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MWCNT/AC Electrode Synthesis on Supercapacitor Performance with NaCl Electrolyte

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ABSTRACT

The increase in the use of electronics requires high enough energy storage so that the use of supercapacitors is very necessary. The solution is obtained by the presence of carbon-based electrode material (MWCNT / AC). Our research used MWCNT and AC because it has high conductivity using *the doctor blade method* and a three-electrode system. Electrochemical analysis was performed by adding electrolyte NaCl and tested with CV and EIS. Electrolyte concentration of 2 M NaCl which has a high value of 11.1559 F / g with an energy density of 1580.58 Wh / kg and a power density of 1138017 W / kg. The resistor, capacitor and CPE values in the EIS test are generated respectively $R = 3.1234\,\Omega$, $C = 0.0004$ F, and $Z_{CPE} = 0.0005$ F/s.

Keywords: Supercapacitors, MWCNT, AC, Electrodes, NaCl

I. INTRODUCTION

Supercapacitors are energy storage devices with high power. Its uses vary widely in applications in transportation, military defense and personal consumer electronics. Improvements in supercapacitor performance need to be added in terms of energy density, power density and service life range of supercapacitors [1]. Types of supercapacitors are Electrical Double Layer Capacitors (EDLC) and Pseudocapacitors. Both have differences in payload storage.

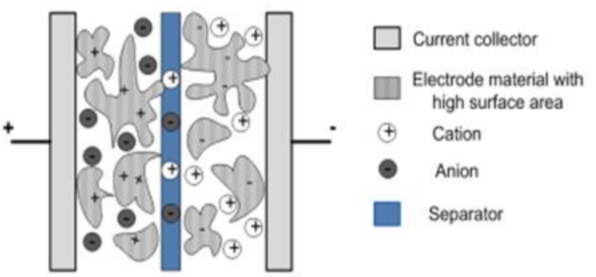

Figure 1: EDLC Scheme (Zhou, 2012)

Figure 1 shows the schematic of a supercapacitor on EDLC. The charging process on the supercapacitor shows that the two electrodes have different charges. Ions from the electrolyte will approach the electrode surface. When viewed from Figure 1, there is no transfer of charge between electrolyte and electrode so that it can be expressed as a process of emptying or storing charge. The process of charging or emptying is referred to as the non-Faradic process. The carbon material used as a supercapacitor electrode must have high conductivity properties, high surface area, not easy to corrosion and also low cost. Other advantages such as different shapes and easy process capabilities are needed in the current state [2].

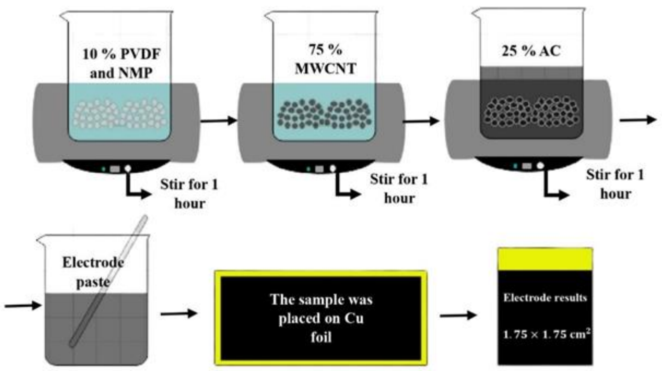

Figure 2: MWCNT/AC Electrode Synthesis

The increase in supercapacitors led to many developments of electrodes and electrolytes with superior uses and properties. This research uses carbon-based materials, namely Multi-Walled Carbon Nanotube (MWCNT) and Activated Carbon (AC). MWCNT has a surface area in diameter 〖100 m〗^2⁄g. This size is still relatively small so that air conditioning needs to be added to the size of the surface area 〖1000-2000 m〗^2⁄g [1]. The performance of the supercapacitor is on the ions of the electrolyte to be adsorbed on the surface of the carbon pore. Electrolytes have two types, namely aqueous electrolytes and non-aqueous electrolytes. The advantage of aqueous electrolyte is high electrical conductivity. Of the various electrolytes, this study used the aqueous electrolyte type NaCl because it is safe for the environment and promising for supercapacitor devices [3]. NaCl electrolyte solutions can produce Na+ ions and Cl- ions so that they have good electrical conductivity because of the strong electrolyte whose constituent ions dissociate and move freely. Because it has good conductivity, the impedance of the material will be low [4]. The electrolyte NaCl shows the capacitance value at the ambient electrode 10.6 μF or 10.6 × 〖10〗^(-6) F [5] It is very small when compared to previous studies stating the capacitance value with NaCl electrolyte reached 0.26 to 0.43 F with chitosan biopolymer material [6].

