Introduction

Catalyst support materials such as Vulcan XC-72R, Black Pearl 2000, Ketjenblack, and others are used in low-temperature fuel cells because of their high surface area, good chemical and mechanical stability, and good electrical conductivity, but not because of catalytic properties. The supports are known to be only weakly active toward the electroreduction of oxygen. However, Wang et al. reported making nitrogenated carbon particles that were active toward oxygen reduction. They oxidized Vulcan XC-72R (surface area ~250 m²/g) with 30% HNO₃ under refluxing condition, reacted the product with NH₃ at 600 °C, and then heat-treated it in Ar at 900 °C. The nitrogenated product exhibited greater catalytic activity toward oxygen reduction in sulfuric acid than the untreated carbon, and there was a 210 mV anodic shift in the oxygen reduction peak.

Carbon—nitrogen materials prepared in other ways can be inactive toward oxygen reduction. Lalande et al. reported that CN₄ particles prepared by pyrolysis of nitrogen-containing organic compounds in Ar at 1000 °C or by pyrolysis of a hydrocarbon, followed by heat treatment in NH₃ at 1000 °C, did not show any activity toward oxygen reduction.

Carbon has a long history as a support in the heterogeneous catalysis literature, and only recently have the effects of adding N been studied. For example, compared to their nondoped counterparts, some N-doped carbon particles show more oxidation resistance. Some show catalytic activities toward NO₃ reduction. Others are oxidation catalysts. In the case of NO₂ oxidation and O₂ reduction, the O₂⁻ superoxide radical was proposed to explain the enhanced activity. These properties have been attributed to electronic or structural changes caused by the nitrogen incorporation into the graphite layers. However, the compositions and structures of the active sites are not yet known.

Carbon nitrides (CNₓ) in thin film forms have been studied over the past decade. They possess high hardness, low coefficients of friction, chemical inactivity, and low work functions. Recently, Hellgren et al. studied the electronic structures of carbon nitride thin films by using a combination of experimental electronic structure probes and density functional theory. From comparisons of experimental spectra with calculated electronic properties for different model systems, they identified three bonding structures for the nitrogen: nitrile bonds (C≡N), pyridine-like nitrogen where N bonded to two C atoms, and graphite-like N, i.e., N bonded to three C atoms, N substituting into the graphitic network. In the present paper, the last of these is referred to as “nitrided graphite” or “graphite nitride”. They also reported that thin films made by dc magnetron sputtering at low temperatures, <150 °C, were amorphous. For temperatures above 200 °C, when the N concentration was greater than 5%, the structures were fullerene-like, but for N concentrations below 5%, graphite nitride formed. The graphitic CNₓ thin films exhibited better thermal stability than the films grown at low temperature.

The mechanisms for oxygen reduction, both in the presence and in the absence of substitutional N in the graphite, and the cause of the anodic shift are not known. The catalytic effect of nitriding is a worthwhile issue to explain. To understand the mechanisms and catalytic effect, we have undertaken a quantum chemical study of nitrided graphite using a small and a large cluster model, both terminated on the edge by bonding to hydrogen atoms.

This paper reports new oxygen reduction results for nitrided Ketjen Black EC 300 J. The surface area of pristine ketjen black is 886 m²/g. A comparison of the experimental and theoretical results will be made. The comparison will indicate that two-electron oxygen reduction to hydrogen peroxide takes place on the edges of the graphite sheets or on nitrided graphite basal...
planes, where it is activated by radical carbon sites adjacent to substitutional N atoms in the graphite sheet. The idea that a carbon radical is involved was motivated by a previous study of hydrogen evolution over radical sites on boron-doped diamond electrodes. A subsurface substitutional boron atom gave a second-layer carbon atom radical character, allowing it to chemisorb an H atom weakly. This atom then participated in electrochemical H₂ evolution. The same is found for the OOH intermediate formed in the first step in oxygen reduction: it is stabilized by bonding to a radical carbon site that is created by the substitutional N, and its reduction forms H₂O₂. It is found that, at potentials below the OOH(ads) formation potential, the carbon radical has H bonded to it, but the H is predicted to be oxidized off at higher potentials.

