# MODELING ELECTROCATALYTIC ACTIVITY OF NITROGEN RADICALS

## ABSTARCT

It has recently been shown that nitrogen radicals electrochemically deposited on carbon nanotube paper can catalyze reactions at the cathode of fuel cells. Density functional theory (DFT) is used to show that $O_2$ and $O_2H$ could adsorb on nitrogen radicals such as $N_2^-$, $N_4^-$, and $N_8^-$.The bond dissociation energy to remove an O atom from $O_2$ and OH from $O_2H$ bonded to these radicals is calculated. The results show that $N_4^-$ and $N_8^-$ could be effective catalysts for the $O_2H$ dissociation but not $O_2$ dissociation. The results support the previous conclusion that $N_8^-$ could be a catalyst for the reactions at the cathode of fuel cells.

Key words: catalysis, nitrogen radicals, oxygen reduction reaction, fuel cells.

## I 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 $O_2$ dissociation followed by atomic oxygen undergoing the following reaction,

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

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,

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

The object of this paper is to use theoretical methods such as Density Functional Theory (DFT) to determine whether nitrogen radicals can catalyze these reactions. Modeling has been used to understand the role of platinum as a possible catalyst.[3,4] It also has been employed to predict possible new catalysts. For example molecular orbital theory has been used to predict that nitrogen doped graphene, coronene and pentacene could be an effective catalysts .[5,6,7]

It has been shown that electrolysis of sodium azide solutions can be used to deposit nitrogen molecules on carbon nanotube paper.[8] The carbon nanotube paper having the deposited nitrogen molecules was shown by cyclic voltammetry to be an effective catalyst for the ORR reaction in fuel cells. Based on the agreement of density functional calculations of frequencies and measured Raman and IR values the species responsible for the catalytic effect was attributed to an $N_8^-$ chain molecule.[8] The possibility of $N_8^-$ is plausible because it has an unpaired electron and thus an available bond for the $O_2$ and $O_2H$ to bind to. However, other radical species such as $N_4^-$ and $N_3^0$ could also catalyze the ORR reaction. The $N_4^-$ radical has been detected in uv photolyzed monovalent azides by electron paramagnetic resonance and has been shown to be stable above room temperature.[,9,10,11] The $N_2$- has also been observed in irradiated azides but is not stable at room temperature.[12]

Generally the modeling has been used 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 produce O or OH is less than the BDE to dissociate free $O_2$ or $O_2H$. This approach has been used to obtain understanding of the mechanism of platinum catalysis and the modeling of nitrogen doped graphene and coronene as a cathode catalyst in fuel cells.[5,6,7]

## II METHODS

The minimum energy structures of $XO_2$ ,XO, and $XO_2H$ where X is $N_2^-$ , $N_4^-$ , and $N_8^-$ are calculated using DFT. The calculations are performed using the Gaussian 03 software package at the B3LYP/6-31 G* level.[13] The BDE is defined as ,

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

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,

$$E_{zpe} = (1/2)h \sum_{i}^{3N-6} f_i \qquad (4)$$

where $f_l$ are the vibrational frequencies of the normal modes and N the number of atoms in the molecule. The calculated BDE given by equation 3 is compared with that to dissociate free $O_2$ or $O_2H$. If it is significantly less, it can be argued that X is a good catalyst for the reactions.

Another issue that needs to be considered in assessing these radicals as catalysts for the reactions at the cathode is whether $O_2$ or $O_2H$ can bond to them . This can be evaluated by calculating the adsorption energy, $E_{ads}$, given by,[14]

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

where X is $N_2^-$, $N_4^-$ and $N_8^-$ and Y is $O_2$ or $O_2H$. If the result is a negative value, it indicates $O_2$ or $O_2H$ can form a stable bond with the radicals.

## III RESULTS

Figure 1a and 1b show the optimized minimum energy structure of $N_8O^-$ and $N_8O_2^-$. The structures have no imaginary frequencies. The bond dissociation energy to remove an O atom from $N_8O_2^-$. Is calculated to be 4.67 eV slightly less than the calculated BDE to dissociate free $O_2$ which is 5.03 eV. Figure 2a and 2b illustrate the calculated minimum energy structure of $N_4O_2^-$ and $N_4O^-$ which have no imaginary frequencies. The BDE calculated to remove an O atom from $N_4O_2^-$

is 4.08. Figure 3a and 3b show the minimum energy structures of $N_2O_2^-$ and

$N_2O^-$ . The calculated BDE to remove an O atom from $N_2O_2^-$ is 4.67 eV. These results indicate that these nitrogen radicals would not be highly effective catalysts for $O_2$ dissociation as the BDEs are only slightly less than that needed to dissociate free $O_2$.

