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Research paper

# Prediction of electrocatalytic activity of boron nanostructures

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ABSTRACT

The dissociation of $O_2$ and $HO_2$ are important reactions that occur at the cathode of fuel cells producing $H_2O$ and use platinum as a catalyst. There is a need to replace platinum with less expensive catalysts. Here the possibility of boron nanostructures as catalysts for the reactions is considered using density functional theory. The calculations show that the bond dissociation energies to remove O and OH from $O_2$ and $O_2H$ bonded to boron nanostructures are less than those necessary to dissociate free $O_2$ and $O_2H$ indicating that some of the boron nanostructures could be catalysts for the dissociation of $O_2$ and $HO_2$.



## 1. Introduction

Presently platinum is employed to catalyze the reactions that produce $H_2O$ at the cathode of fuel cells. Platinum is expensive and susceptible to time dependent drift and CO poisoning [1,2]. These issues are significant obstacles to the development of large scale commercial application of fuel cells. Likely reactions that produce $H_2O$ at the cathodes are the dissociation of $O_2$ bonded to the catalyst followed by atomic oxygen undergoing the following reaction,

$$2O + 4H^+ + 4e \rightarrow 2H_2O \quad (1)$$

Another possibility is the formation of $O_2H$ which bonds to the catalyst followed by the removal of OH which could then undergo the following reaction,

$$OH + H^+ + e \rightarrow H_2O \quad (2)$$

For the catalyst to be effective the energy needed to dissociate O and OH from $O_2$ and $O_2H$ bonded to the catalyst should be significantly lower than that required to dissociate free $O_2$ and $O_2H$. Modeling has been used to successfully understand the role of platinum as a catalyst in fuel cells [3]. It also has been employed to predict possible new catalysts. For example molecular orbital theory has been used to predict that boron nitride nanoribbons as well as nitrogen doped graphene could be effective catalysts for reactions at the cathode of fuel cells [3–6]. The object of this paper is to use theoretical methods such as Density Functional Theory (DFT) to determine minimum energy structures of boron nanoribbons and sheets and investigate whether the structures can catalyze the reactions at the cathode of fuel cells.

The modeling approach follows the procedure used to successfully predict the catalytic effect of platinum on the ORR reactions [3]. In that work no involvement of the acidic electrolyte was assumed in the ORR reaction and is justified by the success of the results. These calculations most likely apply to PEM fuel cells which have a nafion electrolyte having little acidity. The approach seeks to identify a material X that bonds to $O_2$ or $O_2H$ to form X-$O_2$ or X-$O_2H$ such that the bond dissociation energy (BDE) to remove O or OH is less than the BDE to dissociate free $O_2$ or $O_2H$.

## 2. Methods

The minimum energy structures of $XO_2$, XO, and $XO_2H$ where X is a boron nanostructure are calculated using DFT. The calculations are performed using the Gaussian 03 software package at the B3LYP/6-31G* level [7]. The BDE is defined as,

$$BDE = [E(XO) + E(Z)] - [E(XY)] \quad (3)$$

where Y is $O_2$ or $O_2H$ and Z is O or OH. E is the total electronic energy plus the zero point energy (ZPE) of the minimum energy structure. The ZPE is the total ZPE of all of the normal modes of vibration given by,

$$E_{zpe} = (1/2)h\,\Sigma_i^{3N-6} f_i \quad (4)$$

where $f_i$ are the vibrational frequencies of the normal modes and N the number of atoms in the molecule. The calculated BDE given by Eq. (3) is compared with that to dissociate free $O_2$ or $HO_2$. If it is significantly less, it can be concluded that X is a good catalyst for the dissociation of $O_2$ and $HO_2$.

Another issue that needs to be considered in assessing whether boron nano-structures catalyze the reactions at the cathode is

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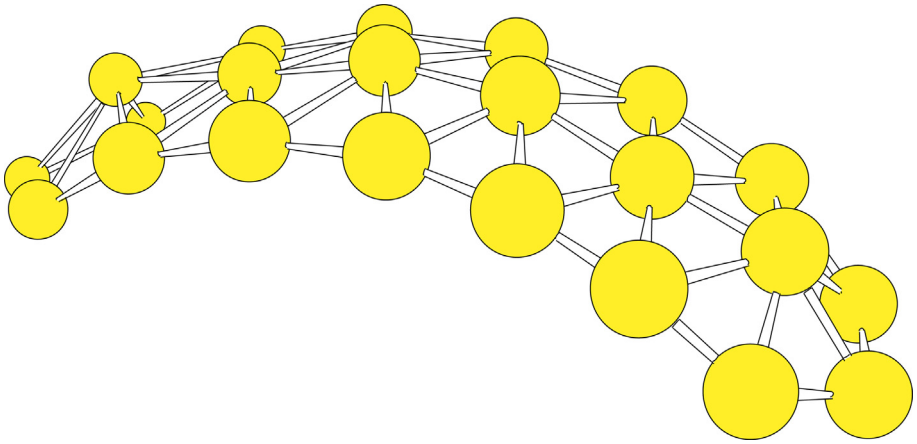

