BAB V

KESIMPULAN DAN SARAN

5.1. Kesimpulan

Kegiatan penelitian yang dilakukan terdapat beberapa hal yang dapat disimpulkan. Adapun kesimpulan yang dihasilkan adalah sebagai berikut:

1. Proses sintesis melalui proses HTC dan pirolisis menghasilkan *yield* produk *N-doped hard carbon* sebesar 22,39 % untuk rasio *hydrochar*:$NaNH_2$ 1:1 pada suhu aktivasi 500 °C dan seiring penambahan $NaNH_2$ serta kenaikan suhu aktivasi, %*yield* akan menurun hingga 13,47 % untuk rasio *hydrochar*:$NaNH_2$ 1:2 pada suhu aktivasi 700 °C. Sedangkan, proses sintesis melalui proses *direct pyrolysis* memiliki *yield* produk *N-doped hard carbon* yang lebih besar yaitu 51,8 % hingga 33,67 % dan memiliki kecenderungan yang sama seperti sintesis proses 2 tahap.
2. Pada hasil analisis SEM, didapati hasil sintesis proses HTC dan pirolisis menghasilkan *hard carbon* dengan struktur *microspheres* dan sedikit pori, sedangkan pada sintesis proses *direct pyrolysis*, struktur yang dihasilkan acak dengan permukaan yang tidak merata dan berpori serta terbentuk *flakes*. Penambahan *sodamide* ini juga berpengaruh terhadap pembentukkan struktur *hard carbon*, semakin banyak *sodamide* yang ditambahkan, semakin banyak pori yang terbentuk pada prekursor karbon.
3. Berdasarkan analisis komposisi sampel dengan metode EDS, *N-doping* berhasil dilakukan pada kedua variasi tahap. Metode dengan proses HTC dan pirolisis menghasilkan *N-doped hard carbon* yang lebih tinggi unsur nitrogen dibandingkan dengan proses *direct pyrolysis* dengan % unsur nitrogen sebesar 0,88 % hingga 1,58 %. Pada proses *direct pyrolysis* didapatkan hasil % unsur nitrogen sebesar 0,67 % hingga 0,96 %. Kenaikan suhu dan jumlah penambahan *sodamide* juga berbanding lurus dengan kenaikan unsur nitrogen yang berhasil ter*doping*.
4. Pada hasil analisis XRD, didapatkan *N-doped hard carbon* hasil penelitian ini memiliki struktur *amorphous* (mencapai 72,57 % amorf) yang lebih dominan dibandingkan struktur kristalin yang memiliki jarak *interlayer* (d_{002}) berkisar

0,363 *nm* hingga 0,393 *nm* dan jarak *intercrystallite* (d_{100}) yang berkisar 0,203 *nm* hingga 0,211 *nm*. Nilai d_{002} didapatkan dari proses *direct pyrolysis* sedikit lebih besar dibandingkan dengan proses yang melewati HTC terlebih dahulu, dengan kecenderungan kenaikan suhu akan meningkatkan nilai dari d_{002}.

5. Produk *N-doped hard carbon* yang melewati karbonisasi dua tahap (HTC + pirolisis) lebih baik dibandingkan dengan proses karbonisasi satu tahap (*direct pyrolysis*) karena memiliki kandungan % unsur nitrogen yang lebih banyak.

5.2. Saran

Demi kepentingan pegembangan penelitian selanjutnya, penelitian ini memiliki beberapa saran yang dapat dipertimbangkan sebagai berikut:

1. Analisis hasil penelitian ini dapat dikembangkan dengan melakukan uji karakteristik elektrokimia seperti *electrochemical performance* dan *cycling performance*, sehingga dapat diketahui bahwa hard carbon yang dihasilkan menunjukkan kecocokkan untuk penggunaan *sodium ion batteries*.
2. Selain analisis SEM-EDS dan XRD, juga dapat dilakukan analisis XPS dan FTIR untuk mengidentifikasi komposisi dan gugus fungsi nitrogen dengan lebih akurat.
3. Analisis BET dapat dilakukan untuk mengetahui *surface area* dan distribusi pori dari produk N-*doped hard carbon* yang dihasilkan.
4. Variasi temperatur aktivasi dapat dilakukan lebih lanjut sehingga dapat diketahui variasi temperatur aktivasi yang lebih berpengaruh terhadap pembentukan *hard carbon* yang cocok untuk *sodium ion batteries*.

