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Anode performance of boron-doped graphites prepared from shot and sponge cokes

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ABSTRACT

The structures and anode performances of graphitized pristine and boron-doped shot and sponge cokes have been comparatively studied by means of scanning electron microscope (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and galvanostatic measurement. The results show that high degree of graphitization can be obtained by the substituted boron atom in the carbon lattice, and boron in the resultant boron-doped graphites mainly exist in the form of boron carbide and boron substituted in the carbon lattice. Both of boron-doped graphites from shot and sponge cokes obtain discharge capacity of 350 mAh g^{-1} and coulombic efficiency above 90%. Apart from commonly observed discharge plateau for graphite, boron-doped samples in this study also show a small plateau at ca. 0.06 V. This phenomenon can be explained that Li ion stores in the site to be void-like spaces that are produced by "molecular bridging" between the edge sites of graphene layer stack with a release of boron atoms substituted at the edge of graphene layer. The effect of the amount of boron dopant and graphitization temperature on the anode performance of boron-doped graphite are also investigated in this paper.

1. Introduction

Synthetic graphite has been well applied to the anodic material of commercial Li ion battery due to its large reversible capacity and long plateau in the low voltage [1–6]. It is usually prepared from graphitizable carbon such as needle coke, mesocarbon microbeads (MCMB) and mesophase pitch-based carbon fibers (MPCF) through graphitization above 2800 °C. Such high temperature heat-treatment incurs high cost in mass production.

It has been well established that, boron, as a graphitization catalyst, can enhance the graphitization of carbons. Thus, Boron doping can help graphitizable carbon obtain the high degree of graphitization under a lower graphitization temperature. Furthermore, boron doping can modify the electronic properties of the host carbon materials due to boron atom substituted for carbon atom in the carbon lattice [7–18]. Theoretically, the presence of boron should be beneficial for lithium intercalation/de-intercalation behavior of carbon material, because the substituted boron atom acts as an electron acceptor. Many studies on the boron doping into MCMB [10,11], MPCF [12–14] and pitch coke [15–17] have approved that boron doping can improve the discharge capacity and initial coulombic efficiency.

Shot and sponge cokes are byproducts of delayed coking operations that use petroleum feedstocks to produce valuable needle coke [19,20]. Both of them are anisotropic in nature. Shot coke is an undesirable product in the form of small spheres and no commercial application has been identified. Sponge coke can be used for fuel or to manufacture carbon anodes for electrolytic aluminum production. Therefore, compared with other currently used precursor materials, shot and sponge cokes are attractive in their low cost.

In this study, graphitized shot and sponge cokes and boron-doped graphites were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Their anode performances were investigated by galvanostatic measurement. Furthermore, the effects of the amount of boron dopant and graphitization temperature on the anode performances of boron-doped graphites were also studied.

2. Experimental

2.1. Materials

Shot coke and sponge coke were used in this study, and their compositions of as-received forms are summarized in Table 1.

After grinding into the size of less than 75 μm, shot and sponge cokes were calcined at 1300 °C (abbreviated as SHC13

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Table 1
Industrial analysis and elemental analysis of as-received shot and sponge cokes (wt.%).

Cokes	Fixed carbon	Volatile	Ash	Water	C	H	N	Diff.
SHC	88.74	11.08	0.18	1.26	88.54	3.93	3.06	4.47
SPC	89.26	10.21	0.53	5.40	90.09	3.66	2.31	3.94

and SPC13, respectively), and then were graphitized at 2400 and 2800 °C, respectively, under Ar atmosphere (abbreviated as SHC24, SHC28, SPC24 and SPC28). Boric acid powder (H_3BO_3) was mixed with SHC13 and SPC13 by 20 wt.%, respectively, and then were heat-treated at 800 °C for 1 h under Ar atmosphere, followed by graphitization at 2800 °C under Ar atmosphere (abbreviated as SHCB28-2 and SPCB28-2, respectively). To investigate the effect of the amount of boron dopant on the anode performances of the resultant boron-doped graphites, H_3BO_3 was also mixed with SHC13 by 10 and 30 wt.% followed by the same treatment as SHCB28-2, and the resultant boron-doped graphites were abbreviated as SHCB28-1 and SHCB28-3. SHCB24-2/SPCB24-2 was prepared by graphitizing the mixture of SHC13/SPC13 and 20 wt.% H_3BO_3 at 2400 °C to compare with SHCB28-2/SPCB28-2.

2.2. Characterization of samples

The microtexture of the prepared samples was studied by a scanning electron microscope (SEM; JSM-6700F JEOL, Japan). The crystallographic data were collected using an X-ray diffractometer (Ultima III Rigaku, Japan) with Cu Kα (λ = 0.15406 nm) radiation, and the crystallographic parameters were calculated according to the revised Gakushin method [21]. The standard silicon powder (200 Mesh, 99.99%, Soekawa Chemical Co., Japan) was mixed with each sample to be measured by 10 wt.% as an internal standard. The chemical state of boron and carbon in the boron-doped samples was analyzed using an X-ray photoelectron spectroscopy (JPS-9010MC JEOL, Japan) with Mg Kα radiation (1253.6 eV). The C 1s peak of carbon was used as a reference for the chemical shift determination, assuming that its binding energy is 284.2 eV.

