



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 8, Issue 1, January 2019

Nitrogen Doping by Urea Decomposition for Making Activated Carbon Derived from Shochu Waste

Takashi Fujita, Daisuke Tashima, Masumi Fukuma Seiji Kumagai,

Abstract—Activated carbon was produced from shochu waste, which is a kind of industrial waste. Nitrogen doping into activated carbon was attempted by using powder urea in the activation process for producing activated carbon. The heating rate was changed within the thermal decomposition temperature of urea, and the physical properties of activated carbon were investigated. The result was revealed that with content nitrogen activated carbon makes the pores size change. And in the same activation temperature but used a different on increasing heating rate mesopores increased by 60.7%, and the nitrogen percentage in activated carbon was decreased to 0.45 %. In addition, a compound derived from nitrogen was formed in the activated carbon with containing, and the measurement of the surface functional group, in the activated carbon by using urea, a double bond spectrum of the amide carbon and oxygen was observed. It was revealed that by this nitrogen doping,, it is possible to maintain higher capacitance than the activated carbon in the long-term cycle test.

Index Terms—Supercapacitor, Activated carbon, Nitrogen doping, Urea decomposition.

I. INTRODUCTION

Today, environmental problems are getting more serious, the solving environmental and energy problems is urgent task in the world. In 2015, the Paris Agreement has been concluded about environmental problem and has a lot of development are underway to reduce CO₂ around the world. Among them, the transport sector accounts for 24% of the world's energy-originated CO₂ emissions, and greening of automobiles is regarded as important. In addition, power generation by using renewable energy such as photovoltaic power generation and wind power generation; it has been actively researched to reduce generation which depend on fossil fuels. However, stable power supply and power leveling are challenge Energy storage technology is effective for these problems. And, supercapacitors are attracting attention among power storage. Recently, supercapacitors are loaded in automobiles as storage of regenerative energy [1]. Also, in Europe, the running test of a hybrid overhead wireless trams using supercapacitor and a battery have been carried out [2] and supercapacitor application is expanding rapidly. The electric storage principle of the supercapacitor is the electrolyte ions are adsorbed on the pores of powder activated carbon surface of the electrode and the surface of the carbon is charged by applying a voltage to this electrode [3]. Unlike batteries, charging and discharging of supercapacitor don't use chemical reaction, the electrode deterioration is extremely small for long cycles and rapid charging and discharging is possible [4]. In addition, activated carbon can be made from any raw material. Because, it is an organic material that is no depletion of resources. Studies have been made to prepare activated carbon from various industrial wastes based on this feature and to apply it to electrodes of supercapacitors [5-6]. Moreover, it is estimated that by creating activated carbon from industrial waste, it is possible to drastically reduce the manufacturing cost of supercapacitors [7]. However, the supercapacitor has a problem about the capacity is very small when compared with any storage battery, because supercapacitor can store electricity only surface of activated carbon. To increase the capacity of the supercapacitor, the pore structure of the activated carbon has been optimized and the specific surface area has been increased, although the capacity increase by them is approaching the limit today [8]. However, recent studies have reported that by doping activated carbon with nitrogen, the physical properties of the activated carbon surface is changed and sometimes show higher capacity than expected from the specific surface area due to the influence of pseudo capacity [9-11]. Methods of doping nitrogen in activated carbon have many methods such as using raw material containing a large amount of nitrogen and treating under a high temperature in NH₃ gas atmosphere. In the previous method, there is also an example in the nitrogen content of the activated carbon about 10 wt% by adjusting the oxidation treatment temperature [12]. However, this method requires high temperature treatment, and materials are also limited. The latter method has the disadvantage that ammonia gas is toxic and expensive. In this study, shochu waste was used as

raw material for making activated carbon. Shochu is Japanese distilled liquor, and shochu waste treatment is one of serious problem in Japan. In order to improve a material of supercapacitor, we try to heat treatment by using powdered urea instead of ammonia and measured the specific capacitance and physical properties of those activated carbon.

II. EXPERIMENTAL

A. Preparation of activated carbon

Black sesame shochu waste was used as the raw material to produce activated carbon. The waste was dehydrated and dried at 100 °C for 70 h. The thermal analysis (TG8120, Rigaku Co., Japan) of black sesame shochu waste was carried out under Ar gas and the optimum carbonization temperature was investigated. Fig.1 show thermal analysis of black sesame shochu waste. Fig. 1 indicated that thermal decomposition is almost completed at 700 °C.

