

Comparing the Effect of 2nd Row Dopants on the Carbon Support to improve Pt Catalytic Activity and Durability

M.N. Groves*, A.S.W. Chan**, C. Malardier-Jugroot*** and M. Jugroot****

* Royal Military College of Canada, Kingston, ON, Canada, michael.groves@rmc.ca

** Royal Military College of Canada, Kingston, ON, Canada, anita.chan@rmc.ca

*** Royal Military College of Canada, Kingston, ON, Canada, cecile.malardier-jugroot@rmc.ca

**** Royal Military College of Canada, Kingston, ON, Canada, manish.jugroot@rmc.ca

ABSTRACT

Density functional theory is used to calculate the binding energy between a platinum atom and singly doped surfaces using the second row elements beryllium, boron, nitrogen, and oxygen. The change in Gibbs free energy of adsorption of H_2 and O_2 gas is also determined as a marker for catalytic activity. The results show that the oxygen doped surface produced the largest binding energy and the smallest ΔG of adsorption which implies that it will form the most durable and active catalyst system of all the supports evaluated.

Keywords: density functional theory, proton exchange membrane fuel cell, binding energy, catalyst activity

1 Introduction

Transitioning away from fossil fuels requires large improvements in alternative technologies so that they may compete based on performance and cost. The proton exchange membrane fuel cell (PEMFC) presents the potential to create, store, and use its fuel on demand and in a delocalized fashion that both promotes sustainable and energy security ideals. This work outlines another step towards this reality by improving the platinum catalyst durability and activity by modifying the carbon catalyst support.

Computational methods have shown that nitrogen [1], [2] and boron [3] substitution in a carbon substrate increases the durability of a Pt catalyst. The beneficial effects of the nitrogen doped case has also been verified experimentally [4], [5]. Given that these two dopants have already been shown to improve the substrate, a comprehensive evaluation including two other second row dopants, beryllium and oxygen, are presented for the case where they are singly substituted into the carbon matrix. Comparison of these four doped surfaces with the undoped case for catalytic activity and durability will use density functional theory (DFT).

2 Computational Methods

Gaussian 03 [6] revision C.02 was used on the High Performance Computing Virtual Laboratory (HPCVL) as well as revision E.01 on a native Mac running OSX.

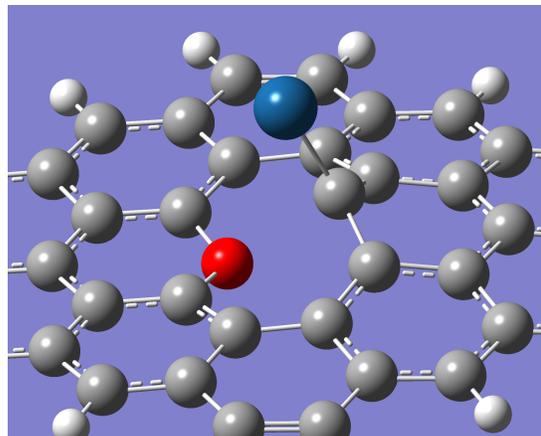


Figure 1: An example of a single substitution (oxygen is in red) into the carbon (in grey) lattice. Hydrogen is in white and platinum is in light blue.

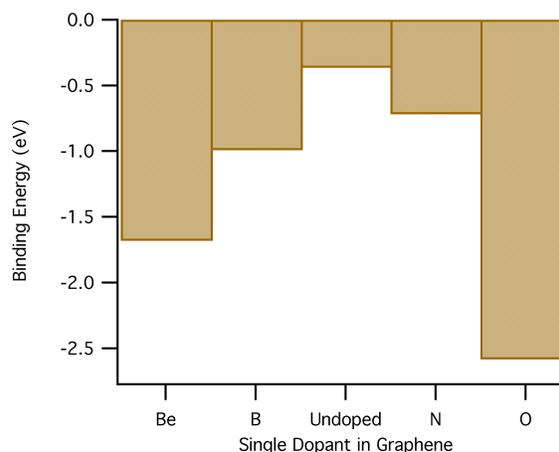


Figure 2: Second row binding energy results.

