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Effect of TiO_2 on Duck Eggshell Membrane as Separators in Supercapacitor Applications

D. Dahlan[1,a], N. Sartika[1], Astuti[1], E. L. Namigo[1] and E. Taer [2]

[1]Material Physics Laboratory, Department of Physics, Andalas University, Limau Manih Padang 25163, West Sumatera Indonesia
[2]Department of Physics,University of Riau, Simpang Baru 28293, Riau Indonesia
[a]dahyunir@yahoo.com (Corresponding author)

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ABSTRACT. A study concerning the effect of TiO_2 on duck eggshell membrane as separator in supercapacitor applications. Concentration of TiO_2 on duck eggshell membrane are 1 %wt, 5 %wt and 10 %wt respectively. Construction capacitor cell is shaped sandwich system. Membrane separator placed in the midst of the two carbon electrodes containing H_2SO_4 solution. From the micrograph Scanning Electron Microscopy (SEM), it observed that TiO_2 particles in all samples are uniform in size. At concentration of 1 %wt, TiO_2 particles covered all fiber of duck eggshell membrane, but not many pore is formed while at concentration of 5%, the TiO_2 particles fill the pores between the fibers, thus causing the pores between the fibers get smaller and multiplied in number. However, if the TiO_2 particles added is the more than 10 %wt, the particles will actually cover the pores between the fibers of the membrane. Characteristics of the capacitor was measured by using Edaq cyclic voltameter. Maximum value of specifics capacitance (C_{sp}) was 2.3 F / g, with current 0.007 mA and voltage of 0.002 V. This value occurs at a concentration of 5 wt% TiO_2 on the charging time for 20 seconds.

Introduction

In recent years research on supercapacitors has attracted worldwide attention as a source of high-capacity energy storage [1]. Supercapacitors have been used widely in the fields of electronics and transportation [2], the power system applications in electronics and telecommunication [3].

Supercapacitor construction is similar to a regular capacitor, which consists of a pair of electrodes filled with electrolyte and separated by insulating dielectric material. The insulating can be a membrane that has a shape that is compact, durable, and free from leaks. This membrane is semi-permeable so that it should allow movement of electrolyte ions between the two electrodes.

Utilization of membrane as supercapacitor separator has been done using avian eggshell membrane as separator of natural supercapacitors [4]. While [5] conducted tests on some eggshell membranes, i.e. the duck eggshell membrane, chicken egg shell membrane, and a goose egg shell membrane. He found that the uptake of duck egg shell membrane electrolyte is greater than the membranes of chicken and goose egg shell. In general, the membrane of duck eggs is superior to the membrane of chicken (Gallus domesticus) [6].

Development of titania (TiO_2) as supercapacitor materials over time showed promising results. Deposition of TiO_2 on RuO_2 electrode surface can increase the value of the capacitance of materials for supercapacitor. The process of hydrogenation of TiO_2 on MnO_2 at temperatures of 300^0C - 600^0C produces specific capacitance of 912 F/g at sweep rate 10 mV/s [7]. TiO_2 layer has been used as dielectric thin film [8]. The addition of TiO_2 can also increase the physical strength of the membrane [9].

In this study, membrane is coated with TiO_2 nanoparticles using dip coating method with variations of concentration of TiO_2 powder. Soaking the membrane in solution of TiO_2 is expected to minimize the pores of the membrane and electrolyte uptake. As separator supercapacitor, resulting capacitance value is expected to increase in the order of farads thus greater storage capacity.

Experimental procedure

Duck eggshell were washed thoroughly using distilled water and then immersed in a solution of hydrochloric acid (HCl) for 30 minutes, until the membrane completely detached from the shell. The membrane was rinsed again to remove the influence of HCl so that the membrane becomes neutral (pH = 7). Digital PH meters from Luxtron was used to measure the pH of membrane. The membrane was cut into small circular shape adapted to the size of the collector electrode surface. The collector electrode is made of carbon materials. The entire membrane was soaked in 1M H_2SO_4 solution for 24 hours. Furthermore, the membrane was also soaked in a solution of TiO_2 with 3 variations of concentration is 1 wt%, 5 wt% and 10 wt% for 24 hours. Phase formed on the membrane were characterized using X-ray diffraction instrument X'Pert Proanalytical. The morphology of the membrane surface was characterized using electron microscopy (SEM) Hitachi S3400N.

