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Superior capacitive performance of active carbons derived from Enteromorpha prolifera

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ABSTRACT

Enteromorpha prolifera (E.prolifera), an ocean biomass, was used as raw materials to prepare active carbons by a two-step strategy (pre-carbonization followed by chemical activation). The as-prepared active carbons have been characterized by a variety of means such as N_2 adsorption, field emission scanning electron microscope, transmission electron microscope, Raman spectroscopy. The results showed that the carbons have large surface area and developed porosity with micro-meso hierarchical pore texture. As evidenced by electrochemical measurements, the specific capacitance of the carbons can reach up to 296 F g^{-1}. More importantly, the carbons can maintain a high capacitance of up to 152 F g^{-1} at a very high current density of 30 A g^{-1}, highlighting the promise of the carbons for high power applications.

1. Introduction

Electrochemical capacitor (EC), also called supercapacitor, is a novel energy storage component, which has become one of highlights in the field of energy research. EC not only possesses higher energy density than traditional capacitors but also has higher power output than conventional batteries. EC often works as a supplement to batteries to meet high power demand of electric vehicles in starting, accelerating and climbing. According to the energy storage mechanism, EC could be classified into electrical double-layer capacitors (EDLCs) and pseudocapacitors. The energy storage in EDLCs is mainly based on electrostatic attraction to generate charge accumulation in the electric double layer formed at the electrode/electrolyte interface [1,2]. EDLCs have been widely used in electrical vehicles, digital devices, portable electronics, pulsing techniques, etc. due to their virtues of reliable cycle life, high energy and power density, fast charging-discharging mechanism [3,4].

The performance of EC is determined, to a large extent, by the electrode materials used, which include conducting polymers, metal oxides and porous carbon materials. Among them, carbon materials are always preferred electrode materials for commercial EC due to their low cost, high corrosion resistance, high surface area and good electrochemical stability [5]. Traditional carbon electrode materials were mainly produced from coal, petroleum or their derived products through a series of activation procedures. However, coal and petroleum are non-renewable resources that we will lose forever once we consume them. With the development of global energy crisis and environmental deterioration, it is a big challenge to look for other renewable resources to prepare carbon materials for EC. As a result, people are focusing on biomass precursors, which could be constantly reproduced and updated under natural or artificial maintenance [6]. The biomass precursors are cheap, environmental friendly and porosity-intrinsic, which include watermelon [7], rice husk [8], bamboo [9], coconut shell [2], argan seed shell [10], waste coffee beans [11], dead leaves [3], celtuce leaves [12], hemp [13], potato starch [14], cattail [15], peanut shell [16], rice straw [17], seaweed [18], sugar cane bagasse [19], sunflower seed shells [20] and tea leaves [21].

Enteromorpha prolifera (E.prolifera) is not only an ocean waste but also one of renewable biological resources with the characteristic of easy growing, rapid propagating, high yield, and high regeneration ability. The accumulating of massive E. prolifera is named as “green tide” and the outbreak of green tide is due to global climate change and water body eutrophication, which may damage the marine ecosystem, block waterways, decrease biodiversity, at the same time may threaten coastal aquaculture, fishery and tourism industry. According to statistics, the E. prolifera disasters broke out in China’s yellow sea in the summer of 2008, which

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led to a direct economic loss of 1.322 billion RMB. And the cumulative pickup of E. prolifera was about 80,000 tons merely in Qingdao city [22]. Moreover, through the years the green tide broke out frequently along coastline and caused extensive ocean pollutant and big economic losses. Thus, a practical and feasible technology to solve this problem is to take advantage of these wastes to produce value-added products [23]. The aim of this work is to use E. prolifera as a precursor to prepare active carbon for EC, which could not only solve this ocean pollutant problem but also afford a new electrode material for EC.

In this study, E. prolifera is used, for the first time, as a precursor to prepare carbon electrode material for EC by KOH activation. The effects of KOH dosage on the surface area and pore structure of the resulted carbon are investigated intensively. The relations between the structure parameters of the carbons and their capacitive performances are also elucidated. It has been demonstrated that the as-prepared carbons have large surface area and micro-meso hierarchical pore texture, which enables excellent capacitive performances of these carbons. The specific capacitance of the carbons can reach up to 296 F g^{-1} and maintains a high capacitance of up to 152 F g^{-1} at a very high current density of 30 A g^{-1}, highlighting the promise of these carbons for high power applications.

