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Surface Modification of Carbon Nanotubes (Cnnts) as Electrode of Hybrid Energy Storage Device (Supercapacitor)

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Abstract
Supercapacitors have an advantage in the form of a higher specific capacitance than conventional capacitors. This alternative is the right idea if it is used to solve the problem of using hybrid energy storage demand. This study aims to analyze the variation in the ratio between activator and carbon nanotubes (Cnnts) that function as electrodes. Electrodes are one of the constituent components of supercapacitors, so they are important to review. Electrodes in the form of Cnnts activated using H_2SO_4 and HNO_3 were analyzed through SEM and FTIR characterization. The activation process produces mesoporous size on the electrode. The activation method is also able to form aromatic compounds that are important for heat stability and electrical conductivity.
Keywords: Supercapacitors, Cnnts, Electrode, Activation, Heat Stability, Electrical Conductivity

Introduction
The supercapacitors, known as a hybrid energy storage system (HES System), have an important role in ensuring energy consumption and preserving a clean environment. The use of supercapacitors that are integrated directly with lithium-ion batteries can extend the life of these batteries. This is evident that supercapacitors make a real contribution as a solution to reducing Lithium-ion battery waste which is identified as hazardous waste (Universal Eco.id, 2024). Supercapacitors have higher energy density and the best performance efficiency when compared to conventional capacitors (Testbook.com, 2024).

The performance of supercapacitors is judged by the charging and discharging process which is quite short because it only occurs on the surface of the electrode-electrolyte. On the basis of this short charging and discharging rate, supercapacitors are suitable for use in portable devices that are easy to charge as needed. Interesting applications of supercapacitors to observe are applied to household devices (Hernandez et al., 2021; Karunanithi et al., 2022), mobile phones (Reddy et al., 2018), and electric vehicles (Zhang et al., 2020; Song et al., 2014; Guo et al., 2023; Atvare et al., 2023). Of course, these applications have different capacitance requirements. Increasing capacitance requirements require supercapacitors to be continuously developed. The development that has been carried out is the basis that the use of supercapacitors as energy storage is promising for a long period of time.

A number of studies have been carried out by previous researchers with the aim of improving the performance of supercapacitors in terms of capacitance value. As far as the author's observations, the efforts that have been made include variations in the type of electrode used (Forouzandeh et al., 2020; Arumugam et al., 2023), activation of biomass-based activated carbon as an electrode (Emriadi, 2020), variations in operating conditions and activator concentrations during activated carbon synthesis (Prasetya et al., 2019; Rahmah et al., 2017), analysis on the type of electrode and electrolyte (Sharma et al., 2020; Shah et al., 2024). Natural and synthetic carbon-based electrodes are known to have less impact on the environment. Therefore, researchers are deepening the analysis of carbon-based electrodes. Previously, researchers have observed the characterization of activated carbon from kepok banana peel biomass (Reza et al., 2022). Activated carbon, which acts as an electrode for electrical energy storage, must have a pore size of up to nanometers. Based on this consideration, the researchers continued to observe the electrode of Cnnts activated using H_2SO_4 and HNO_3 compounds.

Materials & Methods
In principle, the stages of the research as shown in Figure 1 include the preparation of Cnnts (Jiangsu XFNano Materials

Tech Co., ltd, Nanjing, China), activator solution in the form of H_2 SO_4 and HNO_3 (Sumber Ilmiah Persada, Surabaya, Indonesia), activation process, pH neutralization and drying. Characterization was performed using FTIR (Thermo Fisher Scientific) and SEM (FEI Quanta FEG 650) to analysis the characteristic after activation.

