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## Integration of capacitors with carbon-lignin based electrodes in rail vehicles for enhanced energy efficiency

Beata Kurc<sup>a,b</sup>, Krystian Woźniak<sup>b,a</sup>, Łukasz Rymaniak<sup>a,\*</sup>, ktalia Szymlet<sup>a,b</sup>

<sup>a</sup> Faculty of Civil and Transport Engineering, Poznan University of Technology, Poland

<sup>b</sup> Center of Rail Vehicles, Łukasiewicz Research Network – Poznan Institute of Technology, Poznan, Poland

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Braking energy Capacitors Energy consumption Lignin Railbus The article presents considerations regarding the possibility of recovering braking energy of a rail vehicle. The energy parameters obtained during acceleration and braking of the loaded railbus were taken as input data. It was found that over 13 kWh of energy was lost irretrievably in the braking resistors. Due to the speed of the discussed process, capacitors with an original design were proposed for energy recovery. For the purposes of this study, electrodes were fabricated using carbon derived from lignin carbonization at two distinct temperatures: 900°C and 1000°C. Based on the electrochemical tests carried out, it was found that the second proposed solution achieves a significantly better power-to-weight ratio -13 kW/kg.

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#### 1. Introduction

The European Union (EU) conducts continuous activities aimed at protecting the environment and implementing a sustainable development policy. Recent announcements and decisions are intended to lead the EU to achieve climate neutrality in 2050. As a result, there will be no net emissions of greenhouse gases and economic development will not depend on natural resources [2]. This is to be achieved while simultaneously developing the overall well-being of the inhabitants of the EU community. Therefore, extensive development activities should be carried out aimed at energy saving and recovery in all industrial and transport zones, where this is possible.

Research is carried out on rail vehicles regarding their energy consumption [4, 6, 8]. Due to the development of measuring equipment and its miniaturization, pollutant emission tests in real operating conditions are becoming more and more common [10, 11]. Nonetheless, emission measurements should be combined with the assessment of the energy consumption of other electrical components in order to create more energy-efficient structures.

The railway market is dominated by conventional drive systems with CI engines. Manufacturers are trying to create solutions that reduce the carbon footprint, e.g. developing hybrid designs, designing drives based on fuel cells, creation of exhaust gas after treatment systems etc. [3, 12, 13]. However, these activities require continuous research in order to obtain maximum benefits ecologically but also economically [7, 14].

In 2022, 246.8 million tons of cargo and 342.2 million passengers were transported by rail [15]. The rolling stock in Poland includes locomotives -478vehicles (including 123 diesel); motor wagons -79vehicles (including 2 diesel vehicles) and multiple units -1477 vehicles (including 1206 combustion vehicles) [15]. The problem of energy efficiency of vehicles is related not only to ecology, but also to transport economics. During the operation of rail vehicles, significant amounts of energy are irretrievably lost during braking. The high inertia of the machine related to its mass has the greatest impact on the ener-

<sup>\*</sup> Corresponding author: lukasz.rymaniak@put.poznan.pl (Ł. Rymaniak)

gy balance of the facility. This problem is being solved more and more effectively in motor vehicles with hybrid and electric drives. Braking energy recuperation is also used in city buses equipped with alternative drive systems. The rapid braking process of vehicles is unfavorable in terms of battery charging. Therefore, it is possible to use recuperators in the form of capacitors.

Capacitor power, often referred to as "capacitor energy" or "capacitor storage" is a fundamental concept in electronics and electrical engineering. Capacitors are passive electronic components designed to store and release electrical energy. They play a crucial role in various applications, from filtering noise in power supplies to timing circuits and energy storage systems. Understanding how capacitors store and release power is essential in designing efficient and reliable electronic system.

A capacitor consists of two conductive plates separated by an insulating material called a dielectric. When a voltage is applied across the plates, an electric field is established within the dielectric. This electric field stores electrical energy in the form of an electric charge on the plates.

