Supporting Information For

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

Chen Ling*, and Fuminori Mizuno

Toyota Research Institute of North America

1555 Woodridge Ave, Ann Arbor, Michigan, USA, 48105

Corresponding Author: chen.ling@tema.toyota.com
**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).\textsuperscript{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$_{y}$C$_{1-y}$)$_{4}$, 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.\textsuperscript{41} 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

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

The chemical potential of Na on the cathode equals to

$$\mu_{Na,\text{cathode}} = \left( \frac{\partial G}{\partial N_{Na}} \right)_{T,P,B,C} \quad (S2)$$

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

$$\mu_{Na,\text{cathode}} = \left( \frac{\partial E_{NaBC}}{\partial N_{Na}} \right)_{T,P,B,C} \quad (S3)$$

where $E_{NaBC}$ is the energy of Na$_x$(B$_y$C$_z$) with fixed values of y and z.

So the sodiation requires

$$\left( \frac{\partial E_{NaBC}}{\partial N_{Na}} \right)_{T,P,B,C} \leq \mu_{Na,\text{metal}} \quad (S4)$$

In the manuscript, the formation energy is defined as

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

Eq. 4 and Eq. 5 gives

$$\left( \frac{\partial E_f}{\partial N_{Na}} \right)_{T,P,B,C} \leq 0 \quad (S6)$$

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); \(\Delta v\): volumetric expansion;

The energy density is calculated with a cathode voltage 3.4 V.

<table>
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<tr>
<th>anode</th>
<th>sodiation voltage (V vs Na/Na(^+))</th>
<th>capacity (mAh/g)</th>
<th>energy density (Wh/kg)</th>
<th>volumetric expansion</th>
<th>Reference</th>
</tr>
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<tbody>
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<td>930</td>
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<td>BC(_3) boron-doped graphene</td>
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<td>762</td>
<td>2256</td>
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<td>current work</td>
</tr>
</tbody>
</table>
**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:


