The Effect of doped Nanostructured TiO₂/Activated Carbon Composite as Electrodes for Supercapacitor

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Abstract: Research has been carried out to make supercapacitors based on carbon nanopores and transition metal oxides. Carbon nanopores have been made from coconut shells using a simple heating method with a carrier gas with various activation temperatures to produce carbon nanopores. The activation process is carried out with the chemical compound potassium hydroxide (KOH) by heating tube flowing with nitrogen gas. The resulting carbon nanopores have a specific surface area of 1056 to 1469 m²/g with pores at nanopore size. Size of pore between mesopore and macropore sizes. The maximum specific capacitance was obtained from the nanoporous fraction. Cyclic voltammetry test results show that the specific capacitance does not only depend on the specific surface area but is also determined by the pore size distribution, especially in the mesoporous and sub-nanoporous ranges. The effect of porosity and crystallinity of carbon nanopores on supercapacitor performance was also investigated. The results show that the degree of crystallization of carbon has a significant effect on the specific capacitance. To increase the conductivity, specific surface area, and increase the nanoporosity of activated carbon, which ultimately increases the specific capacitance of the supercapacitor, the use of nano size TiO₂ materials has been investigated. From the results it is evident that the addition of TiO₂ nanoparticles affects the capacitance.

Keywords: supercapacitor, carbon, nano porous, coconut shell, KOH, composite, TiO₂, nanoparticles

INTRODUCTION

Supercapacitor, as a store of energy, has been used widely in the fields of electronics such as digital telecommunications systems, computer and pulse laser system, and so on. Supercapacitor has many advantages compared with other energy storage devices such as batteries. From the technical side, supercapacitor has a high energy density, the ability to store large energy, the principle is simple and easy construction. In terms of user friendliness, supercapacitors are not corrosive and less toxic materials[1]. The material used for the manufacture of supercapacitor electrodes include graphene, carbon nanotubes, porous carbon. Currently, the active electrode material using porous carbon supercapacitors made from natural materials are coconut shell activated carbon for products produced from coconut shell charcoal has many pores and a large surface area[2]. Porous carbon potential to be used as a supercapacitor electrode material because it has the potential for high energy density, pore accessibility is good, and the cost of making relatively cheap[3]. To increase the capacitance of a supercapacitor energy can be done by preparing a porous carbon material which has a mesoporous fraction and a high surface area. Porous carbon can be prepared by further carbonized charcoal activated carbon to form the internal pores in the form of mesoporous and microporous resulting in a larger surface area. The activation process involves mechanisms of physics gasification or insertion of a chemical compound[4]. The activation process also involves heating at relatively high temperatures. The chemical activation has several advantages, among others, require low temperatures, yield higher and micropores can be controlled. Some of the chemical compounds that are widely used such as phosphoric acid, zinc chloride, NaOH and KOH[5]. In this study, carried out the synthesis of carbon nanopore by varying the amount of KOH used in the activation process to see how the number KOH against nanopore carbon electrode surface area and its contribution to the value of the capacitance of the supercapacitor.

Based supercapacitor electrode material, it is divided into two groups: (i) carbon material with a high surface area, such as activated carbon, carbon aerogel, etc.; (ii) metal oxides such as Ru, Ni, Co, Zn, etc., and the addition of the polymer[6]. In order to improve the conductivity, the approach to incorporate nanostructured TiO₂ into

carbonaceous materials is great effectiveness and significance, which provide high electroactive surface area and reliable electrical connection for a maximum utilization of TiO2. Relative to the formers, the activated carbon (AC), one of the promising carbonaceous materials for supercapacitor, is selected because of its relatively high power density, high specific surface area, and low cost. The combination of TiO2 and AC may take advantage of the excellent electrical conductivity.

The general requirements for metal oxides are (1) The electrons in the metal oxide to be conductive, (2) the metal can exist in two or more oxidation states that coexist over a continuous range with no phase changes involving irreversible modifications of a 3-dimensional structure and (3) the protons can freely intercalate into the oxide lattice on reduction, allowing facile interconversion of O2- ↔ OH- [7]. The nanostructured metal oxide is a good material to achieve a high specific capacitance because has pseudo capacitance behavior[8]. Maryati et all, has research MnO_2 /activated carbon (AC) composite, where use variation MnO_2. Because that we try to made variation percentage TiO_2[9].