According to dai, et al said that CNT/AC with NaCl electrolyte can efficiently remove Na+ and Cl- from NaCl solution through electrical adsorption. This can be seen from the surface area and pore volume of the electrode [7]. Similar studies on CNT/PTFE electrodes with NaCl electrolyte experienced a steady increase in current with a potential of 0 to 1.2 V thus showing ion adsorption behavior on the electrode surface. There are peaks that appear that indicate the process of redox reactions. The increase in adsorption rate is due to active oxidation or increased electrorption [8]. Different research with Graphene/MWCNT-MnO2 material with NaCl electrolyte resulted in adsorption capacity (65.1 mg)⁄g. The performance of this material has a high apparent capacitive behavior and the electrode performance can be changed to anode mode by adjusting the material [9].

Based on the above problems, MWCNT and AC materials can be used in the manufacture of supercapacitor electrodes with NaCl electrolyte. The use of NaCl can reduce corrosiveness on electrodes and show good conductivity and do not cause damage to carbon-based composite materials. The function of this research is to improve the performance of supercapacitors in energy storage and determine the electrochemical properties in carbon-based electrodes. This research was conducted using the doctor blade method and tested electrodes with CV and EIS tests with output in the form of current data against potential and impedance data.

II. METHODS AND MATERIAL

This research was conducted at the Nanotechnology Laboratory of Diponegoro University. This research is by making electrodes using 75% MWCNT material with a diameter of 10 nm and 25% AC with a surface area 〖1000 m〗^2⁄g purchased from Sigma-Aldirich. The binding material and solvent in the electrode use PVDF and NMP.

An illustration of the process of making electrode paste can be seen in Figure 2, which starts by mixing PVDF and NMP for 1 hour with a magnetic stirrer at a speed of 300 rpm and room temperature. After the PVDF dissolves, MWCNT is added and again stirred for 1 hour. After everything dissolves, air conditioning is added and stirred again for 24 hours. The stirring will cause the liquid solution to turn into a homogeneous paste. The paste is then applied to Cu foil as a substrate with the doctor blade method using a micrometer adjustable film application with a thickness of 25 mm. the paste is dried using an oven for 2 hours with temperature of 80°C.

This study uses two tests, namely CV and EIS tests which are used to determine the electrochemical properties of MWCNT / AC electrodes and also determine the current in them. In the test, it requires electrolyte as a source of charge so that it requires ions from the electrolyte solution, namely NaCl. A sample of dried electrodes is cut to size 1.75 ×1.75 cm^2. Figure 3 shows the CV and EIS test process with MWCNT/AC electrode array as working electrode (WE), platinum plate as auxiliary electrode (CE) and Ag/AgCl as reference electrode (RE).

Analysis of graphic data between electric current to potential from CV test results will produce a specific capacitance value of the MWCNT / AC electrode by calculating based on equation [10].

$$Cp = \frac{A}{2mk\,(v_2 - v_1)} \quad (1)$$

Cp is the specific capacitance (F/g), A is surface area, m is the total mass (gram), k is scan rate (V/s) and $(v_2 - v_1)$ is the controlled potential in CV testing. The calculation is done using Microsoft Excel software then the data is converted in graphic form using Origin 2018 software.

III.RESULTS AND DISCUSSION

This research was conducted using the doctor blade method and carbon-based electrode materials. NaCl electrolyte solutions with concentration variations of 0.5, 1, and 2 M in CV and EIS testing through a three-electrode system. From the results of the CV test, results are obtained in the form of graphs between current and potential.

