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STUDY OF CHEMICAL STRUCTURE AND ELECTRICAL PROPERTIES OF NITROGEN-DOPED ACTIVATED CARBON FROM CANDLENUT SHELL (ALEURITES MOLUCCANA)

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Abstract. Li-Sulphur batteries have a high theoretical energy density of 1300 Ah/kg which is about 3 times of commercial lithium ion batteries today. It has several problems in application, especially low electrical conductivity ($5x10^{-30}$ S/cm) and the swelled volume during the charge/discharge process due to the formation of polysulfide. The solution of this problem is binded the Sulphur particles in porous carbon host. Binder Carbon/Sulphur will increase electrical conductivity while preventing swell the volume of Sulphur during the charge/discharge. In this paper, the nitrogen doped of activated carbon from candlenut shell was investigated for host material of carbon. The chemical structure and electrical conductivity of activated carbon doped nitrogen was studied. The synthesis of activated carbon was carried out by the pyrolysis process at 700°C and then activated by impregnation process for 24 hours using KOH as activator. The pyrolysis process is followed by nitrogen doped using NH_3 as a source of nitrogen. The weight ratio of carbon and NH_3 is 1:3 using 10% and 25% of NH_3 concentrations. The sample was then heated in a furnace at 850°C for 3 hours. The results of BET characterization can be determined the surface area of activated carbon from candlenut shell around 681 m^2/g. The process of nitrogen doping of activated carbon has been carried out successfully proved by the presence of C-N functional groups through FTIR analysis. Based on the results of SEM-EDS analysis, the nitrogen content in activated carbon is around 0.52% and 0.34% for NH^3 concentration of 25% and 10% respectively. The electrical conductivity of nitrogen doped activated carbon is around 2,31 x 10^2 S/cm and 2,03 x 10^2 S/cm for NH_3 concentration of 25% and 10% respectively.

Keywords: Candlenut shell, Li-Sulphur batteries, activated carbon, nitrogen doped

Abstrak. Baterai Li-Sulfur memiliki kerapatan energi teoretis yang tinggi sekitar 1300 Ah/kg atau 3 kali lebih besar dibanding baterai lithium ion komersial saat ini. Di dalam aplikasinya, baterai Li-Sulfur memiliki beberapa kendala terutama karena nilai konduktivitasnya rendah ($5x10^{-30}$ S/cm) dan terjadi pertambahan volume selama proses pengisian/pengosongan akibat terbentuknya polisulfida. Solusi dari masalah tersebut adalah mengikat partikel Sulfur dengan material karbon berpori. Komposit Karbon/Sulfur akan meningkatkan konduktivitas listrik sekaligus mencegah bertambahnya volume Sulfur selama proses pengisian/pengosongan. Pada penelitian ini telah dilakukan kajian doping nitrogen dari karbon aktif tempurung kemiri sebagai material pengikat Sulfur. Struktur kimia dan konduktivitas listrik dari karbon aktif yang didoping nitrogen telah dikaji. Sintesis karbon aktif dilakukan dengan proses pirolisis pada suhu 700°C kemudian diaktivasi dengan proses impregnasi selama 24 jam menggunakan KOH sebagai aktivator. Proses pirolisis dilanjutkan dengan doping nitrogen menggunakan NH_3 sebagai sumber nitrogen. Perbandingan berat karbon dan

NH_3 adalah 1:3 menggunakan konsentrasi NH_3 10% dan 25%. Sampel kemudian dipanaskan dalam furnace pada suhu 850°C selama 3 jam. Hasil karakterisasi BET dapat diketahui luas permukaan karbon aktif dari tempurung kemiri sekitar 681 m^2/g. Proses doping nitrogen karbon aktif telah berhasil dibuktikan dengan adanya gugus fungsi C-N melalui analisis FTIR. Berdasarkan hasil analisis SEM-EDS, kandungan nitrogen dalam karbon aktif sekitar 0,52% dan 0,34% masing-masing untuk konsentrasi NH_3 25% dan 10%. Konduktivitas listrik karbon aktif yang didoping nitrogen adalah 2,31 x 10^2 S/cm dan 2,03 x 10^2 S/cm masing-masing untuk konsentrasi NH_3 25% dan 10%.

