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

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Abstract
This study focuses 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 corn cob at three different temperatures (600, 800, and 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 oxide (RuO2 or Fe3O4) 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 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 preload) showed that a prepelletization of the samples is not necessary to obtain reliable results. By analyzing the obtained EC values while taking mechanical and physicochemical 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% RuO2, 10 wt% Fe3O4), while the treatment with additives leads to a decrease of EC. The EC values among all samples varied between 0.8 S/m (biochar) and 408 S/m (AC/RuO2 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.

KEYWORDS
biobased materials, bioeconomy, biomass carbonization, carbon materials, carbonaceous powders, electrical conductivity, electrochemical double-layer capacitor (EDLC), energy storage, nanocomposites
1 | 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 & Dietmeier, 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 physicochemical properties, which favor 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; 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 (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 Holm (2000) and Mrozowski (1957), the compression of powders is necessary to reduce the voids between particles and thus increase the interparticle 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 as 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. As it was shown that exactly these heterogeneous materials show promising capacitive behavior as electrode materials for EDLCs because of their pseudocapacitively properties (Frackowiak & Béguin, 2001; Hulicova-Jurcakova et al., 2009; Raymundo-Piñero et al., 2009; Su, Wu, Bao, & Yang, 2007; Wang, Zhang, & Zhang, 2012; Zhao, Xia, & Zheng, 2012; Zhi, Xiang, Li, Li, & Wu, 2013), this study focusses on EC measurements of such 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, Darmstadt, Kaliaguine, Sümmchen, & Roy, 2001) and that composites of activated carbon (AC) and certain metal oxides (e.g., Al$_2$O$_3$, Fe$_2$O$_3$, 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 (Pantea, Darmstadt, Kaliaguine, & Roy, 2003).

This study presents the results of conductivity measurements under moderate pressure (max. 637 kPa) of 12 different biobased materials including AC, carbon composites with metal oxides (AC + RuO$_2$ or Fe$_3$O$_4$), and electrode materials (AC + binder or conductive additives). The results were obtained by applying two different
measurement methods (with and without preload), and they were analyzed considering the different material compositions and their effect on conductivity. Besides, the two measurement methods were compared. Since in the literature, to the best of knowledge, no works dealing with EC measurements of biobased carbonaceous powder materials based on corncob and composites can be found, this study 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 study, 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 (EC) of carbonaceous powders including the above-mentioned models, it is referred to the work of Celzard et al. (2002).

2  | MATERIALS AND METHODS

2.1  | 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°C or 800°C with a constant heating rate of 10°C/min. After reaching the temperature, the chars were left to react for 1 hr. 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 hr. This was followed by a second ramp with a heating rate 5°C/min up to 900°C and a reaction time of 1 hr.

Another sample was an AC (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 hr. 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 EC of the leachate was lower than 30 μS/cm. Finally, the AC were dried for at least 16 hr 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.

These composites can be classified into three groups: One group was the activated carbon combined with different percentages of Fe₃O₄ (5, 10, 20, 40 wt%), another group was the activated carbon treated with different percentages of RuO₂ (10, 40 wt%), and the last group was 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 are 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.

2.2  | Methods

2.2.1  | 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 (HEKAttech) according to the DIN standard 51,732. The ash content was determined by difference (Equation 1).

\[
\%\text{Ash} = 100 - \%\text{C} - \%\text{H} - \%\text{N} - \%\text{S} - \%\text{O}
\]  

Elemental analysis was conducted only for the four carbon samples including three biochars P600, P800, P900 and the activated carbon AC-600-800. As 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 has been considered to be redundant and therefore unnecessary.

2.2.2  | DC electrical conductivity measurements

Conductivity measurements were conducted using a self-constructed device based on a procedure described elsewhere (Barroso-Bogeat et al., 2014; Celzard et al., 2002; Sánchez-González, Maclás-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 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).

Pretests with a constant mass of 0.09 g for each sample showed that the height of the sample varies significantly between the different materials. As 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 min 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 preload 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 (Solvex, 2018) and is ±0.5 S/m.

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

The EC was calculated using the following formula

\[ \kappa = \frac{h}{R + A} \]  

with \( \kappa \) = 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 \( A = 0.79 \text{ cm}^2 \), the exact height was determined by the altimeter of the Instron device, and the electrical resistance was measured with the multimeter.

3 | RESULTS

3.1 | Elemental composition of the carbon materials

The EC of carbon materials is directly related to 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 noncondensable...
volatile and char in a temperature range between 200 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 corncob from 46.2 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.

