.22 cm^3/g).

10.3.3. Step 3: activation

Usually after the thermal treatment the SSA of the (hydro)chars does not exceed few hundreds of m^2 / g ¹⁰⁰ and their pore structure is rather poorly developed (especially in the case of hydrochars)¹³⁶, therefore precluding these materials from attaining specific capacitances comparable or greater than those of commercial capacitors. Fortunately, both the SSA and the pore structure can be enhanced through activation. Activation can be carried out chemically, physically or physio-chemically. The first of the three, which is usually but not necessarily paired to carbonization (pyrolysis or HTC) (Figure 6), is chosen for this purpose twice as often as the physical activation because of: i) lower temperature and shorter time required to activate the (hydro)char, ii) higher SSA of the end-product (Figure 7 *versus* Figure 8), iii) better control of the textural properties, in particular the micropore size distribution, and iv) overall higher carbon yield. However, it always carries a risk of introducing inorganic impurities to the AC and requires thorough post-washing¹³⁰.

Figure 6 Summary of different “waste to wealth” pathways for converting sugar cane into activated carbon. Sugar cane graphic was designed by Freepik¹³⁷. (Top right) SEM picture is reprinted in part with permission from reference ¹³⁸. Copyright 2018 American Chemical Society. (Bottom right) SEM picture is reprinted in part from reference ¹³⁹, with the permission of Elsevier.

In a typical procedure, biomass carbon precursor or its pre-carbonized counterpart is mixed or impregnated with chemical agent and subsequently thermally treated under inert atmosphere.¹³⁰

H₃PO₄ and ZnCl₂ are recommended for ligninocellulosic materials, whereas K₂CO₃ and KOH, and other alkaline carbonates and hydroxides, respectively, can be considered as more universal activating agents for biomass rich and low in lignin. In one case or another, the physical and chemical properties of the end-products, ACs, are to a large extent dependent on the concentration of the activating agent and its ratio with respect to the material subjected to activation (Figure 7, top), the temperature (also the heating rate) of the carbonization and its dwell time, and to a smaller extent to the carbonization atmosphere^{130, 140}.

Figure 7 (Top) SEM images of bio-char and activated carbons, adapted from reference ¹⁴¹ with the permission from Elsevier; (Bottom) Comparison of the specific surface area of the carbons derived from different bio-precursors, activated chemically either with H_3PO_4 ¹⁴²⁻¹⁴⁵, or $ZnCl_2$ ^{144, 146-150}, or KOH^{141, 151-152}, or K_2CO_3 ^{141, 153-154}, a concept adapted from reference ¹³⁰.

Carbonization temperature and dwell time are also important processing variables for the physical activation during which a carbon-source material does not react anymore with chemical agent but with the oxidizing agent, that is CO_2 , air, steam, or a mixture of these^{130, 155} (Figure 8). The selection of the oxidizing agent is non-negligible for attaining application-desired SSA, pore volume and pore size distribution. Usually the use of CO_2 endows the end-products with narrow pore size distribution and relatively high micropore volume¹⁵⁶, whereas the steam-activated carbons are characterized by lower micropore volume and overall widen micropores¹⁵⁷.

Thus, in a pursuit of high capacitance a preference would be given to CO₂ activation because higher micropore volume results in larger SSA and, thus, more active sites available for interactions with the electrolyte ions.¹⁵⁷ As can be seen in Figure 9, however, this micropore volume-SSA relationship initially established for olive stones-based carbons¹⁵⁷ is not always a rule of thumb and depends on the interplay between all processing parameters.

Figure 8 Comparison of the specific surface area of the carbons derived from different bio-precursors, activated either physically with CO₂^{142, 151-152, 158}, or H₂O¹⁵⁹⁻¹⁶¹, or physico-chemically with H₃PO₄ and steam¹⁶², HNO₃ and steam¹⁶², and H₂SO₄ and air¹⁶³, a concept adapted from reference¹³⁰.

Even if physical activation is considered as cost-effective waste-free process, high activation temperature (800 - 1000°C), low carbon yield¹⁶⁴, and limited control over the developing porosity (mainly microporosity with the average pore size < 2 nm, Figure 9, right)¹⁶⁴, do not speak in favor of implementing it as a part of industrial process.

In addition, with the capacitor application in mind, the ideal carbon electrode material should have both meso- and micropores, which, respectively, facilitate mobility of electrolyte ions and are responsible for storing the transferred charge.

To improve the development of the meso- and microporosity and render the ACs with tailor-made textural and chemical properties sometimes chemical and physical method are combined into one as for example in the case of coconut shell-derived carbon prepared by Jain and co-workers¹¹⁹. Through careful analysis of the HTC-activation conditions and the interplay between the annealing temperature and ZnCl_2 : shell ratio not only did they enhance the SSA and the mesoporosity of the coconut shell-derived carbon, but also they defined the optimal conditions for hydrochar upgrading¹¹⁹. The latter included also optimization of the material in terms of micropore volume, very important SC application-driven property (Figure 9, right). Certainly, the work of Jain and co-workers can serve as a roadmap for preparing carbons with well-developed meso-microporous structures from biomass other than the coconut shell. Among the examples of physico-chemically activated carbons with highly developed porosity are also ACs derived from date-¹⁶² and olive-stones with SSA largely exceeding $900 \text{ m}^2/\text{g}$ ¹⁶⁵.

