



Article Development of Disposable and Flexible Supercapacitor Based on Carbonaceous and Ecofriendly Materials

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Abstract: A novel flexible supercapacitor device was developed from a polyethylene terephthalate substrate, reused from beverage bottles, and a conductive ink based on carbon black (CB) and cellulose acetate (CA). The weight composition of the conductive ink was evaluated to determine the best mass percentage ratio between CB and CA in terms of capacitive behavior. The evaluation was performed by using different electrochemical techniques: cyclic voltammetry, obtaining the highest capacitance value for the device with the 66.7/33.3 wt% CB/CA in a basic H₂SO₄ solution, reaching 135.64 F g⁻¹. The device was applied in potentiostatic charge/discharge measurements, achieving values of 2.45 Wh kg⁻¹ for specific energy and around 1000 W kg⁻¹ for specific power. Therefore, corroborated with electrochemical impedance spectroscopy assays, the relatively low-price proposed device presented a suitable performance for application as supercapacitors, being manufactured from reused materials, contributing to the energy storage field enhancement.

Keywords: disposable device; supercapacitor; carbon material; carbon black; cellulose acetate

1. Introduction

The energy issue has been one of the great discussions around the world due to the depletion of fossil fuels, which has attracted the search for new sources of energy conversion and storage. This issue arises from the constant demand for fast, economically efficient, and ecologically correct technological devices, to meet the world's growing population's desire for frequent information [1-3]. In such industry, electrochemical energy conversion systems function as key technologies, allowing the management of renewable energy while diminishing the pollution caused by other sources, such as the greenhouse effect [2]. Common batteries are widely researched, discussed, and employed, especially in electric or hybrid vehicles [2,4,5]. On the other hand, they have some lifetime and power issues, such as low power density, requiring a longer charge and/or discharge time, and capacitors can operate at short charge-discharge times (<0.1 s) resulting in low production and maintenance costs. As demonstrated by Libich et al. [1], electrochemical capacitors, also known as supercapacitors, present high energy densities, close to that of batteries, while also bringing the higher power densities of pure metal capacitors. Moreover, they have been gaining prominence due to relatively low-cost, renewable materials usage, and highefficiency energy storage capability [6-8]. It is also known that even at high discharge rates,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). their efficiency and reversibility exceed 90% [9,10], further suggesting that supercapacitors could be ideal for renewable energy storage.

Hence, technological development has opened new applications and, in this scenario, flexible supercapacitors have attracted great interest in the industry. This class of materials meets the technological requirements for advances in the field of wearable, compact, and portable electronics, such as flexible displays on phones, health tracking devices, computers, televisions, electronic textiles, artificial electronic skin, and distributed sensors [11–15]. Furthermore, the key challenge for the conception of the commercial supercapacitors is the development of devices with excellent mechanical flexibility and adjustable dimensions along with decreasing production costs [16,17].

In this context, various carbon materials have been applied as electrode materials for electric double-layer capacitors, and among them, carbon black (CB) stands out due to the structure of the graphitic domains in the concentric particles, ensuring adequate electrical conduction, combined with the porosity of the carbonaceous material, having the capacity to store energy in the form of electrical charges [18–20].

In addition, CB can form stable dispersions of polymeric matrices [21], which is applied for the fabrication of 2D-printed electrodes, using a technology known as screenprinting [22,23]. This technology consists of the application of a conductive ink over a screen, delimiting the form of the desired electrodes on the surface of an inert substrate. This conductive ink is conventionally made by the dispersion of electrically conductive particles on a polymeric matrix, and, among renewable options, cellulose acetate (CA) could be an interesting choice as it is a biodegradable polymer of biological sources, synthesized from cellulose with relatively low production cost [24–26]. The literature also presents screen-printed systems as possible disposable materials [27–29], due to their reduced production cost, when compared to conventional electrodes. This, however, also demands an ecofriendly inert substrate, such as reusable beverage bottles (polyethylene terephthalate, PET) [27] and sandpaper [30]; or recyclable materials, such as paper [31], waterproof paper [32], fiberboard [33], and polyvinyl chloride [34]. The selection of electrode materials directly affects the electrochemical performance, physical properties, and further applications of the device. Therefore, the development of flexible supercapacitors is very important for different technologies, making essential the search for cheaper and renewable materials, with optimal operational parameters. In this work, we propose the development of a disposable and flexible supercapacitor, using the screen-printing technique, with a conductive and lab-made ink of CB and CA, deposited over a PET substrate, presenting and discussing its behaviors, characteristics, and efficiencies in different pH media.

2. Materials and Methods

2.1. Reagents and Solutions

All chemicals used in this work were purchased from Sigma-Aldrich (Taufkirchen city, Bavaria state, Germany) and/or Fluka (Muskegon, MI, USA), with analytical grade. In addition, all aqueous solutions used for electrochemical characterizations, including the supporting electrolytes, sulfuric acid (H₂SO₄), potassium hydroxide (KOH), and sodium sulfate (Na₂SO₄), were prepared by an ultrapure water system Synergy[®] (type 1) from Merck Millipore, Merck Group (Burlington, MA, USA), with resistivity > 18 M Ω cm. For ink preparation, VULCAN[®] XC-72 powder was provided by CABOT (Boston city, Massachusetts state, USA), and substrates were obtained by reusing different beverage bottles.

2.2. Apparatus

The CB-based electrodes were prepared and assembled with the aid of Silhouette Studio 4.4[®] (Silhouette, Brazil) software, used to elaborate the capacitor mask design, and command the Silhouette Cameo 3[®] cutting machine, Silhouette (São Paulo city, São Paulo state, Brazil). For the ink preparation, a magnetic stirrer and heater (Biomixer AM-10), and an ultrasonic bath purchased from Cristófoli (Campo Mourão, Paraná state, Brazil) were used.

