Ag nanoparticles effect on BaTiO$_3$-Graphite-AC/Aluminum foil symmetric supercapacitor

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Abstract. Many supercapacitor studies focus on materials that are inflexible and have low specific capacitance. The addition of low dimension metals such as silver nanoparticles (AgNP) into the BaTiO$_3$-Graphite-Activated Carbon (AC)/Aluminum foil showed a change in structure and morphology. The AC and graphite are generally used as necessary materials for supercapacitors. Adding AgNP is expected to increase the general mobility and specific capacitance of BaTiO$_3$-Graphite-AC/Aluminum foil. In this study, we report the effect of AgNP into Graphite-AC-BaTiO$_3$/Al foil symmetric supercapacitors. In the first step, we prepared nanocomposite comprises (x)AgNP-graphite-AC-BaTiO$_3$. The dense solution then deposited on to clean aluminum foil as an electrode. The symmetric supercapacitors were sandwiched using two electrodes separated by a separator and electrolyte. It is shown that the crystal structure and morphology change with the addition of AgNP. The Optimum capacitance of Ag-BaTiO$_3$-Graphite-AC/Aluminum foil supercapacitor obtained from LCR meter of $1.9 \times 10^{-5}$ F/g and dielectric constant of $1.03 \times 10^6$. The cyclic voltammetry test for three-electrode systems produces a specific capacitance of 8.95 F/g and 0.83 F/g for testing two electrode systems. We obtained that the increase of AgNP increases the specific capacitance of the electrode and supercapacitor to the optimum at 0.06 g Ag.

1. Introduction

Recently, the rapid growth of the human population requires fossil fuels as a sustainable source of energy is very inefficient [1]. Therefore, meeting energy needs with environmentally friendly and high efficiency is now significant and necessary [2]. Energy storage technology systems are needed [3], which are as crucial as generators and harvesting energy. At present, batteries and supercapacitors have been developed as energy storage devices [4,5]. Supercapacitors receive more attention because of their high power density, upper operational age, and charging speed [6,7]. Supercapacitors have experienced significant development in recent years [8]. Recalling the emergence and development of portable electronic devices has become very widespread in everyday life [8]. In general, supercapacitors are divided into three categories: symmetric, asymmetric, and hybrid SC [9].

So far, symmetric supercapacitor research has been carried out by composites metal oxides with conductive carbon and polymers [10–13]. Researchers have produced AC-based supercapacitors [14], graphene [15], CNT [8], and graphite [16]. The carbon material is used because it shows excellent chemical / physical stability of high electrical and thermal conductivity, cheap, and environmentally friendly [17]. Graphene with maximum porosity has large capacitance values of 135 and 99 F/g [8]. But
Graphene is relatively expensive, so alternative materials such as graphite are needed. Graphite is an electrode candidate with superior chemical stability in electrical properties, mechanical properties, and large surface area [18].

Barium titanate (BaTiO$_3$) is a porous ceramic formed by ionic or covalent bonds [19]. BaTiO$_3$ is a good dielectric material [20]. Because of these beneficial properties, BaTiO$_3$ is widely applied in various fields such as semiconductors, capacitors, solar cells, microphones, electrodes, etc. [19,21]. To optimize the performance of BaTiO$_3$ as a dielectric material, it is necessary to compose with material which has superior properties such as graphite and carbon. Research has been carried out that the addition of AgNP material to activated carbon increases the porosity and capacitance of Ag@Carbon active film [14]. This is because Ag is an electroactive porous material suitable for electrolyte ions with high capacitance. Because it is difficult to find in the study literature on Ag-BaTiO$_3$-Graphite-AC electrode-based supercapacitors, this research needs to be done. The addition of AgNP with mass variations is needed to determine the optimum capacitance value. Whereas the flexibility requirements can be obtained from the use of aluminum foil substrate which is conductive, inexpensive, and is often used to improve the performance of supercapacitor electrodes [22]. This research is focused on making Ag-BaTiO$_3$-Graphite-AC/Aluminum foil material by increasing the capacitance of the material and forming a flexible supercapacitor device.