Figure 9 Evolution of the micropore volume, V_{micro} , for the coconut shell-derived carbons prepared by (left) classical pyrolysis accompanied by CO_2 activation and (right) HTC- ZnCl_2 activation; for the latter figure the data points were extracted from reference¹¹⁹ (from Table 2 in the main body of the text and from Supplementary data) and ¹⁶⁴. The coconut graphics was designed by BSG Studio¹⁶⁶.

Despite the wide range of activation methods and considerable knowledge acquired from studying the effect of activation conditions on the properties of the end-products from different carbon-rich precursors, extensive porosity development and relatively wide pore size distribution remain a sore point of “waste to wealth” conversion process described in this chapter. Recently, it has been shown that porous high-surface-area carbon can be obtained also without the activation step. This was accomplished by Beguin *et al.*¹⁶⁷, who took an advantage of Na, K, Ca and Mg, and their derivatives (earlier referred as to “impurities”) naturally present in Neem dead leaves and known to be efficient porogens¹⁶⁸ promoting dehydration of the parent materials. As a result, the dead leaves-derived carbon prepared in this way outperformed other biomass-derived ACs in terms of SSA (1230 m²/g) and well-organized porous ion-conducting network built-up from micropores matching the size of solvated ions, and, thus, allowing more efficient charge storage. Similar work has been carried out on seaweeds¹⁶⁹. Although in this case the SSA of the carbons prepared also without the activation step was on average lower than that of Neem dead leaves corresponding materials (from 416 to < 1300 m²/g), impurity-induced engineering of the pore structure eventually led to competitive performance characteristic (high capacitance at low SSA).

Certainly, high SSA easily accessible to ions is important for efficient charge storage at the electrode / electrolyte interface and, thus, for attaining high specific capacitance but it is not a “must have”. Well-engineered meso-microporous ion-conducting network is equally or even more important when aiming at high-performance capacitor electrodes.

10.3.4. Doping of the biomass-derived carbons

Another strategy to enhance the performance of the biomass-derived carbon in capacitor and, thus, to satisfy the current energy storage demands, is to functionalize the surface of the material by introducing heteroatoms such as boron (B), oxygen (O), nitrogen (N), phosphorous (P), and sulphur (S). The functional groups which contain these heteroatoms alter the wettability and polarity of the carbon surface, as well as its electronic conductivity, and, thus, allow for enhancing the capacitance

through Faradaic reactions with electrolyte ions and, in some cases, to enlarge the potential window and extend the life time of the capacitor.

There are two main strategies to incorporate heteroatoms into the carbon framework, namely *in situ* and *ex situ* doing. The first of the two is based on a simple pyrolysis of either the biomass containing heteroatoms in its structure or a mixture of biomass with a heteroatom-containing compound. Many biomass sources have been explored to obtain heteroatom-doped or co-doped carbons, and it has been concluded that the nature and quantity of heteroatoms and resulting functional groups strongly depend on both biomass composition and synthesis procedure (pyrolysis temperature and time, nature and amount of activating agent, and post-treatment procedure, if any). Antolini *et al.* compared nitrogen content of several types of biomass originating from botanic plants, algae and animals (Table 1 in reference ¹⁷⁰). Interestingly, the animal-based biomass such as egg white and crustacean contains always higher amount of nitrogen, between 12 and 17.5 %, and, therefore, may be of potential interest to achieve high amount of these dopants in resulting carbons. Zhao *et al.* ¹⁷¹ pyrolyzed tobacco rods at 800°C in the presence of KOH activating agent and obtained N-doped carbon with low nitrogen content (1.1 -1.4 at%). Xu and co-workers¹⁷² reported on the synthesis of N- and S-co-doped carbon from shell beans by pyrolysis/activation with KOH at 650°C. The use of bio-precursors other than shell beans, such as natural silk¹⁷³, *Endothelium corneum gigeriae galli*¹⁷⁴, willow catkins¹⁷⁵ or *Enteromorpha prolifera*¹⁷⁶ led to materials doped with N, O, and S.

The second approach to introduce heteroatoms in the carbon structure, the *ex-situ* doping, involves pyrolysis of biomass followed by additional treatment at high temperature using either “doping” gases (N₂, NH₃, H₂S) or chemical agents (melamine, urea). For the latter the examples might be N-doped porous carbons derived from the wood, coconut shell or potato wastes, and mixed with melamine and/or urea¹⁷⁷⁻¹⁷⁹. In these materials, the nitrogen amount reached maximum 6 at% while that of oxygen was higher, at 10 at%. The oxygen functionalities though are always present on the surface of resulting carbon not only as a consequence of the activation processes but also as a residue from the parent material. One more example might be fruit stones-derived shiitake

mushroom AC mixed with phosphoric acid (H_3PO_4) to give P-doped carbon that exhibited higher capacitance, better stability, and was able to work within wider voltage window compared to its undoped carbon counterparts¹⁸⁰⁻¹⁸¹.