In testing the capacitance, the membrane was immersed in a solution of 1M H_2SO_4 electrolyte. The membrane was placed in the midst of a carbon counter electrode. Carbon electrodes clamped on each side by a sandwich structure (Fig. 1). Each side of the electrodes is given an offset of 1 cm for electrical contacts. Cyclic voltametric measured using the potentiostat EA160 Quadstat electrochemistry. Each measurement frequency of 1 kHz was used, the voltage potential of 1 volt and 1 mA maximum current, in order to obtain the maximum time span of 80 second cycle to charge and discharge the capacitor. Span of 10 point measurements was performed during capacitor charging between 4 second - 40 second with measurement internal of 4 seconds.

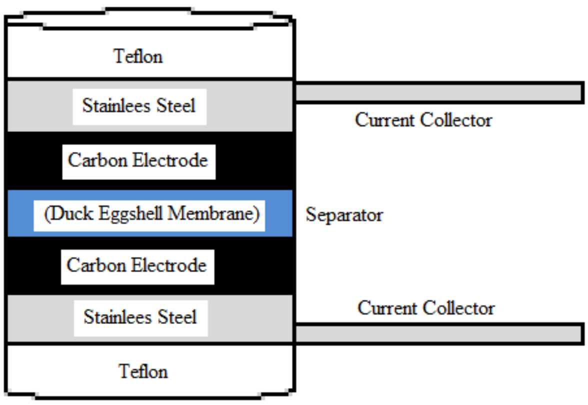

Figure 1. Compiler Components supercapacitor cells

Result and Discussion

XRD characterization showed that TiO_2 particles adhere well to the duck eggshell membrane. This can be understood because the TiO_2 particles were still detected, although the membrane had been washed with distilled water and rubbed H_2SO_4 solution. The diffraction pattern shows that there are peaks of anatase TiO_2 phases (Fig. 2). Characteristic peaks of TiO_2 membranes clearly appear in the diffractogram at 2θ angles = 25 130, 25 660, 37.790, 47.960 and 62. 440 degrees with successive crystal planes are (101), (101), (004), (200) and (204). These phases correspond to the characteristics of the anatase crystalline phase (ref. JCPDS 01-075-2553).

From the value of FWHM (Full Width Half Maximum) at various peaks obtained an average crystal size was 64.4 nm (using Scherer equation). TiO_2 crystal size at the nanometer scale can accommodate charges accumulated while charging the capacitor.

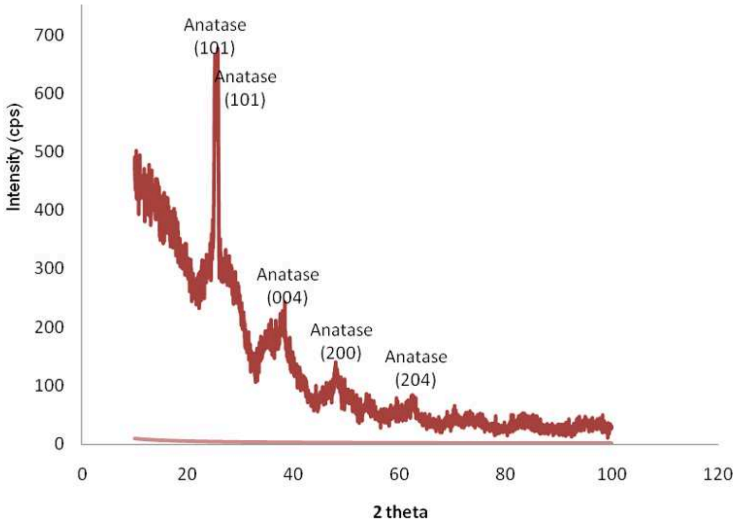

Figure 2. XRD pattern of soaking duck egg membrane with a solution of 5 wt% TiO2 powder

Figure 3. shows some of the conditions that duck egg membrane coated by TiO_2. Soaking the membrane in a solution of TiO_2 with different concentrations influences the shape and pore size significantly. The morphology of the membrane surface is immersed in a solution of 1 wt% TiO_2 are shown in Figure 3a. TiO_2 particles seemed to coat around the fibers of the duck eggshell membrane, but the pores formed are significant in number. This attributed to the TiO_2 concentration is relatively low so it only coats the surface of the membrane.

