

Eggs Shell Membrane as Natural Separator for Supercapacitor Applications

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Abstract: Various eggs shell membranes (ESMs) have been used as a separator for supercapacitor application. The separator was prepared from different membranes such as chicken eggs shell membrane (CESM), duck eggs shell membrane (DESM) and goose eggs shell membrane (GESM). The ESMs were tested as a separator in a two-electrode system, the sandwich-type supercapacitor cell consists of two activated carbon monoliths as electrodes, two stainless steel as current collectors and 1 M H₂SO₄ solution as an electrolyte. The electrochemical performance of the ESMs was characterized by an electrochemical impedance spectroscopy, a cyclic voltammetry and a galvanostatic charge-discharge. The results of this study exhibit all of the ESMs as a good candidate for supercapacitor separator. However, the CESM was shown excellence electrochemical properties, such as low resistance, high energy density and power density. The scanning electron microscope (SEM) micrograph and X-ray diffraction analysis were also proved that the ESMs are a promising low-cost separator for supercapacitor application.

Introduction

Supercapacitor or electrochemical capacitor is an energy storage device that exhibits higher power density and longer cycling life compared with traditional dielectric capacitors, batteries or fuel cells as other energy storage devices [1]. Supercapacitor consists of current collectors, electrodes, separator, and electrolyte. Many researchers had given their efforts to produce a high performance supercapacitor for various focused studies such as the studies on the electrode, electrolytes and current collectors to have their high energy and power were reported [2-4]. On the other hand, only a few papers reported about the study of separator for the cell [5-6]. Separator in a supercapacitor cell was placed between the two electrodes to prevent the transfer of electrons between the two electrodes. Moreover, the separator should be quite thin with having a macropore structure. It is to ensure a smooth drainage of the ions in the electrolyte to diffuse into the pores in both electrodes. Yu et al shown a good supercapacitor performance by using a separator from natural membrane derived from avian egg shell membrane [7]. This paper demonstrates the use of egg shell membrane from several types of birds, such as chickens, ducks and geese as a natural separator for supercapacitor. From this study, the contribution of knowledge relies that the different of the fibers of egg shell membrane thickness and size affects the performance of a supercapacitor cell.

Experimental Procedure

Preparation of egg shell membrane followed method that has been reported earlier [7]. The egg shells membranes have been characterized such as the electrolyte absorption, structure and morphology. The structure of the membranes was elucidated by mean of XRD. A Bruker D8 Advance XRD diffractometer with CuK_α radiation with a 2 θ range of 10 to 70° was used to obtain the XRD pattern. The morphological structures of the egg shells membranes were elucidated on a FESEM (Supra PV 55 model). The electrochemical properties of egg shell membrane have been

studied by fabricating a supercapacitor cell with coin type structure which consists of two electrodes using activated carbon monolith from oil palm empty fruit bunches, two pieces of steel stainless used as current collectors and 1 M sulfuric acid as electrolyte. The performance of the supercapacitor cells was studied by a galvanostatic charge-discharge (GCD), EIS and cyclic voltammetry (CV) technique by using a Solatron 1286 electrochemical interface measurement. The specific capacitance was determined using the standard formula [8].

Results and Discussion

Physical characteristic. Fig. 1 (a) shows the percentage of electrolyte adsorption at various types of ESMs. From the data, it shown that the DESM gave the highest adsorption capacity and the other hand, GESM have minimum adsorption capacity of electrolyte. Fig. 1(b) showed the X-ray diffractogram of the ESMs. The figure shows that the ESMs have a crystal structure. The sharp peaks exist at 20° , 30° and 40° and correlated with (001), (002) and (101) plane. These crystallites peak showed the existing of CaCO_3 element [9]. Fig. 1(c) showed the SEM micrograph for the CESM, DESM, GESM, respectively. The thickness for every ESM can be observed from the cross-section of as 0.03 mm, 0.10 mm and 0.14 mm for CESM, DESM, GESM, respectively. From the figure of all samples, it were observed like a nano-fiber network, which represents average diameter of fibers for CESM, DESM and GESM are 1.177 nm, 1.314 nm and 937 nm, respectively.