Besides that, the simple one-step *in-situ* pyrolysis without the addition of any chemical agent or supplementary thermal treatment step still remains the most efficient way to introduce heteroatoms in the carbon structure. The activation of carbon following its doping, which is necessary to develop the porosity and to achieve optimal SSA requires, however, high temperature. High temperature improves the structure of carbon (especially its conductivity) but also eliminates some of the functional groups, restricting pseudocapacitive properties of these materials. As illustrated before, the most common dopants naturally occurring in biomass are oxygen and nitrogen. Oxygen is present on the carbon surface in the form of carboxyl, ether, phenol, quinone or ketone functional groups (Figure 10a). While it contributes to the wettability of the carbon, high amount of this heteroatom might be detrimental to the electronic conductivity and induce side reactions leading to the electrolyte decomposition. Nitrogen is usually found therein in four different forms, namely graphitic (quaternary N), pyridinic, pyrrolic N, and in the form of oxidized species¹⁸²⁻¹⁸³ (Figure 10b).

Figure 10 Possible functional groups on a pyrolytic carbon surface as related to the presence of a heteroatom: (a) oxygen, (b) nitrogen and (c) sulphur. Basic and acidic functionalities are indicated in blue and red, respectively. Reprinted from reference ¹⁸⁴ with the permission from The Royal Society of Chemistry.

The strong electron donor behavior of nitrogen enhances π bonding and the basic property of the carbons and, thus, its specific interactions with polar species *via* either electrostatic forces or hydrogen bonding. Additionally, the pyridine and pyrrolic groups lead to the increase of the capacitance through redox reactions^{178, 185}.

Figure 11, left, shows the evolution of the amount of oxygen and nitrogen as a function of pyrolysis temperature for different selected biomass: cabbage, corn gluten, *gigeria galli*, and prawn shells. As can be seen, the amount of both elements depends on the source of the biomass and the conditions used to prepare the doped-carbons. Also, the amount of oxygen is always much higher than that of nitrogen due to the higher abundance of the former in the parent material. As soon as the pyrolysis

temperature increases, however, the amount of the two heteroatoms decreases, which is driven by the decomposition of O- and N-functional groups accompanied by the release of NH_3/HCN and CO/CO_2 .

Figure 11 (Left) Evolution of the amount of nitrogen (open symbols) and oxygen (closed symbols) as a function of the pyrolysis temperature for different biomass-derived carbons. Data points extracted from references ^{176, 186-187}; (Right) Evolution of the pyridinic, pyrrolic and quaternary N as a function of the pyrolysis temperature plotted using the data points from reference ¹⁸⁸.

In the case of nitrogen, not only does the amount of N-functional groups decreases but also the ratio between the different N-groups changes as a function of temperature (Figure 11, right)¹⁸⁸⁻¹⁹⁰. Generally, at low carbonization temperatures (600°C) most of the nitrogen is present in the pyrrolic form. The amount of pyridinic and quaternary N increases together with the pyrolysis temperature, in particular at 800°C. Also, at low temperatures, nitrogen tends to appear in functional groups external to the aromatic ring (with localized charge), whereas at higher temperatures it is mainly placed within the aromatic ring with either delocalized or no charge (Figure 10). As can be seen in Figure 11, right, high pyrolysis temperature favors the removal of heteroatom-containing groups from carbon materials. One approach to preserve these functionalities might be for example to turn to microwave-assisted carbonization. This method in combination with KOH activation was used by Liang *et al.*¹⁹¹ to prepare ACs derived from camellia oleifera shell rich in oxygen functionalities (around 35 wt%).

Processing of the biomass into carbon with application-tuned properties and the performance of this “wealth” in capacitor are two different things. That is why the following subchapters are built up on concrete examples showing how do the physico-chemical properties of the biomass-derived carbons influence performance characteristics of the actual device. Through multiple comparisons to the state-of-the-art commercial ACs we will refer to a question as to whether biomass-derived carbons are already viable alternative to Maxsorb, Norit, and other commercial ACs ¹⁰⁰.

10.4. Electrical double-layer capacitors

The mechanism of energy storage in the most classical system, that is, electric double-layer capacitor (EDLC) is based on charge accumulation at the electrode / electrolyte interface in the form of the double layer. Usually the average specific capacitance of commercial EDLC with standard ACs does not exceed 110 F/g and 150 F/g in organic and aqueous (KOH) electrolyte, respectively, which leaves the door wide open to biomass-derived carbons¹⁹².

According to Signorelli *et al.*¹⁹³, the electrode surface area, the gravimetric and volumetric specific capacitance (C_s), the frequency-dependent impedance response (the equivalent series resistance and the “knee” frequency), and the shape of the cyclic voltammetry (CV) curves are the basic metrics of EDLC performance. In addition, given the energy storage mechanism underlying the operation of EDLC, all of these metrics are, to a variable extent, a function of the electrode material, its morphology and physico-chemical properties, as well as the function of the electrolyte¹⁹⁴. The requirements for ideal capacitor component are, however, not the same for the two. While the selection criteria for the ideal electrolyte can be narrowed down to high ionic conductivity, high ion mobility, and wide potential and temperature working range, many more criteria have to be considered when selecting a promising carbon-based electrode material. The ideal candidate in this case should feature high electrical conductivity and low electrical resistivity, high surface area easily accessible to electrolyte ions, optimal pore size, length and connectivity (hierarchical pore structures are preferred), low self-discharge, and relatively low cost¹⁹⁴. Also, it should be designed and

synthesized in accordance with the principles of green chemistry (i.e., cost-effective and energetically efficient processes utilizing low-risk, environmentally benign precursors). That is why biomass-derived (activated) carbons have entered the “energy storage war” and quickly become a strong competitor to commercial products.

Although the specific capacitance of the “real” EDLC electrodes is not directly proportional to their SSA, tuning the SSA of the biochar is often the first intuitive step towards high-performance energy carriers. As can be seen on the examples of corn waste-derived carbons given in Figure 12, it is not a foolish approach because higher SSA is directly translated into higher C_s of the symmetric capacitor.

Figure 12 Carbons derived from different corn wastes¹⁹⁵⁻¹⁹⁸ and their corresponding SSA, V_{micro} , and C_s . The corncob graphics was designed by BSG Studio¹⁹⁹. The corn grains were designed by Omelapics²⁰⁰.

In this way, however, the EDLC capacitance cannot be increased infinitely. Starting from 2000 m^2/g the gain in C_s is usually smaller, if any,¹⁶⁷ because the large surface area is not supported by well-organized pore network, enabling efficient charge transfer and storage. Moreover, the contribution of

the pore size, length, and connectivity to the charge storage ability of the electroactive material is often underestimated. As we will show at the end of this subchapter it may significantly add to the energy-storage-value of the biomass-derived carbon even if its surface area is low.

Cellulose-rich biomass has in general a wide appeal for manufacturing of (micro)porous carbons for EDLCs. The reason for this lies in i) an adequate carbon content (around 40%)²⁰¹, ii) the presence of natural activating agents (earlier described as impurities in Chapter 10.3.1), and iii) relatively narrow thermal decomposition range, all of which render this biopolymer a fairly good carbon precursor²⁰². Adding a well-thought-out thermal processing conditions and carefully selected activation method, it is almost a ready recipe for high-SSA EDLC carbon with pore size distribution matching to that of commercial AC, e.g. Norit Super 50. This has been demonstrated by Wang and co-workers¹⁹⁵, who studied the influence of the activation temperature of biomass-derived carbon on its surface area, morphology, and microstructure. Through pyrolysis followed by chemical activation with KOH, they prepared a series of corncob-based ACs and assessed their charge storage abilities in two-electrode symmetric system with either acidic or basic electrolyte. The results are summarized in Figure 13.

Figure 13 Comparison of the electrochemical performance of different corncob-derived carbons in two-electrode system (left) in 0.5M H₂SO₄ and (right) 6M KOH electrolyte. Data points extracted from Table 4 from reference ¹⁹⁵.

Contrary to the previous example shown in Figure 12, herein the specific capacitance increased proportionally to the SSA of the corn waste-derived carbons. Interestingly, C_s values were on average

50 F/g higher when H_2SO_4 was used as the electrolyte, which might be due the presence of quinone groups on the surface of the carbon, bringing pseudocapacitance into the system¹⁹⁵.

In one case or the another, the best-performing corncob-based carbon was that activated at 850°C (C850) with the highest proportion of meso- to micropores (0.651 to 0.492 cm^3/g). The use of a pair of C850-based electrodes in EDLC instead of that based on Norit A Supra carbon resulted in almost two times higher capacitance at low current density. The values of the capacitance dropped off about 20 to 60 F/g and 30 to 10 F/g for the C850- and Norit A Supra-based EDLCs, respectively, at high current density, at which the specific capacitance is controlled mainly by the average micropore width²⁰³ and the number of groups generating CO_2 ⁶⁶, yet still the corncob-derived carbon was able to store more charge. This was possible not only due to the well-developed surface area of the latter carbon but also a great variety of functional groups present thereon that improved its wettability and electrical conductivity.

Another interesting bio-precursors containing cellulose in its structure (in the cell-walls) are seaweeds (Figure 14). The carbon derived from this biomass is also a good example illustrating the importance of matching the pore size to the ion size¹⁶⁷. This kind of materials were prepared by Raymundo-Piñero et al.¹⁶⁹ through direct pyrolysis of *Lessonia Nigrescens* (LN, no activation).

Seaweeds are rich in hydrocolloids, e.g.:

= carbon precursors

Carbon derived from ...

***Durvillaea Antarctica*: $S_{\text{BET}} = 416 \text{ m}^2/\text{g}$**

***Lessonia Nigrescens*: $S_{\text{BET}} = 746 \text{ m}^2/\text{g}$**

$S_{\text{BET}} = 1307 \text{ m}^2/\text{g}$

Figure 14 Carbons derived from different seaweeds and their corresponding SSA. Seaweeds graphics was designed by Artsybunnies²⁰⁴.

