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Characterization and Electrochemical Investigation of Boron-Doped Mesocarbon Microbeads Anode Materials for Lithium-Ion Battery

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Abstract: The anodic performances of boron-doped and undoped mesocarbon microbeads (MCMBs) were comparatively studied and the structures were characterized by XPS, SEM, XRD and electrochemical measurements. It was found that boron-doping samples greatly increased the degree of graphitization and the crystallite size, leading to quite different morphology. Electrochemical discharge/charge cycle tests indicate that lithium intercalation occurred at a little higher potential for the boron-doped MCMBs, being attended by greater irreversible capacity loss.

Key words: MCMBs, Boron-doped MCMBs, Electrochemical property, XPS, SEM, XRD

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1 Introduction

In recent years, boron-doped carbons have been received much attention for their interest as host materials for lithium intercalation[1~3]. It is convinced that boron-doping can modify the electronic properties of carbon graphitic network as boron is neighboring to carbon in periodic table and has one electron deficient. Experimental and theoretical investigations pointed out that boron-doping is prompting the creation of electron acceptor level[1,2], inducing positive holes in the energy band of matrix graphite, and hence improved battery performance can be expected if boron-doped carbons are used in lithium ion batteries as anode[4]. In carbonaceous materials, boron atom is a graphitization catalyst, can alter the host structure of carbon greatly[5]. If the

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change is concerned with the structural factors of a-b axis crystallite size, stacking fidelity and defect of the basal planes, the great effect on anode characteristics will be proposed[6].

In various soft carbonaceous materials applied in lithium ion batteries, mesocarbon microbead (MCMB) is the most attractive one because of its unique spherical structure and low surface area, which lead to high parking density and suppress extended side reactions with electrolyte during cycle[7]. In the present study, the effect of boron-doping on the microstucture characteristics and electrochemical properties of MCMB will be investigated and discussed in details.

2 Experimental

The undoped and boron-doped MCMBs were supplied by Kawasaki Steel Co. (Japan) and used without any pretreatment. The boron-doped MCMBs were prepared by mixing the pristine MCMBs and 4 wt % B_2O_3 and then heat-treating the resulting material to 2 800 ℃. After received, both samples were characterized by instrument analyses, such as XPS, SEM and XRD.

All electrochemical measurements were performed using three-electrode test cell made of glass. The working electrodes were prepared by mixing 95 wt % undoped or boron-doped MCMBs with 5 wt % PTFE as binder. The gum-like mixture was spread to a thin film and pressed onto a nickel mesh (5 mm × 5 mm) at 10 MPa, and then vacuum dried for 24 h at 120 ℃. The electrolyte used was 1 mol/L $LiPF_6$ dissolved in a mixed solvent of 50 % ethylene carbonate (EC) and 50 % dimethyl carbonate (DMC) by volume. Lithium metal was used both as the counter electrode and as the reference electrode. Cell assembly operations were carried out in a glove box filled with argon gas, where water and oxygen concentrations were kept less than $w = 3 \times 10^{-6}$. Discharge/charge cycle testing was implemented on Arbin BT-2043 battery test system in a voltage range from 0.005 V to 3.0 V and with a constant discharge/charge rate at 40 mA/g.

3 Results and Discussion

3.1 XPS of the Materials

The whole XPS patterns of the two samples are comparatively shown in Fig. 1. It can be seen clearly that besides the common C_{1s} and O_{1s} peaks, the boron-doped MCMB has a unique B_{1s} peak at about 186.5～190.5 eV and an additional N_{1s} peak at about 398.0～399.0 eV.

For the sake of clarity, the peaks of C_{1s}, B_{1s} and N_{1s} were rescanned in high resolution. In Fig. 2, it was shown more clearly that the C_{1s} peak of boron-doped MCMB is located at slightly lower binding energy compared with the undoped MCMB. The lowering of the binding energy of the C_{1s} peak for boron-doped samples might be due to the lowering of Fermi level because the chemical bond formation of carbon atoms with the electron deficient boron atoms is lowering the density of π electrons in the graphite layer[8].

Fig. 3 shows the B_{1s} spectrum of boron-doped sample consists of a main peak around 190.3 eV and a shoulder peak at 186.5 eV. The peak at 190.3 eV may be attributed to B_xC_{1-x} or hexagonal boron nitride. The lower energy component at 186.5 eV is corresponding to boron cluster[9].