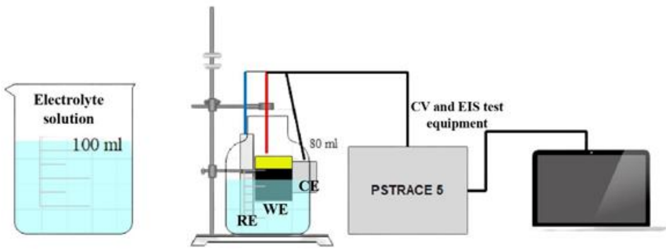

Figure 3: CV and EIS Characterization Techniques

The 4d figure is a curve of all three concentrations of electrolyte NaCl. From the figure it can be seen physically at concentrations of 0.5 and 2 M has a current disconnection at a certain point. However, if the curve is enlarged it still has a current at a certain potential so that it can be concluded that even if the potential given in the CV test will produce current even though the increase is only 1%. Of the three concentrations that have an almost quasi-rectangular shape, the concentration of 1 M can be seen in Figure 4b. This concentration indicates that there is a charge stored in the electrode due to adsorps or desorption of NaCl electrolyte ions that are reversible. It also shows redox reactions due to peaks of reduction (-0.3 V) and oxidation (-0.5 V) due to little phadic contribution to charge or energy storage [11]. Figure 4a shows a controlled potential of about -1.0 to 0 V where redox peaks are observed. The oxidation peak is located at about 0 V and the reduction peak is not significantly visible. While Figure 4c shows a potential that there is the same redox peak but a reduction peak of about -0.1 V. Redox reactions include the formation of solid phases with different speeds between concentrations of 0.5 M and 2 M [12].

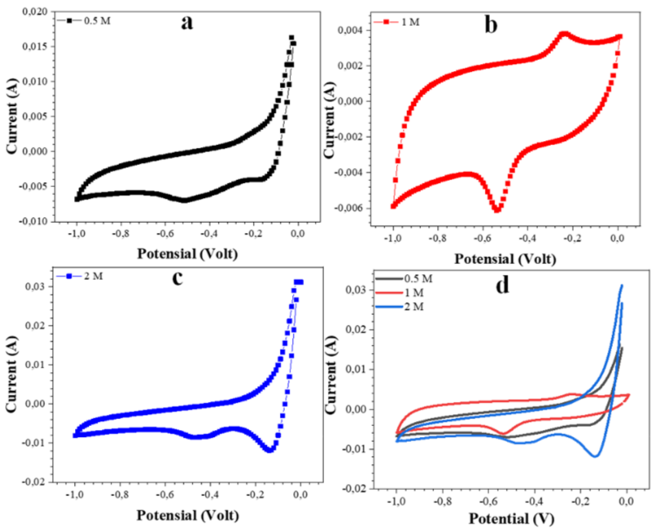

Figure 4 : CV Curve of NaCl Electrolyte with Concentrations of (a) 0.5 M, (b) 1 M, (c) 2 M, and (d) All NaCl Concentrations

Of the three concentrations, the highest capacitance value is 2 M NaCl of 11,156 F / g. Material differences that can cause different Cs values. However, in some studies on MWCNT with other composites for supercapacitors will show the presence of good intercalation and de-intercalation in improving electrochemical performance [13]. Previous research suggested higher redox reaction peaks of about 1.6 to 1.9 V with the material of Fe_2O_3 with reversible reaction [14]. In this study, the addition of activated carbon in the MWCNT material will result in expansion in the MWCNT surface and increase the current so that it can include sodum ions for adsorption into the carbon structure.

Figure 5 shows the resistance curve to frequency that occurs at MWCNT/AC electrodes with NaCl electrolyte. The curve can show the occurrence of the charging process at the electrode. When the potential is given to the electrode, there will be a transmission process to electrolyte ions in the pores of the electrode with a frequency range of (10^{-2}- 10^{5}) Hz which describes the stable charging process. The smaller frequency will increase the resistance because if the AC (Alternating Current) potential is applied in a capacitor or inductor it will cause resistance to change current. From this it can be concluded that Figure 5 horizontally in the EIS test mentioned resistance equal to real impedance (Z') [15].