Figure 4 shows the calculated minimum energy structure of $N_2O_2H^-$. The structure has no imaginary frequencies. The calculated BDE to remove an OH from it is 2.58 eV. Figure 5 shows the minimum energy structure of $N_4O_2H^-$ .The BDE to remove OH from it is calculated to be 0.49 eV. Figure 6 shows the minimum energy structure of $N_8O_2H^-$. This structure had no imaginary frequencies. The BDE to remove an OH from it was calculated to be 0.54 eV. which is much less than calculated BDE to remove OH from free $O_2H$ which is 5.79 eV. The calculated minimum energy structure of $O_2H$ had no imaginary frequencies indicating it can exist as a free entity.Table I tabulates all the BDEs to remove an O atom from $O_2$ bonded to all the nitrogen radicals and to remove an OH from $O_2H$ bonded to the radicals.

Table II presents the calculated adsorption energy for $O_2$ and $O_2H$ to bond to all the nitrogen radicals considered, showing that because they are negative, a stable bonds can form. Interestingly, a calculation of $E_{ads}$ for non paramagnetic molecules such as $N_2$, $N_3^-$, $N_8^0$ yield positive values suggesting that nitrogen radicals are necessary for potential catalysts. This is plausible in that the radical species have an available bond for the $O_2$ or $O_2H$ to bind with.

## CONCLUSION

Density functions calculations of the minimum energy structure of $N_2O_2^-$, $N_2O^-$ ,$N_4O_2^-$, $N_4O^-$ $N_8O_2^-$ and $N_8O^-$ indicate the structures have no imaginary frequencies and are therefore at a minimum on the potential energy surface. The calculated bond dissociation energy to remove an O atom from, $N_2O_2^-$ , $N_4O_2^-$, and $N_8O_2^-$ are only slightly less than that needed to dissociate free $O_2$ into two O atoms. This suggests that these molecules would not be highly effective catalysts for the molecular oxygen dissociation in fuel cells. However, the bond dissociation energy to remove OH from $O_2H$ bonded to $N_4^-$ and $N_8^-$ is considerably smaller than that needed to dissociate free $O_2H$ into O and OH. These nitrogen radicals are predicted to be effective catalysts for the $O_2H$ dissociation. Calculation of the adsorption energy for $O_2$ and $O_2H$ on all the radicals yield a negative value indicating they can bond with the radicals.

The results support the explanation for the recently observed catalytic effect of electrochemically deposited nitrogen radicals on carbon nanotube paper which were attributed to $N_8^-$ but suggest the $O_2H$ reaction is being catalyzed.[7]

Table I Calculated bond dissociation energy to remove an O atom from $O_2$ bonded to the nitrogen radicals and OH from $O_2H$ bonded to the radicals.

| REACTION | BOND DISSOCIATION ENERGY ,eV |
|---|---|
| $N_2O_2^- \rightarrow N_2O^- + O$ | 4.85 |
| $N_4O_2^- \rightarrow N_4O^- + O$ | 4.08 |
| $N_8O_2^- \rightarrow N_8O^- + O$ | 4.67 |
| $N_2O_2H^- \rightarrow N_2O^- + OH$ | 2.58 |
| $N_4O_2H^- \rightarrow N_4O^- + OH$ | 0.49 |
| $N_8O_2H^- \rightarrow N_8O^- + OH$ | 0.54 |

Table II Calculated adsorption energies for $O_2$ and $O_2H$ on nitrogen radicals.

| Radical | ADSORBED MOLECULE | $E_{ads}$ (eV) |
|---|---|---|
| $N_8^-$ | $O_2$ | -0.32 |
| $N_4^-$ | $O_2$ | -20.53 |
| $N_2^-$ | $O_2$ | -9.80 |
| $N_8^-$ | $O_2H$ | -1.33 |
| $N_4^-$ | $O_2H$ | -22.07 |
| $N_2^-$ | $O_2H$ | -3.04 |

Figures

1. ((a) Structure of $O_2$ bonded to $N_8^-$ and (b) O bonded to $N_8^-$ .
2. Minimum energy structure of (a) $N_4O_2^-$ and (b) $N_4O^-$ .
3. Minimum energy structure of (a) $N_2O_2^-$ and (b) $N_2O^-$ .
4. Calculated minimum energy structure of $O_2H$ bonded to $N_2^-$.
5. Minimum energy structure of $N_4O_2H^-$ .
6. Calculated minimum energy structure of $O_2H$ bonded to $N_8^-$ .

- coordinates of optimized structures will be provided on request.

