Sci. Bull. (2016) 61(14):1138–1144
DOI 10.1007/s11434-016-1118-7

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Article

Engineering Sciences

Ab initio prediction of borophene as an extraordinary anode material exhibiting ultrafast directional sodium diffusion for sodium-based batteries

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Received: 9 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published online: 18 June 2016

Abstract Density functional theory calculations and ab initio molecular dynamics simulations are performed to study the feasibility of using borophene, a newly synthesized two-dimensional sheet of boron, as an anode material for sodium-ion and sodium–oxygen batteries. The theoretical capacity of borophene is found to be as high as 1,218 mAh g^{-1} ($Na_{0.5}B$). More importantly, it is demonstrated that the sodium diffusion energy barrier along the valley direction is as low as 0.0019 eV, which corresponds to a diffusivity of more than a thousand times higher than that of conventional anode materials such as $Na_2Ti_3O_7$ and Na_3Sb. Hence, the use of borophene will revolutionize the rate capability of sodium-based batteries. Moreover, it is predicted that, during the sodiation process, the average open-circuit voltage is 0.53 V, which can effectively suppress the formation of dendrites while maximizing the energy density. The metallic feature and structural integrity of borophene can be well preserved at different sodium concentrations, demonstrating good electronic conductivity and stable cyclability.

Keywords Borophene · Sodium anode · Directional diffusion · Ultrafast diffusivity

1 Introduction

Sodium-ion and sodium–oxygen batteries have recently drawn considerable attention as a promising alternative to lithium-based batteries due to the abundance and low price of sodium element [1–6]. However, sodium is a highly reactive metal with low melting temperature, and also shares the same dendrite problem with lithium, all of which pose sever safety concern [7, 8]. Finding a suitable anode material is one of the most urgent tasks before the commercialization of sodium-based batteries. As the size of sodium atom, 1.02 Å, is bigger than that of lithium, 0.76 Å, many of the anode materials that are good for lithium-based batteries are unsuitable for sodium-based batteries. For example, graphite, a widely used anode material in lithium-ion batteries, showed extremely low capacity when used as a sodium intercalation anode [1]. Many possible materials, such as hard carbon, $NiCo_2O_4$ and Sn, have been tested for sodium-based batteries, but these materials suffer from low intercalation utility, slow kinetics and sever volume expansion [9–11]. Thus, finding a proper anode material with a large reversible capacity, high sodium diffusion rate and good structural stability is critically important for the development of sodium-based batteries.

In recent years, two-dimensional (2D) materials draw great attention as a new class of potential candidates for the anode material of sodium-based batteries. The loose packing between the 2D layers can accommodate the volume expansion caused by the insertion of sodium atoms and maintain the structural integrity. Many 2D materials, such as defective/doped graphene [12, 13], transition metal dichalcogenides (TMD) [14, 15], transition metal carbides (MXenes) [16, 17] and phosphorene [18, 19], have been explored as potential candidates for the anode material of

Electronic supplementary material The online version of this article (doi:10.1007/s11434-016-1118-7) contains supplementary material, which is available to authorized users.

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sodium-based batteries using first-principle method, and some of the predicted good performance have already been proven in experiments [20, 21]. Recently, borophene, a 2D sheet of boron, has been successfully synthesized by Mannix et al. [22]. The atomic structure of borophene was resolved experimentally for the first time after many theoretical predictions [23–25]. The 2D metallic feature and low atomic weight of borophene make it an attractive potential choice for the anode of sodium-based batteries. In this work, we comprehensively investigated the feasibility of employing borophene as anode material for sodium-based batteries using density functional theory (DFT) method. The calculation results show that borophene can not only provide a superhigh capacity (1,218 mAh g^{-1}), but also exhibit a directional ultrahigh sodium diffusivity, which is estimated to be more than a thousand times higher than that of conventional anode materials such as $Na_2Ti_3O_7$ [26] and Na_3Sb [27] and one to seven magnitudes higher than other previously reported 2D materials [12–19]. The ultrahigh diffusivity will revolutionize the rate capability of sodium-based batteries. At different sodium concentrations, the metallic feature and structural integrity of borophene can be well preserved, which ensure good electronic conductivity and stable cyclability. The calculated average open-circuit voltage (OCV) is 0.53 V, which is an appropriate value for sodium-based batteries to maintain a high energy density while effectively suppressing the dendrite formation. All the calculation results show that borophene is a prospective material for the anode of both sodium-ion and sodium–oxygen batteries.

