N-Doped and Chemically Activated Carbons Derived from Shrimp Shells Waste as Potential Electrode Materials for Electrochemical Supercapacitors

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ABSTRACT. Supercapacitors are widely recognized as energy storage solutions due to their high-power densities and long cycle life. Furthermore, there is growing scientific and technological interest in converting biomass waste into carbon materials for manufacturing supercapacitor electrodes. In addition to their abundance and cost-effectiveness, the appeal of carbons derived from biomass lies in their tuneable porosity, which enables the rational design of carbon materials to achieve the desired performance of supercapacitors. This work presents the synthesis of activated carbons from shrimp shells waste and its application for supercapacitor electrodes, with an activation treatment using phosphoric acid (H_3PO_4) and nitrogen doping (N-doped). The activator concentration was varied at 3, 6, and 9 M; while the N-doped ratios were 1:3, 1:5, and 1:7. The characteristics of activated carbon and supercapacitor electrodes was analysed with BET, SEM, CV, and GCD. The resulting materials exhibited amorphous and predominant microporous structures. Increasing the activation concentration gave smaller specific surface area, from 17.522 to 9.509 $m^2\,g^{-1}$. The electrochemical properties of these activated carbons for supercapacitor applications were investigated by cyclic voltammetry, galvanostatic charge–discharge, with KOH electrolyte. The best activated carbon produced was mesoporous with the highest specific surface of 17.522 m^2/g, obtained at 3 M H_3PO_4 and a nitrogen doping ratio of 1:3. At the same activator concentration and nitrogen doping ratio (3 M; 1:3), the highest capacitance was obtained 16.320 Farad, with current charging and discharging stop at 475 seconds and 1235 seconds, respectively. This work showcases the efficient and sustainable utilization of shrimp shells waste as a carbon source for supercapacitor applications and highlights their value in a circular economy.

Keywords: Activated carbon, Activator H_3PO_4, Nitrogen doping, Shrimp shell, Supercapacitor

INTRODUCTION

Environmental worries over the continuous use of non-renewable resources and the growing complexity of power distribution networks have spurred the urgent exploitation of sustainable and renewable energy sources, such as wind and solar energy (Fu et al., 2023). The energy crisis and growing concerns about the environmental impact of non-renewable energy sources have driven recent technological revolutions in the energy sector (Chaiammart et al., 2024). Supercapacitors or batteries can be used as energy storage components in energy storage systems. Depending on the systems and applications for which it is designed, each energy storage technology has unique advantages (Tafete et al., 2024). The advancement of energy storage equipment and technology is fuelled by rising energy usage. Supercapacitors are impressive devices with steady cycle performance and good charge-discharge efficiency, but their low energy density remains a

significant problem that requires attention (Zhou & Yao, 2022). Conventional batteries in the form of dry cells as used in TV remotes or clocks are only used once, then become waste and pollute the environment. To avoid environmental pollution due to battery waste, rechargeable battery components have been developed as electrical energy storage devices. Apart from batteries, electrical energy storage can be in the form of capacitors.

Waste or by-products from natural resources can offer an alternative to the electrode material used for renewable energy storage, thereby addressing the issues of cost and environmental impact (Boamah et al., 2023). The development of capacitors continues, one of which is called a supercapacitor (Sharma & Bhatti, 2010). Supercapacitors have some advantages including high capacity, large power density, and fast charging (González et al., 2016; Park et al., 2013; Senthil & Lee, 2021). To improve the performance of supercapacitor, electrochemically double layer

capacitors (EDLC) or electrical double layer supercapacitors have been developed which consist of two layers of electrodes separated by a separator (Liu et al., 2018; Qu et al., 2015; Raj et al., 2018; Taer et al., 2013). Electric double-layer capacitance (EDLC) is the electrostatic storage of charges in pure carbon materials (Zhou & Yao, 2022). EDLCs are based on the separation of charge at the electrode–electrolyte interface while PCs involve reversible Faradaic redox reactions, similar to those occurring in batteries (Chaiammart et al., 2024).

