Dielectric Properties of Dirt Sugarcane Sediment (DSS) Extract-BaTiO₃ for Organic Supercapacitors

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Abstract. Filter cake (or Blotong) is a dirt sugarcane sediment (DSS) obtained from refining sugarcane. Organic Supercapacitors is a new technology combined battery and capacitor for advanced energy storage. The elements and compound containing in the DSS have potential be used as an electrode for supercapacitor. Firstly we prepared three different samples, i.e., heating at 100 °C for an hour, and addition method with H₂SO₄ and carbonation method at high temperatures. To control the specific capacitance, BaTiO₃ nanoparticles fraction was added. It has been successfully fabricated with a structure of DSS/BaTiO3/aluminum films. This supercapacitor produces an average grain size of 31.81 ± 0.29 nm and porosity of 0.63. The capacitance and specific capacitance respectively reaches to 2.44×10⁶ pF and 1100×10⁶ pF/g.

Keywords: Filter cake, supercapacitor, BaTiO₃, and specific capacity.

1. Introduction

Besides the filter cake or dirt sugarcane sediment (DSS) [1] problem, the fulfillment of electrical energy is necessary to overcome. The electricity consumption continues to increase with increasing economic activity in all sectors of energy users in the industrial, transportation, household, and commercial areas. Currently, fossil energy sources remain an option in the energy generation sector, especially electrical energy [2]. It is because the use of fossil energy has increased from year to year and the amount is decreasing, the search for alternative energy continues to be encouraged to replace the fossil energy source. The stored energy is always important in many conditions. One kind of device in storing the electrical energy is supercapacitor.

A supercapacitor is an electrochemical energy storage device that plays a role in meeting electrical energy needs. Unlike batteries, supercapacitors can provide power density with a fast charge and discharge process and a high level of stability [3]. Active carbon is becoming important in the supercapacitor electrode. The carbon-based material is relatively low prices, easy to obtain from various natural materials, easy to synthesize, and easy to be controlled. Carbon electrodes are easily polarized, stable in different solutions (acids, bases and aprotic), and stable in a certain temperature range [3]. The properties of carbon materials are strongly influenced by the method of manufacturing. Thus, the choice of the synthesis procedure, the type of precursor, type of activator, heating rate, and combustion...
temperature or pyrolysis provide ease in controlling the final product but can also design the targeted carbon type[3].

There are many studies related to the effort to find natural possible supercapacitor electrode such as supercapacitors made from CA-Nano ZnO/ITO films with capacitances reaching 2.15765 µF [4]. Cellulose acetate (CA) has been extracted from the water hyacinth which has 67.72% purity; this CA-Nano ZnO/ITO film is categorized as a porous film [5] and supercapacitors made of carbon nanosheets with graphene hydrogel which has a large specific capacitance of 242 F/g. In contrast to natural carbon, the price of graphene is very high [6]. A study of electrical properties of TiO2 nanoparticles doped flavonoids from *Pterocarpus Indicus Wild* (PIW) gum extract reported showing a dielectric constant of 75.8 [7]. The PIW flavonoid is good natural polymer sources contain flavonoids of C6-C3-C6 carbons conjugated configuration[8][9].

By far supercapacitor electrodes from DSS filter cake have not been found. The activated carbon of DSS can be prepared in 2 methods, namely carbonation [1] and the addition of H2SO4. It is known that BaTiO3 nanoparticles shows an excellent dielectric substance [10] and has a high capacity[11]. We aimed to find out the potential of DSS filter cake as a supercapacitor with and without BaTiO3 nanoparticles.

## 2. Methods

### 2.1. Materials

In this work, we used a filter cake of dirt sugar cane sediment (DSS) from local sugarcane industry. We also used H2SO4, distilled water, alcohol as solvents. BaTiO3, PVA, aluminum foil, DMF, and H3PO4.

