

MISS VIOLA HOFFMANN (Orcid ID : 0000-0003-4014-5119)

Article type : Original Research

Study of the electrical conductivity of biobased carbonaceous powder materials under moderate pressure for the application as electrode materials in energy storage technologies

Viola Hoffman, Catalina Rodriguez Correa, Dennis Sautter, Emilio Maringolo, Andrea Kruse*

University of Hohenheim, Institute of Agricultural Engineering, Department of Conversion Technologies of Biobased Resources, Garbenstrasse 9, 70599 Stuttgart, Germany

Keywords: biomass carbonization, carbon materials, electrical conductivity, energy storage, electrochemical double-layer capacitor (EDLC), bioeconomy, biobased materials, carbonaceous powders, nanocomposites

Paper type: Original Research

E-Mail addresses: catarod@uni-hohenheim.de (C. Rodriguez Correa), sautter-dennis@web.de (D. Sautter), emilio.maringolo@freenet.de (Emilio Maringolo), andrea_kruse@uni-hohenheim.de (A. Kruse)

* Corresponding author: Viola Hoffmann, *Phone:* 0711-459 23933, *E-Mail address:* viola.hoffmann@uni-hohenheim.de

Abstract

This paper focusses on the assessment of the electrical conductivity (EC) of biobased electrode materials for the application in energy storage devices and presents a simple and reproducible method to measure the EC of carbonaceous powders under moderate pressure (10 - 50 N). Based on the pyrolysis of corncob at three different temperatures (600 °C, 800

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/gcbb.12545

This article is protected by copyright. All rights reserved.

°C, 900 °C) and further treatments of the biochar obtained at 600 °C, 11 different carbonaceous powder materials were produced including biochars, activated carbons and composites. Composite materials were obtained by adding either metal oxides (RuO_2 or Fe_3O_4) in different proportions or additives which are commonly used in electrode production (5 wt% binder and 15 wt% conductive additive). Furthermore, one physically activated commercial AC based on peat with a known EC of 33 S m^{-1} was treated with additives and used as a reference. For all materials, an increase of applied pressure resulted in higher EC values due to closer particle contact. The comparison of two methods (with and without pre-load) showed that a pre-pelletisation of the samples is not necessary to obtain reliable results. By analysing the obtained EC values while taking mechanical and physico-chemical properties into account, it could be shown that a high carbonization temperature and high specific surface area favor the increase of EC. Furthermore, certain proportions of metal oxides lead to an improvement of EC (40 wt% RuO_2 , 10 wt% Fe_3O_4) while the treatment with additives lead to a decrease of EC. The EC values among all samples varied between 0.8 S m^{-1} (biochar) and 408 S m^{-1} (AC/ RuO_2 composite) at the highest pressure level (637 kPa). Thus, promising biobased electrode materials for environmentally friendly energy storage technologies are presented with the aim of contributing to the establishment of a biobased resource and product platform for Bioeconomy.

Introduction

Establishing a circular economy as an essential part of a sustainable bioeconomy within the framework of the decoupling of economic growth from fossil resources requires, inter alia, the development of innovative biobased materials for future-oriented energy conversion and storage technologies. Electric Double Layer Capacitors (EDLC) represent a key technology in the field of energy storage as they combine extraordinarily high capacities (up to 8 000 F)

and relatively high power densities (up to 10^4 W/kg) (Sharma & Bhatti, 2010; Yassine & Fabris, 2017). Due to these properties, EDLCs are of special interest for the application in electric or hybrid vehicles, as integrated storage in electronic devices or in the field of renewable energy storage (Kotz et al., 2000; Kurzweil & Dietlmeier, 2015). As a result, the global market volume for EDLCs reached EUR 980 million in 2015 and an increase up to EUR 4 billion until 2025 is anticipated – a development which will mainly be driven by the expanding demand for emission-free driving technologies (Lux Research, 2013).

An increasing demand for EDLCs implies the need for large amounts of electrode materials which, at best, exhibit high specific surface areas (SSA), tailored pore size distributions and certain surface functionalities (Frackowiak & Béguin, 2001; Ghosh & Hee, 2012; Hu et al., 2010; Pandolfo & Hollenkamp, 2006; Wang et al., 2015). By carbonization of biomass under inert conditions (pyrolysis), it is possible to produce environmentally friendly materials with the above-mentioned properties (Raymundo-Piñero, Cadek, & Béguin, 2009). In addition to these physico-chemical properties, which favour high power and energy densities, high electric conductivity (EC) of the electrode materials is crucial to ensure electron mobility and avoid high internal resistances of the EDLC (Bonnefoi, Simon, Fauvarque, Sarrazin, & Dugast, 1999; Pandolfo & Hollenkamp, 2006).

However, to the best of knowledge, only few studies of biobased carbon materials consider the EC when assessing the electrochemical performance (Pandolfo & Hollenkamp, 2006; José Sánchez-González, Stoeckli, & Centeno, 2011). The reason for this may be the fact that there is no standard method for determining the EC of carbonaceous powders despite extensive studies in this field have been conducted since the 1950s (Euler, 1978; Marinkovic, Suznjevic, & Djordjevic, 1971; Mrozowski, 1957). Besides, the EC in carbonaceous powders and the underlying mechanisms are highly complex and are determined by different factors such as the particle morphology and size distribution, the intrinsic resistances of the particles,

the mean coordination number of a certain grain, the contact area and the resulting conducting pathways (Celzard, Maréché, Payot, & Furdin, 2002). Rough surfaces of the particles allow only small contact areas between them which lead to constriction resistances. Additionally, the tunnel effect contributes to the conductivity when conducting electrons pass thin contact films between two particles (Holm, 2000). However, the tunnel effect is taking place especially in the case of thin oxide films on metallic powders (Celzard et al., 2002).

Attempts to mathematically describe constriction resistances were done by Holm (Holm, 2000), but apply only for perfectly spherical particles. Hence, this is not applicable for carbon powders which contain rough particles with varying diameters and morphologies. Besides, according to the contact theory established by Mrozowski and Holm (Holm, 2000; Mrozowski, 1957), the compression of powders is necessary to reduce the voids between particles and thus increase the inter-particle contact area. Only in this way, conducting pathways are established and conductivity measurements are possible. Nevertheless, the obtained results can always only be an approximation of the real intrinsic conductivity value of the carbon particles since some void spaces always remain despite compression (Holm, 2000).

The application of moderate pressure on carbon powders leads to a partial deformation of the particles which results in an irregular formation of conducting pathways throughout the sample. Functional surface groups and heterogeneous composite materials (e.g. metal oxides or additives) modify both the capacity and the conductivity of the carbon materials. Since it was shown that exactly these heterogeneous materials show promising capacitive behaviour as electrode materials for EDLCs because of their pseudo-capacitive properties (Frackowiak & Béguin, 2001; Hulicova-Jurcakova et al., 2009; Raymundo-Piñero et al., 2009; Su, Wu, Bao, & Yang, 2007; G. Wang, Zhang, & Zhang, 2012; Zhao, Xia, & Zheng, 2012; Zhi, Xiang, Li, Li, & Wu, 2013), the present study focusses on EC measurements of such

Accepted Article

heterogeneous materials. Past studies on carbon blacks (CB) already showed that conductivity increases with decreasing content of oxygen- and nitrogen-containing surface groups on the carbon surface (Pantea et al., 2001) and that composites of activated carbon (AC) and certain metal oxides (e.g. Al_2O_3 , Fe_2O_3 , SnO_2) show lower conductivity values than the pure AC (Barroso-Bogeat, Alexandre-Franco, Fernández-González, Macías-García, & Gómez-Serrano, 2014). Furthermore, the EC of CB is positively correlated with graphitic structures on the surface of the carbon (Dana Pantea, Darmstadt, Kaliaguine, & Roy, 2003). This paper presents the results of conductivity measurements under moderate pressure (max. 637 kPa) of 12 different biobased materials including activated carbons (AC), carbon composites with metal oxides (AC + RuO_2 or Fe_3O_4) and electrode materials (AC + binder or conductive additives). The results were obtained by applying two different measurement methods (with and without pre-load) and they were analysed considering the different material compositions and their effect on conductivity. Besides, the two measurement methods were compared. Since in literature, to the best of knowledge, no works dealing with EC measurements of biobased carbonaceous powder materials based on corn cob and composites can be found, this paper aims to close that data gap, thereby contributing to the development of biobased electrode materials for EDLCs and thus indirectly to the implementation of bioeconomic principles in the field of energy storage technologies.

In order to not exceed the framework of this paper, the content is limited to the presentation and discussion of experimental data while considerations regarding the mathematical description of the experimental data by applying different models such as the percolation theory, the effective media theory or the general effective media approximation are not included. For a detailed discussion on the mathematical description of electrical conductivity of carbonaceous powders including the above-mentioned models, it is referred to the work of Celzard et al. (Celzard et al., 2002).