DAFTAR PUSTAKA

Ahmad, W. R. W., M. H. Mamat, A. S. Zoolfakar, Z. Khusaimi, dan M. Rusop. 2016. "A review on hematite α-Fe_2O_3 focusing on nanostructures, synthesis methods and applications." *Proceedings - 14th IEEE Student Conference on Research and Development: Advancing Technology for Humanity*, SCOReD 2016 2–7.

Alcázar-Alay, Sylvia Carolina dan Maria Angela Almeida Meireles. 2015. "Physicochemical properties, modifications and applications of starches from different botanical sources." *Food Science and Technology* 35(2):215–36.

Beda, A., Taberna, P. L., Simon, P., & Matei Ghimbeu, C. (2018). Hard carbons derived from green phenolic resins for Na-ion batteries. *Carbon*, *139*, 248–257.

Beda, A., Rabuel, F., Morcrette, M., Knopf, S., Taberna, P.-L., Simon, P., & Ghimbeu, C. M. (2020). Hard carbon key properties allow for the achievement of high Coulombic efficiency and high volumetric capacity in Na-ion batteries. *Journal of Materials Chemistry A*, *2021*(3), 1743–1758.

Bunaciu, A. A., Udriştioiu, E. gabriela, & Aboul-Enein, H. Y. (2015). X-Ray Diffraction: Instrumentation and Applications. In *Critical Reviews in Analytical Chemistry* (Vol. 45, Issue 4, pp. 289–299). Taylor and Francis Ltd.

Chayambuka, K., Mulder, G., Danilov, D.L., Notten, P.H., 2018. Sodium-ion battery materials and electrochemical properties reviewed. *Advanced Energy Materials* 8 (16), 1800079.

Chen, H., Wang, C., Ye, J., Zhou, H., Tao, R., & Li, W. (2018). Preparation of Starch-hard Carbon Spherules from Ginkgo Seeds and Their Phenol-adsorption Characteristics. *Molecules*, *23*(1).

Chen, C., Zhao, K., La, M., & Yang, C. (2022). Insight into a Nitrogen-Doping Mechanism in a Hard-Carbon-Microsphere Anode Material for the Long-Term Cycling of Potassium-Ion Batteries. *Materials*, *15*(12).

Cornejo-Ramírez, YI, Ramírez-Reyes, F., Cinco-Moroyoqui, FJ, Rosas Burgos, EC, Martínez-Cruz, O., Carvajal-Millán, E., & Wong-Corral, FJ. 2016. (X Triticosecale Wittmack). Kimia Sereal, 93(1), 64– 70.

da Silva, V. A., & Rezende, M. C. (2018). Effect of the morphology and structure on the microwave absorbing properties of multiwalled carbon nanotube filled epoxy resin nanocomposites. *Materials Research*, *21*(5).

Dahn, J. R., Tao Zheng, Yinghu Liu, dan J. S. Xue. 1995. "Mechanisms for lithium insertion

in carbonaceous materials." *Science* 270(5236):590–93.

Deraman, M., Sazali, N. E. S., Hanappi, M. F. Y. M., Tajuddin, N. S. M., Hamdan, E., Suleman, M., Othman, M. A. R., Omar, R., Hashim, M. A., Basri, N. H., Nor, N. S. M., Dolah, B. N. M., Noor, A. M., & Jasni, M. R. M. (2016). Graphene/semicrystalline-carbon derived from amylose films for supercapacitor application. *Journal of Physics: Conference Series*, *739*(1).

