МРНТИ 44.00.00; 31.00.00; 61.67.33 https://doi.org/10.18321/cpc22(3)269-277

Food waste-derived activated carbon for supercapacitors

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ABSTRACT

This research investigates the utilization of activated carbon synthesized from food waste biomass, specifically, peels of orange, apple, cucumber, and onion, as electrode materials for high-performance supercapacitor applications. The peels were first pre-carbonized at 600 °C and then activated at 700 °C with KOH. The research involved developing a supercapacitor using the synthesized activated carbon as the electrode material and 6 M KOH as the electrolyte. The results indicated that electrodes made from orange peel, apple peel, cucumber peel, and onion peel exhibited specific capacitances of 238.5 F/g, 201.2 F/g, 236.9 F/g, and 118.9 F/g, respectively, at a current density of 1 A/g. When the current density was increased to 2 A/g, the elec-trodes maintained up to 90% of their capacitance.

Keywords: food waste, activated carbon, supercapacitor, orange peel, apple peel, cucumber peel, onion peel

1. Introduction

Energy presents a major environmental challenge. Conventional energy sources like coal, gas, and oil are not only depleting but also contributing to ecosystem damage, loss of biodiversity, and pollution. The fundamental problem with fossil fuels is their unsustainability over the long term, which is prompting a shift toward sustainable and renewable energy solutions. Recently, there has been substantial research growth in renewable energy sources such as solar, geothermal, wind, and biofuels.

Moreover, there is significant focus on electrochemical energy storage systems, including supercapacitors and batteries. The effective development and deployment of renewable energy technologies, such as wind turbines and solar panels, are highly dependent on advanced and efficient energy storage systems.

Energy storage and transmission technologies such as supercapacitors are capable of storing and transmitting energy at extremely high speeds, allowing large currents to be generated in a short time. They also have a virtually unlimited lifespan with high specific capacity and demonstrate better performance at extreme temperatures than batteries, especially at low temperatures [1].

In recent decades, considerable efforts have been made to improve the characteristics of supercapacitors. Research aimed at increasing the energy and power density of supercapacitors is pursued in two main directions: 1) the development of multicomponent organic electrolytes, including electrolytes based on ionic liquids, to increase the range of operating voltages; 2) enhancing the power characteristics of supercapacitors primarily through improvements in electrode materials. The electrode is a crucial component of supercapacitors, leading to extensive research aimed at enhancing its quality. Utilizing renewable materials for supercapacitor electrodes is particularly significant, as these materials are cost-effective and environmentally friendly [2].

Carbon obtained from food waste biomass is well-suited for use as electrode material in supercapacitors, often demonstrating exceptional electrochemical performance. The key factors for enhancing the performance of carbon supercapacitors are a high specific surface area and optimal pore size. Various food wastes, such as banana peel [3-5], coconut shell [6-9], lemon peel [10, 11], garlic peel [12, 13], rice husk [14-17], cucumber peel [18] etc., have been used as precursors for the production of activated carbon. Compared with traditional carbon sources,

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Дата поступления: 18 августа 2024 г.

these biomass materials are a cheaper carbon source because they are diverse, clean and renewable. Furthermore, converting biomass into activated carbon helps alleviate the problem of biowaste disposal. In this study, food waste such as onion peels, orange, apple and cucumber peels were used to obtain carbon materials used as the active substance of supercapacitor electrodes.

2. Experimental part

2.1. Materials and Chemicals

Food waste materials, including apple, cucumber, orange peels, and onion peels were selected for their relevance in sustainable materials research. These materials are rich in organic content, making them suitable precursors for activated carbon production, as demonstrated in previous studies [10-13, 18]. Prior to use, the peels were rinsed with water and dried at 80 °C for 24 h before being crushed. Chemically pure reagents were employed: hydrochloric acid (HCl, 36.6%), potassium hydroxide (KOH, ≥ 85%, Sigma Aldrich), polyvinylidene fluoride (PVDF, MTI Corporation), carbon black (MTI Corporation), 1-methyl-2-pyrrolidone (NMP, Sigma Aldrich), argon gas (Ikhsan Technogas Ltd), and titanium foil (MTI Corporation). All solutions were prepared using distilled water.

