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Lithium and sodium storage in highly ordered mesoporous nitrogen-doped carbons derived from honey

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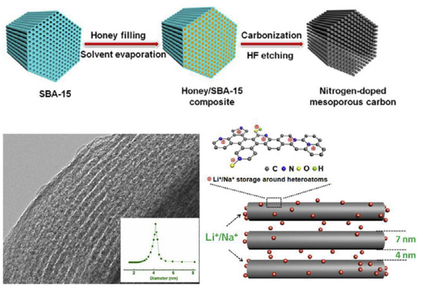
HIGHLIGHTS

- Honey is employed as a nitrogen-containing carbon precursor.
- A novel highly ordered nitrogen-doped mesoporous carbon is obtained.
- The obtained HMNCs exhibit excellent lithium and sodium anodic performance.
- The mechanism of Li^+/Na^+ storage in HMNCs is investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Honey, a widely existent biomass, consists mainly of carbohydrate and other nitrogen-containing substances such as proteins, enzymes and organic acids. It can be mixed homogeneously with mesoporous silica template for its excellent water-solubility and moderate viscosity. In this work, honey was employed as a nitrogen-containing carbon precursor to prepare nitrogen-doped ordered mesoporous carbons (OMCs). The obtained honey derived mesoporous nitrogen-doped carbons (HMNCs) with dilated interlayer spacings of 0.387–0.395 nm, narrow pore size distributions centering at around 4 nm and satisfactory N contents of 1.38–4.32 wt% offer superb dual functionality for lithium ion battery (LIB) and sodium ion battery (NIB) anodes. Tested against Li, the optimized HMNC-700 delivers a superior reversible capacity of 1359 mA h g^{-1} after 10 cycles at 100 mA g^{-1} and excellent rate capability and cycling stability of 722 mA h g^{-1} after 200 cycles at 1 A g^{-1}. For NIB applications, HMNC-700 offers a high initial reversible capacity of 427 mA h g^{-1} and stable reversible capacity of 394 mA h g^{-1} at 100 mA g^{-1}.

1. Introduction

Lithium ion batteries (LIBs) as the main energy storage devices have been dominating the battery market over the last three decades and will continuously boom in the future, because of the steadily increasing demands for electronic devices, such as smartphones, notebook computers and electric vehicles [1–3]. In recent

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years, sodium ion batteries (NIBs) have attracted a great deal of attention due to the wide abundance and low cost of sodium resources [4–7]. Graphite is the most commonly used anode carbon material for commercial rechargeable lithium batteries for its low cost and low electrochemical potential with respect to lithium metal. However, it possess limited storage capacity (372 mA h g^{-1} in theory) and rate performance which cannot meet the requirement for high-energy and high-power LIBs [2,8]. Moreover, graphite is not suitable for NIB anodes because of the larger ionic radii of the Na *versus* Li (0.102 nm *versus* 0.076 nm) and the relatively small interlayer distance of graphite (~0.34 nm, the minimum interlayer distance required for Na^+ insertion is 0.37 nm) [9–12].

Porous hard (poorly or non-graphitizable) carbons with high specific surface areas, shorter diffusion pathways and large interlayer distances can offer large electrode/electrolyte interfaces for charge-transfer reaction, and facilitate ion transport and Li^+/Na^+ insertion-extraction. Consequently, porous hard carbons are highly recommended for the fabrication of high-performance anodes for LIBs and NIBs [13–16]. Especially, the porous carbons doped by heteroatom (such as N, B, S and P) exhibit improved electrochemical performance since the presence of these elements at carbon's surface can enhance its reactivity and provide extra Li/Na ion storage sites [17–26]. Among the heteroatoms, nitrogen has received more attention for its high electronegativity and hybridization of nitrogen lone pair electrons with the π electrons in the carbon which are believed to make favorable binding sites for Li^+/Na^+ storage [17,27–29].

Biomass, as a renewable resource, has been widely used as precursors for porous carbons, because of its low cost, huge availability, rapid regeneration, easy access and environmental friendliness [16,30,31]. Recently, many researchers focus on the preparation of nitrogen-doped porous carbons for battery anodes derived from biomass containing nitrogen resources such as gelatin [27], peat moss [32], egg white [15], wheat straw [19], ox horn [18], silk [20], corn starch [33] and cotton [34]. Among such research, Mitlin et al. [15] utilized egg white as a protein-based precursor to synthesize mesoporous nitrogen-doped carbons by a template process. The mesoporous nitrogen-rich carbon obtained under the optimum condition demonstrates an ultra-high capacity of 1780 mA h g^{-1} as a LIB anode at 100 mA g^{-1} and 390.4 F g^{-1} as an electrochemical capacitor electrode at 250 mA g^{-1}, which is impressive.