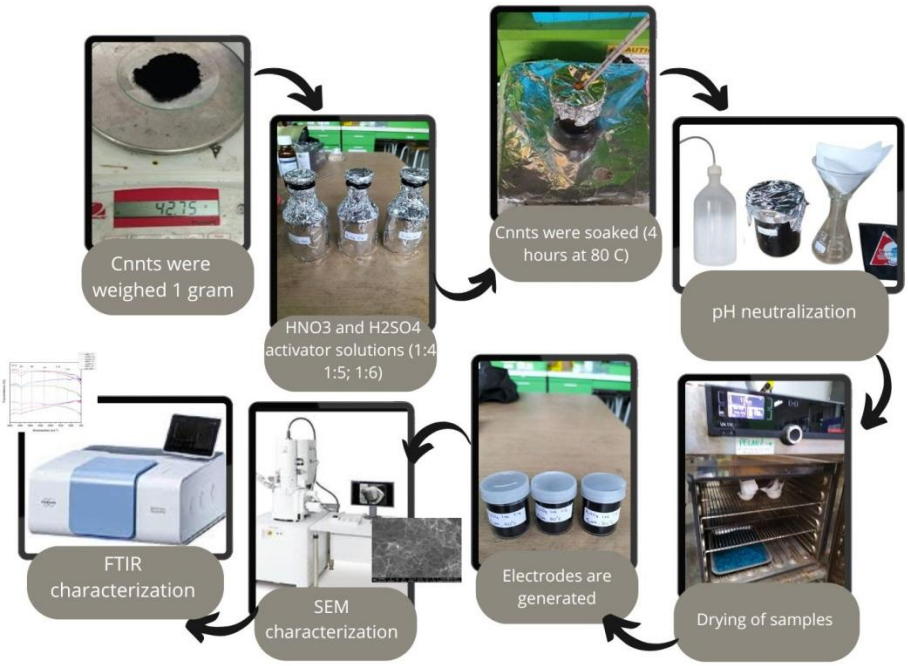


Figure 1. Activation Stages

Preparation of Cnnts Material

A total of 1 gram of Cnnts was activated at 80°C for 4 hours. The activator solutions were H_2SO_4 and HNO_3 with a concentration of 1M respectively. The ratio between Cnnts and activator solution used is 1:4, 1:6, and 1:7 as stated in Table 1. The variation of ratio aims to observe the difference in characterization of Cnnts. The Cnnts purification stage was continued by separating the Cnnts from the activator solution. Cnnts were rinsed using distilled water until reaching a stable pH and heated at 110°C for 1 hour. The temperature usage will ensure that the remaining distilled water in the rinsing process will evaporate completely, so that the sample reaches an optimum dry condition. This dried material is referred to as an electrode which is then characterized (Imelda et al., 2019; Mathias, 2022).

Table 1. H_2SO_4 and HNO_3 Solution Ratio Comparison

Type of activator	Ratio	Volume (ml)
H_2SO_4	1:4	2.8
	1:6	4.2
	1:7	4.9
HNO_3	1:4	2.2
	1:6	3.3
	1:7	3.8

Characterization Phase

The electrodes were analyzed with SEM and FTIR characterization. This step aims to evaluate the results of each variable, including the changing functional groups and surface morphology of the activated samples. The data obtained were observed for changes in the chemical and physical properties based on the results of the test.

Fourier Transform Infra Red (FTIR)

Characterization of functional groups is done through the Fourier Transform Infrared (FTIR) method, which simplifies the identification of chemical changes in molecular structures. This FTIR technique is used for qualitative analysis to determine chemical bonds based on vibrational spectra formed in chemical compounds with a wavelength range of 400-4000 cm^{-1}. Deutratef Triglycine Sulfate (DTGS) detector with reading through KBr pellet is used in this process. The test aims to detect changes in molecular structure based on the sorption of infrared light by the material. The infrared radiation exposed to the sample is measured and produces a spectrum that describes the chemical composition and molecular structure. The FTIR method enables in-depth identification of functional groups by comparing the spectra obtained against a reference database of infrared spectra of various materials. Through Fourier Transformation, the spectral information is converted into optical signals, which are then translated into spectra to identify changes in functional groups and molecular structures in more detail (Nugraha, 2021; Putri, 2020).