2. Methods

2.1. Synthesis Ag nanoparticles
Ag nanoparticles are synthesized using chemical reduction methods. The raw material used in this work were silver nitrate (AgNO$_3$ 99.9%), Sodium Borohydride (NaBH$_4$ 99.9%), and mercaptosuccinic acid (MSA 99.9%). Initially, 0.03 M MSA was dissolved in 400 mL of methanol and then stir at a speed of 700 rpm in an ice bath at a temperature of 5-10 °C. We add 0.3 M AgNO$_3$ in the mixed solution. Furthermore, we added 0.2 M NaBH$_4$ drop-by-drop using a burette for 2 hours into the solution. After completed, the solution was further stirred for 30 minutes at a speed of 700 rpm at 5-10 °C. The yielded solution was then washed three times using 200 mL methanol. Then, Ag nanoparticle powders were filtered using Whatman paper and subsequently dried at 50 °C.

2.2. Fabrication of Ag-BaTiO$_3$-Graphite-AC/Aluminum foil electrode
The working electrode was fabricated by mixing 75 wt% of the active material Ag-BaTiO$_3$-AC, 15 wt% of a conductive agent (graphite), and 10 wt% of the binder (PVDF). The materials were purchased from Sigma-Aldrich and Merck. Powder crushed for 1 hour using a pestle and mortar. Then, the homogenous powder was dissolved in NMP solvent with a speed of 500 rpm at 80 °C for 3 hours until a homogeneous slurry was achieved. The coating process on Aluminum foil (1 x 2 cm$^2$ working area) using a doctor blade method. After that, the film was dried on a hotplate at 80 °C for 3 hours. The process was repeated with the same steps for variations of 0, 0.02, 0.04, 0.06, 0.08, and 0.1 g AgNP mass.

2.3. Assembly of symmetric supercapacitor
Ag-BaTiO$_3$-Graphite-AC/Aluminum foil electrode was selected as active materials for the positive and negative electrode. The electrolyte solution was made by mixing H$_3$PO$_4$ with DI water at a magnetic stirrer at a speed of 800 rpm at 80 °C, and the separator was polyethylene paper. The schematic illustration arrangement of a symmetric supercapacitor, as illustrated in Figure 1.

The structure and phase of the electrode were identified using the X-Ray Diffractometer instrument with Cu-Kα radiation (λ = 1.5418 Å). The electrode morphology was characterized by SEM. The capacitance under the influence of frequency was recorded using LCR AC Keithley merk. The electrochemical studies of the electrodes and supercapacitors were carried out from instrument Cyclic voltammetry (CV) using Gamry Instrument Interface 6000 in a standard two and three-electrode cell system.
Figure 1. Schematic illustration of symmetric supercapacitor

3. Results and Discussion

3.1. Structural analysis

3.1.1. Ag nanoparticles

The silver nanoparticles (AgNP) have been successfully synthesized using a chemical reduction method with a crystal size of 43.1678 nm using the Debye Scherrer equation. AgNP has five diffraction peaks at 2θ of 38.05°, 44.21°, 64.35°, 77.33°, and 81.49° associated to the Bragg’s planes of (111), (200), (220), (311) and (222) respectively. This result is suitable with the reported work of Singh et al., where the main peak of AgNP is at an angle of 2θ = 38.08°, 44.26°, 64.37°, 77.30°, and 81.44°[23]. Further analyses of the crystal parameters were fitted using a model of AMCSD no. 001135. The crystal lattice parameters of the AgNP model are $a = b = c = 4.08620 \text{ Å} = 4.0905 \text{ Å} = 4.0905 \text{ Å}$, ($\alpha = \beta = \gamma = 90^\circ$), the crystal lattice volume was 68.23 Å$^3$ under Fm-3m cubic space group. The result of the refinement using GSAS software is shown in Figure 2. The lattice parameter $a = b = c = 4.0905 \text{ Å}$, ($\alpha = \beta = \gamma = 90^\circ$), and the crystal lattice volume is 68.447 Å$^3$. The results obtained are not much different between AgNP synthesis and model data.

