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# Using eggshell membrane as a separator in supercapacitor

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ABSTRACT

A separator is prepared based on natural and flexible eggshell membrane (ESM) for supercapacitor application. Morphology observation shows that the ESM is consisted of hierarchically ordered macroporous network. With a high decomposition temperature (>220 °C), enough mechanical strength ($\sigma_{max}$ = 6.59 ± 0.48 MPa, $\varepsilon_{max}$ = 6.98 ± 0.31%, respectively), and low water uptake and swelling property (<10%), ESM could be a promising candidate for supercapacitor separator. As expected, the supercapacitor with ESM separator exhibits outstanding electrochemical performances, such as low resistance, quick charge–discharge ability ($\tau$ is 4.76 s), and good cyclic stability (92% retention after 10,000 cycles). However, the one with PE separator shows worse properties (high resistance, low specific capacitance, etc.). This research provides new insight into the preparation of natural, low-cost and high-performance separator for supercapacitor and other applications.



## 1. Introduction

In recent years, great efforts have been devoted to the development of alternative energy storage/conversion devices in response to the depletion of fossil fuels and related environmental issues [1–3]. Supercapacitor, also known as electrochemical capacitor or double electric layer capacitor, is an important energy-storage device, which has attracted increasing attentions because of its high power density, long cycle life, and environment-friendly feature [4–7]. One of the key questions about designing high-performance supercapacitor is the choice of separators [8]. In particular, the utilization of high-surface-area electrodes and the high-efficient electrolytes in supercapacitors have aroused intense researches on separators. Separators used between electrodes in supercapacitor have been constructed of rubber, plastic, aquagel, resorcinol formaldehyde polymers, polyolefin films, etc. to prevent the conduction of electrons between the electrodes, but such prior known separators have had a tendency to dry out or collapse over a period of time, or exhibit poor ionic conductivity [9–11]. Consequently, a need exists for supercapacitor separators, which are made of highly porous materials that provide minimal resistance for electrolyte ion's movement and that at the same time, have electronic insulator properties between opposing electrodes.

Now, the most common separator used in commercial supercapacitors is Nafion membrane, which is composed of a hydrophobic Teflon backbone and side chains terminated with hydrophilic sulfonic acid ($-SO_3H$) groups [12,13]. Although Nafion membrane employs efficient properties for the role of supercapacitor separator, the expensive spend and limited raw materials from fossil resources limits the large-scale application of supercapacitors [14–16]. In other words, although the industrialization of Nafion membrane can be realized at acceptable cost in the foreseeable future, it fails to meet the requirements of the development of low-carbon society. Thus, it is very valuable and significative to develop natural membrane materials with excellent properties for supercapacitors.

It is known that avian eggshells are formed by layered organization of calcified shell and organic ESM containing collagen types I, V, and X, and glycosaminoglycans [17]. ESMs are consisted of the outer shell membrane, inner shell membrane, and limiting membrane surrounding the egg white. The outer shell membrane, which can be easily isolated from eggshells, was used as separate for supercapacitors in this work. ESM can keep good stability in aqueous and alcoholic media and undergo pyrolysis on heating [18]. Furthermore, it is actually the most abundant material in biosphere with non-toxicity and low-cost properties. So our present work can be regarded as a novel attempt to utilize a natural membrane to alternate the conventional polymer separator derived from oil resources.

## 2. Experimental

### 2.1. Materials and reagents

Activated carbon material was supplied by Shanghai Heda carbon Co., Ltd. (nitrogen BET surface area of 1900 $m^2\ g^{-1}$) and

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used as received without further treatments. Polytetrafluoroethylene (PTFE) and nickel foil were purchased commercially from Guangzhou Xingshengjie Co. Ltd. and Changsha Lyrun new material Co. Ltd., respectively. Graphite, sodium sulfate ($Na_2SO_4$), N-methyl-2-pyrrolidone (NMP), and polypropylene (PP, 0.9 mm) were commercially available materials from Sinopharm Chemical Reagent Co., Ltd. and used without further treatments.

### 2.2. Separation of ESM

The separation of the outer shell membrane from eggs has been described previously [19]. Briefly, eggs were gently broken and emptied via the blunt end. The eggshells were washed with deionized water and then the inner shell membrane and the limiting membrane were manually removed. The remaining eggshells were immersed in 1 mol L$^{-1}$ HCl aqueous solution to dissolve the $CaCO_3$ shell, leaving the organic outer shell membrane. After the outer shell membrane was washed with water thoroughly, the resultant ESM (0.8 mm) was prepared for supercapacitor applications.