Supercapacitor electrode materials are usually chemicals containing heavy metals such as lead, mercury, and nickel. However, heavy metals are expensive and pose a risk of polluting the environment. The use of electrodes from cheap and safe materials has been developed. Electrodes and electrical energy storage in electronic devices can use activated carbon-based materials (Gao et al., 2017; Treeweranuwat et al., 2020; Tumimomor & Palilingan, 2018). Carbon electrode materials have some unique advantages: (1) resource-rich, (2) no concern for price, (3) easily manufacturing, (4) hierarchical porous structure, (5) high thermal and chemical stability, (6) good electronic conductivity, (7) wide working temperature range (Lesbayev et al., 2023). This is reasonable due to the characteristics of activated carbon in which it has a high specific surface and good electrical conductivity.

Activated carbon naturally exhibits high surface area and porosity, which are critical for applications like energy storage (Zhou & Yao, 2022). While graphene and carbon nanotubes may offer higher conductivity and mechanical strength, these advantages are often unnecessary or marginal in cost-sensitive applications like supercapacitors, where activated carbon's properties suffice (Thi et al., 2023). Activated carbon stands out due to its affordability, resource abundance, and well-suited properties for supercapacitor applications. While graphene and carbon nanotubes may offer superior performance metrics in specific high-end applications, their high costs and complex production processes limit their practicality in cost-sensitive and large-scale deployments (Fu et al., 2023). This makes activated carbon a more viable and sustainable choice for most supercapacitor applications (Boamah et al. 2023).

Activated carbon can be produced from natural materials such as coconut shells, wood, or fruit peels (Liu et al., 2016; Rawal et al., 2021; Trinh et al., 2020). Activated carbon has many pores obtained from the combustion process of materials having carbon content of 85-90% with a specified pore surface area (Elmouwahidi et al., 2017). Activated carbon can be made according to its purpose after carbonation and activation processes are conducted, tailored to the desired characteristics. Besides plant materials, carbon sources can also be found in animal materials which are processed through both physical

and chemical activation processes. The carbon sources from animal materials include shrimp shell waste, which is not consumed because of its hard texture (Sun et al., 2014). Shrimp shells contain 40-50% calcium carbonate (Gao et al., 2016), so the carbon content in carbonate has the potential to be used as activated carbon for energy storage electrode materials. The presence of calcium carbonate in shrimp shells can significantly influence the outcomes of the carbonization process due to its chemical properties. During carbonization, calcium carbonate undergoes thermal decomposition, releasing carbon dioxide (CO_2) and leaving behind calcium oxide (CaO). The release of CO_2 during decomposition can create pores within the carbon structure, enhancing its surface area and porosity. This is particularly useful for applications like adsorption or catalysis. The release of CO_2 during decomposition can create pores within the carbon structure, enhancing its surface area and porosity. This is particularly useful for applications like adsorption or catalysis. Residual calcium compounds in the final product can change the chemical reactivity of the carbon, affecting its suitability for specific applications.

Activated carbon having a high specific surface can improve the performance of EDLC in supercapacitor devices. The literature demonstrates that because of their large specific surface area, superior electrical conductivity, affordability, and environmental friendliness, activated carbon (AC) materials have emerged as a potential material for electrostatic accumulation (EDLC) (Hounkanrin et al., 2023). (Tong et al., 2016) found that the capacitance of activated carbon in supercapacitors is influenced by the activation process, both activation time and activator concentration. With carbon activated by 9 M KOH solution and a nitrogen doping ratio of 1:7 (mass of carbon : mass of urea) (Qu et al., 2015) obtained a supercapacitor capacitance of 25 Farad. Even though it is not too high, this capacitance meets the IEC 62391-1:20026 standard, i.e. 0.6-700 Farad. Recent research indicates that nitrogen doping on carbon surfaces results in charge delocalization, which facilitates the binding and transfer of certain molecules onto carbon (Gao et al., 2019). Such doping also increases the conductivity of the porous carbon.

Considering the potency of shrimp shells waste, this work presents the synthesis of activated carbons from shrimp shells waste using an activator of phosphoric acid (H_3PO_4) and nitrogen doping. The effects of activator concentration and N-doped ratio on the characteristics of activated carbon and the electrochemical properties of manufactured supercapacitors were investigated. The supercapacitor was made of a stainless-steel collector, and the electrolyte in the separator was a KOH solution. For the purpose of characterizing activated carbon and supercapacitors, Brunauer-Emmet-Teller (BET) test, Scanning Electron Microscopy (SEM), Cyclic

Voltammetry (CV), and Galvano charge discharges (GCD) were used.