Scanning Electron Microscopy (SEM)

Surface morphology analysis was performed using a Scanning Electron Microscope (SEM) to obtain detailed visualization of changes in the topography and surface structure of the material. SEM utilizes an electron beam that is scanned regularly across the surface of the sample, resulting in an image that is magnified up to 300,000 times. High-energy electrons are emitted from an electron gun, focused with a magnetic lens, and scanned over the surface of the specimen. The signal generated from the interaction of the electrons with the sample is collected by a detector, converted into an electrical signal, and processed into an imaging. SEM displays only the surface of the sample without color, but provides three-dimensional visualization. The scale bar on the SEM image is used to calculate the size of the features in the image (Rahmawati et al., 2020).

Results and Discussion

Fourier Transform Infra Red (FTIR) Analysis

The FTIR spectrum shown in Figure 2 shows that Cnnts before activation (pure Cnnts) has absorption bands at 3427 cm^{-1} and 1636 cm^{-1}. After activation, there is a significant displacement in these absorption bands. Cnts that have been activated using HNO_3 solvent (1:4) show absorption bands at 3443 cm^{-1} and 1621 cm^{-1}. The absorption band in the range of 3423-3443 cm^{-1} according to Table 2 indicates the presence of hydroxyl groups (O-H), which indicates an increase in oxygen content on the surface of Cnts (Salmawati, 2016).

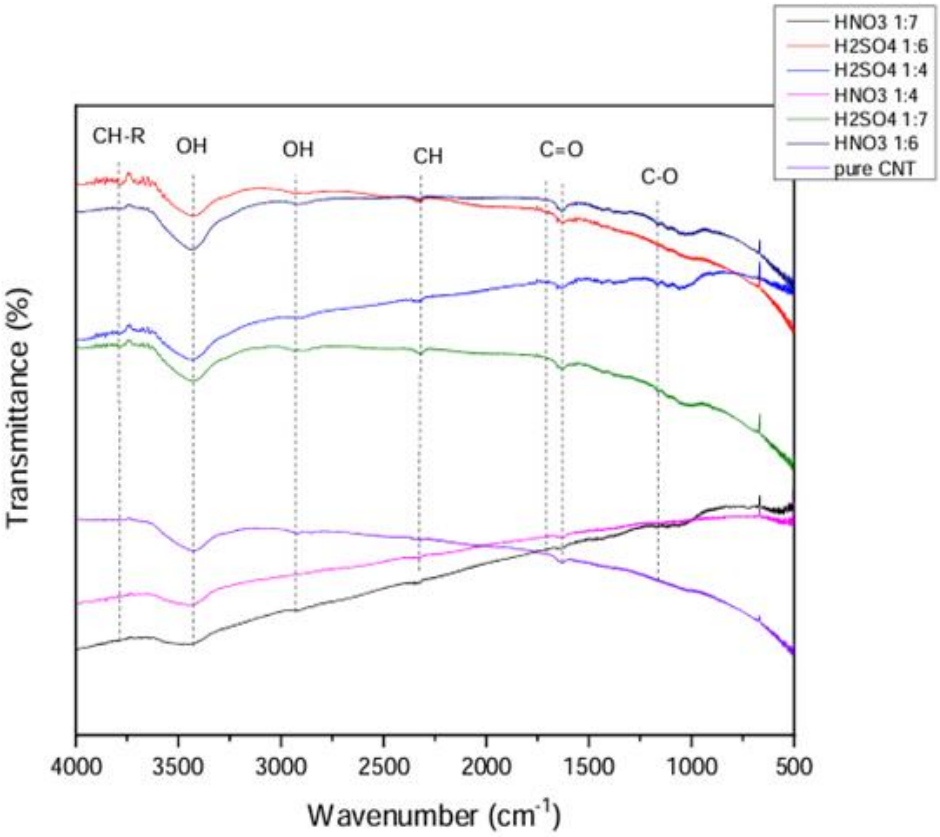


Figure 2. FTIR Spectrum

Table 2. Wave Number of Cnnts

Sampling	Wave Number (cm^{-1})
Cnnts before activation	3427, 1636
HNO_3 1:4	3443, 1621
HNO_3 1:6	3787, 3420, 1628
HNO_3 1:7	3434, 2919, 2325
H_2SO_4 1:4	3794, 3430, 1630, 1170
H_2SO_4 1:6	3790, 3423, 2916, 2320, 1727, 1168
H_2SO_4 1:7	3794, 3430, 2322, 1629