Even if the surface area of these carbons did not significantly exceed $1300 \text{ m}^2/\text{g}$, the capacitor assembled with a pair of LN900-based electrodes (900 denotes the carbonization temperature) outperformed that with commercial AC, Norit Super 50, in both aqueous (175 *versus* 119 F/g, respectively, in 1 M H_2SO_4) and organic electrolyte (94 *versus* 79 F/g, respectively, in 1 M tetraethyl ammonium tetrafluoroborate (TEABF_4) in acetonitrile). The result is even more impressive given that the LN900 carbon was “activated” taking the advantage of natural porogens present in the seaweed, mainly Na- (sodium alginate) and K-derivatives (usually carrageenan – a potassium-rich carbohydrate), homogeneously distributed in the bulk of this biomass¹⁶⁹. The auto-activation of the LN seaweeds during the carbonization resulted in hierarchically porous material with meso- and micropores in the range of 3.0 -4.0 nm and 0.7 – 0.8 nm, very beneficial for double-layer formation¹⁶⁷.

Figure 15 (Left) Comparison of the electrochemical performance of different seaweed-derived carbons in symmetric two-electrode capacitors in 1 M H_2SO_4 electrolyte. Data points extracted from Table 1 from reference ¹⁶⁹; (Right) Electrochemical performance of LN600- and LN750-based capacitors in three different electrolytes: 0.5M Na_2SO_4 , 6M KOH, and 1M H_2SO_4 . Data points extracted from Table 5 from reference ⁶⁶.

Certainly, these results are a good prognostic for successful implementation of the biomass-derived carbons in commercial EDLCs. Therein, however, paring the AC with H_2SO_4 electrolyte, in which the capacitance values for seaweeds-derived carbon were the highest (Figure 15, left), is not

recommended. H_2SO_4 is corrosive to current collector, cable connections and other metallic components of the capacitor⁶⁶. That is why the pursuit of “green carbon” electrode material for capacitor application is often accompanied by the pursuit of high-performing electrolyte, and once the promising carbon material is found, it is subsequently tested with different electrolytes, for example with KOH and Na_2SO_4 ⁶⁶ (Figure 15, right).

Organic electrolytes such as for example TEABF₄ in ACN are usually used to study and understand the relationship between the capacitance and the pore size²⁰⁵⁻²⁰⁶. In general, the capacitance increases with the pore size approaching that of the bare electrolyte ions, i.e., 0.7 nm. However, if other electrolytes are used (LiTFSI in alkyl carbonates: EC/PC/3DMC), the optimal carbon pore size required to obtain the maximum capacitance is often no longer 0.7 nm as it depends on the electrolyte/solvent(s) pair used. In the case of LiTFSI in ACN, this value remains at 0.7 nm (Figure 16, left, b and c). For the EC/PC/3DMC electrolyte, however, the optimal pore size increases up to almost 1.0 nm (Figure 16, left, a). This might be due to the stronger interactions between the LiTFSI salt and the alkyl carbonate solvent, leading to a difficulty in desolvating the LiTFSI ions and, thus, requiring wider pores to accommodate such ions. This is not the case for the ACN solvent, the ions of which are more easily desolvated and, thus, able to access smaller pores. In addition, the described electrolyte pore penetration becomes even more important with increasing current density (Figure 16).

Figure 16 Relation between the specific capacitance normalized by specific surface area and the pore size in 1 mol/L LiTFSI in EC/PC/3 DMC (a), TEABF₄ in ACN (b), LiTFSI in ACN (c) for activated carbon derived from coconut shells activated with CO₂ gas, at (left) 100 mA/g and (right) 1000 mA/g. Reprinted from reference ¹⁶⁴ with the permission from Elsevier.

The choice of the electrolyte/solvent(s) pair is, however, not solely limited to the ease of ion-pair formation, high ionic conductivity, and high ion mobility, but also to the affinity of the functional groups present on the surface of carbon to the electrolyte ions⁶⁶. The latter brings about the pseudo-faradaic reactions and, thus, is a source of additional capacitance in the system, which will be the subject of the following subchapter.

10.5. Carbon-based capacitors with pseudocapacitive effects

A common approach to trigger the pseudo-faradaic reactions in the system is to employ electrodes based on doped carbons. Nitrogen is the most reported dopant^{186-187, 207-210}. It does not, however, stand alone, and is always accompanied by the oxygen naturally present in the biomass. Sometimes besides nitrogen (and oxygen), carbon is also doped with S^{207, 211}, P¹⁷⁷ or a mixture of heteroatoms²¹¹. It should be reminded here that during the pyrolysis of biomass various oxygen and nitrogen groups are formed (see Figure 10 in Chapter 10.3.4), the chemical composition of which depends mainly on the biomass source, pyrolysis temperature, and activation conditions. In addition, the oxygen groups

might be either acidic (anhydride, carboxyl) or basic (ether, phenol, quinone)²¹², which, in turn, define their interactions with the electrolyte. In the alkaline electrolyte (KOH) acidic O-groups react with hydroxyl ions (OH⁻) ((1) and (2)), whereas in the acidic electrolyte (H₂SO₄) basic O-groups interact with protons (H⁺) (3)²¹³⁻²¹⁵. These and other redox reactions originating from the interactions of the surface functionalities with the active species in the electrolyte are usually tracked by means of cyclic voltammetry performed in three-electrode cells.