The electrochemical characterizations were performed in a Potentiostat/Galvanostat (Metrohm, Autolab/PGSTAT204) with an expansion module for Electrochemical Impedance Spectroscopy (EIS) FRA32M performance. Managed by NOVA software 2.1.4 version (Utrecht, The Netherlands) at the open circuit potential (OCP) with sine wave type, 10 mV amplitude, in the frequency range of 0.1–10 MHz. Morphological characterizations were conducted using SEM (Scanning Electronic Microscope) images obtained in a Vega-3 LMU Tescan electronic microscope, in 5.0 kV voltage acceleration and 50 P low vacuum mode. The electrochemical impedance spectroscopy (EIS) data were obtained in three different 1.0 mol L⁻¹ electrolytes: H₂SO₄, KOH, and Na₂SO₄. The data was obtained with the following parameters: applied potential corresponding to the OCP of each system, obtained after 300 s stabilization, being –26 mV for H₂SO₄ and –56 mV for KOH; potential amplitude of 10 mV, sine waves type throughout all analysis, and 10 frequency increments per decade, in the range of 1.0×10^5 to 1.0×10^{-2} Hz.

2.3. Production of the Ink and Manufacture of the Disposable Electrodes

To guarantee optimal ink formulation and material dispersion, two solvent solutions were prepared, with a mixture of N, N-Dimethylformamide (DMF), and acetone (ACE) of distinct volume %. The solvent to best disperse CA had a 52.5/47.5% ratio, while the solvent that better dispersed CB presented a ratio of 42.4/57.6%. The CA dispersion was prepared by adding 250 mg of the acetate in the mentioned solvent, and subsequently stirring it for 10 min at room temperature. Meanwhile, the CB dispersion was produced by adding a desired amount of CB to the corresponding DMF/ACE mixture and placing it in an ultrasonic bath, for 30 min, to enhance homogenization. Finally, these two dispersions were mixed in different proportions, following another ultrasonic bath for 30 min. After, the final dispersion was magnetically stirred for 10 min, finishing the conductive ink. The final CB:CA proportions are presented in Table 1.

To assemble the electrode systems, the polyethylene terephthalate (PET) substrates, obtained by reusing beverage bottles, were cut, properly washed, and polished to enhance ink adhesion. After, adhesive paper sheets were cut with the cutting machine with a proper design, based on the three-electrodes system. These adhesive masks were attached to the PET surface, and the ink was applied over them. After 10 min of drying, a second ink layer was produced, and it was left to dry at 19 °C. After the paper masks were removed and the system was ready to use. Figure 1 illustrates the whole process.



Figure 1. Experimental procedure representation: (1) elaboration of the CB and CA base dispersions; (2) ink preparation; (3) electrode assembly with screen printing technique over PET substrates; (4) finalized capacitor electrode ready for (5) electrochemical analyses.

Formulation N°	CB (mg)	CA (mg)	CB/CA (wt%/wt%)
1	125	250	33.3/66.7
2	250	250	50.0/50.0
3	375	250	60.0/40.0
4	500	250	66.7/33.3

Table 1. CB/CA proportions at the different prepared inks.

3. Results

3.1. Electrochemical and Morphological Characterizations

To understand the CB/CA ink capacitive behavior, different characterization procedures should be investigated. Therefore, the first electrochemical study performed was a profile determining the cyclic voltammetry (CV) technique, aiming to analyze and compare the four different ink formulations, based on each specific capacitance (SC) response at different electrolytes: an acid (H₂SO₄), a saline (Na₂SO₄), and a basic (KOH) media, with respective 1.0 mol L⁻¹ concentration. Properties such as active surface area, porosity, and conductivity are crucial points in the development of electrochemical capacitors, and this is directly influenced by the amount of carbonaceous material used [35]. Thus, the voltammetric profiles in Figure 2A–C, obtained with different CB/CA compositions, demonstrate that, majorly, the capacitive current is predominant, even though a few electrodes presented redox interactions, limiting their use as capacitive devices. This highly capacitive behavior indicates that the materials perform energy storage through an expansion in the electrical double layer, storing charges directly on the double-layer [36]. This class of devices is commonly called an expanded double-layer capacitor (EDLC) [37,38].

This characteristic profile observed is possibly caused by the presence of discrete pores, typical of carbonaceous materials, where the carbon atoms of the CB are compacted at the edges of the channel [39]. In Figure 2, the voltammograms demonstrate an approximately rectangular voltammetric profile, a characteristic near-ideal capacitor behavior, which is justified by diffusion processes. Additionally, this study shows that the variation in current flowing through the circuit increases linearly with the CB concentration, indicating that the larger amounts of CB enhance the capacitive behavior. Probably, this functions to increase the number of active sites, due to the higher atomic density, contributing to the double layer formation process [38]. It is also interesting to highlight the presence of anodic and cathodic peaks in Figure 2C, mainly for the 60.0/40.0 and 50.0/50.0 % (w/w). These phenomena have been attributed to the result of electroactive surface functional groups redox reactions, such as phenols, ketones, and carboxylic structures [40,41]. This process could generate pseudocapacitance, but with uncertain benefits, as the self-discharge rate of such groups is higher than the overall surface [40,42]. Herewith, the ink containing the highest quantity of CB (66.7/33.3%, w/w) was chosen to continue this work.