Materials and methods

Materials

The EC of 12 powdered carbon materials and composites was determined. Three of the powders were biochars (referred to as P for pyrolysis) produced from corncob (*Zea Mays*) collected from the agricultural experiment station Heidfeldhof of the University of Hohenheim. The corncob was dried, cut into pieces of approximately 10 cm and pyrolyzed under constant N₂ flow of 3 l/min following two different heating programs. The first program consisted in heating up the corncob pieces up to either 600 or 800 °C with a constant heating rate of 10 °C/min. After reaching the temperature, the chars were left to react for 1 h. The second pyrolysis program consisted of two sets of heating ramps: first, the corncobs were heated up to 300 °C with a constant heating rate of 5 °C/min and were left to react for 1 h. This was followed by a second ramp with a heating rate 5 °C/min up to 900 °C and a reaction time of 1 h.

Another sample was an activated carbon (in the following referred to as AC-600-800) produced from the pyrolysis char produced at 600 °C. For the activation, the pyrolysis char was mixed with KOH with a char:KOH mass ratio of 1:4 in nickel crucibles. The crucibles were put inside a reactor that was constantly purged with a N₂ flow of 5 L/min. The reactor was inserted into a muffle furnace previously heated to 800 °C and when the reactor reached the furnace temperature, the samples were left to react for 2 h. Subsequently, the reactor was cooled down to room temperature and the mixtures were washed with distilled water, aqueous HCl (2 mol/L) and distilled water again until the electrical conductivity of the leachate was lower than 30 µS/cm. Finally, the activated carbons were dried for at least 16 h and stored for further analysis.

The last eight samples were composite and electrode materials produced using the activated carbon AC-600-800 as basis material.

Accepted Article

These composites can be classified in three groups: One group was the activated carbon combined with different percentages of Fe_3O_4 (5 wt%, 10 wt%, 20 wt%, 40 wt%), another group was the activated carbon treated with different percentages of RuO_2 (10wt %, 40 wt%) and the last group were the two different activated carbons (AC-600-800 and one commercial AC) mixed with 5 wt% Teflon binder (PTFE) and 15 wt% acetylene black (AB). These last two samples are also referred to as electrode materials as the preparation additives such as binder and conductive agent is necessary during the electrode production. That is why the influence of these additives on the conductivity of a sample is of great interest and is additionally assessed here.

Table 1 gives an overview about the starting material, the additives and the abbreviation of the composite materials.

Methods

Elemental composition

The elemental composition (C, H, N, S and O) of the pyrolysis chars and activated carbon was determined with an EA CHNSO Elemental Analyzer (HEKAtech) according to the DIN standard 51732. The ash content was determined by difference (Eq. 1).

$$\%Ash = 100 - \%C - \%H - \%N - \%S - \%O$$

(1)

Elemental analysis was conducted only for the four carbon samples including three biochars P600, P800, P900 and the activated carbon AC-600-800. Since the elemental composition of the carbons does not change during the treatment with metal oxides or other additives, an elemental analysis of the composite and electrode materials have been considered to be redundant and therefore unnecessary.

DC electrical conductivity measurements

Conductivity measurements were conducted by using a self-constructed device based on a procedure described elsewhere (Barroso-Bogeat et al., 2014; Celzard et al., 2002; J. Sánchez-González, MacÍas-García, Alexandre-Franco, & Gómez-Serrano, 2005). The device consists of two parts: the bottom part is made of a brass bracket with a fixed glass cylinder (inner diameter: 1 cm) and the upper part is a movable brass-stamp on which different pressures can exactly be applied by using a material testing system of Instron (Instron GmbH) with an integrated altimeter for determining the height of the respective sample after applying different pressures.

Two different methods based on the 2-pin method were tested to determine the conductivity of the samples. A 4-probe technique was not considered useful here as it is known to be less reliable concerning inhomogeneous, powdery samples (Celzard et al., 2002).

Pre-tests with a constant mass of 0.09 g for each sample showed, that the height of the sample varies significantly between the different materials. Since the length of the sample has a great influence on the EC, the results would not be comparable. Therefore, it was decided to develop a method during which the height of the sample remains constant instead of a constant mass with the aim to reach a higher comparability and reproducibility of the method. Hence, for both methods, it was focussed on holding the sample height constant at 1.1 cm under 50 N.

For the first method (M1), the sample after oven-drying at 105 °C overnight was poured into the hollow thick-walled glass cylinder (inner diameter of 1 cm), and compressed in air between two close-fitting brass plungers forming the electrodes. The resistance was measured with a multimeter (Voltcraft M-4650B) which was connected to the brass bracket and the stamp. Before measuring the resistance, a 5 kg weight was applied to the samples for 2 minutes to compact the powder and to get a regular contact surface between the sample and

the stamp. To test the reproducibility of the measurements, this procedure was conducted three times for each material. During the second method (M2), no pre-load was applied before starting the measurement. Apart from that, the same procedure as during M1 was applied. The accuracy of the device was determined by conducting EC measurements with the conductive additive AB with a known EC of 400 S m⁻¹ (Soltex, 2018) and is ± 0.5 S m⁻¹.

Figure 1 shows a CAD sketch of the measuring device and a scheme of the measurement set-up used for both measuring methods (M1 and M2).

The EC was calculated by using the following formula

$$\kappa = \frac{h}{R \cdot A} \quad (2)$$

with

κ = electrical conductivity [S/m]

h = height of the sample [m]

R = electrical resistance [Ω]

A = area of the sample [m²]

The area of the sample A was $A = 0.79$ cm², the exact height was determined by the altimeter of the Instron device and the electrical resistance was measured with the multimeter.

Results

Elemental composition of the carbon materials

The EC of carbon materials is directly related with their carbon content. More specifically with the polyaromatic carbon content. Polyaromatic carbon in carbonized biomass is organized in randomly organized sheets of graphene, which are directly influenced by the temperature and reaction time of the carbonization process. The elemental composition of the carbon materials is shown in Table 2. During pyrolysis, biomass is decomposed into condensable and non-condensable volatiles and char in a temperature range between 200 °C and 600 °C. The volatiles are composed of organic compounds rich in H, N, S and O; thus, most of the carbon remains in the char. This explains the carbon content increase of the corn

cob from 46.2 wt.% to 81.7 wt.% and the strong decrease of H, N, S and O. At temperatures higher than 600 °C, some volatiles are released but mainly the carbon atoms are reorganized into randomly organized polyaromatic carbon sheets (graphene) (Rodriguez Correa, Otto, & Kruse, 2016). For this reason, at higher temperatures the carbon increase of the samples was less pronounced. The carbon content showed a further increase after the chemical activation with KOH whereas the ash content significantly decreased after KOH activation.

Conductivity studies

Method comparison (M1 versus M2)

The influence of the different measuring methods on the EC is presented in Table 3 for four selected materials (one biochar, one AC, one composite, one AC plus additives). The density for each material was calculated based on Eq. 3:

$$\rho = \frac{m}{l * A} * 1000 \text{ [g/cm}^3\text{]} \quad (3)$$

with

m = mass of the sample [g]

l = length of the sample [mm]

A = cross-sectional area of the sample [mm²]

The density values in Table 3 show the average value of each sample under a force of 10 N (127.32 kPa) or 50 N (636.62 kPa).

The indicators IoEC and IoD have been defined as follows:

$$IoEC = \frac{\kappa_2 - \kappa_1}{\kappa_1} * 100 \quad (4)$$

$$IoD = \frac{\rho_{50N} - \rho_{10N}}{\rho_{10N}} * 100 \quad (5)$$

These indicators allow better comparability of the two methods. By comparing the percentage increase of electrical conductivity and density from 10 N (= 127.32 kPa) to 50 N (= 636.62 kPa) applied force (pressure), some interesting correlations can be observed.

With respect to the sample densities, the comparison of the two methods based on IoD shows,

that with M2, a higher compaction is reached for all materials shown in Table 3. The *IoD* reached with M2 is between 3 - 9 % higher than the *IoD* reached with M1 (Figure 2). With respect to the EC increase, a more differentiated picture emerges. For the biochar (P-600) for example, the *IoD* of M2 is 8 % higher than the *IoD* of M1, which means, that the sample compaction was higher when applying M2. Simultaneously, for P600 the *IoEC* of M2 is 120 % higher than the *IoEC* of M1 (Figure 2). In contrast, the results for the activated carbon (AC-600-800) show a decrease of *IoEC* of 13 % between M1 and M2, even though the *IoD* was slightly higher for M2. The same negative correlation can be observed for the activated carbon with additives (AC-600-800-add), where an increase of 9 % in *IoD* led to a decrease of 10 % in *IoEC* comparing M1 and M2 (Figure 2, left). The results for the composite material containing RuO₂ showed again a clear positive correlation between *IoD* and *IoEC*. A 7 % higher *IoD* was reached with M2 which led to a 48 % higher *IoEC* compared to M1.