2.2. Activated Carbon Production

Activated carbons were derived from the food waste peels as follows. The crushed peels were carbonized in a tube furnace under an argon atmosphere. Apple, cucumber, and orange peels were carbonized at 600°C for 2 hours, while onion peels were carbonized at 300°C for 2 hours. This lower temperature was optimal for onion peels to avoid producing an ultralight carbonized mass. The resulting carbonized materials were then mixed with KOH in a 1:2 weight ratio and subjected to activation at 700 °C for 2 h in an argon atmosphere. The activated materials were washed with 1 M HCl and distilled water until a neutral pH was achieved, then dried at 60°C overnight. The final samples were labeled as activated orange peel (AOP), activated apple peel (AAP), activated cucumber peel (ACP), and activated onion peel (AOnP).

2.3. Characterization

Morphological analysis was performed using scanning electron microscopy (SEM, JEOL JSM-6490LA), and elemental composition was examined via energy-dispersive X-ray spectroscopy (EDAX). The specific surface area was measured by nitrogen adsorption at -196 °C using the Brunauer-Emmett-Teller (BET) method.

2.4. Electrode Preparation

Electrodes were prepared using a suspension of 75 wt.% activated carbon (AOP, AAP, ACP, or AOnP), 15 wt.% PVDF, and 10 wt.% carbon black in NMP. A 0.4 g suspension was mixed for 20 minutes and applied to a 1 cm × 2 cm titanium foil area. The titanium foils were pretreated by sanding, cleaning, and drying. The electrodes were dried at 130°C for 12 hours. The mass of active material was calculated by subtracting the mass of the foil from the total electrode mass, and multiplying the result by 0.75.

2.5. Electrochemical Measurements

Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) techniques were employed to assess electrochemical properties using a P-45X potentiostat-galvanostat. Electrode pairs with the most similar active material mass were selected and immersed in a 6 M KOH solution. The electrodes were assembled with a separator in between, and iron weights were used to secure them. The lower electrode was connected to auxiliary and reference electrodes, while the upper electrode was connected to the working and counter electrodes.

For CV measurements, testing is performed at scan rates of 5 mV/s, 10 mV/s, 20 mV/s, 40 mV/s, 80 mV/s, 160 mV/s.

The specific capacitance (C_m) is determined from the voltammetric curves of the two-electrode cell using the equation provided:

$$C_M = \frac{A}{m \times k \times (V_2 - V_1)} \tag{1}$$

where, A – the integral of the CV curve; m – the mass of the active substance of one electrode, g; k – the scanning rate, mV/s; V_2-V_1 – potential window of the cell, V.

For measurement by the galvanostatic charge-discharge method, testing is carried out at current density values of 100 mA/g, 250 mA/g, 500 mA/g, 1000 mA/g, 2000 mA/g.

The specific capacitance according to the GCD curves of a two-electrode cell is calculated:

$$C_M = \frac{2I \times t}{m \times (V_2 - V_1)} \tag{2}$$

where, I – the current density, A/g; t – the discharge time, s; m – the mass of the active substance of one electrode, g; V_2-V_1 – the potential window of the cell, V.

Figure 1 shows a typical scheme for creating electrodes for supercapacitors based on activated carbon derived from orange, cucumber, apple, and onion peels.

3. Results and discussions

The morphology of the prepared AAP, AOP and ACP was studied using SEM, and the results are shown in Fig. 2. The figures show that the carbonized orange peels have pore sizes ranging from 9 to 28 μm (Fig. 4a), cucumber peels from 2 to 33 μm (Fig. 2b) and apple peels from 7 to 31 μm (Fig. 2c). Fig. 2d shows SEM images of onion peel after preliminary carbonization, where micron-sized carbon structures comprising several parts of the carbonized onion peel are visible.