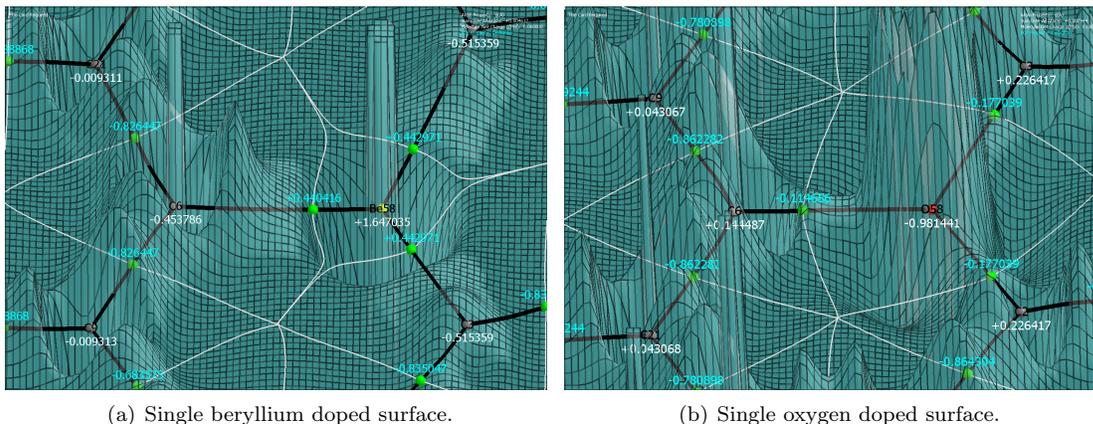


Figure 3: Relief images produced by AIMAll in plane along the C/dopant axis without the platinum atom.

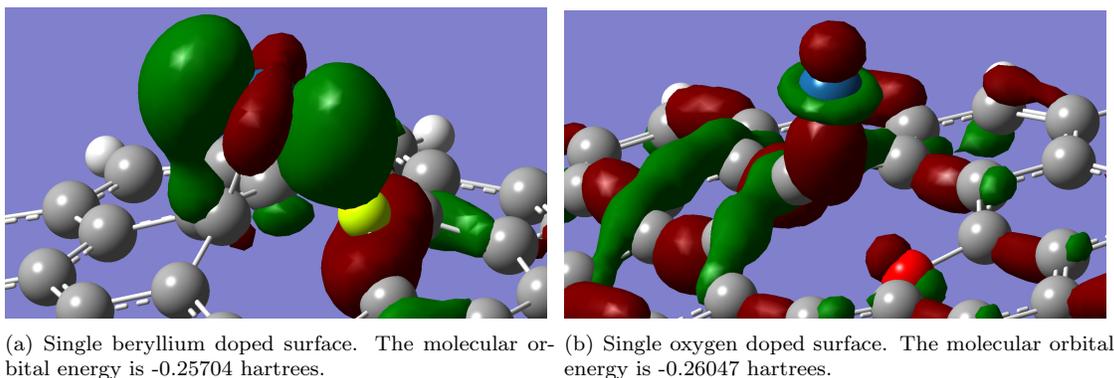


Figure 4: Molecular orbital images of platinum adsorbed onto the beryllium (in yellow), and oxygen (in red) doped carbon (in grey) surfaces. Hydrogen is in white and platinum is in light blue.

The B3LYP hybrid functional [7] was used along with the GenECP basis set. Platinum, being a very large atom, is very expensive computationally when calculating a molecular orbital for each electron. Effective core potentials (ECPs) can be used to greatly reduce the computational time necessary to complete a calculation involving these large atoms. The GenECP basis set allows an ECP to evaluate a platinum while split valence basis sets can be used for the lighter atoms, such as hydrogen, carbon, beryllium, boron, nitrogen and oxygen. Previous work has shown that the combination of using the SDD basis set for transition metals [8], [9] and 6-31G(d) for the light atoms [10], [11] is more accurate than using an ECP such as Lanl2DZ on its own [12]. This is the basis set combination that will be used in this work unless otherwise noted. The only exception is to use 6-31G(d,p) for the hydrogen atoms that directly interact with the platinum atom so that interactions involving their p-orbitals are also considered.

The undoped surface consists of 42 carbon atoms arranged as a single sheet of graphite with hydrogen atoms terminating the dangling bonds along the edges.

The four other surfaces considered involve substituting a single atom of beryllium, boron, nitrogen or oxygen in to the lattice. An example of this can be seen in figure 1 where an oxygen atom is doped into the surface. The other three dopant systems follow this template.