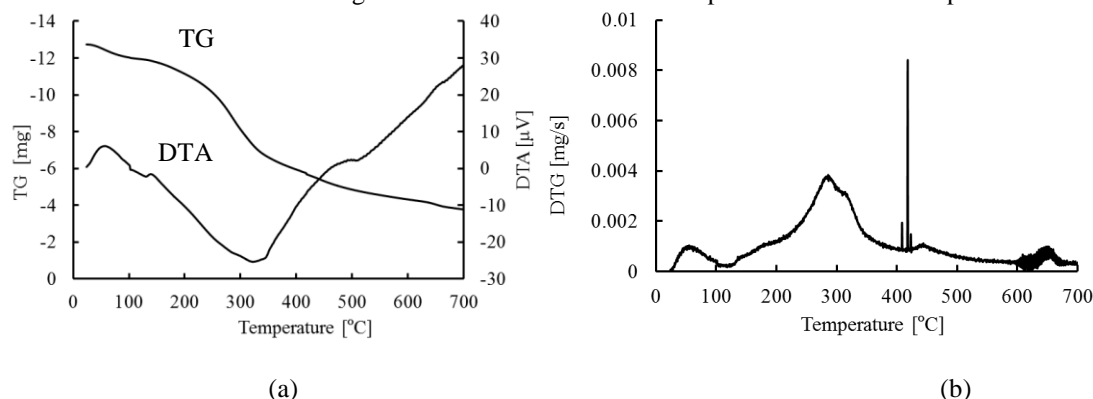


Fig. 1. The graph of black sesame shochu waste thermal analysis. (a) Thermogravimetry and differential thermal analysis data; (b) Differential thermogravimetry data.

Therefore, carbides were obtained by heating black sesame shochu waste at 700 °C for 1 h. This carbide (2 g) was mixed with KOH (14 g). Powdered urea (2 g) and mixed carbide and KOH was placed in electric tubular furnace, activated by placing powdered urea in front of the mixed carbide and KOH in the temperature 800 °C for 1 h. This heating rate was 5 °C/min. In considering sufficient thermal decomposition of urea, the heating rate was changed to 2.5 °C/min, 5 °C/min, and 10 °C/min between 200 - 400 °C. Those activated carbons were called U2.5, U5, and U10, respectively. In thermal decomposition of urea, NH₃ and CO₂ are generated as shown in the formulas (1) and (2). It is also reported that urea thermally decomposed varies with temperature [13]. Activated carbon was activated by using only KOH and heating rate was 5 °C/min. The activated carbon was prepared by not using urea and same condition of U5. This activated carbon was called as N5.



B. Measurement of surface area, pore volume

Activated carbons were measured by using nitrogen gas (-196 °C) adsorption analysis (BELSORP-mini II MicrotracBEL Co., Japan). The surface area and pore size were calculated by Brunauer-Emmett-Teller (BET) method [14], Barrett-Joyner-Halenda (BJH) method [15], and micropore (MP) method [16].

C. Organic element analysis

Activated carbons were analyzed by organic element analysis (MT-6 CHN Corder, Yanaco, Corp, Japan) to measure the nitrogen ratio in activated carbons.

D. Surface functional group analysis

U5 and N5 were analyzed by Fourier transform infrared spectrometer (Cary610, Agilent Technologies, Inc, America) between 400-4000 cm⁻¹. The sample made by mixing KBr and activated carbon, and pressed 2 t.

