

Electronic Supplementary Information (ESI) *for*

Highly active Fe₃BO₆ as an anode material for sodium-ion batteries

Jianliya Tian^a, Baofeng Wang^{a,b,*}, Fei Zhao^a, Xiao Ma^a, Yong Liu^c, Hua Kun Liu^b and Zhenguo Huang^{b,*}

^a Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai, 200090, China

^b Institute for Superconducting and Electronic Materials, University of Wollongong, NSW, 2522, Australia

^c School of Ophthalmology and Optometry, Wenzhou Medical University, Wenzhou, Zhejiang, 325027, China

*Corresponding author:

E-mail: wangbaofeng@shiep.edu.cn

zhenguo@uow.edu.au

Experimental details

Preparation of Fe₃BO₆

The Fe₃BO₆ nanoparticles were synthesized via a facile solid state method. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai) without further treatment. In a typical experiment, FeC₂O₄·2H₂O and H₃BO₃ were mixed by ball milling in a molar ratio of 3:1.2 with a proper amount of deionized water as a dispersant. After the grinding and mixing, the obtained rheological phase was transferred into an autoclave and kept at 80 °C for 12 h. The precursor was then calcined at 800 °C for 5 h with a heating rate of 3 °C /min in air. After cooling down to ambient temperature, the product was washed 3 times using boiling water to remove the unreacted boron oxide. In addition, the Fe₃BO₆@C sample was prepared by mixing Fe₃BO₆ with oleic acid and then heating it at 500 °C in N₂.

Characterization of the materials

The crystal structure of the samples was characterized by an X-ray diffractometer (XRD, Rigaku RINT 2200). XRD data were gained with Cu K α_1 radiation ($\lambda = 0.15406$ nm) in the 2θ range of 20–80° with a step size of 0.02° and a scan rate of 2° per minute. The morphologies and structure of the Fe₃BO₆ nanoparticles were investigated by scanning electron microscopy (SEM, Hitachi S-3500N) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) tests were carried out on a Kratos Axis UltraDLD spectrometer (Kratos Analytical - A Shimadzu Group company) with monochromatic Al K α radiation ($h\nu = 1486.6$ eV).

Electrochemical measurements

The Fe₃BO₆ powders were mixed with sodium carboxymethyl cellulose (CMC, WALOCEL™ CRT 2000 PPA 12, Dow Wolff Cellulosic) and acetylene black to form a slurry with a weight ratio of 80:10:10. The working electrode was manufactured by casting the slurry on copper foil substrate, which was dried at 80°C overnight. Disks with an area of 1.54 cm² were punched out of the foil, and the

average mass loading of active material on each disk was about 1.0 mg. In CR2016 coin cells, the Fe_3BO_6 samples and metallic sodium were using as working electrode and counter electrode, respectively. 1 M NaClO_4 (98% Sigma Aldrich) in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) was used as the electrolyte. The cells were assembled in an argon-filled glove box (Mikrouna-China Super 1220/750). The electrochemical properties of the cells were tested using a battery tester (LAND CT2001A Wuhan, China) in the voltage range of 0.01-3.0 V under different current densities. The cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (Autolab PGSTAT 302N) at a scan rate of 0.01mV s^{-1} in the voltage range of 0.01-3.0 V. The electrochemical impedance spectroscopy (EIS) analysis was conducted on an Autolab PGSTAT 302N electrochemical workstation from 100 kHz to 0.1 Hz with potentiostatic signal amplitude of 5 mV in the fully charged state. The working potential for EIS tests is stable at open circuit potential (about 1.7 V) after charging to 3.0 V (vs. Na^+/Na) and resting for 6 h.

Fig. S1

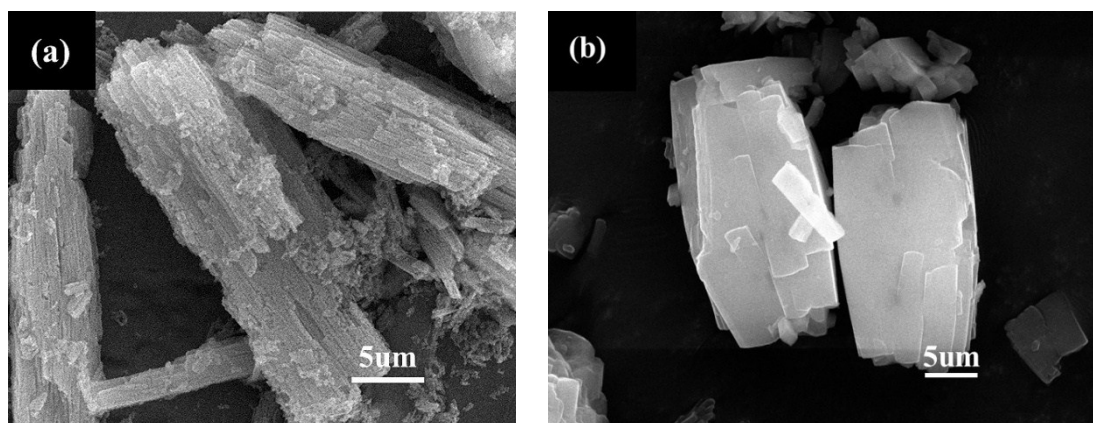


Fig. S1 (a) Low-magnification SEM image of as-prepared Fe_3BO_6 ; (b) SEM image of the $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor.