For this purpose, various metal oxides are cheap and abundant have been investigated, TiO_2 as the alternative to metal oxides. TiO_2 is a good dielectric material and exhibits faradaic capacitance. Activated carbon has a high specific surface area, good electrochemical stability, good conductivity and high supercapacitor cycle life[10]. Therefore, the combination of the surface area of activated carbon with a capacitance of TiO_2 nanoparticles is expected to form composite materials with both the faradaic capacitance of the metal oxide and the double layer capacitance of the activated carbon. This study aims to obtain the capacitance value of supercapacitors by observing the effect of adding TiO_2 nanoparticles

MATERIALS AND METHOD

Materials

The materials used are coconut shell waste as precursors, KOH as the chemical activator, HCL 0.5 M, PVDF, DMAC, distilled water, electrolyte 3M KOH, MnO_2 nano particles (20 nm) Sigma-Aldrich and separator.

Method

A. Synthesis Nano porous Carbon

Synthesis of nano porous carbon was done begins with the carbonization of coconut shell that has been destroyed. Carbonization performed at a temperature of 800 °C for 4 hours by using furnace without the aid of gas. This process produces carbon charcoal which is then crushed and screened to obtain the fine carbon powder size of 200 mesh. The charcoal is then mixed with KOH with variations in the mass ratio of carbon to KOH include 1: 3. The mixture stirred for 2 hours to ensure the continuity of the process of diffusion into the inside of the pores of charcoal, dry in open air for 24 hours at room temperature. Next process was the carbonizing process in N_2 gas atmosphere at a temperature of 700 °C for 1 hour. The last process is washing the charcoal with 0.5M HCl and distilled water repeatedly. Nanoporous carbon dried at a temperature of 100 °C to evaporate off the water contained. The surface morphology of the composite was observed using a field-emission scanning electron microscope (FESEM, X-Mex Horbia). Surface area measurement using Brunauer-Emmett-Teller (BET) by adsorption analyzer NOVA 4200 (Quantachrome) at 77 K surface area analyzer under N_2. Morphology study and the size of the crystals were analyzed by XRD Rigaku SmartLab type 3KW.

B. Preparation of Electrodes

Manufacture of sheet electrodes

The mixture of polyvinylidene difluoride (PVDF) and Dimethylacetamide (DMAC) was stirred at 80 °C for 1 hour. In this solution added activated carbon and super-P. Next MnO_2 nanoparticles with the concentration is 0%, 5%, 10%, 15% and 20% and stirred for 3 hours to reach homogeneous condition. We then paste the sludge on the aluminum sheet using Dr. Blade method and dry it on open air to make the electrode. They are then dried in the oven at a temperature of 80 °C for 1 hour.

C. Assembly the supercapacitors cells

The capacitor cells were constructed with an electrolyte-impregnated polypropylene separator sandwiched between two symmetrical Activated carbon/TiO$_2$ composite electrodes. The electrodes were pre-wetted with electrolyte before used. The supercapacitors performance was tested using a cyclic voltammogram, Electrochemical Impedance Spectroscopy, and galvanostatic instrument test. Use testing as to two electrodes system of symmetric supercapacitors.
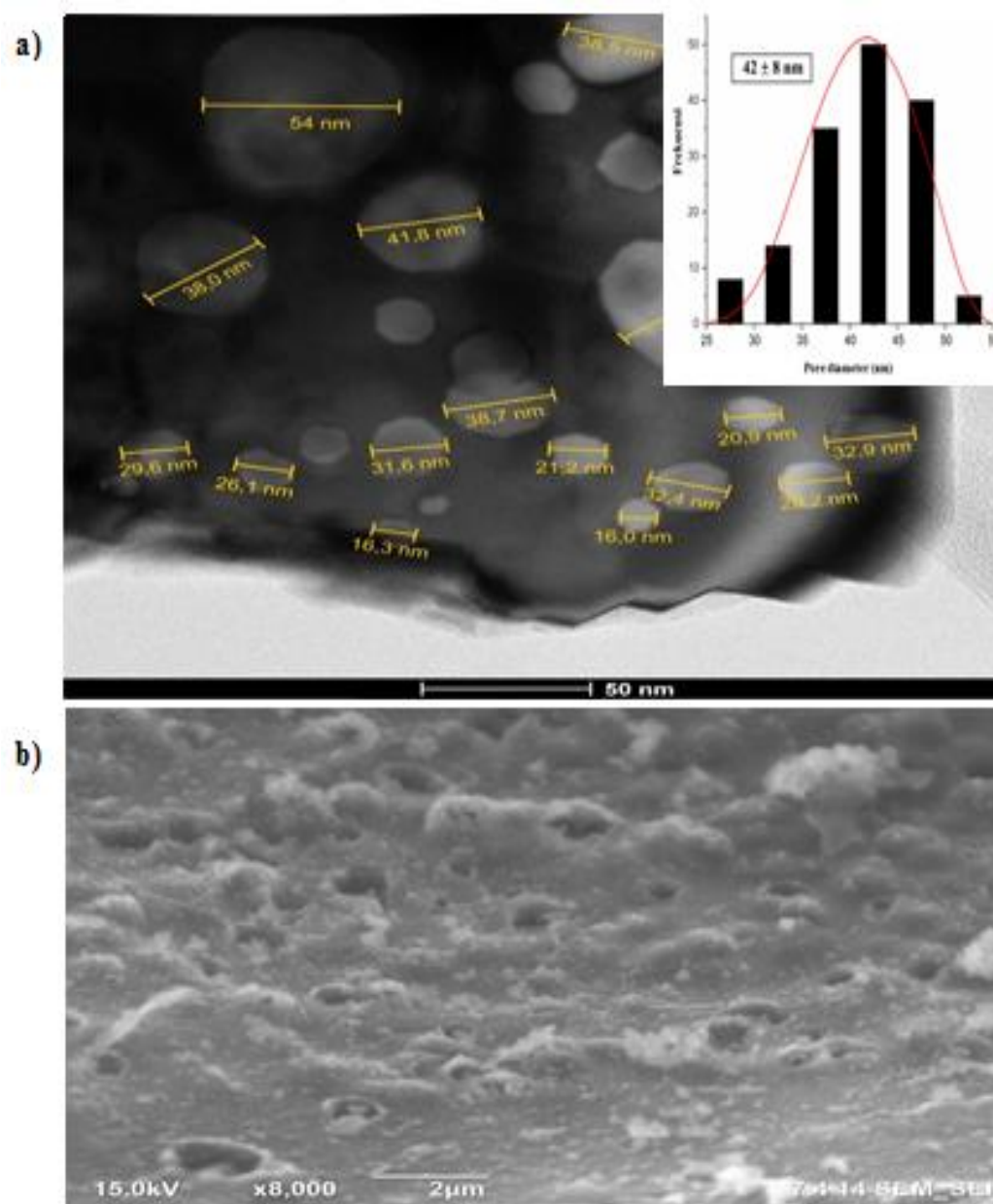
RESULTS AND DISCUSSION