### 2.2. Procedure

Before combining with several additions with BaTiO3 nanoparticles, we firstly prepared three different samples. The first sample was a DSS filter cake synthesized by heating at 100 °C in the oven. The second sample was prepared by dissolving using H2SO4. The precipitate was filtered using Whatman filter paper and subsequently heated in an oven. The third samples were prepared under high-temperature heating at 350, 500, and 700 °C for two hours.

From these three different procedures, we obtained a different form of powders. The obtained powders subsequently were pulverized to yield a fine and homogeneous powder. The fine DSS filter cake powder was then pressed into pellets. The filter cake samples which have the most significant capacitance were combined with BaTiO3. The pellets were annealed at 700 °C for 2 hours. The annealed samples were pulverized again and mixed with DMF solvent using a magnetic stirrer with under 600 rpm for 30 minutes. The samples that have been dissolved was spin-coated onto the aluminum foil substrate with a rotation speed of 2000 rpm for 30 seconds. The samples in the form of the film were characterized using XRF, SEM-EDX, XRD, and the capacitance testing was performed using LCR DC.

### 2.3. Data Analysis Technique

In this research, the data analysis from capacitance measurement was performed using LCR DC. Having obtained the measured capacitance values on the LCR DC, the specific capacitance value was calculated using Equation (1)

\[
C_{sp} = \frac{C}{m} \tag{1}
\]

Where \(C_{sp}\) is specific capacitance (F/g), \(C\) is capacitance measured on LCR DC (F), and \(m\) is electrode mass (g). Meanwhile, dielectric constant values were calculated using Equation (2)

\[
\varepsilon_r = \frac{C}{\varepsilon_0 \cdot A} \tag{2}
\]
where $\varepsilon_r$ is dielectric constant, $C$ is constant values measured on LCR DC (F), $\varepsilon_0$ is vacuum permittivity value, $d$ is electrode diameter (m), and $A$ is the surface area of the electrode (m$^2$).

3. Results and Discussion

The XRF data of DSS samples which were synthesized using the first and second methods showed that Mo and Si experienced reduced elements as described in Table 1. The decrease of metallic elements on the samples of the first compared to the second method is strongly due to the dissolving in H$_2$SO$_4$.

| Compound | Conc Unit (%) heated at 100 °C | Conc Unit (%) with H$_2$SO$_4$ precipitation |
|----------|-------------------------------|---------------------------------------------|
| Al       | 4.10                          | 1.50                                        |
| Si       | 21.90                         | 6.80                                        |
| P        | 2.80                          | 4.91                                        |
| S        | 17.00                         | 1.30                                        |
| Ca       | 7.72                          | 50.20                                       |
| Fe       | 7.88                          | 18.20                                       |
| Mo       | 35.00                         | 7.40                                        |

Table 1. The XRF of DSS filter cake sample using different methods

To confirm the elemental composition, we further analyzed using EDX which was complimentary in SEM machine. The results of EDX test DSS filter cake samples were synthesized using the first method (100 °C heating) showed that the C, O, Si and Ca elements was the most dominant as indicated in Table 2.

| Element | Wt%  | At%  |
|---------|------|------|
| C       | 31.40| 43.30|
| N       | 2.05 | 2.43 |
| O       | 40.23| 41.65|
| Al      | 2.75 | 1.69 |
| Si      | 6.29 | 3.71 |
| P       | 3.62 | 1.94 |
| K       | 0.56 | 0.24 |
| Ca      | 9.81 | 4.06 |
| Fe      | 3.30 | 2.43 |

Table 2. The elemental composition by EDX of DSS sample prepared under 100 °C heating

Comparing the elemental composition of DSS prepared by 100 °C heating of Table 1 and Table 2 are relatively the same. By excluding O and C as XRF could not detect them, the Ca, Si, Fe, and Al is the most prominent elements. This chemical composition is comparable to the works of similar work [1].

