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Synthesis and Electrochemical Characterization of Sodium-Ion Battery Anode Carbon Biomassa Based on Sunflower Seed Husk (*Helianthus annuus*)

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ABSTRACT

This study aimed to synthesize materials from the carbon biomass of sunflower seed husk (*Helianthus annuus)* for sodium ion battery anode. A simple carbonization process was carried out by roasting. The chemical activation process was conducted by adding KOH as much as 4 M in 100 mL water solution for 20 hours. Then drying was done in the oven at a temperature of 100°C for 20 hours, and then continued with the sintering process at a temperature of 900°C for 2 hours. The sintered results were washed and hydrothermal for 20 hours at 200°C with 4 mL H_2O_2 and 1 mL EG in 50 mL Teflon. The resulting acid degree was neutralized (pH ~ 7) with distilled water and then dried at 100°C for 20 hours. The hydrothermal powder was pulverized using a mortar and pestle and then sieved on a 325 mesh sieve. Anode sheets were prepared by mixing active ingredients : PVDF : Super-P with a composition of 85 : 10 : 5 by adding 2 mL of DMAC solvent. Electrochemical characterization testing was carried out to see the resulting performance. The results obtained from EIS, CV, and CD show that commercial hard carbon is better.

Keywords: Anode, Hard Carbon, *Helianthus annuus*, Sodium

ABSTRAK

Penelitian ini bertujuan untuk mensintesis bahan dari biomassa karbon sekam biji bunga matahari (*Helianthus annuus*) untuk anoda baterai ion natrium. Proses karbonisasi sederhana dilakukan dengan pemanggangan. Proses aktivasi kimia dilakukan dengan menambahkan KOH sebanyak 4 M dalam 100 mL larutan air selama 20 jam. Kemudian dilakukan pengeringan dalam oven pada suhu 100°C selama 20 jam, kemudian dilanjutkan dengan proses sintering pada suhu 900°C selama 2 jam. Hasil sinter dicuci dan hidrotermal selama 20 jam pada suhu 200°C dengan 4 mL H_2O_2 dan 1 mL EG dalam 50 mL Teflon. Derajat asam yang dihasilkan dinetralkan (pH ~ 7) dengan akuades kemudian dikeringkan pada suhu 100°C selama 20 jam. Serbuk hidrotermal dihaluskan menggunakan lumpang dan alu kemudian diayak pada ayakan 325 mesh. Pembuatan lembaran anoda dilakukan dengan mencampurkan bahan aktif : PVDF : Super-P dengan komposisi 85 : 10 : 5 dengan menambahkan 2 mL pelarut DMAC. Pengujian karakterisasi elektrokimia dilakukan untuk melihat kinerja yang dihasilkan. Hasil yang diperoleh dari EIS, CV, dan CD menunjukkan bahwa karbon keras komersial lebih baik.

Keywords: Anoda, Karbon Keras, *Helianthus annuus*, Natrium

1. Introduction

A battery is a device that stores electrical energy in chemical form, which can then be converted into electrical energy to obtain the desired electric current needed to power various devices [1]. Lithium-ion batteries are among the most common types of batteries encountered in today's technology [2]. An example of their use is in cell phones, which have become an essential part of daily life [3]. The high demand for lithium materials has increased scarcity and difficulty sourcing [4]. Consequently, alternative options are being sought as substitutes for lithium-ion batteries (LiBs) [5]. This has brought sodium-ion batteries (SIBs) into focus as an attractive alternative to lithium-ion secondary batteries [6].

However, finding a suitable constituent material for SIB batteries remains a challenge. Determining the anode material for SIBs is more complex compared to the cathode. Anode materials for Sodium-Ion Batteries are primarily categorized into metal oxides, metal alloys, and carbons [7]. Carbon, one of the most abundant elements in nature, serves as the fundamental building block for all organic chemistry [8]. Carbon materials can be efficiently and inexpensively produced through straightforward conversion processes [9].