E. Raman spectroscopy analysis

U2.5, U5 and U10 were analyzed by Microscopic Raman spectroscopy (DXR, Thermo Fisher Scientific, Inc, America) using 532 nm between 100 -3500 cm⁻¹.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 8, Issue 1, January 2019

F. Measurement of specific capacitance

The activated carbon electrode was prepared by mixing 80 wt% activated carbon, 10 wt% conductive assistant carbon (Ketjenblack EC600JD, Lion Specialty Chemicals co., Ltd, Japan), and 10 wt% polytetrafluoroethylene (PTFE). The electrode material (10mg) was packed in mold which have 10 mm diameter with Al foil, and pressed in hot press machine in 10 MPa and 130 °C for 15 min. The separator was intermediate between two electrodes. The capacitance was measured using cyclic voltammetry (CV) method by potention/galvanost analyzer (ECstat-300, EC FRONTIER, co., Ltd, Japan). 0.8 mol/L $(C_2H_5)_4NBF_4$ in propylene carbonate (PC) (TOYO GOSEI Co., LTD) was used as electrolyte. The voltage range was 2.5 V, sweep speed was 10 mV/s. And, the long cycle characteristic was measured 1000 cycles by charge / discharge device (HJ1001SD8, Hokuto Denko Corp., Japan) at current density of 0.1 A/g. The specific capacitance carbon electrode of under aqueous electrolyte was measured in 1 mol/L Potassium hydroxide (KOH) (Wako Pure Chemical Industries, Ltd.) by automatic polarization system (HZ-5000, Hokuto Denko Corp., Japan).

III. RESULT AND DISCUSSION

A. Pore size distribution

Fig. 2 shows the nitrogen adsorption isotherm. Hysteresis characteristics were observed in using urea activated carbons. This result indicates using urea activated carbons are mesoporous. Table.1 show specific surface area, micropore and mesopore volume of activated carbons. N5 using KOH activation has highest surface area. The activated carbon using urea show high mesopore volume (V_{meso}). V_{meso} is depend on heating rate due to the thermal decomposition of urea is generated CO_2 , and with increasing the heating rate the generated CO_2 was filled in the interior tubular furnace. And the gas activation using CO_2 reported to develop mesopore [17]. Fig. 3 (a) show micropore distribution of using urea activated carbons. High heating rate activated carbon had a higher second peak of micropores due to in high heating rate potassium can enter into activated carbon better than in low heating rate. Fig. 3 (b) show mesopore distribution of using urea activated carbons. The distribution of mesopores depended on the heating rate.

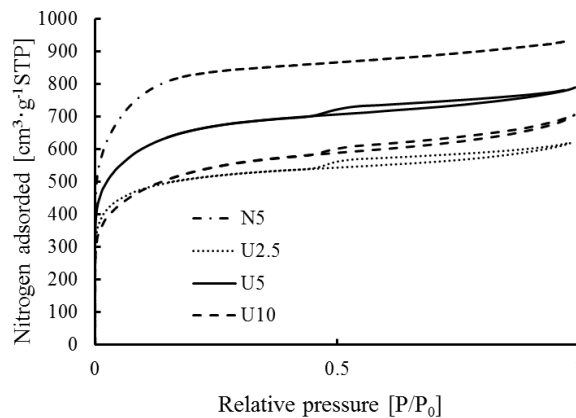


Fig. 2. Nitrogen adsorption isotherm.

Table. 1 specific surface area, micropore and mesopore volume of samples.

Sample	S_{BET} [m^2/g]	V_{micro} [cm^3/g]	V_{meso} [cm^3/g]
N5	2946	1.39	0.3
U2.5	1860	0.84	0.28
U5	2292	1.11	0.36
U10	1821	0.89	0.45

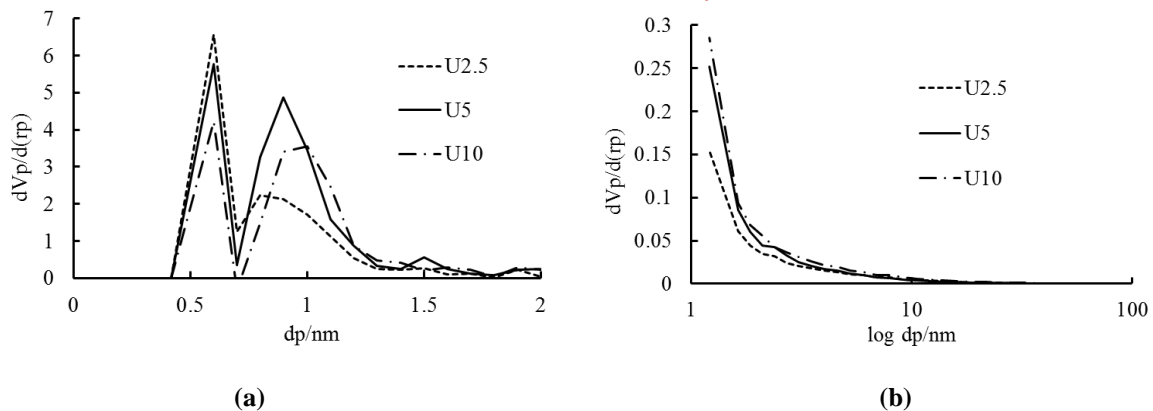


Fig. 3. Pore size distribution of activated carbons. (a) Micropore distribution; (b) Mesopore distribution.

