The effect of spincoating speed on ZnONR microstructure and it's potential of ZnONR/Aluminum foil electrodes symmetric supercapacitors

I Luthfiyah\textsuperscript{1}, J Utomo\textsuperscript{1}, M Diantoro\textsuperscript{1,2,*, N Mufti\textsuperscript{1,2}, T Suprayogi\textsuperscript{1}, Y Yudyanto\textsuperscript{1}, and A Aripriharta\textsuperscript{2,3}

\textsuperscript{1}Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
\textsuperscript{2}Center of Advanced Material for Renewable Energy (CAMRY), Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
\textsuperscript{3}Department of Electrical Engineering, Faculty of Engineering, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia

*Corresponding author: markus.diantoro.fmipa@um.ac.id

Abstract. Many studies on symmetric capacitors have been extensively conducted. Not only the specific capacitance and energy density, but release rate energy are also necessary. Thus, continuous research is needed to improve capacitor performance by modifying ZnONP (nanoparticles) to ZnONR (nanorods) because the surface area of ZnONR is higher than ZnONP so that the interaction performance may increase. The spin coating speed needed to find out the appropriate ZnONR levels and morphology influencing supercapacitor performance. This research is focused on the influence of spin coating speed on the structure, morphology, and electrochemical performance of ZnONR/Aluminum foil electrodes. The deposited content, microstructure, and morphology of ZnONR are strongly influenced by the coating process. ZnONP coating on the surface of the substrate was carried out at a spin coater speed of 1500, 2500, and 3000 rpm. As the spin-coating speed increases, the porosity also increases, while the size of the grain, crystallinity, and specific capacitance reduce. Therefore, the best performance is shown by the lowest speed of 1500 rpm with the condition show ZnONR more deposited, and porosity, the highest cycle stability, and the specific capacitance reach to 0.0086 F/g with energy density 0.00433 Wh/g.

1. Introduction

The life of the people in the modern era is inseparable from the need for higher electricity consumption. According to the International Energy Agency, the government plans for sustainable development related to the electricity technology sector in Indonesia to 85% by 2040 [1]. This effort was made to reduce the dependence on petroleum and reduce air pollution due to the use of fuel or biofuel given the increasingly limited availability of fossil fuels that cannot be renewed [2,3]. Electric energy storage is the most vital component in harvesting renewable alternative energy such as solar, wind, and heat, as well as a reservoir of energy reserves whenever needed. Weather conditions strongly influence electricity production from renewable energy sources (especially wind and solar), so the power generation tends to be unstable [4,5].
The role of energy storage in modern electricity networks is a crucial issue to study. Various energy storage devices, such as conventional capacitors, lithium-ion batteries, and supercapacitors, have been widely developed and used widely in various technology industries [2]. Lithium batteries are B3 waste that is difficult to break down in the environment, low power density, life cycle and limited availability of lithium resources, and relatively high costs [6,7]. Supercapacitors are attractive candidates for consumers because they can produce higher power densities compared to lithium-ion batteries and fuel cells; energy density is better than conventional capacitors. It is proven to have fast charge storage capabilities and life cycles) longer than conventional lithium-ion batteries and capacitors [8–11].

Zinc oxide or commonly called Zinc Oxide (II-V) type semiconductor material that has high electron mobility and electrical conductivity and excellent chemical stability [12–14]. Electron mobility, energy density, and electrical conductivity of the ZnO material are 5 cm²V⁻¹S⁻¹, 650 Ahg⁻¹, and 230 Scm⁻¹ [15–17]. ZnO shows excellent electrochemical properties, is environmentally friendly, and has low production costs [16,18], so this material is widely used in fabricating electrical energy storage devices. Specific material such as ZnO with different dimensions significantly affect storage performance. ZnO nanorods may possess a higher due to its specific surface area produce superior capacitor performance compared to its nanoparticles [14,19]. Several studies reported the use of ZnONR as electrode material to support active materials because it has fast ion diffusion and easy electron transfer. The spin coating speed is needed to determine the appropriate ZnONR content in enhancing capacitor performance using a measured method. Thus, in this study, specifically the influence of ZnONR Morphology on the performance of ZnONR/Aluminum foil symmetric supercapacitors without any actives materials.

