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Nori-based N, O, S, Cl co-doped carbon materials by chemical activation of $ZnCl_2$ for supercapacitor

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ABSTRACT

Plant biomass has gained much attention as raw materials for preparing porous carbon materials used in supercapacitors. In this paper, nori-based N, O, S, Cl co-doped carbon materials are prepared by a method of direct $ZnCl_2$ activation in high carbon yields over 30%. The prepared carbons are systematically characterized by N_2 adsorption/desorption, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Raman spectroscopy, infrared spectroscopy and X-ray photoelectron spectroscopy. The electrochemical capacitive performances are investigated in 6 M KOH electrolyte. Although the prepared carbons possess relative undeveloped porosity with low specific surface area and small pore volume, the nori-based carbons exhibit good capacitive performance due to the combined contributions of electrochemical double layer and pseudo-capacitance. The nori:$ZnCl_2$-2:1 carbons show a high capacitive performance of 220 F g^{-1}, good rate capability (61.5% in the range of 0.1–10 A g^{-1}), and good long-term cycle stability (96.6% after 5000 cylces). More importantly, the Nori:$ZnCl_2$-2:1-800 exhibits a very high specific volumetric capacitance of up to 307.7 F cm^{-3}. This work shows that direct $ZnCl_2$-activated seaweed carbon materials are promising electrode materials for supercapacitor applications.

1. Introduction

Supercapacitor has been one of most charming devices for storage of electric energy due to its unique merits of high power, fast charge-discharge stability, long cycle life, appropriate dimension/weight and low cost [1,2]. This device is typically composed of electrode materials, current collectors, membranes and electrolytes, in which the electrode material are the main factor that determines supercapacitor's performance. Based on the energy storage mechanism of electrode materials, supercapacitors are generally divided into electrical double layer (EDL) capacitors and pseudo-capacitors. In EDL capacitors, the charges store at the interface of electrolyte/electrode, and carbon materials with high accessible surface area are widely used [3–5]. In pseudo-capacitors, the charge/discharge process is achieved by reversible redox reactions, and transition metals oxide/hydroxide, conducting polymers and their composite materials [6–10] are mainly used. However, the large-scale applications of pseudo-capacitors are still limited due to the high price and poor cycle stability of these pseudo-capacitive materials.

Due to their tailored porosity, good conductivity, low cost, and excellent capacitive performance, porous carbons still get the most attentions in supercapacitor field. Many substances, such as petroleum cokes [11–13], phenolic resins [14–16], conductivity polymers [17,18] and metal-organic frameworks [19–21], have been used as raw materials for preparation of carbon materials. In recent years, plant biomass have gained much attentions as carbon precursors due to that the plants are abundantly available, reproducible, and low cost [22,23]. The plant biomass ever investigated are mainly obtained from terrestrial plants, including but not limited to: corn husk [24], pectin [25], rice husk [26], waste tea-leaves [27], peanut shells [28], cotton stalks [29], camellia oleifera shells [30], distillers dried grains [31], sunflower seed shells [32], potato [33], sugar cane bagasses [34], apricot shells [35], polar woods [36], coffee endocarps [37], bamboos [38], banana fibers [39], cherry stones [40]. Chemical activations, especially KOH and $ZnCl_2$ activation, are widely employed in the preparation of biomass-based carbon materials. After a chemical activation treatment, the plant biomass, mainly composed of hemicelluloses, celluloses and lignins, could be converted into porous carbon materials in moderate yields.

Roughly 2/3 of Earth's surface is covered by the oceans. Every

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year, the oceans supply a huge amount of seaweeds up to millions of tons. The seaweeds are widely various, quickly produced and easily harvested. Besides C and O elements, seaweeds always contain N, S or other elements, meaning that the seaweed-derived carbons may be doped by N, O or S. The heteroatom doping is considered to be helpful to improve the performance of carbon materials because some specific heteroatom-containing species on the carbon surface could contribute pseudo-capacitance [41,42]. Thus, seaweeds should be paid more attentions as carbon precursors. However, seaweeds are typically composed of water-soluble polysaccharide, protein and fat that is different from terrestrial plants. In a direct KOH activation, these matters always strongly degrade into small molecular and lost majority of carbon atoms due to the strong activation effect of KOH, thus leading to a very low yield of carbon materials. Although the combination process of pre-carbonization and post-KOH activation can give acceptable carbon yield, this process is completed and time-consuming [43]. Compared with KOH, $ZnCl_2$ is a milder activating agent, but sufficiently effective in creating porosity, and may be suitable to the production of seaweed-based porous carbon materials.

