

1 MODELING ELECTROCATALYTIC ACTIVITY OF NITROGEN RADICALS

2

3 ABSTARCT

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

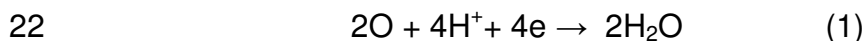
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13 Key words: catalysis, nitrogen radicals, oxygen reduction reaction, fuel cells.

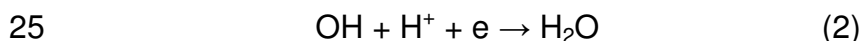
14 I INTRODUCTION

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16 Presently platinum is employed to catalyze the reactions that produce H_2O at the
17 cathode of fuel cells. Platinum is expensive and susceptible to time dependent drift and
18 CO poisoning.^{1,2} These issues are significant obstacles to the development of large
19 scale commercial application of fuel cells. Likely reactions that produce H_2O at the
20 cathodes are the O_2 dissociation followed by atomic oxygen undergoing the following
21 reaction,



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



26 The object of this paper is to use theoretical methods such as Density Functional
27 Theory (DFT) to determine whether nitrogen radicals can catalyze these reactions.
28 Modeling has been used to understand the role of platinum as a possible catalyst.^{3,4} It
29 also has been employed to predict possible new catalysts. For example molecular

30 orbital theory has been used to predict that nitrogen doped graphene, coronene and
31 pentacene could be an effective catalysts.^{5,6,7}

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

44 Generally the modeling has been used to identify a material X that bonds to O_2 or
45 O_2H to form $X-O_2$ or $X-O_2H$ such that the bond dissociation energy (BDE) to produce O
46 or OH is less than the BDE to dissociate free O_2 or O_2H . This approach has been used
47 to obtain understanding of the mechanism of platinum catalysis and the modeling of
48 nitrogen doped graphene and coronene as a cathode catalyst in fuel cells.^{5,6,7}

49 II METHODS

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

53
$$\text{BDE} = [E(\text{XO}) + E(\text{Z})] - [E(\text{XY})] \quad (3)$$

54 where Y is O₂ or O₂H and Z is O or OH. E is the total electronic energy plus the zero
55 point energy (ZPE) of the minimum energy structure. The ZPE is the total ZPE of all of
56 the normal modes of vibration given by,

57
$$E_{\text{zpe}} = (1/2)h \sum_i^{3N-6} f_i \quad (4)$$

58
59 where f_i are the vibrational frequencies of the normal modes and N the number of atoms
60 in the molecule. The calculated BDE given by equation 3 is compared with that to
61 dissociate free O₂ or O₂H. If it is significantly less, it can be argued that X is a good
62 catalyst for the reactions.
63

64 Another issue that needs to be considered in assessing these radicals as catalysts for
65 the reactions at the cathode is whether O₂ or O₂H can bond to them. This can be
66 evaluated by calculating the adsorption energy, E_{ads}, given by,¹⁴

67
$$E_{\text{ads}} = E(\text{XY}) - E(\text{X}) - E(\text{Y}) \quad (5)$$

68 where X is N₂⁻, N₄⁻ and N₈⁻ and Y is O₂ or O₂H. If the result is a negative value, it
69 indicates O₂ or O₂H can form a stable bond with the radicals.

70 III RESULTS

71 Figure 1a and 1b show the optimized minimum energy structure of N₈O⁻ and N₈O₂⁻.
72 The structures have no imaginary frequencies. The bond dissociation energy to remove
73 an O atom from N₈O₂⁻. Is calculated to be 4.67 eV slightly less than the calculated BDE
74 to dissociate free O₂ which is 5.03 eV. Figure 2a and 2b illustrate the calculated
75 minimum energy structure of N₄O₂⁻ and N₄O⁻ which have no imaginary frequencies.
76 The BDE calculated to remove an O atom from N₄O₂⁻
77 is 4.08. Figure 3a and 3b show the minimum energy structures of N₂O₂⁻ and

78 N_2O^- . The calculated BDE to remove an O atom from N_2O_2^- is 4.67 eV.

79 These results indicate that these nitrogen radicals would not be highly effective
80 catalysts for O_2 dissociation as the BDEs are only slightly less than that needed to
81 dissociate free O_2 .