It has to be considered that *IoD* and *IoEC* only serve as comparison indicators between M1 and M2 and that, based on these indicators, it is not possible to draw conclusions regarding correlations between density and EC of each material. Furthermore, the absolute density values of M1 at 10 N are already higher than the same values of M2 (Table 3) because of the pre-load (50 N) which can be a reason why the *IoD* for M1 is 3 - 8 % smaller compared to M2.

Considering the absolute EC and density values in Table 3, it becomes clear that a higher density generally leads to higher EC values. However, it is remarkable, how different the materials behave. For P600 for example, it can be observed, that the low sample densities during M2 led to significantly lower EC values (0.02 S m^{-1} and 0.08 S m^{-1}) compared to M1 (3.05 S m^{-1} and 8.54 S m^{-1}), where the sample densities were almost double as high. In

contrast, the RuO₂-composite shows even higher EC values at lower densities (e.g. 316 S m⁻¹ at 1.19 g cm³ (M1) and 408 S m⁻¹ at 1.01 g cm³ (M2)) whereas the sample containing additives again shows higher EC values with higher densities.

Variation of EC with different parameters (M1 versus M2)

EC versus applied pressure (P)

The variation of EC depending on the applied pressure is shown in Figure 3 for both methods and nine different materials each. It can be observed a positive linear correlation between applied pressure and conductivity for all materials, even though the correlation strength is slightly varying depending the material and the chosen method. The correlation coefficient r between EC and P lies between 0.84 - 1 for M1 (Fig. 3a,c) and from 0.97 - 1 for M2 (Fig. b,d) which indicates a strong to perfect linear correlation between the parameters.

The two graphs Fig. 3a, b show the above-average performance of the composite material AC-RuO-40 with conductivity values of up to 408 S m⁻¹ (at 637 kPa). This means a conductivity value nearly six times higher than that of the composite with only 10 wt% RuO₂ (69 S m⁻¹ at 637 kPa).

For the composites with Fe₃O₄, the opposite can be observed: the higher the amount of Fe₃O₄, the lower the EC of the respective composite. By doubling the share of Fe₃O₄ from 10 to 20 wt%, the EC of the composite decreases by almost 25 % for both methods under the highest pressure (M1: from 94.01 S m⁻¹ to 71.14 S m⁻¹; M2: from 80.28 S m⁻¹ to 61.23 S m⁻¹).

By again doubling the share of Fe₃O₄ from 20 to 40 wt%, the EC even decreases by 35 % under the highest pressure. At the same time, an inconsistency occurs for the composite with only 5 wt% Fe₃O₄. It shows almost the same EC values as the composite AC-600-800-FeO-20 for all pressures applied (Figure 4).

Since during electrode manufacturing for EDLCs, additives are added to the active material (Lee et al., 2016; D. Liu & Cao, 2010; Pandolfo & Hollenkamp, 2006; Zhu et al., 2016), the influence of these additives on the EC performance is of great interest. The graphs in Figure 5 shows the EC values obtained with M1 (Fig. 5a) and M2 (Fig. 5b) for the pure activated carbon AC-600-800 and the same AC plus additives. Furthermore, the EC values of the commercial AC plus additives (AC-add) are shown.

Here again it becomes obvious, that the results obtained with M1 and M2 vary widely. While M1 shows almost no effect of the additives on the EC values of AC-600-800, the values obtained with M2 show a clear decrease in EC for AC-600-800-add compared with AC-600-800. In this context, AC-add shows the lowest EC values for both methods.

Considering the standard deviations (in %) of the EC value of the respective material (Table 4), it becomes evident, that the values obtained from M2 are much more reliable. While for M2 a maximum standard deviation of 9.39 % is reached, for M1 standard deviation goes up to 24.89 % (for AC-600-800 at 40 N). In most cases, the standard deviation of the EC values during M1 is many times higher than the standard deviation of the measured values during M2 (by maximal factor 5.9).

Figure 6 gives an overview of the EC values obtained for the three biochars with M2, showing that the higher the carbonization temperature, the higher the EC values, especially at the highest pressure level. Besides, it is notable which strong increase in EC the KOH activation of P600 causes. The EC increases from 0.08 S m^{-1} before activation (P600) to 80 S m^{-1} after activation (AC-600-800).

It was not possible to reach a maximum EC with any of the measurement methods. Therefore, it was assumed, that the pressures applied were too low. To gain information about the EC under higher pressures, a sample of AC-600-800 was measured with a professional Powder Resistivity Meter (PD-51 MCP-T700 from Mitsubishi Chemical

Analytech Co., Ltd.). During this measurement, forces between 2 kN and 20 kN were applied to the sample while the electrical resistivity was determined. The obtained EC values are shown in Figure 7.

The positive correlation between pressure and EC remain unchanged ($r = 0.99$) as well as the lack of a constant value of EC after a certain pressure. However, it has to be pointed out that a certain flattening of the curve takes place as the slope of the EC curve is decreasing with increasing pressure.

EC versus volume (V)

The volume of the samples was calculated with the following formula:

$$V_j = \pi * r^2 * h_j \quad (6)$$

with

r = inner radius of sample holder

h = height of the sample

$j = 10 - 50$ N

The calculated volumes are set in relation with the respective EC values (Figure 8) to understand the influence of the sample volume on EC and specifically to be able to compare M1 and M2. Firstly, it can be noted that there is a negative linear correlation between V and EC for almost all samples. The higher the volume of the sample, the lower is the respective EC value. The main difference between M1 and M2 is the dispersion of the volume values. Whereas for M1, the volume of the samples only changes slightly with increasing pressure, the volumes during M2 are changing within a broader range. Furthermore, the values of M1 show some irregularities, e.g. for P600 and AC-600-800-FeO-20 whereas the curves of M2 are almost linear for every sample.

Concerning differences between the samples, it is worth noting how the activation of P-600 to AC-600-800 and the treatment with additives and metal-oxides changes the behavior of the materials under compression. Whereas for P600, there is almost no change in EC when V is changing, the EC of AC-600-800 is increasing by a magnitude of almost three between lowest and highest volume (26.97 S m^{-1} at 0.1 cm^3 ; 80.32 S m^{-1} at 0.09 cm^3 (M2) (Fig. 8b). Surprisingly, the content of additives (AC-600-800-add) generally leads to lower sample volumes and within M2 even to lower EC values compared to the raw AC (AC-600-800) (Fig. 8c, d).

Comparing P600 and P900, it can be stated that with the same volume P900 reaches EC values up to 224 times higher than P600 (0.08 S m^{-1} for P600 versus 17.95 S m^{-1} for P900 at $V = 0.09 \text{ cm}^3$ both (M2) (Fig. 8a, b)).

Considering the composite materials, it can be observed that given the same pressure a content of 40 wt% of RuO_2 leads to lower volumes and higher EC values compared to 10 wt% of RuO_2 which shows higher volumes and at the same time lower EC (Fig. 8e, f). Comparing M1 (Fig. 8e) and M2 (Fig. 8f), the curves of the RuO_2 -containing composites cover a broader range of EC and V values than the same curves of M1.

Concerning the Fe_3O_4 -containing composites, the opposite case can be observed (Fig. 8g, h). A higher content of the metal-oxide leads to lower volumes (in the case of M2 the same volumes) and lower EC. Besides, it is remarkable that for M2 (Fig. 8h) the curves of the two composites are nearly congruent whereas for M1 (Fig. 8g) this is not the case.

EC versus density (ρ)

The change of EC with sample density ρ is illustrated in Figure 9. As expected, the curve shapes of the EC – ρ plot are similar to the respective ones of the EC – V plots. Nevertheless, there are some interesting observations to be mentioned regarding the EC – ρ relation. For

example, for the non-composite materials (Figure 9a, b), the materials with the lowest densities show the highest EC values. Although, comparing the biochars P600, P800 and P900, higher densities are related with a higher EC. The same behavior is observed for the composite materials (Figure 9c, d). A positive linear correlation between ρ and EC can be observed.

In general, the curves of M2 (Fig. 9b, d) seem to be more consistent and with less anomalies.

EC versus mechanical work (MW)

The mechanical work (MW), which is necessary to compress the respective sample to a certain density, was calculated by using the following formula (Grivei & Probst, 2003):

$$MW = \sum_{j=1}^i p_j \cdot A \cdot (h_{j-1} - h_j) \quad (7)$$

with

h_j = sample height [m]

p_j = pressure applied at h_j [Pa]

A = sample area [m²]

By relating MW to the respective density and comparing the values obtained with M1 and M2, it became clear that with M1 higher densities were reached with much less MW compared to M2. However, the absolute value of MW is not that important in this context but rather the course or slope of the $MW - \rho$ plot. Regarding this point, there are no significant differences between M1 and M2, the reason why, in the following, only data of M2 is presented.