Activation using HNO_3 solution (1:6) resulted in an increase in hydroxyl and aldehyde (C=O) groups, and indicated the formation of aromatic compounds important for heat stability and electrical conductivity (Farnane et al., 2022; Yuan.Z., et al., 2023). Activation using H_2 SO_4 solution (1:6) showed a significant increase in acidic groups on the activated carbon surface, with an absorption band around 3787 cm^{-1}, indicating the presence of aldehyde groups (CH-R). The 3787 cm^{-1} absorption band shows that H_2 SO_4 is more effective in enriching the oxygenation properties of

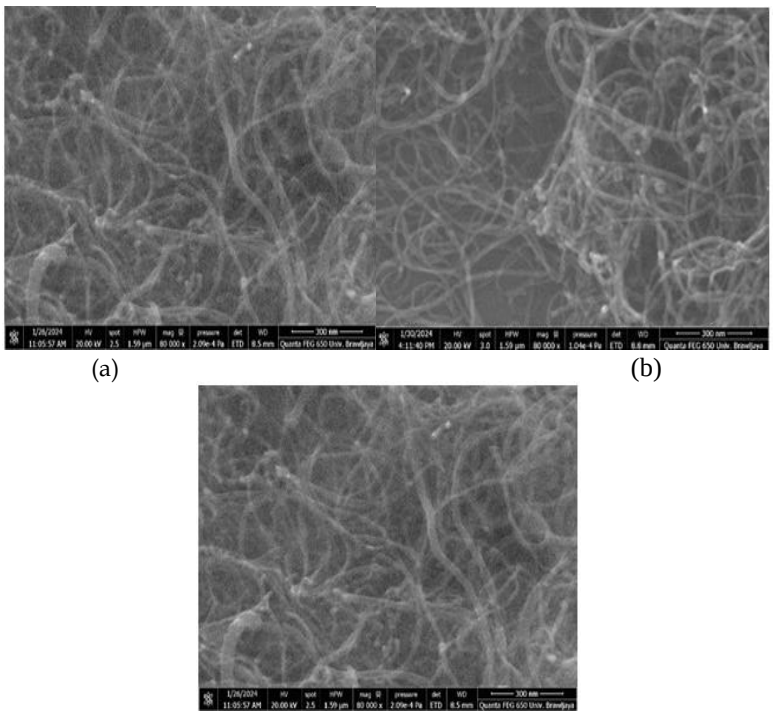
carbon, which is crucial in increasing surface area and energy storage capacity. Overall, FTIR analysis shows that chemical activation of Cnnts using H_2 SO_4 and HNO_3 solutions, increases the number and variety of functional groups. This contributes to the increase in surface area, porosity, as well as energy storage capacity in supercapacitor applications (Kim et al., 2023).