In the activated carbons obtained using KOH, the pore size in the orange samples decreased to the range of 5-11 μm (Fig. 2e), in the cucumber samples to 0.9-16 μm (Fig. 2f) and in the apple samples to 2-9 μm (Fig. 4g). The presence of a three-dimensional macroporous cellular-structural network consisting of carbon walls is also observed for AAP, AOP and ACP. Activated onion peel also exhibits a three-dimensional porous channel structure connected to each other. This porous architecture increases the surface area of the material, facilitating more efficient electrolyte penetration and improved diffusion of electrolyte ions within the electrode.

Table 1 shows the specific surface areas of the carbon materials as measured by the BET method.

Non-activated porous carbons obtained by conventional heat treatment have a surface area from 0.58 to 7.51 m^2/g. Activated carbons treated with potassium hydroxide have the following surface area values: 510.2 m^2/g for AOP samples, 575.2 m^2/g for AAP samples, 421.8 m^2/g for ACP samples, and 447.1 m^2/g for AOnP samples. In the presence of KOH, decomposition reactions occur, consisting of two processes [18]:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \tag{3}$$

1) Reaction of carbon with potassium hydroxide:

2) The reaction of decomposition of potassium carbonate and/or the reaction of carbon with CO_2, K_2CO_3, K_2O:

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{4}$$

$$CO_2 + C \rightarrow 2CO \tag{5}$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \tag{6}$$

$$C + K_2O \rightarrow 2K + CO \tag{7}$$

During the gas release process, numerous pores are formed, which positively impacts the properties of the active electrode material for supercapacitor applications.

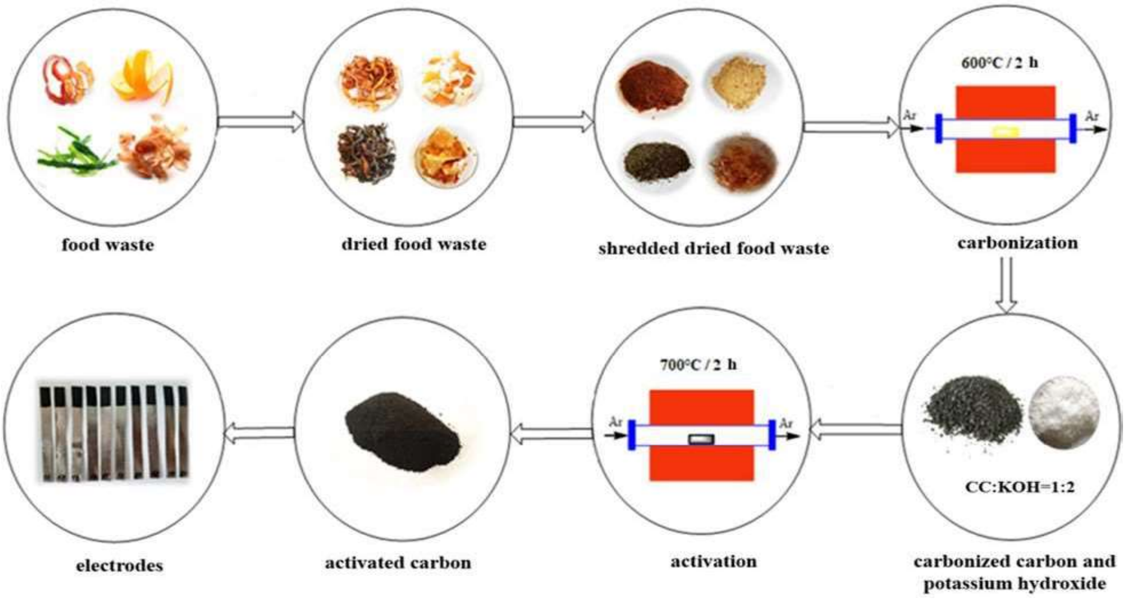
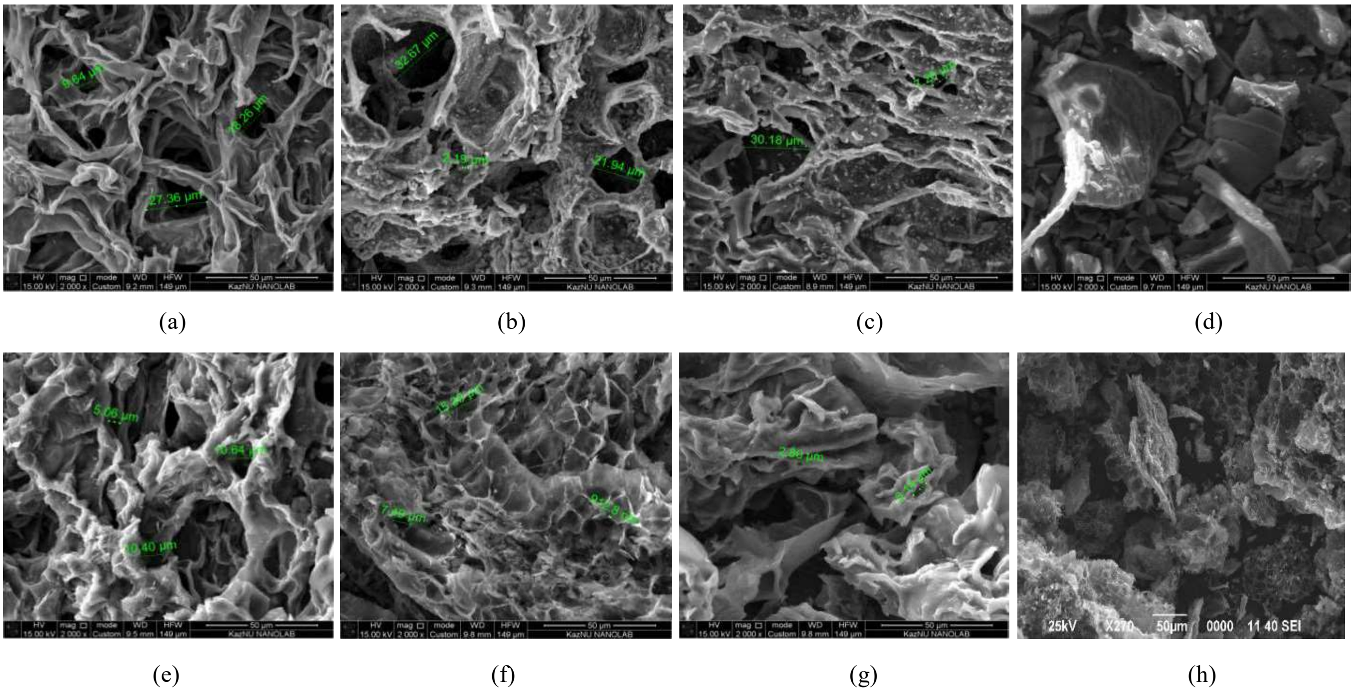