Dou, X., Hasa, I., Hekmatfar, M., Diemant, T., Behm, R. J., Buchholz, D., & Passerini, S. (2017). Pectin, Hemicellulose, or Lignin? Impact of the Biowaste Source on the Performance of Hard Carbons for Sodium-Ion Batteries. *ChemSusChem*, *10*(12), 2668–2676. https://doi.org/10.1002/cssc.201700628

Dou, Xinwei, Ivana Hasa, Damien Saurel, Christoph Vaalma, Liming Wu, Daniel Buchholz, Dominic Bresser, Shinichi Komaba, dan Stefano Passerini. 2019. "Hard carbons for sodium-ion batteries : Structure , analysis , sustainability , and electrochemistry." *Materials Today* 23(March):87–104.

Dutrow, B.L. dan Clark C. M., 2020. X-ray Powder Diffractio (XRD), https://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html

Ehara, H., Toyoda, Y., & Johnson, D. V. (2018). *Sago Palm* (1st ed.). Springer Nature. pp. 247-257

Fajaroh, F., H. Setyawan., W. Widiyastuti., dan S. Winardi. 2009. "Synthesis of Magnetite Nanoparticles by Surfactant-Free Electrochemical Method in an Aqueous System". Advanced Powder Technology. (23): 328-333.

Fan, X., Zhou, Y., Jin, X., Song, R. bin, Li, Z., & Zhang, Q. (2021). Carbon material-based anodes in the microbial fuel cells. In *Carbon Energy* (Vol. 3, Issue 3, pp. 449–472). John Wiley and Sons Inc.

Franklin, Rosalind E. 1951. "Crystallite growth in graphitizing and non-graphitizing carbons." Hal. 196–218 in *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*. Vol. 209. Royal Society.

Funke, Axel dan Felix Ziegler. 2012. "Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering." *Biofuels, Bioproducts and Biorefining* 6(3):246–56.

Goodge, J., 2017, Energy-Dispersive X-Ray Spectroscopy (EDS), https://serc.carleton.edu/research_education/geochemsheets/eds.html

Henry, D., Eby, N., Goodge, J. dan Mogk D., 2016, X-ray reflection in

accordance with Bragg's Law, https://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html

Hou, C., Liu, K., Yu, X., Yang, X., Wang, J., Liu, H., Liu, C., & Sun, Y. (2021). Nitrogen-doped porous carbons synthesized with low-temperature sodium amide activation as metal-free catalysts for oxidative coupling of amines to imines. *Journal of Materials Science*, *56*(30), 16865–16876.

Hu, Mingxiang, Le Yang, Kai Zhou, Chengshuang Zhou, Zheng-hong Huang, Feiyu Kang, dan Ruitao Lv. 2017. "Enhanced sodium-ion storage of nitrogen-rich hard carbon by NaCl intercalation." *Carbon* 122:680–86.

Huang, K., Chai, S.-H., Mayes, R. T., Tan, S., Jones, C. W., & Dai, S. (2016). Significantly increasing porosity of mesoporous carbon by NaNH 2 activation for enhanced CO 2 adsorption. *Microporous and Mesoporous Materials*, 230, 100–108.

Huang, S., Li, Z., Wang, B., Zhang, J., Peng, Z., Qi, R., Wang, J., & Zhao, Y. (2018). NDoping and Defective Nanographitic Domain Coupled Hard Carbon Nanoshells for High Performance Lithium/Sodium Storage. Advanced Functional Materials, 28(10), 1–10.

Jeżowski, P., Chojnacka, A., Pan, X., & Béguin, F. (2021). Sodium amide as a "zero dead mass" sacrificial material for the pre-sodiation of the negative electrode in sodium-ion capacitors. Electrochimica Acta, 375, 137980.

Kamal, M. M., Baini, R., Mohamaddan, S., Selaman, O. S., Zauzi, N. A., Rahman, M. R., Rahman, N. A., Chong, K. H., Atan, M. F., Samat, N. A. S. A., Taib, S. N. L., & Othman, A. K. (2017). Effect of temperature to the properties of sago starch. *IOP Conf. Series: Materials Science and Engineering*, *206*, pp. 1–13.

Keller, M., Vaalma, C., Buchholz, D., & Passerini, S. (2016). Development and Characterization of High-Performance Sodium-Ion Cells based on Layered Oxide and Hard Carbon. *ChemElectroChem*, *3*(7), 1124–1132.

