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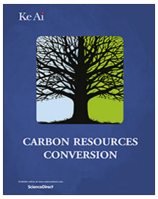

Pyrolytic carbon derived from spent coffee grounds as anode for sodium-ion batteries

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ABSTRACT

This paper reported the facile preparation of pyrolytic carbon derived from spent coffee grounds and the evaluation of its electrochemical performance when used as anode in sodium-ion battery. X-ray diffraction analysis, scanning electron microscope, Brunauer–Emmett–Teller were employed to characterize the structure of pyrolytic carbon. Electrochemical performances were tested by constant current charge–discharge, cyclic voltammetry and electrochemical impedance spectroscopy. Results showed that the pyrolytic carbon possess a porous structure (1–2 μm) and a specific surface area of 94.35 $m^2 g^{-1}$. When used as anodes in sodium-ion batteries, a reversible capacity of 154.2 mA h g^{-1} at a current density of 200 mA g^{-1} after 50 cycles was obtained. Several electrolytes were evaluated and their electrochemical performances were compared. The result indicated that this material has excellent storage capacity and good cycling stability. Our method provided a preparation of pyrolytic carbon from environmentally friendly resources.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used as working power supplies for various electronic products because of their large energy density, long cycle life, and small self-discharge [1–6]. However, limited lithium resources, safety issue and poor low-temperature performance have limited the large scale applications of LIBs. Thus, there is an urgent need to look for other storage batteries to replace LIBs.

Sodium ion batteries (SIBs) appeared to be an attractive greener alternative for LIBs. There are abundant sodium resources; and sodium extraction technology from sea is already mature. In addition, both lithium and sodium belong to the same group of elements; and thus, sharing similar chemical properties [7–11]. Nevertheless, more work needs to be done to search for a suitable anode material for use in SIBs. Conventional anode material that has been used for LIBs are unsuitable for use in SIBs. For example, graphite which has a capacity of 372 mA g^{-1} when used as anode for LIBs demonstrated only ~15 mA h g^{-1} in SIBs [12,13]. In addition, the lattice structure of graphite can be easily destroyed during Na ion insertion and extraction resulting in rapid capacity fading in SIBs.

Hard carbon has been demonstrated to be good candidate as anode material for SIBs. Table 1 shows the carbon source, fabrication process and electrochemical performance of the hard carbon in previous studies. Dahn's group has successfully prepared hard carbon using glucose as precursor for the first time. A reversible sodium capacity of 300 mA g^{-1} was achieved which is close to that for lithium insertion in graphitic carbon anode [14]. Most of the hard carbon currently investigated is derived directly or indirectly from petrochemical or environmentally unfriendly resources. For example, Yang et al. prepared carbon material derived from pitch by oil-bath heating which showed an initial discharge and charge capacity of 233.3 mA h g^{-1} and 79.2 mA h g^{-1}, respectively [15].

Recently, there are an increasing number of researches on synthesis of pyrolytic carbon from bio-resources such as coconut shells [16], peanut shell [17], lignin [18], etc. In 2014, more than 9.1 million tons of coffee fruit were produced globally. Every kg of instant coffee produces 0.9 kg of spent coffee grounds. Spent coffee grounds which are relatively rich in carbon can be used as a potential source for pyrolytic carbon and represent a kind of concentrated biomass resource. For example, Kim et al. reported that carbon derived from waste coffee grounds can be used for methane storage [19]; Xu et al. reported the conversion of coffee grounds into middle-caloric product gas [20,21]; Park et al. reported the fabrication of supercapacitors by nanoporous carbonaceous materials that obtained from coffee grounds [22]; Jang et al.

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Table 1
Carbon source, fabrication process and electrochemical performance of pyrolytic carbons.

Carbon source	Fabrication process	Capacity retention	References
Spent coffee ground (C700)	Simple sintering method	154.2 mA h g^{-1} after 50 cycles at 200 mA g^{-1}	Present study
Natural graphite		– 100 mA h g^{-1} after 500 cycles at 200 mA g^{-1} (Ether-based Electrolyte Systems) – 15 mA h g^{-1} for the 3rd cycle at 200 mA g^{-1} (Carbonate-based Electrolytes Systems)	[12]
Polystyrene cups	Moderate temperature and high pressure fabrication process in a sealed reactor	116 mA h g^{-1} after 80 cycles at 20 mA g^{-1}	[25]
Sucrose	Microwave-assisted reaction	183 mA h g^{-1} after 50 cycles at 30 mA g^{-1}	[26]
Coal tar pitch	Pyrolysis condensation method	133 mA h g^{-1} after 200 cycles at 100 mA g^{-1}	[27]
Mesitylene (C_9H_{12})	Controlled thermal decomposition	92 mA h g^{-1} after 50 cycles at 150 mA g^{-1}	[28]
Commercial hard carbon		75 mA h g^{-1} after 50 cycles at 150 mA g^{-1}	[28]
Reduced graphene oxide (RGO)		93.3 mA h g^{-1} after 250 cycles at 200 mA g^{-1}	[29]
Hollow carbon nanowires (HCNWs)		206.3 mA h g^{-1} after 400 cycles at 50 mA g^{-1}	[30]