Fig. 1. Flow diagram of the electrode fabrication process using activated carbon produced from food waste.


(a) (b) (c) (d)

(e) (f) (g) (h)

Fig. 2. SEM images of peels: after carbonization – (a) orange; (b) cucumber; (c) apple; (d) onion and after activation – (e) orange; (f) cucumber; (g) apple; (h) onion.

Table 1. Specific surface area of carbonized and activated carbon masses according to BET

Raw materials	Sample name	Specific surface area, m^2/g
orange peel	Carbonized orange peel at 600 °C (COP600)	7.51
	AOP	510.20
apple peel	Carbonized apple peel at 600 °C (CAP600)	4.94
	AAP	575.20
cucumber peel	Carbonized cucumber peel at 600 °C (CCP600)	0.58
	ACP	421.80
onion peel	Carbonized onion peel at 300 °C (COnP300)	0.87
	AOnP	447.10

Thus, it can be concluded that pyrolysis of fruit peels using KOH as an activator helps to increase the specific surface area and improve the porous structure of the material.

Elemental analysis of the samples was carried out using the EDS method, the results are grouped in Table 2. The results show that the high activation temperature (700 °C) has a positive effect on the final products, since the percentage of carbon in the activated carbon samples increased to 88-91%. While after carbonization at a temperature of 600 °C, the percentage of carbon in the samples is only 67-80%.