The calculation of MW versus density serves to draw conclusions on the internal structure of the different materials by assessing how much energy is needed to reach a certain density for a certain material. In Figure 10 the $MW - \rho$ plots based on the data obtained with M2 are shown. Furthermore, the relationship between the different samples is indicated by means of labelled arrows. First of all, it is remarkable that with increasing carbonization temperature

(P600 < P800 < P900) the relation between MW and ρ is turning from a non-linear to a linear correlation ($r_{P900} = 0.99$). Furthermore, compared to P600, ten times less energy is needed to achieve even higher density values for the samples with higher carbonization temperatures (P800, P900). In addition to that, the slopes of the curves decrease with increasing carbonization temperature which supports the assumption that the breakdown of the structure of P800 and P900 requires less energy compared to P600.

The $MW - \rho$ plot of the activated carbon AC-600-800 shows even more irregularity than that one of the precursor material P600. At the same time, however, it has to be noted that the MW and ρ values are much smaller than those obtained for P600. The observed irregularity of the curve after activation become even worse after the treatment of AC-600-800 with Fe_3O_4 . The energy which is necessary to increase the sample density is highly variable and shows no consistent pattern.

In contrast, the curves of the AC-600-800- RuO_2 composites show again a certain degree of regularity. Especially for the composite containing 10 wt% of RuO_2 , a linear correlation ($r_{AC-600-800-RuO_2-10} = 0.96$) and an increase in the slope of the curve is observed. This implies that the structure of this composite is more resistant to pressure and more energy is needed to increase the density compared to the other materials including the composite containing 40 wt% of RuO_2 . For the latter, the highest densities among all samples are reached using a relatively small amount of energy.

These observations lead to the conclusion, that those materials with a higher mechanical stability (higher MW required) are less conductive whereas less required MW is connected with higher EC values.

Compression Ratio (CR)

The compression ratio (*CR*) was calculated to be able to compare M1 and M2 concerning the degree of compression reached with each method. Besides, this indicator allows to compare the different sample materials regarding their compressibility. The *CR* was calculated by dividing the respective sample volume at 10 N (V_{10N}) by the sample volume at 50 N (V_{50N}), as can be seen from the following formula:

$$CR = V_{10N} / V_{50N} \quad (8)$$

The comparison of the *CR*s obtained for M1 and M2 are depicted in Figure 11. It can be noted that a higher compression is achieved with M2 for all samples except for the composites containing Fe_3O_4 .

Figure 12 illustrates the differences in *CR* for all studied materials based on data obtained with M2.

The highest *CR* values are reached by the commercial AC plus additives (AC-add) followed by P800 and P600. Thus, these samples resulted in experiencing the highest compressions among all samples. In contrast, the non-commercial AC (AC-600-800) has the lowest *CR*. The AC treatment with additives leads to a slightly higher *CR*. The same applies for the addition of Fe_3O_4 to the AC-600-800. However, it is notable that with increasing content of Fe_3O_4 , the *CR* constantly decreases which implies an increase in compressibility. In contrast, for the RuO_2 -composites the opposite is the case. With increasing RuO_2 -content the *CR* increases from 1.15 to 1.19 which implies a lower compressibility of AC-600-800- RuO_2 -40 compared to AC-600-800-10.

Discussion

As already mentioned, the aim of this paper is to discuss two main questions:

- 1) Which method is more suitable to characterize the samples concerning their EC?
- 2) Which material shows the best EC values and why?

By answering these questions, it can be contributed to the creation of a knowledge base for the development of sustainable, biomass-based electrode materials for energy storage technologies such as EDLCs.

Method comparison

Regarding the first question, it has been shown, that focussing on a constant sample height is reasonable. Previous studies have been conducted by setting a constant mass instead of a constant height (Barroso-Bogeat et al., 2014). However, pre-tests conducted during this work showed that keeping the height constant delivers more reliable and reproducible results. A reason for this is the direct dependence of EC on the height of the sample (see Eq. 2).

The results presented above seem to indicate that M2 represents the best method to assess the EC of the studied materials. Due to the pre-load of 50 N within M1, pelletisation of the sample took place to a certain extent. The intention behind this was to ensure the contact area between the particles to be high enough for EC measurements. However, it could be shown that the pre-pelletisation was only of relevance for the sample P600 which showed almost no EC during M2 while with M1 the increase of density due to the pre-load led to a 100-fold increase of EC. The higher content of functional groups on the surface of P600 compared to the other samples is assumed to be responsible for this behaviour since they hinder electron transport through the sample and hence a higher compression is needed to establish electrical contact between the particles. For the other samples, by contrast, EC values obtained with M2 at lower densities were often equal or even higher than those obtained with M1 at higher densities.

Accepted Article

Because of the lack of a pre-load during M2, the compaction (*CR*), increase in density (*IoD*) or decrease in volume respectively was higher for all materials. Hence, M2 allows the EC assessment within a wider range of compression, density and volume values. Furthermore, the plots of M1 often show irregularities and anomalies (e.g. concerning EC-V and EC- ρ). It is assumed that this is because of the partial decompression after the removal of the pre-load. Depending on the material this proceeding (compression with 50 N \rightarrow partial decompression \rightarrow compression with 10 – 50 N) could have led to the irregularities within the obtained data. Since during M2 no pre-load was applied, the samples were compacted in a linear manner (from 10 to 50 N) which lead to a higher stability of the samples because of less decompression.

This uncertainty regarding the data obtained with M1 is further confirmed by the high standard deviations obtained for M1 compared to M2 (Table 4). Considering the facts described above, M2 seems to provide much more reliable data than M1.

Therefore, the second above-mentioned question will be discussed based on the data obtained within M2.

Discussion of the results of M2

To be able to identify which material properties lead to which EC values, a range of totally different carbons and their composites were produced out of the same precursor (corn cob) by pyrolysis at different temperatures and further treatments. By determining the EC values of all produced materials and additionally of one commercial AC based on peat and comparing the obtained values with each other, it is possible not only to identify which material shows the highest EC but also to draw conclusions on the influence of different parameters or treatments on the EC of the respective material. Within the framework of this work, the following parameters/ treatments and their influence on EC are of special interest:

- carbonization temperature

- KOH activation
- treatment with additives
- treatment with metal oxides

By discussing the results described in the previous paragraph while taking the above-mentioned parameters/ treatments into account, some valuable conclusions can be drawn with respect to the EC of biobased carbonaceous powders and their composites and the suitability of each material as electrode material in EDLCs.

Influence of carbonization temperature on EC

Considering carbonization temperature and its influence on EC, the results show clearly that an increase of heat treatment temperature favours higher EC values which can be attributed to different underlying processes: the increase in ash content in the char with increasing pyrolysis temperature (Naeem, Khalid, Arshad, & Ahmad, 2014), the gradual change of carbon structures from mainly σ -bondings and carbon in the sp^3 state (in the biomass precursor) to conjugated carbon in the sp^2 state during carbonization (Biniak, Pakula, Radovic, & Swiatkowski, 2001), the decrease of acidic functionalities on the carbon surface after 600°C-700°C (Radovic, 1994) and the reorganization of the carbon from amorphous to crystalline structures (up to graphite at < 2.500 °C) (Pandolfo & Hollenkamp, 2006).

However, it is questionable if the increase of the ash content significantly contributes to the increase in EC as in Table 2 the ash content of P800 is lower than that of P600 but P800 shows higher EC values. Even though, in past studies, it has been shown that the ash content as well as the EC values independently increase with increasing pyrolysis temperature without directly relating EC and ash content (Naeem et al., 2014; Singh, Singh, & Cowie, 2010). However, it is undisputable that the volatilisation of basic cations such as Ca^+ or Mg^{2+} only starts when temperatures of about 1000°C are reached (Neary, Klopatek, DeBano, &

Ffolliott, 1999) while non-mineral components start volatilizing at 100°C (Knoepp, DeBano, & Neary, 2005) which is why an ash concentration after carbonization can be observed. Nevertheless, it is assumed that the other processes taking place during carbonization are more determining for the EC than the increasing ash content.

Biniak et al. state, for example, that the EC is directly related to the material structure (Biniak et al., 2001). While biomass is an insulator ($EC < 10^{-10} \text{ S m}^{-1}$ (Pandolfo & Hollenkamp, 2006)) due to the high proportion of σ -bonds between sp^3 -hybridized carbon atoms, the formation of carbon atoms in the sp^2 -state and the associated π -bonds during carbonization lead to the delocalization of electrons (Biniak et al., 2001). The consequence is the conversion from an insulator (biomass) to a conductor (biochar). This explanation corresponds well with the obtained results for P600, P800 and P900 (increase of EC in this sequence, see Figure 6), which show ECs in the range of semiconductors.

However, the difference in EC between P600 and P800 was remarkable (increase by a factor of more than 100) and implies that at 600 °C some mechanisms which affect the EC were still not activated. Considering the facts that the conversion of surface functionalities into volatiles (mainly H_2O and CO_2) starts at a temperature range between 600 °C and 700 °C and that the surface oxygen content, inter alia, acts as a barrier for electrons resulting in a higher resistivity (Biniak et al., 2001), the reason for the low EC of P600 (compared to P800) might be the presence of surface functionalities which are not volatilized yet and hence hinder the electron flow through the carbon.