82 Figure 4 shows the calculated minimum energy structure of $\text{N}_2\text{O}_2\text{H}^-$. The structure
83 has no imaginary frequencies. The calculated BDE to remove an OH from it is 2.58 eV.

84 Figure 5 shows the minimum energy structure of $\text{N}_4\text{O}_2\text{H}^-$. The BDE to remove OH from
85 it is calculated to be 0.49 eV. Figure 6 shows the minimum energy structure of $\text{N}_8\text{O}_2\text{H}^-$.

86 This structure had no imaginary frequencies. The BDE to remove an OH from it was
87 calculated to be 0.54 eV, which is much less than calculated BDE to remove OH from
88 free O_2H which is 5.79 eV. The calculated minimum energy structure of O_2H had no
89 imaginary frequencies indicating it can exist as a free entity. Table I tabulates all the
90 BDEs to remove an O atom from O_2 bonded to all the nitrogen radicals and to remove
91 an OH from O_2H bonded to the radicals.

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

98 CONCLUSION

99 Density functions calculations of the minimum energy structure of N_2O_2^- , N_2O^-
100 N_4O_2^- , N_4O^- , N_8O_2^- and N_8O^- indicate the structures have no imaginary frequencies and

101 are therefore at a minimum on the potential energy surface. The calculated bond
 102 dissociation energy to remove an O atom from, $N_2O_2^-$, $N_4O_2^-$, and $N_8O_2^-$ are only
 103 slightly less than that needed to dissociate free O_2 into two O atoms. This suggests that
 104 these molecules would not be highly effective catalysts for the molecular oxygen
 105 dissociation in fuel cells. However, the bond dissociation energy to remove OH from
 106 O_2H bonded to N_4^- and N_8^- is considerably smaller than that needed to dissociate free
 107 O_2H into O and OH. These nitrogen radicals are predicted to be effective catalysts for
 108 the O_2H dissociation. Calculation of the adsorption energy for O_2 and O_2H on all the
 109 radicals yield a negative value indicating they can bond with the radicals.
 110 The results support the explanation for the recently observed catalytic effect of
 111 electrochemically deposited nitrogen radicals on carbon nanotube paper which were
 112 attributed to N_8^- but suggest the O_2H reaction is being catalyzed.⁷
 113 Table I Calculated bond dissociation energy to remove an O atom from O_2 bonded to
 114 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

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117 Table II Calculated adsorption energies for O₂ and O₂H 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 ₂ H	-1.33
N ₄ ⁻	O ₂ H	-22.07
N ₂ ⁻	O ₂ H	-3.04

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119 Figures

- 120 1. ((a) Structure of O₂ bonded to N₈⁻ and (b) O bonded to N₈⁻ .
- 121 2. Minimum energy structure of (a) N₄O₂⁻ and (b) N₄O⁻ .
- 122 3. Minimum energy structure of (a) N₂O₂⁻ and (b) N₂O⁻ .
- 123 4. Calculated minimum energy structure of O₂H bonded to N₂⁻ .
- 124 5. Minimum energy structure of N₄O₂H⁻ .
- 125 6. Calculated minimum energy structure of O₂H bonded to N₈⁻ .
- 126 • coordinates of optimized structures will be provided on request.

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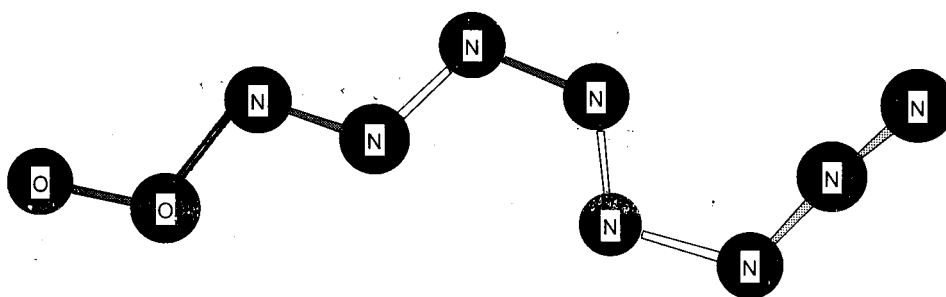