The voltammetric characteristics of the electrodes based on activated carbons from food wastes were measured in a two-electrode cell in the potential range from -0.2 to 0.8 V. For all samples of activated carbons obtained from food peels, the voltammetry characteristic curves at scan rates from 5 to 160 mV/s demonstrate a typical rectangular shape characteristic of supercapacitors with a double electric layer (Fig. 3). With an increase in the scan rate, the shape of the graphs retains its rectangularity even at high rates (160 mV/s), which indicates a good speed capability of the cell. However, with an increase in the scan rate, the curves become slightly rougher, which indicates the presence of noticeable ohmic resistance in the pores. The integral area of the voltammetric curves corresponds to the capacitance of the supercapacitor. Thus, the specific capacity of the cell at different scanning rates is presented in Table 3. Calculations showed that the samples of synthesized activated carbons demonstrate high specific capacity at a scanning rate of 5 mV/s. With an increase in the scanning rate, the capacity decreases, which is associated with the limited availability of electrolytic ions for the active zones of the electrodes.

Table 2. Elemental composition of the samples

Element		C	O	Na	Mg	Al	Si	K	Ca	Cl	P	S
atomic concentration, %	COP600	80.39	18.02	-	0.11	-	-	0.99	0.42	0.07	-	-
	AOP	88.99	7.91	0.05	0.17	0.08	0.10	2.13	0.57	-	-	-
	CAP600	78.35	18.77	-	0.02	-	-	2.74	-	-	0.12	-
	AAP	90.08	8.54	0.02	0.22	0.06	0.02	0.97	0.07	-	-	-
	CCP600	67.64	20.02	0.23	0.39	0.07	0.42	9.60	-	0.47	0.98	0.17
	ACP	91.69	7.04	0.33	0.04	0.07	0.12	0.02	0.16	0.55	-	-
	COnP300	79.30	17.59	-	0.35	0.26	0.65	0.61	0.97	-	-	-
	AOnP	80.79	13.18	-	0.81	0.21	0.62	0.72	3.66	-	-	-

