



Boron-doped carbon prepared from PFO as a lithium-ion battery anode



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ABSTRACT

A petroleum-based Li-ion battery anode was prepared by thermal condensation of pyrolysis fuel oil (PFO) and a subsequent carbonization process. H_3BO_3 was used as a catalyst for efficient thermal condensation, carbonization and battery performance. The influence of the carbonization temperature on the carbon structure and battery performance was also investigated. Notably, H_3BO_3 promoted thermal condensation and formation of a graphitic carbon structure and acted as a boron doping agent. Boron-doping attenuated the highly active sites in carbon and effectively controlled formation of the SEI layer, which resulted in an increase in the initial efficiency of the anode. For the sample carbonized at 900 °C, a reversible capacity of 301 mAh/g and an initial efficiency of 78.6% were obtained. In addition, the samples obtained at different carbonization temperatures were all highly stable over 50 cycles, with capacity retentions greater than 90%.

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1. Introduction

Carbon-based materials have been extensively studied and applied as Li-ion battery (LIB) anodes [1–5]. Because of their low material cost, excellent stability, safety and affordability, carbon materials are considered promising candidates for LIB anodes in hybrid electric vehicles (HEVs) and plug-in HEVs [6–8].

Pyrolysis fuel oil (PFO) is a high-boiling-point, aromatic hydrocarbon product that is a residue from the petroleum refining process; it has attracted considerable interest as a carbon precursor because of its low cost and high carbon content. PFO-derived carbon also has the advantages of being ash-free and having excellent graphitizable properties and a thermoplastic nature [9].

The conversion from PFO to carbon usually includes two processes: thermal condensation of PFO to form pitch or coke and subsequent carbonization to obtain the carbon product. The thermal condensation of PFO via heat treatments at temperatures greater than 400 °C has been reported [10], and this temperature can be lowered to approximately 300 °C through the use of Br_2 gas

as a catalyst [11]. However, the toxic nature of Br_2 gas makes this procedure non-environmentally friendly and difficult to scale up.

Boron doping to enhance the degree of graphitization in non-graphitic carbonaceous materials has been studied. It was presented that Boron can be penetrated between graphene layers and doped on defects of graphene surface [12]. Kurita suggested that boron-substituted disordered carbon atoms could more easily accept electrons from absorbed Li atoms via the creation of a lower electron-acceptor level caused by boron substitution [13]. Yoon et al. suggested that the rate performance of carbon can also be improved by boron doping [14].

In the current work, we present a process for preparing carbon from PFO using H_3BO_3 as a catalyst; this approach provides an attractive alternative to existing protocols for obtaining pitch from heavy oil. Readily available, low-cost, nontoxic, and environmentally friendly H_3BO_3 could constitute a highly effective catalyst for pitch formation reactions that does not require removal during the subsequent carbonization process. In this study, H_3BO_3 was used as a catalyst to produce boron-doped carbon structures for use as LIB anodes. The influence of the thermal condensation conditions and the carbonization temperature on the chemical and structural properties of the product was investigated, and the boron-doped carbon products were tested as LIB anodes.

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2. Experimental

PFO, which was used as a starting material, was obtained from GS Caltex. The thermal condensation of PFO was conducted in a pressurized 1 L reactor. 600 g of PFO and 30 g of H_3BO_3 (Aldrich, 99.97% trace metals basis) were first stirred for 30 min with N_2 purging to remove oxygen before the mixture was heated. The reactor was heated to 400 °C over a period of 2 h and was maintained at this temperature for 2 h using self-generated pressure. Next, the light component was removed and maintained at 400 °C at a pressure of 1 bar for another 3 h. After cooling to room temperature, the resultant product was collected as a carbon precursor, and the carbonization was performed in a tube furnace under a N_2 atmosphere. The tube furnace was heated to a target temperature of 600, 900, 1200, or 1400 °C over a period of 5 h, and the holding time was 1 h. The obtained carbon products were ground into powders with diameter that ranged from 20 to 30 μm and were collected for battery tests.

X-ray diffraction patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode and a Cu $K\alpha$ radiation source ($\lambda = 0.15418$ nm). X-ray photoelectron spectroscopy (XPS) was performed using a MultiLab 2000 spectrometer (Thermo Electron Corporation, UK) and was used to identify the chemical bonding in the samples. For the LIB tests, the product was mixed with Super P and polyvinylidene difluoride binder in a weight ratio of 8:1:1 in NMP and the resulting mixture was subsequently coated onto Cu foil. The half-cell tests were conducted using a coin-type (CR2032) two-electrode cell in which lithium foil was used as the counter electrode. The electrolyte was a 1.0 M $LiPF_6$ ethylene carbonate/dimethyl carbonate solution (volume ratio 1:1). All of the electrochemical measurements were conducted using a WBCS-3000 battery cycler (Xeno Co.).