Figure 6 shows the results of a Nyquist plot with an impedance spectrum measured by DC current 10 mA or 10-5 A. The curve moves from right to left, there is a semicircle at the point of real impedance of about 1.6 ohms. This suggests that these electrodes can be applied to double-layer supercapacitors (EDLC) and pseudocapasitance. It can be shown that this pseudocapasitance has a semicircle and if applied to the equivalent series there is a CPE component [16]. The equivalent circuit simulation is shown in Figure 7 which has components of one resistor (R), one capacitor (C) and three constant dase elements (CPE). Capacitors are used as charge storage so that in Nyiquist plots the curve experiences a steady rate in charge storage. The next component, CPE, is often referred to as a phase element, which can indicate that the electrode behaves the same as a double-layer supercapacitor. CPE can show that the supercapacitor does not have an imperfect dielectric. The dielectric is in the form of an electrolyte solution NaCl.

$$Z_{CPE}=T^{-1}(j\omega)^{-n} \qquad (2)$$

Equation 2 is a formula for determining the impedance of CPE based on calculations. T represents the apparent capacitance and n is the parameter that indicates the resistive properties of the MWCNT/AC electrode from 0 to 1. j represents an imaginary number and ω represents the frequency (Hz) [17]. The values of the equivalent circuit components and the n values in CPE can be seen in Table 1.

Electrochemical properties are properties that describe the relationship between chemical reactions and lytric currents. Research uses NaCl electrolyte because there are ions that can produce electrical energy composed of ions Na^+ and ions Cl^-[18].

Figure 5 shows the relationship between energy density and power density. The data points are adjusted for electrochemical performance at the scan rate 0.05 mV/s the greatest energy density value at an electrolyte concentration of 2 M is produced 1580.58 Wh/Kg and a power density value of 1138016.9 W/Kg. Electrochemical properties can be described by specific capacitance values, energy density and power density. Of these three values, it will increase with increasing the concentration of electrolyte NaCl. Electrolytes with low concentrations will produce low voltage and low electrochemical values [19].

Table 1: Component Values from NaCl Electrolyte Equivalent Circuit Simulation

Sample	Rs (Ω)	C (F)	CPE1 (F/s^{n-1})		CPE2 (F/s^{n-1})		CPE3 (F/s^{n-1})	
			P1	n1	P2	n2	P3	n3
0,5 M	11,987	0,0005	0,0005	1	0,0005	0,9967	0,0005	0,9999
1 M	8,3354	0,0005	0,0005	1	0,0005	0,9551	0,0004	1
2 M	3,1234	0,0004	0,0005	1	0,0005	1	0,0003	1

IV. CONCLUSION

Combining MWCNT and AC with PVDF as binder using *doctor blade* and Cu Foil method as substrate. Electrochemical properties are determined using CV and EIS tests. Of the three concentrations of 0.5, 1, and 2 M NaCl, 2 M NaCl has the largest value with a specific capacitance yield of 11.1559 F/g, an energy density of 1580.58 Wh/kg and a power density of 1138017 W/kg. EIS results show low electrolyte resistance values $R = 3.1234\,\Omega$ thus showing that carbon-based electrodes have good conductivity.

V. ACKNOWLEDGEMENTS

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VI. REFERENCES

[1] Zhang, W. Lu, R. Hartman, L. Qu, and L. Dai, "Nanocomposite Electrodes for High-Performance Supercapacitors," J. Phys. Chem. Lett., vol. 2, no. 6, hlm. 655–660, Mar 2011, doi: 10.1021/jz200104n.

[2] P. Login, "An Experimental Study of All-Solid-State Mediator Supercapacitor and Fundamental Study of Interfaces in Polymer Electrolyte Fuel Cell".

[3] H. Onodera and T. Tsubota, "Fabrication of NaCl aqueous electrolyte electric double layer capacitor as practical device and dependence of cell performance on pore structure of activated carbon," In Review, preprint, Okt 2022. doi: 10.21203/rs.3.rs-2160366/v1.

[4] C. S. Widodo, H. Sela, and D. R. Santosa, "The effect of NaCl concentration on the ionic NaCl solutions electrical impedance value using

electrochemical impedance spectroscopy methods," presented on THE 8TH ANNUAL BASIC SCIENCE INTERNATIONAL CONFERENCE: Coverage of Basic Sciences toward the World's Sustainability Challanges, East Java, Indonesia, 2018, hlm. 050003. doi: 10.1063/1.5062753.

[5] Y. Fujii, Y. Muramoto, and N. Shimizu, "Analysis of electric double layer in aqueous solutions of sodium chloride," dalam 2010 Annual Report Conference on Electrical Insulation and Dielectic Phenomena, West Lafayette, IN: IEEE, Okt 2010, hlm. 1–4. doi: 10.1109/CEIDP.2010.5724027.[6] J. Keskinen, A. Railanmaa, and D. Lupo, "Monolithically prepared aqueous supercapacitors," Journal of Energy Storage, vol. 16, hlm. 243–249, Apr 2018, doi: 10.1016/j.est.2018.02.008.

