



Bio-derived hierarchically macro-meso-micro porous carbon anode for lithium/sodium ion batteries



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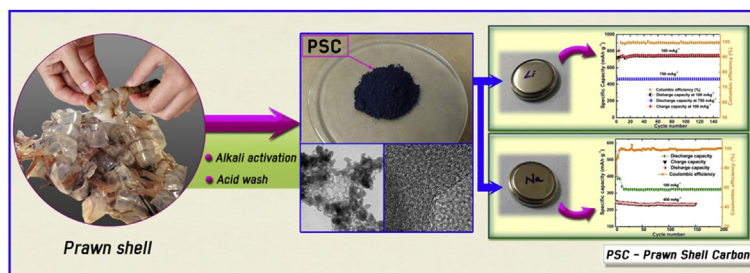
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HIGHLIGHTS

- Prawn shells are converted into porous carbon through economically viable process.
- The derived carbon exhibits excellent capacity in both Li/Na ion batteries.
- NMR (Li^6 , Li^7 & Na^{23}) and EPR studies on intercalated derived carbon carried out.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen doped hierarchically porous carbon derived from prawn shells have been efficiently synthesized through a simple, economically viable and environmentally benign approach. The prawn shell derived carbon (PSC) has high inherent nitrogen content (5.3%) and possesses a unique porous structure with the co-existence of macro, meso and micropores which can afford facile storage and transport channels for both Li and Na ions. PSC is well characterized using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Transmission electron Microscopy (TEM), High resolution TEM (HR-TEM) and X-ray photoelectron spectroscopy (XPS). Electron Paramagnetic Resonance (EPR) and Solid state-Nuclear Magnetic Resonance (NMR) studies have been conducted on pristine PSC and Li/Na intercalated PSC. PSC as anode for Lithium ion batteries (LIBs) delivers superior electrochemical reversible specific capacity (740 mAh g^{-1} at 0.1 Ag^{-1} current density for 150 cycles) and high rate capability. When used as anode material for Sodium ion batteries (SIBs), PSC exhibits excellent reversible specific capacity of 325 mAh g^{-1} at 0.1 Ag^{-1} for 200 cycles and rate capability of 107 mAh g^{-1} at 2 Ag^{-1} . Furthermore, this study demonstrates the employment of natural waste material as a potential anode for both LIB and SIB, which will definitively make a strike in the energy storage field.

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1. Introduction

Lithium ion batteries (LIBs) have become the universal power source for most of the portable consumer electronics since they were launched in 1981. Currently, they are the technology of choice to develop electric vehicles and large scale storage of renewable energy because of their high energy density and high voltage. But these applications call for higher specific capacities and faster rate performance. A typical modern LIB cell consists of a cathode made from a lithium-intercalated layered oxide, a graphite anode and an organic electrolyte. The battery operates following a “rocking chair” concept in which the Li^+ ions shuttle between the anode and cathode through the electrolyte during the charge/discharge cycles [1]. In spite of extensive research on electrode materials for LIB, still they are lacking in terms of rate capabilities, capacities and economic viability. Novel highly structured and cheap electrode materials have to be investigated for improved performances.

In this context, if LIBs are to gain a significant place in the future, there is going to be an increasing demand for Li, resulting in concerns about the increasing cost and limited abundance of Li. Sodium ion battery (SIB) is one possible alternative to LIB owing to its low cost and higher natural abundance of sodium particularly when large scale applications are considered. The state of the art anode for LIB is graphite but exhibiting low capacities when used in SIBs as only a small amount of Na can intercalate into graphite [2]. Disordered carbon with porous morphology appears to be very promising as anode for SIBs.

Many carbonaceous materials with various morphologies and structures like carbon nanotubes (CNTs) [3], hollow nanospheres [4], graphene [5] etc. have been investigated as anode materials for rechargeable batteries. However, the complex synthesis methods, expensive equipments and the use of toxic/harmful chemicals make it less attractive. Recently, carbonaceous material derived from biomass has been explored widely as anode material for LIBs [6–9]. Biomass derived carbon has the advantage of being a renewable, low cost source, and also can provide excellent porous 3D nanostructure which is of very particular interest for high lithiation/sodiation capacity and excellent cyclability in batteries [10].