![Figure 2. The diffraction pattern of AgNP refinement by GSAS software](image)

3.1.2. Ag-BaTiO$_3$-Graphite-AC/Aluminum foil electrode

Positive and negative electrodes of symmetric supercapacitors were made of Ag-BaTiO$_3$-Graphite-AC materials. The diffraction pattern of Ag-BaTiO$_3$-Graphite-AC/Aluminum foil with mass variations 0.02 – 0.1 Ag is shown in Figure 3. Composite films were successfully synthesized by the presence of Ag, BaTiO$_3$, AC phase as an active material, and graphite as a conductive agent.
Figure 3. The diffraction pattern of Ag-BaTiO₃-Graphite-AC/Aluminum foil electrodes

The most definite diffraction peaks of Ag nanoparticles appeared at an angle of 2θ = 38.03°, 44.17°, 64.37°, 77.33°, and 81.43° which were specific to Ag nanoparticles. AgNP mass increases from 0.02-0.1 g. The peak intensity of Ag is increase as the mass of AgNP in the film is increasing. This result will further be discussed by comparing it with the results of EDX. The diffraction pattern of BaTiO₃ on the nanocomposite film showed 2θ = 21.86°, 31.32°, 38.60°, 45.24°, 50.52°, 56.04°, and 74.44° with cubic phase and space group Pm-3m. This diffraction pattern is not much different from previous studies by Singh et al. namely, at 2θ peaks at 22.208°, 32.17°, 38.898°, 45.590°, 50.812°, 56.127°, and 74.788° correspond to the (100), (110), (110), (111), (200), (210), (211), (310) planes of BaTiO₃ (COD no. 4124442) [19]. Furthermore, the diffraction pattern of graphite at 2θ = 26.58° with tetragonal phase and space group Fm-3m which is accordance with Devrim et al research that is the highest diffraction peak at 2θ = 26.5° in the (002) plane (AMCSD no. 0000049) [24]. Besides that, visible diffraction peaks of aluminum foil as an electrode substrate due to its conductive nature and film thickness are also one of the factors. Manikanda et al, have shown that the strong diffraction 20 peaks at 38.52°, 44.76°, 65.14°, 78.26°, and 99.11° which appropriate with planes of (111), (200), (220), (311), (400) respectively. It indicates the pure aluminum phase [25]. The results of crystal structure analysis of Ag-BaTiO₃-Graphite-AC composite films using the GSAS software to determine the lattice parameters, atomic position, and crystal size are shown in Table 1.