One of the most explored areas in SIB anodes is the utilization of hard carbon (HC). Three categories of carbon materials are commonly considered for sodium-ion insertion: hard carbon, soft carbon, and graphite [10]. Among these, hard carbon exhibits the highest sodium-ion storage capacity due to its inherently random carbon bond structure, resulting in a larger gap or pore than graphite and soft carbon [11].

Hard carbon is a non-graphitizable carbonaceous material produced through the pyrolysis of carbon-containing materials in an inert atmosphere [12]. One method of synthesizing HC involves utilizing biomass. Utilizing biomass as a raw material for hard carbon is an excellent alternative due to its cost-effectiveness and sustainability [6]. The crystalline nature of activated carbon is pivotal in its electrode application, enhancing its intercalation and ion transport capabilities [13]. Biomass refers to a collection of organic materials derived from plant or animal sources, including materials resulting from natural or artificial transformation [14]. In this study, sunflower seed husks derived from the *Helianthus* annuus plant are categorized as biomass due to their organic nature [15]. The utilization of sunflower seed husk is particularly suitable as it contains up to 70% carbon [16]. The performance of biomass-derived hard carbon will be compared with commercially available HC materials commonly used today.

2. Method

The synthesis process of hard carbon biomass material from sunflower seed husk initiates with the carbonization process, followed by chemical activation of carbon. Subsequently, sintering will be conducted at a temperature of 900°C. A hydrothermal procedure will then follow the outcomes of sintering.

2.1. Materials and Instruments

In this study, a sunflower seed husk (*Helianthus annuus*) was employed and transformed into hard carbon. Creating hard carbon involved using KOH 4 M, H_2O_2, and EG. Furthermore, a commercial hard carbon material was utilized for comparative analysis. Super P, PVDF, and NMP were used to fabricate anode sheets. Electrochemical testing methods were employed to evaluate the anode's performance, including Cyclic Voltammetry, Charge-Discharge, and Electrochemical Impedance Spectroscopy.

2.2. Preparation of Hard Carbon from sunflower seed (Helianthus annuus) husk

The skin of the sunflower seeds will be cleaned initially. Subsequently, it will undergo roasting until the skin turns black. Following the roasting process, the skin will undergo activation. Currently, chemical and physical activation methods are commonly used for activating biomass carbon [13]. In this research, activation is accomplished by adding KOH. The resulting mixture will be heated again at 110°C. Afterward, the solution will be separated from the activated carbon. The separated activated carbon will be dried and sintered at 900°C for 2 hours. The sintered product will be washed and subsequently subjected to a hydrothermal process for 20 hours, with the addition of ethylene glycol.

2.3. Preparation of Slurry

Firstly, grinding will be performed, followed by sieving through a 325-mesh sieve to achieve sensitivity. Subsequently, the mass calculation is conducted to produce commercial HC and dwarf slurry HC. A ratio of 85 : 5 : 10 for Active Material : Super P : PVDF will be employed. Following this, the materials will be thoroughly mixed until homogenous, with the addition of 2.5 mL of NMP.