To determine the binding energy between the platinum atom and the surface, the zero point energy (ZPE) of the surface and an individual platinum atom are subtracted from the geometrically optimized surface with a platinum atom adsorbed onto it. The initial position of the platinum atom was determined using a potential energy scan to determine the position of lowest energy. For these scans, the surface was evaluated using the smaller 3-21G basis set while the Pt still used the SDD basis set. The position corresponding to the lowest energy was then reoptimized using the basis set combination described above.

Once the binding energy calculations were completed, the change in Gibbs free energy of adsorption (ΔG_{ad}) of the H_2 and O_2 gas were performed. In the literature, a combination of experimental and theoretical studies have shown that measuring the ΔG_{ad} is a good indica-

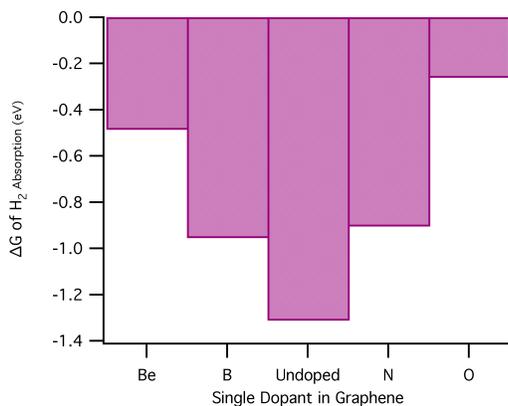


Figure 5: ΔG of H_2 adsorption when the surface dopant is varied.

tor of activity of a catalyst[13]. To calculate this value a geometry optimization of the gas adsorbed onto the catalyst. From that, the Gibbs free energy of the gas and catalyst/substrate systems were both subtracted to give ΔG_{ad} .

3 Results and Discussion

The results from the binding energy calculations can be seen in figure 2. The oxygen doped system shows the strongest interaction between the support and the platinum atom and is five times stronger than the undoped case. This result is related to how the dopant changes the local bonds in the surface of the support. When there is no doping present, the delocalized double bonds are present throughout the surface and that is where the platinum atom will interact to adsorb onto the surface [1]. The dopant will locally create an electron hole either on the adjacent carbon atoms or possess the hole itself depending on if the dopant has more or less valence electrons respectively relative to carbon. This can be seen in figure 3 which are $\nabla^2\rho$ relief plots of the beryllium and oxygen doped systems produced by AIMAll[14] which is based on atoms in molecules computational theory[15]. These images are orientated so that peaks reflect areas of electron localization and minimums reflect electron deficiencies.

This hole seems to be what attracts the platinum atom to form bonds with the surface. This explains why the single boron doped surface has a stronger binding energy than the single nitrogen doped surface. The nitrogen atom can not induce a hole on the surrounding carbon atoms that compare to the hole present on the boron atom. Moving out one additional column, the oxygen and beryllium atoms interact very weakly with the adjacent carbon atoms. This frees up an sp_2 hybridized orbital on the adjacent carbon atom to bond with the platinum atom. In addition to this, the oxygen atom creates a large hole on that same carbon atom to allow

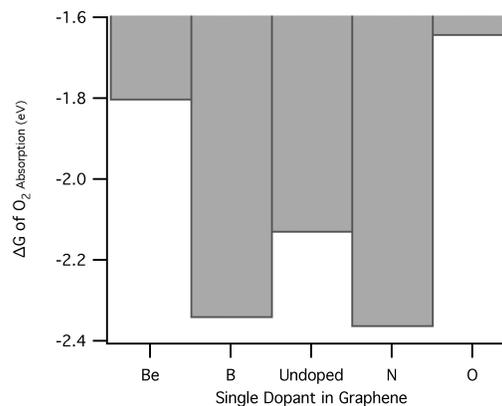
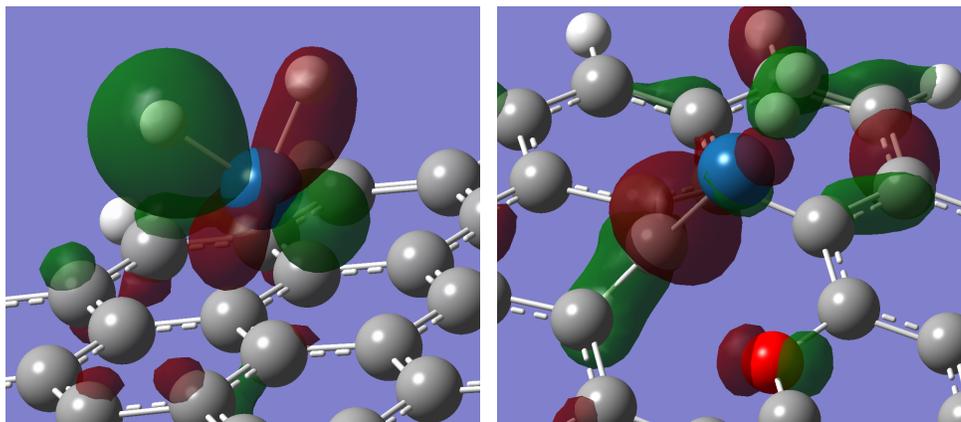


Figure 6: ΔG of O_2 adsorption when the surface dopant is varied.

for the platinum to bond quite strongly. The beryllium doped surface on the other hand presents two different bonding sites, the underutilized sp_2 hybridized carbon orbital and the hole on the beryllium atom. This delocalized bonding arrangement lowers the overall strength of the interaction the platinum has with the surface. This is illustrated in figure 4 which shows an example of similar molecular orbitals for oxygen and beryllium doped surfaces and the difference in bonding described above.

The results for the ΔG of H_2 and O_2 gas adsorption are shown in figures 5 and 6. For the adsorption of hydrogen, as the binding energy increases between the surface and the platinum atom, the ΔG decreases. The stronger the platinum/surface interaction allows fewer electrons to be available to interact with the incoming hydrogen atoms. This is illustrated in figure 7 which shows similar molecular orbitals for the undoped and oxygen doped systems. In the undoped case, the platinum, having a weak interaction with the surface, interacts quite strongly with the two hydrogen atoms. Conversely, the oxygen doped surface has a very strong bond between the surface and the platinum atom. The hydrogen atoms weakly associate with the platinum catalyst and presumably can adsorb/desorb easily.

When adsorbing oxygen gas the relationship between binding energy and ΔG no longer holds. In this case boron and nitrogen perform worse than the undoped case. According to molecular and natural bond orbital (NBO) analysis, in order to reduce the ΔG_{ad} , the oxygen atoms need to have a relatively strong interaction with the platinum atom. The nitrogen doped system produced the largest ΔG_{ad} and had the weakest platinum/oxygen interaction. The molecular orbitals from this catalyst show that there are surface/platinum interactions and an association between the two oxygen atoms but very little between the oxygen and platinum atoms. The NBO analysis confirms that there is no significant platinum/oxygen interaction. The oxygen



(a) Hydrogen atoms interacting with the platinum above the undoped surface. The molecular orbital energy is -0.37208 hartrees. (b) Hydrogen atoms interacting with each other and not with the platinum over the oxygen doped surface. The molecular orbital energy is -0.36607 hartrees.

Figure 7: Molecular orbital images of hydrogen (in white) adsorption onto an undoped and oxygen (in red) doped surfaces. Carbon is in grey and platinum is in light blue.

doped system had the lowest of the five ΔG_{ad} . Its calculated molecular orbitals and NBOs shows many interactions involving the carbon, platinum and oxygen gas atoms together. It seems that oxygen atoms need to be adsorbed on to the catalyst so that hydrogen atoms can also be adsorbed to form water and complete the reaction. Presumably, if this interaction does not exist, then the remaining steps to the oxygen reduction reaction can not occur.

4 Conclusion

The binding energy, and ΔG_{ad} of H_2 and O_2 gas for singly doped graphene surfaces supporting a platinum catalyst are presented. Oxygen doping provides the strongest carbon/platinum bond, and lowest ΔG_{ad} of the four doped systems. The increase in binding energy is attributed to the oxygen atom having a minimal interaction with an adjacent carbon atom freeing up its sp_2 hybridized orbital to interact with the platinum atom. In addition to this, the platinum seems to favour bonding with electron holes which the oxygen atom induces on the the binding carbon atom. The low ΔG of H_2 adsorption is attributed to the strong binding energy between the surface and the platinum atom which does not allow for the platinum to strongly interact with hydrogen atoms. The lower ΔG of O_2 adsorption is attributed to an interaction between the platinum and the oxygen atoms which allows for the oxygen reduction reaction to occur and then desorb the water.

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