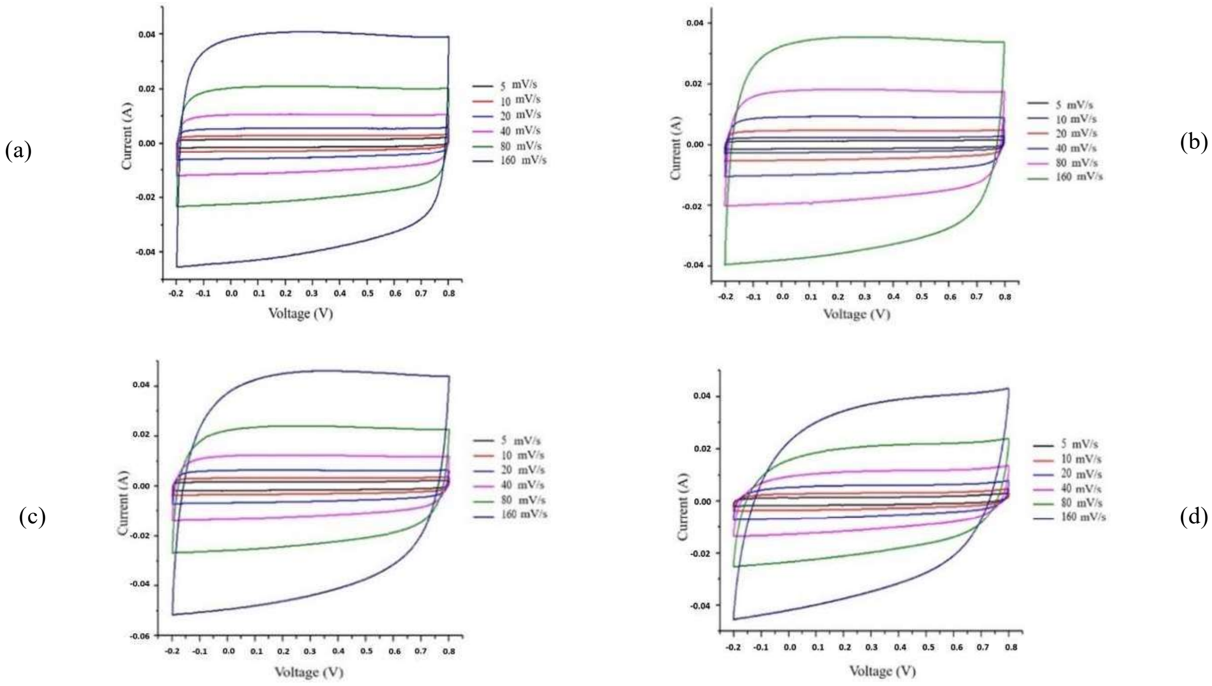


Fig. 3. I-V curves of electrodes based on (a) AOP; (b) AAP; (c) ACP; (d) AOnP in 6M KOH electrolyte (- 0.2 – 0.8 V) at different scanning rates (5, 10, 20, 40, 80 and 160 mV/s).

To obtain more accurate capacitance values, GCD curves were recorded at different current densities. Figure 4 shows typical charge-discharge curves for capacitor cells, demonstrating a highly symmetrical isosceles triangle shape at different current densities. This indicates good electrochemical reversibility. After the first ohmic decrease, an almost linear discharge line is observed. The typical charge-discharge capacitance profile is maintained even at high current densities, indicating excellent cell speed characteristics. The gravimetric capacitance values obtained from GCD measurements for electrodes based on activated carbons made from food waste are presented in Table 4.

Table 3. Gravimetric capacities of electrodes based on AOP, AAP, ACP, and AOnP samples, derived from CV measurements

Scan rates, mV/s		5	10	20	40	80	160
Gravimetric capacity, F/g	AOP	255.9	246.5	239.8	233.1	225.4	214.5
	AAP	220.3	213.5	207.6	201.1	193.0	180.5
	ACP	252.1	241.9	233.4	223.6	210.1	189.4
	AOnP	119.5	116.7	112.6	106.9	99.2	89.3

