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Full Length Article

Surface functionalization of nitrogen-doped carbon derived from protein as anode material for lithium storage

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ABSTRACT

Carbon has received an intensive consideration in view of its application as an anode in lithium storage and is characterized by high electrical conductivity, excellent chemical and physical properties, and outstanding stability for insertion and deinsertion of Li ions. However, the due to the high-cost production requiring a high temperature process, a limited storage capacity, and a poor rate capability. In the present study, we suggest a novel protein as a raw material of carbon using simply carbonization. The nitrogen-doped carbon indicates the nitrogen (N)-doped sites with graphitic–N and pyridinic–N sites, as well as high crystallizability. The optimized electrode delivers an excellent cycling stability (284 mA h g^{-1} after 100 cycles at 100 mA g^{-1}), an impressive rate performance (154 mA h g^{-1} at 2000 mA g^{-1}), and a remarkable ultrafast cycling stability (112 mA h g^{-1} after 500 cycles at 2000 mA g^{-1}). Therefore, this unique nitrogen-doped carbon offers attractive advantages in terms of the functional N-doped sites, a simple fabrication process, and a low-cost production.

1. Introduction

In the future technological life, energy is an essential demand for use in electric vehicle, electric robotics, and so on [1–3]. Therefore, a large number of approaches have been performed to respond to the ever-increasing requirements of energy storage. In this regard, due to their high energy density, high average output voltage, long cycle life, eco-compatibility, low self-discharge rate, and low memory loss, lithium ion batteries (LIBs) can be considered as a promising storage technology for portable electronic devices such as smart phones, cameras, laptops, etc. [4–7] LIBs are composed of four main components: the anode electrode, cathode electrode, separate, and electrolyte. Among them, the storage capacities and cost of anode materials of LIBs still cannot gratify the fast development of future applications such as electric vehicles and electric robotics [8–10]. Graphite anode with a limited storage capacity and a poor rate capability, which is mostly used in commercial LIBs, is commonly synthesized from oil residues such as coal-tar pitch and petroleum coke at the high temperature of 2000–3000 °C, leading to a high-cost production [11–15]. Therefore, extensive research has sought to explore functional carbon with high capacity, high-rate capability, easy approach, and low cost to replace conventional graphite.

Previous studies have focused on various carbons as anode materials for LIBs, including carbon nanofibers [16,17], carbon nanotubes [18], and graphene [19,20]. However, most of the fabrication processes require a particular precursor, unique equipment, and intricate process. Thus, as a renewable source, biomasses such as coffee shells [21], coconut [22], rice straw [23], and cherry stones [24] have recently acquired much consideration as promising candidates in the fabrication of carbon. The main reason of this interest was the abovementioned biomaterials' low cost and richness. In addition, it is widely known that the physicochemical properties of carbon-based systems can be modified by means of surface dopants [25–28]. The N-doped carbon can be further increased to active sites and defects sites, leading to an improvement of electrochemical performance [29–31]. Specifically, the defects sites onto the surface can be helped to provide electrochemical reaction sites for Li^+ adsorption to increase the rate performance at high current densities. However, the formation of N-doping sites in carbon implies a unique synthetic method, such as the hydrothermal method, as well as an additional precursor for doping sites, which creates some challenges. Said differently, the fabrication of N-doped carbon from natural biomasses with ample amounts of nitrogen appears to be a very attractive alternative.

In addition, another issue related to the application of carbon as an

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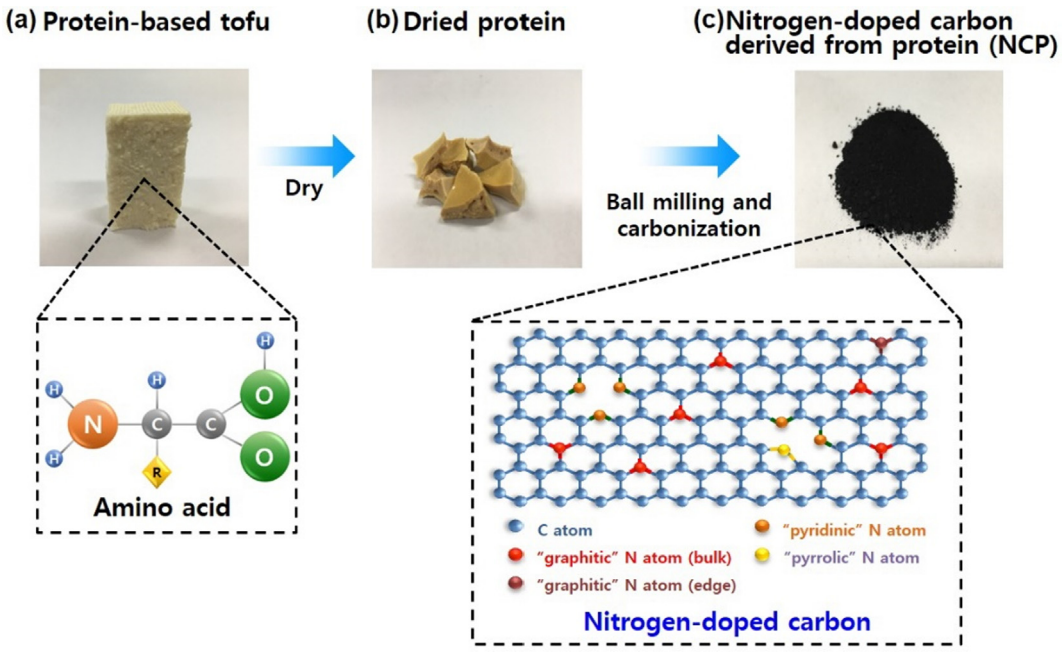

