

## Synthesis and Characterization of Nitrogen-Doped Activated Carbon for Lithium Battery Anode Applications

Prihanto Trihutomo, Poppy Puspitasari, Muhammad Bustomi Radja\*, Milzam Rahmat Busono

*Mechanical Engineering, Universitas Negeri Malang, Malang, 65114, Indonesia*  
*\*Corresponding authors: radjabustomi22@gmail.com*

### Article history:

Received: 4 November 2022 / Received in revised form: 27 January 2023 / Accepted: 8 April 2023

Available online 30 April 2023

### ABSTRACT

Nitrogen-doped activated carbon was synthesized to see its effect on the characterization of the nitrogen surface functional groups, crystal size, and morphology of the resulting sample. Synthesis of nitrogen-doped activated carbon was carried out by varying the addition of Urea as a nitrogen doping source. Activated carbon compared its characteristics with variations in the concentration of added Urea to activated carbon, at 1:3 and 1:5. The FTIR results obtained were the presence of functional groups indicating the presence of nitrogen bonds in each sample. The crystallinity results showed that the samples were classified as crystalline and nitrogen doping influenced the size of the crystallinity of each sample. The morphology of nitrogen-doped activated carbon shows differences in the grain size of nitrogen-doped activated carbon. Crystallinity and morphology have been shown to affect battery anode performance. The more crystalline of anode material, the electrochemical properties are better. The smaller the grain size of the sample morphology, the stability of the battery cycle is to be great.

Copyright © 2023. Journal of Mechanical Engineering Science and Technology.

**Keywords:** *Activated carbon, characterization, nitrogen concentration, nitrogen doping, surface*

## I. Introduction

New and renewable natural resources are needed, especially due to increasing global warming and limited fossil resources [1]. The utilization of renewable energy, such as wind, solar, ocean waves, and biomass, has shown a positive trend in the last few decades [2]. One of the most important aspects of utilizing new and renewable energy sources is access to energy transmission and storage technology. Currently, the limitations of renewable energy development are hindered by storage and transmission technologies due to environmental impacts [3]. The environment consisting of thousands of islands makes it difficult for energy, such as electricity, to reach remote areas [4].

Alternative solutions for downstream renewable energy development are through superior storage technology. Lithium battery is an excellent energy storage device that can easily convert chemical energy and electrical energy, which is also popularly used as a portable electronic device [5]. However, making these batteries with high energy and power density through an economical and environmentally friendly process is still a big challenge. Existing anode materials exhibit high specific capacities, cycle stability, and safety, but their high cost and relatively small current densities limit their practical applications [6].



Activated carbon with a large surface area, high absorption capacity, and minimal charging time is suitable for application in several materials, including the anode material in batteries [6]. During maximizing the potential of activated carbon in the form of its capacity properties, nitrogen doping can be utilized to increase the capacity of activated carbon. Nitrogen, with an atomic size almost the same as the carbon atom, can be an electron donor for N-doping substitution. After nitrogen is doped, the interaction between electrons and ions becomes relatively negative [7].

Silicon (Si) is also used as an anode material for lithium-ion batteries due to its high theoretical capacity (~4200 mAh/g). However, a large volume expansion occurs during the charge-discharge process, which significantly affects the stability of the silicon anode. Silicon also tends to be expensive, increasing the cost of producing anodes. Therefore, it is necessary to develop a new carbon-based anode material that has a high energy storage capacity and low volume expansion during the charge-discharge process [2]

The focus of this research is the synthesis and modification of activated carbon. Urea is added as a nitrogen source to form nitrogen functional groups. Nitrogen atom doping was chosen because it is relatively stable, easy to obtain, and affordable. The next process is chemical activation with KOH as an activator agent. The synthesized material was analyzed for surface functional groups, crystallinity, and morphology in its application as a lithium battery anode.