Thus, with the previous charge data acquisition used for the CV technique, the resultant charge data influence, at each electrolyte, with different scan rates (ν), guided by SC values would be estimated by the Equation (1):

$$SC = \frac{\Delta Q}{m \times \Delta V} \tag{1}$$

where *SC* is expressed in (F g⁻¹); ΔQ is the charge variation in terms of C s⁻¹; *m* is the electrode mass, which was estimated at around 0.134 mg for the chosen formulation; and ΔV is the working potential used, represented in *V*. Therefore, the resultant *SC* values vs. different ν (mV s⁻¹) are shown in Figure 2D, for each electrolyte. The resultant dispersion, in general, presented a capacitance decrease with the increase in ν . This was expected behavior, especially because of the velocity of surface formation processes, including surface resistance, double-layer thickness, and charge diffusion as well, which are all processes in progress during data collection. It is important to highlight, however, that

the CB/CA electrode demonstrated a more stable *SC* vs. ν curve in the acidic electrolyte, with a decrease of only 75%, when compared to the other media (93% for KOH and 87% for Na₂SO₄).



Figure 2. Cyclic voltammograms of different CB/CA formulations: 33.3/66.7 (**black**), 50.0/50.0 (**red**), 60.0/40.0 (**blue**), and 66.7/33.3% (**pink**); in (**A**) 1.0 mol L^{-1} H₂SO₄, (**B**) 1.0 mol L^{-1} KOH, and (**C**) 1.0 mol L^{-1} Na₂SO₄; v = 10 mV s⁻¹ (**D**) SC vs. scan rate plots for 66.7/33.3% CB/CA at equimolar 1.0 mol L^{-1} H₂SO₄ (**A**); Na₂SO₄ (**•**) and KOH (**■**) solutions.

The EIS technique configures a very important tool for mapping processes in the electrode interface, which may include redox reactions, adsorption, and forced mass transfer processes. It responds with the function of the relation between frequency and a given potential, in contrast with the most used electroanalytical methods. This technique is useful for electrochemical devices, especially energy storage systems, such as batteries, capacitors, and supercapacitors, especially as they need more comprehensive information about resistivity and charge transfer of electrode materials.

In this study (Figure 3A), it was observed that the acidic profile presents a lowfrequency region almost in parallel to the imaginary axis, which characterizes an ideal capacitive behavior due to minimal material resistance effects being observed in lower frequencies. This could imply that the double-layer ion transport has ceased, achieving equilibrium, and only dielectric behavior is being observed [43,44]. This behavior is described by a [R(RQ)C] equivalent circuit. For the KOH medium, the electrode shows a profile containing deviations from ideal capacitor behavior, especially by the formation of two semicircles, probably caused by proper material hybrid capacitive/resistive behavior, better described with the [R(RQ)([RW]C)] equivalent circuit. The first semi-circle is, potentially, due to the device geometry [43], while the second could originate from the surface redox reactions, as presented in Figure 2B. The literature proposes a few explanations for such reactions: the device could be functionalized by the basic electrolyte, adsorbing hydroxyl ions [45], or promoting rise to pseudocapacitance by oxygen-involved redox processes [46].



Figure 3. (**A**) Nyquist diagrams for H_2SO_4 (**D**) and KOH (•). (**B**) Cyclic voltammograms obtained in OCP by 66.7/33.3% CB/CA electrode, in equimolar 1.0 mol L⁻¹ H₂SO₄ (**—**) and KOH (**—**); $\nu = 10 \text{ mV s}^{-1}$. Capacitance retention dispersion plots of 100 cycles in (**C**) 1.0 mol L⁻¹ KOH and (**D**) 1.0 mol L⁻¹ H₂SO₄.

Each system was then evaluated for its behavior against the OCP values used in EIS, and the profiles are presented in Figure 3B. As can be noted, both presented characteristic voltammograms with the only capacitive current generation. It could also be highlighted that the acidic system is considered a more rectangular shape than the basic one, implying a higher energy storage capability. By increasing the number of cycles in CV to 100, the capacitance retention of each system was evaluated against previously obtained data (100%). In alkaline solution (Figure 3C), the device rapidly presented an increase in capacitive current, equivalent to 130%, but quickly dropped to around 65%. The device then linearly increased the retention to 74% after all scans. This behavior implies a non-stable surface. In acidic solutions (Figure 3D), the retentions started at around 80%, increasing to 84% after all cycles, suggesting higher stability. This data also corroborates the use of acidic electrolytes to properly employ the proposed device as a supercapacitor.

Morphological characterizations were required to better understand the proposed material and confirm its electrochemical behavior. Therefore, SEM was carried out for the optimal 66.7/33.3% (w/w) CB/CA ink without CB (Figure 4A–C), without CA (Figure 4D–F),

and in its complete form (Figure 4G–I). In the images without CB (only CA), it is possible to observe a roughish polymeric structure, with small, intertwined wing-like structures. For the ink without CA (only CB), purely carbonaceous structures can be observed, with high roughness and flake-like formation. Additionally, this sample presented a high cracking rate, as can be observed in Figure 4D right side, probably due to the electrostatic interaction between CB agglomerates being destroyed as the solvents are eliminated. In the last sample, it is possible to observe the roughness of the whole surface, with pores distributed throughout the film structure, corroborating with the data discussed previously. Additionally, the carbonaceous structure of CB is still observed, and without cracks, proving a homogeneous distribution of CB in CA. This active distribution of amorphous carbon can be associated with the overall material conductivity.



Figure 4. SEM images of the 66.67% CB/CA ink without CB (**A–C**), without CA (**D–F**) and the complete ink (**G–I**) at (**A,D,G**) $500 \times$, (**B,E,H**) $1000 \times$, and (**C,F,I**) $2000 \times$ magnification.

3.2. Potentiostatic Charge/Discharge Evaluation

Charge and discharge tests were carried out by performing a potentiostatic charge/ discharge technique (PCD). These tests are extremely important for a more complex analysis of the behavior of the device in an applied situation, by inserting the material under charging and discharging phenomena, at distinct current density (CD) values, through time. Thus, it is expected to observe profiles with a triangular shape, that results from the device's double-layer charge/discharge response. This process depends on the charge movement rate through each material gram. As such, this behavior is principally affected by resistance and diffusion layer processes in the electrolyte/electrode interface.