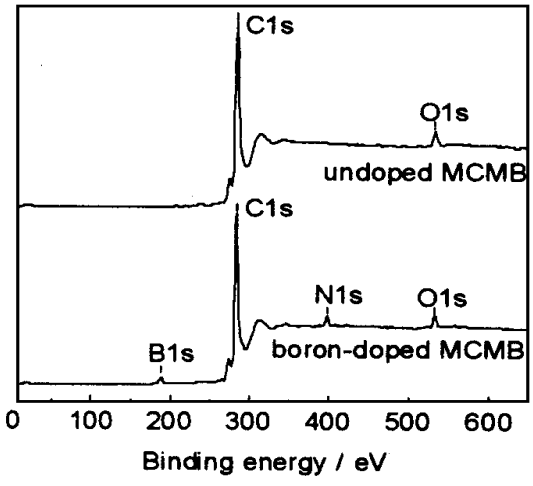

Fig. 1　Wide-scan XPS survey spectra

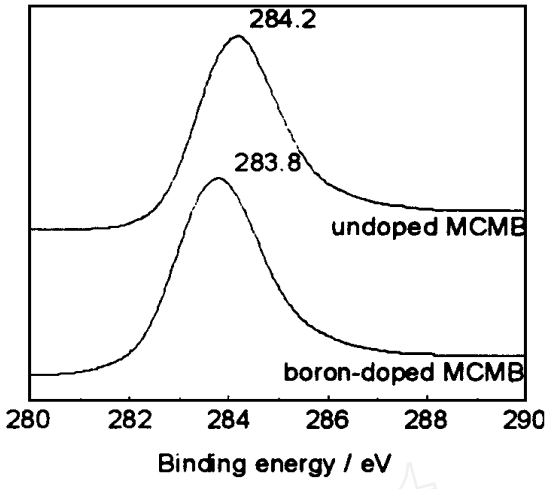

Fig. 2　XPS C_{1s} spectra in comparison

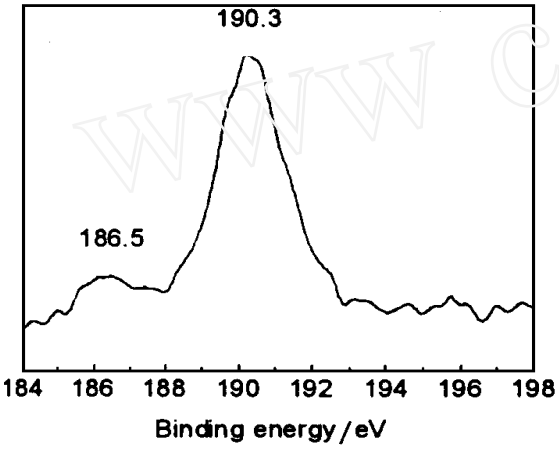

Fig. 3　XPS B_{1s} spectra of boron-doped MCMBs

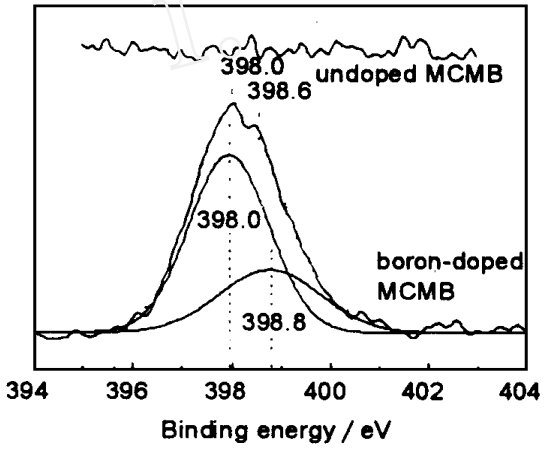

Fig. 4　XPS N_{1s} spectra in comparison

Fig. 4 illustrates that the N_{1s} peak of boron-doped sample is constitued with two peaks. The main peak is located at 398.0 eV, which can be vested in the B_3N structure[10]. From the Gaussian multi-peak fitting, the hypo-peak at 398.8 eV can be assigned to N-C sp^3 bonding of C_3N_4-like local structure (C-N σ bonds). Boron can stabilize nitrogen in hexagonal carbon layer. That is why the N_{1s} peak is observed only in boron-doped sample, as illustrated in Fig. 4 and Fig. 1. Its appearance is presumed due to the raw materials.

