

Article

MODELING COPPER NANOPARTICLES AS CATALYSTS FOR THE OXYGEN REDUCTION REACTION IN FUEL CELLS

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ABSTRACT

The dissociation of O₂ and HO₂ are important reactions that occur at the cathode of fuel cells producing H₂O and use platinum as a catalyst. There is a need to replace platinum with less expensive catalysts. Here the possibility of copper nanostructures as catalysts for the reactions is considered using density functional theory. The calculations employing density functional theory at the B3LYP/6-31G* level show that the bond dissociation energies to remove OH from O₂H bonded to copper nanostructures Cu₆, Cu₈, and Cu₁₀ are significantly less than those necessary to dissociate free O₂H indicating that copper nanostructures could be catalysts for the dissociation of O₂H. However, the copper nanostructures are shown not to catalyze O₂ dissociation.

Keywords: copper nanostructures, Density Functional Theory, catalysis, oxygen reduction reaction.

1. INTRODUCTION

Presently platinum is employed to catalyze the reactions that produce H₂O 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 H₂O at the cathodes are the dissociation of O₂ bonded to the catalyst followed by atomic oxygen undergoing the following reaction,



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Another possibility is the formation of O₂H which bonds to the catalyst followed by the removal of OH which could then undergo the following reaction,



For the catalyst to be effective the energy needed to dissociate O and OH from O₂ and O₂H bonded to the catalyst should be significantly lower than that required to dissociate free O₂ and O₂H. The traditional approach to developing new catalysts is to identify a candidate based on the known properties of a material. The material is then synthesized and tested by such methods as cyclic voltammetry. Such an approach is time consuming and does not always lead to the best catalyst. Theoretical modeling of catalysts has the potential to provide a rapid, reliable and a less costly method to identify new catalysts. Further it can often identify the details of the reaction which is not always possible from the cyclic voltammetry measurement. Modeling has been used to understand the role of platinum as a catalyst in fuel cells [3]. It also has been employed to predict possible potential 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 [4, 5, 6].

2. METHODS

The minimum energy structures of Cu_NO₂, Cu_NO, and Cu_NO₂H, where Cu_N is a copper nanostructure, are calculated using DFT at the B3LYP/6-31G* level employing Gaussian software.⁷ The frequencies of the structures are calculated to insure the absence of imaginary frequencies which indicates the obtained structures are at a minimum on the potential energy surface. To determine if the copper nanoparticles can catalyze the production of O and OH from O₂ and O₂H bonded to Cu_N, nanoparticles the bond dissociation energy (BDE), to remove O and OH from these structures is calculated.

$$BDE = [E(Cu_N O) + E(OH)] - [E(Cu_N O_2 H)] \quad (3)$$

where 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,

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

where f_i are the vibrational frequencies of the normal modes and N the number of atoms in the molecule. An analogous expression is used for the dissociation of O₂. The calculated BDE given by equation 3 is compared with that to dissociate free O₂ or O₂H. If it is significantly less, it can be concluded that Cu_N is a good potential catalyst for the dissociation of O₂ and O₂H. Bond dissociation energies calculated by DFT have been shown to be in reasonably good agreement with experimentally measured activation energy values [8, 9].

Another issue that needs to be considered in assessing whether copper nano-structures catalyze the reactions at the cathode is whether O₂ or O₂H can bond to the structures. This can be evaluated by calculating the adsorption energy, E_{ade}, given by [10],

$$E_{ade} = E(Cu_N O_2 H) - E(Cu_N) + E(O_2 H) \quad (5)$$

where E is the total electronic energy of the system at the minimum energy structure. If the result is a negative value, it indicates O_2 or O_2H can form a stable bond with the copper nanostructures.

3. RESULTS

Figures 1, 2 and 3 show the calculated minimum energy structure of O_2H , O_2 and O bonded to a Cu_6 nanoparticle. The structures have no imaginary frequencies indicating they are at a minimum on the potential energy surface. The calculated BDE to remove O from O_2 bonded to Cu_6 is 5.5eV which is slightly greater than that needed to dissociate free O_2 . This indicates that Cu_6 would not be a catalyst to dissociate O_2 . It turns out this is also true of the larger Cu nanostructures Cu_8 and Cu_{10} considered.