B. Organic element analysis

Table 2 shows the results of elemental analysis. Compared with N5, the nitrogen ratio of using urea activated carbons are high. From this result, it is possible to contain nitrogen into activated carbon by using thermal decomposition method. Also, the proportional between nitrogen percentage and heating rate trend is inverse with each other. In addition, in low heating rate the ammonia can be stay inside the tubular furnace better than in high heating rate. Which means in low heating rate, nitrogen is enter into the activated carbon better.

C. Surface functional group analysis

Fig. 4 (a) shows transmission spectrum of N5, and Fig.4 (b) shows the transmission spectrum of U5. Transmission spectra of ether C = O stretching (1284 cm^{-1}), aldehyde or ketone C = O stretching (1733 cm^{-1}) and alkane C –H stretching (2956 cm^{-1}) were observed remarkably in N5 transmission data. On the other hand, Transmission spectra of N, N- disubstituted amid C = O stretching (1652 cm^{-1} and 1558 cm^{-1}) [18] was observed remarkably in U5 transmission data. This suggests that functional groups containing nitrogen can be formed by activation using urea method.

D. Raman spectra

Fig. 5 (a) shows the Raman spectrum of activated carbon using urea. The band at 1360 cm^{-1} is called D band, and it is derived from the disorder of the structure. Also, the band near 1580 cm^{-1} is the Graphite original band called G band. The intensity ratio (I_{1360} / I_{1580}) of D band and G band can be used to evaluate the degree of graphitization and the ratio of edge and crystal boundary on the graphite surface. The half band width ($\Delta\nu_{1580}$) of the G band is used for the evaluation of the graphitization degree. Characteristic features of the carbon material can be known with I_{1360} / I_{1580} on the vertical axis and $\Delta\nu_{1580}$ on the horizontal axis, and the upper right part of the graph is a carbon material with an amorphous structure. When three activated carbons are applied to this graph, they are as shown in Fig.5 (b). The linearity due to the heating rate is observed, and the structure of the activated carbon tends to be amorphous by slowing the heating rate.

Table.2. Constituent element ratio of activated carbons.

Sample	H [%]	C [%]	N [%]
N5	1.32	79.8	1.54
U2.5	1.77	72.9	2.75
U5	1.75	75.4	2.60
N10	1.58	59.6	2.30

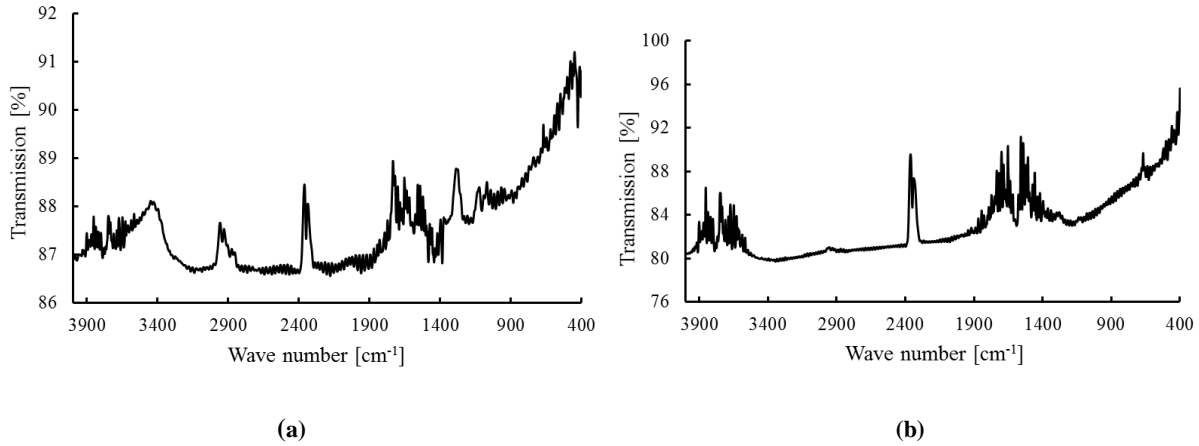


Fig. 4. Comparison of transmittance spectra. (a) In the case of N5; (b) In the case of U5.