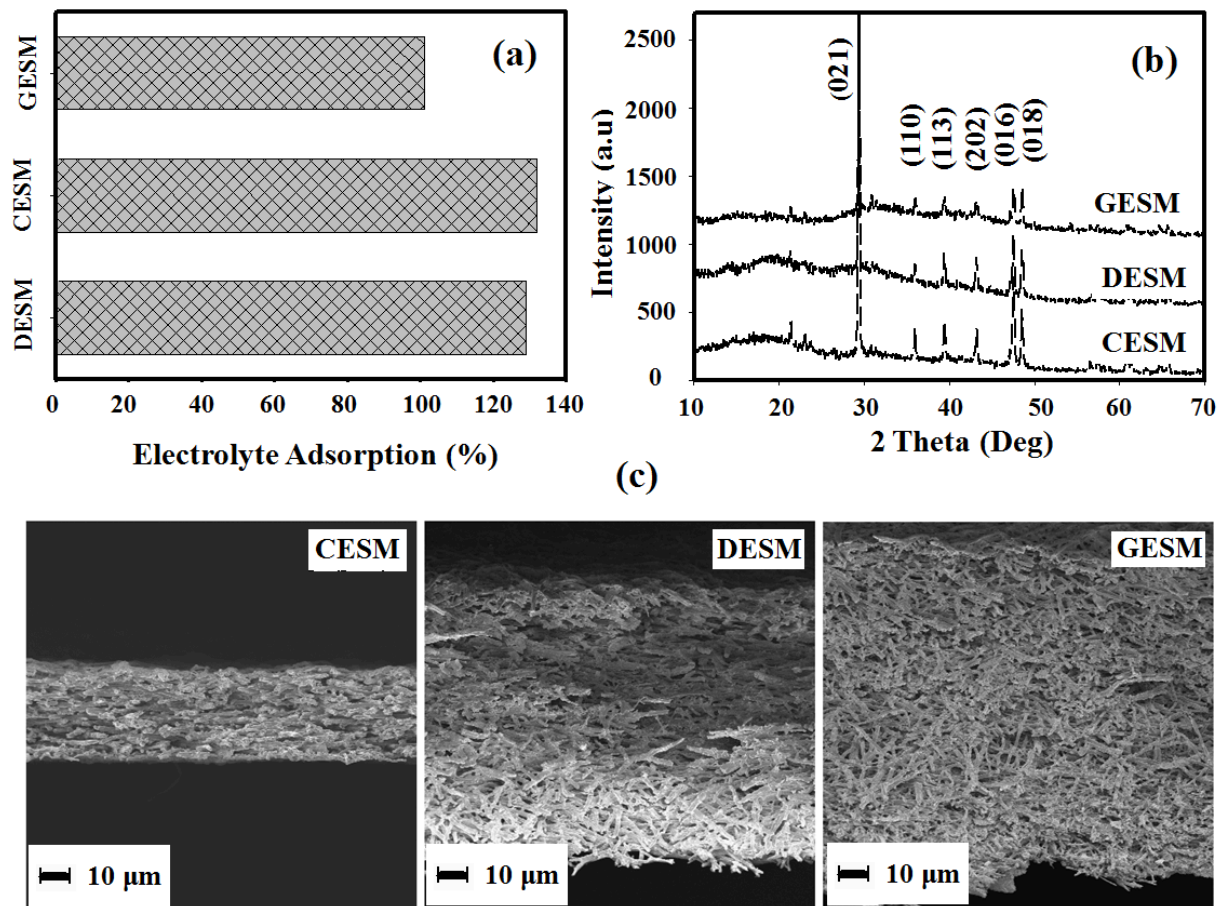


Figure 1. (a): Electrolyte adsorptions capacity of ESM, (b): X-ray diffractogram of ESM and (c): SEM micrographs of ESMs' cross-section observation at 300 X.