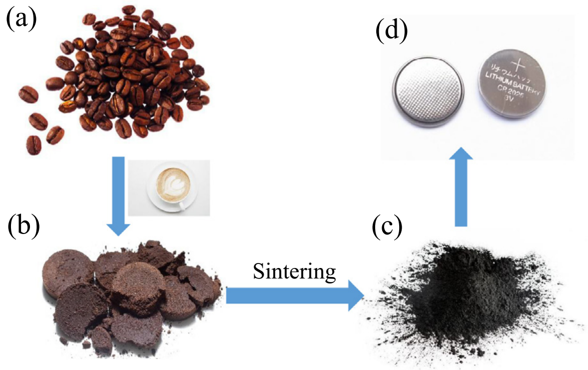

Fig. 1. Schematic illustration of pyrolytic carbon derived from spent coffee grounds as anode for batteries. (a) Coffee bean; (b) spent coffee grounds; (c) pyrolytic carbon; (d) batteries.

demonstrated the possibility of direct power generation from waste coffee grounds via a high-temperature carbon fuel cell technology [23]. However, to the best of our knowledge, researches about pyrolytic carbon derived from coffee grounds as anode materials for SIBs are rarely reported. Therefore, present study aims to investigate the possibilities of synthesizing pyrolytic carbon from spent coffee ground for use as anode materials in SIBs. Development of anode materials from coffee grounds will reduce the cost of SIBs and add value to spent coffee grounds. In this work, pyrolytic carbon was derived from spent coffee grounds by sintering process at elevated temperature (Fig. 1). The morphology of the as-prepared pyrolytic carbon was characterized by X-ray diffraction analysis (XRD), scanning electron microscope (SEM), specific surface area and porosity analysis. The pyrolytic carbon was then used as active material of anode in SIBs. Battery performance was analyzed using constant current charge–discharge test, cyclic voltammetry and AC impedance test.

2. Experiment section

2.1. Preparation of pyrolytic carbon

Spent coffee grounds were put into beaker and washed several times with deionized water to clean and adequately remove floating and water soluble impurities in raw materials. Spent coffee grounds were then filtered and transferred into Teflon-lined stainless autoclave at 150 °C for 2 h. Following that, the spent coffee grounds were soaked in sodium carbonate solution (1 g L^{-1}) for more than 6 h to neutralize the remaining oil in the material. The obtained materials were washed with deionized water and dried in a drying oven. Finally, pyrolytic carbons were obtained by heating the obtained materials at a heating rate of 10 °C min^{-1} to 600, 700, 800, and 900 °C under flowing argon for 1 h. The four samples obtained at 600, 700, 800, and 900 °C were denoted as C600, C700, C800, C900, respectively.

2.2. Characterization of pyrolytic carbon

The obtained pyrolytic carbon were characterized by X-ray diffraction (XRD, D8 Discover, Broker AXS, Cu radiation, $\lambda = 1.540596$ Å), scanning electron microscopy (SEM, S-4800, Hitachi). Brunauer–Emmett–Teller (BET, Micromeritics, ASAP 2020M) and X-ray Photoelectron Spectroscope (XPS, AXIS ULTRA DLD).

2.3 Electrochemical measurement

Electrodes were prepared by mixing active material, conductive agent (super-p) and adhesive (PVDF) at a mass ratio of 7:2:1. N-methyl pyrrolidone (NMP) was chosen as dispersant and the obtained slurry was spread on copper foil. Metallic sodium was used as counter and reference electrode. Three different electrolytes were used namely 1 M $NaClO_4$ solution in tetraethylene glycol dimethyl ether (TEGDME), ethylene carbonate: dimethyl carbonate (EC:DMC) (1:1 w/w) and EC:DMC (1:1 w/w) + 20 wt% of fluoroethylene carbonate (FEC) with $NaClO_4$ as conductive salt. Glass fiber was used as separator. Coin cells (CR 2032) were assembled in a glove box filled with argon. During the assembling operation, the moisture and oxygen levels were both kept below 0.1 ppm. Constant current charge and discharge test was conducted in battery testing system within a voltage range of 0.01–3.00 V. Cyclic voltammetry (CV) measurement and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (Ametek 1470E) at a frequency range from 1 MHz to 10 mHz. CV measurement was conducted at a scan rate of 0.05 mV s^{-1}.

3. Results and discussion

3.1. Structural and morphological characterization of the pyrolytic carbon

Fig. 2 shows the XRD pattern of C700. Two typical characteristic peaks of hard carbon can be observed at approximately 26° and 43°, which corresponds to the (002) and (100) crystal planes of hard carbon. The intensive characteristic peak obtained at 26° indicates parallel accumulation of graphite sheets. The weak peak at 43° demonstrates the obtained product existed in the form of honeycomb structures formed by sp^2 hybridized carbons [16,17,24]. The Barrett–Joyner–Halenda (BJH) pore size distribution curve of

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