| Table 1. Crystal structure parameters of AgNP | 0.02 | 0.04 | 0.06 | 0.08 | 0.1 |
|---------------------------------------------|------|------|------|------|-----|
| Parameter                                  |      |      |      |      |     |
| Crystal system                              | Cubic| Cubic| Cubic| Cubic| Cubic|
| Space group                                 | Fm-3m| Fm-3m| Fm-3m| Fm-3m| Fm-3m|
| a = b = c (Å)                               | 4.1002| 4.0944| 4.0997| 4.1002| 4.0994|
| Atomic position of Ag                       | 0; 0; 0 | 0; 0; 0 | 0; 0; 0 | 0; 0; 0 | 0; 0; 0 |
| χ²                                         | 2.626 | 2.453 | 1.893 | 1.812 | 1.756 |
| Rwp                                         | 0.3215 | 0.3185 | 0.2794 | 0.2702 | 0.2639 |
| Rp                                          | 0.2361 | 0.2346 | 0.2039 | 0.1983 | 1.962 |
The particle sizes of Ag, BaTiO$_3$, and graphite on Ag-BaTiO$_3$-Graphite-AC/Aluminum foil composite films were obtained from a calculation using the Scherrer equation. Particle size of AgNP with the addition of Ag mass 0.02, 0.04, 0.06, 0.08, and 0.1 g respectively produced AgNP sizes of 41.70, 32.75, 26.11, 39.9, and 40.01 nm. The particle size of BaTiO$_3$ has changed along with the addition of AgNP mass, namely 42.67, 38.24, 32.37, 39.50, and 39.74 nm. Besides, the particle size of graphite also changed, namely 49.87, 43.96, 36.25, 48.06, and 48.35 nm. The addition of AgNP mass resulted in an optimum decrease of particle size at 0.06 g which can be seen in Figure 4. From the Figure, it can be seen that the addition of AgNP mass has a specific limit. This limit is estimated to be a competition between the amount of AgNP and the interaction between AgNP and other compounds. This interaction is believed to be a surface interaction with hydrogen bonds or van der Waals which allows the modification of some Ag into Ag ions. The pattern of particle size change due to the addition of AgNP mass is believed to affect other physical properties.

![Figure 4. AgNP particle size as a function of adding Ag mass](image)

### 3.2. Morphology Analysis of AG-BaTiO$_3$-Graphite-AC/Aluminum foil electrodes

The morphology of the Ag-BaTiO$_3$-Graphite-AC/Aluminum foil electrode film with the mass variation of AgNP particle mass is shown in Figure 5. Figure 5a shows AgNP powders forming granules that spread and have very wide pores. Ag-BaTiO$_3$-Graphite-AC/Aluminum foil composite electrode film with AgNP mass variation from 0-0.1 g can be seen in Figure 5 (b-g). The more AgNP in the composites shows that the distribution of grains in the film also enhanced. Agglomerated particles of AgNP and BaTiO$_3$ spread on the surface of the graphite sample in the form of plates/layers [16] and fill the cavities of activated carbon. This phenomenon is originated by activated carbon material, which pore size tends to the larger, rough, and irregular surface [25]. Figure 5h is a diagram of the percentage of elemental content (Ag, C, Ba, Ti, O) on the nanocomposite film, which is the result of EDX. EDX analysis is to confirm the elemental composition of the samples. The existence of the C element is indicating the presence of activated carbon and graphite [24]. The Ba, Ti, O are elements building of BaTiO$_3$ [26]. While the Ag is an element showing AgNP, which was intentionally added into the composites [27]. Increasing variations in the mass of AgNP causes the value of percent atomic AgNP to be even higher. The mass of AgNP from EDX results is 5.73, 10.39, 12.21, 15.62, and 18.1%.
Dielectric properties of the symmetric supercapacitor

Dielectricity is obtained from the calculation of capacitance supercapacitor (C), which has been measured using LCR AC with the application of a frequency of 100 Hz - 200 kHz. Before composite with AgNP, the value of the film capacitance is $1.5 \times 10^{-5}$ F/g. This proves that the addition of AgNP mass can increase the capacitance of BaTiO$_3$-Graphite-AC/Aluminum foil films. Capacitance is affected by the frequency charged. In this discussion, frequency is the time taken by supercapacitors to reach half of the low dielectric relaxation time to determine the capacitance value [28]. It can be seen that the greater the frequency given; the resulting capacitance value of the film decreases. The increase of frequency provides the transmitted waves to increase every second. Before the polarization is fully formed, a vacuum occurs due to the direction of the electric current reversing so that the capacitance is reduced [29]. Figure 6a shows the capacitance as a function of frequency variation. We found that, as the frequency increases, the capacitance decreases. Maximum capacitance at 0.06 g AgNP mass at 100Hz gram frequency is $1.9 \times 10^{-5}$ F/g and decreases when adding Ag mass 0.08 g to 0.1 g. Similar studies have been carried out that the addition of AgNP increases the value of capacitance [30]. This pattern is influenced by the additional mass of AgNP, which will cause the supercapacitor film to decrease [31]. On the other hand, capacitance is also affected by the grain size of the film electrode. The smaller AgNP size causes the capacitance to increase because AgNP plays a role in facilitating ion transfer at the electrodes [32].