Another mechanism which contributes to the increase of EC after carbonization is the structural reorganization during heat treatment. An ideal development of the carbon structure from amorphous to graphitic depending on the carbonization temperature is depicted in Figure 13 (Downie, 2011). Along the plane of the aromatic rings (Figure 13 C) (a-axis), graphite crystals show specific resistivities of $\sim 10^{-5} \Omega \text{ cm}$ whereas in the c-axis direction

(perpendicular to a-axis) the specific resistivities are higher ($\sim 10^{-2} \Omega \text{ cm}$) (Kinoshita, 1988).

This corresponds to a EC of $\sim 10^7 \text{ S m}^{-1}$ in the a-axis and $\sim 10^4 \text{ S m}^{-1}$ in the c-axis of the graphite crystals. Single graphite crystals thus show EC values similar to semi-metals and the highest EC values among all carbon materials (Thrower, 1997).

It can therefore be stated that with an increasing proportion of graphitic structures in a specific material and hence with a higher carbonization temperature, the EC increases. This, in addition to the mechanisms described above, explains well the increase of EC from P600 to P900 and, additionally, the effect of the activation process on the EC.

Influence of KOH activation on EC

Nevertheless, the increase of EC after the activation of P600 with KOH deserves a more detailed examination as the EC of the AC-600-800 was thousand times higher than that of P600 and more than three times higher than that of P900. These observations imply that the EC does not only depend on the level of the temperature itself but is also significantly affected by the mechanisms taking place during the activation process. In this context, two main mechanisms are of special interest: firstly, the activation was conducted with the sample P600 at 800 °C, which means that during the activation some volatiles were released and the proportion of ordered carbon structures was increased. Secondly, the activation was conducted with KOH, which has proven to be a catalyst for gasification and volatilization reactions (McKee, 1983). Consequently, the release of oxygen-containing volatiles as well as the carbon increase and the formation of conjugated aromatic carbon was favored. At the same time, however, the ash content was significantly lower after activation which generally would lead to a lower EC. Here again, the above-mentioned assumption that the ash content is of minor significance for the EC of carbonaceous materials is confirmed. Indeed, the catalytic effect of KOH regarding volatilization and consequently the lower content of

Accepted Article

surface functionalities is assumed to be one of the main reasons for the high EC of AC-600-800. Nevertheless, this assumption has to be verified by conducting e.g. X-ray photoelectron spectroscopy (XPS) measurements. Another important contribution to the increase of EC can be attributed to the higher porosity after KOH activation. Upon compression, the higher porosity in combination with smaller carbon particles lead to higher contact areas between the single particles (Kennedy, Vijaya, & Sekaran, 2005) which, according to the contact theory (see above), favors higher EC values. This corresponds well with the obtained EC data for AC-600-800 under compression, as the EC - P curve of AC-600-800 shows a higher gradient than that of P600. Nevertheless, simultaneously, the CR of P600 is higher than that of AC-600-800 which shows that in spite of a higher compression and density of P600, the contact area under the same force levels was obviously higher for AC-600-800 due to its higher porosity.

Influence of additives on EC

Since during electrode manufacturing, the pure materials are always mixed with binder and other additives (Bernstein, 2015), the influence of these additives on the EC of each material is of special interest with regard to the application in EDLCs. The decrease of EC after treatment with PTFE and AB is due to PTFE, which has insulator properties and consequently decreases the EC even when added in small quantities (here 5 wt%) and despite the addition of a conductive additive (15 wt% AB). Such conductive additives generally enhance the EC of a polymer as their EC ranges between 10 S m^{-1} and 10^4 S m^{-1} (Donnet, Bansal, & Wang, 1993) but in this case, the insulating properties of PTFE on EC seem to overlap the positive effects of AB. Hence, it can be concluded that the binder content should be reduced to a minimum or that binder should even be avoided in electrode manufacturing. Liu et al. already made first attempts to develop such binder-free electrodes based on banana peel (B. Liu et al., 2016), but this approach is relatively new and far from being able to be

implemented in electrode production on an industrial scale. The higher EC values of AC-600-800-add compared to those of AC-add can be explained by the lower surface area of the commercial AC in comparison with AC-600-800 (Hoffman et al., 2018), which is a consequence of the different production process and precursor of the commercial AC (precursor: peat, carbonization temperature: 500°C, physical activation).

Influence of metal oxides on EC

Concerning the composite materials, the obtained results were highly heterogeneous which was, to a certain extent, expected due to the different electronic properties of RuO₂ and Fe₃O₄. Among the six oxides of the transition metal ruthenium, RuO₂ is technologically of special interest because of its high pseudocapacitive properties and its high EC (Table 5).

However, the literature-based values in Table 5 show that the EC values of RuO₂ highly depend on its structural properties. Especially, the EC significantly decreases when RuO₂ is in an amorphous state. Due to the sol-gel method, which was used to produce the AC-RuO₂-composites studied in this work, and the low annealing temperature of 150 °C, it must be assumed that the RuO₂ occurs in its amorphous state here. This assumption agrees well with the results obtained with XRD measurements in the work of Su et al. (Su et al., 2007). Nevertheless, this does not explain, why the composite containing 40 wt% RuO₂ shows the highest EC values among all studied materials while the composite with 10 wt% RuO₂ shows lower EC values than AC-600-800 and even lower EC values than the composite containing 10 wt% of Fe₃O₄. One explanation could be the better compressibility of AC-600-800-RuO₂-40 compared to the other composites. The better compressibility is proven by the high CR, the relatively high densities (or low volumes) and the low *MW* values. It is assumed that due to the high content of RuO₂ and the size of the RuO₂-particles (10-20 nm (Su et al., 2007)), the mesopores of the AC (2 - 50 nm) are partially filled or clogged by the metal oxide

nanoparticles. This assumption is proven by SEM measurements of the composite material (Hoffman et al., 2018) which, in addition, show a smooth distribution of the metal oxide particles on the surface of the AC. It is assumed that due to the high content of RuO₂ nanoparticles, their distribution on the surface and their presence in the pores of the AC the mechanical properties of the composite (e.g. density, compressibility) are modified in a manner which allows higher densities under moderate pressure. This, in turn, leads to a higher amount of electrical contacts between neighboring particles and hence a higher EC. Nevertheless, amorphous RuO₂ show much lower EC values than the pure AC (Table 5) and should therefore rather act as an insulating layer which increases resistivity and decreases the EC of the carbon support. Such a behavior has been observed at least for other AC-metal oxide composites (including Al₂O₃, Fe₂O₃, ZnO etc.) and as a result, it has been stated that the EC of a hybrid material is mainly determined by the intrinsic EC of the respective metal oxide and not by the altered mechanical properties of the composite compared to the pure AC (Barroso-Bogeat et al., 2014). Concerning the AC-RuO₂ nanocomposites, the statement of Barroso-Bogeat et al. does not seem to apply as, compared to the raw AC, both the compressibility and the density are significantly higher, which indicates that the mechanical changes are the crucial factors for the increase in EC. However, this is contradicted by the facts that the density values of P900 and AC-add are only slightly lower and the CR values of P600, P800 and AC-add are even higher than the respective ones of AC-600-800-RuO-40. This suggests that the high EC value obtained for AC-600-800-RuO-40 is a consequence of both the properties of the supported nanoparticles (e.g. morphology, content, distribution, intrinsic EC) and the changed mechanical properties of the composite due to the surface and pore modification. Consequently, on the one hand the RuO₂-nanoparticles led to an increase in density which caused a further approximation to the intrinsic EC value of AC and on the other hand it cannot be excluded that a certain amount of RuO₂ occurs in a polycrystalline

Accepted Article

state (with an EC of 10^5 S m^{-1} , Table 5) contributing to the increase in EC. Nevertheless, the crucial factor seems to be the amount of the metal-oxide on the surface of AC since the composite with only 10 wt% of RuO_2 showed even lower EC values than the raw AC, especially under higher pressures (382 – 637 kPa). This corresponds well with the finding of Barroso-Bogeat et al. that the supported nanoparticles act as an insulator between the carbon particles. By increasing the pressure, the contact area between carbon and metal-oxide particles is increased and as a consequence the EC decreases. It is assumed that only a high content of RuO_2 (40 wt%) can affect the mechanical properties of the composite sufficiently to cause such a sharp increase in EC.