Fig 1. TEM of Image of Nanoporous Activated Carbon

Morphology observation Activated Carbon

Figure 1 TEM image of nanoporous activated carbon with a surface area (SA) = 1469 m2/g, it appears that the majority of the pore sizes are in the mesoporous phase (2-50 nm) and appear to still be present at the macropore size (>50 nm). according to the pore diameter graph generated by BJH BET data. The nanoporous activated carbon

produced was prepared for supercapacitor performance tests. This nanoporous activated carbon supercapacitor uses a 3M KOH electrolyte. This electrolyte will later wet the pores on the electrode which is also a source of ions during the charging process.
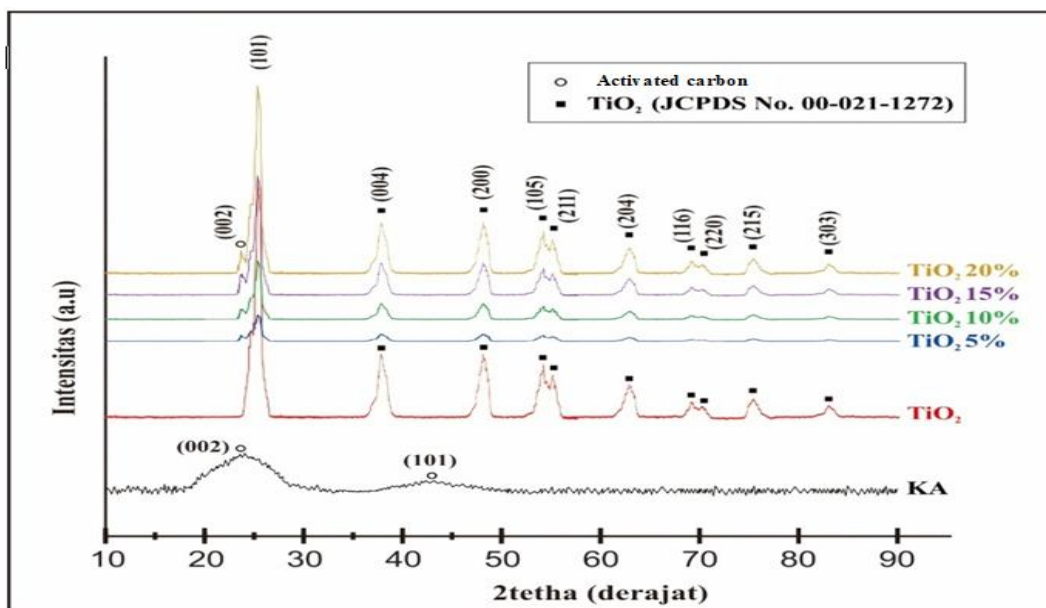