EXPERIMENTAL SECTION

The materials used in this research include shrimp waste, distilled water, H_3PO_4, KOH, dimethyl sulfoxide (DMSO), polyvinylidene fluoride (PVDF), technical grade urea, and ethanol. The tools and analysers used standard analytic laboratory glass wares, BET, SEM, CV, and GCD. The experimental work was carried out through several stages, namely preparation of raw materials, carbonation of shrimp waste, carbon activation, manufacture of supercapacitors, as well as testing the characteristics of activated carbon and electrochemistry of supercapacitors.

The shrimp waste in the form of shrimp shells and tails was cleaned with clean water, and then cleaned using distilled water. The cleaned shrimp waste was dried in the sun for 3 days. The results were dried in the oven for 5 hours at 100°C. Then, the dried shrimp waste was ground using a blender and sieved through a 150-mesh sieve for 7 hours. A total of 12 g of urea was dissolved in ion-free water to 100 mL. Dry shrimp waste from the furnace was weighed as much as 20 g, to be put into an impregnation flask, refluxed using a temperature of 70°C, and stirred using a magnetic stirrer with the addition of urea until a mixture of slurry was produced. The shrimp waste slurry was put into an autoclave reactor for carbonation. After impregnation with urea, the mixture was separated and rinsed using ethanol.

A total of 10 g of shrimp shell biochar that had been impregnated with urea was soaked in a phosphoric acid activator solution (H_3PO_4) with concentration variations of 3, 6, and 9 M. Soaking was carried out for 24 hours to ensure the diffusion process reached the inside of the charcoal, carbonization, subsequent activation, and modification of their surface have a significant impact on the structure and properties of activated carbon (Lesbayev et al., 2023). Then, the activated carbon was dried in an oven for 24 hours. The carbon that has been activated was then washed using distilled water until the pH was neutral. The washing results were filtered and then the activated carbon was dried again in the oven for 2 hours.

5 g of activated carbon material was mixed with PVDF and DMSO, with a ratio of 40% PVDF and 4 mL DMSO. The gluing technique used the solid-state reaction or wet mixing method. The solution was heated and stirred using a hot plate until a gel forms. The gel was used as a supercapacitor electrode.

The type of capacitor made was an Electrical Double Layer Capacitor (EDLC) in a symmetrical shape using two activated carbon electrodes with dimensions of 2 x 2 cm, and two stainless steel mesh plates that have been sprinkled with carbon composite with PVDF and DMSO. The activated carbon electrode was separated by a separator in the form of a 6 M KOH solution electrolyte. The EDLC scheme is illustrated in **Figure 1**.

Sample Analysis

The characteristic of activated carbon was measured from the specific surface using the BET test (Rawal et al., 2021). The electrochemical characteristics of supercapacitors were determined from the capacitance and charge-discharge time. The capacitance and charge-discharge time were measured by GCD (Kampouris et al., 2015). The GCD test applied a voltage range of 0.1-1 V. The capacitance value C (in Farad) was calculated using the following formula (Lin et al., 2019):

$$C = \frac{\int IdE}{2\gamma VE} \approx \quad = \left| \frac{Ic \, x \ln\ln \, \Delta E \, x \, A}{2\gamma} \right|$$

where γ is the scane rate (V/s), ΔE is the potential windows (Volt), Ic is the current density (A/m²), and A is the surface area (m²).

RESULTS AND DISCUSSION
Surface Morphology of Activated Carbon

The activated carbon electrodes from shrimp waste which were activated using H_3PO_4 solution can be seen in **Figure 2**. Meanwhile, the surface morphology of the activated carbon as influenced by the H_3PO_4 activator concentration (3, 6, 9 M) is shown respectively in **Figure 3a, 3b,** and **3c**. The characterization of activated carbon to determine the physical properties and surface morphology of activated carbon used SEM (De et al., 2023; Salawu et al., 2022).
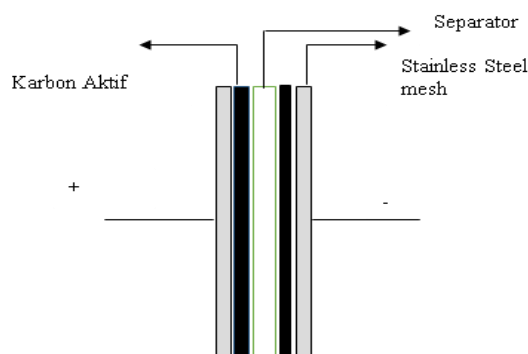