The energy stored in a capacitor is proportional to the square of the voltage across it and the capacitance (C) of the capacitor. The formula for calculating the energy stored in a capacitor is:

$$E = \frac{CV^2}{2}$$
(1)

where E represents energy in joules, C is the capacitance in farads, and V is the voltage across the capacitor in volts. This equation illustrates that increasing the voltage or capacitance of a capacitor results in more energy storage.

While capacitors are valuable components in electronic systems, they have limitations. The amount of energy they can store is generally much lower than batteries, and they can discharge quickly, making them less suitable for long-term energy storage. Additionally, capacitors can have limitations in terms of size, cost, and lifetime.

In the era of sustainable economic progress, the quest for creative solutions to make the most of available raw materials is a critical concern. A particular focus is placed on the efficient utilization of natural resources, which also contributes to lowering atmospheric carbon dioxide levels. This inclination underscores the interest in lignin, a byproduct generated in substantial quantities during cellulose pulp production. Although this byproduct is primarily employed for energy purposes, the latent potential within lignin's structure opens up extensive avenues for scientific and industrial advancement. It's imperative to recognize the extraction of low-molecular-weight substances from lignin and its chemical modification (functionalization) at this juncture. This biopolymer can also be harnessed in crafting functional hybrid materials. By preserving the synergistic properties of lignin alongside other components within such systems, it becomes feasible to create products endowed with distinctive qualities for a wide range of applications [5].

The presented article considered energy recovery through the use of proprietary capacitor designs using carbon derived from lignin.

### 2. Energy during vehicle braking

Braking energy recuperation contributes to improving the energy balance of vehicles. This type of solutions are being introduced in passenger cars and city buses. This applies to facilities equipped with hybrid and electric drives. As shown in publication [9] during the RDE (Real Driving Emission) tests, in accordance with the homologation requirements, the recovered energy from the braking process constitutes approximately 10% of the total energy demand to complete the route. In city buses, these values reach about 16%, and their construction increasingly uses supercapacitors, in addition to electrochemical batteries [16].

In order to estimate the value of energy lost in braking, tests were carried out on the traction properties and energy consumption of the diesel-electric multiple unit on the test track. During the tests, the heating, air conditioning and interior lighting systems were turned off. The remaining electrical and electronic equipment of the vehicle was in normal operation. The mass of the research object ready to move was approximately 120,000 kg. The tests were performed for the vehicle with a load of: 11,211 kg: all seating positions occupied and standing positions occupied for a density of 2 people/m<sup>2</sup>. The research object was accelerated with maximum power to 160 km/h, and then electrodynamic braking was implemented with full efficiency until stopping on a straight line. The energy consumption results obtained for a representative trip are presented in Table 1. The energy needed to accelerate the object  $(E_z)$  was 56.948 kWh, while the energy transferred to the braking resistors (E<sub>r</sub>) was 13.048 kWh. To determine electricity consumption, a set of measuring equipment was used, consisting of a digital recorder equipped with advanced mathematical functions and voltage and current transducers adapted to measure direct and alternating components. The speed and distance were determined based on the readings of odometry devices and the GPS signal.

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Parameter	Unit	Value
E <sub>z</sub> electricity taken from the grid	kWh	56.948
E <sub>0</sub> electricity fed into the grid	kWh	0
E <sub>r</sub> electrical energy fed into the braking resistors	kWh	13.048
E <sub>c</sub> total energy	kWh	43.9
E <sub>b</sub> electricity balance	kWh/km	9431

Table 1. List of characteristic values of energy parameters during the test of the research object

Based on the obtained characteristics, it can be calculated that the average energy consumption during acceleration was 1620 kWs. The average energy in the braking process was 1152 kWs (Fig. 1).