Fig 2 is an XRD spectrum of activated carbon nanopores,

TiO₂ nanoparticles and composited

Figure 2 is an XRD spectrum of activated carbon nanopores, TiO₂ nanoparticles, and composites. The XRD pattern shows the peaks of nano porous activated carbon in the (002) and (101) planes. TiO₂ peaks are in the planes (101), (004), (200), (105), (211), (204), (116), (220), (215), (303). From this pattern, it can be seen that there is no change in the crystal structure and changes in the crystal lattice spacing of nano porous activated carbon due to the addition of metal oxides. Diffraction peaks of nano porous activated carbon and metal oxides still appear in the composite electrode material. This concluded that there was no reaction due to the addition of TiO₂ nanoparticles. Composite properties are a combination of physical and chemical properties of TiO₂ and carbon nanoparticles. In this composite, between TiO₂ and carbon nanoparticles only interfacial bonds occur and are not compounded.
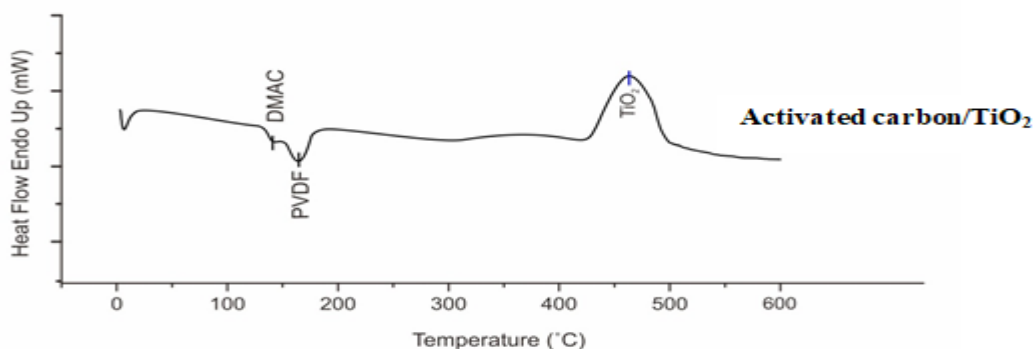

Fig 3. DSC of Composited materials

In the process of mixing composite materials, the required temperature is 90°C to maintain the bond between the materials. From the DSC data profile it can be seen the melting point of the materials used, it appears that in the composite there are still DMAC, PVDF, TiO₂, and activated carbon materials, because materials such as DMAC,

PVDF, TiO_2, and activated carbon have melting points of 165°C, 170°C, respectively. 1800°C, 3500°C. In Figure 3 the peak of TiO_2 indicates that the crystallinity temperature of TiO_2 ranges between 450-600°C.