In the case of N-functional groups, the attribution of the pseudocapacitance is still under intense debate in the community. Some authors associate it to the pyrrolic and pyridinic N-groups, which are negatively charged and located at the edges of carbon. Also, although quaternary-N groups are known to mainly enhance the electron transport, some studies showed that they might bring the pseudocapacitance into the system, in both acid and basic electrolytes^{188, 216}. Possible redox reactions involving pyridinic, pyridone, and pyrrolic N-groups are given below^{177, 217}:

Figure 17, left, shows the relation between specific capacitance, C_s , of different biomass-derived carbons in alkaline electrolyte, KOH, as a function of the atomic percentage of nitrogen and SSA. As can be seen, there is no clear correlation between these parameters, which might be related, among others, to: i) the material characteristics, ii) the interactions of the doped-carbon with the electrolyte, and iii) the electrode formulation and the testing conditions, each of which has a strong impact on the electrochemical performance. As explained before, the presence of nitrogen in the carbon structure is always accompanied by the presence of oxygen, which, in turn, leads to a large variety of possible pseudo-faradaic interactions with the electrolyte ((1) - (5)). In addition, the nature and the amount of N- and O-groups directly influence the wettability and the electronic conductivity of the material and, thus, also the diffusion of the electrolyte ions and the charge propagation. Carbon texture (e.g. SSA), important for the formation of EDL, has also its large share in defining the performance of the capacitor and if composed of very small pores inaccessible to the electrolyte ions it might as well limit C_s .

Figure 17 (Left) Specific capacitance of different biomass-derived carbons tested in 6M KOH electrolyte as the function of the amount of nitrogen (at%) and SSA, plotted using data points extracted from the following references: ^{174, 179, 186-188, 191, 207-211, 218-219}; (Right) Gravimetric capacitance

vs. number of basic groups at different current loads. Adapted from reference¹⁷⁷ with the permission from Elsevier.

Therefore, it is very difficult to unambiguously evaluate the role of N-and O-functional groups in enhancing the performance of the capacitor due to their co-existence, and different amount and types present in carbon. In an attempt to do so, N-free carbon materials with similar characteristics (SSA, pore size distribution, morphology, and structure) to those of the carbon doped with nitrogen should be prepared. This is, however, a very difficult and challenging task to fulfill. In addition, the variety of electrode preparation recipes (the active material loading, the type of binder used and the formulation as such), electrode testing conditions and capacitance calculation (from two- or three-electrode cell configuration, from different current densities) contributes to the difficulty of obtaining reliable correlations in most of the cases. Despite that, Seredych *et al.*¹⁷⁷ demonstrated that in the acidic medium a linear correlation between the number of basic nitrogen (pyridinic and pyrrolic) and the oxygen surface groups (quinone) could be established¹⁷⁷ (Figure 11, right). In addition, the correlation coefficient increases together with the current density, reaching almost linear dependence at 1 A/g. This, as explained by the authors, is because of a strong contribution of the electrochemically active basic functionalities to the capacitance at high current densities. At lower current densities (mild operation conditions), however, SSA and the formation of double-layer are the main contributors to the C_s . To the contrary, no correlation was found between the number of acidic surface groups and the obtained capacitance.

10.6. Asymmetric and hybrid capacitors

As already mentioned, today's capacitors are expected not only to provide high power and, thus, to support the batteries in successfully fulfilling their tasks, but also to store more energy. For this purpose, according to the following equation: $\frac{1}{2} C_s \cdot U^2$ not only should the specific capacitance, C_s , be enhanced but also the operational voltage (U) window. It can be achieved by either employing wide-voltage-window electrolyte (organic electrolyte or ionic liquid) or further elaborating on the concept

of the SC. For the latter, asymmetric and hybrid capacitors are the “returning newbies” in the field. Although both are built-up from a pair of dissimilar electrodes and, thus, offer significantly wider operational voltage window (compared to ≈ 1.0 V and ≈ 2.7 V in aqueous and organic electrolyte, respectively²²⁰), and enhanced energy density, they do not have the same working principle²²¹. Asymmetric capacitor (AsC) can be considered as an adduct of the pseudocapacitive and electric double-layer Cs (Figure 18, left). Hybrid capacitor (HEC) also utilizes capacitor-like electrode, either pseudocapacitive or EDLC electrode. It pairs it, however, with a battery-like counterpart²²², aiming at simultaneous gain in energy and power densities. It is therefore obvious that the requirements for the biomass-derived carbon for both applications are not exactly the same as we will try to point it out herein on the selected examples. The focus will be therefore on the material and its performance in SC, without entering into the discussion as to whether the described system is still asymmetric or already a hybrid one.