Fig. 1. Vehicle speed (V), electrical energy taken from the grid (Ez) and electrical energy fed into the braking resistors (Er) over time during the test

# **3.** Development of new capacitors utilizing carbon derived from kraft lignin

Lignin is a complex, three-dimensional polymer that plays a crucial role in the structural integrity of plant cell walls. Kraft lignin is characterized by its intricate and robust chemical structure. The properties of kraft lignin can vary depending on the type of wood used and the specific pulping conditions. This variability makes it suitable for a range of applications, as its characteristics can be tailored to meet different requirements. Researchers are exploring its use in bioplastics, carbon materials, antioxidants, and as a precursor for high-value chemicals. Kraft lignin is a versatile and sustainable resource with the potential to play a significant role in the development of environmentally friendly and value-added products. Its utilization is not only environmentally responsible but also economically promising as researchers continue to unlock its potential in various industrial and scientific applications. The proposed material was used in the construction of the capacitor, the author's prototype of which is presented in this chapter.

Carbon materials derived from kraft lignin were synthesized through carbonization within a nitrogen-

rich environment (inert gas) using a Nabertherm tube furnace. The entire procedure extended over 6 hours, featuring a temperature increment of 300°C per hour, a carbonization phase of 4 hours, and a 2-hour furnace heating phase. The flow rate of nitrogen gas reached 50 liters per hour. Before the carbonization commenced, the system was preconditioned in an inert gas atmosphere for 1 hour. The technical gas used maintained a purity level of 99.998%. Samples carbonized at two temperatures: 900°C and 1000°C.

Carbon electrodes were prepared in tablet form by measuring out precise quantities of the following components: carbon material; PVdF binder and acetylene black. This mixture was meticulously ground in an agate mortar to achieve a uniform mass for the electrode. Subsequently, portions of this mass, were transferred onto copper collectors. After drying these electrodes at 105°C, the tablets were weighed and paired based on their similar mass (approximately 6 mg each).

Electrodes with known mass were then set up within a Swagelok® measuring vessel. The working electrode, slightly lighter in mass, was positioned on the lower current collector to facilitate proper electrolyte wetting through gravity flow. A glass fiber separator was introduced on this electrode to prevent any physical contact between the electrodes. Finally, the opposing electrode was placed, and the entire system was filled with electrolyte and sealed using the current collector of the opposing electrode.

To assess the electrochemical characteristics of materials, a multi-channel potentiostat provided by Gamry Industries was employed. This potentiostat featured seven identical modules of model 1000. This apparatus is not limited solely to cyclic voltammetry for electrochemical property measurements; it offers the versatility to evaluate materials using various techniques such as linear voltammetry, stripping voltammetry, pulsed voltammetry, chronoamperometry, and more. The testing of capacitors was conducted within a two-electrode symmetrical system, using processed lignin.

Cyclic voltammetry (CV) represents one of the fundamental techniques for exploring the electrochemical characteristics of materials. It relies on the ability to electrochemically oxidize and reduce the substance under examination. In this method, three electrodes are employed: the working electrode, the reference electrode, and the auxiliary electrode. In the classic three-electrode setup, current flows from the working electrode to the auxiliary electrode to maintain a constant potential at the reference electrode. This arrangement allows precise polarization of the working electrode while simultaneously obtaining accurate potential readings between the working and reference electrodes.

The reference electrode is commonly a silver chloride electrode (Ag, AgCl|Cl<sup>-</sup>) or a calomel electrode (Hg, Hg<sub>2</sub>Cl<sub>2</sub>|Cl<sup>-</sup>). The auxiliary electrode can be constructed from any highly conductive material, with the specific reactions at this electrode being of little significance as long as they do not interfere with current conduction. Platinum is often the material of choice for the auxiliary electrode. While measurements can be carried out in a two-electrode system (working and reference), the addition of an auxiliary electrode enhances the stability and precision of the results. The analytical signal is determined by the change in current relative to the change in electrode potential.