3. Results and discussion

3.1. Characterization of petroleum-based pitch according to the introduced catalyst and the thermal condensation process

The products obtained from the different thermal condensation processes are compared in Table 1; the results in the table indicate that the use of H_3BO_3 as a catalyst increased the yield from PFO to pitch compared to the yields of the reactions without the catalyst. H_3BO_3 is a Brønsted acid and can provide protons through successive ionization steps in the thermal condensation process. These protons can produce protonated complexes of aromatic hydrocarbons. This complex attacks the second aromatic molecule at the position with the highest basicity to achieve polymerization. Such reactions repeat to produce high-molecular-weight pitch from PFO [14]. Thus, a high yield of pitch can be achieved. In Table 1, compared with step 1 process (S1), step 2 process with catalyst (S2-C) and step 2 process without catalyst (S2-N) have much higher softening points because the light components were removed in

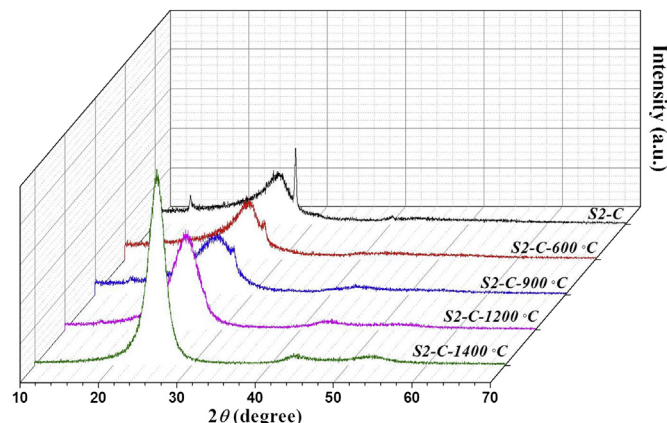


Fig. 1. XRD pattern of the products obtained at different carbonization temperatures.

the second temperature step. The S2-C and S2-N series were chosen for further carbonization and battery tests because of their relatively high softening points, which is an important factor for carbon yield in the final product.

3.2. Physical properties of boron-doped carbon

The structures of the products obtained at different carbonization temperatures were characterized by XRD, as shown in Fig. 1. The XRD pattern of product before carbonization showed a broad peak at approximately 26°, corresponding to the interlayer space between the carbon nanosheets (002), which was less ordered before carbonization. A sharp peak near 30° is attributed to H_3BO_3 and its dehydrated derivatives. After carbonization, the peak near 30° gradually attenuated, whereas the intensity of the carbon (002) peak increased with increasing carbonization temperature. The disappearance of H_3BO_3 can be explained by its vaporization and doping into carbon lattices during the carbonization process; the increased crystallinity of carbon at elevated temperatures has also been reported by numerous other authors [15].

XPS analysis was conducted to identify the chemical bonds in the produced samples (Fig. 2). The C1s data showed a shifted peak at 281.1 eV. This peak is explained by boron doping lowering the binding energy in the carbon structure because of boron's low Fermi level [16]. After carbonization, the C1s peak shifted to the prevalent graphite peak at approximately 284.5 eV because of the removal of the boron catalyst located around the carbon structure [17]. This result was in agreement with the XRD analysis data. The B1s peak was deconvoluted into two peaks at approximately 190 and 192 eV, which are associated with boron–carbon bonding and BN particles, respectively. BN particles were generated during the high-temperature reaction with N_2 gas in the reactor [18]. With increasing reaction temperature, the intensity of the BN peak at 192 eV increased. The boron–carbon bonding peak at 190 eV

Table 1
Experimental conditions for the thermal condensation of PFO.

Sample name	Catalyst	Step 1	Step 2	Softening point [°C]	Pitch yield [%]
S1-C (Step 1 process with catalyst)	5% H_3BO_3	400 °C, 5 h Self-generated pressure (Final 39 Bar)	None	79	51
S1-N (Step 1 process without catalyst)	No catalyst	400 °C, 5 h Self-generated pressure (Final 27 Bar)	None	76	46
S2-C (Step 2 process with catalyst)	5% H_3BO_3	400 °C, 2 h Self-generated pressure (Final 38 Bar)	400 °C, 3 h Pressure (1 Bar)	Semi-coke	45
S2-N (Step 2 process without catalyst)	No catalyst	400 °C, 2 h Self-generated pressure (Final 27 Bar)	400 °C, 3 h Pressure (1 Bar)	183	32

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