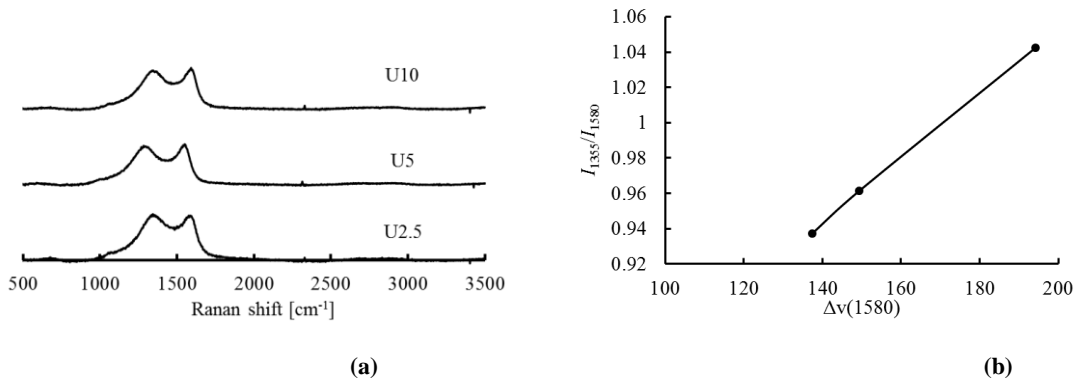


Fig. 5. Raman Characteristic of using urea activated carbon. (a) Raman spectra; (b) Relationship between I_{1335}/I_{1580} and $\Delta\nu(1580)$

E. Capacitance of activated carbons and comparison with other study

Fig. 6 (a) shows the specific capacitance in KOH. The capacitances are depending on surface area. Especially U2.5 having a lot of small micropores which has relatively high capacitance. Fig. 6 (b) shows capacitance in $(C_2H_5)_4NBF_4/PC$. U10 having a lot of mesopores relatively high capacitance. Fig. 6 (c) shows the results of the long cycle charge and discharge test. The capacitance shows a high value of N5 with a large specific surface area, however the capacitance efficiency after 1000 cycles was down to 27% potential. But, activated carbon using urea showed efficiency was only 40%. It is found that the using urea activated carbon maintain a capacitance efficiency. Fig. 7 shows the chemical formula [16] of the nitrogen-derived functional group that is thought to occur during NH_3 treatment. The structure of the activated carbon was strengthened by the surface modification of the activated carbon by NH_3 and that the strong hydrophobic carbon decreased the hydrophobicity due to nitrogen contain. Table. 3 shows the data of this study and other study data on activated carbon using various raw materials and processing methods. Black sesame shochu waste activated carbon has higher nitrogen content ratio than palm husk which is a general raw material for activated carbon Improvement of nitrogen content by urea treatment was observed to improve the nitrogen content by about 1% while using the same amount of urea as carbon material and high surface area. Since, the activated carbon prepared in this study has a large specific surface area, capacitance expression due to the surface area and pore volume was dominant. However, since the process of preparing activated carbon is fewer than that of other nitrogen doping studies, it is found the life of activated carbon can be extended.

Table.3. Nitrogen doped activated carbon from various source

Name	S_{BET} [m ² /g]	N [%]	C_g [F/g]	Condition/ electrolyte	Cell type	Reference
N5	2946	1.54	319	10 mV/s, 1 M KOH	Three	This study
U5	2292	2.60	280	10 mV/s, 1 M KOH	Three	This study