### 3.2 | Conductivity studies

#### 3.2.1 | Method comparison (M1 vs. 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, and one AC plus additives). The density for each material was calculated based on Equation 3:

\[
\rho = \frac{m}{l \times A} \times 1000 [g/cm^3]
\]  

where \( m \) is the mass of the sample [g], \( l \) is the length of the sample [mm], and \( A \) is the cross-sectional area of the sample [mm²].

The 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:

\[
\text{IoEC} = \frac{\kappa_2 - \kappa_1}{\kappa_1} \times 100
\]  

\[
\text{IoD} = \frac{\rho_{50N} - \rho_{10N}}{\rho_{10N}} \times 100
\]

These indicators allow better comparability of the two methods. By comparing the percentage increase of EC 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 as shown in.
Table 3. The IoD reached with M2 is between 3% and 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 preload (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 and 0.08 S/m) compared to M1 (3.05 and 8.54 S/m), 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 at 1.19 g cm⁻³ (M1) and 408 S/m at 1.01 g cm⁻³ (M2)), whereas the sample containing additives again shows higher EC values with higher densities.

### Variation of EC with different parameters (M1 vs. M2)

**EC vs. 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

| Method | Sample | \(\kappa_1\) [S/m], 10 N | \(\kappa_2\) [S/m], 50 N | IoEC a [%] | \(\rho_{10N}\) [g/cm³] | \(\rho_{50N}\) [g/cm³] | IoD b [%] |
|--------|--------|-------------------|-------------------|----------|-------------------|-------------------|----------|
| M1 (with preload) | P-600 | 3.05 | 8.54 | 180 | 0.7 | 0.79 | 13 |
| | AC-600-800 | 25.89 | 80.41 | 211 | 0.39 | 0.43 | 10 |
| | AC-600-800-RuO-40 | 140.37 | 316.05 | 125 | 1.06 | 1.19 | 12 |
| | AC-600-800-add | 34 | 81.22 | 139 | 0.6 | 0.66 | 10 |
| M2 (without preload) | P-600 | 0.02 | 0.08 | 300 | 0.39 | 0.47 | 21 |
| | AC-600-800 | 26.97 | 80.32 | 198 | 0.24 | 0.27 | 13 |
| | AC-600-800-RuO-40 | 149.7 | 408 | 173 | 0.85 | 1.01 | 19 |
| | AC-600-800-add | 24.23 | 55.5 | 129 | 0.36 | 0.43 | 19 |

*Increase of electrical conductivity in % (from 10 to 50 N). Increase of density in % (from 10 to 50 N).
correlation between applied pressure and conductivity for all materials, even though the correlation strength is slightly varying depending on the material and the chosen method. The correlation coefficient $r$ between EC and $P$ lies between 0.84 and 1 for M1 (Figure 3a,c) and from 0.97 to 1 for M2 (Figure 3b,d) which indicates a strong to perfect linear correlation between the parameters.

The two graphs (Figure 3a,b) show the above-average performance of the composite material AC-RuO$_4$-40 with conductivity values of up to 408 S/m (at 637 kPa). This means a conductivity value nearly six times higher than that of the composite with only 10 wt% RuO$_2$ (69 S/m at 637 kPa).

For the composites with Fe$_3$O$_4$, the opposite can be observed: the higher the amount of Fe$_3$O$_4$, the lower the EC of the respective composite. By doubling the share of Fe$_3$O$_4$ 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 to 71.14 S/m; M2: from 80.28 to 61.23 S/m).

By again doubling the share of Fe$_3$O$_4$ 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% Fe$_3$O$_4$. It shows almost the same EC values as the composite AC-600-800-FeO-20 for all pressures applied (Figure 4).

As during electrode manufacturing for EDLCs, additives are added to the active material (Lee et al., 2016; Liu & Cao, 2010; Pandolfo & Hollenkamp, 2006; Zhu et al., 2016), and the influence of these additives on the EC performance is of great interest. The graphs in Figure 5 show the EC values obtained with M1 (Figure 5a) and M2 (Figure 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 before activation (P600) to 80 S/m 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 and 20 kN were applied to the sample, while the

### Table 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    |
| 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 |

![Figure 4](image1.png)

**Figure 4** Change of electrical conductivity (EC/S/m) vs. applied force (10–50 N) for the composites containing between 5 and 40 wt% of Fe3O4 (all values from Method 2)

![Figure 5](image2.png)

**Figure 5** Electrical conductivity (EC/S/m) vs. 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
electrical resistivity was determined. The obtained EC values are shown in Figure 7.

The positive correlation between pressure and EC remains 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 vs. volume \((V)\)
The volume of the samples was calculated with the following formula:

\[
V_j = \pi r^2 h_j
\]  

with \( r \) = inner radius of sample holder, \( h \) = height of the sample, \( j = 10–50 \) N.