Experimental Approach

Synthesis of Nitrogen-Doped Carbon. Commercially available carbon black, namely Ketjen Black EC 300 J, was treated in HCl and HNO₃ to remove the metallic impurities. The as-received Ketjen Black EC 300 J was pre-washed twice with 6 M HCl for 24 h. Next, the chloride impurities present in the sample were washed out with distilled water. The pre-washed carbon was subjected to oxidation in 70% HNO₃ for 7 h under reflux conditions. It was then washed in distilled water and dried in an oven at 75 °C. For brevity, as-received Ketjen Black EC-300J is denoted as K, HCl-treated carbons as K₁, and HNO₃-treated carbons as K₂. The HNO₃-treated carbon was subjected to heat treatment in NH₃ at 900 °C to obtain nitrogenated carbon (K₃).

Electrochemical Characterization. Electrochemical characterizations were performed in a single-compartment three-electrode cell. The electrocatalytic activity of the modified carbon was studied using the rotating ring disk electrode (RRDE) technique. Briefly, a rotating ring disk electrode from Pine Instruments employing a glassy carbon disk (5 mm o.d.) and Pt ring (5.52 mm i.d., 7.16 o.d.) was used as the working electrode. Platinum wire was used as the counter electrode, and a standard Hg/HgSO₄ electrode was used as the reference electrode. The potentials presented in this study are referred with respect to standard hydrogen electrode (SHE). A catalytic film was produced at the disk electrode according to the following procedure: 8 mg of the modified carbon was suspended in isopropyl alcohol and ultrasonically blended for 10 min. 15 μL of this suspension was applied as an ink on the disk electrode in steps of 5 μL. A 5 μL Nafion solution [1(5 wt % Nafion)/10(water)/10(isopropyl alcohol)] was added on top of the film. 0.5 M H₂SO₄ was the electrolyte in all of the studies, and prior to measurements, the solution was purged with nitrogen. Cyclic voltammograms (CVs) were recorded by scanning the disk potential from 1.04 to 0.04 V vs SHE at a scan rate of 5 mV s⁻¹. For all electrochemical measurements, the ring potential was maintained at 1.2 V vs SHE in order to oxidize any hydrogen peroxide produced. First, CVs were recorded at 5 mV s⁻¹ using nitrogen atmosphere to obtain the background capacitive currents. Next, the CVs were recorded using the oxygen-saturated electrolyte. The electrolyte solution was purged with oxygen for 15 min before commencing oxygen reduction on the disk electrode. Linear sweep voltammograms for disk potentials were recorded from 1.04 to 0.04 V vs SHE at a scan rate of 5 mV s⁻¹ for different rotation rates of the RRDE. The linear sweep voltammograms shown in this paper were obtained at 900 rpm unless specified otherwise. The net faradic current was obtained by subtracting the background capacitive current from the N₂ CV. All measurements were obtained with a bipotentiostat (model AFRDE from Pine Instruments).

Experimental Results and Discussion

The as-received carbon (K), HCl-treated carbon (K₁), HNO₃-treated carbon (K₂), and nitrogenated carbon (K₃) were tested for activity toward oxygen reduction. Figure 1a shows typical polarization curves for oxygen reduction by these carbons on a rotating disk electrode in 0.5 M H₂SO₄. The highest activity is for the HNO₃-treated carbon that was subjected to heat treatment in NH₃. A performance trend of K₃ > K₂ > K₁ is clearly seen in Figure 1a. The as-received carbon support shows greater activity than the HCl-treated carbon, and this is attributed to the presence of metallic impurities. The HCl treatment evidently removes the metallic impurities, and K₁ represents the activity of bare carbon. Oxidized carbon K₂ shows about 100 mV less activation overpotential for oxygen reduction reaction compared to K₁. Electrochemical analysis indicated that oxidation of carbon in nitric acid introduces oxygen, probably as quinone groups, on the carbon surface. The 0.55 V vs SHE peak in the linear sweep voltammograms of K₂ is characteristic of the quinone-hydroquinone redox couple. The onset potential for oxygen reduction reaction is 0.3 V vs SHE. Further introduction of nitrogen, by heat treatment at 900 °C in a NH₃ atmosphere, increases the activity of the catalyst by nearly 200 mV in the anodic direction. The onset potential is as high as 0.510 V vs SHE.
Oxygen electroreduction in acid can be either a four-electron discharge to form water or a two-electron reduction to form peroxide. Figure 1b gives the ring currents of the carbons K, K1, K2, and K3. The ring currents were measured to estimate the amount of generated hydrogen peroxide. It can be observed that the ring currents initiate at the same potentials as the onset potentials for oxygen reduction in the disk, indicating that the generation of hydrogen peroxide is taking place. For nitrided carbon, the ring current initiates at the onset potential of 0.51 V vs SHE. Also, the bell-shaped curve of the ring current is characteristic of hydrogen peroxide produced on non-noble metal catalysts and activated carbon. The number of electrons transferred \( n \) and the percentage of hydrogen peroxide produced \( \% \text{ H}_2\text{O}_2 \) can be determined by the following equations:

\[
\begin{align*}
    n &= \frac{4I_D}{(I_D + I_R/N)} \quad (1) \\
    \% \text{ H}_2\text{O}_2 &= 100(4 - n)/2 \quad (2)
\end{align*}
\]

where \( N, I_D, \) and \( I_R \) are the collection efficiency, disk current, and ring current, respectively. We assumed the collection efficiency to be a constant at an estimated value of 0.25 for all the catalysts studied. Figure 2 shows the number of electrons and \% \text{ H}_2\text{O}_2 generated for the nitrogenated carbon K3. The obtained values clearly indicate that oxygen reduction on the nitrogenated carbon surface becomes predominantly two-electron at higher overpotentials, leading to the production of hydrogen peroxide. At still higher overpotentials, the decrease in percentage hydrogen peroxide produced is attributed to the reduction of oxygen to water through a four-electron process or through two two-electron processes. The high O=O bond strength of 494 kJ/mol has been discussed in this context. The series pathway, through peroxide production and its subsequent reduction to water, and the direct four-electron pathway can occur in parallel on some surfaces, though at high overpotentials to the four-electron process. The formation of peroxide does not require the breaking of the O=O bond, but does weaken it to an O–O single bond. Further reduction to water requires that this bond be broken. Thus, on less reactive surfaces, such as the synthesized graphite and nitrided carbon, hydrogen peroxide is the reduction product.

### Theoretical Method

#### A. Cluster Calculations

In this study, a cluster approach was used with the B3LYP hybrid density functional theory in Gaussian 03. The basis sets used for O, N, and H were 6-31G*. Graphite models used in this work contained four and fourteen hexagonal rings with delocalized \( \pi \) electrons and terminated with C–H bonds. For modeling the nitrided basal plane sheet of graphite, a nitrogen atom was placed substitutionally as shown in Figure 3. Adsorption of reaction intermediates on sites a–d and others of the graphite and nitrided graphite models was examined. The bond strength values were calculated using the formula

\[
BS = E(\text{cluster}) + E(\text{adsorbate}) - E(\text{adsorbate on cluster})
\]

#### B. Calculating Reversible Potentials for Forming Adsorbed Reaction Intermediates

The reversible potentials were calculated by a Gibbs linear free energy relationship. The essence of this free energy relationship is that, if one has the reversible potential for a redox reaction in solution bulk, then the electrode surface value can be approximated as a perturbation to this because of bonding to the surface. It is assumed that when the intermediates are bonded to the surface the solvation interactions of the reactants and the products of the electron transfer are equally reduced. Thus, the adsorption bond strengths may be used to make predictions of reversible potentials. As
an example, consider OH reduction in solution and on the Pt surface. The reversible potential for forming the intermediate on the electrode surface is

$$U_{\text{surface}}^o = U^o + (\text{product adsorption bond strength} - \text{reactant adsorption bond strength})/F$$

(4)

where $F$ is the Faraday constant.

