Biomass derived hierarchical porous carbons as high-performance anodes for sodium-ion batteries

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ABSTRACT

The electrochemical performance of sodium ion battery was improved by using peanut skin derived hierarchical porous carbon as an anode. By the utilization of the structure/composition of the peanut skin, hierarchical porous carbons with high surface area and sheet-like structure are successfully achieved through combined carbonization and activation with or without hydrothermal pretreatment. Tested against sodium, peanut skin derived carbon exhibits good rate capability and cycling stability, delivering a high initial charge capacity of 431 mAh g^{-1} at 0.1 A g^{-1}, retaining a reversible capacity of 47 mAh g^{-1} at 10 A g^{-1}, and showing a capacity retention of 83–86% after 200 cycles. The reason that peanut skin derived carbon works so well is that it uniquely combines highly accessible surface area and nanopores, dilated intergraphene spacing, and intrinsically open sheet-like structure, which are capable of reversibly accumulating sodium ions through surface adsorption and sodium intercalation.

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1. Introduction

Fabricating devices for high-performance energy storage has great importance for the solvation of energy shortage and related environmental issues [1]. Lithium ion batteries, as one of the most important energy storage systems, have been widely applied in electric vehicles, portable devices and grid storage owing to their long cycle life and high energy density [2]. However, as the use of large format lithium ion batteries, there is increasing concern regarding lithium's cost and continued availability [3]. Recently, sodium ion batteries are attracting renewed interest as a potentially lower cost alternative to lithium ion batteries because of the widespread distribution of sodium resources [4–6]. Because the sodium ion has a larger ionic radius than that of the lithium ion, the design of suitable host materials with larger space for intercalating and accommodating sodium ions is very difficult [7,8].

Currently, carbon is recognized as one of the promising electrode materials for energy storage systems due to its low cost, high electrical conductivity, stable physicochemical property, and long cycle life. It is well acknowledged that the commonly-used commercial graphite anode in today's lithium ion batteries shows a low reversible capacity in sodium ion batteries due to the graphene interlayer spacing that cannot host the larger Na ions

[2,9]. On the other hand, a variety of carbon materials including carbon black [10], hard carbon [11,12], carbon spheres [13,14], hollow carbon nanowires [15], carbon nanofibers [16,17], carbon nanotubes [9,18], and graphene [19,20] were found to facilitate the insertion/extraction of sodium ions and accelerate solid-state diffusion kinetics. Charge storage in carbons as anodes for sodium ion batteries can be clarified into several mechanisms, including chemisorption on surface heteroatoms or at defect sites, physisorption on the surface of pores, intercalation between graphene layers, and metal pore fillings [9,15,21]. Recent results indicate that the improvement of electrochemical performance of carbon anodes for sodium ion batteries strongly depend on their morphology, pore structure, and heteroatom doping. Noteworthy examples of high performance carbon anodes include nitrogen-doped carbon naofibers (a capacity of 134 mAh g^{-1} after 200 cycles at 0.2 A g^{-1}) [16], nitrogen-doped porous carbon sheets (a capacity of 155 mAh g^{-1} after 260 cycles at 0.05 A g^{-1}) [8], peat moss derived carbon nanosheet (a capacity of 255 mAh g^{-1} after 200 cycles at 0.1 A g^{-1}) [22], hollow carbon nanowire (a capacity of 206 mAh g^{-1} after 400 cycles at 0.05 A g^{-1}) [15], nitrogen-doped graphene foams (a capacity of 594 mAh g^{-1} after 150 cycles at 0.05 A g^{-1}) [23]. Besides, carbon material can be used as a promising matrix for loading of nanostructured metals, metal oxides, and sulfides, to increase the electronic conductivity, accommodate the volume change during cycling, and improve the rate capability [24,25].

Recently, extensive attention has been focused on using natural biomass to construct carbon materials [26–41]. Such carbon

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electrodes derived from biomass waste would be truly green. In terms of the preparation technique and the electrochemical performance, some biomass derived activated carbons with microscale particulates and tortuous pore networks exhibited similar electrochemical performance with commercial activated carbon products [42,43]. In the present work, we selected peanut skin as the precursor to design nanostructured carbons by using two different synthesis routes. Approximately more than 30 million metric tons of peanut produced per year in the word [44]. Peanut skin is the by-product of the manufacturing of peanut-based products, such as peanut butter, snack peanuts and confectionary. Peanut skin contains about 12% protein, 16% fat, and 72% carbohydrate [45]. Although the peanut skin, to some extent, is nutritive and expensive than other biomass precursors, we selected peanut skin as the precursor in the present work in order to give a case study that marrying the intrinsic structure/composition of the precursor to a tailored synthesis route can prepare sheet-like porous carbons [32]. The obtained hierarchical porous carbon (HPC) with sheet-like structure and high surface area (>1400 $m^2 g^{-1}$) derived from peanut skin delivers a reversible capacity as high as 148 mAh g^{-1} at a current density of 0.5 A g^{-1} after 200 cycles, and maintains a capacity of 47 mAh g^{-1} even at a very high current density of 10 A g^{-1}. The observed excellent electrochemical performance of the obtained carbon anodes in sodium ion batteries can be attributed to synergistic effects associated with the sheet-like morphology with a well-defined porosity, large surface area, and enlarged lattice spacing between graphene layers.

2. Experimental

2.1. Material preparation

Hierarchical porous carbons were prepared by carbonization and activation of peanut skin with and without hydrothermal pretreatment. The employed peanut skins were peeled off from peanuts grown in the Shandong region of China. **Route one**: 2.0 g of peanut skin and 50 mL of diluted sulfuric acid were placed in a 100 mL stainless steel autoclave. The autoclave was heated at 180 °C for 24 h and then cooled down naturally. The resulting biochar was collected by filtration, washed with distilled water, and dried. The activation agent (KOH) and dried biochar, in a mass ratio of 1:1 or 2:1, were thoroughly ground in an agate mortar, and then the mixture was heated at 800 °C with a heating rate of 5 °C min^{-1} for 1 h under argon flow. After that, the activated samples were thoroughly washed with 2 M HCl and distilled water, and finally dried in an oven at 100 °C for 12 h. The obtained carbons were denoted as HPC-1-n, where n represents the KOH to biochar mass ratio. **Route two**: 1.0 g of peanut skin was impregnated in 50 mL KOH solution (2 M or 4 M) for 2 days. After that, the peanut skin-KOH mixture was collected by filtration and drying. Activation was also carried out in a tubular furnace at 800 °C (5 °C min^{-1}) for 1 h under argon flow. The activated sample was also thoroughly washed with 2 M HCl and distilled water, and finally dried in an oven at 100 °C for 12 h. The resultant carbon was labeled as HPC-2-m, where m represents the concentration of KOH solution.

2.2. Material characterization

The microscopic feature of the samples was observed with scanning electron microscopy (SEM, Hitachi S4800, 15 kV) and transmission electron microscopy (TEM, JEOL 2010F, 200 kV). X-ray diffraction patterns (XRD) were obtained on a Bruker D8 ADVANCE diffractometer using Cu Kα radiation. The Raman spectra were recorded at ambient temperature with a confocal microprobe Raman system (Thermo Nicolet Almega XR Raman Microscope).

The surface areas and pore structures of the samples were investigated using physical adsorption of nitrogen at 77K on an automatic volumetric sorption analyzer (Autosorb-1, Quantachrome). Prior to the gas sorption measurements, the samples were outgassed at 250 °C for 6 h under a vacuum. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ULTRA (Kratos Analytical) spectrometer using monochromatic Al-Kα radiation.

2.3. Electrochemical measurement

The electrochemical characterization of all the samples was carried out using coin cells. All the electrodes were prepared by coating the electrode materials with carbon black and polyvinylidenedifluoride (PVDF) binder, at a weight ratio of 8:1:1, on stainless steel spacers. N-methyl-2-pyrrolidone (NMP) was used as the blending solvent for the mixture. The fabricated electrodes were dried at 120 °C under vacuum. The typical mass loading of the electrodes was ~0.5–1 mg cm^{-2}. The obtained electrode, polyethene separator, and Na metal counter electrode were assembled into a 2032-type button cell filled with electrolyte (1 M NaClO$_4$ in a 1:1 volume ratio of ethylene carbonate and diethyl carbonate), in an Ar-filled glovebox. Cyclic voltammetry (CV) was carried out using a CHI 660 workstation at a scan rate of 0.1 mV s^{-1}. The charge-discharge measurements were performed using Land battery measurement systems (CT2001A) at various current densities. Electrochemical impedance spectroscopy measurements were performed using a Gamry Interface 1000 workstation. All electrochemical tests were conducted at room temperature.

3. Results and discussion

3.1. Physicochemical characterization

The decision to employ two different synthesis strategies for hierarchical porous carbons was based on the plant structure, and how it can be transformed to final carbons with unique structures. Fig. 1 illustrates the material synthesis process employed for the electrodes, as well as the relevant charge storage mechanisms (discussed later). For route one, the hydrothermal pretreatment of biomass was firstly applied before carbonization/activation. The hydrothermal process involves hydrolysis, dehydration, decomposition, and condensation, which would increase the porosity of the biomass and introduce high levels of oxygen-containing functional
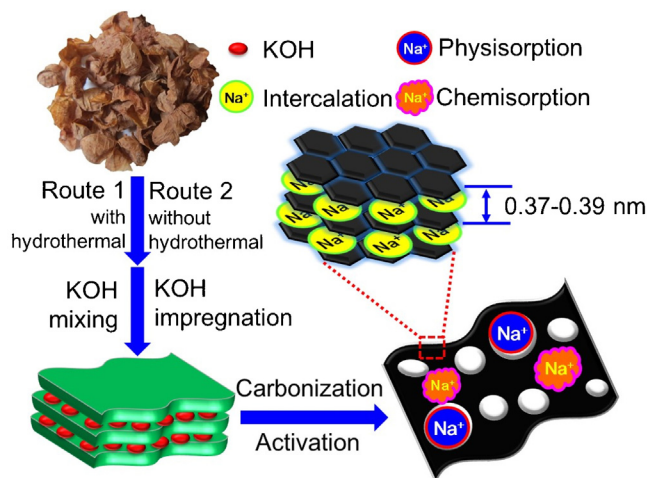
Fig. 1. Schematic illustration of the formation of hierarchical porous carbons and the relevant charge storage mechanisms.