Scanning Electron Microscopy (SEM) Analysis

Activation of Cnnts using HNO_3 and H_2SO_4 solutions is important in modifying the pore distribution and size, thereby improving the morphological characteristics and performance of the material in energy storage applications. The activation process is used to expand the pore size, as shown in Figure 3. Table 3 displays the pore size of Cnnts calculated using the ImageJ application which displays the average value of pore diameter in various samples. The pore sizes of Cnnts before and after activation (HNO_3 and H_2SO_4 ratio 1:6) were 26.303 nm, 30.104 nm and 42.175 nm, respectively. Chemical activation aims to open more pores, so as to increase interaction with energy molecules and ions. This morphological analysis can be seen using SEM, where the variation in the diameter of the Cnnts is clearly visible after going through the activation process. This activation is important as the larger surface area allows for higher energy absorption. In general, pores in carbon materials are divided into three categories: micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm). Cnnts that have been activated are likely to have a higher proportion of mesoporous pores. This condition is ideal for supercapacitor applications, as mesopores allow efficient absorption and release of ions, as well as accelerate charge transfer in the electrode. Study results show that mesoporous pores also contribute to improved electrochemical performance through capacitance and cycle stability during charge and discharge (Zhu et al., 2019). The more open pore structure and larger surface area result in increased charge storage in supercapacitors and facilitate the absorption and release of ions, which are closely related to maintaining capacitance stability during charge and discharge cycles (Sa'diyah et al., 2020; Munawarah, 2010; Lu.X., et al, 2020). Increasing the number of functional groups on the surface of Cnnts through activation methods not only favorably affects the chemical properties of the material, but also improves the conductivity and reactivity of the electrode. This makes the activated Cnnts suitable for application as a supercapacitor electrode. The surface area porosity of the electrode is an indicator in storing electric charge.

Tabel 3. Cnnts Pore Size

Variable	Pore Size (nm)
Cnnts pure	26,303
HNO_3 1:6	30,104
H_2SO_4 1:6	42,175



(a) (b)

(c)

Figure 3. (a) Cnnts pure, (b) HNO_3 1:6, H_2 SO_4 1:6

Conclusions

Cnnts activated using HNO_3 and H_2 SO_4 solutions with varying ratios produce different functional groups and porosity. Electrodes activated with HNO_3 and H_2 SO_4 solutions in a ratio of 1:6 produce mesoporous porosity sizes.

The activation method used is able to form optimal electrodes in the energy storage process applied to supercapacitor devices.

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References

Atvare, E., Gravelsins, A., Kudurs, E., Rozakis, S., Blumberga, D. (2023). When the household becomes environmentally friendly—dynamic simulation of hybrid energy system's feasibility. *Journal Environments,10(9)*. 1-21.

Arumugam, B., Mayakrishnan, G., Manickavasagam, S.K.S., Kim, S.C., & Vanaraj, R. (2023). An overview of active electrode materials for the efficient high-performance supercapacitor application. *Crystals, 13*(7), 1-28.

Emriadi, E. (2020). Effect of KOH activator on the performance of activated carbon from oil palm kernel shell as supercapacitor electrode material. *Journal of Aceh Physics Society, 9*(1), 13-19.

Forouzandeh, P., Kumaravel, V., & Pillai, S.C. (2020). Electrode materials for supercapacitors: a review of recent advances. *Catalysts, 10*, 1-73.

Guo, L., Hu, P., & Wei, H. (2023). Development of supercapacitor hybrid electric vehicle. *Journal of Energy Storage, 65*.

Imelda, Khanza, M., & Wulandari, N. (2019). Pengaruh aktivasi karbon nanotube terhadap luas permukaan dan sifat elektroda. *Jurnal Teknik Material, 17*(2), 45-55.

Kim, J-H., Kim, S-K., Kim, B-J., & Lee, H-M. (2023) Effects of oxygen-containing functional groups on the electrochemical performance of activated carbon for EDLC. *Nanomaterials, 13(2),* 1-16.

Lee, H., Park, J., Kim, J., Kim, S., & Cho, Y. (2020). Surface modification of carbon nanotubes for enhancing electrochemical performance in supercapacitors. *Electrochimica Acta, 324*.

Lu, X., & Yang, H. (2020). Designing mesoporous carbon materials with high specific surface area for electrochemical applications. *Journal of Materials Chemistry A, 8(9),* 4291-4305.

Mathias, L. (2022). Teknik peningkatan luas permukaan CNT dengan aktivasi kimia. *Jurnal Kimia Fisika, 30*(1), 23-31.

Munawarah, M. (2010). Pengaruh aktivasi kimia terhadap adsorben karbon aktif. *Universitas Mulawarman*.

Nugraha, H. (2021). Karakterisasi gugus fungsi material menggunakan FTIR. *Jurnal Material dan Teknologi Indonesia, 20*(3), 200-208.