## II. Material and Methods

### 1. Material

The main materials are activated carbon, pore diameter on activated carbon, mesoporous carbon (2 nm to 50 nm), Urea as a doping source, and KOH as an activator. In addition, other materials needed include distilled water and HCl acid. Activated carbon, demineralized water, Urea, and KOH were obtained from CV Makmur Sejati, Malang, Indonesia. The chemical activation method was used to increase the surface area of nitrogen-doped activated carbon. The pore diameter of activated carbon decreases, and the surface area increases. This mechanism is through adding KOH and reacting to form CO and CO<sub>2</sub> gases that evaporate into the air. Synthesis results from nitrogen-doped activated carbon samples were tested for their Fourier Transform Infrared/FTIR functional groups using the Shimadzu IR Prestige 21, X-ray Diffraction/XRD using PAN-Analytical Expert Pro, and their morphology with SEM using FEI Inspect-S50.

### 2. Methods

Activated carbon is impregnated in a solution of Urea and KOH activator. The ratio of the mass of activated carbon: KOH: Urea (NH<sub>2</sub>)<sub>2</sub>CO is 1:2:X (X = 3 or 5). The solution was then homogenized using a stirrer for 2 hours at 750 rpm and then sonicated for 30 minutes. After sonication, the solution was heated in an oven at 200 C for 4 hours, then the material became solid and then crushed for 1 hour until it became powder. The resulting powder is then soaked in HCl for 24 hours to neutralize the pH. The solution was then titrated and dried in an oven. The resulting solid is then crushed for 1 hour. Each sample was named according to the ratio of Urea doping as a nitrogen source (NDAC 3 and NDAC 5). In addition, the pure sample of activated carbon without doping and treatment was also given the name NDAC 0 for comparison. The resulting sample was then characterized as a lithium battery anode potential material.

### III. Results and Discussions

#### 1. Surface Functional Group

The nitrogen doping process and chemical activation gave changes in the chemical structure of NDAC 0, NDAC 3, and NDAC 5. The FTIR spectrum of each sample is shown in Figure 1. The figure shows the stretching of chemical bonds in the aromatization reaction and heteroatom doping. Oxygen functional groups are seen in the C-O, C=O, and O-H bonds [8]. Nitrogen functional groups are seen in the C-N and N-H bonds [9]. At the same time, the bonds between C atoms are seen in the C-H, C=C, and C=CH bonds [10]. The addition of nitrogen doping can increase electrochemical properties due to the presence of nitrogen donors from doping [11]. The table of bond types with respect to absorbed wavelengths is shown in Table 1.

**Table 1.** Bonding Type Based on FTIR Result

No	Wave Number	Bonding type
1	670-900	C-H
2	1020-1220	C-N
3	1250-1300	C-O
4	1560-1640	O-H
5	1640-1680	C=C
6	1710	C=O
7	3020	C=CH
8	2400-3000	N-H
9	3200-3400	O-H

Source : Withrow, (2013)

The intensity of the C-H bond at NDAC 0, NDAC 3, and NDAC 5 seems to be increasing, which can be seen in the range of 900-670  $\text{cm}^{-1}$ . The intensity of the C-N bond itself increases. This increase in absorption occurred in the range of 1020-1220, indicating that nitrogen doping occurs effectively [13].