2 Computational details

All the calculations were performed using ABINIT software package [28–30], with Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [31] and projector augmented-wave (PAW) method [32]. The cutting-off energy was set to be 20 Ha, and the k-point mesh was set to be <0.01 $Å^{-1}$. All the structures have been fully optimized with a force tolerance of 0.01 eV $Å^{-1}$. A 5 × 3 supercell was used to study the binding and diffusion of sodium with a 20 Å vacuum spacing along the z-direction.

The binding energy was calculated as [33]

$$E_b = E_{\text{borophene+Na}} - E_{\text{borophene}} - \mu_{\text{Na}}, \quad (1)$$

where $E_{\text{borophene+Na}}$ is the total energy of the borophene after bind with sodium, $E_{\text{borophene}}$ is the total energy of borophene and μ_{Na} is the chemical potential of metallic sodium.

According to the Arrhenius equation [33, 34], the diffusion coefficient (D) of sodium can be estimated by

$$D \sim e^{\frac{-E_a}{k_B T}}, \quad (2)$$

where E_a is the activation energy (diffusion barrier), k_B is the Boltzmann constant and T is the environment temperature.

Ab initio molecular dynamics (AIMD) was used to evaluate the structural stability of borophene and the diffusion of sodium atom. The simulations were performed on a 5 × 3 borophene supercell at 300 K using NVT ensemble. The time step was set to be 1 fs and both simulations last 3 ps.

3 Results and discussion

3.1 Structure of borophene

The top and side view of the optimized structure of borophene is shown in Fig. 1a, b. Different from the flat honeycomb structure of graphene [35], according to Mannix et al. [22], borophene belongs to the *pmmn* space group and shows a buckling structure. Here, we distinguish the boron atoms at different heights with "peak" and "valley", where "peak" denotes those atoms at higher positions in the z-axis considered, and "valley" denotes those atoms at lower positions. The optimized lattice parameters are $a = 1.62$ Å and $b = 2.87$ Å, which agree well with experiment and previous calculation results [22, 36, 37]. According to previous calculations [22, 36], the phonon spectrum of free-standing borophene shows a small imaginary frequency near the Γ point, indicating its instability against long-wavelength transversal waves, which can be fixed by defects and may explain the observed stripe formation in experiment. In this work, AIMD simulation was performed to check the thermal stability of borophene at 300 K using a 5 × 3 supercell. The snapshot during the

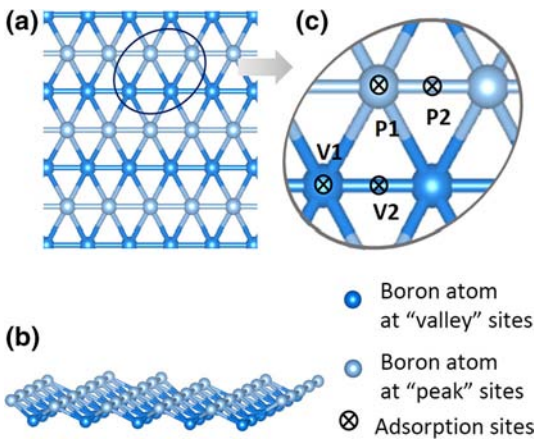

Fig. 1 (Color online) **a** Optimized borophene structure from top view and **b** side view, **c** the chosen adsorption sites on borophene