2.4. Anoda Sheet Fabrication

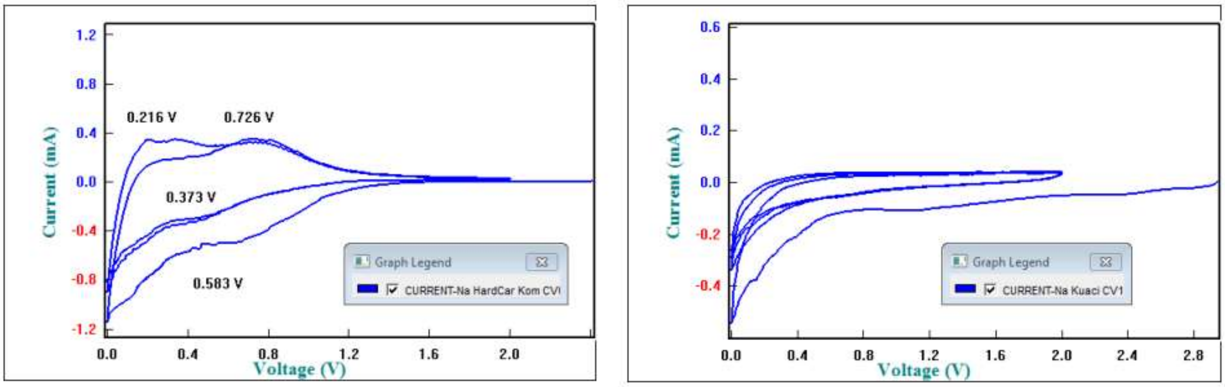
Anode sheet fabrication for commercial HC and dwarf HC uses a coating tool. The copper sheet is positioned on the tool and cleaned using ethanol. The doctor blade's thickness is set to 0.2 mm. The slurry is poured onto the copper sheet and processed through the machine. The coated results will be dried at 80°C for approximately 2 hours, resulting in a circular coating with a diameter of 16 mm.

2.5. Assembly Coin Cell

The coin cell assembly process for Commercial HC and sunflower seeds HC will be conducted within a glove box under vacuum conditions. The assembly procedure forms a half-cell configuration (half-cell testing), wherein the anode comprises HC, and the cathode consists of sodium metal (complimentary).

3. Results and Discussion

3.1. Cyclic Voltammetry (CV) Analysis



a b

Figure 1. Voltammogram of CV test on samples: a. Commercial hard carbon b. Dwarf hard carbon.

Cyclic Voltammetry (CV) testing measures the current response to potential changes that occur when an electrode undergoes polarization, inducing an oxidation-reduction reaction within the sample [14]. CV testing aims to identify the oxidation-reduction reactions taking place at the electrode. In this study, half-cell testing was conducted to assess the sodium-ion performance of the coin cell, utilizing hard carbon material as the anode. The resulting curve in the cyclic voltammetry method exhibits a characteristic hysteresis shape, where a broader curve indicates a higher capacitance value [17]. A comparison between the performance of commercial hard carbon material and synthesized hard carbon from dwarf as the anode will be carried out. Sodium metal is the cathode, and a separator is employed between them. The electrolyte used is NaPF6. CV samples underwent testing with a scan rate of 0.1 mV/s within a potential range of $0<V<2$ volts [18]. The curve depicted in Figure 1 illustrates the oxidation reaction leading to the peak at the top of the curve, known as the anodic peak. Conversely, the reduction reaction corresponds to the peak at the bottom of the curve, identified as the cathodic peak.

In Figure 1.a, the commercial HC exhibits an anodic peak at 0.216 V and a cathodic peak at 0.373 V. Conversely, in Figure 1.b, the anodic peak is observed at 0.4 V, while the cathodic peak is at 0.01 V. A larger distance between the curve peaks indicates easier intercalation and deintercalation of sodium ions. Analyzing the data reveals that the hard carbon derived from the dwarf source performs better in the intercalation process. This is attributed to the greater peak separation distance of 0.39.

3.2. Charge Discharge (CD) Analysis

Charging is the process of discharging electrons from the cathode, where electrons leave the cathode and move toward the anode, resulting in a negative charge. Discharging, however, involves utilizing the battery's capacity [19]. Charge-Discharge (CD) testing is employed to determine a battery's capacity. This study determined the battery capacity using the charge-discharge (CD) test tool for commercial and dwarf HC samples. CD testing serves to ascertain a battery's capacity [20]. The resulting curves are depicted in Figure 2, illustrating the CD curve in the Half Cell test with voltage ranging from 0 to 2 volts. Notably, the commercial HC samples exhibit a charge-discharge reaction with a coulombic efficiency of 100.9% in two cycles, outperforming sunflower seed HC, which exhibits a coulombic efficiency of 119.3%.