Therefore, the CD values were selected randomly for the PCD procedure and the chosen values were 0.5, 1.0, 2.0, 3.0, and 4.0 A g^{-1} , and their resulting profiles for the CB

ink are presented in Figure 5. In Figure 5A, the charge and discharge relationship at H_2SO_4 presented the discussed triangular profile, as expected for a capacitor. Nonetheless, plotline inclination suggested a smooth charge transition. This type of profile indicates a closer relationship with supercapacitor behavior, which conventionally shows relatively high energy and power densities with smooth rate transitions.



Figure 5. E vs. t plots of CB/CA PCD profiles in 1.0 mol L^{-1} (**A**) H₂SO₄, (**B**) Na₂SO₄, (**C**) KOH, at different CD values: 0.5, 1.0, 2.0, 3.0, and 4.0 A g⁻¹. (**D**) SP vs. SE (Ragone plots) for CB/CA in different and equimolar 1.0 mol L^{-1} electrolytes: H₂SO₄ (**A**), Na₂SO₄ (**•**), and KOH (**I**). (**E**) Dispersion plot of PCDs SC vs. different current densities (0.5, 1.0, 2.0, 3.0, and 4.0 A g⁻¹) for CB/CA in different and equimolar 1.0 mol L^{-1} electrolytes: H₂SO₄ (**A**), Na₂SO₄ (**•**), and KOH (**I**). (**F**) Capacitor efficiency, in equimolar 1.0 mol L^{-1} H₂SO₄ (**A**), Na₂SO₄ (**•**), and KOH (**I**). (**F**) Capacitor efficiency, in equimolar 1.0 mol L^{-1} H₂SO₄ (**A**), Na₂SO₄ (**•**), and KOH (**I**), for CB/CA devices.

Hereupon, profiles for Na_2SO_4 presented in Figure 5B also demonstrated the triangular tendency through CD rising, but started to show some alterations in shape resolution, probably due to process alterations at the double layer, like a pseudocapacitance rising phenomenon [47]. This tendency is accentuated at KOH profiles (Figure 5C), especially at discharge lines, where its definition intensifies the pseudocapacitance growth hypothesis, added to a possible decrease in activity, due to the higher pH, since water-based electrolytes were used [48,49]. Table 2 shows the calculated rate capacitance for each of the aforementioned systems, in which the alkaline performance starts as the highest, but is diminished to ~4% of its initial value. In saline solution the observed behavior is similar, while in H₂SO₄ only a third of the initial rate capacitance is observed to be lost with the increase in current density, further demonstrating higher stability for the device in such media. With these data, it is possible to conclude that the charge and discharge time increases with saline and alkaline solutions, while the acidic electrolyte seems to have more attractive features for this supercapacitor, including a flatter profile and lower PCD time.

Electrolyte	Rate Capacitance (F g ⁻¹)				
	$0.5 \ A \ g^{-1}$	$1.0 \ {\rm A} \ {\rm g}^{-1}$	$2.0 \ { m G} { m g}^{-1}$	$3.0 \ \mathrm{A} \ \mathrm{g}^{-1}$	$4.0 \ { m A g}^{-1}$
H ₂ SO ₄	30.01	28.23	24.38	24.13	20.7
КОН	100.6	64.85	15.70	8.280	4.242
Na ₂ SO ₄	55.79	25.29	13.10	4.172	2.590

Table 2. Rate capacitance obtained by CB/CA in different 1.0 mol L^{-1} electrolytes and current densities.

3.3. Energy and Power Density Calculations

Energy and power density values present a relevant form to cross and compare data between different energy storage devices, especially through the Ragone plot (Figure 5D), which are composed of specific power (*SP*) and specific energy (*SE*) magnitudes. Therefore, the Ragone graphic was plotted by utilizing two equations, one for the device-specific energy (*SE*, Equation (2))

$$SE = \frac{I \times \Delta V \times \Delta t}{2 \times m} \tag{2}$$

where *SPe* is expressed in Wh Kg⁻¹; *I* the PCDs discharge current in A; Δt the discharge time in seconds (s); *m* the working electrode mass g; ΔV is voltage variation through the discharge process in *V*; and the other is for its specific power (*SP*, Equation (3)):

$$SP = \frac{I \times \Delta V}{2 \times m} \tag{3}$$

where SPw is in terms of W Kg⁻¹. The graphic obtained by plotting SP vs. SE presents a comparison of the electrode performance in different media, and shows a very interesting behavior between the two axes, especially for the acidic medium, which get closer to a storage device behavior, with high SP per SE.

To better understand the *SC* behavior of the device, obtained by PCD, the *SC* values were converted with a different *SC* formula, which considers the proper time data obtained by PCD assays, expressed by Equation (4):

$$SC = \frac{I \times \Delta t}{m \times \Delta V} \tag{4}$$

where *SC* is the PCD *SC* in terms of F g⁻¹; *I* is the applied current in terms of A; Δt *is* the discharge time (s); *m* is the work electrode mass (g); and ΔV is the voltage variation through the discharge process in *V*. Herewith, the *SC* calculated values were plotted against the previously chosen CD values, for each electrolyte studied, as can be seen in Figure 5E.

At low CD values, the saline and alkaline electrolytes presented higher *SC* values than the acidic ones. Although, with the CD increase, this tendency decays and, in general, the acidic medium presented more stability throughout the *SC* variation. This behavior shows an interesting feature that justifies a supercapacitor-like performance, in sulfuric acid, especially because of its flat and stable PCD profile.