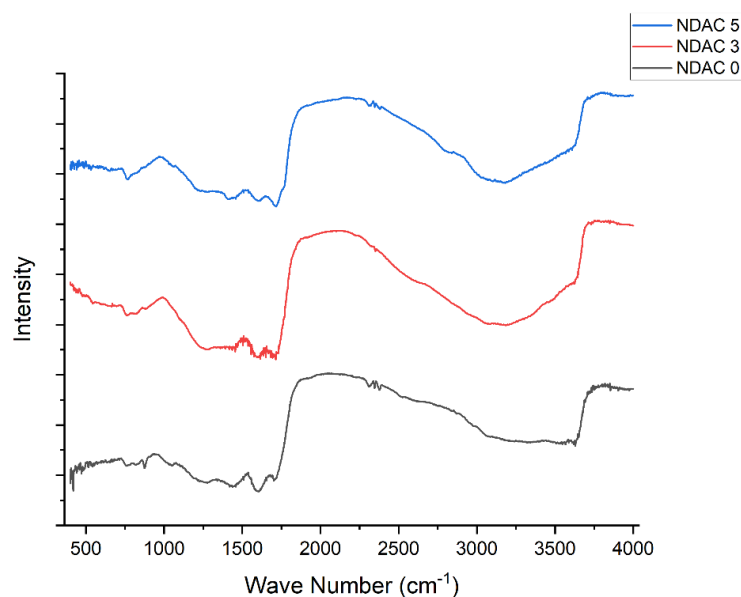


Fig. 1. The FTIR spectrum

The intensity of the C-O bond occurring in the range of 1300-1250  $\text{cm}^{-1}$  also increases as the nitrogen doping concentration in the sample increases. In addition, the O-H bond that occurs in the range of 1640-1560  $\text{cm}^{-1}$  also tends to increase. The bond between C=C at 1680-1640  $\text{cm}^{-1}$  also tends to increase in absorption. At wave number 1700, it is seen that the double bond between C and O atoms also increases with the addition of nitrogen doping [12].

The double bond between C and CH atoms increased in intensity in the NDAC 3 sample but decreased again in the NDAC 5 sample. In addition, the absorption intensity of the N-H bond was also clearly seen to increase as the nitrogen doping concentration increased [13].

## 2. Crystallization

Synthesis of nitrogen-doped activated carbon was prepared in several stages. Nitrogen doping on activated carbon is synthesized by impregnation in urea solution [13]. Activation uses a chemical activation method through KOH as an activator agent to increase the surface area of nitrogen-doped activated carbon [14][15]. This impregnation and activation process affects the lattice structure of activated carbon [16].

The XRD patterns on the NDAC 0, NDAC 3, and NDAC 5 samples are shown in Figure 2. In the observed patterns, all samples showed the highest diffraction pattern centered at  $2\theta = 24^\circ, 28^\circ,$  and  $40^\circ$  [17]. The NDAC 3 and NDAC 5 samples showed increased diffraction intensity than NDAC 0. The highest diffraction peaks among the 3 samples occurred in NDAC 3 samples. The degree of crystallization was used to calculate the crystal size of each sample using equation 1 [1],

$$D = \frac{k \cdot \lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

where  $k$  is the material constant of 0.9,  $\lambda$  is the wavelength of the X-ray (nm),  $\beta$  is the maximum half-peak width (rad),  $\theta$  is the Bragg angle of the diffraction peak, and  $D$  is the crystal size (nm) [4].