The dielectric constant of the Ag-BaTiO$_3$-Graphite-AC/Al foil supercapacitor is calculated using Equation 1.

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A}$$  

(1)
The greater the capacitance may increase linearly the dielectric constant. Figure 6b the dielectric constant decreases with increasing frequency. Large dielectric constants at low frequencies can be associated with lower electrostatic binding forces, which arise due to the polarization of the space charge near the grain boundary interface [33]. The greater addition of AgNP increases the capacitance and dielectric constant because of the higher the mass of the polarized part [11], [13]. But in this study, the optimum addition of AgNP to produce the best dielectric constant is at the mass of AgNP 0.06 g and then begins to decrease at a higher mass of AgNP 0.08 to 0.1 g. This relates to the specific capacitance, which is influenced by grain size. The smallest grain size is at the addition of 0.06 g AgNP mass, which is 26.11 nm. The maximum capacitance value is $1.9 \times 10^{-5}$ F/g to produce a dielectricity of $1.03 \times 10^6$.

Figure 6. The capacitance of (a) supercapacitor Ag-BaTiO$_3$-Graphite-AC/Aluminum foil and (b) dielectricity at different frequencies

3.4. Electrochemical Studies

3.4.1. Three electrode cell assembly

The electrochemical performance of the supercapacitor electrode is represented from the voltammetric cyclic curve area of the three-electrode system using a 0.5 M H$_3$PO$_4$ electrolyte solution. Figure 7 is a voltammetric cyclic curve from Ag-BaTiO$_3$-Graphite-AC/Aluminum foil electrode measurements with variations in the addition of AgNP at a scan rate of 20 mV/s. The rectangular shape of the CV curve shows the ideal pseudocapacitive behavior of all electrodes [34] and shows that the electrodes have excellent capacitance performance [35]. The specific capacitance value can be calculated from the voltammetric cyclic curve using Equation 2.

$$C_s = \frac{1}{2 \times v \times \Delta m \times \Delta V} \int I(V) dV \tag{2}$$

The graph of adding AgNP on the specific capacitance of the electrode is shown in Figure 7a. The addition of AgNP affects the capacitance of the electrode. The specific capacitance of AgNP variations of 0, 0.02, 0.04, 0.06, 0.08, and 0.1 g are 4.50, 6.81, 7.73, 8.95, 6.99, and 4.66 F/g at the scan rate of 5 mV/s, respectively. BaTiO$_3$-Graphite-AC/Aluminum foil electrodes show a specific influence on specific capacitance as AgNP increase. According to previous studies that the addition of AgNP increases specific capacitance due to increased contact between electrolyte ions and the surface of the electrode [35]. The optimum specific capacitance is at the addition of 0.06 g AgNP mass of 8.95 F/g and then decreases. This decrease in capacitance is influenced by the excess of AgNP in the composite so that AgNP is oxidized to Ag(1) [36]. Besides, the decrease in capacitance is influenced by the particle size of AgNP.
Figure 7. The CV curves of (a) electrode supercapacitor (x)Ag-BaTiO$_3$-Graphite-AC/Aluminum foil and (b) specific capacitance

3.4.2. Two electrode cell assembly
Symmetric supercapacitor capacitance performance can be obtained through the voltammetric cyclic curve area of the two electrode system tests. Figure 8a is a voltammetric cyclic curve from Ag-BaTiO$_3$-Graphite-AC/Aluminum foil symmetric supercapacitor measurements with variations in the addition of AgNP at a scan rate of 20 mV/s. The rectangular shape of the CV curve shows the ideal pseudocapacitive behavior of all electrodes [34] and shows that the electrodes have excellent capacitance performance [35]. The specific capacitance of the supercapacitor on the addition of Ag 0, 0.02, 0.04, 0.06, 0.08, and 0.1 g are respectively of 0.37, 0.49, 0.6, 0.83, 0.76, and 0.49 F/g as shown in Figure 8b.