Figure 5F shows the device efficiency plot in the function of the selected different current densities, calculated by Equation (5):

n

$$=\frac{Dt}{Ct}$$
(5)

where *n* is the estimated efficiency in percentage (%); *Dt* is the PCD discharge time in seconds (s); and *Ct*, the PCDs charge time, also in seconds. This plot shows the device efficiency at the selected electrolyte. This is an important indicator to corroborate device performance over a range of current densities. Unlike before, the device presents more stable efficiencies in acidic and alkaline media, but with a considerably higher value for the first one. This further justifies the previous hypothesis about this device super capacitive behavior. Whereas, saline medium showed a more linear behavior with the previous tests, presenting certain instabilities under the studied current densities, compromising the device in optimized supercapacitor applications.

3.4. Flexibility Study

Flexibility is, as discussed previously, an important attribute for capacitors and supercapacitors, enabling the production of different and adaptable technologies. To evaluate it, tests were carried out by twisting the electrode and subsequently collecting its response with CV at 50 mV s⁻¹, with a torsion interval of 20 torsions, for a total of 200. This process was repeated twice, with different configurations for data obtention, one with the device still twisted and the other with the device laid flat, to better understand the effect of such strain in the ink. The voltammograms were recorded in 1.0 mol L⁻¹ H₂SO₄ solution, from -0.5 to 0.5 V, and the data was collected at 0.0 V for all torsions. As can be seen in Figure 6A,B, both obtained profiles presented stable profiles across all cycles, with little difference between the curved and the flat electrode system, as can be noted in Figure 6C. As the PET substrate has a geometrically curved shape, due to the circumference of beverage bottles, the forced flattering of electrodes puts the ink under increased stress, diminishing the current obtained. Besides that, the electrode shows considerable stability under mechanical stress, effectively working as a flexible device.

Similar supercapacitors were chosen for comparison with the values of specific capacitance, power, and energy, which are comparable to the literature (Table 3). The data collected suggests the interesting performance of the developed device in terms of specific energy and capacitance, implying its use as an energy storage device. The majority of the selected works describe different capacitor, micro-capacitor, and supercapacitor systems, usually utilizing relatively higher-cost materials with complex processes such as vaporliquid-solid chemical vapor deposition [50], and hydrogel synthesis [51]. On the other hand, the proposed work used a simple synthesis method, while still employing relatively low-cost and ecologically friendly materials.

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Types of Cell	Composition	Specific Capacitance	Specific Power	Specific Energy	Works
Three electrodes	Highly doped silicon nanowires	$46~\mu F~cm^{-2}$	$1.6 \mathrm{mF} \mathrm{cm}^{-2}$	Not specified	[50]
Two electrodes	N-doped Graphene/ PANI hydrogel	$584.7 \mathrm{mF}\mathrm{cm}^{-2}$	-0.5 mW cm^{-2}	$\sim 0.1 \text{ mWh cm}^{-2}$	[51]
Two electrodes	PANI-N/CNT	$341.0 \ \mathrm{F} \ \mathrm{g}^{-1}$	$40.0 \ {\rm W \ kg^{-1}}$	11.5 Wh kg ⁻¹	[52]
Two electrodes	ACTIVATED CARBON-PTFE	$2.1 \mathrm{mF}\mathrm{cm}^{-2}$	Non-specified	Non-specified	[23]
Two electrodes	PANI-MLG	$110 {\rm mF} {\rm cm}^{-2}$	$0.15 \mathrm{~mW~cm^{-2}}$	$\sim 0.01 \text{ mWh cm}^{-2}$	[6]
Two electrodes	PANI/cellulose/Ag	$310.9 \ \mathrm{F} \ \mathrm{g}^{-1}$	$238.2 \mathrm{W}\mathrm{kg}^{-1}$	$0.7 \mathrm{Wh}\mathrm{kg}^{-1}$	[13]

Types of Cell	Composition	Specific Capacitance	Specific Power	Specific Energy	Works
Two electrodes	PANI-MLG	$451.0 \mathrm{F}\mathrm{g}^{-1}$	$3610.0 \mathrm{W kg^{-1}}$	17.0 Wh kg^{-1}	[6]
Three electrodes	Vanadium nitride and nickel oxide thin film	$1.85 \mathrm{mF}\mathrm{cm}^{-2}$	$28 \mathrm{~mW~cm^{-2}}$	$0.7 \ \mu Wh \ cm^{-2}$	[53]
Two electrodes	IPCN-alkaline carbon metal	$200 {\rm ~F~g^{-1}}$	Non-specified	Non-specified	[54]
Three electrodes	Carbon black- cellulose acetate	$313.53 \mathrm{F}\mathrm{g}^{-1}$	$455.691 \mathrm{W \ kg^{-1}}$	$5.84 \mathrm{~Wh~kg^{-1}}$	This work
		$168.05 \mathrm{mE}\mathrm{cm}^{-2}$	$0.24437 \text{ mW cm}^{-2}$	$0.00313 \text{ mWh cm}^{-2}$	This work

Table 3. Cont.

Highly doped silicon nanowires: silicon nanowire-based electrodes for micro-capacitor applications, elaborated with highly n and p type doping in silicon nanowires grown with the gold catalyst in chemical vapor deposition (CVD) reactor. *N-doped GraphenelPANI hydrogel*: N-type doped PANI hydrogel/graphene oxide (GO) composite electrode synthesized by hydrothermal process, for flexible supercapacitor assemble. *PANI-NICNT*: electrode based on activated carbon nanoparticles doped with nitrogen, obtained from PANI nanoparticles pyrolysis for capacitor application. *ACTIVATED CARBON-PTFE*: Ink-jet printed electrode with an ink formulation obtained by mixing activated carbon powder, polytetrafluoroethylene (PTFE) polymer, ethylene glycol, and surfactant. Subsequently printing over a silicon substrate for micro-capacitor applications. *PANI-MLG*: PANI modified multilayer graphene electrodes. *IPCN-alkaline carbon metal*: interconnected porous carbon nanosheets with controllable pore size.