Kata Kunci: Tempurung kemiri, baterai Li-Sulfur, karbon aktif, doping nitrogen

1. Introduction

The development of lithium-ion batteries based on Li-Sulphur cathodes has several advantages i.e., high energy density, low production costs, raw materials abundance in Indonesia and more environment friendly. Li-Sulphur has a high theoretical energy density, gravimetrically 1300 Ah/kg and volumetrically 1400 Ah/L, these energy densities are about 3 times of current commercial lithium-ion batteries [1]. In experimentally application, Li-Sulphur batteries have several disadvantages, especially their low electrical conductivity ($5x10^{-30}$ S/cm) and have volume expansion during the charge/discharge due to the formation of polysulfide [2]. The solution to overcome this disadvantage is to bind Sulphur particles in activated carbon host doped by nitrogen. The use of nitrogen-doped activated carbon will increase the electrical conductivity while preventing volume expansion of sulphur because it bonds in a strong carbon structure. Furthermore, the nitrogen doped carbon structure will facilitate the lithiation/de-lithiation process during the charge/discharge. The utilization of carbon from organic waste able to solving environmental problems and allows pore size engineering as well as nitrogen doped engineering which can improve carbon quality and facilitate the formation of bonds with Sulphur [3].

Activated carbon is a type of carbon that has been activated using chemical process or by heat treatment which formed many pores in the order of micro until nanometres and produce a high specific surface area [4]. Activated carbon can be synthesized from various type of biomass, such as: wood, coconut shells, water hyacinth, oil palm bunches, bamboo, rice husks, corn cobs and others [5] [6]. Candlenut shell waste is one of biomass which has a high carbon content however has not been widely studied. Candlenut shell contains high percentage of hemicellulose and lignin [7]. Previous research show that candlenut shell activated carbon has better adsorption effectiveness than coconut shell activated carbon [8].

Activated carbon has been known having a widely application including as supercapacitor material [5], [9], additive material for battery electrode [10], adsorbent of metal pollutants [11], [12], and catalyst material [2], [13]. Activated carbon has unique characteristics, i.e., large specific surface area and its surface functional groups allow to interact with any ions. In activated carbon from biomass, the surface functional group is dominated by OFG (oxygenated functional group) which serves as the active region for redox reactions [14]. Moreover, the addition of nitrogen functional groups through doping process has been shown to increase the distribution of electrons which contribute to increasing the value of conductivity [15].

Candlenut shell as a raw material for activated carbon has a high carbon content in hemicellulose compounds (49,22%) and lignin (54,46%) [7]. Candlenut shell

activated carbon is obtained through a carbonization process followed by an activation process and a modification process by adding impurities or doping into the matrix carbon bond. In the nitrogen doping process, NH_3 is added as a nitrogen source on activated carbon which aims to form nitrogen functional groups on activated carbon. NH_3 compound is a source of nitrogen which stable, easily obtained and relatively low price [15]. In this study, variations of NH_3 concentration as dopants and the heating time of the nitrogen doping process were carried out to determine the effect on the chemical structure and electrical conductivity of activated carbon.

2. Methods

The experiment was started with the synthesis of activated carbon from candlenut shell waste. The candlenut shell was crushed into small pieces and then washed by aquadest to remove dust and other dirt. The carbonization process was carried out in a furnace at 700°C for 1 hour. After the carbonization process, the sample was crushed by mortar and pestle following by ball milling process then sieved using 200 mesh. The next step is the activation process using 30% KOH solvent as an activator. The activation process is carried out by impregnation for 24 hours which the ratio of carbon sample and activator is 1:3. The next process is filtering followed by washing process using 3 M HCl until the filtrate solution is neutral. The sediment from the filtering process was then rinsed with distilled water to remove residual activator and HCl. Furthermore, the sample was dried in an oven at 110°C for 3 hours and the activated carbon was obtained in a fine powder.