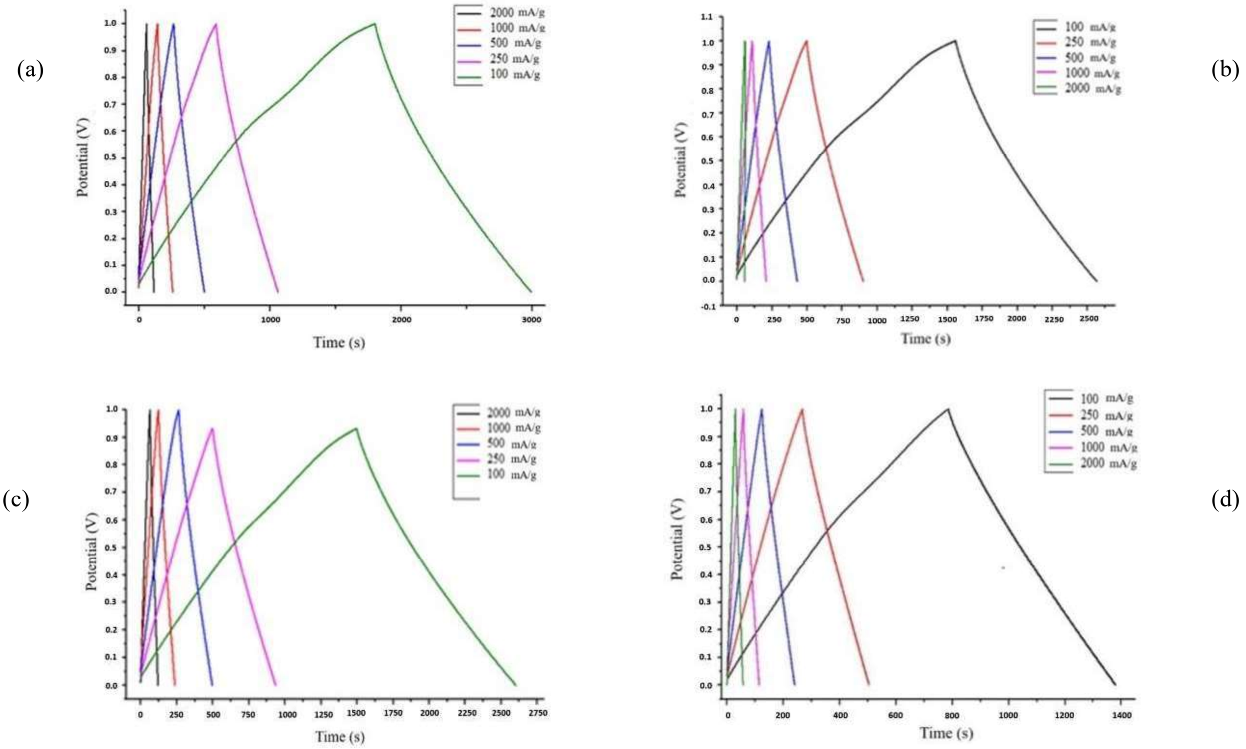


Fig. 4. GCD curves of electrodes based on (a) AOP; (b) AAP; (c) ACP; (d) AOnP in 6M KOH electrolyte (potential window 0 – 1.0 V) at different current densities (100, 250, 500, 1000 and 2000 mA/g).

Table 4. Gravimetric capacities of electrodes based on AOP, AAP, ACP, and AOnP samples, derived from GCD measurements.

Current density, mA/g		100	250	500	1000	2000
Gravimetric capacity, F/g	AOP	238.5	235.7	234.1	232.4	224.9
	AAP	201.2	200.9	199.9	197.9	194.7
	ACP	236.9	234.1	232.2	227.8	222.4
	AOnP	118.9	118.5	116.2	112.3	106.7

According to the results of CV and GCD, the AOnP sample showed the lowest value of gravimetric capacity: 119.5 F/g at 5 mV/s and 118.9 F/g at 100 mA/g. This is due to the fact that when activated with potassium hydroxide in a ratio of 1:2, a material with low porosity is obtained. The specific capacity of activated carbons obtained from orange, apple and cucumber peels is approximately the same. The low capacity of activated carbon from onion peels compared to other samples is due to its structural features. The highest specific capacity was demonstrated by activated orange peel: 255.9 F/g according to the CV method and 238.5 F/g according to the GCD method, which can be explained by the preservation of the unique structure of the orange peel even after carbonization.

Figure 5 shows the gravimetric specific capacity values of activated carbons obtained from food waste at different current densities. Measurements using the GCD method showed that the capacity of AOP at a current density of 0.1 A/g is 238.5 F/g, and at 2 A/g - 224.9 F/g, which corresponds to a capacitive stability of 94.3%

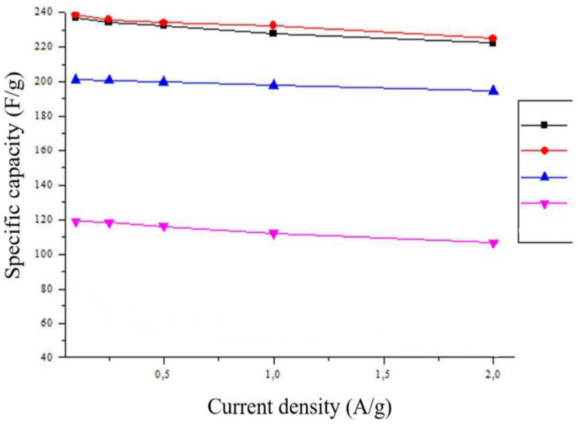


Fig. 5. Gravimetric capacity values of electrodes measured at different current densities.

While activated carbon from apple peel at current densities of 0.1 A/g and 2.0 A/g has a capacity of 201.2 and 194.7 F/g, respectively, providing a stability of 96.8%. The capacity of ACP at a current density of 0.1 A/g is 236.9 F/g, and at 2 A/g - 222.4 F/g, which provides a specific capacity stability of 93.7%. Carbons obtained from onion peels have a capacitive stability of 89.7%.

4. Conclusion

In this work, orange peels, which retain their structural characteristics even after high-temperature pyrolysis, as well as apple peels, cucumber peels and onion peels, which are widely available and inexpensive, were selected to obtain activated carbon from food waste used as an active substance for supercapacitor electrodes. The possibilities of obtaining activated carbons through preliminary carbonization and subsequent activation with potassium hydroxide from these food wastes were investigated.