Number of torsions

Figure 6. Cyclic voltammograms of the flexibility study on the (**A**) curved device and (**B**) flat device, in 1.0 mol L^{-1} H₂SO₄; $\nu = 50$ mV s⁻¹. (**C**) I vs. the number of torsions dispersion plots for (**A**) curved and (•) flat electrodes. Data was collected at 0.0 V.

4. Conclusions

The production of a flexible supercapacitor electrode was demonstrated in this paper, using a polyethylene terephthalate (PET) substrate. The mass quantity of CA and carbon

black was tested in different aqueous media to optimize the capacitance response. The device is potentially disposable as it is obtained from eco-friendly and relatively low-cost materials, compared to others employed in electrochemical capacitors development. The optimal composition was achieved with 66.7/33.3 wt% CB/CA, and its storage mechanism is predominantly by the electrical double layer, as evidenced by cyclic voltammetry, presenting an outstanding capacitive behavior on acidic media, demonstrating the absence of redox reactions in this condition. In the PCD technique, the device presented more defined charge/discharge graphics, leading to more capacitive behaviors in both acidic and basic solutions. In these conditions, specific power of 1000 W Kg⁻¹ in the acidic medium was obtained. Through the EIS technique, it was possible to observe a highly capacitive behavior in acidic media and a hybrid capacitive/resistive profile in the basic electrolyte. The device also presented 84% capacitance retention after 100 cycles and is quite stable after 200 torsions. All these data suggest that the device is indeed optimal in lower pH systems, but some energy storage can still be obtained in higher pH electrolytes. The proposed device also demonstrated interesting charge-storage capacity and cyclic stability, especially in acidic solutions, affirming its path as an alternative environmentally friendly supercapacitor with simple fabrication.

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References

- Libich, J.; Máca, J.; Vondrák, J.; Čech, O.; Sedlaříková, M. Supercapacitors: Properties and applications. J. Energy Storage 2018, 17, 224–227. [CrossRef]
- Badwal, S.P.S.; Giddey, S.S.; Munnings, C.; Bhatt, A.I.; Hollenkamp, A.F. Emerging electrochemical energy conversion and storage technologies. *Front. Chem.* 2014, 2, 79. [CrossRef] [PubMed]
- 3. Rapisarda, M.; Marken, F.; Meo, M. Graphene oxide and starch gel as a hybrid binder for environmentally friendly highperformance supercapacitors. *Commun. Chem.* **2021**, *4*, 169. [CrossRef]
- Faggioli, E.; Rena, P.; Danel, V.; Andrieu, X.; Mallant, R.; Kahlen, H. Supercapacitors for the energy management of electric vehicles. J. Power Sources 1999, 84, 261–269. [CrossRef]
- Kouchachvili, L.; Yaici, W.; Entchev, E. Hybrid battery/supercapacitor energy storage system for the electric vehicles. J. Power Sources 2018, 374, 237–248. [CrossRef]
- 6. Augusto, G.D.S.; Scarminio, J.; da Silva, P.R.C.; de Siervo, A.; Rout, C.S.; Rouxinol, F.; Gelamo, R.V. Flexible metal-free supercapacitors based on multilayer graphene electrodes. *Electrochim. Acta* **2018**, *285*, 241–253. [CrossRef]
- Lekakou, C.; Moudam, O.; Markoulidis, F.; Andrews, T.; Watts, J.F.; Reed, G.T. Carbon-based fibrous EDLC capacitors and supercapacitors. J. Nanotechnol. 2011, 2011, 409382. [CrossRef]
- Kandalkar, S.; Dhawale, D.; Kim, C.-K.; Lokhande, C. Chemical synthesis of cobalt oxide thin film electrode for supercapacitor application. *Synth. Met.* 2010, 160, 1299–1302. [CrossRef]
- 9. Chmiola, J.; Largeot, C.; Taberna, P.-L.; Simon, P.; Gogotsi, Y. Monolithic carbide-derived carbon films for micro-supercapacitors. *Science* 2010, 328, 480–483. [CrossRef]
- Simon, P.; Gogotsi, Y. Materials for electrochemical capacitors. In Nanoscience Technology: A Collection of Reviews from Nature Journals; World Scientific Publishing: Singapore, 2010; pp. 320–329.
- 11. Palchoudhury, S.; Ramasamy, K.; Gupta, R.K.; Gupta, A. Flexible supercapacitors: A materials perspective. *Front. Mater.* **2019**, *5*, 83. [CrossRef]