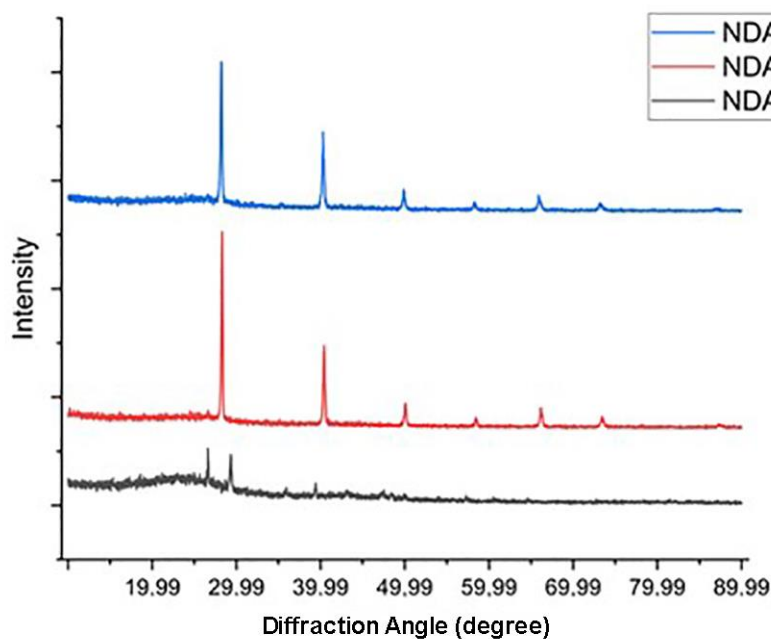


Fig. 2. The XRD pattern of samples

Based on Equation 1, the crystal size was obtained in the NDAC 0 sample of 72.65 nm, the NDAC 3 sample of 48.338 nm, and the NDAC 5 sample of 43.490 nm. Diffraction intensity and peak shift are affected by the concentration of nitrogen doping on activated carbon [18]. Figure 2 shows that the higher the nitrogen doping concentration, the diffraction intensity will increase. However, at a certain point, the intensity reaches a peak, and the intensity will decrease as the nitrogen doping increases. This is due to the relationship between crystallinity and nitrogen doping in activated carbon [5].

Activated carbon modified with heteroatoms will improve its electrochemical properties as an application in lithium battery anodes [7]. This is very useful for modifying the electrochemical properties of carbon which is a type of porous carbon. The tendency of carbon to lose capacity after several cycles can be solved by modification with heteroatoms, one of which is the nitrogen atom [19].

### 3. Morphology

The results of the SEM (Scanning Electron Microscope) test showed that pure activated carbon (1:0) had the largest size among the three samples, followed by nitrogen-doped activated carbon with a ratio of 1:3 and 1:5 (Figure 3). This is because pure activated carbon does not go through the synthesis process, while samples that get nitrogen doping have a reduction in particle size [13].

The addition of nitrogen doping on activated carbon also increases surface area due to more potassium hydroxide (KOH), which reacts with C atoms to produce CO and CO<sub>2</sub> gases, which will then evaporate and form a pore structure. The pores function as access and pathways for ions or adsorbents to bind nitrogen to activated carbon. The results show that the nitrogen functional group in carbon serves as an ideal functional group to improve energy storage properties [20]

According to Han (2020), activated carbon, without adding KOH, shows a dense and smooth surface with small pores. Upon activation by KOH, many large pores (2  $\mu\text{m}$ ) can be found in carbon materials. KOH is a good chemical activator on carbon because it can increase its surface area up to 3000  $\text{m}^2/\text{g}$  and release CO<sub>2</sub> during N-AC activation [22]. The released CO<sub>2</sub> passes through the carbon material at high temperatures, creating many large pores. These results are consistent with other studies using KOH as a pore-forming agent in manufacturing activated carbon.