2.3. Measurement of anode performance

Test electrode was fabricated by spreading a slurry mixture of active material (90 wt.%) and PVdF (polyvinylidene fluoride, 10 wt.%) dissolved in NMP (1-methyl-2- pyrrolidone) solution onto the copper foil, and rolling it after drying under vacuum for 12 h at 120 °C. Two-electrode test cell was assembled by using lithium foil as the counter electrode, 1 M $LiPF_6$ in EC/DEC (1:1, v/v) as the electrolyte and polyethylene film as the separator. The cell assembly was carried out in an argon-filled glove box.

Electrochemical evaluation was performed using TOSCAT-3100 battery testing unit (TOYO SYSTEM CO. LTD., Japan). The carbon electrodes were first charged from open circuit voltage to 0 V at 30 mA g^{-1}, and then constant voltage (CV) charging was applied at 0 V until current decreased to 3 mA g^{-1}. Constant current (CC) discharging was performed at 30 mA g^{-1} until 2 V.

3. Results

3.1. Characterization of as-prepared samples

Fig. 1 shows SEM images of as-received shot and sponge cokes, SHCB28-2 and SPCB28-2. Microtexture of cokes evidently changes from bulky form to a highly developed plate-like texture with parallel alignment of the layers. Compared with boron-doped graphite from sponge coke, more byproducts, which are boron carbide according to XRD and XPS results later, are observed on the surface of boron-doped graphite from shot coke.

Fig. 2 shows XRD patterns of graphitized shot and sponge cokes and boron-doped graphites. As graphitization temperature increases, the (0 0 2), (0 0 4) and (0 0 6) peaks shift to a higher diffraction angle, in corresponding to the decrease of interlayer spacing, d_{002}. The (1 0 1), (1 0 3) and (1 1 2) peaks become clearer, which indicate a more developed three-dimensional stacking layer structure of graphite. Compared with undoped samples, boron-doped samples also show a similar tendency in spite of the same graphitization temperature. It implies improvement of graphite crystallinity with boron doping. In addition, the peaks attributed to B_4C are observed in the range of 30–40° for SHCB28-2, while they do not appear in XRD pattern of SPCB28-2, which is in consistence with their SEM images.

The calculated lattice sizes of as-prepared samples are shown in Table 2. Boron-doped sample shows a lower d_{002} and a growth in crystallite thickness ($L_{c(002)}$) and lattice constant (a_0). The decrease of d_{002} is thought to be related to the depleted p-electrons between graphite layers [13]. The increase of a_0 is because B–C bond caused

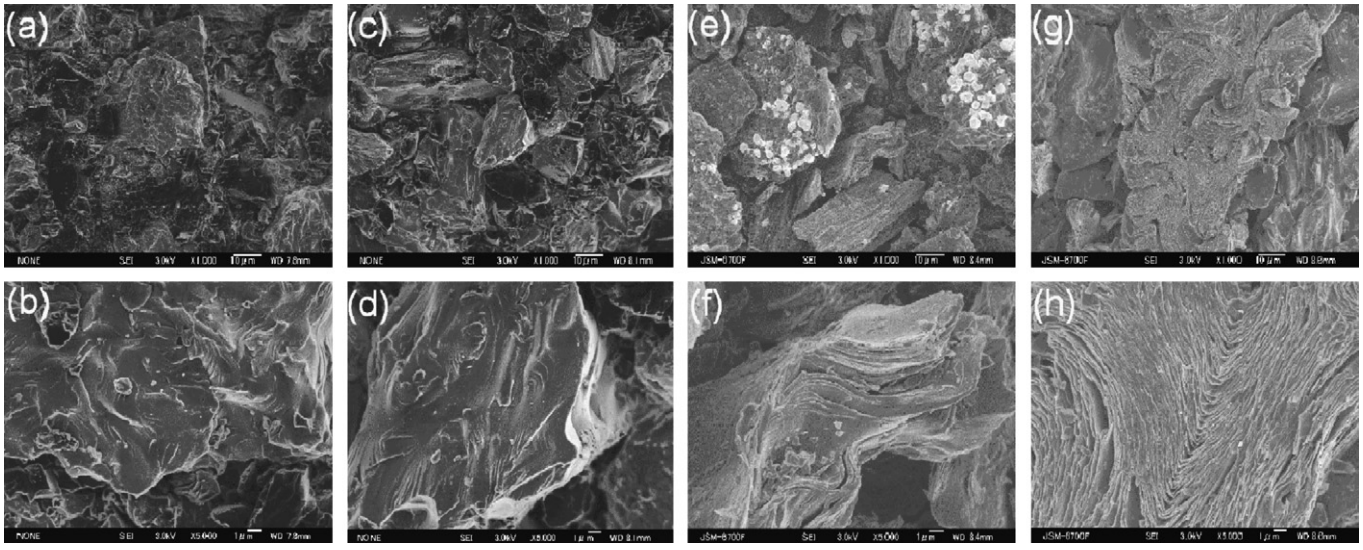

Fig. 1. Low and high magnification SEM images of as-received shot coke (a and b), as-received sponge coke (c and d), boron-doped shot coke (e and f) and boron-doped sponge coke (g and h) graphitized at 2800 °C.