Figure 1: Minimum energy structure of O_2H bonded to a Cu_6 copper particle.

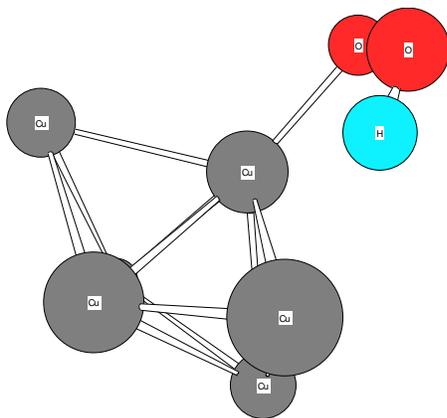


Figure 2: Minimum energy structure of O_2H bonded to a Cu_6 copper particle.

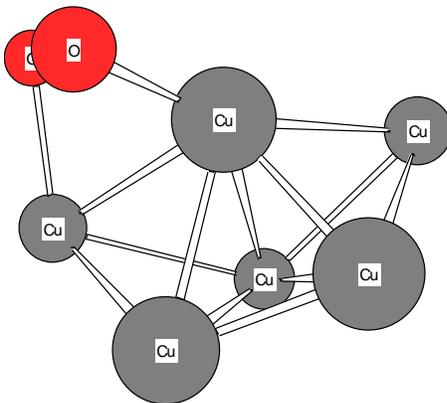
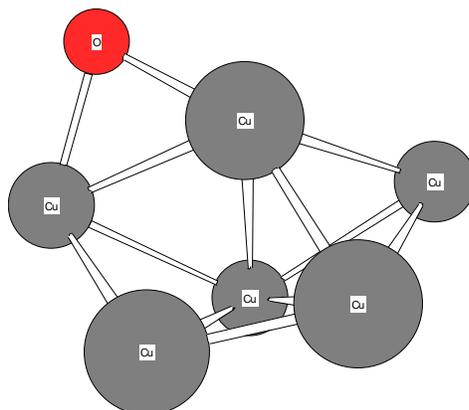


Figure 3: Minimum energy structure of an O atom bonded to Cu₆.

Thus the remainder of the paper will focus on O₂H dissociation. The calculated BDE to remove OH from O₂H bonded to Cu₆ is 0.21 eV, much smaller than that needed to dissociate free O₂H which is calculated to be 5.0 eV. This indicates that Cu₆ could be an effective catalyst for removing OH from O₂H. The calculated BDEs for removal of OH from O₂H bonded to all the structures considered are given in Table I. The calculated ades for O₂H to bond to all the Cu nanoparticles considered are given in Table II and are negative indicating that O₂H can bond to all the structures.

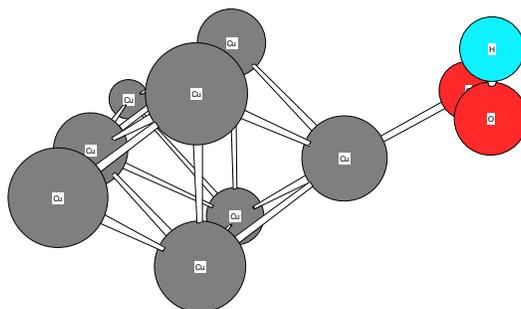
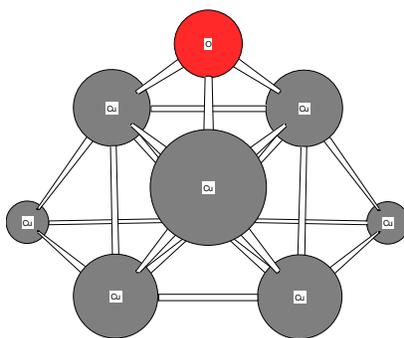
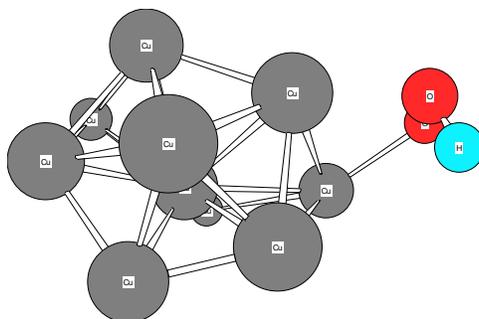
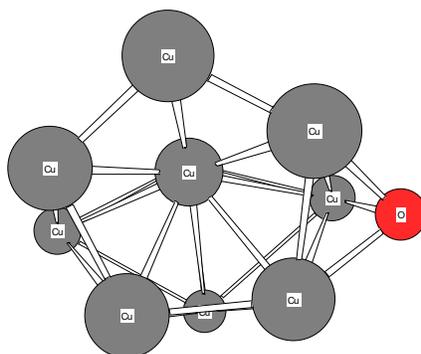
Table 1: Calculated bond dissociation energy to remove OH from O₂H bonded to Cu_N nanoparticles.