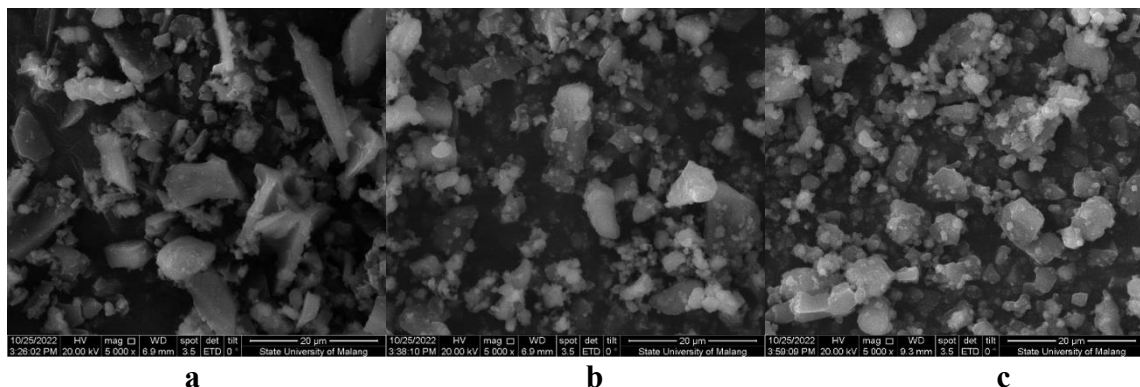


Fig. 3. SEM morphology (a) NDAC 1:0 (b) NDAC 1:3 (c) NDAC 1:5

#### IV. Conclusions

Nitrogen-doped activated carbon can be a solution to replace graphite in lithium batteries due to their low capacity. Modification of nitrogen doping in ratios (1:3 and 1:5) using the chemical activation method has an ideal function to increase energy storage. Nitrogen can bond with carbon atoms if the atomic structure has many pores. The small pore size will increase the surface area and improve the cycle stability of the battery. The smaller grain size in the SEM test shows a large surface area. Nitrogen functional groups in the FTIR and XRD results showed the most optimal performance at a ratio of 1:3 and decreased at a ratio of 1:5. This was due to the increasing number of nitrogen atoms, which would inhibit the formation of pores. Research on the application of nitrogen-doped activated carbon in lithium battery anodes should be carried out to determine its effect on lithium battery performance.

#### Acknowledgment

This research was funded by the Universitas Negeri Malang grant through a student innovation scheme in 2022.

#### References

- [1] S. Zong, "Preparation of N-doped porous carbon materials and their supercapacitor performance Dissertation Submitted for the Degree of MTech: Engineering: Chemical Prepared by," no. January, 2021.
- [2] J. Yan, C. E. Ren, K. Maleski, C. B. Hatter, B. Anasori, P. Urbankowski, A. Sarycheva, and Y. Gogotsi, "Flexible MXene/Graphene Films for Ultrafast Supercapacitors with Outstanding Volumetric Capacitance," *Adv. Funct. Mater.*, vol. 27, no. 30, pp. 1–10, 2017, doi: 10.1002/adfm.201701264.
- [3] A. D. Roberts, X. Li, and H. Zhang, "Porous carbon spheres and monoliths: Morphology control, pore size tuning and their applications as Li-ion battery anode materials," *Chem. Soc. Rev.*, vol. 43, no. 13, pp. 4341–4356, 2014, doi: 10.1039/c4cs00071d.
- [4] H. Susana and Astuti, "Pengaruh Konsentrasi LiOH terhadap Sifat Listrik Anoda Baterai Litium Berbasis Karbon Aktif Tempurung Kemiri," *J. Fis. Unand*, vol. 5, no. 2, pp. 136–141, 2016.
- [5] J. Wang, W. Zhang, J. Li, B. Wang, C. Xu, and C. Lai, "In situ self-assembly assisted synthesis of N-doped mesoporous hierarchical carbon aerogels-wrapped Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> composite for high-rate lithium ion batteries," *J. Mater.*, vol. 7, no. 5, pp. 1083–1093, 2021, doi: 10.1016/j.jmat.2021.01.013.
- [6] A. H. Abdul, N. Ramli, A. N. Nordin, and M. F. Abd. Wahab, "Supercapacitor performance with activated carbon and graphene nanoplatelets composite electrodes, and insights from the equivalent circuit model," *Carbon Trends*, vol. 5, p. 100101, 2021, doi: 10.1016/j.cartre.2021.100101.
- [7] M. Inagaki, M. Toyoda, Y. Soneda, and T. Morishita, "Nitrogen-doped carbon materials," *Carbon N. Y.*, vol. 132, pp. 104–140, 2018, doi: 10.1016/j.carbon.2018.02.024.
- [8] A.N.A. El-Hendawy, "Variation in the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions," *J. Anal. Appl. Pyrolysis*, vol. 75, no. 2, pp.