2. Methods

To fabricate simple symmetric supercapacitors of Al/ZnONR-Electrolyte, we first prepared the ZnONR electrodes with various speeds of spin-coating. The speed of spin-coating is intended to modify the microstructure of ZnONR electrodes. In the first step, we dissolved a 0.878 g Zinc Acetat dihydrate into 20 mL ethanol. The solution was heated at 70 °C while stirred under 600 rpm for about 45 mins and subsequently dropped a 0.24 mL MEA wisely for about 2 hours. The solution then kept for 24 hours to obtain a clear solution around 6 pH and ready to be deposited on 3 × 3 cm² aluminum foil with various speed rotation of 1500, 2500, and 3000 rpm. The total deposited solution was kept about 400 μL and spin-coated for about 2 seconds. On the other hand, we also prepare a solution made of 0.92 g Zinc Acetat tetrahydrate, 100 mL DI water, and 0.5 g HMT under 600 rpm and 25 °C. The three samples were then immersed in the solution for 5 hrs under 600 rpm at 90 °C. The samples then cleaned using DI water and followed by annealed at 500 °C for 2 hrs. These three samples called electrodes for further microstructure characterization and also fabricated as simple symmetric supercapacitors.

Figure 1. Schematic illustration of Symmetric ZnONR/Aluminum foil Supercapacitors
The structure and morphology of the ZnONR/Aluminum foil were characterized using SEM and X-RD. The scanning electron microscopy (SEM) we used FEI, Type: Inspect-S50. The X-ray diffraction (X-RD) pattern was recorded using an X-RD ’Xpert Pro PANalytical with Cu-κα. The diffractometer was set using a step size of 0.02°, λ of 1.54060 Å, and 2θ diffraction recorded in the range of 10-90°. The electrochemical properties were characterized (Cyclic Voltammetry and Electrochemical Impedance Spectroscopy) using Gamry reference 3000.

3. Results and Discussion

X-ray diffraction analysis was used to determine crystal structure, lattice parameters and detect that samples have a single or multi-phase phase [20]. Figure 1 shows the results of the refinement of ZnONR/Aluminum foil electrodes. The samples indicated by ZnONR 1500, ZnONR 2500, and ZnONR 3000 are associated with the electrodes, which were deposited under 1500, 2500, and 3000 rpm.

From this figure, we found that the ZnONR electrode is a single-phase, although the peaks of the substrates also exist in the patterns. It also shows the changes in diffraction intensity as a function of spin coating speed. Different intensity patterns supposed originated from different ZnONR content and morphology. The higher the spin-coating speed supposed to the lower the thickness and intensity of ZnONR. Bragg peaks in the XRD pattern can be analyzed well into the ZnO phase with COD 900887. The crystal structure model of ZnO with the hexagonal wurtzite structure which has a lattice constant a = b = 3.2495 Å, c = 5.2069 Å (α = β = 90°, γ = 120°) dan space group P63mc (number 186) and the Wyckoff position in 2b. A detailed observation of the lattice parameters extracted from the refinement we obtain that there is a change with an increase in the speed of spin coating as listed in Table 1.
Besides grown on thicker seeds. With research conducted in the last row of Table 1, the crystallinity of the electrodes with the peaks intensity is respectively shown by the electron diffraction. As seen in Figure 2, we may observe the (010) and (011) peaks, which is closely fit to work reported by Shamhari et al [21]. Figure 3 describes a specific structure of hexagonal wurtzite of our work.

Crystallinity is strongly related to the intensity of diffraction peaks compare to the total background. As seen in Figure 2, we may observe the (010) and (011) peaks. In qualitative view, we may obtain that the peaks intensity is respectively shown by the electrode with 1500, 2500, and 3000 rpm. The ZnONR crystallinity of the electrodes was calculated using our previous method [22,23]. The results are listed in the last row of Table 1. These results show the best crystallinity due to the high content of ZnONR, where most free suppressed to initiate nucleation and less pressure to grow. These results are consistent with research conducted by Jia et al [24], Which showed that ZnONR has better crystallinity when grown on thicker seeds. The thickness of our electrodes is inferred from the SEM images as follows. Besides, we further explore the diameters of ZnONR of the electrodes.

Figure 4 shows the surface morphology of the ZnONR/Aluminum foil film with a spin coating speed of 1500, 2500, and 3000 rpm. The average diameter was calculated using ImageJ software from measurements of 240 points.