Prasetya, F.A., Anggarini, U., Zakaria, Y., & Putri, R.D.S. (2019). Synthesis and characterization of supercapacitor electrode from fiber of *Borassus flabelifer L.* by activation method. *Trans Publications Ltd, Switzerland, 966*, 444-450.

Putri, A. (2020). Penerapan metode FTIR dalam analisis struktur kimia. *Jurnal Sains Nano dan Material, 15*(1), 89-97.

Rahmah, A., Zainollah, A., Fitriani, N.A., Ramadhan, D.S., Cahayo, M., & Masruroh, M. (2017). EDLC type supercapacitor electrode based on banana peels activated carbon. *Indonesian Journal of Applied Physics, 7*(1), 46-51.

Rahmawati, N., Wijayanti, E., & Kurniawan, A. (2020). Aplikasi SEM dalam analisis morfologi material. *Jurnal Teknologi Material Indonesia, 18*(2), 134-140.

Reddy, A.E., & Kim, H.-J. (2018). Supercapacitor applications in electric home appliances and smartphones. *International Conference on Information and Communication Technology Robotics (ICT-ROBOT)*, Busan: Korea, 1-3.

Reza, M., Ernawati, L., Pusfitasari, M.D., Sylvia, N., Noor, A.H., & Ali, L.G. (2022). Karakterisasi karbon aktif dari kulit pisang kepok sebagai superkapasitor. *Jurnal Teknik Kimia, 16*(2), 53-60.

Sa'diyah, K., Lusiani, C.E., & Chrisnandari, R.D. (2020). Pengaruh proses aktivasi kimia terhadap karakteristik adsorben dari kulit pisang kepok (*Musa acuminata L.*). *Jurnal Chemurgy, 4*(1).

Salmawati, S. (2016). FTIR analysis on carbon nanotube activation. *Jurnal Sains Material Indonesia, 15*(2), 89-98.

Shah, S.S., & Aziz, Md.A. (2024). Properties of electrode materials and electrolytes in supercapacitor technology. *Journal of Chemistry and Environment*, 1-45.

Sharma, P., & Kumar, V. (2020). Study of electrode and electrolyte material of supercapacitor. *Materials Today: Proceedings, 3*(33), 1573-1578.

Song, Z., Hofmann, H., Li, J., Hou, J., Han, X., & Ouyang, M. (2014). Energy management strategies comparison for electric vehicles with hybrid energy storage system. *Applied Energy, 134*, 321-331.

Testbook.com. (2024, November 02). Supercapacitor: Know Definition, Types, Working Principle, Properties, Advantages & Applications. Retrieved from https://testbook.com/physics/supercapacitor

Universal Eco.id. (2024, November 02). Bahaya limbah baterai bekas jika tidak terkelola dengan baik. Retrieved from https://www.universaleco.id/blog/detail/bahaya-limbah-baterai-bekas-jika-tidak-terkelola-dengan-baik/141

Wardani, W. (2017). Transformasi struktur kimia karbon melalui aktivasi. *Indonesian Journal of Chemistry, 21*(2), 150-160.

Wulandari, I., et al. (2016). Chemical activation of CNT using sulfuric acid. *Indonesian Journal of Chemistry, 18*(4), 305-315.

Yuan, Z., He, Y., Wang, R., Mao, Y., Bai, J., & Dou, Y. (2023). Modification of multiwalled carbon nanotubes and their mechanism of demanganization. *Molecules, 28*(4).

Zhang, Q., & Li, G. (2020). Experimental study on a semi-active battery-supercapacitor hybrid energy storage system for electric vehicle application. *IEEE Transactions on Power Electronics, 35*(1), 1014-1021.

Zhu, Y., Murali, S., Stoller, M. D., Ganesh, K. J., Cai, W., Ferreira, P. J., ... & Ruoff, R. S. (2019). Carbon-based supercapacitors produced by activation of graphene. *Science, 332*(6037), 1537-1541.