2. Experimental

2.1. Preparation of active carbon

2.1.1. Raw materials

The E. prolifera used in this experiment was collected from Jinshatan beach in Qingdao, China (as shown in Fig. 1). The collected E. prolifera was thoroughly washed and cleaned to remove any impurities such as sediment and sea salt. Then, E. prolifera was dried at 60 °C for 12 h. Ash content was obtained by burning E. prolifera for 4 h under 550 °C in air till constant weight. Organic elements of E. prolifera were determined by element analysis. Oxygen content is calculated from: O (wt.%) = 100- (Ash + C + H + N + S) (wt.%). The composition analysis results are shown in Table 1.

2.1.2. Carbon preparation

Cleaned and dried E. prolifera was pre-carbonized in tubular furnace under nitrogen flow at 350 °C for 12 hours, resulting in a coke. Active carbons were prepared by mixing solid KOH and coke with agate mortar at KOH/Coke weight ratio of X (X = 3, 2, 1, 1/2). Then the mixture were heated to 800 °C at a heating rate of 5 °C min^{-1} and maintained at 800 °C for 1 hour under N_2 atmosphere in a tube furnace. The resulted carbons were washed with excessive 1 mol L^{-1} HCl solution two times and with distilled water three times until the PH value of filtrate was neutral. The resultant was dried at 100 °C overnight and grounded in a mortar to get fine powder. The as-prepared carbons are named as CK-X, where X stands for the weight ratio of KOH/coke. Fig. 1 schematically represents the preparation process for the carbon electrode material of EC from E. prolifera.

Table 1
Chemical composition of E. prolifera.

sample	Element analysis (%)					Ash (%)
	C	H	O	N	S	
E.prolifera	37.13	5.46	33.25	1.72	3.30	19.14

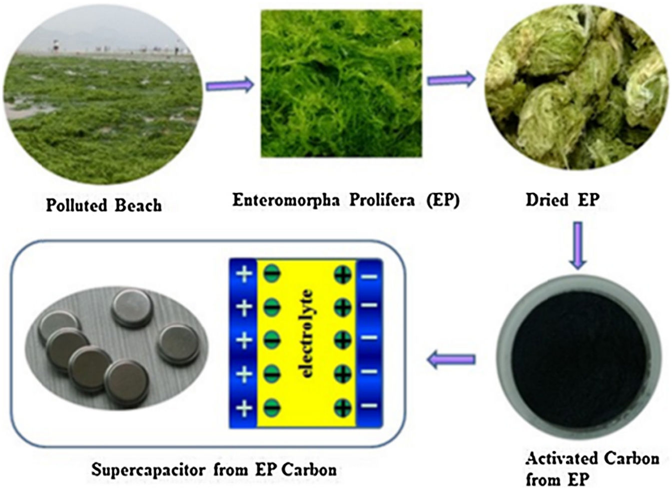

Fig. 1. Schematic diagram for the synthesis of active carbon material for supercapacitor from an ocean biomass E. prolifera.

2.2. Materials characterization

The specific surface area and pore volume of the carbons were determined by N_2 adsorption at 77 K on a porosity analyzer (Tristar 3000, Micromeritics). The specific surface area was calculated using BET (Brunauer-Emmett-Teller) equation. The total pore volume was obtained at the relative pressure of 0.995. The mesopore size distribution was calculated by BJH (Barret-Joyner-Helenda) method. The micropore volume was obtained using t-plot method. The micropore distribution of the carbons was determined using CO_2 adsorption at 0 °C and calculated by DFT (Density Function Theory) method. The microscopic morphology of the carbons was observed by field emission scanning electron microscope (FESEM, Sirion 200, FEI) and transmission electron microscope (TEM, JEM-2100, JEOL). The Raman analyses of the carbons were performed on a laser Raman spectrometer (RM2000, Renishaw).

2.3. Preparation of the electrode and electrochemical measurements

The active carbon materials were ground with 5 wt% of PTFE as binder and pressed between two pieces of nickel foam under 300 kg/cm^2. The prepared electrodes contained about 5 mg carbon materials. Before electrochemical tests, the electrodes were vacuum impregnated with electrolyte to guarantee that the electrode material was thoroughly wetted by the electrolyte of 30 wt % potassium hydroxide solution. The electrochemical capacitive performances of samples were studied on a CHI660D electrochemical workstation. All electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed in a three-electrode system using the carbon electrode as working electrode, a platinum film as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. A potential window of -1~0 V vs. SCE reference electrode was applied to the electrochemical measurements. From the GCD curves, the specific capacitance of the carbon was calculated using the following equation: [2]

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where C is the specific capacitance (F g^{-1}), I is the discharge current (A), Δt is the time spent in discharge (s), m is the mass of the active carbon in the electrode (g) and ΔV is the potential drop during discharge (V).