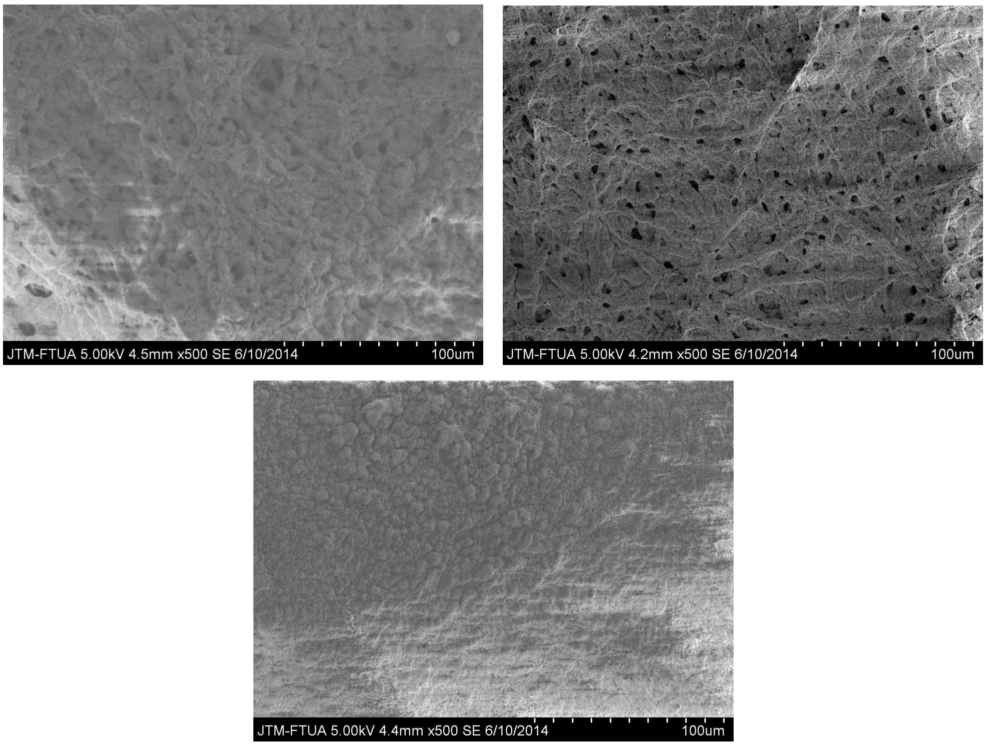

Figure 3. SEM image of membrane surface with a duck egg dyeing using % TiO2 ;
(a) 1 wt% , (b) 5 wt% , and (c) 10 wt%. (Magnification 1000X)

For membrane soaked in 5 wt% TiO_2 shown in Figure 3b, it can be seen that the morphology of the surface has more pores. The use of TiO_2 is able to reduce the size of the pores of the duck eggshell membrane. This is consistent with the research (Johan, 2009), that the TiO_2 potentially minimize pores and increase the density of the membrane. Small and deep pores were performed between the fibers due to thick TiO_2 particles attached to membrane. Membrane pore size is in the range between 10-40µm. These sizes can still be grouped in the membrane pore macropores classification according to the classification of IUPAC (International Union of Pure and Applied Chemistry).

Figure 3c. shows the duck eggshell membrane coated with 10 wt% TiO_2. The more TiO_2 particles were added, the more pores between the fibers membranes were covered. This would inhibit the flow of ions in the electrolyte membrane which automatically affects its ability as capacitor.

Cyclic Voltametry measurements are shown in Fig. 4. For all the variations of concentration, it can be seen is seen that the value of the membrane capacitance is maximum at half of the charge time of the capacitor. The maximum capacitance value occurs after 20 seconds with a scan rate of 50 mV rate/s. At the beginning of the charging capacitor, current and voltage increases linearly up to half of the charge time. However, before the capacitor is fully charged it already experienced a reduction in flow. This is due to linearly increasing voltage resulting in reduction of current flow.