The distribution of material supercapacitor composite electrode observed with SEM-EDX and mapping based on material which results are displayed in different colors. The results of the EDX mapping test are shown in Figure 4 for activated carbon/TiO_2 nanoparticle composite material. Results of the EDX spot, the distribution spectrum and identification of the elements in the sample are obtained. It appears that the distribution of the three elements is homogeneously distributed, and the TiO_2 nanoparticles in macropores of the activated carbon.
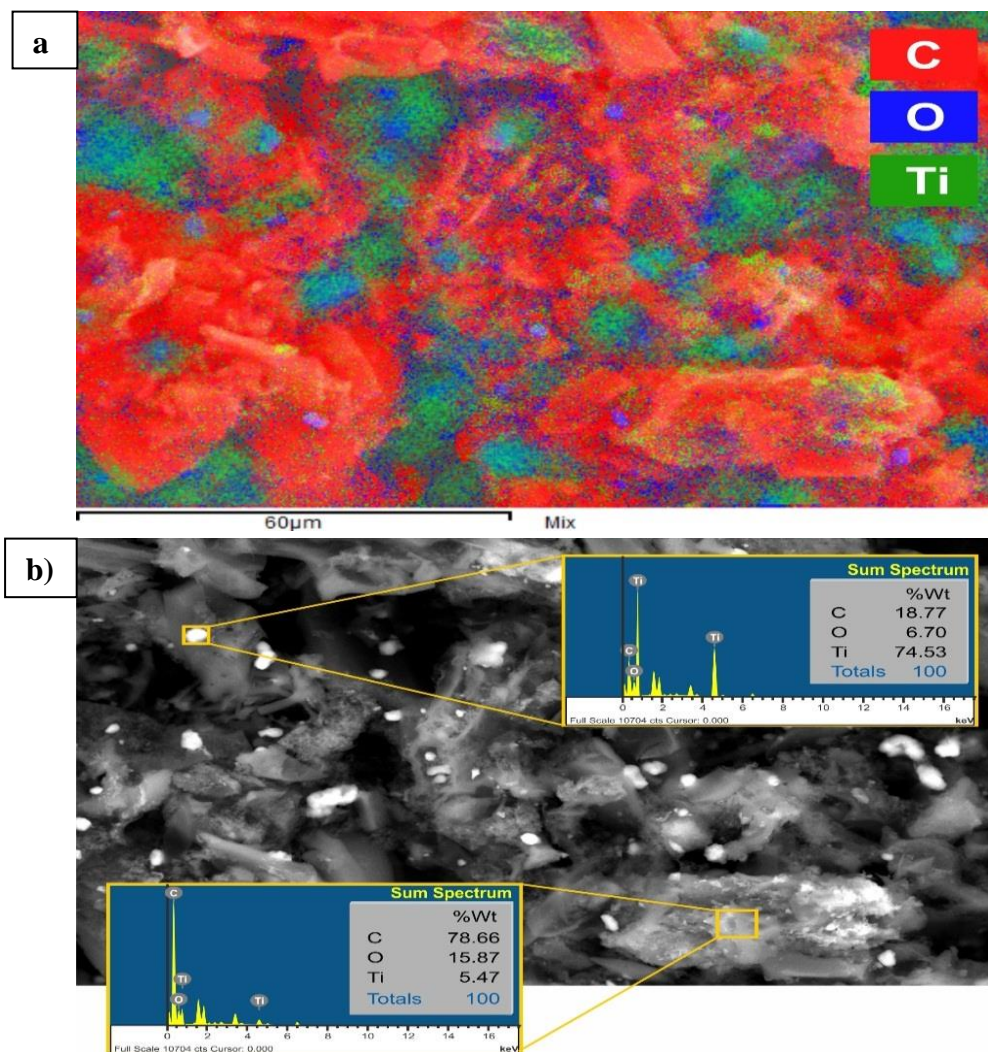

Fig 4. Mapping Activated carbon/ Nanoparticle TiO_2

The capacitance of 5% TiO_2 has the maximum value due to the large pore size distribution in the mesoporous. In addition, this is possible with the presence of crystal orientation which can increase the electrical conductivity[11]. The presence of metal oxide nanoparticles TiO_2 serves to increase the value of the supercapacitor capacitance through a redox reaction on the electrode surface. in the supercapacitor and increase the electricity of the supercapacitor. Given that the amount of energy stored in a supercapacitor depends on the amount of ion deposited, then the oxidation state in the crystal structure of TiO_2 will have a contribution in increasing the capacitance. In the cyclic voltammetry test, it appears that the more TiO_2 composition is added, the lower the capacitance value is because the added nanoparticles cover the pores in the composite, causing the surface area to decrease, resulting in a decrease in the capacitance value. The mechanism of charge storage that occurs on the surface of the electrode which is a nanoporous activated carbon/TiO_2 composite is:
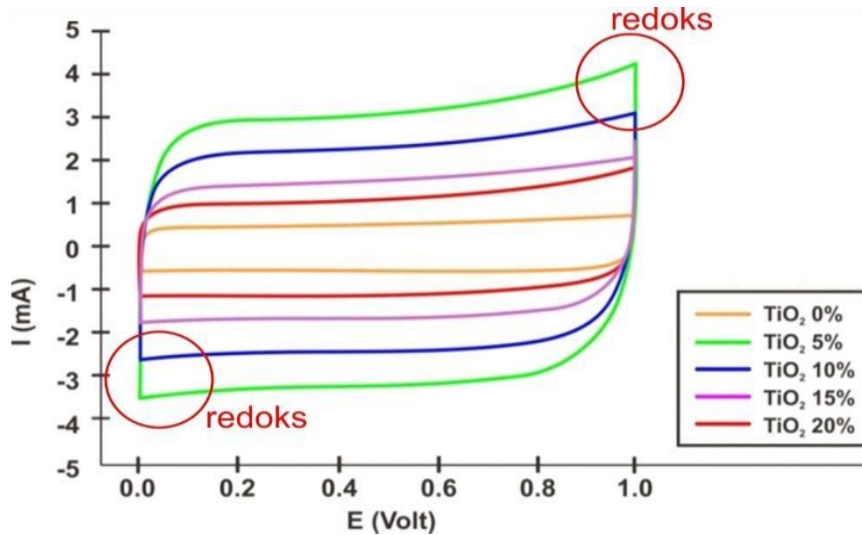
$$(TiO_2)_{surface} + K^+ + OH^- \leftrightarrow (TiO_2 K^+ OH^-)_{surface} \qquad (1)$$