Figure 1. A schematic supercapacitor of EDLC

Figure 2. The carbon-based electrode activated with H_3PO_4 and nitrogen doping
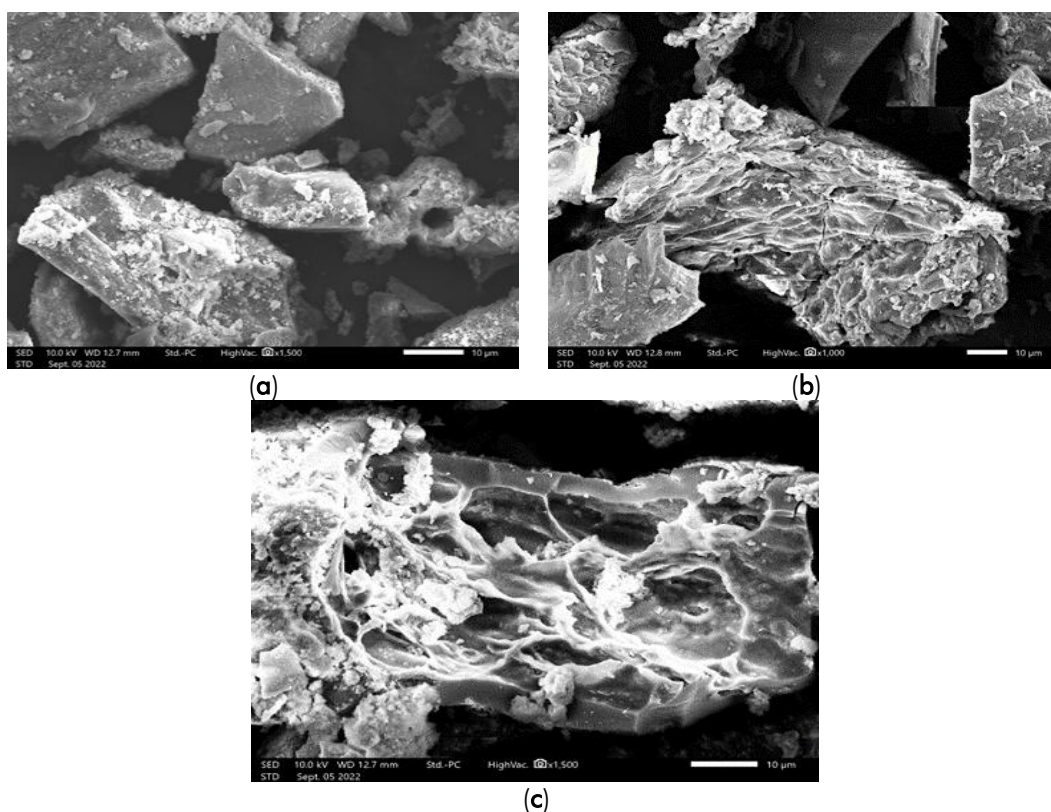

Figure 3. The morphological structure of activated carbon from shrimp waste with activator concentration of 9 M doping ratio 1:7 (**a**), 6 M doping ratio 1:5 (**b**), and 3 M doping ratio 1:3 (**c**).

The results of surface analysis of activated carbon using SEM (3000 × magnification) show that there are differences in morphology because of variations in activator concentration. The role of the activator in the activation process is to absorb the mineral content in the material and to prevent the formation of ash on the carbon (Prayogatama et al., 2022). The content of oxygen groups in the raw material allows reactions to occur with acid (H_3PO_4). H_3PO_4 is also able to remove hydrocarbon compounds and to open pores on the surface of materials. At a concentration of 9 M H_3PO_4, the particle size is not uniform and looks like irregular chunks, with a pore size of around 10 μm. At a concentration of 6 M H_3PO_4, it appears that the pores are more numerous and more uniform with a smaller pore size, around 5 μm. At a concentration of 3 M H_3PO_4, more and smaller pores are visible with a pore size of around 1.6 μm. It can be concluded that the lower the concentration of the H_3PO_4 activator in fact opens more pores in the carbon. H_3PO_4 is a weak acid, thus the ionization process is reversible and undergoes through 3 stages to form $H_2PO_4^-$, HPO_4^{2-}, and PO_4^3, so that pore formation in carbon occurs more effectively at low H_3PO_4 concentrations. The results of this work are different from those conducted by (Qu et al., 2015) which used HCl acid as an activator to activate carbon from shrimp head waste. HCl is a strong acid, almost completely ionizes into H^+