Khaniabadi, Y. O., Jafari, A., Nourmoradi, H., & Taheri, F. (n.d.). *Adsorption of 4-chlorophenol from aqueous solution using activated carbon synthesized from aloe vera green wastes A Survey on Average Lead Concentration of Most Conventional Lipstick and Eye shade in Isfahan city at 2011. View project Nursing Care Quality in the Cardiac Care Unit: A Cross-Sectional Study View project*.

Khosravi, M., N. Bashirpour, dan F. Nematpour. 2014. "Synthesis of hard carbon as anode material for lithium ion battery." *Advanced Materials Research* 829:922–26.

Kroschwitz, J. 1990. Polymer Characterization and Analysis. Canada: John Wiley and Sons, Inc.

Kubicka, M., Bakierska, M., Chudzik, K., Świętosławski, M., Molenda, M.. Nitrogen-Doped Carbon Aerogels Derived from Starch Biomass with Improved Electrochemical Properties for Li-Ion Batteries. *International Journal of Molecular Sciences*. 2021; 22(18):9918

Li, W., Chen, M., & Wang, C. (2011). Spherical hard carbon prepared from potato starch using as anode material for Li-ion batteries. *Materials Letters*, 65(23–24), 3368–3370. https://doi.org/10.1016/j.matlet.2011.07.072

Li, Rui dan Abolghasem Shahbazi. 2015. "A Review of Hydrothermal Carbonization of Carbohydrates for Carbon Spheres Preparation." *Trends in Renewable Energy* 1(1):43–56.

Li, Y., Hu, Y. S., Titirici, M. M., Chen, L., & Huang, X. (2016). Hard Carbon Microtubes Made from Renewable Cotton as High-Performance Anode Material for Sodium-Ion Batteries. *Advanced Energy Materials*, *6*(18).

Li, Z., Bommier, C., Chong, Z. sen, Jian, Z., Surta, T. W., Wang, X., Xing, Z., Neuefeind, J. C., Stickle, W. F., Dolgos, M., Greaney, P. A., & Ji, X. (2017). Mechanism of Na-Ion Storage in Hard Carbon Anodes Revealed by Heteroatom Doping. *Advanced Energy Materials*, *7*(18).

Liu, S., Ma, R., Hu, X., Wang, L., Wang, X., Radosz, M., & Fan, M. (2020). CO2 Adsorption on Hazelnut-Shell-Derived Nitrogen-Doped Porous Carbons Synthesized by Single-Step Sodium Amide Activation. *Industrial and Engineering Chemistry Research*, *59*(15), 7046–7053.

Libra, Judy A., Kyoung S. Ro, Claudia Kammann, Axel Funke, Nicole D. Berge, York Neubauer, Maria Magdalena Titirici, Christoph Fühner, Oliver Bens, Jürgen Kern, dan Karl Heinz Emmerich. 2011. "Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis." *Biofuels* 2(1):71–106.

Luo, W., Bommier, C., Jian, Z., Li, X., Carter, R., Vail, S., Lu, Y., Lee, J. J., & Ji, X. (2015). Low-surface-area hard carbon anode for Na-ion batteries via graphene oxide as a dehydration agent. *ACS Applied Materials and Interfaces*, *7*(4), 2626–2631

Mirzaeian, M., Abbas, Q., Hunt, M.R.C., Galeyeva, A., Raza, R., 2021. Na-Ion Batteries, Encyclopedia of Smart Materials, ISBN 9780128157336,

https://doi.org/10.1016/B978-0-12-815732-9.00052-8.

Mischnick, P. & Momcilovic, D., 2010. Chemical Structure Analysis of Starchand Cellulose Derivatives. Advances in Carbohydrate Chemistry and Biochemistry, Volume 64, pp. 117-210.

Mua, JP, & Jackson, DS (1997). Struktur halus fraksi amilosa dan amilopektin jagung dengan berbagai berat molekul. Jurnal Kimia Pertanian dan Pangan, 45 (10), 3840–3847.

