



## Research article

## Preparation of synthetic graphite from bituminous coal as anode materials for high performance lithium-ion batteries



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## ABSTRACT

An earth-abundant and low cost bituminous coal was used as precursor to prepare synthetic graphite materials through preliminary carbonization coupled with further high temperature graphitization treatment at 2000–2800 °C. The microstructure characteristics of the obtained synthetic graphite materials were characterized by means of X-ray diffraction, scanning electron microscope, transmission electron microscope, Raman spectroscopy and nitrogen adsorption–desorption. The results show that the microstructures of synthetic graphite materials are strongly dependent on the graphitization temperature. The synthetic graphite graphitized at 2800 °C has perfect ordered layered structure with high graphitization degree and relatively large surface area with well-developed mesopores, which offers a favorable pathway for the electrochemical intercalation–deintercalation of lithium ions in carbon matrix. Such synthetic graphite applied as anode materials for lithium-ion batteries presents a maximum reversible capacity of 310.3 mAhg<sup>-1</sup> at current rate of 0.1C and still remains as high as 143.9 mAhg<sup>-1</sup> at current rate of 5C. Moreover, the synthetic graphite also exhibits superior rate capability and outstanding cycling performance with over 95.3% initial capacity retention after 100 cycles. This study demonstrates a promising feasibility for large-scale production of synthetic graphite materials from bituminous coal for high performance lithium-ion batteries.

## 1. Introduction

Global energy crisis and environmental pollution have led to a great demand for sustainable energy sources and high performance energy storage devices. Lithium-ion batteries (LIBs), regarded as one of the most attractive energy storage and conversion devices, have attracted extensive attention during the past decades due to their high energy density, flexible lightweight design, long cycling life [1–3]. LIBs have widespread application in portable electronic devices, electric and hybrid electric vehicles, and their electrochemical performance is significantly depended on the choice of appropriate anode materials [4,5]. Up to date, various anode materials have been extensively investigated including graphite, amorphous carbon, graphene, silicon, tin and transition metal oxides [6–8]. Among these advanced materials, graphite is considered as the most promising candidate in practical applications because of its high reversible capacity, excellent conductivity, desirable charge-discharge potential profile and relatively low cost [9–11]. Generally, there are two types of graphite materials

widely used as anode materials for LIBs: natural graphite and synthetic graphite. The former usually possesses anisotropic structure feature, which restricts the random transportation and diffusion of lithium ions into the graphite structure during the charge-discharge process, leading to a poor rate capability [11–13]. As a result, natural graphite used for anode materials often needs a series of complex modification processes such as spheroidization and amorphous carbon coating [11,14–16]. Moreover, natural graphite that can be used as anodes for LIBs is a limited natural resource and is mainly distributed only in a few countries (i.e. China, Mexico, Czech and Brazil), hindering its worldwide supply in the medium to long-term [17,18]. Therefore, it is highly desirable to explore the possibility to use synthetic graphite as high performance anode materials.

Many attempts have been made recently to prepare graphite materials for LIBs from a variety of precursors including mesocarbon microbead [19], petroleum coke and needle coke [20], sponge coke [21], pitch [13], unburned carbon from fly ash [22] and anthracite [23]. Among these anode candidates for LIBs, mesocarbon microbead is the

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most commonly used as industrial anode materials due to its merits of high specific capacity, excellent cyclic performance as well as superior rate capability. However, the tedious production processes and high manufacture cost hindered its large-scale production and commercial applications [13,24]. Therefore, the search for inexpensive, abundant and environmental friendly precursors for anode materials is urgently needed due to the increasing demand of high performance LIBs.

Coal, a conventional fossil fuel, is known as the cheapest and most abundant natural carbon source in the world, which has been exploited as an important resource for the production of a wide variety of carbon materials such as activated carbon [25], carbon nanotube [26], fullerene [27], graphene nanosheets and carbon quantum dots [28–30]. Most recently, several groups have intensively investigated the possibility and feasibility of preparing synthetic graphite or graphite-like products focusing on using anthracite as starting materials. For instance, Gao et al. prepared coal-derived graphite from Chinese anthracite as carbon source to synthesize graphene sheets [31]. Cabiellés et al. reported that graphite materials were prepared from anthracite combustion fly ashes through high temperature treatment [32]. Caméan et al. also prepared graphite materials derived from anthracite combustion fly ashes, and studied their electrochemical behaviors applied as the potential anode in LIBs [33]. García and co-workers reported the successful production of synthetic graphite from anthracite via high temperature treatment under inert atmosphere, and the electrochemical properties of resultant graphite product as anode materials for LIBs were investigated systematically [23].