Figure 8. The CV curves of (a) symmetric supercapacitor (x)Ag-BaTiO$_3$-AC/Aluminum foil and (b) specific capacitance

Supercapacitors with the addition of AgNP have greater capacitance than BaTiO$_3$-Graphite-AC/Aluminum foil supercapacitors. In accordance with previous studies that the addition of AgNP increases the specific capacitance of the supercapacitor due to increased contact between the electrolyte ion and the surface of the electrode [35]. The optimum specific capacitance of the supercapacitor is at the mass variation of AgNP 0.06 g as in the electrode capacitance. Furthermore, the capacitance value can determine the value of the supercapacitor energy density by Equation 3.

$$ED = \frac{1}{2}C_{\text{b}}(\Delta V)^2 = \frac{1}{2}m(\Delta V)^2$$

Equation 3

The energy densities of supercapacitor are 0.03, 0.04, 0.05, 0.07, 0.06 and 0.04 Wh/kg at a scan rate of 20 mV/s associated to the increase of AgNP of 0, 0.02, 0.04, 0.06, 0.08, and 0.1 g respectively. This
supercapacitor energy density is just lower than the supercapacitor's energy density, which is 1-10Wh/kg. This is because the scan rate charged for testing two electrodes is higher than the three-electrode testing systems, resulting in low specific capacitance, which then affects the energy density value. The energy density of the electrodes at the 5 mV/s scan rate is 0.20, 0.31, 0.35, 0.40, 0.31 and 0.21 Wh/kg with the addition of AgNP mass 0, 0.02, 0.04, 0.06, 0.08 and 0.1 g.

Furthermore, the optimum capacitance i.e., the addition of Ag 0.06 g, is measured by the variation of the scan rate on the electrode and the supercapacitor device to determine the capacitance performance as shown in Figure 9. The specific capacitance decreases with increasing scan rate. This is related to the mechanism of ion exchange. At a low scan rate, the time needed for ions or molecules to enter into and interact with the active electrode is more, while at a high scan rate the time required is less so that the ions only interact with the electrode surface, which results in reduced specific capacitance [37].

![Figure 9](image)

**Figure 9.** The CV curves of (a) electrode and (b) symmetric supercapacitor at various scan rates

At the same scan rate of 20 mV/s, the specific capacitance of the three-electrode system is greater than that of the two electrode system because in the three-electrode system the only electrode is tested so that it gets the capacitance of electrode only. As for the two electrode system (supercapacitor device) will get the actual capacitance value of the material. Another factor is that the current in the two-electrode system will be half of the current in the three-electrode system [38]. The two different systems will produce different specific capacitance values.

4. Conclusion

The greater the mass of AgNP in BaTiO$_3$-Graphite-AC/Aluminum foil reduces the AgNP size to the optimum value at 0.06 g and rises for a larger AgNP mass. The symmetric supercapacitor shows the performance of the dielectric constant to the optimum value at 0.06 g and falls for a larger Ag mass for all frequency ranges. The application of frequencies from 100 Hz-200 kHz causes the capacitance to decrease exponentially. Fabricated electrode film systems have shown values far above conventional capacitors and are at the lower limit of the supercapacitor system. The greater the mass of AgNP added to the Ag-BaTiO$_3$-Graphite-AC/Aluminum foil film increases the specific capacitance and energy density to the optimum value at 0.06 g and decreases for greater Ag mass. The pattern of changes in AgNP mass variation to specific capacitance is also shown by the symmetric supercapacitor system.

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