The calculated volumes are set in relation to 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. First, 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, for example, 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 at 0.1 cm\(^3\); 80.32 S/m at 0.09 cm\(^3\) (M2) (Figure 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) (Figure 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 for P600 vs. 17.95 S/m for P900 at \( V = 0.09 \) cm\(^3\) both (M2) (Figure 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 (Figure 8e,f). Comparing M1 (Figure 8e) and M2 (Figure 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\(_3\)O\(_4\)-containing composites, the opposite case can be observed (Figure 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 (Figure 8h) the curves of the two composites are nearly congruent, whereas for M1 (Figure 8g), this is not the case.

EC vs. density \((\rho)\)
The change of EC with sample density \( \rho \) is illustrated in Figure 9. As expected, the curve shapes of the EC–\( \rho \) plot are similar to the respective ones of the EC–\( V \) plots. Nevertheless, there are some interesting observations to be mentioned regarding the EC–\( \rho \) relation. For example, for the noncomposite 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 \( \rho \) and EC can be observed.
In general, the curves of M2 (Figure 9b,d) seem to be more consistent and with less anomalies.

**EC vs. mechanical work (MW)**

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

\[
MW = \sum_{j=1}^{J} p_j \cdot A \cdot (h_{j-1} - h_j)
\]  
(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 vs. 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 labeled arrows. First of all, it is remarkable that with increasing carbonization temperature (\( P600 < P800 < P900 \)) the relation between MW and \( \rho \) is turning from a nonlinear 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–ρ 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 becomes even worse after the treatment of AC–600–800 with Fe3O4. 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–RuO2 composites show again a certain degree of regularity. Especially for the composite containing 10 wt% of RuO2, a linear correlation ($r_{AC-600-800-RuO_{20}} = 0.96$) and an increase in the slope of the curve are 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 RuO2. 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.

### 3.2.3 | 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:

$$CR = \frac{V_{10N}}{V_{50N}}$$

The comparison of the CRs obtained for M1 and M2 is depicted in Figure 11. It can be noted that a higher compression is achieved with M2 for all samples except for the composites containing Fe3O4.

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 noncommercial 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 Fe₃O₄ to the AC-600-800. However, it is notable that with increasing content of Fe₃O₄, the CR constantly decreases which implies an increase in compressibility. In contrast, for the RuO₂-composites, the opposite is the case. With increasing RuO₂-content, the CR increases from 1.15 to 1.19 which implies a lower compressibility of AC-600-800-RuO₁₀ compared to AC-600-800-10.

**FIGURE 10** Mechanical work (MW/J) vs. density (ρ/g/cm³) of biochars, activated carbon AC-600-800 (-add), AC-add, and composites (M2)

**FIGURE 11** Comparison of M1 and M2 via compression ratio

4 | **DISCUSSION**

As already mentioned, the aim of this study was 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.

4.1 Method comparison

Regarding the first question, it has been shown that focusing 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, pretests 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 Equation 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 preload of 50 N within M1, pelletization 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 prepelletization 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 preload 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 behavior as 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.

Because of the lack of a preload during M2, the compaction (CR), increase in density (IoD), or decrease in volume, respectively, were higher for all materials. Hence, M2 allows the EC assessment within a wider range of compaction, 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 preload. Depending on the material, this proceeding (compression with 50 N → partial decompression → compression with 10–50 N) could have led to the irregularities within the obtained data. Since during M2, no preload was applied, and 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.

4.2 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.

4.3 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 favors 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 sp² state (in the biomass precursor) to conjugated carbon in the sp³ state during carbonization (Biniak, Pakula, Radovic, & Swiatkowski, 2001), the decrease of acidic functionalities on the carbon surface after 600–700°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 increases 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 volatilization of basic cations such as Ca⁺ or Mg²⁺ only starts when temperatures of about 1,000°C are reached (Neary, Klopatek, DeBano, & Ffolliott, 1999), while nonmineral 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 S/m; Pandolfo & Hollenkamp, 2006) due to the high proportion of σ-bonds between sp³-hybridized carbon atoms, the formation of carbon atoms in the sp²-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 H₂O and CO₂) starts at a temperature range between 600 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** 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 (>2,500°C) (Downie, 2011) (Copyright: Adriana Downie)
(Figure 13c) (a-axis), graphite crystals show specific resistivities of \(\sim 10^{-3} \text{ } \Omega \text{ } \text{cm}\), whereas in the c-axis direction (perpendicular to a-axis) the specific resistivities are higher (\(\sim 10^{-2} \text{ } \Omega \text{ } \text{cm}\)) (Kinoshita, 1988). This corresponds to a EC of \(\sim 10^7 \text{ } \text{S/m}\) in the a-axis and \(\sim 10^4 \text{ } \text{S/m}\) in the c-axis of the graphite crystals. Single graphite crystals thus show EC values similar to semimetals 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 the increase of EC from P600 to P900 and, additionally, the effect of the activation process on the EC.