Corn²²³, potatoes²²⁴ and other starch-rich biomass are among the good candidates for ASC negative electrode material. In general, the structure of starch built-up from glucose-based repeat units resembles that of the cellulose. Unlike the cellulose, however, it contains not one but two glucose units, linear amylose and branched amylopectin, which tend to self-assemble into organized lamellar structures²²⁵. This intrinsic ability is used for the synthesis of pore-size-controlled mesoporous materials, the preparation of which usually requires the templating agent, e.g. mesoporous silica²²⁵, and is associated with aggressive and potentially hazardous strong acid/alkali reactions upon the removal of the template²²⁵⁻²²⁶. It was also the seed of the bio-based family of mesoporous materials known under the tradename Starbon®. The SSA of the starch-based carbons prepared through classical pyrolysis followed by chemical activation typically exceeds 1300 m²/g. It drops, however, sharply to almost one-third of this value when pyrolysis is preceded by HTC and the resultant biochar is not activated anyhow¹⁹⁶. The latter was the case of potato starch-derived carbon prepared by Rubinin and the co-workers²²⁴. Bound to acetylene black with Nafion, and paired with reduced graphene oxide (rGO) positive electrode, this biomass-derived carbon showed very promising and

highly reversible capacitive characteristics with less 12 F/g difference between the extreme values of applied current densities, that is, 1 and 20 A/g (68.7 and 57 F/g, respectively) (Figure 18, right). The practical potential window of potato starch derived-carbon // rGo capacitor utilizing aqueous electrolyte (1M KOH) was up to 1.5 V, leading to 21.5 Wh/g and, thus, rendering the concept of ASC an interesting solution to store more energy.

Figure 18 (Left) Configuration of the asymmetric capacitor assembly; (Right) Specific capacitances calculated from galvanostatic charge/discharge curves of the asymmetric capacitor with 1M KOH electrolyte as a function of current density. Data points extracted from reference ²²⁴. The potatoes graphics was designed by BSG Studio²²⁷

Besides the precursors rich in starch, other raw materials containing less of this polymeric carbohydrate (usually between 1 and 4 wt% of pectin)²²⁸ were also considered for the preparation of high-performance ASC negative electrodes. The representatives of this low-starch materials group, banana-²²⁹ and hemp stem-fibers²³⁰, have proven to be promising precursors for high-performance porous carbon materials. Interestingly, although both biowastes were not processed in the same conditions, the morphology of the end-product was almost alike, with well-arranged arrays of mesopores forming a 3D honeycomb (Figure 19). Even though this highly ordered open-pore structure does not have a high SSA, it certainly offers high electrical conductivity, which, in turn facilitates the electron and ion transport at the electrode/electrolyte interface²³⁰. Paired with

carefully selected transition metal-based counter electrode, bringing in pseudocapacitance and significantly adding to structural stability during cycling, these materials can cycle up to 2.0 V (in aqueous electrolyte – 1M KOH), without apparent distortions in nearly rectangular CV profiles. Moreover, a synergy between the unique structural and electrochemical properties of each and every material used to assemble given ASC resulted in energy density higher than 30 Wh/kg, leaving other biomass-derived competitors, such as jackfruit peel-based carbon²³¹, behind.

Figure 19 Configuration of the asymmetric capacitor assembly in which the EDLC-like electrode is derived from either banana- or hemp stem-fibers. The SEM picture showing the 3D honeycomb-like morphology of the derived carbons is reproduced from reference ²²⁹ with the permission of Elsevier.

In all the examples of ASCs given thus far, the negative electrode was based on biomass-derived material storing the energy through the formation of double-layer. Although the results were promising, the capacitance of the entire system, expressed as a sum of specific capacitances of both electrodes, C_{s+} and C_{s-} , was always limited by carbon, whose charge storage ability is certainly lower than that of transition metal oxide. One idea to tackle this might be to employ biomass-derived carbons with highly-developed surface chemistry, in particular those containing nitrogenated functional groups, which trigger the redox reactions and, thus, boost the specific capacitance remarkably (few orders of magnitude)²³². To this end, Li and co-workers²¹⁰ converted N-rich bio-

precursor, chicken egg whites, into high functionality – high surface area capacitor electrode. Knowing that the activation temperature higher than 600°C risk the loss of nitrogen functionalities, they proposed an alternative processing of the denatured proteins, which does not require the use of template. Low-temperature activation under the flow of argon resulted in highly microporous material (SSA and total volume up to 1405 m²/g and 0.73 cm³/g, respectively) containing high amount of both nitrogen and oxygen functional groups. Therefore, it is not a surprise that the ASC assembled with this highly functionalized AC and NiCo₂O₄ / graphene positive electrode delivered twice the energy density of the same capacitor with commercial activated carbon (48 *versus* 23 Wh/kg).

With their pseudocapacitive properties N- and other heteroatom-doped carbons can be also used as positive electrodes. This is the case of the hybrid capacitors (HCs) combining carbon-based electrode with that employed in high-energy Li-ion batteries (Figure 20). For the latter, the choice usually falls on silicon offering high theoretical energy (and power) density. There are, however, also examples of other materials, such lithium titanate (Li₄Ti₅O₁₂) and metallic lithium¹⁰², used in HCs. Similar to the case of conventional positive electrodes in Li-ion batteries, the capacitor-like electrode also struggles to match the specific capacity (or capacitance) with that of the counter electrode. Fortunately, high diversity of biomass precursors with different, often unique, structural properties and wide range of their processing/converting methods enable obtaining materials with performance tailor-made characteristics.