The assumption that the amount of the metal-oxide in the composite is crucial for the EC is further proven by the obtained results for the AC- Fe_3O_4 composites. Here, 10 wt% Fe_3O_4 seem to be the ideal proportion regarding EC (EC values higher than those of AC-600-800) while 40 wt% Fe_3O_4 lead to a decline in EC of about 50 % for all pressure levels. Here, the conclusions made by Barroso-Bogeat et al. for other AC-metal oxide composites seem to fit quite well since the Fe_3O_4 particles cause almost no changes in the mechanical properties of the material (density and *CR*). However, considering the EC value of Fe_3O_4 (Table 5) the EC value of the composite should increase with increasing content of the metal oxide. Rather, it appears that the Fe_3O_4 particles, after a certain amount, hinder the electron transport through the composite. This might be due to their morphology or size which could lead to less contact area between the composite particles.

Concluding, it can be noted that a high carbonization temperature, a high specific surface area and as a result high porosity generally favor the EC of carbonaceous powders because these properties directly influence the structure of the carbon lattice as well as the mechanical properties of the carbon powder. Especially the direct relation between increasing surface area and increasing EC can be observed by comparing the EC values of the biochar (P600)

before and after KOH activation (0.08 S m^{-1} to 80.32 S m^{-1}). KOH activation is the preferred activation method as it leads to higher surface area compared to physical activation (Ahmadpour & Do, 1997) and hence higher EC values, which was proven by comparing the EC of AC-600-800 (KOH activation, SSA of raw AC = $2\,333 \text{ m}^2 \text{ g}^{-1}$ (Hoffman et. al., 2018)) and AC-add (physical activation, SSA of raw AC = $950 \text{ m}^2 \text{ g}^{-1}$ (Wolf, 2014)). The EC of the commercial AC is given with 33 S m^{-1} (Wolf, 2014) which fits well to the obtained results for AC-add with slightly lower EC values.

The treatment with metal oxides and additives highly alters the mechanical properties of the raw AC in terms of compressibility and density which consequently leads to varying EC values under moderate pressures. It can be observed, though, that the development of the EC highly depends on the metal oxide used, especially on its physico-chemical properties, morphology, particle size and intrinsic EC and the respective interactions between these specific properties and the carbon particles. An increasing proportion of RuO_2 nanoparticles, for example, lead to increasing EC values of the respective composite while for Fe_3O_4 the opposite can be observed. These results and the assessment of the mechanical behavior of the composites and their components lead to the assumption that high shares of RuO_2 nanoparticles (40 wt%) favor the establishment of greater contact areas between the particles whereas high shares of Fe_3O_4 particles block electron pathways and act as an insulator because of their morphology and particle size. However, lower proportions of Fe_3O_4 (10 wt%) lead to increasing EC values compared to the raw AC which suggests that the positive effect of the high intrinsic EC of Fe_3O_4 neutralizes the negative effect of the Fe_3O_4 on the establishment of conducting pathways. In conclusion, it has been found that the material AC-600-800-RuO-40 shows the best EC values and is, in this context, the most promising material.

Regarding additives, it can be concluded that even 5wt% of PTFE binder considerably reduce the EC of AC and invalidates any positive effects of the conductive additive AB ($EC = 400 \text{ S m}^{-1}$ (Soltex, 2018)) (15 wt%) on the EC. However, it has to be considered that without any conductive additive the EC would probably be even lower due to the insulation effect caused by the binder. The aim should be to develop binder-free electrode materials to avoid negative effects on the EC of the electrodes and also to diminish the use of non-biobased chemicals in the electrode production.

Concerning the method development, it has been shown that a pre-pelletisation of the samples powder materials lead to undesirable anomalies during the measurements (e.g. partial decompression) which resulted in high standard deviations. Reliable results were obtained by using M2 which represents a simple and reproducible method for EC measurements of carbonaceous powders.

Nevertheless, the results regarding EC should not be considered on their own but in combination with other results concerning their capacitive properties. Only in this way, it is possible to assess the materials regarding their suitability as bio-based electrode materials in EDLCs and thus make a contribution to the development of biobased and sustainable solutions in the framework of Bioeconomy.

Acknowledgements

This work was funded by German Federal Ministry of Education and Research and the ERANet LAC initiative (ELAC2014/BEE-0367). Financial support by the Ministry of Science, Research and the Arts of Baden-Württemberg by means of a LGF grant for V. Hoffmann is gratefully acknowledged. Furthermore, we thank N&H Technology GmbH for conducting EC measurements with the Powder Resistivity Meter.

References

- Ahmadpour, A., & Do, D. D. (1997). The preparation of active carbons from macadamia nutshell by chemical activation. *Carbon*, 35(12), 1723–1732.
- Barroso-Bogeat, a., Alexandre-Franco, M., Fernández-González, C., Macías-García, A., & Gómez-Serrano, V. (2014). Electrical conductivity of activated carbon–metal oxide nanocomposites under compression: a comparison study. *Phys. Chem. Chem. Phys.*, 16(45), 25161–25175. <https://doi.org/10.1039/C4CP03952A>
- Bernstein, H. (2015). Bauelemente der Elektronik. Berlin, München, Boston: Walter de Gruyter GmbH. https://doi.org/10.1007/978-3-7091-7946-8_1
- Biniak, S., Pakula, M., Radovic, L. R., & Swiatkowski, A. (2001). *Chemistry and Physics of Carbon*, Vol. 27. New: Marcel Dekker, Inc.
- Bonnefoi, L., Simon, P., Fauvarque, J. F., Sarrazin, C., & Dugast, A. (1999). Electrode optimization for carbon power supercapacitors. *Journal of Power Sources*, 79(1), 37–42. [https://doi.org/10.1016/S0378-7753\(98\)00197-9](https://doi.org/10.1016/S0378-7753(98)00197-9)
- Celzard, A., Marêché, J. F., Payot, F., & Furdin, G. (2002). Electrical conductivity of carbonaceous powders. *Carbon*, 40(15), 2801–2815. [https://doi.org/10.1016/S0008-6223\(02\)00196-3](https://doi.org/10.1016/S0008-6223(02)00196-3)
- Cornell, R. M., & Schwertmann, U. (1996). *The Iron Oxides: Structure, Properties, Occurrences and Uses*. Weinheim, New York: VCH.
- Donnet, J. B., Bansal, R. C., & Wang, M. J. (1993). *Carbon Black. Science and Technology* (Vol. 2). New York: Marcel Dekker, Inc.
- Downie, A. (2011). *Biochar Production and Use: Environmental Risks and Rewards*. The University of New South Wales.
- Euler, K. J. (1978). The conductivity of compressed powders. A review. *Journal of Power Sources*. [https://doi.org/10.1016/0378-7753\(78\)80011-1](https://doi.org/10.1016/0378-7753(78)80011-1)

- Frackowiak, E., & Béguin, F. (2001). Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*, 39(6), 937–950. [https://doi.org/10.1016/S0008-6223\(00\)00183-4](https://doi.org/10.1016/S0008-6223(00)00183-4)
- Ghosh, A., & Hee, Y. (2012). Carbon-Based Electrochemical Capacitors. *ChemSusChem*, 5, 480–499. <https://doi.org/10.1002/cssc.201100645>
- Grivei, E., & Probst, N. (2003). Electrical conductivity and carbon network in polymer composites. *KGK. Kautschuk, Gummi, Kunststoffe*, (9), 460–464. Retrieved from <http://cat.inist.fr/?aModele=afficheN&cpsidt=15156571>
- He, P., Yang, K., Wang, W., Dong, F., Du, L., & Liu, H. (2013). Nanosized Fe₃O₄-modified activated carbon for supercapacitor electrodes. *Russian Journal of Electrochemistry*, 49(4), 354–358. <https://doi.org/10.1134/S1023193513040095>
- Hoffman, V., Correa, C. R., Sachs, S., Kruse, A., Sandoval, A. D. pilar R., Rodriguez, J. P. E., ... Zimmermann, M. (2018). Study of physico-chemical and electrochemical properties of AC-RuO₂-composites for the application in energy storage technologies. in progress.
- Holm, R. (2000). *Electric contacts: Theory and Applications*. Springer (4th ed., Vol. 221). Berlin Heidelberg New York: Springer. <https://doi.org/10.1016/j.powtec.2012.01.024>
- Hu, B., Wang, K., Wu, L., Yu, S. H., Antonietti, M., & Titirici, M. M. (2010). Engineering carbon materials from the hydrothermal carbonization process of biomass. *Advanced Materials*, 22(7), 813–828. <https://doi.org/10.1002/adma.200902812>
- Hu, C.-C., Chen, W.-C., & Chang, K.-H. (2004). How to Achieve Maximum Utilization of Hydrous Ruthenium Oxide for Supercapacitors. *Journal of The Electrochemical Society*. <https://doi.org/10.1149/1.1639020>
- Hu, C. C., & Chen, W. C. (2004). Effects of substrates on the capacitive performance of RuO_x·nH₂O and activated carbon-RuO_x electrodes for supercapacitors. *Electrochimica*

Acta, 49(21), 3469–3477. <https://doi.org/10.1016/j.electacta.2004.03.017>

Hulicova-Jurcakova, D., Kodama, M., Shiraishi, S., Hatori, H., Zhu, Z. H., & Lu, G. Q.