Particle type	Bond dissociation energy (eV)
Cu ₁₀	0.42
Cu ₈	0.61
Cu ₆	0.21

Table 2: Calculated adsorption energy for O₂H to bond to Cu_N nanoparticles.

Particle Type	Adsorption Energy (eV)
Cu ₁₀	-3.5
Cu ₈	-3.7
Cu ₆	-1.9

Figure 4 shows the minimum energy structure of O₂H bonded to Cu₈. Figure 5 is O bonded to Cu₈. The structures have no imaginary frequencies. The calculated ade given in Table II is negative indicating that O₂H can bond to Cu₈. The calculated BDE to remove OH from the structure is 0.61 eV suggesting that Cu₈ could also be a catalyst for O₂H dissociation. Figure 6 shows the calculated minimum energy structure of O₂H bonded to Cu₁₀. Figure 7 is the calculated structure of O bonded to Cu₁₀. The calculated ade given in table II is negative showing that O₂H can bond to Cu₁₀. The calculated BDE to remove OH from Cu₁₀ is 0.42eV suggesting that this structure can also be a good catalyst for O₂H dissociation.

Figure 4: Minimum energy structure of O_2H bonded to a Cu_8 nanoparticle**Figure 5:** Minimum energy structure of an oxygen atom bonded to Cu_8 **Figure 6:** Minimum energy structure of O_2H bonded to Cu_{10} **Figure 7:** Minimum energy structure of an O atom bonded to Cu_{10} 

Stability of Cu_NO_2H structures

It is also necessary that the O_2H bonded to the copper nanostructures be thermally stable over the usable temperature range of a fuel cell which for a polymer electrolyte membrane (PEM) fuel cell is 50 °C to 100 °C. The calculated BDEs to remove O_2H from the copper nanostructures, given in Table III, are all large enough to suggest the structures are thermally stable over the usable temperature range of PEM fuel cell.

Table 3: Calculated bond dissociation energy to remove O_2H from copper particles

Particle type	Bond dissociation energy (eV)
Cu_{10}	3.1
Cu_8	3.2
Cu_6	2.0

*The bond lengths of the structures shown below will be provided on request.

4. CONCLUSION

The model used here based on bond dissociation energies calculated by DFT at the B3LYP/6-31G* level has been shown to predict catalytic activity in small copper nanoparticles. The minimum energy structure of O, O_2 and O_2H bonded to Cu_6 , Cu_8 , and Cu_{10} have been calculated by density functional theory. The bond dissociation energy to remove OH from O_2H bonded to the structures was quite low, less than 0.61 eV suggesting that these structures could be catalysts for this ORR reaction. However, the structures were not indicated to be catalysts for O_2 dissociation. The calculations indicate that O_2H bonded to the structures should be stable over the operating temperature range of a PEM fuel cell. Interestingly there have been some experimental observations that copper nanostructures can be catalysts for the ORR reaction lending support to the theoretical approach employed [11].

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