Glucose activated carbon	1210	2.81	313	10mV/s, 6 M KOH	Three	[6]
Polyaniline activated carbon	34	7.0	157	40mA/g, 1 M H ₂ SO ₄	Three	[8]
Polyacrylonitrile activated carbon	970	7.50	—	—	—	
Polyacrylonitrile activated carbon treatment of urea	940	5.6	—	—	—	[10]
Palm husk activated carbon	898	0.28	—	—	—	
Palm husk activated carbon treatment of NH ₃	691	2.06	—	—	—	[20]
Celery activated carbon	1186	1.56	245	5mV/s, 6 M KOH	Three	[21]
Squid gladius activated carbon	1129	4.04	204	0.5 A/g, 1 M H ₂ SO ₄	Two	[22]

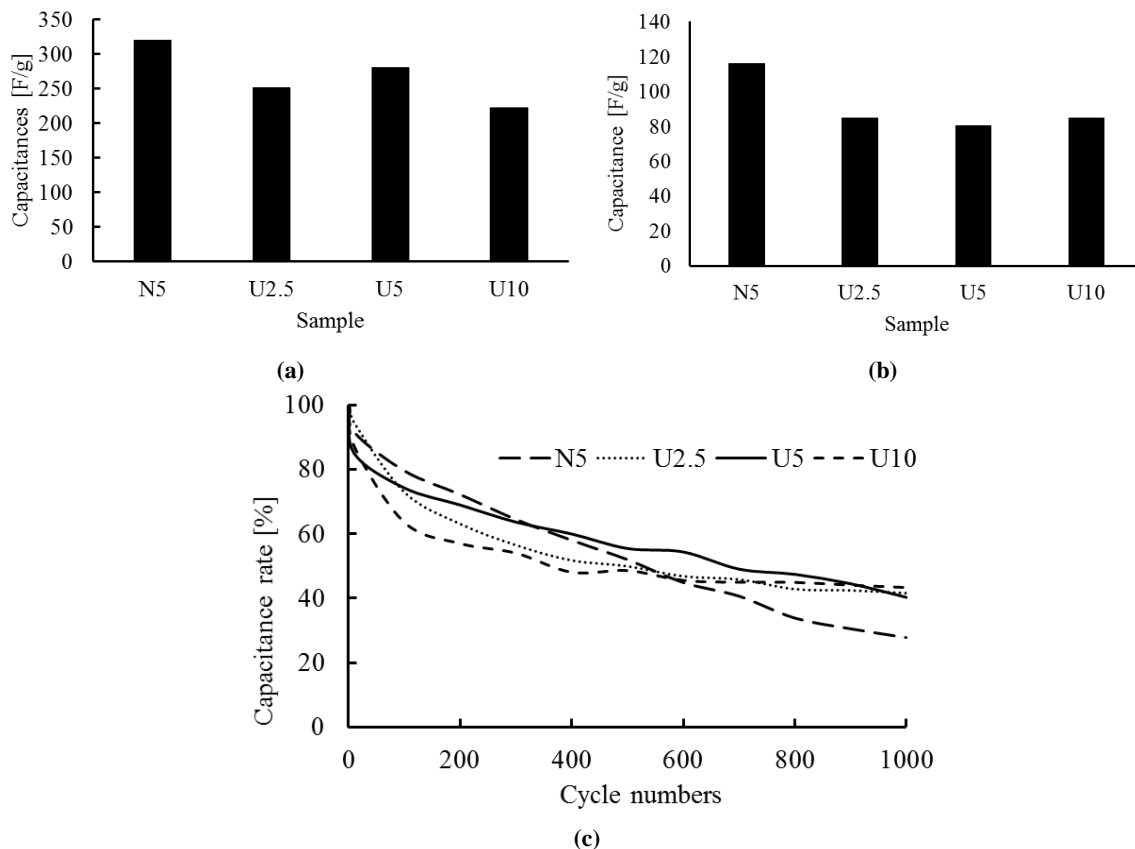


Fig. 6. Capacitance characteristic. (a) Capacitance in KOH; (b) Capacitance in (C₂H₅)₄NBF₄/PC; (c) Capacitance reduction ratio in (C₂H₅)₄NBF₄/PC.