Fig 5. Cyclic Voltammetry of composited activated carbon/TiO$_2$

When the KOH electrolyte dropped on the electrode, a wetting process occurs where the ions from the KOH are absorbed into the pores of the electrode. When cations from the electrolyte enter and are absorbed on the surface of the TiO$_2$ nanoparticles, a storage process occurs[12]. The process of ion movement (velocity) entering the electrode will affect the speed of the storage process, so that the storage lasts a long time, the ion size must match the pore size. In this case, the ion size is K = 0.13 nm and OH = 0.1 nm. In order for the ions to move freely, the pore size is at least 10 times the size of the ion[13]. In this case the appropriate ion size is at least 2 nm. Therefore, the pore size that is expected to become a supercapacitor electrode is in the mesoporous phase range. The relationship between the specific surface area and the specific capacitance of the supercapacitor is proportional. Where the greater the value of the specific surface area of a material, the more ions (cations and anions) that can be absorbed on the surface of the electrode so that the specific capacitance increases. Besides being influenced by the specific surface area, capacitance is also proportional to the total pore volume, where pore volume increases, the capacitance value increases. The supercapacitor was made of symmetric composite electrode TiO$_2$/AC and 3M KOH as electrolyte. The capacitance was determined using equation:

$$C_e \ (F) = \frac{\int I dv}{\Delta v . vs} \tag{2}$$

$$Csel = \frac{2Ce}{m} \tag{3}$$

Where C$_e$ is the electrode capacitance, I is the current, ΔV is potential, vs is scan rate, C$_{sel}$ is the specific capacitance of the supercapacitors cell and m is the mass of the material active electrode[14]. The CV curves of the composite electrodes reveal that the mechanism of electrochemical storage could be described by the electrical double layer theory. Energy storage in these electrodes is the accumulation of ionic charge in the double layer at the electrode/electrolyte interface and this may be due to high surface area and the porosity of the activated carbon. The results of the cyclic voltammetry test showed that the use of a carbon/transition metal oxide electrode of 0.002 g at a thickness of about 10 micrometers resulted in a specific capacitance of 100 F/g (0% TiO$_2$), 290 F/g (5% TiO$_2$), 190.80 F/g (10% TiO$_2$), 146 F/g (15% TiO$_2$), 115.6 F/g (20% TiO$_2$). This result is equivalent to a power density between 156.1- 470.8 kWh/kg, and an energy density between 50-186 kJ kg. The high capacitance achieved in these may be due to effective electrical and ionic conductivity. *C-V* tests for the variation percentage TiO$_2$ at a scan rate of 10mV/s are shown in Figure 5.

Figure 6. is the result of the Charge discharge test which shows the relationship between the length of charging and discharging time when a load current of 1A given. Of the three types of supercapacitors, the fastest charging process occurs in EDLC (Electrochemical Double Layer Capacitor) because in this process only ion transfer occurs, while in pseudocapacitance it takes time for oxidation and reduction processes[15].
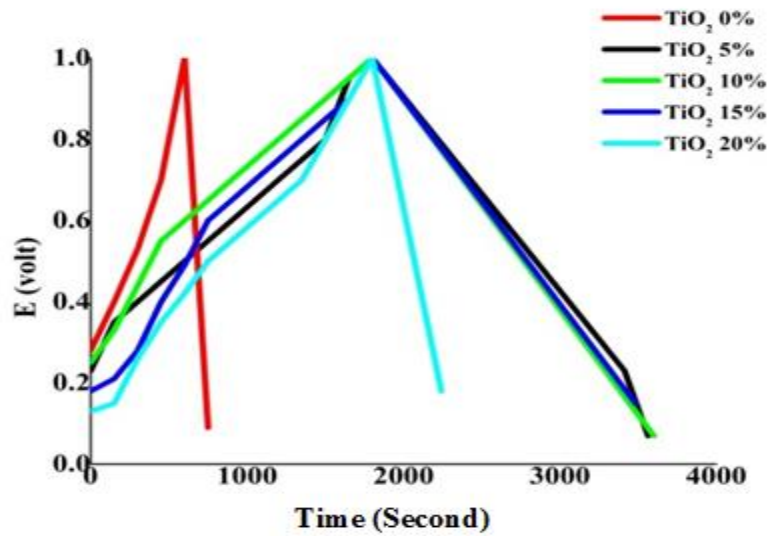
Fig 6. Charge Discharge profile

From the figure 6, it can be learned that supercapacitor cells have been able to have basic properties as electrical energy storage devices, characterized by two characteristics, namely a decrease in current with the passage of charging time and the cells can withstand the voltage level characteristic of supercapacitor cells.
From charge discharge profile, can be calculated by equation:

$$C_{sp} = \frac{4I\Delta t}{m\Delta V}$$ (4)