Figure 1 shows the phase identification of X-RD patterns data using GSAS application. From the analyses, we found that the DSS filter cakes samples with the addition of 0.125 g BaTiO$_3$ contained 51.36% BaTiO$_3$ and 48.64% SiO$_2$ crystalline phases. The sample combined with 0.175 g BaTiO$_3$ contained 63.24% BaTiO$_3$ and 36.76% SiO$_2$. The DSS filter cake combined with 0.2 g BaTiO$_3$ included 63.79% BaTiO$_3$ and 36.21% SiO$_2$. The major phase of BaTiO$_3$ in the composites show a significant amount with the BaTiO$_3$ as prepared raw materials as also reported previously[10] [11].
Figure 1. The phase of crystalline phase identification using GSAS of DSS combined with (a) 0.125, (b) 0.175, and (c) 0.2 g BaTiO$_3$.

The average of grain size was obtained from SEM images which have been analyzed using ImageJ and Origin software. We found that the average grain size is 31.81 $\pm$ 0.29 nm as shown in Figure 2. Meanwhile, for the morphology obtained from the data of SEM image is shown in Figure 3. The morphology just slightly differs from the other works [10,12]. The small discrepancy may be due to the different the dopant incorporated into the significant phase of BaTiO$_3$. 
Further electrochemical analysis of the BaTiO3 doped DSS samples was performed using CV equipment as depicted in Figure 4. From the graph of cyclic voltammetry measurement, we obtained that the increasing amount of BaTiO3 affects to the widening of the curves. It means that the capacity to carry electrical energy storage also increase.
Figure 4. I-V plots of DSS combined with (a) 0.1, (b) 0.125, (c) 0.15, (d) 0.175, and (e) 0.2 g of BaTiO$_3$

The performance of I-V of the current work is a little bit smaller compared to PANI doped [13], PANI [14] carbon-based supercapacitors. By employing Equation (1) and (2) the capacitance, specific capacitance, and its dielectric constant of various DSS filter cake samples are presented in Table 3.

| DSS                   | Capacitance (pF) | Specific Capacitance (pF/g) | Dielectric Constant |
|-----------------------|------------------|----------------------------|---------------------|
| Pure                  | 5.80             | 11.60                      | 53.27               |
| Pure + Carbonation 350 °C | 5.50             | 11.00                      | 49.09               |
| Pure + Carbonation 500 °C | 7.80             | 15.60                      | 46.10               |
| Pure + Carbonation 700 °C | 23.00            | 46.00                      | 153.59              |
| Carbonation 700 °C+0.1 g BaTiO$_3$ | $1.10 \times 10^6$ | $1100 \times 10^6$ | $2.90 \times 10^5$ |
| Carbonation 700 °C+0.125 g BaTiO$_3$ | $2.44 \times 10^6$ | $305 \times 10^6$ | $4.28 \times 10^5$ |

It is shown in Table 3 that the addition of BaTiO$_3$ affects the increase of its capacitance, specific capacitance, and dielectric constant of the sample. The more BaTiO$_3$ is added, the more capacitance, specific capacitance and dielectric constant of the sample. Since the density of BaTiO$_3$ is the highest one, the particular capacitance optimum is reached by 0.1 g BaTiO$_3$. It is seen that the undoped DSS is less dielectric than cellulose based supercapacitors [5], while the BaTiO$_3$ doped samples is consistent with previous similar research [15] but its dielectric constant is higher than our organic based film [7].

4. Conclusion
It can be obtained that DSS mostly contain elements C, Ca, Si, and Fe, which means that the DSS sample can be used as a raw material for supercapacitor electrode. The combination between carbonation about 700 °C and addition of BaTiO$_3$ fraction is promising for the use of DSS for supercapacitors. The average grain size and porosity are 31.81 ± 0.29 nm, and 0.63 respectively. From the CV analysis, the more samples with the highest energy storage are shown by the sample with 0.15 g BaTiO$_3$. We further obtained that the capacitance, specific capacitance, and dielectric constant are $2.44 \times 10^6$ pF, $1100 \times 10^6$ pF/g, and $4.28 \times 10^5$. It is suggested to further exploration for any combination of the DSS sample associated with the electrochemical properties.
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