(2009). Nitrogen-enriched nonporous carbon electrodes with extraordinary supercapacitance. *Advanced Functional Materials*, 19(11), 1800–1809. <https://doi.org/10.1002/adfm.200801100>

Kennedy, L. J., Vijaya, J. J., & Sekaran, G. (2005). Electrical conductivity study of porous carbon composite derived from rice husk. *Materials Chemistry and Physics*, 91(2–3), 471–476. <https://doi.org/10.1016/j.matchemphys.2004.12.013>

Kinoshita, K. (1988). Carbon: electrochemical and physicochemical properties. *Journal of the American Chemical Society*, 110(18), Medium: X; Size: Pages: 541. <https://doi.org/978-0-471-84802-8>

Knoepp, J. D., DeBano, L. F., & Neary, D. G. (2005). *Soil Chemistry. U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station*. Ogden: UT.

Kotz, R., Carlen, M., Kötz, R., Kötz, R., Carlen, M., & Carlen, M. (2000). Principles and applications of electrochemical capacitors. *Electrochim. Acta*, 45, 2483–2498. [https://doi.org/10.1016/S0013-4686\(00\)00354-6](https://doi.org/10.1016/S0013-4686(00)00354-6)

Kurzweil, P., & Dietlmeier, O. K. (2015). *Elektrochemische Speicher - Superkondensatoren, Batterien, Elektrolyse-Wasserstoff, REchtliche Grundlagen*. Springer.

Lee, K. K., Hao, W., Gustafsson, M., Tai, C.-W., Morin, D., Björkman, E., ... Hedin, N. (2016). Tailored activated carbons for supercapacitors derived from hydrothermally carbonized sugars by chemical activation. *RSC Adv.*, 6(112), 110629–110641. <https://doi.org/10.1039/C6RA24398C>

Liu, B., Zhang, L., Qi, P., Zhu, M., Wang, G., Ma, Y., ... Yu, F. (2016). Nitrogen-Doped Banana Peel–Derived Porous Carbon Foam as Binder-Free Electrode for Supercapacitors. *Nanomaterials*, 6(1), 18. <https://doi.org/10.3390/nano6010018>

- Liu, D., & Cao, G. (2010). Engineering nanostructured electrodes and fabrication of film electrodes for efficient lithium ion intercalation. *Energy & Environmental Science*, 3(9), 1218. <https://doi.org/10.1039/b922656g>
- Marinkovic, S., Suznjivic, C., & Djordjevic, M. (1971). Pressure dependence of the electrical resistivity of graphite powder and its mixtures. *Phys. Stat. Sol.*, 4(3), 743–754. <https://doi.org/10.1002/pssa.2210040319>
- McKee, D. W. (1983). Mechanisms of the alkali metal catalysed gasification of carbon. *Fuel*, 62(2), 170–175. [https://doi.org/10.1016/0016-2361\(83\)90192-8](https://doi.org/10.1016/0016-2361(83)90192-8)
- Mrozowski, S. (1957). *Studies of carbon powders under compression. Proceedings 3rd carbon conference*. Buffalo, USA. <https://doi.org/10.1016/j.jnucmat.2013.01.315>
- Naeem, M. A., Khalid, M., Arshad, M., & Ahmad, R. (2014). Yield and Nutrient Composition of Biochar Produced From Different Feedstocks At Varying Pyrolytic ... Yield and Nutrient Composition of Biochar Produced From. *Pak. J. Agri. Sci*, 51(1), 75–82.
- Neary, D. G., Klopatek, C. C., DeBano, L. F., & Ffolliott, P. F. (1999). Fire effects on belowground sustainability: A review and synthesis. *Forest Ecology and Management*, 122(1–2), 51–71. [https://doi.org/10.1016/S0378-1127\(99\)00032-8](https://doi.org/10.1016/S0378-1127(99)00032-8)
- Oh, I., Kim, M., & Kim, J. (2015). Deposition of Fe₃O₄ on oxidized activated carbon by hydrazine reducing method for high performance supercapacitor. *Microelectronics Reliability*, 55(1), 114–122. <https://doi.org/10.1016/j.microrel.2014.09.014>
- Pandolfo, A. G., & Hollenkamp, A. F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources*, 157(1), 11–27. <https://doi.org/10.1016/j.jpowsour.2006.02.065>
- Pantea, D., Darmstadt, H., Kaliaguine, S., & Roy, C. (2003). Electrical conductivity of conductive carbon blacks: Influence of surface chemistry and topology. *Applied Surface*

Science, 217(1–4), 181–193. [https://doi.org/10.1016/S0169-4332\(03\)00550-6](https://doi.org/10.1016/S0169-4332(03)00550-6)

- Pantea, D., Darmstadt, H., Kaliaguine, S., Sümchen, L., & Roy, C. (2001). Electrical conductivity of thermal carbon blacks: Influence of surface chemistry. *Carbon*, 39(8), 1147–1158. [https://doi.org/10.1016/S0008-6223\(00\)00239-6](https://doi.org/10.1016/S0008-6223(00)00239-6)
- Radovic, L. R. (1994). *Chemistry & Physics of Carbon, Vol. 24*. New York: Marcel Dekker.
- Raymundo-Piñero, E., Cadek, M., & Béguin, F. (2009). Tuning carbon materials for supercapacitors by direct pyrolysis of seaweeds. *Advanced Functional Materials*, 19(7), 1032–1039. <https://doi.org/10.1002/adfm.200801057>
- Research, L. (2013). *Power Play: Supercapacitor Innovation for Growth in Transportation and Electronics*. Lux Research. Bosoton. Retrieved from <http://www.luxresearchinc.com/news-and-events/press-releases/read/market-supercapacitors-grow-128-836-million-2018>
- Rodriguez Correa, C., Otto, T., & Kruse, A. (2016). Influence of the biomass components on the pore formation of activated carbon. *Biomass and Bioenergy*, 97, 53–64. <https://doi.org/10.1016/j.biombioe.2016.12.017>
- Sánchez-González, J., MacÍas-García, A., Alexandre-Franco, M. F., & Gómez-Serrano, V. (2005). Electrical conductivity of carbon blacks under compression. *Carbon*. <https://doi.org/10.1016/j.carbon.2004.10.045>
- Sánchez-González, J., Stoeckli, F., & Centeno, T. A. (2011). The role of the electric conductivity of carbons in the electrochemical capacitor performance. *Journal of Electroanalytical Chemistry*. <https://doi.org/10.1016/j.jelechem.2011.03.025>
- Sharma, P., & Bhatti, T. S. (2010). A review on electrochemical double-layer capacitors. *Energy Conversion and Management*, 51(12), 2901–2912. <https://doi.org/10.1016/j.enconman.2010.06.031>
- Singh, B. B. P., Singh, B. B. P., & Cowie, A. L. (2010). Characterisation and evaluation of

biochars for their application as a soil amendment. *Australian Journal of Soil Research*, 48, 516–525.

Soltex. (2018). Acetylene black-01.

Steeves, M. M. (2011). Electronic Transport Properties of Ruthenium and Ruthenium Dioxide Thin Films. *Electronic Theses and Dissertations*, 262, 187.

Su, Y., Wu, F., Bao, L., & Yang, Z. (2007). RuO₂/activated carbon composites as a positive electrode in an alkaline electrochemical capacitor. *New Carbon Materials*, 22(1), 4–9. Retrieved from <http://xxtcl.sxicc.ac.cn/fileup/PDF/070110.pdf>

Thrower, P. A. (1997). *Chemistry and physics of carbon. Materials Science and Technology* (Vol. 25). New York: Marcel Dekker, Inc. <https://doi.org/10.1179/026708397790302007>

Wang, C.-M., Wen, C.-Y., Chen, Y.-C., Chang, J.-Y., Ho, C.-W., Kao, K.-S., ... Shen, Y.-A. (2015). The Influence of Specific Surface Area on the Capacitance of the Carbon Electrodes Supercapacitor. *The Proceedings of the 2nd International Conference on Industrial Application Engineering 2015*, (3), 439–442. <https://doi.org/10.12792/iciae2015.077>

Wang, G., Zhang, L., & Zhang, J. (2012). A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.*, 41(2), 797–828. <https://doi.org/10.1039/C1CS15060J>

Wolf, E. L. (2014). *Applications of Graphene: An Overview*. Heidelberg Dordrecht London New York: Springer.

Worasuwannarak, N., Sonobe, T., & Tanthapanichakoon, W. (2007). Pyrolysis behaviors of rice straw, rice husk, and corncob by TG-MS technique. *Journal of Analytical and Applied Pyrolysis*, 78(2), 265–271. <https://doi.org/10.1016/j.jaap.2006.08.002>

Yassine, M., & Fabris, D. (2017). Performance of commercially available supercapacitors. *Energies*, 10(9). <https://doi.org/10.3390/en10091340>

Accepted Article

Zhao, X., Xia, D., & Zheng, K. (2012). Fe₃O₄ / Fe / Carbon Composite and Its Application as Anode Material for Lithium-Ion Batteries.