The bulk and surface reactions can be related in a reaction cycle

$$\text{OH}_\text{aq} + H^+ + e^- \leftrightarrow H_2O$$  \hspace{1cm}  $U^o = 2.81 \text{ V (SHE)}$  \hspace{1cm} (5)

$$\text{Pr-OH} + H^+(aq) + e^- \leftrightarrow \text{PrOH}_2$$

The reversible potential for the onset of the surface process is then given by

$$U_{\text{surface}}^o = 2.81 - 2.50 + 0.42 = 0.73$$  \hspace{1cm} (6)

where 2.81 V is the experimental reversible potential for the water oxidation and OH reduction in acid solution, and 2.50 and 0.42 eV are the respective measured adsorption bond strengths for OH$^{26}$ and H$_2$O$^{27}$ at low coverage. The predicted water oxidation onset potential of 0.73 V on Pt is within 0.2 V of the observed value of 0.55 V in acid in the absence of anion adsorption.$^{28}$

**Theoretical Results and Discussion**

A. Adsorption Energies for H, O$_2$, OOH, and H$_2$O$_2$ on the Radical Sheet Cluster C$_{41}$NH$_{16}$ and on C$_{42}$H$_{16}$. Figure 3 shows the fully optimized geometry for the 14-ring C$_{41}$NH$_{16}$ sheet radical in the absence of an adsorbate and in the doublet state. It has a C$_2$ symmetry along the C$_{14}$−N axis and is flat with no more than $\pm 0.001$ Å variations from planarity. Because of the symmetric distribution of spin and charge densities along the C$_{14}$−N axis, the display may be simplified: The top half of Figure 4 shows only spin densities, while both spin and charges are shown along the C$_{14}$−N axis, and at the bottom half, only the charge densities are shown. The N atom is quite negative, with a charge of $-0.916$. This is a consequence of N being a radical and more electronegative than carbon. Most of the compensating positive charge is distributed on the three neighboring carbon atoms. The spin density due to the unpaired electron is seen in Figure 4 to delocalize onto adjacent C atoms mostly on the left side of the N atom, with the highest spin densities found on the edge C atom c (defined in Figure 3) and its symmetric counterpart.

As expected, the optimized geometry of the pure graphene sheet, C$_{42}$H$_{16}$, is perfectly planar. A spin-unrestricted calculation revealed no spin polarization.

The adsorption bond strengths for H and OOH on C$_{41}$NH$_{16}$ used in this study are shown for several adsorption sites in Figure 5 and Figure 6, respectively. In Figure 7, it is shown that the adsorption bond strengths of adsorbate radicals, H and OOH, exhibit a correlation with the spin density only when the net spin is $>0.1$. The highest bond strengths within the cluster for H and OOH are 2.238 and 0.891 eV, respectively, on the carbon atom that is directly bonded to N. Structures are shown in Figure 8a,b. When a radical adsorbs on the radical sheet, the changes in the hybridization of the adsorption site atoms distort the planar geometry, raising the adsorption site carbon out of the plane.
toward a tetrahedral structure. If the adsorbate is bonded to an edge carbon atom, it is able to relax to a nearly tetrahedral structure. The adsorption bond strengths of the neutral molecules at the edge of the nitrided cluster is caused in part by the adjacent to the substitutional N in C_{41}NH_{16}. Upon adsorption of OOH to edge site c, which is also stronger than its bonding to site a. The strong bonding at the edge of the nitrided cluster is caused in part by the flexibility of edge sites to adopt the tetrahedral structure and, as will be shown below, the spin density on the site c carbon in the nitrided cluster, which is absent in the case of the undoped cluster. The two H atoms in the methylene group are symmetrically distributed above and below the sheet plane, while the neighboring C and H atoms are nearly unmoved. A similar structure was adopted in the case of OOH adsorption on the edge site c.

To understand better the effect of the substitutional N on the adsorption bond strength of H and OOH radicals, we calculated adsorption bond strengths for sites a–d on the undoped graphite sheet, C_{42}H_{16}. The results are shown in Figure 9. For both radicals, the undoped graphite sheet has stronger adsorption bonds at the edge than at the center, just like the nitrogenated counterpart. However, the bonding is weaker on the undoped graphite sheet. These bond strengths will next be used to explain the catalytic abilities of the doped and undoped graphite.

Figure 7. Bond strengths as functions of spin density for H and OOH bonded to various sites on C_{41}NH_{16}.

Figure 8. Optimized structures for OOH (a) and H (b) when bonded to sites labeled b, c, and d on the C_{41}NH_{16} cluster. The two H atoms in the methylene group are symmetrically distributed above and below the sheet plane, while the neighboring C and H atoms are nearly unmoved. A similar structure was adopted in the case of OOH adsorption on the edge site c. The strong bonding at the edge of the nitrided cluster is caused in part by the flexibility of edge sites to adopt the tetrahedral structure and, as will be shown below, the spin density on the site c carbon in the nitrided cluster, which is absent in the case of the undoped cluster. The two H atoms in the methylene group are symmetrically distributed above and below the sheet plane, while the neighboring C and H atoms are nearly unmoved. A similar structure was adopted in the case of OOH adsorption on the edge site c.