Figure 1a

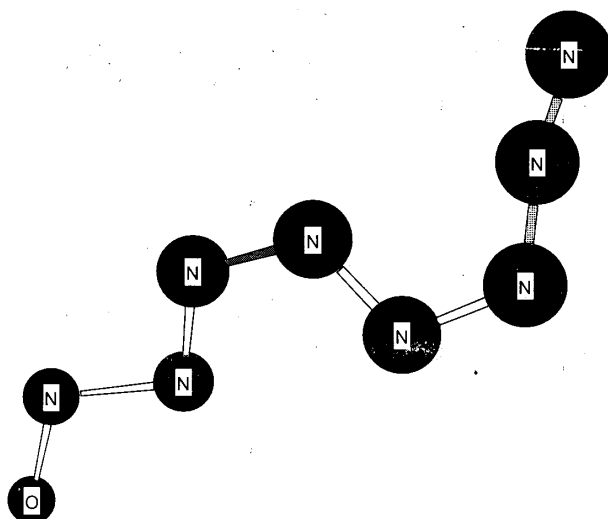


Figure 1b

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Figure 2a

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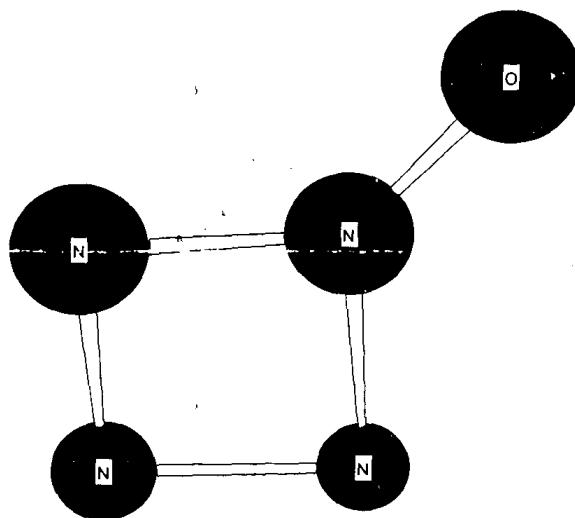
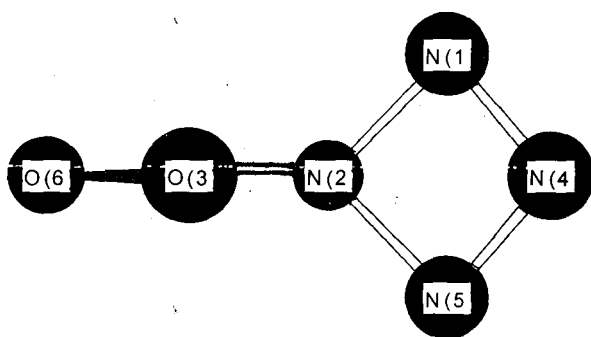
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Figure 2b

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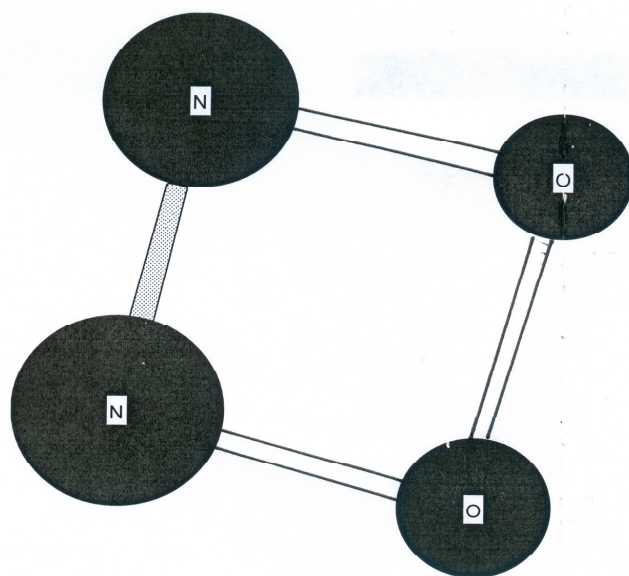