Table 1. Lattice parameters of ZnONR/Aluminum foil electrodes

| Parameters                      | 1500     | 2500     | 3000     |
|--------------------------------|----------|----------|----------|
| $a = b$ (Å)                    | 3.2631   | 3.2583   | 3.2568   |
| $c$ (Å)                        | 5.2151   | 5.2284   | 5.2296   |
| Atomic Position ($z_O$)        | 0.3656   | 0.3556   | 0.3487   |
| $c/a_o$                        | 1.6      | 1.6      | 1.6      |
| $X^2$                          | 1.472    | 1.593    | 1.687    |
| $R_p$                          | 0.1914   | 0.2705   | 0.2117   |
| $R_{wp}$                       | 0.2544   | 0.2031   | 0.2769   |
| $V$ (Å³)                       | 55.529   | 55.507   | 55.469   |
| Crystallinity (%)              | 62       | 50       | 45       |

It is readily seen that the lattice and volume parameters increase significantly compared to the model. The results of the structure analysis show that the lattice parameters for all samples have $c/a_o$ ratio of 1.6. This result is closely fit to work reported by Shamhari et al [21]. Figure 3 describes a specific structure of hexagonal wurtzite of our work.

Figure 4. The diameter of ZnONR on ZnONR/Aluminum foil Spin Coating speed of (a) 1500, (b) 2500, and (c) 3000 rpm.
Figure 5. The thickness of ZnONR on film ZnONR/Aluminum foil Spin Coating speed (a) 1500, (b) 2500, and (c) 3000 rpm

Figure 5. shows the calculation of the thickness of the deposited material using software ImageJ. Measurement was performed by taking 40 different points and averaged to obtain an average thickness. The lower grain size distribution increases the porosity, reactivity, and mechanical properties of the material so that the large surface area and surface mobility become more active [14,25,26]. The effect of spin coating speed on porosity is shown in Figure 6. The average diameter and thickness of ZnONR/Aluminum foil electrodes are listed in Table 2.

Figure 6. The porosity of ZnONR/Aluminum foil Electrodes speed of various Spin Coating.
Table 2. Thickness and Diameter of Film ZnONR/Aluminum foil Electrodes

| Speed of Spin Coating (rpm) | Thickness (μm) | Diameter (nm) |
|-----------------------------|----------------|---------------|
| 1500                        | 6.76           | 282           |
| 2500                        | 5.96           | 106           |
| 3000                        | 3.96           | 103           |

Table 2 shows that the higher the spin-coating speed, the deposited material will be less so that the thickness of the sample decrease. The average diameter of the ZnONR grain size mode may also reduce. The thickness of ZnONR of the electrodes decreases as speed increases [27]. These results are consistent with research conducted by Ghayour et al., the higher the thickness of the ZnONR diameter, the greater the thickness, which increases [28].

Figure 6 shows that the higher the speed of the spin coating, the higher porosity. This result is following the theory that porosity is inversely proportional to the surface area [29]. ZnONR/Aluminum foil 1500 rpm has the highest surface area by using equation (1).

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\text{Porosity} = \frac{\sum A_{\text{porosity}}}{A_{\text{total}}}
\]  

(1)

According to research conducted by M. Wang et al., ZnONR shows good ion diffusion because of its electrolyte binding ability and high electron mobility [18,30]. The composition of ZnONR/Aluminum foil electrodes proven in the SEM-EDAX. The results are shown in Table 3.

Table 3. EDAX films ZnONR/Aluminum foil Electrodes

| Element | % mass (Wt%) | 1500 | 2500 | 3000 |
|---------|--------------|------|------|------|
| Zn      | 87.74        | 84.06| 83.72|
| O       | 12.26        | 15.94| 16.28|

Figure 7. (a) Cyclic Voltammetric Supercapacitor Symmetric ZnONR/Aluminum foil in variated Spin Coating Speed 1500, 2500, and 3000 rpm scan rate 20 mVs⁻¹ (b) Correlation Spin Coating Speed and Capacitance of Symmetric Supercapacitor ZnONR/Aluminum foil

Figure 7 shows the lower spin speed; the specific capacitance of ZnONR will be higher because ZnO nanoparticle material is deposited well on the aluminum foil substrate. High Zn content will be able to improve storage performance because the ZnONR surface area will be higher. Specific capacitance and energy density of ZnONR /Aluminum foil symmetric supercapacitors are shown in Table 4.
Table 4. Specific Capacitance and Energy Density of Supercapacitor Symmetric ZnONR /Aluminum foil scan rate of 20 mVs$^{-1}$

| Speed of Spin Coating (rpm) | Capacitance Specific (Fg$^{-1}$) | Energy Density (Whg$^{-1}$) |
|-----------------------------|----------------------------------|----------------------------|
| 1500                        | 0.00867                          | 0.00433                    |
| 2500                        | 0.00736                          | 0.00368                    |
| 3000                        | 0.00351                          | 0.00175                    |

Table 4 shows the increasing speed of spin coating specific capacitance and decreasing energy density. Cyclic Voltammetric at a scan speed of 20 mVs$^{-1}$ is the most effective way to determine supercapacitor performance because the lower electrolyte scan speed has enough time to enter the micropore, stable ionic response and the micropore is used effectively to form a double layer capacitance [31]. The specific capacitance, as well as the energy density, are the most critical parameters to determine the performance of supercapacitors.

