Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information For

Boron-doped Graphene as Promising Anode for Na-ion Batteries

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Details about DFT calculations

DFT calculations employed the Vienna ab initio Simulation Package (VASP) with projector augmented waves (PAW) pseudopotentials and the exchange-correlation functionals parameterized by Perdew, Burke, and Ernzerhof for the generalized gradient approximation (GGA).[1-3] Numerical convergence criteria were chosen to be less than 10^{-5} eV for the electronic structure and 0.01 eV/Å for the geometry optimization at energy cutoff 400.0 eV. Graphene monolayer calculations were performed with the 16x16 Gamma-centered *k*-point grid for the primitive cell (2.467x2.467 Å). In supercell calculations, *k*-point grids were reduced so as to give an approximately constant reciprocal space sampling density. Gaussian smearing of electronic states with a 0.1 eV spread was used for Brillion zone integration. All atoms are relaxed in the search of stable configurations.

For the adsorption and diffusion of $Na_x(B_yC_{1-y})_4$, supercell containing 72 B and C atoms was used for x=0.167, 0.333, 0.667 and 1.333, while supercell containing 32 B and C atoms was used for x=0.125, 0.25, 0.5, 0.75 and 0.875. The sizes of these two supercells were around 15.5x15.5 Å and 10.3x10.3 Å, respectively. The thickness vacuum layer was set to be 20 Å. The convergence of the adsorption energies was checked for the dilute adsorption and we found further increasing the size of the supercell changed the adsorption energy by less than 2 meV.

For the sodiation of few layer boron-doped graphene, we used DFT-D2 method implemented in VASP to accurately describe the Van der Waals force between graphene layers.[s1] The layered structure showed AB stacking without Na insertion. With Na insertion it changes to AA stacking. For a n-layered BC_3, the maximum amount for Na intercalation is 0.67(n-1) Na per n(BC_3) unit. Based on the analysis presented in the paper, higher intercalation concentration causes much larger structural deformation and thus is ignored in our calculations. Similarly, we take the maximum amount for Na adsorption as 0.67 Na per BC_3 surface.

Estimate the maximum capacity

In the discharge of the cathode, sodium continues to adsorb on the graphene sheet until the chemical potential of Na on the cathode equals to the chemical potential of Na in the metal anode. It requires

$$\mu_{Na,cathode} \leq \mu_{Na,metal} \quad \text{(S1)}$$

The chemical potential of Na on the cathode equals to

$$\mu_{Na,cathode} = (\partial G / \partial N_{Na})_{T,P,N_B,N_C} \quad \text{(S2)}$$

Because $G = E + PV - TS$, if we ignore PV and TS it can be written as

$$\mu_{Na,cathode} = (\partial E_{NaBC} / \partial N_{Na})_{T,P,N_B,N_C} \quad \text{(S3)}$$

where E_{NaBC} is the energy of $Na_x(B_yC_z)$ with fixed values of y and z.

So the sodiation requires

$$(\partial E_{NaBC} / \partial N_{Na})_{T,P,N_B,N_C} \leq \mu_{Na,metal} \quad \text{(S4)}$$

In the manuscript, the formation energy is defined as

$$E_f = E_{NaBC} - E_{BC} - x\mu_{Na,metal} \quad \text{(S5)}$$

Eq. 4 and Eq. 5 gives

$$(\partial E_f / \partial N_{Na})_{T,P,N_B,N_C} \leq 0 \quad \text{(S6)}$$

Thus the sodiation requires the slope of the formation energy curve presented in Figure 1 to be negative. The maximum amount of adsorbed Na corresponds to the concentration at which the slope of the formation energy curve becomes positive.

Energy density of different Na-ion battery anodes

Table S1. Comparison of different anode candidates for Na-ion batteries. V: voltage (unit: volt vs Na/Na+); C: capacity (unit: mAh/g); u: energy density (unit: Wh/kg); Δv: volumetric expansion; The energy density is calculated with a cathode voltage 3.4 V.

anode	sodiation voltage (V vs Na/Na$^+$)	capacity (mAh/g)	energy density (Wh/kg)	volumetric expansion	Reference
hard carbon	0.01	300	1017	~0%	2
tin	0.20	845	2704	318%	3
antimony	0.58	659	1858	285%	4, 5
titanate	0.3	300	930	~10%	6, 7
BC_3 boron-doped graphene	0.44	762	2256	~0%	current work

Adsorption energy of Na on pristine graphene

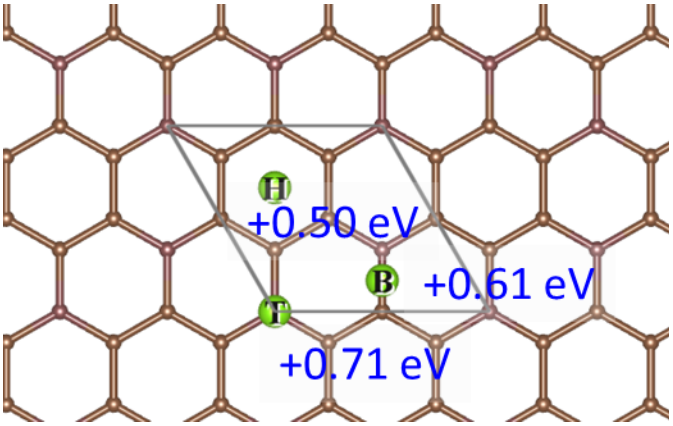

Figure S1. Adsorption energy of single Na atom on pristine graphene sheet. H: hollow site, T: top site; B: bridge site.

Reference:

[S1] Lee, et al. “Li Absorption and Intercalation in Single Layer Graphene and Few Layer Graphene by First Principles”, Nano Lett. 12, 4628, 2012

[S2] Komaba et al., “Electrochemical Na Insertion and Solid Electrolyte Interphase for Hard-Carbon Electrodes and Application to Na-Ion Batteries,” Adv. Func. Mater. 21, 3859, 2011.

[S3] Zhu et al, “Tin Anode for Sodium-Ion Batteries Using Natural Wood Fiber as a Mechanical Buffer and Electrolyte Reservoir” Nano Lett., 13, 3093, 2013

[S4] Qian et al., “High capacity of Na-storage and superior cyclability of nanocomposite Sb/C anode for Na-ion batteries,” Chem. Commun. 48, 7070, 2012.

[S5] Darwiche et al., “Better Cycling Performances of Bulk Sb in Na-Ion Batteries Compared to Li-Ion Systems: An Unexpected Electrochemical Mechanism,” J. Am. Chem. Soc. 134, 20805, 2012.

[S6] Senguttuvan et al., “Low-Potential Sodium Insertion in a NASICON-Type Structure through the Ti(III)/Ti(II) Redox Couple,” J. Am. Chem. Soc. 135, 3897, 2013;

[S6] Sun et al., “Direct atomic-scale confirmation of three-phase storage mechanism in $Li_4Ti_5O_{12}$ Anodes for room temperature sodium-ion batteries,” Nature Communications, 4, 1870, 2013.