Li *et al*²³³ used N-doped activated carbon and Si/C composite to explore the benefits of the multiple almost equally involved energy storage mechanisms, double-layer formation and pseudocapacitance, and alloying / de-alloying reactions with Li, in one system. The carbonaceous material was prepared from corncob in one step, by mixing the pre-dried biomass with KOH and subsequently heat treating it at high temperature (400 or 600°C) under the flow of NH₃/N₂ mixture. Cycled in the hybrid system versus Si/C electrode, it enabled attaining high energy density of 230 Wh/kg without scarifying the power density of the device. Interestingly, when the corncob-derived carbon was replaced by that

obtained from egg white²³⁴, the energy density of the HCs increased even further, almost up to 260 Wh/kg (at a similar high power density). The latter result was ascribed to the synergetic effect of the presence of oxygenated surface functional groups, partial graphitization of the bio-carbon, high SSA and highly developed microporosity, and good electronic conductivity.

Figure 20 Configuration of the hybrid capacitor assembly in which the SC-like electrode is derived from either corn leaves, or chicken egg whites, or (cooking) oil. The corn cob graphics was designed by BSG Studio¹⁹⁹.

Despite the promising C_s and energy densities demonstrated at the cell level, today's green capacitors do not have an easy life. More and more often sustainable high-capacitance performance is expected to go hand in hand with flexibility and an ease of fabrication in any shape and size²³⁵⁻²³⁶. Also in this case the granular self-assembly of starch into various shapes²³⁷, from elongated to polygonal granules²³⁷, is an attribute, particularly in decreasing the inter- and/or intraparticle electrical resistance, shortening the diffusion lengths,²³⁸ and increasing packing density, and, thus, enhancing the rate capability and the amount of energy that can be stored in capacitor at a given mass²³⁹. However, despite the promising performance characteristics described earlier in this chapter, the 3D spherical shape of the potato starch-derived carbon does not seem to be the most optimal geometry for increased charge accumulation (usually it suffers from low ion-accessible

surface area) and rapid electron transfer^{236, 238}, important requirements that can be successfully met using 1D (nano)structures. The latter as shown by Ouyang and co-workers²³⁸ can be produced from biomass not necessarily predisposed to self-assemble into particular shape as is tofu with its irregular particle-like morphology. In the described study, ZnCl₂-molten-salt-assisted calcination of the soybean curd resulted in the formation of 1D carbon nanobelts (CNB) with the SSA between 938 and 1208 m²/g, depending on the residence time, and interconnected pores network. The latter was built up mostly from mesopores, which occupied more than 80% of the total pore volume, lowering the density of the CNB, but giving a promise of fast ion transport and low contact resistance. In addition, the quaternary, pyridinic, and pyrrolic nitrogen doping inherited from parent material significantly enhanced the electronic conductivity of 1D carbon nanobelts and brought in the pseudocapacitance²³⁸, further increasing the amount of charge stored in capacitor. Indeed, the AsC assembled with a pair of nanobelts carbon (CNB)-based electrodes, negative CNB and positive MnO₂-CNB electrode, exhibited an outstanding electrochemical performance (29 Wh/kg) with 96% capacity retention at the high current density of 3 A/g. Moreover, it could have been operated stably up to 2.0 V in aqueous electrolyte. A multiplication of the two, the capacitance and the voltage, resulted in nearly 30 Wh/kg, leaving behind most of the previously reported ASC with MnO₂-based electrodes²⁴⁰⁻²⁴².

10.7. Conclusions and prospects

Sustainable development intensified the research on the electrode materials with “environmental origin”. Activated carbons derived from biomass certainly have a broad spectrum of features beneficial for electrochemical capacitors – high specific surface area, well-developed porosity, and often do contain heteroatoms altering the electrode conductivity and its accessibility for the electrolyte ions. However, the term biomass is sometimes misused, and the parent materials considered as a “waste” and, thus, as good candidates for the carbonization, do serve well in other, often more important applications than the energy storage.

Another important issue is the reproducibility of the carbons obtained from biomass. Large-scale batches of the electrode materials produced for industrial applications need to have similar morphological and structural characteristics to be considered as viable. For some precursors this might not be the case.

For fundamental research, as a starting electrode material, biomass brings in many opportunities for further development of electrochemical capacitor technology. However, the capacitance values reported for SCs with biomass-derived carbon-based electrodes should always be verified at the cell level – specific and/or volumetric capacitance values calculated for the three-electrode cell rarely do coincide with those of the end-device. In addition, the specific and/or volumetric energy can only be estimated for the cell. The same concerns also the cycling stability and cycle-life investigations.

One of the significant advantages offered by biomass-derived carbons is that some of them can be formulated into electrodes without the binder (binder-free electrodes). This is an important step towards the development of sustainable devices free from fluorine-based polymers. This kind of devices – all-solid-state electrochemical capacitors employing biomass-derived materials are recently being developed for portable electronics.

Certainly, despite the numerous efforts and significant progress in the “waste to wealth” conversion of biomass to supercapacitor electrode materials, there is still a room for improvement in specific capacitance and efficient charge propagation. These issues might be, to a large extent, solved by introducing into the system the pseudocapacitive effects through either incorporation of heteroatoms or the choice of the electrolyte. Last but not least, it seems that hybrid devices, bringing together the capacitive and redox-based charge storage phenomena, are the next step in electrochemical capacitors development. Sustainable biomass-derived carbons with their versatile properties will definitely play an important role in this process.

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