Fig. 1. Schematic illustration of the fabrication process for (a) protein-based tofu, (b) dried protein, and (c) nitrogen-doped carbon derived from protein (NCP).

anode material is ultrafast performance to extend the LIB applications [3,5,16]. The ultrafast performance of N-doped carbon is more favorable than that conventional graphite due to the excellent Li^+ adsorption of the latter that results from defects sites [11].

Therefore, in the present study, we prepared N-doped carbon derived from protein as anode material for LIBs. The protein, which contains amino acid with carbon, nitrogen, oxygen, and hydrogen, is one of the novel carbon sources [32,33]. The N-doped carbon area was developed using carbon and nitrogen atoms. Moreover, we demonstrated and optimized the electrochemical performance of N-doped carbon from protein by definite conditions using the optimized synthetic temperature. Our concept would widen the synthesis of carbon from biomass and could contribute to the development of anode materials for high-performance LIBs, including ultrafast performance.

2. Experimental

2.1. Synthesis of nitrogen-doped carbon derived from protein (NCP)

Protein from tofu (Pulmuone Co., Ltd.) was used. The nitrogen-doped carbon derived from protein (NCP) was simply synthesized by carbonization. The protein was firstly dried in an oven at 100 °C to take out water, and then heated at 400 °C for 3 h with the heating rate of 10 °C min^{-1} to remove any impurities as organic materials. Afterwards, to eliminate the inorganic materials, the prepared sample was washed using nitric acid. Finally, the carbonization was performed in N_2 atmosphere. To obtain the optimization of energy storage performance in LIBs, the carbonization was gradationally performed using different temperatures of 1100, 1200, and 1300 °C for 2 h with the heating rate of 10 °C min^{-1}, which are henceforth referred to as NCP 1100, NCP 1200, and NCP 1300, respectively.

2.2. Characterization

The structure and morphology were inspected using scanning electron microcopy (SEM, Hitachi S-4800), and transmission electron microscopy with dispersive spectrometer (TEM-EDS, KBSI Gwangju Center, Tecnai G^2). To investigate the crystal structure, X-ray diffractometry (XRD, Rigaku, D/Max 2500 V) was confirmed in the range from 10° to 90° and by a Cu K_α source. The empirical parameter of intensities for main peaks was used to investigate the crystallinity of carbon. Thus, the ratio of height of the main peak to the background was calculated. Also, the standard deviation of the calculated data is ± 0.1. X-ray photoelectron spectroscopy (XPS, Thermo scientific, ESCALAB 250) was used to analyze the chemical bonding states. The binding energies of the XPS peaks were calibrated by the C 1s core level (284.5 eV) before fitting.

2.3. Electrochemical characterization

Energy storage performance with electrochemical reactions were executed by the half-cell system using coin cells (CR2032). The working electrode was fabricated on copper foil substrate as the current collector from a slurry, made up of the NCP as the active material (80 wt%), Ketjen black (10 wt%) as the conducting material, and polyvinylidene difluoride (10 wt%) as the binder. The prepared electrode was dried in an oven at 100 °C for 10 h. The Li metal foil and a porous polypropylene membrane were used for the counter electrode and the separator, respectively, in a 1.0 M $LiPF_6$ solution in a mixture of ethylene carbonate dimethyl carbonate (1:1) as the electrolyte. The coin cells were prepared in a argon-filled glove box with O_2 and H_2O contents less than 5 ppm. The charging/discharging measurements were tested in the potential range of 0.05–3.00 V (vs Li/Li^+) at the current density of 100 mA g^{-1} up to 100 cycles at 25 °C. The rate capability test was observed at the following current densities: 100, 300, 500, 700, 1000, and 2000 mA g^{-1}. The ultrafast cycling stability was examined at the current density of 2000 mA g^{-1} up to 500 cycles.

3. Results and discussion

Fig. 1 elucidates the synthesis process of NCP by the protein using a facile method, including the dry procedure and carbonization. The