Figure 3a

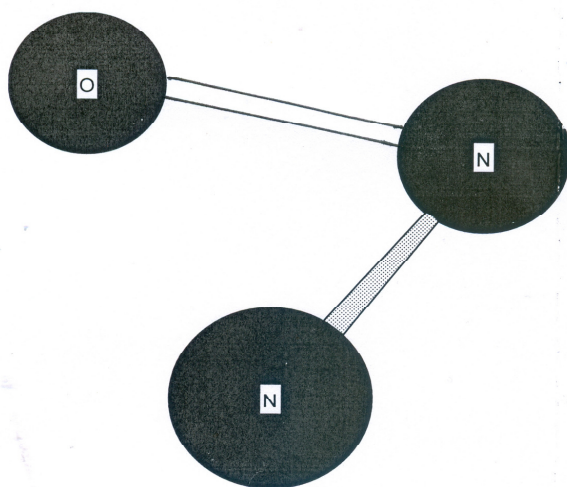
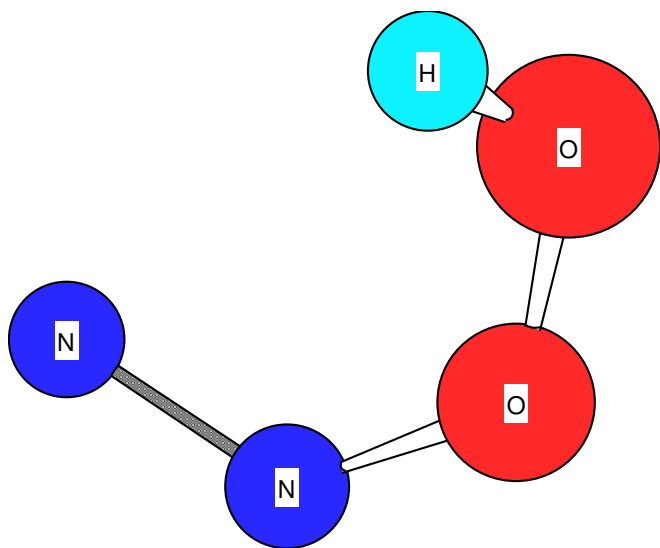


Figure 3b



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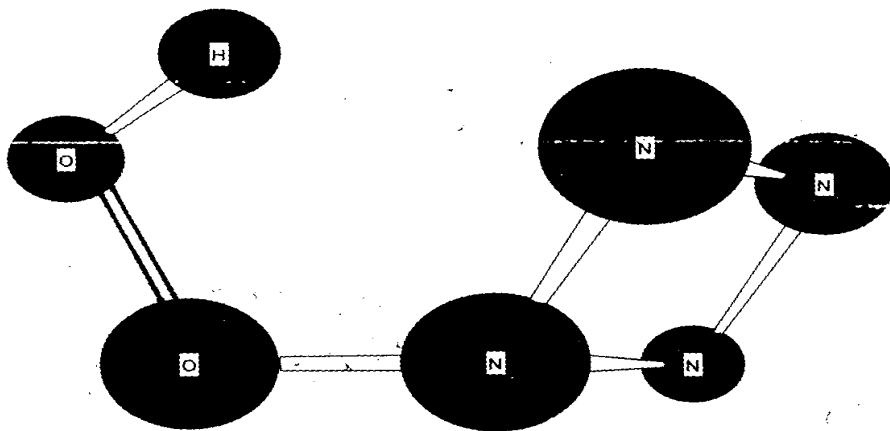
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Figure 4

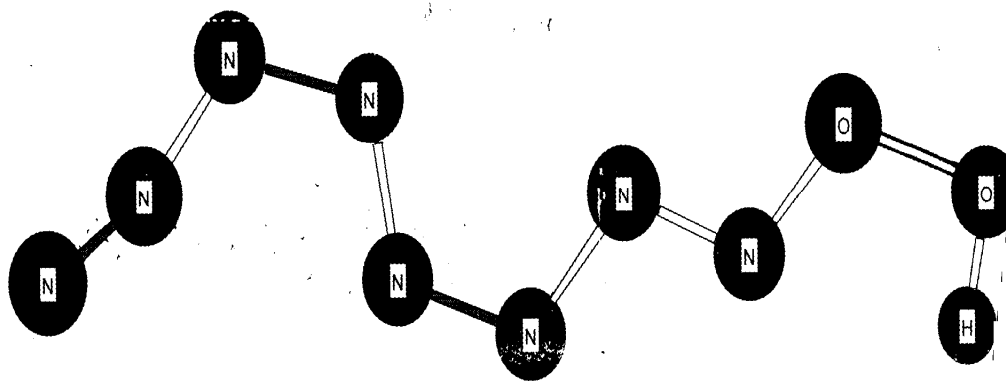


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Figure 5



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Figure 6