[6] K. Dai, L. Shi, D. Zhang, and J. Fang, "NaCl adsorption in multi-walled carbon nanotube/active carbon combination electrode," Chemical Engineering Science, vol. 61, no. 2, hlm. 428–433, Jan 2006, doi: 10.1016/j.ces.2005.07.030.

[7] S. Wang, D. Wang, L. Ji, Q. Gong, Y. Zhu, and J. Liang, "Equilibrium and kinetic studies on the removal of NaCl from aqueous solutions by electrosorption on carbon nanotube electrodes," Separation and Purification Technology, vol. 58, no. 1, hlm. 12–16, Des 2007, doi: 10.1016/j.seppur.2007.07.005.

[8] V. S. Wadi dkk., "Three-dimensional graphene/MWCNT-MnO2 nanocomposites for high-performance capacitive deionization (CDI) application," Journal of Electroanalytical Chemistry, vol. 914, hlm. 116318, Jun 2022, doi: 10.1016/j.jelechem.2022.116318.

[9] H. Jiang, L. Yang, C. Li, C. Yan, P. S. Lee, and J. Ma, "High–rate electrochemical capacitors from highly graphitic carbon–tipped manganese oxide/mesoporous carbon/manganese oxide hybrid nanowires," Energy Environ. Sci., vol. 4, no. 5, hlm. 1813, 2011, doi: 10.1039/c1ee01032h.

[10] F. Escobar-Teran, H. Perrot, and O. Sel, "Ion Dynamics at the Carbon Electrode/Electrolyte Interface: Influence of Carbon Nanotubes Types," Materials, vol. 15, no. 5, hlm. 1867, Mar 2022, doi: 10.3390/ma15051867.

[11] Z. Zhang dkk., "The composite electrode of Bi@carbon-texture derived from metal-organic frameworks for aqueous chloride ion battery," Ionics, vol. 26, no. 5, hlm. 2395–2403, Mei 2020, doi: 10.1007/s11581-019-03389-4.

[12] R. George, K. R. V. Subramanian, F. Jan, and S. Allu, "Sodium ion based supercapacitor development with high capacity and stability," Materials Letters, vol. 313, hlm. 131767, Apr 2022, doi: 10.1016/j.matlet.2022.131767.

[13] M. Chen dkk., "Porous α-Fe 2 O 3 nanorods supported on carbon nanotubes-graphene foam as superior anode for lithium ion batteries," Nano Energy, vol. 9, hlm. 364–372, Okt 2014, doi: 10.1016/j.nanoen.2014.08.011.

[14] L. F. Lima, A. L. Vieira, H. Mukai, C. M. G. Andrade, and P. R. G. Fernandes, "Electric impedance of aqueous KCl and NaCl solutions: Salt concentration dependence on components of the equivalent electric circuit," Journal of Molecular Liquids, vol. 241, hlm. 530–539, Sep 2017, doi: 10.1016/j.molliq.2017.06.069.

[15] J. N. Barisci, G. G. Wallace, D. Chattopadhyay, F. Papadimitrakopoulos, and R. H. Baughman, "Electrochemical Properties of Single-Wall Carbon Nanotube Electrodes," J. Electrochem. Soc., vol. 150, no. 9, hlm. E409, 2003, doi: 10.1149/1.1593045.

[16] D. A. Triana-Camacho, D. A. Miranda, E. García-Macías, O. A. Mendoza Reales, and J. H. Quintero-Orozco, "Effective medium electrical response model of carbon nanotubes cement-based composites," Construction and Building Materials, vol. 344, hlm. 128293, Agu 2022, doi: 10.1016/j.conbuildmat.2022.128293.

[17] S. Z. N. Haq, E. Kurniawan, and M. Ramdhani, "Analysis Of Power Plants Using Salt Water Media As Electrolyte Solutions".

[18] P. Lannelongue dkk., "'Water-in-Salt' for Supercapacitors: A Compromise between Voltage, Power Density, Energy Density and Stability," J. Electrochem. Soc., vol. 165, no. 3, hlm. A657–A663, 2018, doi: 10.1149/2.0951803jes

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