Zhi, M., Xiang, C., Li, J., Li, M., & Wu, N. (2013). Nanostructured carbon-metal oxide composite electrodes for supercapacitors: a review. *Nanoscale*, 5(1), 72–88.
<https://doi.org/10.1039/c2nr32040a>

Zhu, Z., Tang, S., Yuan, J., Qin, X., Deng, Y., & Qu, R. (2016). Effects of Various Binders on Supercapacitor Performances. *International Journal of Electroche*, 11, 8270–8279.
<https://doi.org/10.20964/2016.10.04>

Tables

Tab. 1: Overview about the studied materials including information about precursors, production method, density and abbreviations

Sample Type	Raw material/ Precursor	Production method	Activation (800 °C)	Abbreviation
P	Corncob	Pyrolysis (600°C)	No	P600
P	Corncob	Pyrolysis (800°C)	No	P800
P	Corncob	Pyrolysis (900°C)	No	P900
AC	Corncob	Pyrolysis (600°C) + KOH activation	Yes	AC-600-800
Composite	AC-600-800	Mixing with 5 wt% Fe ₃ O ₄	Yes	AC-600-800-FeO-5
Composite	AC-600-800	Mixing with 10 wt% Fe ₃ O ₄	Yes	AC-600-800-FeO-10
Composite	AC-600-800	Mixing with 20 wt% Fe ₃ O ₄	Yes	AC-600-800-FeO-20
Composite	AC-600-800	Mixing with 40 wt% Fe ₃ O ₄	Yes	AC-600-800-FeO-40
Composite	AC-600-800	Sol-gel method with 10 wt% RuO ₂	Yes	AC-600-800-RuO-10
Composite	AC-600-800	Sol-gel method with 40 wt% RuO ₂	Yes	AC-600-800-RuO-40
Electrode Material	Commercial AC (peat)	Carbonization (500°C) + Steam activation (1000 °C); PTFE (5 wt%) + Acetylene Black (15 wt%)	Yes	AC-add
Electrode Material	AC-600-800	PTFE (5wt %) + Acetylene Black (15 wt%)	Yes	AC-600-800-add

Tab. 2: Elemental Composition of the precursor biomass corncob and the carbon materials P600, P800, P900 and AC-600-800*

Sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	Ash (wt.%)
Corncob ¹	46.2	6.2	1.3	N.D.	47.0	0.9
P600	81.7	1.6	0.9	N.D.	7.8	8.2
P800	84.4	0.6	1.0	N.D.	6.3	8.0
P900	85.7	0.4	0.7	N.D.	5.2	8.9
AC-600-800	95.3	0.1	0.2	N.D.	3.7	0.7

* Elemental composition on a dry basis of the pyrolysis chars and activated carbon. N.D.: not detected

¹(Worasuwanarak, Sonobe, & Tanthapanichakoon, 2007)

Tab. 3: Changes of electrical conductivity and density depending on the force applied (10N and 50N) and the method used (M1 = preload, M2 = no pre-load) for four different materials (biochar, activated carbon, composite with RuO₂, activated carbon with additives)

Method	Sample	κ_1 [S/m], 10 N	κ_2 [S/m], 50 N	IoEC ¹ [%]	ρ_{10N} [g/cm ³]	ρ_{50N} [g/cm ³]	IoD ² [%]
M1 (with preload)	P-600	3.05	8.54		0.7	0.79	13
	AC-600-800	25.89	80.41	180	0.39	0.43	10
	AC-600-800- RuO-40	140.37	316.05	211	1.06	1.19	12
	AC-600-800- add	34	81.22	125	0.6	0.66	10
				139			
M2 (without pre-load)	P-600	0.02	0.08		0.39	0.47	21
	AC-600-800	26.97	80.32	300	0.24	0.27	13
	AC-600-800- RuO-40	149.7	408	198	0.85	1.01	19
	AC-600-800- add	24.23	55.5	173	0.36	0.43	19
				129			

¹ = Increase of Electrical Conductivity in % (from 10 N to 50 N)

² = Increase of Density in % (from 10 N to 50 N)

Tab. 4: Comparison of the standard deviations of k [%] for AC-600-800, AC-600-800-add and AC-add between M1 and M2

Applied Force [N]	AC-600-800		AC-600-800-add		AC-add	
	M1	M2	M1	M2	M1	M2
10	17,12	2,89	10,75	6,69	16,77	7,00
20	21,54	7,72	6,13	9,39	2,40	4,52
30	22,11	1,73	2,53	5,28	1,82	5,62
40	24,89	4,47	10,05	2,00	4,63	3,71
50	18,90	6,25	9,48	4,44	11,15	3,97

Tab. 5: Overview of selected capacitance and EC values of AC, RuO_2 , Fe_3O_4 and the respective composites

Oxides/ Composites	Electrolyte	Capacitance (F g^{-1})	EC (S m^{-1})
AC	Na_2SO_4	79.2 [5]	80.32 (50 N) [o.d]
	Na_2SO_3	99.4 [6]	1.7×10^3 (20 kN) [o.d.]
$\text{RuO}_2, x\text{H}_2\text{O}$	$\text{H}_2\text{SO}_4, \text{Na}_2\text{SO}_4$	1200-2200 (1.23 V) [1]	2.8×10^6 (single-crystal) [2] 10^5 (polycrystalline) [3] ~ 1 (amorphous) [3]
RuO_2/AC	KOH solution (6mol/l)	768 [8]	408 (50 N) [o.d]
Fe_3O_4	H_2SO_4	185 [4]	$10^4 - 10^5$ [7]
$\text{Fe}_3\text{O}_4/\text{AC}$	Na_2SO_4	78.5 (1 V) [5]	80.28 (50 N) [o.d]
	Na_2SO_3	154.3 [5] 202.6 [6]	

¹(C.-C. Hu, Chen, & Chang, 2004) ²(Steeves, 2011) ³(Zhi et al., 2013) ⁴(C. C. Hu & Chen, 2004) ⁵(He et al., 2013) ⁶(Oh, Kim, & Kim, 2015) ⁷(Cornell & Schwertmann, 1996) ⁸(Su et al., 2007); [o.d.] = own data;

Figure captions

Fig. 1: CAD sketch of the measurement device and measurement setup for the conductivity measurements

Fig. 2: Comparison of method 1 (M1) and method 2 (M2) based on the indicators IoEC (left) and IoD (right)

Fig. 3: Electrical conductivity ($k / S m^{-1}$) versus applied pressure (P / kPa) with M1 (left) and M2 (right), (a) and (b): all samples, (c) and (d): without AC-RuO-40

Fig. 4: Change of electrical conductivity ($EC / S m^{-1}$) versus applied force (10 – 50 N) for the composites containing between 5 wt% and 40 wt% of Fe_3O_4 (all values from Method 2)

Fig. 5: Electrical conductivity ($EC / S m^{-1}$) versus applied pressure (P / kPa) for the activated carbon (AC-600-800), activated carbon plus additives (AC-600-800-add) and commercial activated carbon based on peat plus additives (AC-add); (a): M1; (b): M2

Fig. 6: Electrical conductivity ($EC / S m^{-1}$) versus applied pressure (P / kPa) for the activated carbon (AC-600-800) and three biochars produced by pyrolysis at 600 °C (P600), 800 °C (P800) and 900 °C (P900) (values from Method 2)

Fig. 7: Electrical conductivity ($EC / S m^{-1}$) versus applied pressure (P / kPa) for AC-600-800 at high pressures (loads between 2-20 kN)

Fig. 8: Comparison of M1 (8a, c, e, g) and M2 (8b, d, f, h) concerning electrical conductivity ($EC / S m^{-1}$) versus sample volume (V / cm^3) of biochars, activated carbon (plus additives) and composites (lines between data points for visual aid)

Fig. 9: Comparison of M1 (left) and M2 (right) concerning electrical conductivity ($EC / S m^{-1}$) versus sample density ($\rho / g cm^{-3}$) of biochars, activated carbon (plus additives) (above) and composites (below)

Fig. 10: Mechanical work (MW / J) versus density ($\rho / g cm^{-3}$) of biochars, activated carbon AC-600-800 (-add), AC-add and composites (M2)

Fig. 11: Comparison of M1 and M2 via Compression Ratio

Fig. 12: Compression Ratio for all studied materials (M2)

Fig. 13: Theoretical structure development of heat treated biomass with carbonization temperature: (A) increasing content of aromatic C within a highly disordered and amorphous structure; (B) growing sheets of conjugated aromatic carbon without order in the 3rd dimension; (C) structure becomes graphitic with order in the third dimension ($> 2500\text{ °C}$) (Downie, 2011) (Copyright: Adriana Downie)

