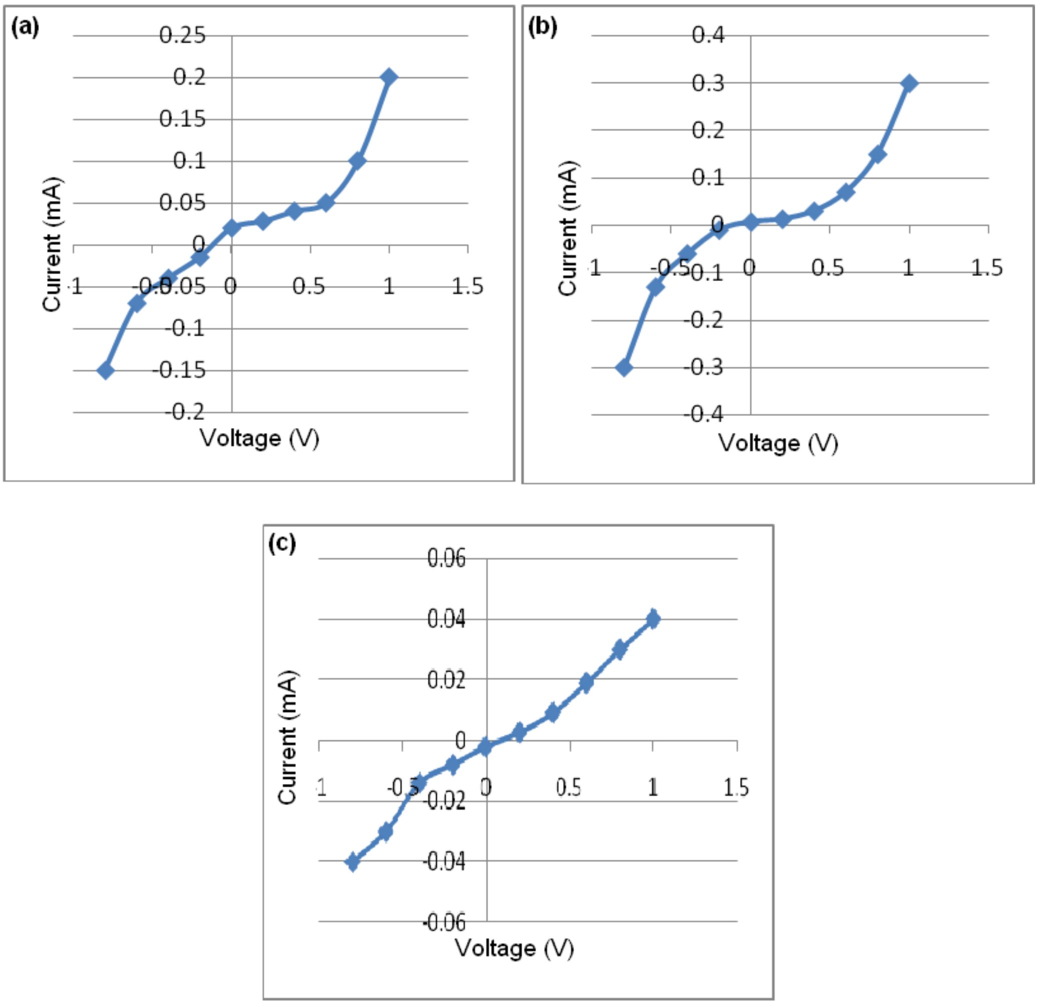

Figure 4. The cyclic voltametric curve of duck membrane coated by TiO_2; (a) 1 wt% , (b) 5 wt% and (c) 10 wt% in 1M H_2SO_4 solution.

Fig. 4a shows the membrane with a concentration of 1 wt% TiO_2. At 10 point measurement with current ranges between -0.15 - 0.2 mA and a voltage range between -0.8 - 1 V maximum cell capacitance values obtained at the time of filling 20 seconds. From these measurements the value obtained was 0.02 mA current, voltages 0.002 V. So we get the results of the calculation of cell capacitance (CSEL) is 0.2 M and the specific capacitance (Csp) was 0.7 F/g.

For membrane with TiO_2 concentration of 5 wt% (Fig. 4b), the current range was between -0.3 - 0.3 mA and a voltage range between -0.8 - 1V. It also produced the maximum capacitance value on measurement after 20 seconds at the rated current of 0.007 mA and voltage of 0,002 V. The calculation data obtained cell capacitance values (C_{SEL}) is 0.7 M and the specific capacitance (Csp) was 2.3 F/g .