Nwokocha et al., 2010. Effect of drying temperature on physiochemical properties of cassaca starch. International Agrophysics, Volume 3, pp. 219-225.

Ngidi, Nonjabulo P. D., Moses A. Ollengo, dan Vincent O. Nyamori. 2019. "Precursors on the Physicochemical , Optical , Nitrogen-Doped Reduced Graphene Oxide." *Materials* 12(20):3376–3401.

Oates, CG Menuju Pemahaman Struktur Butiran Pati dan Ruales, J. Penentuan Kandungan Amilosa Pada Pati Berbeda Menggunakan Kalorimetri Pemindaian Diferensial Termodulasi [J]. Starke pati wiley. 25. Muhammad, HF, Nasser, T., Hossein, Hidrolisis [J]. Tren Ilmu & Teknologi Pangan, 1997. Vol. 8, No.11, hh. 375-382.

Ouyang, L., Xiao, J., Jiang, H., & Yuan, S. (2021). Nitrogen-doped porous carbon materials derived from graphene oxide/melamine resin composites for co2 adsorption. *Molecules*, *26*(17).

Perveen, T., Siddiq, M., Shahzad, N., et al., 2020. Prospects in anode materials for sodium ion batteries – A review. Renewable and Sustainable Energy Reviews 119, 109549.

Raja, Pavan M. V dan Andrew R. Barron. 1934. "Physical methods in chemistry and nano science." *Nature* 134(3384):366–67.

Rao, L., Yue, L., Wang, L., Wu, Z., Ma, C., An, L., & Hu, X. (2018). Low-Temperature and Single-Step Synthesis of N-Doped Porous Carbons with a High CO_2 Adsorption Performance by Sodium Amide Activation. Energy & Fuels.

Reza, M. Toufiq, Janet Andert, Benjamin Wirth, Daniela Busch, Judith Pielert, Joan G. Lynam, dan Jan Mumme. 2014. "Hydrothermal Carbonization of Biomass for Energy and Crop Production." *Applied Bioenergy* 1(1):11–29.

Reza, M. Toufiq, Erwin Rottler, Laureen Herklotz, dan Benjamin Wirth. 2015. "Hydrothermal carbonization (HTC) of wheat straw: Influence of feedwater pH prepared by acetic acid and potassium hydroxide." *Bioresource Technology* 182(April 2015):336–44.

Syahariza, ZA, dan Yong, HY. 2017. Evaluasi Sifat Reologi dan Tekstur Bubur Beras Modifikasi Tekstur Menggunakan Tapioka dan Tepung Sagu Sebagai Pengental. Jurnal Makanan dan pengukuran. (doi.org/10.1007/s11694-017-9538-x)

Sevilla, M. dan A. B. Fuertes. 2009. "The production of carbon materials by hydrothermal carbonization of cellulose." *Carbon* 47(9):2281–89.

Shinn, John H. 1984. "From coal to single-stage and two-stage products: A reactive model of coal structure." *Fuel* 63(9):1187–96.

Singh, S., Singh, N., Isono, N., & Noda, T. (2010). Hubungan distribusi ukuran granul dan struktur amilopektin dengan sifat paste, termal, dan retrogradasi pada pati gandum. Jurnal Kimia Pertanian dan Pangan, 58, 1180-1188.

Smallman, R.E. and Bishop, R.J. 1999. *Modern Physical Metalurgy and Material Engineering.* Hill International Book Company. New York.

Smith, AM, & Martin, C. (1993). Biosintesis pati dan potensi manipulasinya. dalam biosintesis dan manipulasi produk tanaman. Seri Bioteknologi Tanaman, 3, 1–54.

Speirs, Jamie; Contestabile, Marcello; Houari, Yassine; Gross, Robert (2014). The future of lithium availability for electric vehicle batteries. Renewable and Sustainable Energy Reviews, 35(), 183–193.

Stevens, M. P. 2001. Kimia Polimer Edisi Pertama. Jakarta: Pradnya Paramita.