- 12. Xie, P.; Yuan, W.; Liu, X.; Peng, Y.; Yin, Y.; Li, Y.; Wu, Z. Advanced carbon nanomaterials for state-of-the-art flexible supercapacitors. *Energy Storage Mater.* **2021**, *36*, 56–76. [CrossRef]
- 13. Khosrozadeh, A.; Darabi, M.A.; Xing, M.; Wang, Q. Flexible electrode design: Fabrication of freestanding polyaniline-based composite films for high-performance supercapacitors. *ACS Appl. Mater. Interfaces* **2016**, *8*, 11379–11389. [CrossRef] [PubMed]
- Cheng, J.; Zhao, B.; Zhang, W.; Shi, F.; Zheng, G.P.; Zhang, D.; Yang, J. High-Performance Supercapacitor Applications of NiO-Nanoparticle-Decorated Millimeter-Long Vertically Aligned Carbon Nanotube Arrays via an Effective Supercritical CO₂-Assisted Method. *Adv. Funct. Mater.* 2015, 25, 7381–7391. [CrossRef]
- Cheng, J.; Chen, S.; Chen, D.; Dong, L.; Wang, J.; Zhang, T.; Jiao, T.; Liu, B.; Wang, H.; Kai, J.J.; et al. Editable asymmetric all-solidstate supercapacitors based on high-strength, flexible, and programmable 2D-metal–organic framework/reduced graphene oxide self-assembled papers. J. Mater. Chem. A 2018, 6, 20254–20266. [CrossRef]
- 16. Yu, L.; Hu, L.; Anasori, B.; Liu, Y.-T.; Zhu, Q.; Zhang, P.; Gogotsi, Y.; Xu, B. MXene-bonded activated carbon as a flexible electrode for high-performance supercapacitors. *ACS Energy Lett.* **2018**, *3*, 1597–1603. [CrossRef]
- Wang, S.; Liu, N.; Su, J.; Li, L.; Long, F.; Zou, Z.; Jiang, X.; Gao, Y. Highly stretchable and self-healable supercapacitor with reduced graphene oxide based fiber springs. *Acs Nano* 2017, *11*, 2066–2074. [CrossRef]
- Ban, S.; Malek, K.; Huang, C.; Liu, Z. A molecular model for carbon black primary particles with internal nanoporosity. *Carbon* 2011, 49, 3362–3370. [CrossRef]
- 19. Silva, T.; Moraes, F.C.; Janegitz, B.C.; Fatibello-Filho, O. Electrochemical biosensors based on nanostructured carbon black: A review. J. Nanomater. 2017, 2017, 4571614. [CrossRef]
- Delgado, K.P.; Raymundo-Pereira, P.A.; Campos, A.M.; Oliveira, O.N., Jr.; Janegitz, B.C. Ultralow Cost Electrochemical Sensor Made of Potato Starch and Carbon Black Nanoballs to Detect Tetracycline in Waters and Milk. *Electroanalysis* 2018, 30, 2153–2159. [CrossRef]
- 21. Phillips, C.; Al-Ahmadi, A.; Potts, S.-J.; Claypole, T.; Deganello, D. The effect of graphite and carbon black ratios on conductive ink performance. *J. Mater. Sci.* 2017, *52*, 9520–9530. [CrossRef]
- 22. Garcia, D.M.E.; Pereira, A.S.T.M.; Almeida, A.C.; Roma, U.S.; Soler, A.B.A.; Lacharmoise, P.D.; Ferreira, I.M.D.M.; Simão, C.C.D. Large-Area Paper Batteries with Ag and Zn/Ag Screen-Printed Electrodes. *ACS Omega* **2019**, *4*, 16781–16788. [CrossRef] [PubMed]
- 23. Pech, D.; Brunet, M.; Taberna, P.-L.; Simon, P.; Fabre, N.; Mesnilgrente, F.; Conédéra, V.; Durou, H. Elaboration of a microstructured inkjet-printed carbon electrochemical capacitor. *J. Power Sources* **2010**, *195*, 1266–1269. [CrossRef]
- 24. Rodríguez, F.J.; Galotto, M.J.; Guarda, A.; Bruna, J.E. Modification of cellulose acetate films using nanofillers based on organoclays. *J. Food Eng.* **2012**, *110*, 262–268. [CrossRef]
- 25. Wsoo, M.A.; Shahir, S.; Bohari, S.P.M.; Nayan, N.H.M.; Razak, S.I.A. A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: A new perspective. *Carbohydr. Res.* **2020**, *491*, 107978. [CrossRef] [PubMed]
- Xu, Y.; Hao, Q.; Mandler, D. Electrochemical detection of dopamine by a calixarene-cellulose acetate mixed Langmuir-Blodgett monolayer. *Anal. Chim. Acta* 2018, 1042, 29–36. [CrossRef] [PubMed]
- Andreotti, I.A.D.A.; Orzari, L.O.; Camargo, J.R.; Faria, R.C.; Marcolino-Junior, L.H.; Bergamini, M.F.; Gatti, A.; Janegitz, B.C. Disposable and flexible electrochemical sensor made by recyclable material and low cost conductive ink. *J. Electroanal. Chem.* 2019, 840, 109–116. [CrossRef]
- 28. Kondo, T.; Sakamoto, H.; Kato, T.; Horitani, M.; Shitanda, I.; Itagaki, M.; Yuasa, M. Screen-printed diamond electrode: A disposable sensitive electrochemical electrode. *Electrochem. Commun.* **2011**, *13*, 1546–1549. [CrossRef]
- Kadara, R.O.; Jenkinson, N.; Banks, C.E. Characterization and fabrication of disposable screen printed microelectrodes. *Electrochem.* Commun. 2009, 11, 1377–1380. [CrossRef]
- Rocha, D.S.; Duarte, L.C.; Silva-Neto, H.A.; Chagas, C.L.; Santana, M.H.; Filho, N.R.A.; Coltro, W.K. Sandpaper-based electrochemical devices assembled on a reusable 3D-printed holder to detect date rape drug in beverages. *Talanta* 2021, 232, 122408. [CrossRef]
- Li, H.; Wang, W.; Lv, Q.; Xi, G.; Bai, H.; Zhang, Q. Disposable paper-based electrochemical sensor based on stacked gold nanoparticles supported carbon nanotubes for the determination of bisphenol A. *Electrochem. Commun.* 2016, 68, 104–107. [CrossRef]
- Camargo, J.R.; Andreotti, I.A.; Kalinke, C.; Henrique, J.M.; Bonacin, J.A.; Janegitz, B.C. Waterproof paper as a new substrate to construct a disposable sensor for the electrochemical determination of paracetamol and melatonin. *Talanta* 2020, 208, 120458. [CrossRef] [PubMed]
- 33. Orzari, L.; Andreotti, I.A.D.A.; Bergamini, M.F.; Marcolino-Junior, L.H.; Janegitz, B.C. Disposable electrode obtained by pencil drawing on corrugated fiberboard substrate. *Sens. Actuators B Chem.* **2018**, *264*, 20–26. [CrossRef]
- 34. Carvalho, J.H.; Gogola, J.L.; Bergamini, M.F.; Marcolino-Junior, L.H.; Janegitz, B.C. Disposable and low-cost lab-made screenprinted electrodes for voltammetric determination of L-dopa. *Sens. Actuators Rep.* **2021**, *3*, 100056. [CrossRef]
- 35. Liu, B.; Shioyama, H.; Jiang, H.-L.; Zhang, X.; Xu, Q. Metal-organic framework (MOF) as a template for syntheses of nanoporous carbons as electrode materials for supercapacitor. *Carbon* **2010**, *48*, 456–463. [CrossRef]
- 36. Danaee, I.; Jafarian, M.; Forouzandeh, F.; Gobal, F.; Mahjani, M. Mahjani, Electrochemical impedance studies of methanol oxidation on GC/Ni and GC/NiCu electrode. *Int. J. Hydrogen Energy* **2009**, *34*, 859–869. [CrossRef]
- 37. Krause, A.; Kossyrev, P.; Oljaca, M.; Passerini, S.; Winter, M.; Balducci, A. Electrochemical double layer capacitor and lithium-ion capacitor based on carbon black. *J. Power Sources* **2011**, *196*, 8836–8842. [CrossRef]