3.2　Morphology Change of the Materials

SEM observations revealed the boron-doped MCMB is shaped quite differently from the pristine one. It can be seen from Fig. 5 that after boron-doping the spherical shape of undoped MCMB was changed into an irregular and unconsolidated fragmentary-graphite-like form. It can be ex-

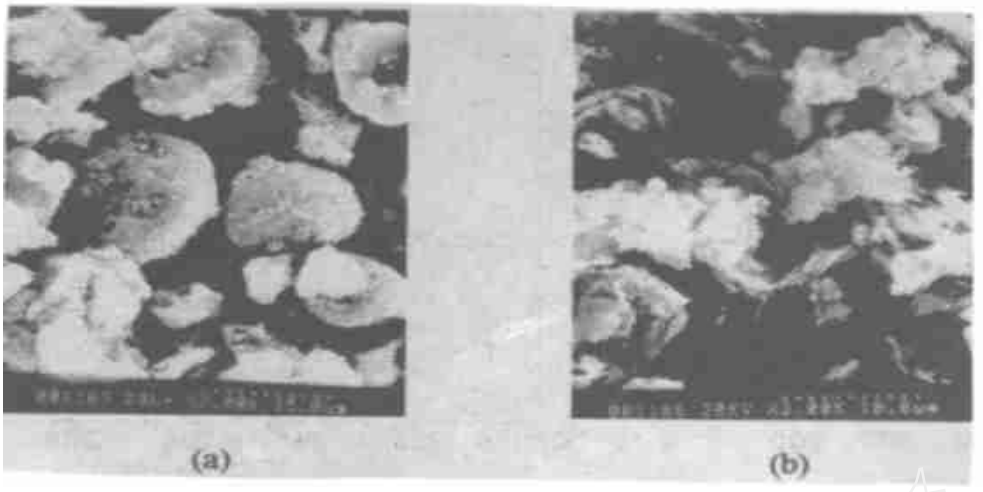

Fig. 5 SEM images of (a) undoped-MCMB and (b) boron-doped MCMB

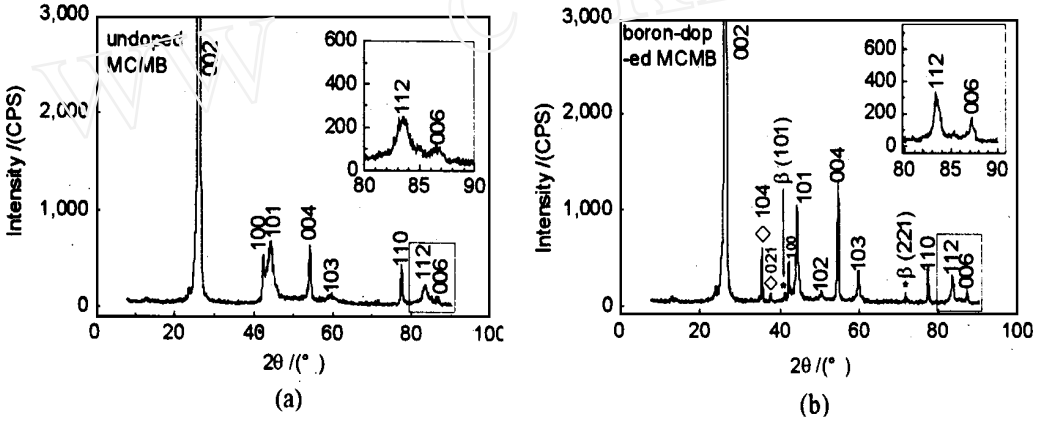

Fig. 6 XRD patterns of (a) undoped MCMB and (b) boron-doped MCMB
(◇:B_xC_{1-x}, * :β-C_3N_4)

pected that this morphology transformation caused by boron doping will tamper with the anodic performance of MCMB because it obliterates the two characteristics of the undoped-MCMB anode materials, *i. e.* the spherical structure and low surface area.

3.3 XRD Diffraction of the Materials

The X-ray diffraction (XRD) patterns of boron-doped and undoped MCMBs are shown in Fig. 6. It's worthwhile to note that the (101), (004), (103), (112) and (006) peaks of carbon in boron-doped MCMBs are sharper than those of the corresponding undoped MCMBs. The results implies that the crystallinity of graphite structure was improved by boron-doping. In Fig 6 (b),