The next step is the process of doping activated carbon using nitrogen. The doping process was carried out by two variations of NH_3 concentration i.e., 10% and 25%. Activated carbon and NH_3 were prepared in a ratio of 1:3, then the nitrogen doping was carried out using impregnation process for 24 hours. The doping process was continued by heating in a furnace at 850°C by two variations of time i.e., 3 hours and 5 hours. At the final step, the sample was cooled at a cooling rate of 5 °C/min until room temperature then crushed to obtain nitrogen-doped activated carbon powder. Samples are labelled for simplify identification i.e., CN 10% 3h for 10% NH_3 by 3 hours heating process, CN 10% 5h for 10% NH_3 by 5 hours heating process, CN 25% 3h for 25% NH_3 by 3 hours heating process and CN 25% 5h for 25% NH_3 by 5 hours heating process. Some characterization has been carried out to determine the quality of the sample which was obtained i.e., FTIR characterization for determine chemical functional groups present in the sample, SEM-EDS for determine the percentage of each element in the sample and four-point probe method for electrical conductivity.

3. Results and Discussion

The product of activated carbon was characterized by FTIR, the results for samples of activated carbon and activated carbon doped by nitrogen were shown in Figure 1. The doping process of nitrogen heteroatom was successfully conducted which indicated by changing the chemical structure of activated carbon before and after doping process. The FTIR spectrum of activated carbon show absorption peaks only come from the C-H, C=C and C-C functional groups. These functional groups were

dominated by carbon bond which indicated the successfully of carbonization process.

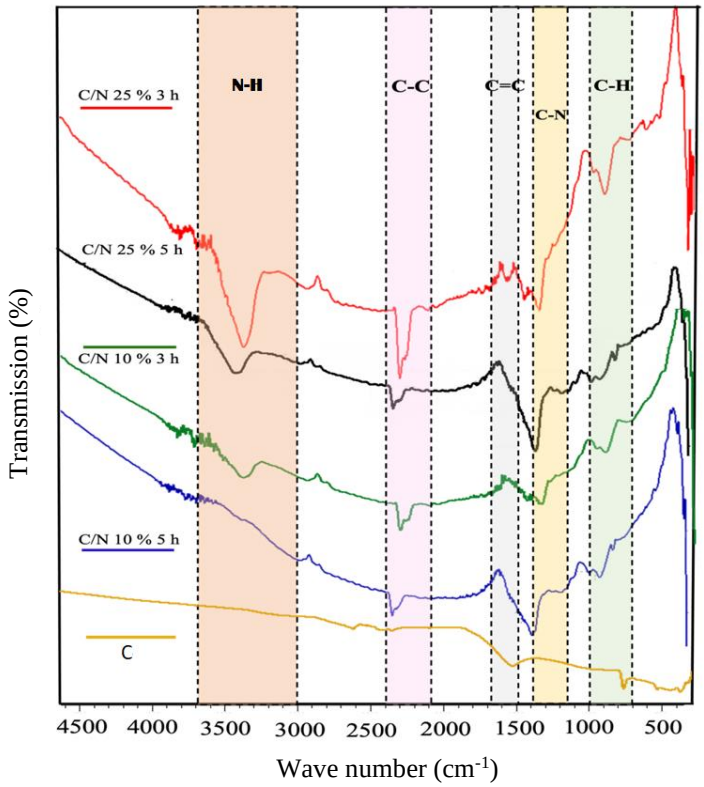

Figure 1. The FTIR spectrum of activated carbon (C) and nitrogen doped activated carbon (C/N)

The FTIR spectrum for activated carbon doped by nitrogen show arising several new absorption peaks i.e., C-N and N-H functional groups. Analysis of FTIR spectrum show the nitrogen doping process disrupted the C=C bond and turned into a C-N functional group which indicated by arising of absorption peaks in the 1180-1360 cm^{-1} region. The presence of C-N functional group was indicated the successfully of nitrogen doping process. In its application as battery electrode, the presence of nitrogen will strengthen the bonding of sulphur and activated carbon. Moreover, the nitrogen doping has also a positive impact on the wettability of activated carbon which will increase the ability of electrochemical reactions in its application as battery electrodes [16][15].