Electrochemical characteristic.

Measurements of electrochemical properties of supercapacitor cells using natural separator of CESM, DESM and GESM were performed by using of EIS, CV and GCD method. EIS measurement results are shown in Fig 2 (a) describes the relationship between the real impedance (Z') and imaginary impedance (Z'') to determine the nature of the resistive and capacitive properties of the supercapacitor cells. Fig. 2 (a) shows the Nyquist plots for the ESM are almost the same, but

more over it still can be observed the difference in the intersection of the plot with the Z' axis at high frequency region and it also shown the different value of Z'' at low frequencies region. Nyquist plots for CSEM was intersects with the Z' axis at a lower value and has a value of Z'' which is smaller than the other two ESM. This indicates that the thickness of 0.03 mm CSEM have given better resistive and capacitive properties than the other samples. Fig. 2 (a) inset is showing semicircular area associated with the values of R_s , R_p and ESR [10] and is listed in Table 1. From the table can be observed that the CSEM has the lowest value of R_s and R_s was associated with the combination of electrolyte resistance and contact resistance between the current collector and the carbon electrode [10]. This is due to the thickness and size of fiber diameter corresponding to the absorption of electrolytes. R_p is the intrinsic resistance of carbon electrode (4) and from the table it shows almost the same. This relates to the use of the same electrodes. ESR or also known as the Equivalent Series Resistance which is a reduction of R_p against R_s (4) and GESM gave the lowest value. Specific capacitance values (C_{sp}) of various types ESMs by using the EIS method was shown in Fig. 2 (b), which describes the relationship between C_{sp} and frequency characteristics.