Fig. S2

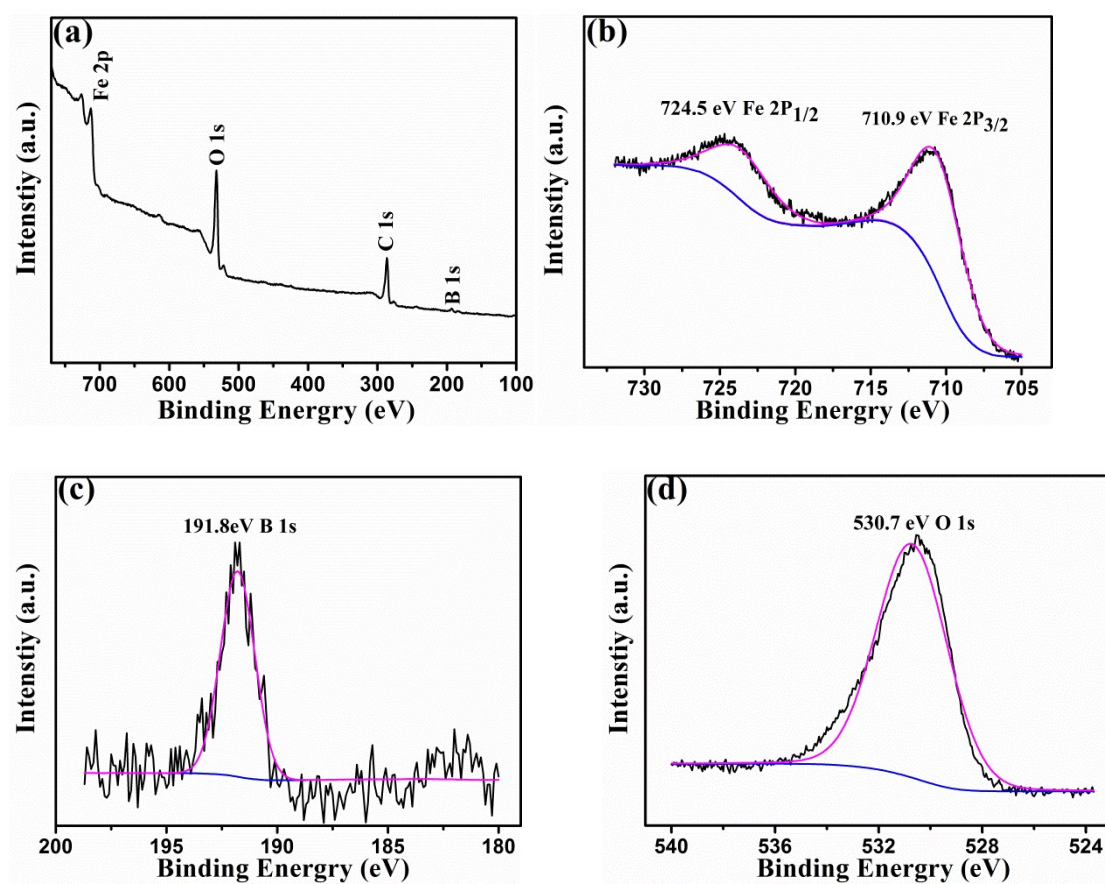


Fig. S2 XPS spectra of the Fe_3BO_6 sample: (a) survey spectrum, (b) Fe 2p, (c) B 1s, and (d) O 1s.

Fig. S3

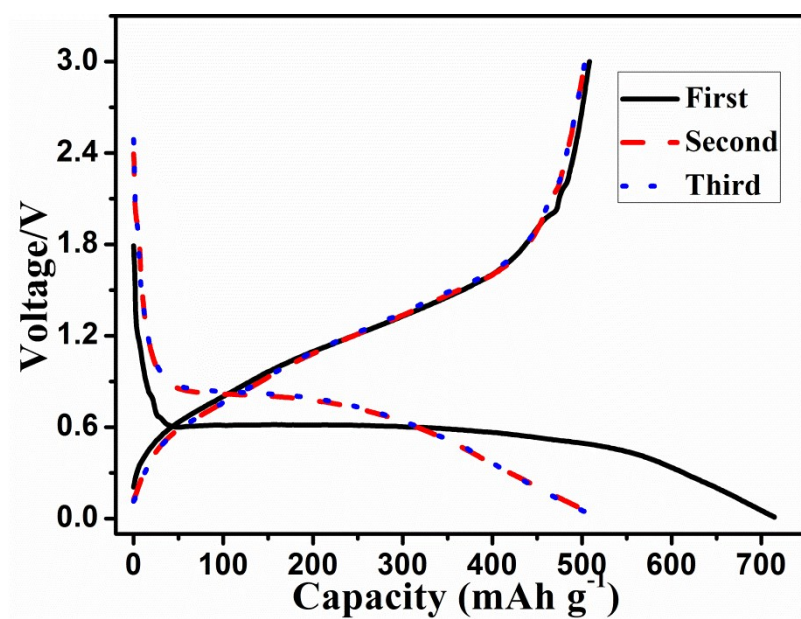


Fig. S3 Initial three charge-discharge curves of Fe_3BO_6 electrode at 100 mA g⁻¹.

Table S1

Table S1: Solution resistance (R_s), charge transfer resistance (R_{ct}), and constant phase angle element (CPE) derived from the equivalent circuit model of EIS curves.

Cycles	R_s/Ω	R_{ct}/Ω	CPE	
			$Y_o/\mu F$	N
1 st	1.98	100	225	0.60
2 nd	2.41	94.4	213	0.63
30 th	2.67	102	192	0.63
80 th	3.24	125	190	0.61