and Cl^- ions and is able to remove $CaCO_3$ from carbon materials so it has a smaller pore structure with a pore size of 3.9 nm. Biocarbon derived from Miscanthus activated KOH thus open channels remained and surface morphology became rough when the KOH/BC ratio increased to 5:1, the BC bulk structure partly collapsed and became interconnected with the channels inside (You et al., 2018).

The greater the carbon pore volume and the smaller the carbon pore diameter, the greater the surface area and adsorbent power of the carbon. The morphological structure of activated carbon is closely related to the electrochemical properties of energy storage devices, where the pores on the carbon electrode can facilitate the process of ion diffusion into the micropores on the electrode surface (Taer et al., 2018), thereby influencing the capacitance value where the pores become the charge storage (Rawal et al., 2018). This cluster can prevent the aggregation of N-doped carbon layers and improve the porosity and roughness of the N-doped carbon electrode, therefore increasing its surface area and catalytic activity. Because of the increased nitrogen content, HC4 has a hollow structural shape and a greater surface area of 560.72 m^2/g (Tafete et al., 2024).

Specific Surface of Activated Carbon

The specific surface was analysed based on the amount of nitrogen gas absorbed by the activated carbon, using the BET method. The specific surface of activated carbon from shrimp waste is shown in **Figure 4**. At H_3PO_4 concentrations of 9 M, 6 M, 3 M, and doping ratios of 1:7, 1:5, 1:3, the specific surfaces are 9.509 m^2/g, 11.581 m^2/g, and 17.522 m^2/g, respectively. This is consistent with the surface morphology of activated carbon shown in **Figure 3a**, **3b**, and **3c**, that at lower H_3PO_4 concentrations it produces more pores with smaller pore diameters. The pore diameter and pore volume affect the specific surface and absorption capacity of carbon. In BET analysis, smaller pore diameters allow more nitrogen molecules to adsorb to the surface, hence increasing the specific surface area. Thus, the smaller the pore diameter, the larger the specific surface.

Capacitance of Activated Carbon Electrode

The ability to store electrical energy by supercapacitor electrodes is measured from the capacitance properties and charge-discharge performance characteristics. A good supercapacitor is one that meets the International Electrotechnical Commission (IEC) 62391-1:2006 double layer supercapacitor standard which is used in electronic component applications. The capacitance is expressed in Farad (F) units. The determination of capacitance used the CV method based on the initial and final voltage characteristics (Rawal et al., 2021). The potential that exists in CV measurements consists of the charging and discharging current density. The electrodes used in the voltammetry cell consist of 3 electrodes, namely working electrode, reference electrode, and auxiliary electrode. The reference, support, and working electrodes are gold disc, platinum wire and Ag/AgCl, respectively. The voltammogram curve of the measurement results with a potential difference of 0-1 V at various activator concentrations and nitrogen doping ratios can be seen in **Figure 5**, **6**, and **7**.

At a potential difference of 0-1 V and a scan rate of 0.002 V/s A slow scan rate, such as 0.002 V/s, allows the system to remain closer to equilibrium during the measurement. This minimizes distortions caused by resistive or kinetic limitations, ensuring more accurate measurement of capacitance. The highest current is obtained at a concentration of 3 M with a nitrogen doping ratio of 1:3. The curve obtained is rhomboid in shape. Referring to the literature (Zhang et al., 2021) the curve has sharp edges because the electric current flow is proportional to the potential difference generated. The shape of the curve is also influenced by the charge and discharge currents, where the greater the charge-discharge current, the wider the shape of the curve (Elmouwahidi et al., 2017). The capacitance values of activated carbon electrodes based on the CV test results are presented in **Table 1** and **Figure 6**. The sample that has the highest capacitance is the AC-001 sample, which was activated by 3 M H_3PO_4 and a nitrogen doping ratio of 1:3, i.e. 16.3206 Farad.
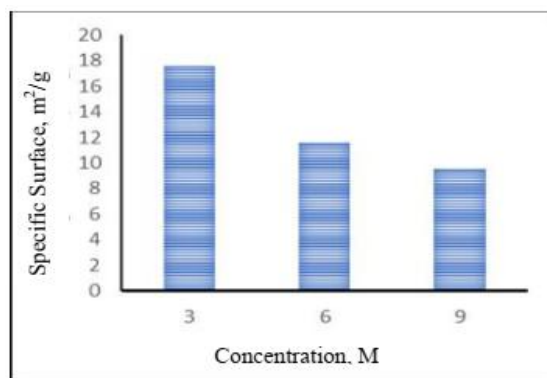

Figure 4. Specific surface of activated carbon from shrimp waste.

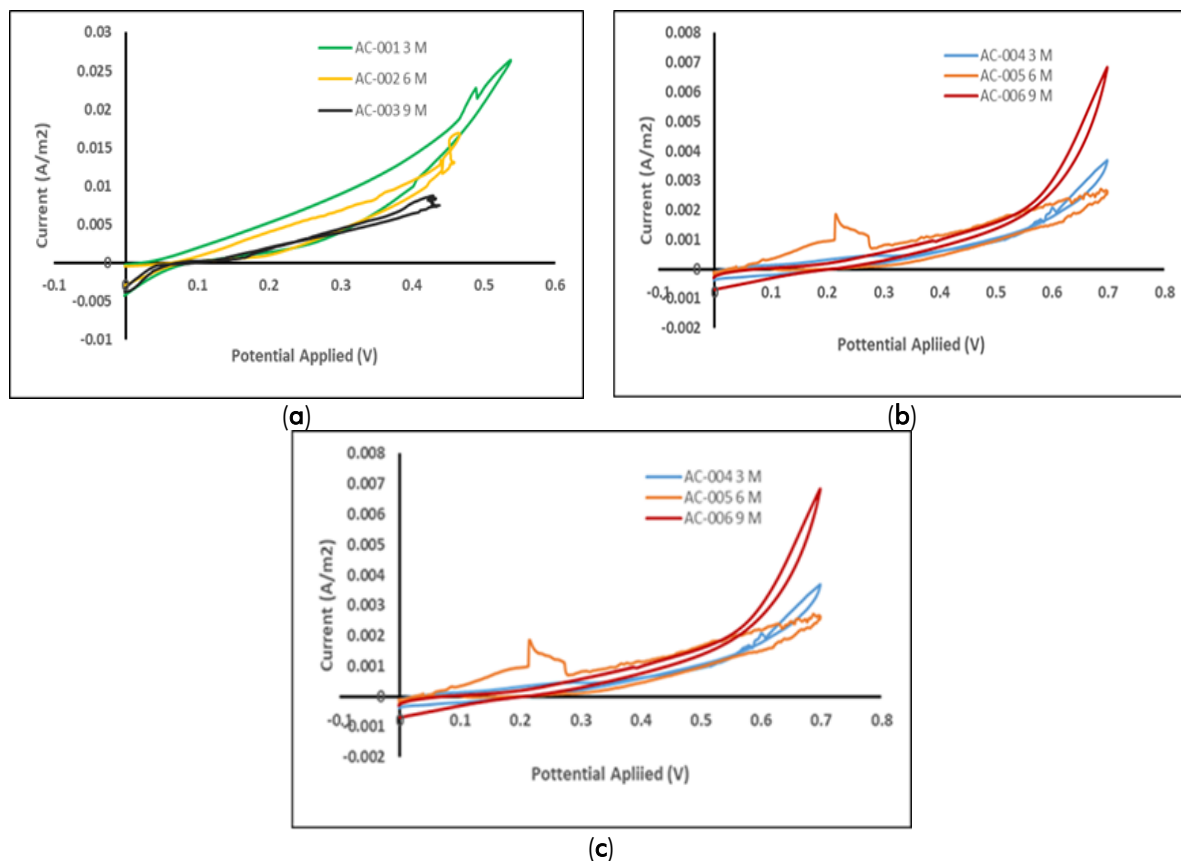(a)   (b)

(c)

Figure 5. The voltamogram curve of H_3PO_4 activator with 1:3 nitrogen doping.