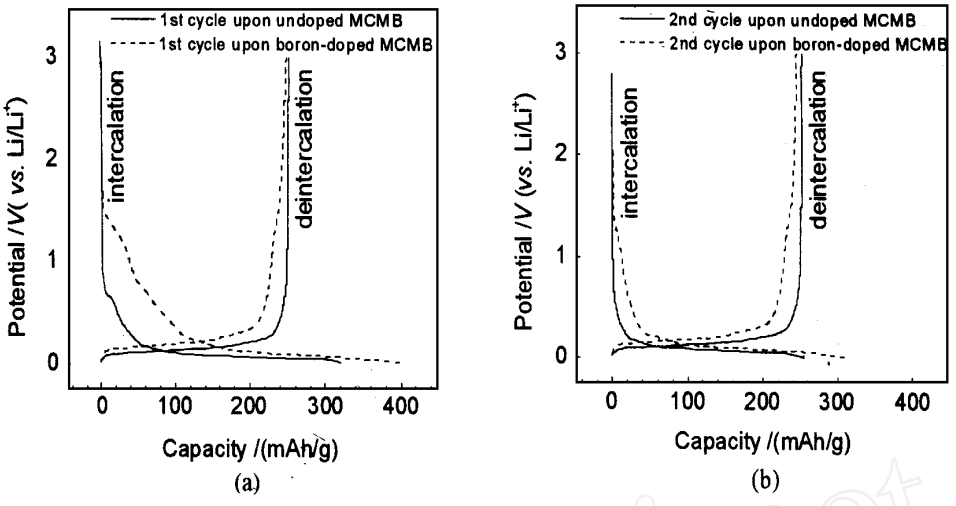

Fig. 7　Discharge/ charge curves for undoped and boron-doped MCMBs at (a) the first cycle and (b) the second cycle

peaks of boron carbide and carbon nitride detected with the boron-doped sample accords with the XPS results and SEM observations very well.

Further calculation (Bragg equation : $n\lambda = 2d\sin\theta$) shows that after boron-doping, d value of (002) plane is decreased from 0.338 1 nm to 0.335 3 nm. It means boron-doping shortens the distance between graphene planes and elongates the side length of the regular hexagon in graphene layer.

3.4　Discharge/ Charge Behavior of the Materials

Fig. 7 illustrates the discharge/ charge curves of both boron-doped and undoped samples. It is obvious that the boron-doped sample carries through the discharge and charge process on a higher potential and finally harvests a larger discharge capacity but less charge capacity than the undoped sample. However, both samples show charge capacities much less than their corresponding discharge capacities in the first two cycles.

Normally, when the SEI is forming, there is a potential plateau or shoulder clearly visible at 0.7～0.8 V (vs. Li/ Li^+) on the discharge curve, as shown in Fig. 7(a). For the boron-doped sample, there is an additional potential shoulder probably occurring at 1.3～1.4 V because of the strengthened chemical bond between the intercalated lithium and boron-doped carbon. As a result, the potential is increased relative to the undoped sample. But radically, the higher potential of boron-doped sample can be ascribed to the electron deficiency of the boron substituent and the lowering of Fermi Level.

For the doped sample, the lower charge capacity is attributed to the development of the ag-

gregated and recrystallized boron carbide and/or boron nitride[5]. The heterogeneous structure of the boron carbide and boron nitride change the graphite structure morphology of the MCMBs. The results accord with the results of XPS, SEM and XRD.

4 Conclusions

Boron-doping is found to lead to a more developed crystallite and complicated structure than that of the undoped MCMBs, as indicated by the XRD/XPS measurements.

To morphologies of MCMB powder, boron-doping is negative for the performance of Li ion battery. SEM observations showed that boron-doped MCMB has an irregular and unconsolidated structure, quite different from the spherical shape of the pristine MCMB.

Aroused from the electrophilic reactivity of substituent boron and the undesirable morphology, boron-doped MCMB exhibits higher potenitial and larger irreversible capacity lose in electrochemical cycle testing experiment. By these results, we suggest the key of boron doping for better electrochemical performance is the concentration of boron-doping and heat-treatment temperature (HTT).

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硼掺杂的中间相碳素微球(MCMB)用作锂离子电池负极材料的性能及表征

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摘要: 本文采用 XPS,SEM,XRD 和电化学充放电测试研究了硼掺杂的中间相碳素微球(MCMB)的结构和性能. 结果表明掺杂硼提高了 MCMB 的石墨化程度和晶粒尺寸,极大地改变了 MCMB 的形貌. 电化学充放电实验说明硼掺杂的中间相碳素微球嵌锂过程处于较高的电位,并有较大的不可逆容量.

关键词: 中间相碳素微球;硼掺杂的中间相碳素微球;电化学性能;XPS;SEM;XRD