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Full Length Article

High performance aqueous symmetric supercapacitors based on advanced carbon electrodes and hydrophilic poly(vinylidene fluoride) porous separator

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ABSTRACT

The main components of a supercapacitor include two electrodes, electrolyte, and a separator, which are all essential to specify the energy storage capability of the device. In this work, two kinds of porous carbon materials have been fabricated via different routes using pomelo peel as raw material. The specific surface area are 1187 $m^2 g^{-1}$ for the nanosized worm-like carbon, and 1744 $m^2 g^{-1}$ for the nitrogen-enriched microsized carbon. Both carbon materials demonstrate excellent energy storage capability as electrodes for aqueous supercapacitors. According to the three-electrode measurements, the worm-like carbon exhibits a high specific capacitance of 316 F g^{-1} at 0.2 A g^{-1} in 6 M KOH, while the other exhibits 471 F g^{-1} due to the highly enriched nitrogen atoms in structure. In addition, two-electrode coin-type cells have been assembled with the carbon materials as electrodes and hydrophilic poly(vinylidene fluoride) porous membrane as the separator. The assembled cells exhibit high specific capacitances, excellent rate performance and superior cycling durability because of a synergistic effect of the high performance carbon electrodes and hydrophilic porous separator.

1. Introduction

In the last decades, severe issues of environmental pollution and energy shortage have arisen from globally excessive consumption of fossil fuels. Therefore, the renewable and clean energy has attracted great attention, which consequently stimulates the rapid development of energy storage technologies. As a novel kind of energy storage systems, supercapacitors generally demonstrate high power density and excellent cycling stability compared with traditional dielectric capacitors, lithium ion batteries or fuel cells [1,2]. However, supercapacitors of today generally suffer from a drawback of low energy density, hence substantial improvement is required for practical applications [3,4].

Great efforts have been devoted in seeking for high performance electrodes including carbonaceous materials, pseudocapacitive metal oxides, conductive polymers and their composites, or alternatively exploring high-voltage stable organic electrolytes [4–8]. For electrical double layer capacitors (EDLCs), the most common electrodes are porous carbon-based materials because they have high specific surface area and excellent physicochemical stability, as energy is theoretically stored by accumulating electrostatic charge at the electrode/electrolyte interface. Therefore, large active surface area and optimum pore structures are essential factors to be considered for carbon materials so as to achieve effective electrolyte accessibility and fast ion transportation. In addition, functionalizing the carbon materials with oxygenic groups including hydroxyl, carboxyl and carbonyl groups, or heteroatoms including nitrogen, sulfur, boron and phosphor species [9–12] can harvest extra pseudo-capacitance due to the their faradaic reactions with electrolyte ions, at the same time, the wettability of carbon electrodes to electrolyte can be enhanced, which accounts for greatly improved energy storage capability.

It has to be noted that a supercapacitor does not only consist of the electrodes and electrolyte, but also the separator. The separator is indeed as important as the others although it is an inactive component. The cell performance strongly relies on appropriate selection of electrodes, electrolyte and separator. However, the researches on separators have not been paid too much attention, and the related papers reported in recent years are not as much as those concerning the electrode materials [13–17]. The separator in a practical cell shall have proper thickness, adequate porosity, as well as high mechanical and electrical properties. A good separator shall efficiently prevent electrons from transferring between the

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two electrodes, at the same time, assures that the free migration of electrolyte ions in the separator during charge/discharge process [18]. Meanwhile, the separators shall be chemically stable in electrolyte, and must not decompose and introduce harmful contaminations into the system. In general, cellulose paper is frequently used for the supercapacitors based on organic electrolytes, but it is not good enough for aqueous ones because of possible cellulose degradation in H_2SO_4 or KOH solution [19–21]. For aqueous cells, it seems that polymer separators are more promising because of their excellent chemical stability and high mechanical strength. On the other hand, the poor wettability of polymers to aqueous electrolyte is a big obstacle for their practical applications, as the hydrophilicity essentially influences the ion conductivity [22]. Therefore, hydrophilic surface modification for polymer separator is needed to achieve high performance aqueous supercapacitors.

In this work, two kinds of porous carbon materials were synthesized via different routes using pomelo peel as the raw material. The electrochemical behavior of the carbon materials for energy storage was investigated in a three-electrode system with 6 M KOH as the electrolyte. At the same time, to simulate the performance of the carbon materials in actual devices, the coin-type cells were assembled using poly(vinylidene fluoride (PVDF) porous membranes as the separator. To increase their surface hydrophilicity, the membranes were modified by polyvinyl alcohol (PVA) and glutaraldehyde (GA) through hydrogen bonds and aldol cross-linking reaction. As shown in Fig. 1, PVA molecules are able to be anchored on the PVDF membrane via strong hydrogen bonds (i.e. F···H—O) formed between hydroxyl groups (—OH) and highly electronegative fluorine atoms, resulting in a hydrophilic surface. In addition, the cross-linking of PVA with GA further enhances the surface hydrophilicity, meanwhile, the cross-linked network can improve the thermal stability and mechanical strength of the membrane [23,24]. As expected, the assembled supercapacitors exhibit significantly enhanced electrochemical performance including high specific capacitance that accounts for high energy density, excellent rate performance that accounts for high power density, as well as superior cycling stability.