Cyclic voltammetry, unlike linear voltammetry, doesn't conclude the measurement once the maximum voltage is reached; instead, the voltage is decreased to its initial value. An important parameter in these measurements is the scanning speed, denoted in millivolts per second (mV/s), which governs the rate of increase or decrease in electrode potential.

The tested system was comprised of two electrodes separated by an electrolyte. Consequently, one can view a capacitor cell as a pair of capacitors connected in series, with their combined capacitance given by the formula (1):

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$$
(2)

where  $C_1$  and  $C_2$  represent the individual electrode capacitances.

Assuming that  $C_1 = C_2 = Cell$  electrodes and substituting these values into formula (2), one obtains the following relationship as shown in (3).

$$C_{Elektrode} = 2C \tag{3}$$

To determine the specific capacity per unit mass of activated carbon, use the formula  $C_{sp}$ , denoted in (4)

$$C_{sp} = \frac{C_{Elektrode}}{m}$$
(4)

where m denotes the mass of a single electrode (mass of activated carbon) in grams.

The capacitance of a capacitor cell can be expressed by the equation illustrated in (5):

$$C = \frac{I}{dU/dt}$$
(5)

where C represents the capacitance of the capacitor in farads, I is the current in miliamperes, and dU/dt signifies the rate of voltage change over time in millivolts per second.

The equations (2)–(5) were used to analyze the data obtained from voltammetric measurements. The capacitance calculations took into account the value of the current flowing through the tested system when the potential reached half of the set value. The scan rate (dU/dt) was 2 mV/s. The potential range to which the selected capacitor was charged was determined based on the width of the electrochemical stability of the electrolyte used. The output potential range was 0-1 V. The change in potential over time was 2 mV/s.

The voltammograms of the constructed electrochemical capacitors, in the potential range of 0–1 V, show an almost perfect course, proving the lack of electrode reactions in the given potential range. For a symmetrical capacitor made of carbon (after carbonization at 900°C) (Fig. 2a), minimal deviations from this shape of the voltammetric curve were observed, consisting in reduced current at higher potential values. Based on the obtained voltammetric curves, using the relationship presented in equation 5, the specific capacities of the constructed electrochemical capacitors were estimated. Values per gram of carbon are calculated. The obtained results imply that the temperature at which carbonization occurs could impact the way charges move, favoring the diffusion of ions.





Fig.2. The voltamperogram of a capacitor cell with a 1 mol/L
H<sub>2</sub>SO<sub>4</sub> electrolyte and carbon electrodes, recorded at a scan rate of 2 mV/s, was obtained for two different samples: a) following carbonization at 900°C, and b) after carbonization at 1000°C

This is likely achieved by enhancing the electrode's ability to interact with the electrolyte (lowering its surface tension) and forming a thin layer of electrolyte that wets the electrode surface. The higher carbonization temperature contributed to obtaining a slightly better specific capacity (Table 2). It should be noted that the capacitance values obtained using the cyclic voltammetry method should be treated as indicative only, because it is a definitely qualitative method. Galvanostatic charging and discharging measurements were performed for the constructed electrochemical capacitors, during which the time of charging and discharging the capacitor to a specific potential with a current was recorded with a previously determined value.

Table 2. Specific capacity calculated from voltammograms

Carbonization	Carbon	C <sub>sp</sub>
temperature [°C]	[mg]	[F/g]
900	6.5	178
1000	6.4	210

In all cases examined, the IRs ohmic drop shown in Fig. 3a (occurring in the section showing the capacitor discharge) is small. The occurrence of a potential drop may result from electrolyte resistance, electrode resistance and resistance related to the penetration of electrolyte into the electrode pores [1].