### 2.3. Characterizations

The morphological structure of ESM was observed and photographed by an S-4700 Hitachi cold field emission scanning electron microscopy (SEM). Thermal gravimetric analysis (TGA) of the samples was performed on TA make a TGA 2050 instrument to monitor the degeneration temperature of ESM. The experimental procedure consisted of heating the samples in flowing nitrogen (99.999% purity, 100 mL min$^{-1}$) at a linear heating rate of 15 °C min$^{-1}$ from room temperature to 750 °C until all the samples were completely consumed.

The tensile strength–elongation test of the ESM and PP were carried out on an INSTRON Model 5583 testing machine (USA) by following the procedure reported in our previous research [20]. The test conditions were controlled as follows: the temperature was set at 25 °C, the size of humid sample was cut with a knife to 2 mm × 10 mm, the distance between two square panels was 5 mm, and the crosshead speed was 5 mm min$^{-1}$. The thickness of the membrane was ∼100 μm from SEM observation. Since the thickness of the ESM was not perfectly uniform, it was average to a yield of 100 μm from measurements at more than 20 points along the horizontal direction of each sample. The strain under stress is defined as the change in length relative to the initial length of the specimen. The tensile strength and strain at break were calculated on the basis of the initial cross-section area. For each set of data, more than 5 samples were prepared and measured at identical conditions. Each data set showed similar stress–strain behavior. As an average, from each measurement one typical data set was selected.

### 2.4. The properties of water uptake and swelling

The dry membrane was weighted ($W_{dry}$) and immersed in 1 mol L$^{-1}$ $Na_2SO_4$ solution for different days at room temperature to reach certain dilation, respectively. And then the membrane was taken out of the solution and carefully wiped with an absorbent paper before it was weighed ($W_{wet}$). The swelling was determined in a similar method, by soaking the dry rectangular membrane (about 1.0 cm × 1.0 cm) with area of $A_{dry}$ in 1 mol L$^{-1}$ $Na_2SO_4$ solution for different days, then re-measuring to obtain the wetted membrane area ($A_{wet}$). The degree of water uptake ($D_w$) and swell ($D_s$) were determined from the differences between the wet and dry membranes according to equation [21,27]:

$$D_w = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

$$D_s = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100\% \quad (2)$$

### 2.5. Fabrication of activated carbon electrodes

The electrodes for supercapacitors were composed of 85 wt.% activated carbon, 10 wt.% graphite, and 5 wt.% PTFE [22]. The activated carbon and graphite powders were added to PTFE/NMP mixture and the mixture was stirred to form carbon slurry at room temperature. And then the carbon slurry was pressed by Decal method to form a thin sheet. Under pressure of 10 MPa, the sheet was painted on nickel foam that acts as the current collector. After being dried at 60 °C for 24 h in a vacuum, an as-prepared electrode was obtained.

### 2.6. Assembly and measurements of supercapacitors

Two as-prepared activated carbon electrodes fitted with the ESM separator and electrolyte solution constitute a classical Swagelok®-type cell [23]. Before assembling the supercapacitor configuration, activated carbon electrodes and ESM were immersed in 1 mol L$^{-1}$ $Na_2SO_4$ electrolyte for 24 h to make aqueous electrolyte solutions homogeneously diffuse into the pores of carbon electrodes. As comparison, the supercapacitor based on PP separator and the same electrolyte was assembled.

Electrochemical measurements were performed on an electrochemical workstation system (CHI 660C, Shanghai ChenHua Co., Ltd.). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge (GCD) measurements were determined to evaluate the performances of the supercapacitor. The supercapacitor specific capacitance ($C$, F g$^{-1}$) and single-electrode specific capacitance ($C_s$, F g$^{-1}$) were evaluated from charge–discharge curves according to the following equation [24,25]:

$$C = \frac{I \times \Delta t}{\Delta V \times m_{ac}} \quad (3)$$

$$C_s = 4 \times C \quad (4)$$

where $I$ (A) is the discharge current, $m_{ac}$ (g) is the weight of active material (including the binder and the graphite), $\Delta t$ (s) is the charge–discharge time, $\Delta V$ (V) represents the actual voltage excluding $iR_{drop}$ of the discharge process. Besides, the coulombic efficiency ($\eta$) was evaluated using the following relation, when the same current is used for charging and discharging [26]:

$$\eta = \frac{t_d}{t_c} \times 100\% \quad (5)$$

where $t_c$ (s) and $t_d$ (s) are the charging and discharging times, respectively.

## 3. Results and discussion

### 3.1. Morphology observation

The typical SEM images of the natural ESM were shown in Fig. 1. One can see that the membrane is a macroporous network composed of interwoven and coalescing shell membrane fibers ranging in diameter from 0.5 to 1 μm. The presence of macropores with pore sizes of 1–3 μm is evident, providing a superhigh way for diffusing ions with a low resistance so as to enhance the performance of supercapacitors [27].

### 3.2. Thermal stability and mechanical strength

High thermal stability and excellent mechanical strength in a separator are prerequisites to obtain high-performance