It is well known that bituminous coal exhibits similar chemical composition and macromolecular structure as anthracite, containing condensed aromatics forming large units bridged or cross-linked by a variety of functional groups such as aliphatic and ether groups. It seems that the aromatics units in bituminous coal could be converted into synthetic graphite materials after a severe heat treatment process. Rodríguez et al. successfully prepared lightweight graphite-like carbon foams from low volatile bituminous coal for anode materials in LIBs through catalytic graphitization treatment [34]. Our previous work described the preparation of graphite-like carbon materials from low rank coal based humic acid by heating treatment at 1800 °C in an inert atmosphere [35]. However, to the best of our knowledge, there has been little information available in the open literature regarding the preparation of synthetic graphite materials from bituminous coal, and their application in anode for LIBs has also hardly been reported. On the other hand, bituminous coal contains a relatively higher volatiles compared to that of anthracite, which may be of great benefits for the formation of porosity in the carbon matrix in the high temperature treatment process. As reported elsewhere that these nanopores not only can provide large capacity for lithium ions accommodation, but also serve as channels for fast lithium ions and electrons transportation, thereby enhancing the electrochemical performance of LIBs [36–40].

In this work, synthetic graphite materials for anode in LIBs were fabricated from bituminous coal with preliminary carbonization coupled with further graphitization treatment at different temperatures. The microstructure of obtained graphite materials was investigated through various characterization techniques. The electrochemical behaviors of these graphite materials applied as anode for LIBs were also systematically evaluated in terms of galvanostatic cycling, cyclic voltammetry and electrochemical impedance spectroscopy.

## 2. Experimental

### 2.1. Materials

A high rank bituminous coal from Shanxi Province of China was used as the starting precursor for the preparation of synthetic graphite materials. The raw coal was ground to powder and then sieved into a particle size less than 75 µm. The proximate analysis and ultimate analysis of bituminous coal are listed in Table 1. Noticeably, a relatively

**Table 1**  
Proximate analysis and ultimate analysis of bituminous coal.

Proximate analysis (wt%)			Ultimate analysis (wt%, daf)			
M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	C	H	O <sup>a</sup>	N
1.53	7.35	11.42	87.08	3.55	8.14	1.23

ad, air dry basis; d, dry basis; daf, dry and ash-free basis; <sup>a</sup> by difference.

high ash content of approximately 7.35% (dry basis) is contained in the original coal. The composition of ash derived from the original coal was analyzed using a new ARL Quant'x energy dispersive X-ray fluorescence (Thermo Fisher Scientific), and the result exhibits that the main chemical composition in the ash are SiO<sub>2</sub> (25.02 wt%), Al<sub>2</sub>O<sub>3</sub> (15.57 wt%), Fe<sub>2</sub>O<sub>3</sub> (21.02 wt%), CaO (26.21 wt%), MgO (11.03 wt%), K<sub>2</sub>O (0.63 wt%) and Na<sub>2</sub>O (0.52 wt%), indicating that the mineral matters in the coal are mainly consisted of elements of Si, Al, Fe, Ca, Mg, K and Na and their compounds.

### 2.2. Carbonization and graphitization of bituminous coal

The bituminous coal powder was placed in a corundum crucible and carbonized at 1000 °C in a tube furnace for 4 h under nitrogen flow with a heating rate of 5 °C·min<sup>-1</sup>. The obtained sample was collected after natural cooling, and then graphitized. The graphitization treatment process was carried out in a high temperature graphite furnace under high purity argon (99.99%) flow. Briefly, about 50 g carbonized powder was placed in a graphite crucible, and heated in a graphite furnace at 1000 °C with a heating rate of 10 °C·min<sup>-1</sup>, followed by further heating to the designated temperature (ranged from 2000 to 2800 °C) at a heating rate of 5 °C·min<sup>-1</sup> and held for 2 h. Such prepared synthetic graphite samples derived from bituminous coal were denoted as BCG-X, where X represents the graphitization temperature.

### 2.3. Characterization of synthetic graphite materials

X-ray diffraction (XRD) patterns of raw coal and synthetic graphite samples were recorded on a Bruker D8 Advance diffractometer using the Cu Kα X-ray radiation source (λ = 0.15418 nm). The interlayer spacing (d<sub>002</sub>) of synthetic graphite materials was calculated from the position of (002) peak in XRD pattern using the Bragg's equation, while the stacking height (L<sub>c</sub>) and crystallite size (L<sub>a</sub>) were evaluated from the (002) and (110) peaks by applying the Scherrer formula [22,23]:

$$L = K\lambda/(\beta\cos\theta) \quad (1)$$

where L is the stacking height (L<sub>c</sub>) or crystallite size (L<sub>a</sub>), K is the Scherrer parameter (K = 0.9 for L<sub>c</sub> and 1.84 for L<sub>a</sub>), λ is the wavelength of X-ray, β is the angular width of the diffraction peak at half maximum intensity and θ represents the diffraction angle.

The morphological characteristics were carried out using a Quanta FEG 250 scanning electron microscope (SEM) and a field emission Tecnai G<sup>2</sup> F20 S-Twin transmission electron microscope (TEM). Raman spectroscopy was analyzed using a Renishaw Raman spectrometer with an argon ion laser (λ = 514 nm) at room temperature. Nitrogen adsorption and desorption isotherms were determined by low temperature nitrogen adsorption at -196 °C on a Quantachrome Autosorb-IQ-MP automatic adsorption instrument. All samples were degassed at 200 °C for 10 h prior to nitrogen adsorption measurement, specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) model, and pore size distribution was evaluated by the density functional theory (DFT) from the adsorption branch.

### 2.4. Electrochemical measurements

The electrochemical measurements were carried out using a two-

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