Fig. 3. Charge/discharge curves of a capacitor cell with a 1 mol/L  $H_2SO_4$  electrolyte, determined using the galvanostatic method with a 5 mA current, were recorded for two different samples: a) following carbonization at 900°C, and b) after carbonization at 1000°C

The charge/discharge curves of all the capacitors we constructed exhibit a similar shape to the charge/discharge curves of an ideal capacitor. This similarity underscores the excellent capacitive characteristics of these capacitors. By analyzing these charge/discharge curves, calculated the specific capacity of the tested capacitor cells (Table 3).

Table 3. Capacities specific to constructed capacitors as estimated from galvanostatic charge/discharge measurements

Carbonization	Carbon	C <sub>sp</sub>
temperature [°C]	[mg]	[F/g]
900	6.5	140
1000	6.4	215

Power P is the product of the voltage U and the current I flowing in the circuit:

$$P = UI \tag{6}$$

The discharge current will cause the potential to decrease from the initial value  $U_0$  to the value U, according to the equation:

$$U = U_0 - IR_S \tag{7}$$

where:  $R_s$  is the serial resistance of the capacitor.

Substituting equation (7) into equation (6) gives:

$$\mathbf{P} = \mathbf{I}\mathbf{U}_0 - \mathbf{I}^2\mathbf{R}_\mathbf{S} \tag{8}$$

Power takes its maximum value when:

$$\frac{dP}{dI} = 0 = U_0 - 2IR_S$$
 (9)

from this it follows:

$$I_{\max} = \frac{U_0}{2R_S}$$
(10)

The maximum value of the potential can be obtained by substituting equation (9) into equation (7):

$$U_{max} = U_0 - I_{max}R_S = \frac{U_0}{2}$$
 (11)

After substituting equations (10) and (11) into equation (6), the final expression for the maximum power  $P_{max}$  is obtained [17]:

$$P_{\max} \frac{U_0}{2R_S} \frac{U_0}{2} = \frac{U_0^2}{4R_S}$$
(12)

A capacitor does not directly generate power; instead, it stores and releases electrical energy. However, it is possible to calculate the rate at which a capacitor stores or releases energy, which is often referred to as the "apparent power" associated with the charging or discharging process. In turn, the energy equation describes how much electrical energy is stored in a capacitor when it is charged to a specific voltage. Energy is stored in the electric field between the capacitor plates and can be released when the capacitor discharges. Additionally, the energy and power of electrochemical capacitors have been calculated, by the formulas presented in equations (Table 4).

Table 4. Power	and	energy	of the	author	`s cap	acitors
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Carbonization	U <sub>max</sub>	E <sub>sp</sub>	P <sub>max</sub>
temperature [°C]	[V]	[kJ/kg]	[kW/kg]
900	3.5	190	3
1000	3.0	165	13

### 4. Summary

Reducing energy consumption and recovering it in all branches of industry and transport is currently the greatest challenge. The article introduces proprietary capacitor solutions utilizing carbon materials derived from lignin. Considering the voltage and energy values obtained from these capacitors, their maximum power based on mass have been determined. Specifically, for the carbon derived from lignin carbonized at 900°C, a power output of 3 kW/kg has been achieved, while for the electrodes based on carbon obtained at 1000°C, the calculated power was 13 kW/kg.

These achieved power values strongly support the feasibility of integrating the capacitor system into rail vehicles. The calculated relationships align well with

### Nomenclature

the energy range typically associated with braking scenarios in rail vehicles, as demonstrated in this study. This suggests that the proposed capacitor system is well-suited for effectively capturing and storing energy during braking events in rail transportation. When estimating, it can be assumed that the mass of the container together with peripheral devices (an innovative capacitor system) for a rail vehicle would constitute a small additional mass of the object, below 0.2‰. At the same time, energy recovery could reach up to several dozen percent. In order to determine the operating speed of the proposed capacitors, it is necessary to extend the research to include quality and durability issues. Moreover, it is necessary to perform tests in real operation in order to collect operational data on a larger sample, in natural conditions and not forced by experiment. Such work will allow to determine more precise parameters of the designed energy storage systems, which is being carried out by the authors.

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