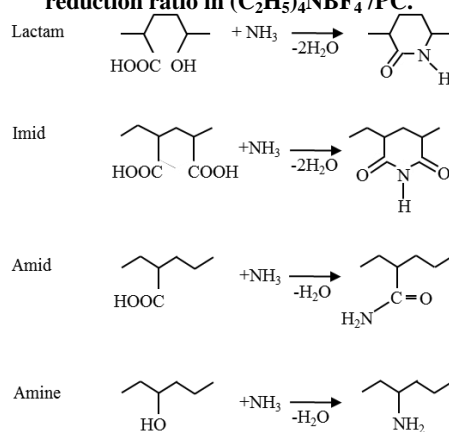


Fig.7. Chemical formula of the nitrogen-derived functional group.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 8, Issue 1, January 2019

IV. CONCLUSION

In this study, shochu waste was used as the raw material of activated carbon, and nitrogen doping was performed using urea in the activation method. It was found that by using urea, the nitrogen ratio in the activated carbon can be increased by about 1%. It was also found that changing the heating rate in the thermal decomposition temperature range of urea affects the nitrogen ratio and the mesopore volume. Using urea activated carbon could keep capacitance in long cycle test. This factor was considered that activated carbon is modified for surface by NH_3 generated urea decomposition to form a nitrogen-derived compound such as amide, and the hydrophobicity of activated carbon is decreased due to the increase in nitrogen ratio. Since nitrogen doping in this study uses urea in the activation process, nitrogen doping is easily performed as compared with other studies.

ACKNOWLEDGMENT

This work was supported by a Scientific Research Grant from the Japan Society for the Promotion of Science KAKENHI Grant number 18K11717.

REFERENCES

- [1] S. Watanabe, "Electric Double Layer Capacitor as an Energy Storage Device for Automotive Applications" The Japan Society of Applied Electromagnetics and Mechanics, Vol.24, No.4, pp.305-310, August 2016.
- [2] H. Hata, "Recent Trends of a R&D of Propulsion Systems in Abroad," RTRI REPORT, Vol.23, No.11, pp.1-6, Nov 2009.
- [3] I. Mochida, S. I. Lee, S. Mitani, S.H. Yoon, and Y. Korai, "Performance, Working Mechanism and Future Development of Activate Carbons in Super Capacitor" TANSO, No.210, Dec 2003.
- [4] H. Hatori, O. Tanaike, Y. Soneda, and M. Kodana, "Capacitor devices for rapid charge/discharge storage" Synthesiology, Vol.6, No.4, pp.228-237, Nov 2013.
- [5] A. Yamashita, Y. Mori, T. Oshima, and Y. Bada, "Preparation of activated carbon with high surface area using crab shell and shochu waste and the development of methane storage technology" TANSO, No.262, pp.53-58, Jan 2014.
- [6] T. Hirose, S. Kakuta, M. Kushibiki, "Pore Properties of Activated Carbon from Pruned Apple Branches" Journal of the Society of Materials Engineering for Resources of Japan, Vol.25, No.1/2, June 2013.
- [7] N. Kamikuri, Y. Hamasuna, D. Tashima, M. Fukuma, S. Kumagai, and J.D.W.Madden, "Low-cost Activated Carbon Materials, Produced from Used Coffee Grounds for Electric Double-layer Capacitor" International Journal of Engineering Science and Innovative Technology, Vol.3 Issue.4, pp.492-501, July 2014.
- [8] S. Shiraishi, H. Mamyouda, "Electrochemical capacitance of carbonized polyaniline" TANSO, No.232, pp.61-66, Jan 2008.
- [9] M. Iwanaga, Y. Amano, M. Aikawa, and M. Machida, "Dechlorination Reaction Compounds on the Surface of Activated Carbon under Ambient Temperature and Pressure" Journal of Environmental Chemistry, Vol.21, No.2, pp.161-167, April 2011.
- [10] M. Furuyado, T. Ohba, Y. Amano, and M. Machida, "Adsorption of Cd (II) onto Activated Carbon Fiber Prepared by Urea Treatment" The Society of Chemical Engineers, Japan, Vol.38, No.4, pp.242-249, April 2012.
- [11] A. K. Mondal, K. Kretschmer, Y. Zhao, H. Liu, H. Fan, and G. Wang, "Naturally nitrogen doped porous carbon derived from waste shrimp shells for high-performance lithium ion batteries and supercapacitors" Microporous and Mesoporous Materials, No.246, pp.72-80, March 2017.
- [12] M. Furuyado, M. A. A. Zaini, M. Aikawa, Y. Amano, and M. Machida, "Adsorption of Cd (II) on Activated carbon Fiber Prepared from Polyacrylonitrile (PAN)" Journal of Environmental Chemistry, Vol.20, No.4, pp.379-384, Sep 2010.
- [13] T. Furuhashi, N. Seki, and M. Arai, "Decomposition Behavior of Urea in High Temperature Atmosphere" The Japan Society of Mechanical Engineers, Vol.77 No.781, pp.170-179, Sep 2011.
- [14] S. Brunauer, J. Skalny, and E.E. Bodor, "Adsorption on nonporous solids" Journal of Colloid and Interface Science, Vol.30, No.4, pp.546-552, August 1969.
- [15] E. P. Barrett, L. G. Joyner, and P. P. Halenda, "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms" Journal of the American Chemical Society, Vol.73, No.1, pp.373-380, 1951.
- [16] A. Ishizuka, M. Machida, and H. Tatsumoto, "Comparison of various pore structure analysis methods for activated carbons using nitrogen adsorption and desorption" TANSO, No.227, pp.103-106, Jan 2007.