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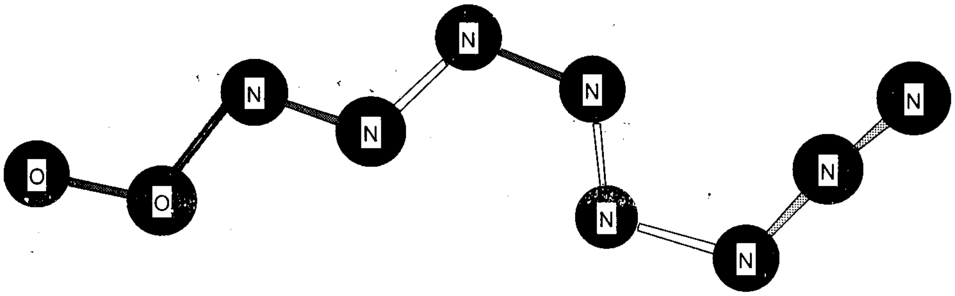


Figure 1a

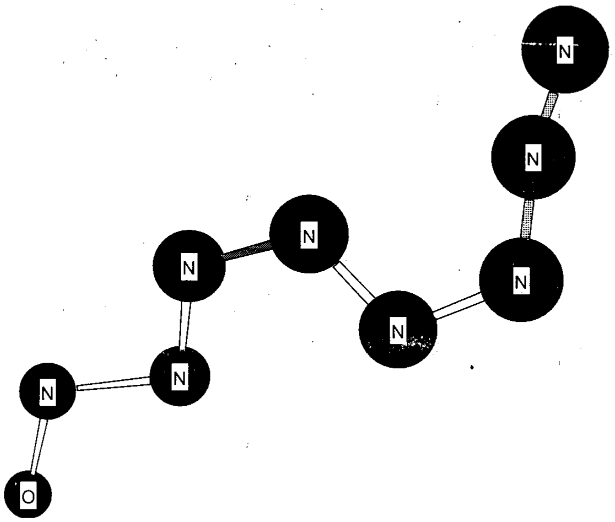


Figure 1b

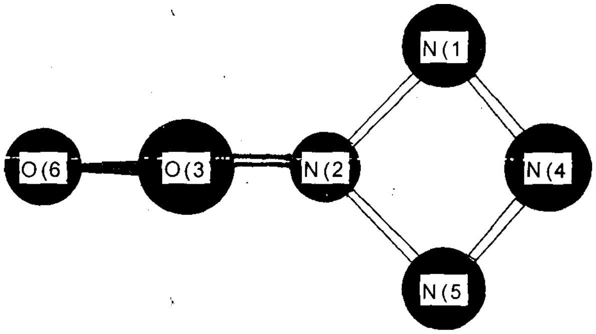


Figure 2a

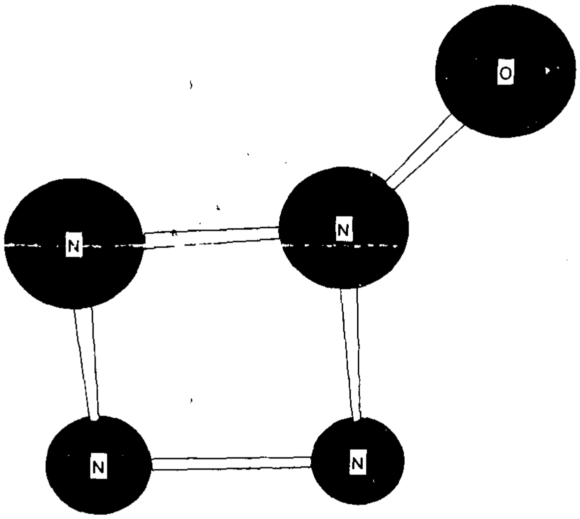


Figure 2b

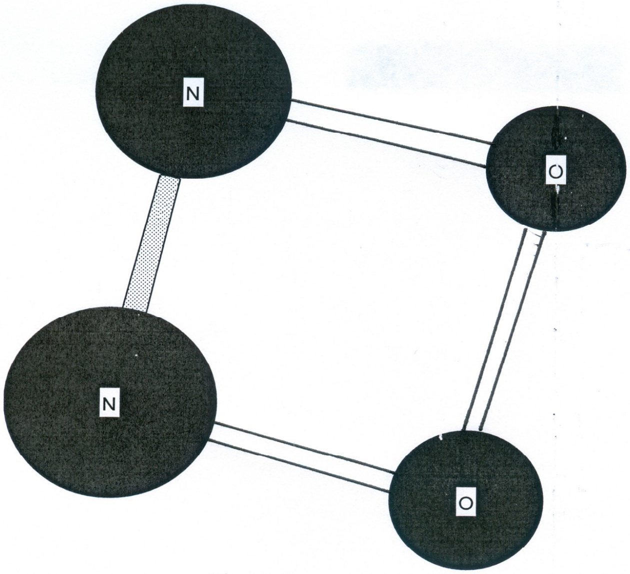
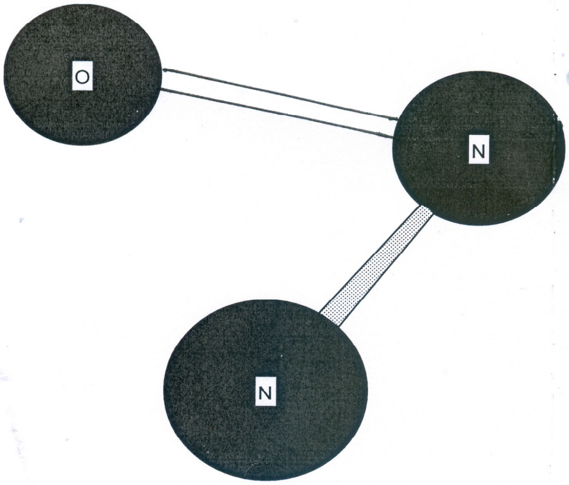