2. Experimental

All chemicals are analytical grade and used without further purification. Pomelo peel was washed with distilled water, dried and crushed into powders prior to the experiment.

2.1. Preparation of carbon materials

Pomelo peel-based activated carbon (AC) was prepared using the hydrothermal method, followed by a high temperature carbonization and activation process. In a typical procedure, 5 g of pomelo peel powders was immersed in 90 mL distilled water for 12 h. The mixture was transferred into a Teflon-lined autoclave, and heated at 180 °C for 12 h. The resultant mixture was filtered, the solid was washed with distilled water and dried at 60 °C. The solid was further carbonized at 800 °C for 2 h in nitrogen atmosphere, and then activated at 700 °C for 2 h using four times mass of KOH. The final product was washed with diluted hydrochloric acid and distilled water for several times, and dried at 120 °C.

Nitrogen-enriched activated carbon (N-AC) was prepared as the follows. A certain amount of pomelo peel powders and urea were homogeneously mixed with a mass ratio of 1:3. The mixture was carbonized at 800 °C for 2 h, and then activated at 700 °C for 2 h using four times mass of KOH. The product was washed with diluted hydrochloric acid and distilled water, and dried at 120 °C.

2.2. Preparation and modification of PVDF porous membrane

PVDF porous membrane was fabricated by the classical phase inversion method using (N, N-Dimethylformamide) DMF as the

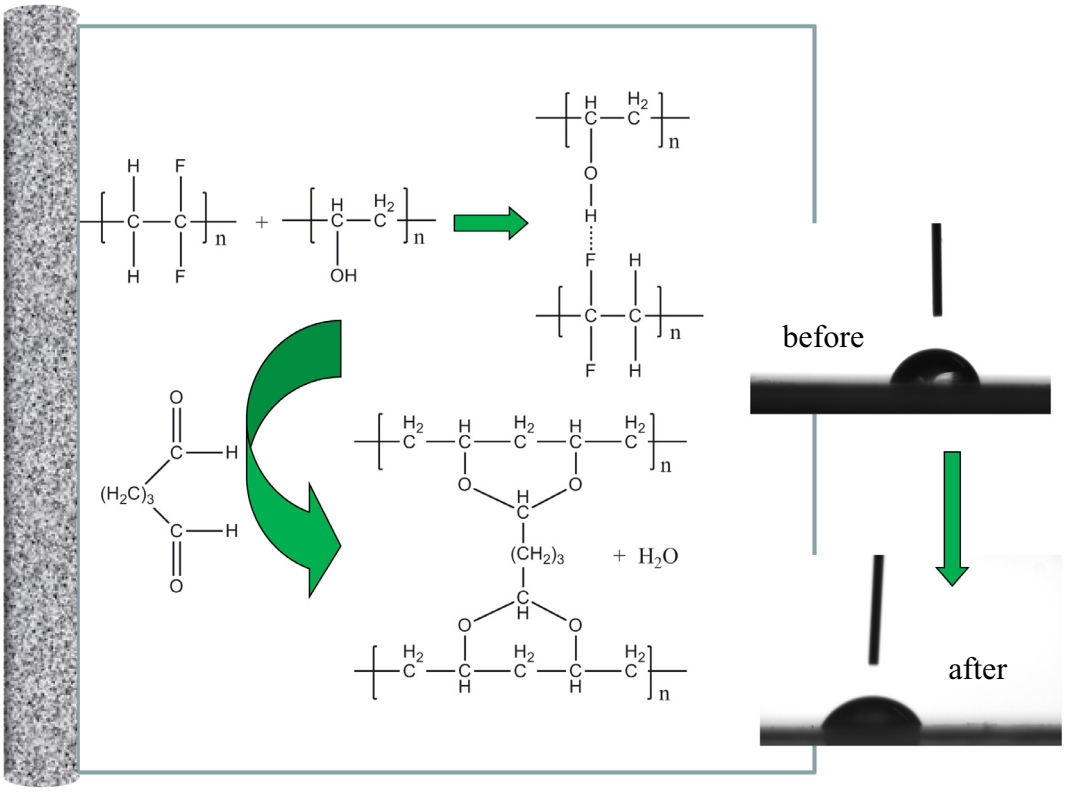

Fig. 1. Schematic illustration of hydrophilic modification of PVDF membrane.