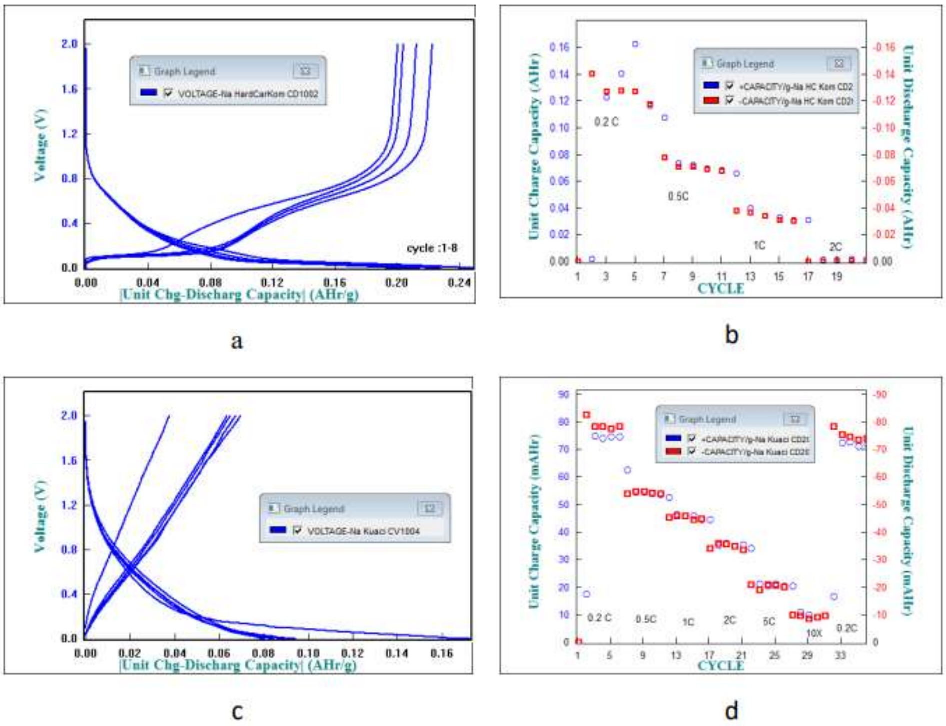


Figure 2. Galvanostatic Charge-Discharge curve: a. CD graph of commercial HC sample, b. Capacity vs cycle variation of commercial HC, c. CD graph of sunflower seeds HC sample, and d. Capacity vs cycle variation of dwarf HC.

3.3. Electrochemical Impedance Spectroscopy (EIS) Analysis

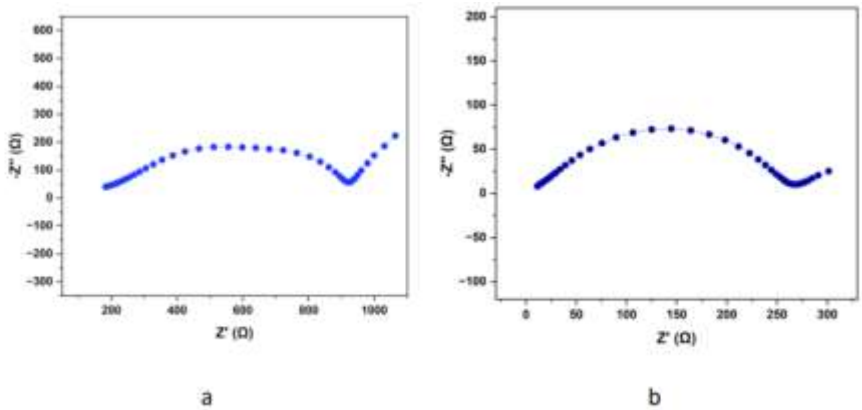


Figure 3. Nyquist plot for a. Commercial hard carbon, and b. Dwarf hard carbon.

Electrochemical Impedance Spectroscopy (EIS) is a versatile tool that provides valuable insights into a battery's behavior [21]. Electrochemical Impedance Spectroscopy (EIS) testing was conducted to determine the electrical conductivity value of the electrochemical cell. Testing was carried out using a coin cell configuration. The results of the EIS test are presented in the form of a Nyquist Plot, with the real resistance value (Z') along the x-axis and the imaginary resistance value (Z'') along the y-axis. The resulting curve typically appears semi-circular and linear. Figure 3 depicts the Nyquist plots for both samples.