From this study, we have learned that the initial speed rotation of ZnO deposition is significantly affected the microstructure as well as the electrochemical performance. The ZnONR/Al electrodes in this study is lower than the criterion of the supercapacitors. This result is acceptable due to the composition of the electrodes merely from the semiconductors. Technically we know that the lower speed of rotation may give rise to better electrochemical performance. The implication for the next research is to combine the ZnONR with higher dielectric constant, other metal oxides as well as carbon-based materials. The ZnONR may help to increase the time-release of energy during the discharging of the supercapacitors of future works.

4. Conclusion
In summary, we found that the higher the spin-coating speed, the less the material capable of depositing on the substrate surface; hence the microstructure as well as the electrochemical performance also reduce. The crystal structure of ZnONR in ZnONR/Aluminum foil electrodes is hexagonal wurtzite. As the spin-coating speed increases, the porosity also increases, while the size of the grain, crystallinity, and specific capacitance reduce. Therefore, the best performance is shown by the lowest speed of 1500 rpm with the condition show Zn more deposited rods, the highest Zn content, the highest cycle stability, and the specific capacitance reaches to 0.0086 Fg$^{-1}$ with energy density 0.00433 Whg$^{-1}$.

References
[1] Outlook W E 2018 World Energy Outlook 2018
[2] Hau W, Sim P, Shee S and Wee C 2018 Recent development of mixed transition metal oxide and graphene / mixed transition metal oxide based hybrid nanostructures for advanced supercapacitors Recent development of mixed transition metal oxide and graphene / mixed transition metal oxide based by J. Alloys Compd. 775 1324–56
[3] Zhang L L and Zhao X S 2009 Carbon-based materials as supercapacitor electrodes 2520–31
[4] Lin R Y 2020 Advanced Solar Power Technology-Multiple Junction Photovoltaics Innovations in Sustainable Energy and Cleaner Environment ed A K Gupta, A De, S K Aggarwal, A Kushari and A Runchal (Singapore: Springer Singapore) pp 505–27
[5] Duan J and Tang Q 2019 A revolution of photovoltaics: persistent electricity generation beyond solar irradiation Dalt. Trans. 48 799–805
[6] Hu J, Chu Y, Tian Q, Guo S, Yang M, Wang X and Zhao L 2017 Electrochemical properties of the NiCl$_2$ cathode with nickel foam substrate for thermal batteries Mater. Lett. 207 198–201
[7] Fibriyanti A A, Fuad A, Astutik W, Hidayat N, Prihandoko B, Mufi N and Diantoro M 2019 Synthesis and Crystal Structure Analysis of LiNiSi x P 1-x O 4 /C as a Cathode Material for the Lithium-ion Batteries Application IOP Conf. Ser. Mater. Sci. Eng. 515
[8] Parveen N, Ansari M O, Han T H and Cho M H 2017 Simple and rapid synthesis of ternary polyaniline / titanium oxide / graphene by simultaneous TiO 2 generation and aniline oxidation as hybrid materials for supercapacitor applications J. Solid State Electrochem. 57–68
Yi C P and Majid S R 2018 The Electrochemical Performance of Deposited Manganese Oxide-Based Film as Electrode Material for Electrochemical Capacitor Application *Semiconductors - Growth and Characterization* ed R Inguanta and C Sunseri (InTech)

González A, Goikolea E, Andoni J and Mysyk R 2016 Review on supercapacitors: Technologies and materials *Materials* **58** 1189–206

Jiang Y and Liu J 2019 Definitions of Pseudocapacitive Materials: A Brief Review *ENERGY Environ. Mater.* 2 30–7

Mufti N, Idiawati R, Wisodo H, Laksono Y A, Fuad A and Diantoro M 2018 The Effect of ZnO Nanorods Morphology on Electrical Properties of Perovskite Solar Cells *J. Phys. Conf. Ser.* 1093

Masrul M Z, Suprayogi T, Diantoro M, Fuad A, Latifah E and Hidayat A 2019 The Effect of Light Irradiation on Performance of Photo-Supercapacitor of FTO/TiO2-ZnO-β Carotene-Quercetin/Carbon/Al/PVDF-BaTiO3 /Al IOP Conf. Ser. Mater. Sci. Eng. 515