Table 1. The results of the capacitance calculation are based on the voltammogram curve

| Sample	Scane Rate/Y (V/s)	Ec (V)	Ic (A/m²)	A (m²)	Ln (ΔE)	C (Faraday)
AC-001	0.002	0.53808	26.33	0.004	0.6197	16.3206
AC-002	0.002	0.46569	16.90	0.004	0.7642	12.9206
AC-003	0.002	0.43223	8.473	0.004	0.8387	7.10726
AC-004	0.002	0.69820	3.692	0.004	0.3592	1.32651
AC-005	0.002	0.69830	2.632	0.004	0.3591	1.94522
AC-006	0.002	0.69715	6.715	0.004	0.3607	0.42250
AC-007	0.002	0.69868	5.538	0.004	0.3585	1.98604
AC-008	0.002	0.69821	3.757	0.004	0.3592	1.34979
AC-009	0.002	0.69718	7.284	0.004	0.3607	0.62744
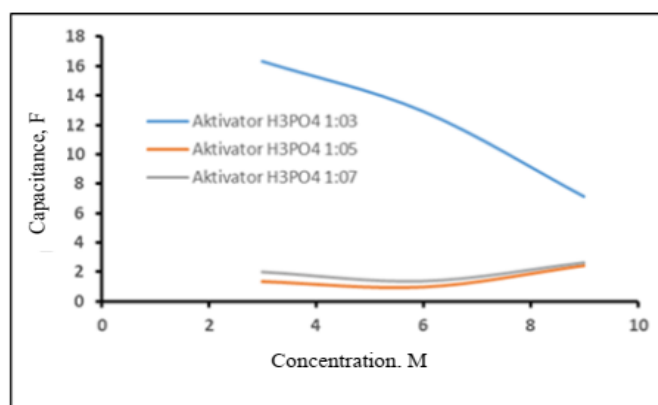
Figure 6. The capacitances of activated carbon electrodes at various activator concentrations and doping ratios

The 9 M concentration with the nitrogen doping ratio of 1:7 has a lower capacitance value. The trend of capacitance is similar to that of specific surfaces in which the higher the concentration and nitrogen doping ratio, the lower the capacitance value. The capacitance is influenced by carbon pores, carbon specific surface, sample thickness, and material permittivity. The wider the specific surface of activated carbon, the more electric charge can be stored, so the higher the capacitance. The BET test shows that the specific surface of activated carbon at a concentration of 3 M and doping ratio of 1:3 is 17.522 m^2/g, greater than at a concentration of 9 M and doping ratio of 1:7, i.e. 9.509 m^2/g.

Characteristics of Charge-Discharge

The performance of supercapacitor electrodes made from shrimp waste activated carbon was measured from the charging and discharging times using the GCD method. The supercapacitors are capable of discharging two voltage points at a constant current. The potential used was 0-2 V at a current of 10 $mAcm^{-2}$. The GCD curves for carbon-based supercapacitors are generally triangularly symmetric, showing almost linear changes in potential as a function of time during charging and discharging (Farma et al., 2013). The generated potential is plotted against time, producing a linear data trend, with both positive and negative slopes. The deviations from linearity can occur due to an increase in voltage with each additional time, so that the same resistance can cause a rapid decrease. The performance of supercapacitors depends on the presence of electrically charged ions, which fill the pore walls of the activated carbon electrode by a diffusion-adsorption mechanism. The electric charge is released when used by a desorption-diffusion mechanism. The potential change profiles during charging and discharging at various activator concentrations and nitrogen doping ratios are shown in **Figure 7**.