With C_{sp} = spesifik capacitance (F/gr), I = discharge current (A) , Δt = discharge time (s), m= mass of material elektrode (g), v = *Potential window* (V)

The voltage achieved is very good because it is close to the standard voltage value for KOH = 1-volt electrolyte (base aqua). During the charging process, the charge occurs to a potential of 1 volt. From the figure, it appears that the charging time for each electrode is different. At 0% TiO_2 charge time 350 seconds discharge 450 seconds, 5% TiO_2 charge 1800 seconds discharge 1800 seconds, 10% TiO_2 charge 1800 seconds discharge 1762 seconds, 15% TiO_2 charge 1800 seconds discharge 1683 and 20% TiO_2 charge 1800 seconds discharge 442 second. When the discharging process the voltage will decrease with the loss of charge, and the voltage never increases again at a reference potential. This decrease reflects the cell's ability to replenish. However, the discharging ability of the cell is still very low because it can only be drawn by a current of no more than 1A and the cell voltage drops drastically to 0 V. From the test results it appears that the charging and discharging time of the supercapacitor cell is the same, which should be fast charging time but this cell can still be considered as a supercapacitor cell because its capacitance is still promising.
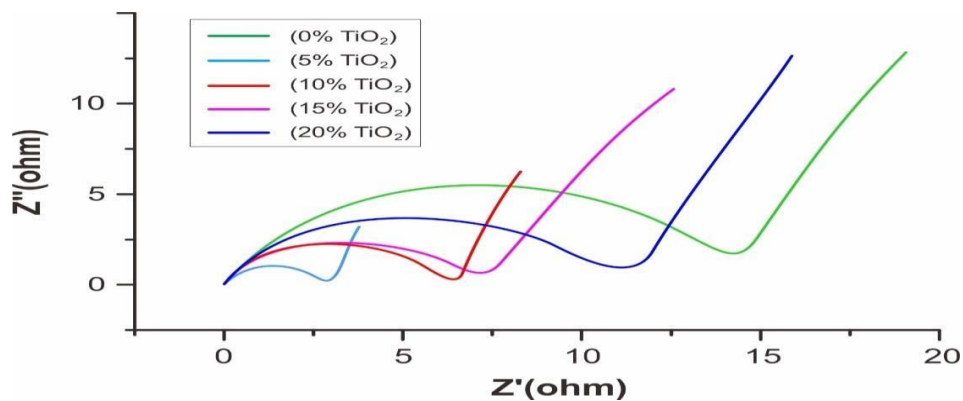

Fig 7. Electrochemical Impendence Spectroscopy (EIS) profile

Electrochemical Impendence Spectroscopy (EIS) measurements were carried out to determine contact resistance, charge transfer resistance, diffusion resistance in the pores of electrolyte ions and observe ion penetration during electrochemical processes. Figure 7, The Nyquist plot shows straight lines at low frequencies and small arcs at higher frequencies which are typical for supercapacitor behavior. Small arcs in high frequency indicate porous electrodes. The diameter of the semicircle is directly related to the resistance of the electrode and the resistance between the electrode and the current collector. The smaller the semicircle concludes that the more internal resistance. It also shows that the electrolyte ions pass through the activated carbon mesoporous very effectively. The line with a steep slope also indicates that the activated carbon obtained has a uniform mesoporous structure. Activated carbon has a higher surface area which provides a double layer forming surface, exhibiting uniform mesopores, easy access for electrolyte ions to pass through the electrode, and hence lower diffusion resistance. From EIS profile, it can be seen whether the curve has formed well. A good electrode will form a semicircle arc pattern. The impedance measurement is done by applying a voltage of 1V. The range of the frequency spectrum is given between 4 Hz - 1 MHz. From this EIS measurement, the cell conductivity can be calculated by equation:

$$R = \rho \frac{t}{A} \qquad (5)$$

From the calculation results obtained conductivity 0% TiO_2 3.55 x 10-04 S/cm, 5% TiO_2 1.98 x 10-03 S/cm, 10% TiO_2 8.06 x 10-04 S/cm, 15% TiO_2 7.30 x 10-04 S/cm, 20% TiO_2 4.72 x 10-04 S/cm. From these results, it can be seen that the highest conductivity is at the 5% TiO_2 position with a resistance of 7.3 ohms. Small resistance indicates fast ion transport. This result is better than research by Selvakumar et al[16] which produces a resistance of 20 ohms. The structural X-ray diffraction on the transition metal oxide used, it shows that there is no change in the crystal structure due to composites with carbon while the change in the distance between the carbon molecules has not been confirmed. The results of the thermal test showed that the crystal structure of the constituent components did not interact with each other so that the electrodes were made in the form of a composite of carbon and transition metal oxides.