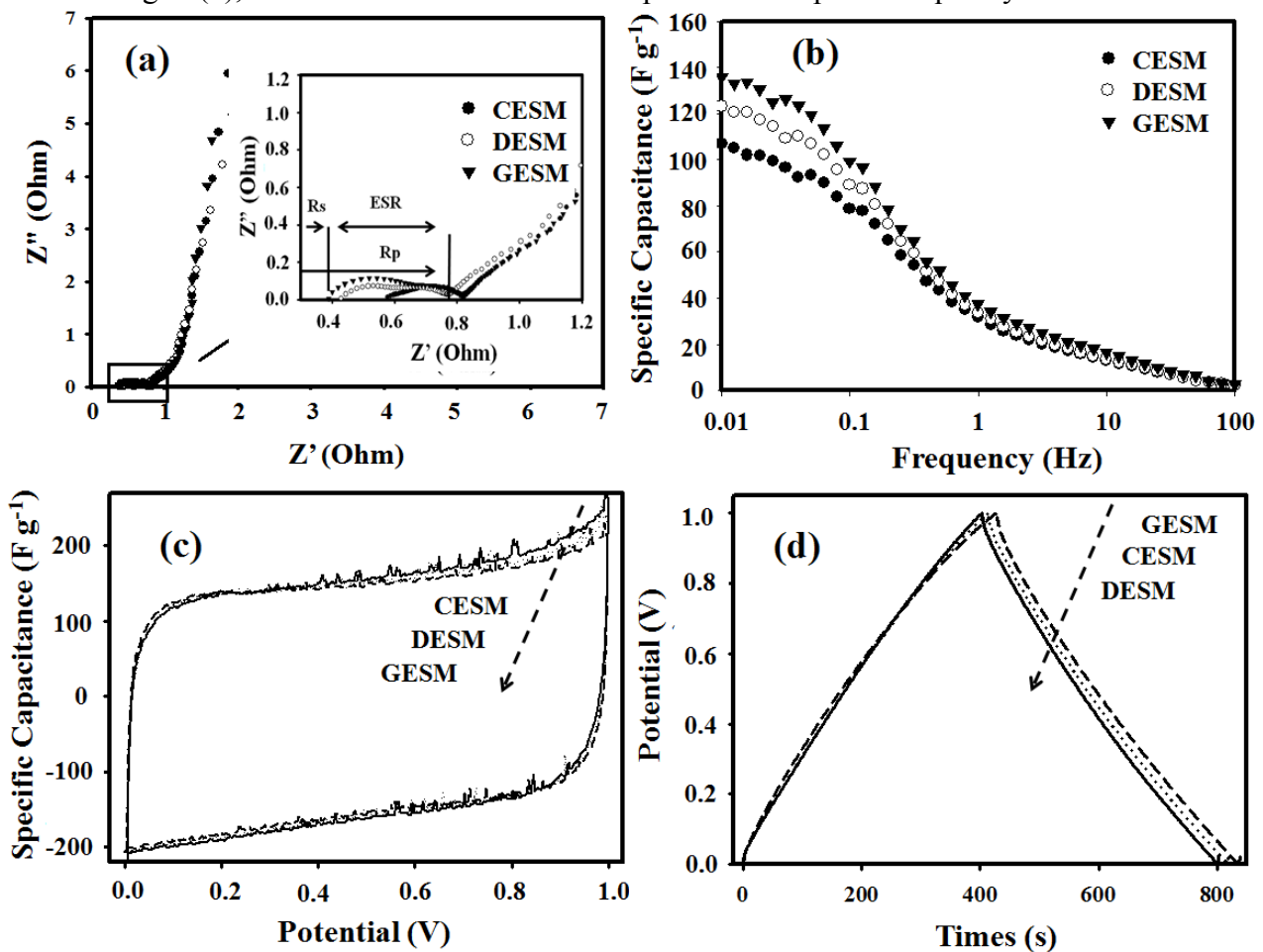


Figure 2. (a): Nyquist plot data for supercapacitor cell with different ESM, (b): The specific capacitance Vs frequency, (c): The CV data for supercapacitor cell with different ESM and (d): The GCD curve at constant current measurement for supercapacitor cell with different of ESM.

Fig. 2 (c) showed the CV measurement curves for various ESMs at a scan rate of 1 mV s^{-1} . Generally, these curves had shown the pattern of charge-discharge which are almost same. The value of C_{sp} are calculated using the formula of $C_{sp} = (2(I_c - I_d)/2)/s \times m$, where large current is generated in the CV curve is determined by taking the midpoint of a large voltage of 0.5 V [2]. C_{sp} values for each separator CSEM, DESM and GESM was 159.22 F g^{-1} , 156.14 F g^{-1} and 153.06 F g^{-1} , respectively. The difference result was clearly influenced by difference thickness of the ESMs, in which the thinner ESMs has the higher C_{sp} value.

Table 1. Resistive properties of supercapacitor cells by type ESM.

Type of ESM	R_s (Ω)	R_p (Ω)	ESR (Ω)
CESM	0.291	0.822	0.530
DESM	0.390	0.814	0.424
GESM	0.574	0.847	0.272

Fig. 2 (d) shows the relationship between the voltages versus time on a charge-discharge current density of 0.01 mA/cm^2 for cells using different ESMs. Generally, the resulting curve resembles the shape of isosceles triangles that almost symmetry. Specific capacitance values is determined in these measurements using the equation of $C_{sp} = (2 \times I \times \Delta t) / (m \times \Delta V)$. Specific capacitance value of each ESM was 163.85 F g^{-1} , 161.84 F g^{-1} and 159.45 F g^{-1} corresponds to GESM, DESM and CESM.

Conclusion

Various types of egg shell membranes have been demonstrated for its good potential for supercapacitor separator. Physical characteristics such as absorption capacity of electrolyte, fiber diameter size and thickness playing a very important role for determining the performance of electrochemical supercapacitor of egg shell membrane as a separator for supercapacitor application.

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