- Ma, X.; Song, X.; Yu, Z.; Li, S.; Wang, X.; Zhao, L.; Zhao, L.; Xiao, Z.; Qi, C.; Ning, G.; et al. S-doping coupled with pore-structure modulation to conducting carbon black: Toward high mass loading electrical double-layer capacitor. *Carbon* 2019, 149, 646–654. [CrossRef]
- Khamkeaw, A.; Asavamongkolkul, T.; Perngyai, T.; Jongsomjit, B.; Phisalaphong, M. Interconnected Micro, Meso, and Macro Porous Activated Carbon from Bacterial Nanocellulose for Superior Adsorption Properties and Effective Catalytic Performance. *Molecules* 2020, 25, 4063. [CrossRef]
- 40. Toupin, M.; Bélanger, D.; Hill, I.R.; Quinn, D. Performance of experimental carbon blacks in aqueous supercapacitors. J. Power Sources 2005, 140, 203–210. [CrossRef]
- 41. Frackowiak, E.; Beguin, F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* **2001**, *39*, 937–950. [CrossRef]
- 42. Conway, B.E. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications;* Springer Science & Business Media: Berlin/Heidelberg, Germany, 2013.
- 43. Orazem, M.E.; Tribollet, B. Electrochemical Impedance Spectroscopy; Whily: Hoboken, NJ, USA, 2008; pp. 383–389.
- Lasia, A. Electrochemical Impedance Spectroscopy and Its Applications, Modern Aspects of Electrochemistry; Springer: Berlin/Heidelberg, Germany, 2002; pp. 143–248.
- Nasibi, M.; Golozar, M.A.; Rashed, G. Nano zirconium oxide/carbon black as a new electrode material for electrochemical double layer capacitors. J. Power Sources 2012, 206, 108–110. [CrossRef]
- 46. Bobacka, J.; Lewenstam, A.; Ivaska, A. Electrochemical impedance spectroscopy of oxidized poly (3, 4-ethylenedioxythiophene) film electrodes in aqueous solutions. *J. Electroanal. Chem.* **2000**, *489*, 17–27. [CrossRef]
- 47. Zhang, C.; Xie, Y.; Wang, J.; Pentecost, A.; Long, D.; Ling, L.; Qiao, W. Effect of graphitic structure on electrochemical ion intercalation into positive and negative electrodes. *J. Solid State Electrochem.* **2014**, *18*, 2673–2682. [CrossRef]
- Mitchell, J.B. Understanding the Role of Structural Water for High Power Electrochemical Energy Storage in Tungsten Oxide Hydrates; North Carolina State University: Raleigh, NC, USA, 2021.
- Orellana, K.P.D. Low Cost, Carbon-Based Micro-and Nano-Structured Electrodes for High Performance Supercapacitors. Ph.D. Thesis, Clemson University, Clemson, SC, USA, 2016.
- 50. Thissandier, F.; Le Comte, A.; Crosnier, O.; Gentile, P.; Bidan, G.; Hadji, E.; Brousse, T.; Sadki, S. Highly doped silicon nanowires based electrodes for micro-electrochemical capacitor applications. *Electrochem. Commun.* **2012**, *25*, 109–111. [CrossRef]
- 51. Zou, Y.; Zhang, Z.; Zhong, W.; Yang, W. Hydrothermal direct synthesis of polyaniline, graphene/polyaniline and N-doped graphene/polyaniline hydrogels for high performance flexible supercapacitors. J. Mater. Chem. A 2018, 6, 9245–9256. [CrossRef]
- 52. Zhou, J.; Zhu, T.; Xing, W.; Li, Z.; Shen, H.; Zhuo, S. Activated polyaniline-based carbon nanoparticles for high performance supercapacitors. *Electrochim. Acta* 2015, *160*, 152–159. [CrossRef]
- 53. Eustache, E.; Frappier, R.; Porto, R.L.; Bouhtiyya, S.; Pierson, J.-F.; Brousse, T. Asymmetric electrochemical capacitor microdevice designed with vanadium nitride and nickel oxide thin film electrodes. *Electrochem. Commun.* **2013**, *28*, 104–106. [CrossRef]
- Lee, J.; Lee, Y.A.; Yoo, C.-Y.; Yoo, J.J.; Gwak, R.; Cho, W.K.; Kim, B.; Yoon, H. Self-templated synthesis of interconnected porous carbon nanosheets with controllable pore size: Mechanism and electrochemical capacitor application. *Microporous Mesoporous Mater.* 2018, 261, 119–125. [CrossRef]