CONCLUSION

A symmetric supercapacitor has been successfully fabricated by the sandwich method. Fabrication of having a composite electrode of TiO_2/AC shows maximum specific capacitance 190,80 F/g at 5% TiO_2. This supercapacitor fairly stable during charge-discharge which can be retained for 1800 cycles. The dopant of TiO_2 nanoparticles in composite electrodes increases the specific capacitance due to the increase the exhibition of a pseudocapacitive mechanism in addition to double layer.

ACKNOWLEDGMENT

REFERENCE

1. Zhu, Z., Hu, H., Li, W., and Zhang, X., vol.45, Resorcinol Formaldehyde Based Porous Carbon as an Electrode Material for Supercapacitors, *Carbon*, (2007) pp. 160-165.
2. Miller, J.R. & Simon, P., 321 (5889), Electrochemical capacitors for energy management, *Science*, 321 (5889), (2008) 651–652.
3. Adinaveen, J. Judith Vijaya, R. Sivakumar, L. John Kennedy, Structural and electrochemical investigation of waste newspaper based electrodes for supercapacitor applications, Materials Science-Poland, 34(2), (2016), pp. 302-314 http://www.materialsscience.pwr.wroc.pl/ DOI: 10.1515/msp-2016-0064.
4. Zhu, Z., Hu, H., Li, W., and Zhang, X., vol.45, Resorcinol Formaldehyde Based Porous Carbon as an Electrode Material for Supercapacitors, *Carbon*, (2007), pp. 160-165.
5. Roldán, S., Granda, M., Menéndez, R., Santamaría, R., and Blanco, C., Mechanisms of energy storage in carbon-based supercapacitors modified with a quinoid redox-active electrolyte, *J. Phys. Chem.* C 115, (2011) 17606–17611. doi:10. 1021/jp205100v.
6. Wang Y, Jin Guo, Tingfeng Wang, Junfeng Shao, Mesoporous Transition Metal Oxides for Supercapacitors, *Nanomaterials* 2015, *5*(4), (2015) 1667-1689; https://doi.org/10.3390/nano5041667.

7. Lee, H. Y.; Goodenough, J. B. *J. Solid State Chem*, *144*, 220. See also a more detailed version of this study in the following: Lee, H. Y.; Manivannan, V.; Goodenough, J. B. C. R. *Acad. Sci. Paris* (1999), *t. 2, Se´rie II c*, 565.

8. C.L. Xu, S.J. Bao, L.B. Kong, H. Li, H.L. Li, J. Solid State Chem. 179 (2006) 1351. *Capacitor Design and Operation*, The Electrochemical Society Interface Conference, Tampa.

9. M. Doloksaribu, Harsojo, K. Triyana, B. P. Handoko, Internat. Jour. of App. Eng. Res. 12 (2017) 8625-8631.

10. Jia-Wei Wang, Ya Chen,z and Bai-Zhen Chen , *Journal of The Electrochemical Society*, 162 (8) , (2015), A1654-A1661.

11. Pandolfo A G, Hollenkamp A F, Carbon properties and their role in Supercapacitor,. *Journal of Power Sources*, 157(1), (2006), 11–27.

12. Jiang, Zhifeng Ren, Shuo Chen, Qinyong Zhang, Xiong Lu, Hongping Zhang and Guojiang Wan, Bio-derived three-dimensional hierarchical carbon-graphene-TiO_2 as electrode for supercapacitors Sci Rep, (2018), doi: 10.1038/s41598-018-22742-7.

13. Mi G, PAN Qun, TU Wenmao, Characteristics of Electric Double Layer in Different Aqueous Electrolyte Solutions for Supercapacitors, Journal of Natural Science, (2012), DOI 10.1007/s11859-012-0828-1.

14. Candelaria, Y.Y. Shao, W. Zhou, X.L. Li, J. Xiao, J.G. Zhang, Y. Wang, J. Liu, J.H. Li, G.Z. Cao, Nano Energy 1 (2012) 195-220).

15. Béguin, F., Raymundo-Piñero, E., dan Frackowiak E, Electrical Double-Layer Capacitors and Pseudocapacitors *Carbons for Electrochemical Energy Storage and Conversion Systems,* CRC Press, USA, (2010).

16. Selvakumar.M, D. Krishna Bhat, 2012, Microwave synthesized nanostructured TiO_2-activated carbon composite electrodes for supercapacitor, *Applied Surface Science* 263, 236–241