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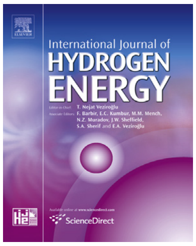

Theoretical limit of reversible hydrogen storage capacity for pristine and oxygen-doped boron nitride

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ABSTRACT

To achieve higher hydrogen storage capacity than that of compressed gas vessels, new advanced materials must be developed. Among the most promising are two-dimensional layered nanomaterials, such as graphene and boron nitride, storing hydrogen via physisorption which is potentially reversible at relatively low pressures. Unlike graphene, boron nitride is a polar material that makes it potentially more attractive for hydrogen physisorption. To quickly evaluate storage capacity of novel materials an efficient theoretical tool is proposed. A customized model combining quantum simulation with thermodynamic calculation is developed and applied for pristine and oxygen-doped boron nitride materials. It is shown that pristine boron nitride has a maximum reversible hydrogen storage capacity of 1.5 wt.% under 5 MPa at room temperature. Oxygen doping increases the capacity to 1.9 wt.% under the same conditions by deepening and widening the adsorption potential. Both gravimetric and volumetric storage properties are found to be strong functions of the interlayer separation distance of the material, with an optimum distance near 7 Å. The present results indicate that pristine and oxygen doped boron nitride materials have a suitable base configuration for potentially high reversible hydrogen storage.

Introduction

The challenge of global warming demands urgent development and implementation of alternative renewable sources of clean and safe energy. Additionally, the intermittent nature of renewable energy sources, e.g., solar and wind, demands reliable, efficient, and inexpensive forms of energy storage. Prospective technologies include pumped hydro, flywheels, rechargeable batteries, power-to-gas systems, or hydrogen storage with subsequent gas utilization to produce power, e.g., onboard storage on fuel cell vehicles. The challenge of

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onboard hydrogen storage is a balance between sufficient amount of hydrogen in acceptable volume and weight as well as its cost and safety: cryogenic temperatures drastically increase the cost while very high pressures cause safety issues. To date there is no satisfactory solution for hydrogen storage onboard vehicles. The difficulty of the problem is indicated by the recent decision of the US Department of Energy (DOE) to revise the time of the gravimetric (5.5 wt.% H_2) and volumetric (0.04 kg H_2/L) hydrogen storage targets for onboard light-duty vehicles and portable power applications from 2015 to 2020 [1]. The gap between the current storage capacities and the DOE targets can be only closed by development of novel materials with much greater storage capacity than existing ones [2–7].

The main research challenge in the context of practical hydrogen storage at near-ambient conditions lies in the choice of storage medium. Several broad categories of materials are available for this purpose based on chemical storage (materials with high hydrogen content released when decomposed) [2], metal-hydrides [3], metal-organic frameworks (MOFs) [4], covalent-organic frameworks (COFs) [5], and two-dimensional layered materials [6–8]. The majority of chemical storage materials irreversibly release hydrogen, which is a major drawback of their exploitation. Materials based on chemisorption, such as metal and chemical hydrides, either require high temperatures for hydrogen desorption or have very low gravimetric capacity because of their heavy metal content (e.g., La and Ni in $LaNi_5$) [3]. Both of these factors severely limit their prospective use in fuel cell vehicles. In contrast, because of their inherently low interaction energy (<0.1 eV), materials based on physisorption, such as carbon-based materials, MOFs, and COFs, can be reversibly used at ambient temperature and low pressure [9]. However, it should be noted that many of these materials are not stable in air or moisture [2,4]. Among these materials one of the most promising candidates are two-dimensional layered nanomaterials, such as graphene and boron nitride (BN), which are stable, robust, mechanically flexible, and have high available surface area [6,7].

Both graphene and boron nitride, as materials for hydrogen storage, showed modest storage capacity at room temperature [10–13]. It was shown experimentally [10,11] and theoretically [14,15] that the hydrogen storage capacity of pure graphene is 0.8–3.3 wt.% under 5 MPa at room temperature. For bulk BN powder, the storage capacity was measured to be around 0.1 wt.% under 6 MPa at room temperature [12]. In other study [13] Reddy et al. reported up to 3 wt.% under 10 MPa at room temperature for boron nitride nanostructures.

One way to improve their storage characteristics is to use doping which can increase hydrogen-material interaction [16]. One of the commonly used elements as a dopant is oxygen [17]. When substituting nitrogen in BN, the oxygen atom donates an extra electron to the surface which can increase the weak van der Waals bonding of hydrogen to the surface of the material. Indeed, Lei et al. recently demonstrated experimentally that O-doped BN (OBN) has a considerably higher storage capacity of 5.7 wt.% under 5 MPa at room temperature, 89% of which can be released at ambient conditions [16]. In that work it was also shown theoretically that BN and OBN materials may possess 5.5 wt.% of hydrogen capacity. That calculation as well as the majority of other modeling works on hydrogen storage is based on the number of adsorbed H_2 molecules estimated by quantum calculations. This approach can only provide an estimation of the maximum possible hydrogen capacity at cryogenic, near absolute zero temperatures, which are impractical for fuel cell vehicle applications. At higher temperatures, it is unavoidably significantly lower as the density decreases drastically with temperature. Therefore, a thermodynamic model is crucial for reliable estimation of hydrogen storage properties at more practical, non-cryogenic levels of temperature and pressure. The novelty of this work is in applying combination of quantum-chemical and thermodynamic approaches to BN and OBN materials to estimate their hydrogen storage capacity at ambient conditions.

The objective of the present work is to compare the theoretical hydrogen storage properties of pristine and O-doped boron nitride by using first principle calculations as well as thermodynamic modeling. The proposed combination of quantum and thermodynamic calculations allows for comprehensive investigations of the hydrogen storage capacity of the materials as a function of temperature and pressure, and hence permits practical evaluation of potential material formulations under application oriented conditions. The scope of this work considers two ways of modifying the material to increase its capacity by chemical (e.g., by doping or decoration) [18–20], and geometrical [14,15] modifications. Geometrical modification implies a change (tuning) of certain spatial parameters of the material. If two-dimensional monolayers can be smartly packed in three-dimensional structures with optimal interlayer separation, then the highest potential can be harnessed [14,15]. Both modification strategies are taken into account in the present work by doping BN with oxygen and tuning its interlayer distance.

Methodology

Pristine and oxygen doped boron nitride materials were modeled using unit cells consisting of 3 × 3 BN primitive surface monolayer cells resulting in eighteen atoms: nine boron and nine nitrogen atoms for pristine BN (pBN); and nine boron, eight nitrogen, and one oxygen atoms for oxygen doped BN (OBN) (Fig. 1). The choice of the 3 × 3 BN unit cell with one oxygen atom in the OBN cell provided an oxygen content of 5.6 at%. A vacuum space of 30 Å was kept normal to the surface to avoid interactions between adjacent layers.

Quantum calculations

Quantum calculations were performed in the plane-wave-based periodic density functional theory (DFT) software package Cambridge Serial Total Energy Package (CASTEP) [21] using a Perdew–Burke–Ernzerhof functional [22] and ultrasoft pseudopotentials. To account for the dispersion interaction responsible for hydrogen physisorption [23], dispersion correction in the form of a Tkatchenko and Scheffler scheme [24] was used as implemented in the DFT semi-empirical dispersion interaction correction module [25]. The electronic occupation numbers were fixed during electronic minimization. Spin-restricted and spin-unrestricted calculations were

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