Honey is the natural sweet substance that consists mainly of carbohydrates, including fructose, glucose, about 25 different oligosaccharides and other nitrogen-containing substances such as proteins, enzymes and organic acids [35]. And honey can be mixed homogeneously with mesoporous silica template for its excellent water-solubility and moderate viscosity. Therefore, honey is expected to be an ideal carbon precursor used to prepare ordered mesoporous carbons (OMCs) by a hard template method. In this work, we employ honey as a nitrogen-containing carbon precursor to prepare highly ordered mesoporous nitrogen-doped carbon by a simple SBA-15 template process for the first time. The as-prepared mesoporous carbons with narrow pore size distributions centering at around 4 nm, N-contents of 1.38–4.32 wt% and dilated interlayer spacings of 0.387–0.395 nm have been studied for LIBs and NIBs applications to explore the improvement of Li^+/Na^+ storage performances.

2. Experimental

2.1. Preparation of honey derived mesoporous nitrogen-doped carbons (HMNCs)

5 g honey and 1 g SBA-15 template with pore size 6–8 nm and wall thickness of about 4 nm (sourced from Nasenmei nano materials, Hangzhou, China) were dissolved and mixed sufficiently in 5 mL double-distilled water. The mixture was under stirring for 4 h and dried at 80 °C, followed by carbonized in an argon-flowing tube furnace (700, 800, 900 °C) for 2 h with a heating rate of 5 °C min^{-1}. Sintered products were treated in 5% HF solution for 12 h to remove the hard template, washed with double-distilled water to neutral, and dried at 100 °C under vacuum for 10 h. The samples carbonized at different temperatures are named HMNC-700, HMNC-800 and HMNC-900.

2.2. General characterization

The obtained products were subjected to various characterization techniques. Nitrogen sorption analysis was carried out with a Micromeritics TriStar II 3020 automatic analyzer (Norcross, GA, USA). The samples were degassed at 120 °C for 48 h before absorption measurements. Specific surface areas were estimated according to the BET model and pore size distributions (PSDs) were calculated by applying the Barrett-Joyner-Halenda (BJH) model. X-ray diffraction (XRD) measurements were performed on a TD-3500 X-ray powder diffractometer (Danton, China). X-ray photoelectron spectra (XPS) were acquired on a Kratos XSAM 800 spectrometer (Manchester, UK). Field emission scanning electron microscopy (SEM) images were obtained with a Hitachi S4800 scanning electron microscope (Tokyo, Japan). Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai G2 20 TEM (Hillsboro, OR, USA) operating at 200 kV. Raman spectra were detected on a Confocal LabRAM HR800 spectrometer, HORIBA Jobin Yvon (Paris, France). Elemental analysis was done by using a Euro EA3000A-nalyzer (Leeman, USA).

2.3. Electrochemical measurements

The electrochemical behavior of as-prepared samples was evaluated using 2032-type coin cells. The slurry of active material, acetylene black (conductive additive) and polyvinylidene fluoride (PVDF, binder) at a weight ratio of 80: 10: 10 in N-methyl-pyrrolidone (NMP) was coated onto a copper foil current collector and then dried at 110 °C overnight in vacuum oven to obtain the working electrode with a loading of around 1.2 mg cm^{-2}. Li/Na metal foil was used as a counter/reference electrode. The Celgard 2400 microporous polypropylene film was used as the separator. The cells were assembled in an argon-filled Dellix glove box with sub-0.1 ppm water and oxygen contents (Chengdu, China). The LIB electrolyte was 1 M $LiPF_6$ in a 1:1:1 vol ratio of ethylene carbonate (EC): dimethyl carbonate (DMC): diethyl carbonate (DEC) and the NIB electrolyte was 1 M $NaClO_4$ in 1:1 by volume EC and DEC. Cyclic voltammetry (CV) measurements were carried out at a scan rate of 0.1 mV s^{-1} on an Autolab PGSTAT 302 electrochemical workstation (Utrecht, the Netherlands) in the voltage range of 0.005–3.0 V (*vs.* Li^+/Li) or 0.005–2.9 V (*vs.* Na^+/Na). The galvanostatic charge-discharge tests were performed between 0.005 and 3.0 V (*vs.* Li^+/Li) or between 0.005 and 2.8 V (*vs.* Na^+/Na) at room temperature on a Newware CT-3008 W battery cycler (Guangdong, China). Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range 0.01–100 kHz at a charged stage with an applied amplitude of 5 mV on an Autolab PGSTAT 302 electrochemical workstation (Utrecht, the Netherlands).

3. Results and discussion

During previous research, we employed wheat straw as a carbon source to prepare hierarchically porous nitrogen-rich carbon (HPNC) by KOH activation assisted with acid pretreatment and