ISSN: 2319-5967

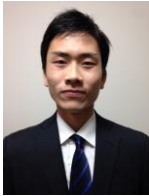
ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 8, Issue 1, January 2019

- [17] I. Abe “Production methods of activated carbon” TANSO, No. 225, pp373-381, Sep 2006.
- [18] M. Hesse, H. Meier, and B. Zeeh, “Spectroscopic Methods in Organic Chemistry 2nd Edition” pp.33-71, 2010.
- [19] D. H. Jurcakova, M. Kodama, S. Shiraishi, H. Hatori, Z. H. Zhu, and G. Q. lu, “Nitrogen-Enriched Nonporous Carbon Electrode with Extraordinary Supercapacitance” ADVANCED FUNCTIONAL MATERIALS, No.19, pp.1800-1809, April 2009.
- [20] B. Xiao, J. P. Boudon, and K. M. Thomas, “Reaction of Nitrogen and Oxygen Surface Groups in Nanoporous Carbons under Inert and Reducing Atmospheres” Langmuir, 2005, Vol.21, No.8, pp.3400-3409, March 2005.
- [21] J. He, D. Zhang, M. Han, X. Liu, Y. Wang, Y. Li, X. Zhang, K. Wang, H. Feng and Y. Wang, “One-step large-scale fabrication of nitrogen doped microporous carbon by self-activation of biomass for supercapacitors application” Journal of Energy Storage, No.21, pp.94-104, Oct 2018.
- [22] C. J. Raj, M. Rajesh, R. Manikandan, K. H. Yu, J. R. Anusha, J. H. Ahn, D.W. Kim, S. Y. Park, B. C Kim, “High electrochemical capacitor performance of oxygen and nitrogen enriched activated carbon derived from the pyrolysis and activation of squid gladius chitin” Journal of Power Sources, No.386, pp.66-76, March 2018.

AUTHOR BIOGRAPHY



Mr. Takashi Fujita

He received a bachelor's degree from the Fukuoka Institute of Technology in 2016 and completed the first stage of the master program in 2017. His research is focused on synthesizing high capacitance activated carbons from shochu waste.



Prof. Daisuke Tashima

He received his B.E degree in Electrical and Electronic Engineering from the University of Miyazaki in 2003, and his doctoral degree from the University of Miyazaki in 2007. He is now an associate professor at in the Department of Electrical Engineering, Faculty of Engineering, Fukuoka Institute of Technology. His research interest includes electric double layer capacitors and proton exchange membrane fuel cells.



Prof. Masumi Fukuma

He received his B.E and M.E degrees from the Department of Electrical and Electronic Engineering at Toyohashi University of Technology in 1983 and 1985, respectively. He received a doctoral Dr. Degree from Toyohashi University of Technology in 1997. He is now a professor at the Department of Electrical Engineering in Matsue College of Technology. His main research interests are space charge measurement techniques in dielectrics and electric double layer capacitors.



Prof. Seiji Kumagai

He received his B.E degree in the Department of Electrical and Electronic Engineering from Akita University in 1995, and his doctoral. Degree from Akita University in 2000. He is now a professor at Akita University. His research interests includes power storage devices and electrical insulating materials