- 159–166, 2006, doi: 10.1016/j.jaap.2005.05.004.
- [9] S. Shi and Y. Liu, “Nitrogen-doped activated carbons derived from microalgae pyrolysis by-products by microwave/KOH activation for CO<sub>2</sub> adsorption,” *Fuel*, vol. 306, no. January, p. 121762, 2021, doi: 10.1016/j.fuel.2021.121762.
- [10] S. Timur, I. C. Kantarli, S. Onenc, and J. Yanik, “Characterization and application of activated carbon produced from oak cups pulp,” *J. Anal. Appl. Pyrolysis*, vol. 89, no. 1, pp. 129–136, 2010, doi: 10.1016/j.jaap.2010.07.002.
- [11] R. Mishra, P. R. Prasad, P. Panda, and S. Barman, “Highly Porous Activated N-Doped Carbon as an Ideal Electrode Material for Capacitive Energy Storage and Physisorption of H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>,” *Energy and Fuels*, vol. 35, no. 17, pp. 14177–14187, 2021, doi: 10.1021/acs.energyfuels.1c02051.
- [12] J. Withrow, *Infrared Spectroscopy*. New York: Research, 2016.
- [13] Y. F. Ferawati and R. F. Susanti, “Peran N-Doping terhadap Karakteristik Pori Karbon Aktif yang Dihasilkan dari Limbah Destilasi Akar Wangi,” *Metalurgi*, vol. 36, no. 2, pp. 59–68, 2021, doi: 10.14203/metalurgi.v36i2.595.
- [14] N. Khoirina, A. F. Nugraheni, A. A. Alfian, and W. D. P. Rengga, “Preparation and characterization of activated carbon derived from the bovine bone doped urea as an electrode material,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 969, no. 1, 2022, doi: 10.1088/1755-1315/969/1/012040.
- [15] H. Marsh and F. Rodríguez-Reinoso, *Activated Carbon*. Elsevier Ltd. 2006.
- [16] S. Ahmed, A. Ahmed, and M. Rafat, “Nitrogen doped activated carbon from pea skin for high performance supercapacitor,” *Mater. Res. Express*, vol. 5, no. 4, 2018, doi: 10.1088/2053-1591/aabbe7.
- [17] Y. Y. García-Guel, E. M. Múzquiz-Ramos, J. C. Ríos-Hurtado, A. Moreno-Santos, S. E. Flores-Villaseñor, and G. B. Escalante-Ibarra, “Surface modification of activated carbon cloth with calcium silicate and hydroxyapatite: bioactive composite material,” *Heliyon*, vol. 8, no. December 2021, p. e11586, 2022, doi: 10.1016/j.heliyon.2022.e11586.
- [18] Q. Li, M. Yuan, Y. Wang, X. Gao, X. Li, M. Yao, H. He, Q. Tan, Z. Zhong, and F. Su, “Designing and preparing carbon anode materials modified with N and Fe-nanoparticle: Creating the interior electric field to improve their electrochemical performance,” *Electrochim. Acta*, vol. 383, p. 138367, 2021, doi: 10.1016/j.electacta.2021.138367.
- [19] R. Naraprawatphong, C. Chokradjaroen, and S. Thiangtham, “Nanoscale advanced carbons as an anode for lithium-ion battery,” *Mater. Today Adv.*, vol. 16, p. 100290, 2022, doi: 10.1016/j.mtadv.2022.100290.
- [20] X. Xue, Y. Weng, Z. Jiang, S. Yang, and Y. Wu, “Journal of Analytical and Applied Pyrolysis Naturally nitrogen-doped porous carbon derived from waste crab shell as anode material for high performance sodium-ion battery,” *J. Anal. Appl. Pyrolysis*, vol. 157, no. January, p. 105215, 2021, doi: 10.1016/j.jaap.2021.105215.
- [21] W. Hana, H. Wanga, K. Xi, S. Chen, P. Yan, T. Deng, and W. Zhu, “Superior nitrogen-doped activated carbon materials for water cleaning and energy storing prepared from renewable leather wastes,” *Environ. Int.*, vol. 142, no. May, p. 105846,

2020, doi: 10.1016/j.envint.2020.105846.

- [22] N. Nurfitria, K. Febriyantiningrum, W. P. Utomo, Z. V. Nugraheni, D. D. Pangastuti, H. Maulida, and F. N. Ariyanti, "Pengaruh Konsentrasi Aktivator Kalium Hidroksida (KOH) pada Karbon Aktif dan Waktu Kontak Terhadap Daya Adsorpsi Logam Pb dalam Sampel Air Kawasan Mangrove Wonorejo, Surabaya," *Akta Kim. Indones.*, vol. 4, no. 1, p. 75, 2019, doi: 10.12962/j25493736.v4i1.5071.