Figure 3a



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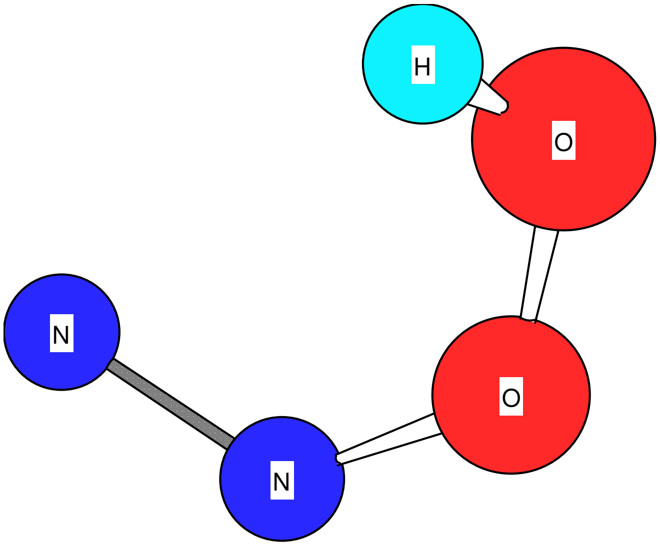

Figure 4

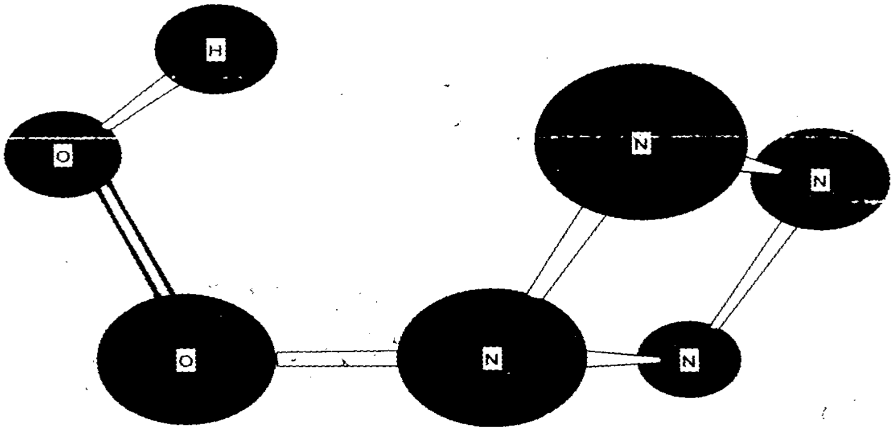

Figure 5

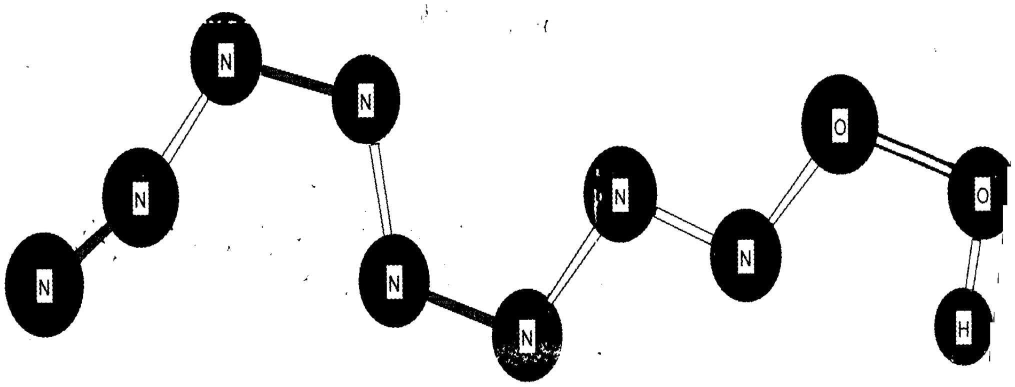

Figure 6