Mustikasari A A, Diantoro M, Mufti N and Suryana R 2018 THE EFFECT OF NANO ZnO MORPHOLOGY ON STRUCTURE, DIELECTRIC CONSTANT, AND DISSIPATION FACTOR OF CA-NANO ZnO/ITO FILMS *J. Neutrino* 10 65

Pruna A, Shao Q, Kamruzzaman M, Zapien J A and Ruotolo A 2015 Enhanced electrochemical performance of ZnO nanorod core/polyaniline shell arrays by graphene oxide *Elsevier Ltd*

Liu X, Liu H and Sun X 2020 Aligned ZnO nanorod@Ni-Co layered double hydroxide composite nanosheet arrays with a core-shell structure as high-performance supercapacitor electrode materials *CrystEngComm* 22 1593–601

Hadi Al-Weally D, Mebdir Holi A and Abdullah Al-Zahrani A 2019 Structural, Optical, Morphological Properties of ZnO Nanoparticle/ZnO Nanorods *J. Phys. Conf. Ser.* 1294

Suprayogi T, Masrul M Z, Diantoro M, Taufiq A, Fuad A and Hidayat A 2019 The Effect of Annealing Temperature of ZnO Compact Layer and TiO 2 Mesoporous on Photo-Supercapacitor Performance *IOP Conf. Ser. Mater. Sci. Eng.* 515

Li Z, Liu P, Yun G, Shi K, Lv X, Li K, Xing J and Yang B 2014 3D (Three-dimensional) sandwich-structured of ZnO (zinc oxide)/rGO (reduced graphene oxide)/ZnO for high performance supercapacitors *Energy* 69 266–71

Khan M I, Bhatti K A, Qindeel R, Alonizan N and Althobaiti H S 2017 Characterizations of multilayer ZnO thin films deposited by sol-gel spin coating technique *Results Phys.* 7 651–5

Shamhari N M, Wee B S, Chin S F and Kok K Y 2018 Synthesis and characterization of zinc oxide nanoparticles with small particle size distribution *Acta Chim. Slov.* 65 578–85

Diantoro M, Fitriana I N, Parasmayanti F, Nasikhudin, Taufiq A, Sunaryono, Mufti N and Nur H 2017 Crystallinity and Electrical Conductivity of PANI-Ag/Ni Film: The Role of Ultrasonic and Silver Doped IOP Conf. Ser. Mater. Sci. Eng. 202

Sawitri R A, Suryanti L, Zuhri F U and Diantoro M 2019 Dielectric Properties of Dirt Sugarcane Sediment (DSS) Extract-BaTiO3 for Organic Supercapacitors *IOP Conf. Ser. Mater. Sci. Eng.* 515

Xu J, Huang J, Zini M, Cheng C, Jin T and Huang B 2020 A facile synthesis of ZnO nanorods on nitrogen-doped graphene sheet for supercapacitor applications *Int. J. Electrochem. Sci.* 15 765–73

Mufti N, Abadi M T H, Yasrina A, Sunaryono, Yudyanto, Diantoro M and Fuad A 2019 Photoelectrochemical Performance of ZnO Nanorods Grown on Stainless Steel Substrate *IOP Conf. Ser. Mater. Sci. Eng.* 515

Hewlett R M and McLachlan M A 2016 Surface Structure Modification of ZnO and the Impact on Electronic Properties *Adv. Mater.* 28 3893–921

Ghayour H, Rezaie H R, Mirdamadi S and Nourbakhsh A A 2011 The effect of seed layer
thickness on alignment and morphology of ZnO nanorods *Vacuum* 86 101–5

[29] Dewi A S P, Mufti N, Fibriyanti A A, Diantoro M, Taufiq A, Hidayat A, Sunaryono and Nur H 2020 The improvement of Triboelectric effect of ZnO Nanorods/PAN in flexible Nanogenerator by adding TiO2 nanoparticle *J. Polym. Res.* 27 1–10

[30] Xiao X, Han B, Chen G, Wang L and Wang Y 2017 Preparation and electrochemical performances of carbon sphere @ ZnO core-shell nanocomposites for supercapacitor applications *Nat. Publ. Gr.* 1–13

[31] Bang J H, Lee H-M, An K-H and Kim B-J 2017 A study on optimal pore development of modified commercial activated carbons for electrode materials of supercapacitors *Appl. Surf. Sci.* 415 61–6

**Acknowledgment**

This research was supported by a research grant [4.3.401/UN32.14.1/LT/2020] of PNBP UM 2020.