N-doping of carbon is proven to improve the electrochemical performance, as it enhances the electrical conductivity and also provide more sites to increase the interaction between carbon and Li/Na during cycling. N-doped carbons are synthesized typically using various expensive, toxic N containing precursors following rigorous/complex experimental procedures. In this point, preparation of N-doped carbon from naturally occurring bio waste/biomass is very appealing as it reduces the environmental pollution, lessens the usage of toxic chemicals and is very inexpensive both in terms of source cost and processing cost. Several studies have been reported recently on biomass derived anode material for LIB/SIBs like carbon material derived from human hair [11–13], ox horn [14], agricultural waste [15], peanut shells [16,17], wheat straw [18], banana peels [19], coconut shell [20], fish scales [21] and plant biomass [8,22,23].

In this work, we have synthesized a hierarchical macro-meso-micro porous, turbostratic, N-doped carbon material derived from marine Indian prawn shells. The Indian prawn (*Fenneropenaeus indicus*, formerly *Penaeus indicus*) [24], is one of the major commercial prawn species of the world. *F. indicus* is known by many common names around the world, including Indian white prawn, Tugela prawn, white prawn, banana prawn, Indian banana prawn and red leg banana prawn. About 10^{10} to 10^{11} tons of prawn shells are produced each year as natural waste. In addition, capture fisheries and aquaculture also contributes enormous quantity of prawn shells as waste side product [25,26]. Prawn/shrimp

crustacean shells contains nitrogen containing polysaccharide, chitin (poly- β (1-4)-N-acetyl -D-glucosamine) and inorganic components mainly CaCO_3 . Hence, prawn shells are an inexpensive, easily available, abundant source of nitrogen containing biomass which can be put into use for a wide variety of applications.

N-doped highly porous carbon has been synthesized from prawn shell by a very simple method, which is not only economical but also environmental friendly. Porous carbon derived shrimp/prawn shells has been used for applications like supercapacitors [27,28] and catalyst for oxygen reduction reaction (ORR) [29] recently. We have evaluated carbon obtained from prawn shells as anode material for LIBs and SIBs and obtained excellent electrochemical performances. Herein, we have successfully converted a waste material to a wonder/wealth material for high end applications. To the best of our knowledge, this is the first time prawn shell derived carbon is used as electrode materials in both LIB and SIBs, which we believe will revolutionize the present energy scenario.

2. Experimental section

All the chemicals used in the study were of analytical grade from Sigma-Aldrich and Merck and used as received without further purification. De-ionized (DI) water was prepared on site using Millipore-Q water system. The Indian prawn shells used in this study were collected from the local fish market (Karaikudi, India), a waste material.

2.1. Preparation of prawn shell derived porous carbon (PSC)

The Indian prawn shells were washed thoroughly with water and dried in air. The material was heated at 300°C and grinded. The pre-carbonized material was immersed in 0.1 M NaOH solution for 24 h followed by heating at 750°C under inert argon atmosphere for 2 h with a heating ramp of 3°C min^{-1} . NaOH is used as an activation agent for creating porous structure by leaching out the acidic impurities. The obtained black material was washed extensively with 1 M HCl to remove the metal impurities like Ca, followed by washing with DI water till neutral pH was attained. The resulting carbon material was dried at 80°C under vacuum. The as-fabricated prawn shell derived carbon material is designated as PSC hereafter.

2.2. Material characterization

The surface morphology of the synthesized powder was examined using a FESEM (Model: KARL ZEISS) and HRTEM (Tecnaï 20 G2(FEI)). XPS of the synthesized powder has been performed using a MULTILAB 2000 (Thermo Scientific) photoelectron spectrometer and the spectra were recorded using an X-ray source (Mg- $K\alpha$ radiation 0–1253 eV). XRD have been carried out with a Bruker D-8 diffractometer equipped with a Cu $K\alpha$ radiation (1.5406 Å) operated at 40 kV and 30 mA. Raman spectroscopy has been carried out at room temperature with Green LASER (excitation line 514 nm at 2.5 mW power) using Renishaw InVia Reflex Micro Raman spectrometer equipped with a CCD detector. EPR studies of PSC before and after interaction with Li and Na, was conducted using EPR spectrometer (Model: BRUKER EMX Plus) at microwave frequency of 9.863,940 GHz and 10 mW power at room temperature. ^6Li , ^7Li and ^{23}Na NMR of PSC after intercalating with Li/Na was recorded using NMR instrument (BRUKER, 400 MHz). N_2 sorption analysis was performed at 77.4 K using QUANTASORB equipped with surface area and pore size analyzer. Sample was degassed at 150°C for 24 h before analysis. BET surface area was determined according to BET model.

The electrochemical measurements were carried out by

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