Figure 1 shows the intensity of the N-H functional group in the CN 10% 3h and CN 10% 5h samples lower than CN 25% 3h and CN 25% 5h, these data indicate the increasing of NH_3 concentration are proportionally to the formation of the N-H functional group [16]. Whereas the C-H functional group is arised consistent before and after the nitrogen doping process. The presence of the C-N functional group was indicated by absorption peak in the region of 1180 – 1360 cm^{-1} which was followed by shrinked the absorption of the C=C functional group in the region of 1500 – 1600 cm^{-1} [17]. These results show the nitrogen functional group from NH_3 reacted with carbon functional group from activated carbon during doping process. The compound of 1-deoxy-2-amino-1-ketose has formed during that reaction can

be dehydrating and deaminating to produce C-N functional group on the carbon bond [18].

The surface morphology and the composition of elemental from activated carbon doped by nitrogen were analysed using SEM-EDS. Figure 2 shows the surface morphology and elements mapping of activated carbon doped by nitrogen. The distribution of elements in the sample is dominated by green color which indicated the percentage of carbon elements is very high. The other elements presence in the sample but very small percentage i.e., calcium, nitrogen, manganese, calcium, and copper.

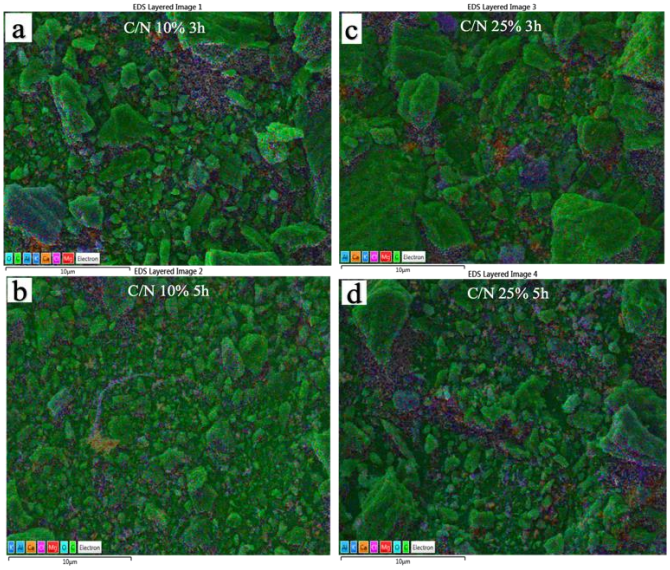

Figure 2. The surface morphology and elements mapping (a) C/N 10% 3h (b) C/N 10% 5h, (c) C/N 10% 3h, (d) C/N 25 % 5h

Table 1. Percentage of elements from SEM/EDS measurement

Element	C/N 10% 3 h		C/N 25% 3 h		C/N 10% 5 h		C/N 25% 5 h	
	Wt (%)	Atomic (%)	Wt (%)	Atomic (%)	Wt (%)	Atomic (%)	Wt (%)	Atomic (%)
C	90.94	94.68	91.58	94.83	87.69	91.85	87.15	91.61
N	0.34	0.12	0.52	0.21	0.26	0.08	0.32	0.14
O	5.15	4.02	5.34	4.15	8.90	7.00	9.02	7.11
Mg	0.07	0.04	0.09	0.05	0.09	0.05	0.12	0.06
Al	0.08	0.04	0.08	0.04	0.10	0.05	0.09	0.04
Cl	1.12	0.39	0.71	0.25	1.04	0.37	0.96	0.34
K	1.60	0.51	1.13	0.36	1.33	0.43	1.28	0.41
Ca	0.92	0.29	1.00	0.31	0.84	0.27	0.24	0.39
Cu	0.12	0.02	0.07	0.01	0.00	0.00	0.16	0.03
Total	100	100	100	100	100	100	100	100

Table 1 shows the results of the SEM-EDS analysis of nitrogen-doped activated carbon. In general, all variations of samples are dominated by carbon and oxygen elements with a few inorganic impurities i.e., potassium, aluminum, calcium, copper, and magnesium. The data in Table 1 shows the percentage element of carbon for all sample above 90% which indicate the success of the carbonization process in decomposing cellulose compounds into carbon bonds. The nitrogen as a doping element was detected with percentage of 0.26% until 0.52% (wt.%). The results of SEM-EDS analysis correlated with the results of FTIR which showed the presence of nitrogen and indicated the successfully of doping process.