### 4.4 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-P600 with KOH deserves a more detailed examination as well (Hoffman et al., 2018). 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.

Concerning the composite materials, the obtained results were highly heterogeneous which was, to a certain extent, expected due to the different electronic properties of RuO\(_2\) and Fe\(_3\)O\(_4\). Among the six oxides of the transition metal ruthenium, RuO\(_2\) 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 RuO\(_2\) highly depend on its structural properties. In particular, the EC significantly decreases when RuO\(_2\) is in an amorphous state. Due to the sol-gel method, which was used to produce the AC-RuO\(_2\)-composites studied in this work, and the low annealing temperature of 150°C, it must be assumed that the RuO\(_2\) occurs in its amorphous state here. This assumption agrees well with the...
results obtained with XRD measurements in the work of 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-RuO-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 shows 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, and ZnO) 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 state (with an EC of 10^5 S/m, 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 as the composite with only 10 wt% of RuO2 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 RuO2 (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-Fe3O4 composites. Here, 10 wt% Fe3O4 seem to be the ideal proportion regarding EC (EC values higher than those of AC-600-800), while 40 wt% 

| Oxides/composites | Electrolyte | Capacitance (F/g) | EC (S/m) |
|--------------------|-------------|------------------|---------|
| AC                | Na2SO4      | 79.2^a           | 80.32 (50 N) [o.d.] |
|                   | Na2SO3      | 99.4^a           | 1.7 × 10^3 (20 kN) [o.d.] |
| RuO2, xH2O        | H2SO4, Na2SO4 | 1.200–2.200 (1.23 V)^c | 2.8 × 10^6 (single-crystal)^d |
|                   | KOH solution (6 mol/L) | 768^f | 10^5 (polycrystalline)^e |
|                   |             | ~1 (amorphous)^f |         |
| RuO2/AC           | H2SO4       | 185^g            | 408 (50 N) [o.d.] |
| Fe3O4             | Na2SO4      | 78.5 (1 V)^a     | 10^4–10^6 |
| Fe3O4/AC          | Na2SO4      | 154.3^a          | 80.28 (50 N) [o.d.] |
|                   | Na2SO3      | 202.6^b          |         |

[o.d.] = own data. ^aHe et al. (2013). ^bOh, Kim, and Kim (2015). ^cHu, Chen, and Chang (2004). ^dSteves (2011). ^eZhi et al. (2013). ^fSu et al. (2007). ^gHu and Chen (2004). ^hCornell and Schwertmann (1996).
Fe₃O₄ lead to a decline in EC of about 50% for all pressure levels. Here, the conclusions made by Barroso-Bageat et al. for other AC-metal oxide composites seem to fit quite well as the Fe₃O₄ particles cause almost no changes in the mechanical properties of the material (density and CR). However, considering the EC value of Fe₃O₄ (Table 5), the EC value of the composite should increase with increasing content of the metal oxide. Rather, it appears that the Fe₃O₄ 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. In particular, 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 to 80.32 S/m). 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 m²/g; Hoffman et al., 2018) and AC-add (physical activation, SSA of raw AC = 950 m²/g; Wolf, 2014). The EC of the commercial AC is given with 33 S/m (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 physicochemical properties, morphology, particle size, and intrinsic EC and the respective interactions between these specific properties and the carbon particles. An increasing proportion of RuO₂ nanoparticles, for example, lead to increasing EC values of the respective composite, while for Fe₃O₄ 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 RuO₂ nanoparticles (40 wt%) favor the establishment of greater contact areas between the particles, whereas high shares of Fe₃O₄ particles block electron pathways and act as an insulator because of their morphology and particle size. However, lower proportions of Fe₃O₄ (10 wt%) lead to increasing EC values compared to the raw AC which suggests that the positive effect of the high intrinsic EC of Fe₃O₄ neutralizes the negative effect of the Fe₃O₄ 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, in this context, the most promising material.

Regarding additives, it can be concluded that even 5 wt % of PTFE binder considerably reduce the EC of AC and invalidates any positive effects of the conductive additive AB (EC = 400 S/m; 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 nonbiobased chemicals in the electrode production.

Concerning the method development, it has been shown that a prepelletization of the samples powder materials leads to undesirable anomalies during the measurements (e.g., partial decompression) which resulted in high standard deviations. Reliable results were obtained 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 biobased electrode materials in EDLCs and thus make a contribution to the development of biobased and sustainable solutions in the framework of bioeconomy.

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