

# EFFECT OF BORON-DOPING ON THE ELECTRONIC STATE OF GRAPHITE SURFACE AND ITS IMPLICATIONS ON THE OXIDATION MECHANISM

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## Introduction

It is known that boron is a unique and efficient dopant for improving the oxidation resistance of graphite. Its effect on the oxidation resistance is considered to be tightly related with the alteration of the electronic density distribution along the surface of graphite[1]. This paper is to investigate the electronic density redistribution of a graphene layer as a result of boron substitution using the semi-empirical molecular orbital package (MOPAC) and large clusters of carbon atoms, which will shed some light on the mechanism mainly responsible for the oxidation inhibition of boron-doped graphite.

## Model

The large cluster with 56 carbon atoms having four active sites on the edge studied was designed as shown in Fig. 1. There are two long edges, labeled as top and bottom, and two short edges, labeled as left and right. On the top edge, there are four surface active sites, 4, 6, 8, and 10. The carbon atoms on the active sites of the bottom and two short edges are saturated by hydrogen atoms. The hydrogen saturation on the bottom, left and right edges of the cluster is made to simulate the behavior of internal bulk, or unreactive, carbon sites in a graphene layer. On the other hand, the hydrogen atoms have been purposely left off the top edge of the cluster in order to simulate the most reactive carbon sites present in the layer. It is obvious that in order for the oxidation reaction between carbon and oxygen to take place, hydrogen would have to be extracted from the carbon surface. Hence, the cluster model shown in Fig.1 describes all the important features at the surface of the graphene layer during oxidation.

Since oxidation is an electrophilic reaction in which an oxygen atom draws electrons from the atoms that it reacts with, the ability of the carbon atoms to donate electrons can be considered to be their oxidation reactivity. In bulk graphite, only the electrons occupying the states around the Fermi surface would contribute to the oxidation reaction [1]. In a larger carbon cluster with edges and corners, the electrons in the highest occupied molecular orbital (HOMO), and those orbitals close to the

HOMO, are considered to make the main contribution to the oxidation reaction [2]. Therefore, the oxidation reactivity of the atoms depends on the populations of their electrons in the HOMO and the orbitals close to the HOMO. Such populations can be used as an index of the oxidation reactivity (R). In MOPAC, this reactivity (R) can be characterized through the coefficient  $C_j^i$ [2],

$$R = \sum_j 2 \sum_i (C_j^i)^2, \quad (1)$$

where  $C_j^i$  is the coefficient of LCAO (linear combination of atomic orbitals) on molecular orbital j, and i labels the atomic orbitals S, Px, Py and Pz, respectively. The summation runs over the high occupied molecular orbitals including the HOMO. In our model, the four highest occupied orbitals were taken into account to determine R. Table 1 gives the populations R in different cases.

## Results and Discussion

Table 1. Reactivities (Rs) of four surface active sites for various cases: (a) pure graphite cluster; (b) the graphite cluster with two boron substitutions on sites 6 and 8; (c) the graphite cluster with two boron substitutions on the shallow internal lattice sites 14 and 15; (d) the graphite cluster with two boron substitutions on the deep internal lattice sites 16 and 17.

#Site	R	(a)	(b)	(c)	(d)
4		0.82	1.68	0.53	0.92
6		1.10	0.07	1.15	1.00
8		1.09	0.07	0.26	1.00
10		0.83	1.68	1.66	0.92

It is shown that boron-doping on the edge and internal lattice sites of the graphene layer produces very different effects on the electronic structure around the edges. It is found in table 1 that the substitutional boron atoms on the edges (case (b)) dramatically alter the density distribution of high energy electrons along the edges and the substitutional boron atoms on the deep internal lattice sites (case (d)) do not produce any significant effect on the density distribution along the edges.

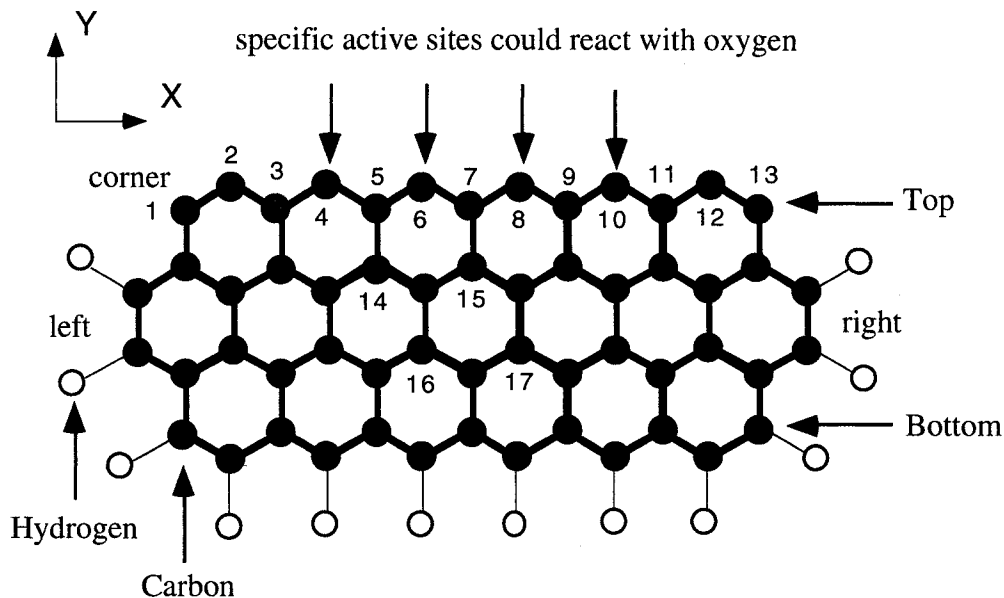


Figure 1. The atomic arrangement in the designed carbon cluster.

Based on the results obtained, a model is proposed for describing the oxidation process in boron-doped graphite. During the initial stage of oxidation, some of the surface sites will be occupied by carbon, and they will react with oxygen and be removed. As a result, new surface active sites will be created. If the new surface sites are again occupied by carbon atoms, the oxidation will most likely continue. The oxidation will be significantly slowed down when all the surface active sites, or their neighbors, are occupied by boron atoms or boron oxide. It is quite reasonable to expect, therefore, that boron atoms can accumulate on the graphite surface during the oxidation process. The prediction of boron accumulation on the surface is consistent with the experimental observation[3].

### Conclusion

In summary, the electronic structures of various carbon clusters have been simulated by MOPAC with AM1 parameters to investigate the oxidation behavior of graphene layers and the oxidation-inhibition in boron-doped graphite. The results show that (1) substitutional boron atoms on the surface play very significant roles in oxidation inhibition of the boron-doped graphene layer by changing the density distribution of high energy electrons along the edges of layer; (2) substitutional boron atoms on the deep internal lattice sites do not produce any significant effect on the electron density distribution along

the edges of graphene layer; (3) a model is proposed for describing the oxidation process in boron-doped graphite. It is concluded that the mechanism of oxidation inhibition due to boron-doping of a graphene layer is chemical inhibition via the reduction of electron density at surface sites, and consequently, a reduction in the total number of active sites for gasification of carbon.

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