In this work, nori is used as a precursor to prepare porous carbon materials for EDL capacitors by a direct $ZnCl_2$ activation. The effects of $ZnCl_2$ dosage and carbonization temperature on the porosity are investigated. After the $ZnCl_2$ activation, the nori-based carbon materials can be obtained in high yields over 30%. Although the as-prepared carbon materials have low surface area and narrow microporosity, these carbons give a specific capacitance up to 220 F g^{-1} and good retention ratio in the range of 0.1–10 A g^{-1} (>60%). More importantly, the prepared carbons exhibit high volumetric capacitive performance.

2. Experimental

2.1. Materials preparation

Cleaned nori was grinded into a fine powder, and was homogeneously mixed with $ZnCl_2$ and a little water. The mixture were heated with a heating rate of 5 °C min^{-1}, and maintained for 2 h at a certain temperature (700 or 800 °C) under N_2 atmosphere in a tube furnace. The nori-based carbons were liberated by washing the carbonization residual with excessive 10% HCl and deionized water. In convenience, the as-prepared carbons are named as Nori:$ZnCl_2$-*m*-*n*, in which *m* and *n* are the weight ratio of nori/$ZnCl_2$ (1:1, 2:1 and 4:1) and carbonization temperature (700 and 800 °C), respectively. For comparison, a KOH-activated nori-based carbon (Nori:KOH-2:1-700) is prepared with nori/KOH weight ratio of 2:1 at 700 °C.

2.2. Materials characterizations

Microscopic morphology of the nori-based carbon materials was observed by scanning electron microscopy (SEM, Sirion 200 FEI Netherlands) and transmission electron microscopy (TEM, JEM2100, JEOL, Japan). Chemical properties of the surface of carbon materials were determined by X-ray photoelectron spectroscopy (XPS, Escalab 250, USA). Crystal structure of the carbon materials were analyzed by X-ray diffraction (XRD) patterns (Brucker D8 Advance diffraction) and Raman spectra (LabRAM HR800, Horiba). The porosities of the prepared carbons were determined by nitrogen adsorption/desorption measurements at −196 °C (Micrometitics ASAP 2020 system, USA). Brunaner-Emmett-Teller (BET) and Langmuir surface area (S_{BET}) were calculated from the N_2 adsorption isotherm data in the relative pressure range of 0.05–0.30. Total pore volume (V_{Total}) was obtained at $p/p_0 = 0.995$. Micropore (<2 nm) volume (V_{micro}), mesopore (2–50 nm) volume (V_{meso}) and pore size distributions (PSDs) were determined by applying the nonlocal density functional theory (NLDFT) model for slit pores on the N_2 adsorption isotherms.

2.3. Electrochemical measurements

The active materials on working electrodes were made up of the nori-based carbons, carbon black and polytetrafluoroethylene (PTFE) with a weight ratio of 90:5:5. Current collectors are nickel foams here. The mass of the active materials loaded on a work electrode is 2.0 mg (8 mg cm^{-2}). Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) test and electrochemical impedance spectroscopy (EIS) were performed on a CHI660D electrochemical testing station in 6 M KOH solutions. EIS test was performed in a three-electrode system with a platinum plate electrode and a saturated calomel electrode (SCE) as the counter and reference electrode, respectively.

Based on the galvanostatic charge/discharge results, the specific capacitances (C_m), energy densities (E) and powder densities (P) at current densities (0.1–10 A g^{-1}) could be calculated by the following equations:

$$C_m = \frac{4I \times t}{V \times m} \quad (1)$$

$$E = \frac{1}{8} \times C_m \times V^2 \quad (2)$$

$$P = \frac{E}{t} \quad (3)$$

in which I, t V and m is the discharge current (A), is galvanostatic discharge time (s), range of work voltage (V), total mass of active materials in the supercapacitor. The volumetric capacitance (C_v) was calculated by the equation of:

$$C_v = \rho \times C_m \quad (4)$$

in which ρ (g cm^{-3}) is the density of carbon materials which is calculated from the equation of

$$\rho = (V_{total} + 1/\rho_T)^{-1} \quad (5)$$

where V_{total} is the total pore volume obtained from N_2 adsorption isotherms at $p/p_0 = 0.995$, and ρ_T is the true density of graphitic materials (2.2 g cm^{-3}).

3. Results and discussion

3.1. Preparation and characterization of nori-based carbon materials

As shown in Fig. 1, the nori-based carbon materials are prepared by direct carbonizing a mixture of nori power and $ZnCl_2$. In this chemical activation process, $ZnCl_2$ acts as dehydrating agent that promotes the condensation reactions of carbonaceous material, inhibit the formation of tar and the gasification of carbon atoms, which results in high carbon yields (>30% here). Comparatively, the KOH-activated carbon material of Nori:KOH-2:1-700 is obtained in a very low yield of about 5%. The possible reason is that the polysaccharide, protein and fat in the nori strongly hydrolyse into small molecular and evaporate during the KOH activation process.

The pore structure, including specific surface area, pore size and its distributions, and pore volume, is very important for the