From Figure 3.a, the commercial hard carbon demonstrates a conductivity of 5.45×10^{-7} S/cm, while Figure 3.b shows a conductivity value of 1.59×10^{-7} S/cm for dwarf hard carbon. It can be concluded that the commercial HC sample exhibits favorable sodium-ion diffusion and good ionic conductivity characteristics.

4. Conclusion

The electrochemical tests enable a comparison of the electrochemical performance between the synthesized carbon anode derived from sunflower seed husk (*Helianthus annuus*) and commercial hard carbon (HC). Characterization results indicate that in the case of sunflower seed HC, the CV test demonstrates a favorable intercalation and deintercalation process due to its larger peak separation of 0.39.

The CD test results highlight that the capacity of commercial HC is higher than that of sunflower seed HC at C-Rate 2, with a charge value of 204 mAh/g and a discharge of 203 mAh/g. EIS testing indicates that commercial HC exhibits higher conductivity and sodium-ion diffusion values, with a 5.45 x 10^{-7} S/cm conductivity

References

[1] Y. Han, Z. Lai, Z. Wang, M. Yu, Y. Tong, and X. Lu, "Designing Carbon-Based Supercapacitors with High Energy Density: A Summary of Recent Progress," *Chemistry - A European Journal*, vol. 24, no. 29, pp. 7312–7329, 2018, doi: 10.1002/chem.201705555.

[2] M. Nasution, "Karakteristik Baterai Sebagai Penyimpan Energi Listrik Secara Spesifik," *JEIT (Journal of Electrical Technology)*, vol. 6, no. 1, pp. 35–40, 2021.

[3] F. A. Perdana, "Baterai Lithium," *INKUIRI: Jurnal Pendidikan IPA*, vol. 9, no. 2, pp. 103-109, 2020, doi: 10.20961/inkuiri.v9i2.50082.

[4] H. P. Nurba, Y. Fauzi, A. G. Djatnika, and K. A. Munastha, "Implementasi Panel Surya untuk Perangkat Baterai Portabel," *Jurnal Infotronik*, vol. 7, no. 2, pp. 110–116, 2022, doi: 10.32897/infotronik.2022.7.2.2259.

[5] H. S. Hirsch, Y. Li, D. H. S. Tan, M. Zhang, E. Zhao, and Y. S. Mieng, "Sodium-Ion Batteries is Paving the Way for Grid Energy Storage," *Advanced Energy Materials*, vol. 10, no. 32, pp. 2001274, 2020, doi: 10.1002/aenm.202001274.

[6] T. E. P. S. Rahayu, M. Nurhilal, and R. Dwityaningsih, "Analisis Porositas, Tekstur, dan Morfologi Karbon Tempurung Nipah Hasil Pirolisis Suhu Tinggi untuk Anoda Baterai Sekunder," *Infotekmesin*, vol. 14, no. 01, pp. 119–129, 2023, doi: 10.35970/infotekmesin.v14i1.1666.

[7] B. Lu et al., "Hard-Carbon Negative Electrodes from Biomasses for Sodium-Ion Batteries," *Molecules (Basel, Switzerland)*, vol. 28, no. 10, pp. 4027, 2023, doi: 10.3390/molecules28104027.

[8] Z. Yang et al., "Recent Advancements of Nanostructured Carbon for Energy Applications," *Chem. Rev.*, vol. 115, no. 11, pp. 5159–5223, 2015, doi: 10.1021/cr5006217.

[9] L. Wang, J. Han, D. Kong, Y. Tao, and Q.-H. Yang, "Enhanced Roles of Carbon Architectures in High-Performance Lithium-Ion Batteries," *Nano-Micro Lett.*, vol. 11, no. 1, p. 5, 2019, doi: 10.1007/s40820-018-0233-1.

[10] G. Wang, M. Yu, and X. Feng, "Carbon materials for ion-intercalation-involved rechargeable battery technologies," *Chem. Soc. Rev.*, vol. 50, no. 4, pp. 2388–2443, 2021, doi: 10.1039/D0CS00187B.

[11] T. E. P. S. Rahayu, M. Nurhilal, and R. Dwiityaningsih, "Analisis Proksimat dan Bilangan Yodium Sebagai Kajian Awal Arang Tempurung Nipah Sebagai Bahan Intermediate Karbon Keras," *Rekayasa Hijau: Jurnal Teknologi Ramah Lingkungan*, vol. 6, no. 3, pp. 248–260, 2022, doi: 10.26760/jrh.v6i3.248-260.

[12] N. Shaji et al., "Efficient Conversion of Non-Biodegradable Waste into Hard Carbon as a Cost-Effective Anode for Sodium-Ion Batteries," *Chemical Engineering Science*, vol. 279, p. 118938, 2023, doi: 10.1016/j.ces.2023.118938.

[13] N. Suryana, O. Nurhilal, and S. Hidayat, "Kajian Pengaruh Temperatur Sintering terhadap Peningkatan Derajat Kristalinitas Karbon dari Limbah Kulit Kemiri," *JIIF (Jurnal Ilmu dan Inovasi Fisika)*, vol. 05, no. 02, pp. 164–169, 2021, doi: 10.24198/jiif.v5i2.35078.

[14] M. A. Peireia-Moreno, F. Manzano-Agugliaro, and A. J. Peireia-Moreno, "Sustainable Energy Based on Sunflower Seed Husk Boiler for Residential Buildings," *Sustainability (Switzerland)*, vol. 10, no. 10, p. 3407, 2018, doi: 10.3390/su10103407.

[15] P. S. Pratiwi, "Penggunaan Tepung Biji Bunga Matahari Sebagai Pengganti Tepung Terigu dalam Pembuatan Cookies," Sekolah Tinggi Pariwisata AMPTA Yogyakarta, 2021

[16] T. S. Hubeitska, N. G. Kobyliinska, and J. R. García, "Sunflower Biomass Power Plant By-Products: Properties and Its Potential for Water Purification of Organic Pollutants," *J. Anal. Appl. Pyrolysis*, vol. 157, p. 105237, 2021, doi: 10.1016/j.jaap.2021.105237.

[17] E. Tahir, Zulkifli, Sugianto, R. Syech, and R. Taslim, "Analisa Siklis Voltametri Supercapacitor Menggunakan Elektroda Karbon Aktif dari Kayu Kareit Berdasarkan Variasi Aktivator KOH," *in Seminar Nasional Fisika SNF 2015*, vol. 4, pp. 105–110, 2015.

[18] A. M. Nureza, "Analisis Pengaruh Komposisi Glycine pada Proses Sintesa Anoda Fe_2O_3 untuk Aplikasi Baterai Ion Lithium," Institut Teknologi Sepuluh November, 2017.

[19] I. Hidayah, Multazam, Yahdi, and A. W. Sakti, "Analisis Teori Energi Desolvasi Ion Natrium pada Pelarut Elektrolit Organik Menggunakan Density Functional Tight Binding (DFTB)," *SPIN: JURNAL KIMIA & PENDIDIKAN KIMIA*, vol. 4, no. 1, pp. 86–94, 2022, doi: 10.20414/spin.v4i1.5147.

[20] K. Hanif, "Pengaruh Penambahan Nanopartikel Hasil Sintesis Arc Discharge terhadap Performa Baterai Lithium Ion," Universitas Sebelas Maret, 2023.

[21] R. Xiong, J. Tian, W. Shein, J. Lu, and F. Sun, "Semi-Supervised Estimation of Capacity Degradation for Lithium-Ion Batteries with Electrochemical Impedance Spectroscopy," *J. Energy Chem.*, vol. 76, pp. 404–413, 2023, doi: 10.1016/j.jechem.2022.09.045.