According to the BET results, the surface areas of the synthesized activated carbons AOP, AAP, ACP and AOnP were 510.2; 575.2; 421.8 and 447.1 m²/g, respectively. Using SEM, it was found that the pore sizes were in the range from 0.9 to 16 μm.

These carbon materials were used as active substances for creating electrodes. The electrochemical characteristics of the electrodes were tested in a 6 M KOH solution. The curves obtained by the CVA method showed that a double electric layer functions in the electrodes, corresponding to the operating principle of supercapacitors. The specific capacitance measured by the GCD method at a current density of 1 A/g was: AOP - 238.5 F/g, AAP - 201.2 F/g, ACP - 236.9 F/g and AOnP - 118.9 F/g. When the current density was increased to 2 A/g, the capacitive stability of the electrodes remained at least 90%.

In conclusion, it can be stated that electrode materials made from orange, apple, cucumber and onion peels demonstrate good electrochemical characteristics when used in two-electrode symmetrical supercapacitor cells.

The work was carried out at the Institute of Combustion Problems.

Acknowledgments

This research has been funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan for financial support ("Grant No. AP19677415 Obtaining nanocomposites from food waste and creating electrode materials based on them for supercapacitors").

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Суперконденсаторлар үшін тағам қалдықтарынан алынған белсендірілген көмір

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АННОТАЦИЯ

Бұл зерттеу өнімділігі жоғары суперконденсаторлар үшін электродтық материалдар ретінде тағам қалдықтарынан синтезделген белсендірілген көмірді, атап айтқанда апельсин, алма, қияр және пияз қабықтарын пайдалануды қарастырады. Қабықтардың суперконденсаторларда қолданылу мүмкіндігін анықтау үшін, шикі қабықтарды алдымен 600 °C температурада көміртектендіреді, содан кейін 700 °C температурада KOH қолдану арқылы активтендіреді. Жұмыс синтезделген активтендірілген көмірді электрод материалы ретінде және 6M KOH-ты электролит ретінде қолданатын суперконденсаторды әзірлеуді қамтиды. Нәтижелер көрсеткендей, апельсин қабығы, алма қабығы, қияр қабығы және пияз қабығынан жасалған электродтар сәйкесінше 1 А/г ток тығыздығында 238,5 Ф/г, 201,2 Ф/г, 236,9 Ф/г және 118,9 Ф/г нақты сыйымдылықты қамтамасыз етеді. Ток тығыздығы 2 А/г дейін артқан кезде, электродтар өз сыйымдылығын 90% деңгейінде сақтап қалады.

Түйін сөздер: тағам қалдықтары, белсендірілген көмір, суперконденсатор, апельсин қабығы, алма қабығы, қияр қабығы, пияз қабығы

Активированный уголь полученный из пищевых отходов для суперконденсаторов

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АННОТАЦИЯ

В данном исследовании рассматривается использование активированного угля, синтезированного из пищевых отходов, а именно кожуры апельсина, яблока, огурца и луковой шелухи, в качестве электродных материалов для высокоэффективных суперконденсаторов. Для определения потенциала использования кожуры в качестве электродных материалов, сырую кожуру предварительно подвергают карбонизации при 600 °C и последующей активации при 700 °C с использованием KOH. В данном исследовании предложен суперконденсатор, в котором в качестве электродного материала используется синтезированный активированный уголь, а в качестве электролита – 6 M KOH. Результаты показали, что электроды из апельсиновой, яблочной, огуречной кожуры и луковой шелухи обеспечивали удельную емкость 238,5 Ф/г, 201,2 Ф/г, 236,9 Ф/г и 118,9 Ф/г, соответственно, при плотности тока 1 А/г. При увеличении плотности тока до 2 А/г электроды сохраняли свою емкость на уровне 90%.

Ключевые слова: пищевые отходы, активированный уголь, суперконденсатор, кожура апельсинов, яблок, огурцов, луковая шелуха