The data in Table 1 shows that the percentage of nitrogen element at a heating time of 5 hours is smaller than the heating time of 3 hours. These results probably due to the longer heating time will break the C-N bond consequently the percentage of nitrogen is smaller for sample at 5 hours heating time. Masud Rana et.al. explains that the nitrogen doping will act as Lewis base which interaction with lithium di-polysulfide acid in its application as a battery electrode. Furthermore, the nitrogen doping on carbon bonds will increase the adsorption of polysulfide on the cathode layer [15].

Table 2. Electrical conductivity of activated carbon before and after nitrogen doping

Sample	$\bar{\sigma}$ **(S/cm)**
C Activator KOH	$1{,}12 \times 10^2$
C/N 10% 3 h	$2{,}03 \times 10^2$
C/N 10% 5 h	$1{,}91 \times 10^2$
C/N 25% 3 h	$2{,}31 \times 10^2$
C/N 25% 5 h	$2{,}44 \times 10^2$
commercially activated carbon	$3{,}27 \times 10^2$

Table 2 shows the electrical conductivity of activated carbon before and after nitrogen doping and its comparing with the electrical conductivity of commercially activated carbon. The data in Table 2 shows that electrical conductivity of nitrogen-doped activated carbon is higher than undoped activated carbon. These results correspond with report from Masud Rana el.al. which the nitrogen doping can increase the value of electrical conductivity [15]. The electrical conductivity of nitrogen-doped activated carbon is still smaller than commercially activated carbon but already in the same order. This is probably due to the purity of the activated carbon from candlenut shell still lower than the purity of commercially activated carbon.

4. Conclusions

The synthesis of activated carbon from candlenut shell and its nitrogen doping have been successfully carried out. The nitrogen doping was impacted of changing the chemical structure of activated carbon which was identified by presence of the C-N functional group through FTIR. The nitrogen doping has proved by SEM-EDS which obtain the highest percentage of nitrogen content around 0.52% for C/N 25% 3 h. The nitrogen doping has also contributed to increasing the electrical conductivity of activated carbon by approximately two time.