Sumardiono, S., Rakhmawati, R.B., Pudjihastuti, I. 2018. Fisikokimia dan Rheologis Pati Dimodifikasi dengan Asam Laktat Hidrolisis dan Pengeringan Rotary UV Khasiat Sagu (MetroxylonSagu). AJCHE. Vol. 18. No. 04.

Svihus, B., Uhlen, AK, & Harstad, OM (2005). Pengaruh struktur granula pati, komponen terkait dan pengolahan pada nilai gizi pati sereal: Tinjauan. Ilmu dan Teknologi Pakan Ternak, 122, 303–320.

Swapp, S. 2017. Scanning Electron Microscopy (SEM), https://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html , diakses Desember 2021.

Wang, Tengfei, Yunbo Zhai, Yun Zhu, Caiting Li, dan Guangming Zeng. 2018. "A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties." *Renewable and Sustainable Energy Reviews* 90(February):223–47.

Wang, N., Liu, Q., Sun, B., Gu ,J., Yu, B., Zhang, W., Zhang, D. 2018. *N-doped catalytic graphitized hard carbon for high-performance lithium/sodium-ion batteries.*

SCiEnTifiC REPOrtS | (2018) 8:9934.

Wang, W.-N. & Wurm, P., 2010. Standard Operating Procedure (SOP) Surface Area & Pore Size Distribution Analysis, s.l.: WUSTL.

Wang, L., Rao, L., Xia, B., Wang, L., Yue, L., Liang, Y., DaCosta, H., & Hu, X. (2018). Highly efficient CO2 adsorption by nitrogen-doped porous carbons synthesized with low-temperature sodium amide activation. *Carbon*, *130*, 31–40.

Widodo, H., Arie, A.A., Bisowarno, B.H. 2021. Pyrolysis Carbonization Of Sago Starch. Jurnal Integrasi Proses Vol. 10, No. 1 (Juni 2021) 42 – 47.

Wong, CW, Muhammad, SKS, Dzulkifly, MH, Saari, N., dan Ghazali, HM. 2007. Produksi Enzimatik Linier Dekstrin Rantai Panjang Dari Sagu (Metroxylon sagu). Makanan Tepung Kimia. Vol. 100, hh. 774-780

Wu, L., Buchholz, D., Vaalma, C., Giffin, G. A., & Passerini, S. (2016). Apple-Biowaste-Derived Hard Carbon as a Powerful Anode Material for Na-Ion Batteries. *ChemElectroChem*, *3*(2), 292–298. https://doi.org/10.1002/celc.201500437

Xing, Z. et al., 2016. One –pot hydrothermal synthesis of Nitrogen-doped graphene as high-performance anode materials for lithium ion batteries. Scientific Reports, Volume 6.

Yamaguchi, Shotaro; Miyaoka, Hiroki; Ichikawa, Takayuki; Kojima, Yoshitsugu (2017). Thermal decomposition of sodium amide. International Journal of Hydrogen Energy, 42(8), 5213–5219.

Zhang, Shicheng, Xiangdong Zhu, Shaojie Zhou, Hua Shang, Jiewen Luo, dan Daniel C. W. Tsang. 2019. "Hydrothermal Carbonization for Hydrochar Production and Its Application." Hal. 275–94 in *Biochar from Biomass and Waste*. Elsevier Inc.

Zheng, H. et al., 2012. Hard Carbon: a promising lithium-ion battery anode for high temperature applications with ionic electrolyte. RSC Advances, Volume 2, pp. 4904-4912.

Zheng, Peng, Ting Liu, Jinzheng Zhang, Lifeng Zhang, Yi Liu, Jianfeng Huang, dan Shouwu Guo. 2015. "Sweet potato-derived carbon nanoparticles as anode for lithium ion battery." RSC Advances 5(51):40737–41.

Zhong, Z., Mahmoodi, S., Li, D., Zhong, S. (2022). Electrochemical Performance and Conductivity of N-Doped Carbon Nanotubes Annealed under Various Temperatures as Cathode for Lithium-Ion Batteries.

Ziegler, A. F. and F. (2009). Hydrothermal carbonization of biomass: a summary and discussion ofchemical mechanism for process engineering. Wiley Interscience.