For membrane with TiO_2 concentration of 10 wt% (Fig. 4c), the current range was between -0.04 - 0.04 mA and a voltage range between -0.8V - 1V. These measurements yielded the maximum capacitance in seconds 20 mA with a current and voltage -0.0021 -0.004 V. The value of cell capacitance (C_{SEL}) is 0.01 M and the specific capacitance (Csp) is 0,035 F/g.

Summary

Has produced duck eggshell membrane coated with TiO_2 as separators for supercapacitor applications. Maximum value of specifics capacitance (Csp) was 2.3 F / g, with the current 0007 mA and voltage of 0002 V. This value Occurs at a concentration of 5 wt % TiO_2 on the charging time for 20 seconds

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References

[1] H. Yu, Q. Tang, J. Wu, Y. Lin, L. Fan, M. Huang, J. Lin, Y. Li and F. Yu, Using eggshell membrane as a separator in supercapacitor , Journal of Power Source 206 (2012) 463-468.

[2] Zhang, H. dan Banfield, J.F, Understanding Polymorphic Phase Transformation Behavior during Growth of Nanocrystalline Aggregates:Insights from TiO2“, J Phys Chem B. 104 (2000) 3481.

[3] X. Lu, G. Wang, T. Zhai, M.Yu, J. Gan, Y. Tong and Y. Li, Hydrogenated TiO2 Nanotube Arrays for Supercapacitors, Nano Lett. 12 (2012) 1690−1696.

[4] H. Yu, Using Eggshell Membrane as a Separator in Supercapacitor. Journal of Power Sources 206 (2012) 463-468.

[5] E. Taer, Sugianto, M. A. Sumantre, R. Taslim, Iwantono, D. Dahlan, M. Deraman, Eggs Shell Membrane as Natural Separator for Supercapacitor Applications, Advanced Materials Research 896 (2014) 66-69.

[6] E. Mahrani, Study of Different Types of Membrane Rheology properties Eggs , Department of Physics . Faculty of Mathematics and Natural Sciences. Bogor : Bogor Agricultural University 2008.

[7] R. A. Young and R.P. Chong, School of Materials Science and Engineering, Seoul National University, Seoul (2007) 151-74.

[8] X. Lu, G. Wang, T. Zhai, M.Yu, J. Gan, Y. Tong and Y. Li, Hydrogenated TiO2 Nanotube Arrays for Supercapacitors, Nano Lett. 12 (2012) 1690−1696.

[9] S. Rohman, 2009. Synthetic polysulfone membrane. http://polisulfon.com/ [14th October 2013].

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DOI References

[1] H. Yu, Q. Tang, J. Wu, Y. Lin, L. Fan, M. Huang, J. Lin, Y. Li and F. Yu, Using eggshell membrane as a separator in supercapacitor , Journal of Power Source 206 (2012) 463-468.
http://dx.doi.org/10.1016/j.jpowsour.2012.01.116
[3] X. Lu, G. Wang, T. Zhai, M. Yu, J. Gan, Y. Tong and Y. Li, Hydrogenated TiO2 Nanotube Arrays for Supercapacitors, Nano Lett. 12 (2012) 1690−1696.
http://dx.doi.org/10.1021/nl300173j
[4] H. Yu, Using Eggshell Membrane as a Separator in Supercapacitor. Journal of Power Sources 206 (2012) 463-468.
http://dx.doi.org/10.1016/j.jpowsour.2012.01.116
[5] E. Taer, Sugianto, M. A. Sumantre, R. Taslim, Iwantono, D. Dahlan, M. Deraman, Eggs Shell Membrane as Natural Separator for Supercapacitor Applications, Advanced Materials Research 896 (2014) 66-69.
http://dx.doi.org/10.4028/www.scientific.net/AMR.896.66
[8] X. Lu, G. Wang, T. Zhai, M. Yu, J. Gan, Y. Tong and Y. Li, Hydrogenated TiO2 Nanotube Arrays for Supercapacitors, Nano Lett. 12 (2012) 1690−1696.
http://dx.doi.org/10.1021/nl300173j