The long-term electrode stability is also an important factor in evaluating carbon materials as supercapacitor electrodes. The characteristic of supercapacitor can be indicated from the time required in charging and discharging. A good capacitor has a short time in charging but a long time in discharging. **Figure 7** shows the variation of gravimetric capacitance with time required in a charge-discharge cycle on a current density of 1 Ag with a KOH electrolyte on both electrodes. The activated carbon electrodes activated by 3 M H_3PO_4 with nitrogen doping ratio of 1:3 show that the current charging stops at 475 seconds, and the current discharging ends at 1235 seconds. The results are significantly different from the concentration of 6 M with a doping ratio of 1:5 particularly in current discharging; the charge stops at 380 seconds and ends with discharging at 665 seconds. This is in line with the capacitance value where at 3 M and doping ratio of 1:3 the highest capacitance was obtained. Meanwhile, the longest charging occurred at a concentration of 9 M with a nitrogen doping ratio of 1:5 with a charging value of 750 seconds. The resulting GCD curve does not show a symmetrical shape due to the higher scanning speed and large barriers to ion transport in the pores, which will inhibit the formation of the electric double layer (Yan et al., 2018).
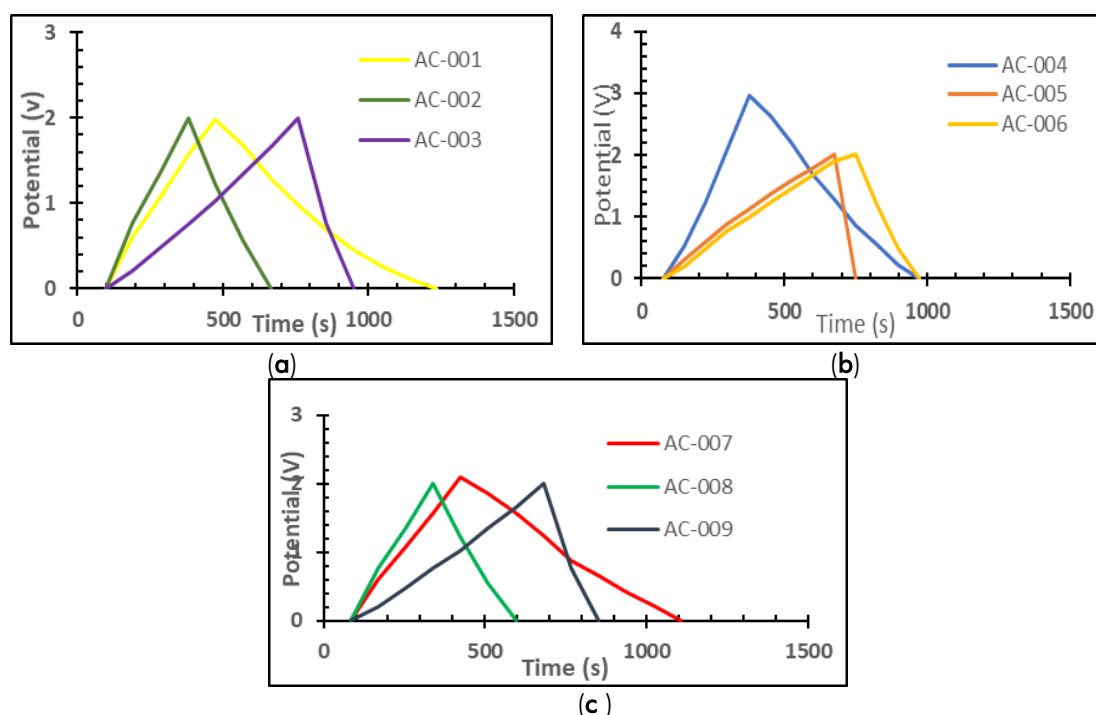

(a)

(b)

(c)

Figure 7. GCD curve at concentrations of 3, 6, 9 M with a doping ratio of 1:3, 1:5, 1:7

CONCLUSIONS

Supercapacitors electrodes were prepared from a renewable, low cost, abundant and sustainable natural resource (i.e. waste shrimp shells), with an activation treatment using N-doping and H_3PO_4. The concentration of H_3PO_4 activator and the addition of nitrogen doping from urea were known to affect the characteristics of activated carbon in terms of morphological surface and specific surface, and the electrochemical properties of supercapacitor in terms of capacitance and current charge-discharge cycle. This effect is likely due to the increased pore formation and enhanced structural properties that facilitate ion diffusion. In the range of H_3PO_4 concentrations and nitrogen doping ratios studied, the highest specific surface of activated carbon and supercapacitor capacitance were obtained at a concentration of 3 M and a doping ratio of 1:3, i.e. 17.522 m^2/g and 16.3 Farad, respectively. In terms of charging and discharging time, the best supercapacitor performance was also obtained at 3 M H_3PO_4 and a nitrogen doping ratio of 1:3, i.e. The best performance was observed with a charging time of 475 seconds and a discharging time of 1235 seconds.

ACKNOWLEDGEMENTS

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