**Fig. 1.** Calculated minimum energy structure of a boron nanoribbon.

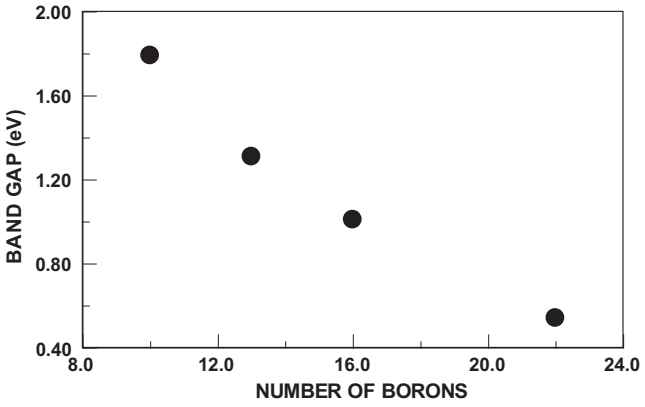


**Fig. 2.** Plot of the calculated band gap of the ribbon versus the number of borons.

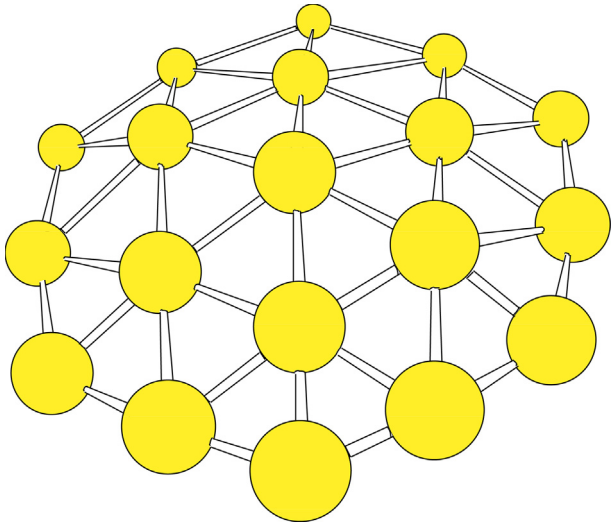

**Fig. 3.** Calculated minimum energy structure of a boron sheet.

whether $O_2$ or $HO_2$ can bond to the structures. This can be evaluated by calculating the adsorption energy, $E_{ads}$, given by [8],

$$E_{ads} = E(XY) - E(X) - E(Y) \quad (5)$$

where X is a boron nanostructure and Y is $O_2$ or $HO_2$. If the result is a negative value, it indicates $O_2$ or $HO_2$ can form a stable bond with the boron nanoribbons

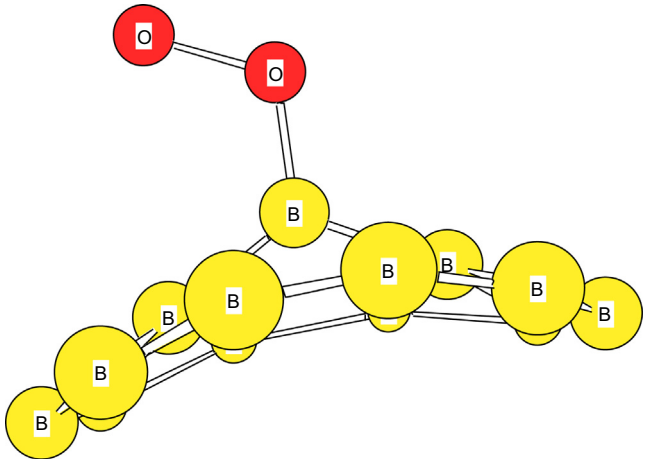


**Fig. 4.** Calculated minimum energy structure of $O_2$ bonded to a boron nanoribbon.

## 3. Results

### 3.1. Structure of boron nanoribbons and nanosheets

Various molecular methods have been used to predict a variety of structures for boron two dimensional sheets and ribbons [9–12]. However, it is not clear that the predicted structures are at a minimum on the potential energy surface because in many instances frequencies of normal modes of vibration were not calculated.

Fig. 1 shows the calculated minimum energy structure of a boron nanoribbon having 22 boron atoms. Calculation of the frequencies of the normal modes of vibration indicated no imaginary frequencies indicating that the structure is at a minimum on the potential energy surface. This structure has previously been suggested based on an aufbau principle in which the structure is built be addition $B_6$ pentagonal structures [9]. However, it was not shown that this was a minimum energy structure by calculation of frequencies. The band gap of this ribbon has been calculated as a function of the number of borons in the ribbon, effectively the length of the ribbon. The calculation is performed using the LSDA approach at the 6-31G* level on the optimized structures. Previous work has suggested this approach for calculation of energy gaps [13]. Fig. 2 shows that the energy gap decreases with increasing ribbon length suggesting the ribbons having more than 30 atoms are metallic. Fig. 3 shows the calculated minimum energy structure of a boron nanosheet. The structure is not two