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References

1. A. Elmouwahidi, Z. Zapata-Benabithe, F. Carrasco-Marín, and C. Moreno-Castilla, "Activated carbons from KOH-activation of argan (Argania spinosa) seed shells as supercapacitor electrodes," *Bioresour. Technol.*, vol. 111, pp. 185–190, 2012, doi: 10.1016/j.biortech.2012.02.010.
2. A. A. Arie, H. Kristianto, I. Suharto, M. Halim, and J. K. Lee, "Preparation of orange peel based activated carbons as cathodes in lithium ion capacitors," *Adv. Mater. Res.*, vol. 896, pp. 95–99, 2014, doi: 10.4028/www.scientific.net/AMR.896.95.
3. N. R. Villarante, R. A. E. Davila, and D. P. Sumalapao, "Removal of lead (α) by lumbang, aleurites moluccana activated carbon carboxymethylcellulose composite crosslinked with epichlorohydrin," *Orient. J. Chem.*, vol. 34, no. 2, pp. 693–703, 2018, doi: 10.13005/ojc/340211.
4. H. Kristianto, "Review: Sintesis Karbon Aktif Dengan Menggunakan Aktivasi Kimia ZnCL2," *J. Integr. Proses*, vol. 6, no. 3, pp. 104–111, 2017, doi: 10.36055/jip.v6i3.1031.
5. S. Mudaim and S. Hidayat, "Effect of Heating Temperature on the Chemical Structure and of Conductivity Carbon from Candlenut Shells (Aleurites moluccana)," Materials Science Forum 1028, pp. 302–307, 2021.
6. R. Rinawati, A. A. Kiswandono, N. L. G. R. Juliasih, and F. D. Permana, "Pemanfaatan Karbon Aktif Sekam Padi sebagai Adsorben Phenantrena dalam Solid Phase Extraction," *al-Kimiya*, vol. 6, no. 2, pp. 75–80, 2020, doi: 10.15575/ak.v6i2.6495.
7. S. Mudaim, S. Hidayat, and Risdiana, "Analisis Proksimat Karbon Tempurung Kemiri (Aleuritas Moluccana) Dengan Variasi Suhu Karbonisasi," *Jurnal Ilmu dan Inovasi Fisika*, vol. 05, no. 02, pp. 157–163, 2021
8. D. Junipuspita *et al.*, "Preparation of porous carbon made from candlenut shell (Aleurites moluccana) as a cathode for lithium ion capacitor," *J. Phys. Conf. Ser.*, vol. 1191, no. 1, 2019, doi: 10.1088/1742-6596/1191/1/012020.
9. B. Li, M. Xie, G. Yi, and C. Zhang, "Biomass-derived activated carbon/Sulphur composites as cathode electrodes for Li-S batteries by reducing the oxygen content," *RSC Adv.*, vol. 10, no. 5, pp. 2823–2829, 2020, doi: 10.1039/c9ra09610h.
10. K. Yang, Q. Gao, Y. Tan, W. Tian, L. Zhu, and C. Yang, "Microporous carbon derived from Apricot shell as cathode material for lithium-Sulphur battery," *Microporous Mesoporous Mater.*, vol. 204, no. C, pp. 235–241, 2015, doi: 10.1016/j.micromeso.2014.12.003.
11. S. S. A. Syed-Hassan and M. S. M. Zaini, "Optimization of the preparation of activated carbon from palm kernel shell for methane adsorption using Taguchi

orthogonal array design," *Korean J. Chem. Eng.*, vol. 33, no. 8, pp. 2502–2512, 2016, doi: 10.1007/s11814-016-0072-z.
12. S. Maulina and M. Iriansyah, "Characteristics of activated carbon resulted from pyrolysis of the oil palm fronds powder," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 309, no. 1, 2018, doi: 10.1088/1757-899X/309/1/012072.
13. Y. Shao, J. Sui, G. Yin, and Y. Gao, "Nitrogen-doped carbon nanostructures and their composites as catalytic materials for proton exchange membrane fuel cell," *Appl. Catal. B Environ.*, vol. 79, no. 1, pp. 89–99, 2008, doi: 10.1016/j.apcatb.2007.09.047.
14. K. Zou, P. Cai, X. Cao, G. Zou, H. Hou, and X. Ji, "Carbon materials for high-performance lithium-ion capacitor," *Curr. Opin. Electrochem.*, vol. 21, pp. 31–39, 2020, doi: 10.1016/j.coelec.2020.01.005.
15. M. Rana *et al.*, "Review on areal capacities and long-term cycling performances of lithium Sulphur battery at high Sulphur loading," *Energy Storage Mater.*, vol. 18, pp. 289–310, 2019, doi: 10.1016/j.ensm.2018.12.024.
16. R. F. S. Yohana Fransiska Ferawati, "Peran N-Doping Terhadap Karakteristik Pori K arbon Aktif Yang Dihasilkan Dari Limbah Destilasi Akar Wangi," pp. 59–68, 2021.
17. J. Chen *et al.*, "Enhanced CO2 Capture Capacity of Nitrogen-Doped Biomass-Derived Porous Carbons," *ACS Sustain. Chem. Eng.*, vol. 4, no. 3, pp. 1439–1445, 2016, doi: 10.1021/acssuschemeng.5b01425.
18. Q. Wu, W. Li, S. Liu, and C. Jin, "Hydrothermal synthesis of N-doped spherical carbon from carboxymethylcellulose for CO_2 capture," *Appl. Surf. Sci.*, vol. 369, pp. 101–107, 2016, doi: 10.1016/j.apsusc.2016.02.022