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because according to the calculated reversible potentials, H(ads) will be unstable to oxidative removal in the potential range of interest.

Graphite Nitride. As can be seen from Figure 5, the highest bond strength site for H adsorption on the nitrided cluster lies at the edge site c, where the bond strength is 2.780 eV. The reversible potential for the oxidation of this H is 0.67 V, based on the reversible potential for the reduction of H\(^{+}\)(aq), \(-2.11 \text{ V}\).\(^{32}\) This potential is too high to account for the observed current onset potential in Figure 1a, where O\(_2\) reduction occurs below 0.67 V. This means that in the 14-ring model the N is too close to the edge, and hence, we conclude that N near a graphite edge will not generate activity. However, when there is no edge site nearby, a C atom adjacent to N is a candidate for being an active site. Of the nonedge sites, it has the highest bond strength for H, and the reversible potential for its oxidation is 0.128 V, which is a good potential for maintaining an active radical site for O\(_2\) reduction.

For the centrally located substitutional N, the spin density is highest on the site a carbon neighboring the N, but other atoms have nonzero spin densities, so adsorption bond strength for reaction intermediates O\(_2\), OOH, and H\(_2\)O\(_2\) were calculated on some of the other sites too. The interactions of O\(_2\) and H\(_2\)O\(_2\) with all sites are very weak, with the highest adsorption bond strengths on the nonedge sites being 0.056 and 0.076 eV, respectively. For the edge sites, the respective results are 0.036 and 0.179 eV. The structure perturbations to the cluster caused by the weak bonds are small, as shown in Figure 10. Bond strengths for OOH on the nitride cluster, as may be seen in Figure 6, range from 0.02 to 1.197 eV, depending on the adsorption site. The most stable edge site is c, just as for H adsorption. By using the highest adsorption bond strength values for OOH, the reversible potentials in Table 2 were obtained for the formation of H\(_2\)O\(_2\) from O\(_2\) reduction in acidic solution. The calculated reversible potential for the overall reaction is the same as the reported standard experimental values of 0.695 V, because as mentioned earlier, (i) the reversible potential for the overall reaction does not depend on the adsorption bond strength of the OOH reaction intermediate, and (ii) the adsorption energies of the O\(_2\) reactant and H\(_2\)O\(_2\) product are taken as zero. As shown in Table 2, for the edge site c, the second electron-transfer step has a reversible potential of 0.239 V, which is too low to account for the experimental current onset potential for H\(_2\)O\(_2\) formation in Figure 1a. However, using the highest bond strength, 0.891 eV, which is for OOH on the site adjacent to N, respective reversible potentials 0.845 and 0.545 V are predicted for the first and second electron-transfer steps. The second matches the observed current onset potentials for H\(_2\)O\(_2\) generation on nitrogenated Ketjenblack quite well, as shown by the curve labeled K3 in Figure 1a.

The spatial extent of the influence of the substitutional N atom is of interest. Calculations of H and OOH bond strengths to a smaller four-ring cluster were made. As is evident from Table 3, bond strengths to C adjacent to N in a 4-ring C\(_{14}\)NH\(_{10}\) cluster increased very little, but the bond strengths at the edge sites increased somewhat more. The bond energies to the edge of the undoped 14-ring cluster approximates the limit for large cluster. These values are in the column labeled “no N”. The bond energies indicate that the biggest perturbation effect of N is local, but when the N is near an edge, it magnifies the reactivity of edge sites toward bonding radical molecules to the extent that they will be passivated against oxygen reduction activity at the potentials shown in Figure 1a, curve K3.

Conclusions

Nitried carbon obtained from oxidized carbon that is heat-treated in NH\(_3\) at 900 °C shows a high 0.510 V vs SHE onset potential toward oxygen reduction. Oxygen reduction is predominantly by the two-electron process to hydrogen peroxide, as observed from RRDE studies. Quantum calculations show that carbon radical sites formed adjacent to substitutional N in graphite are active for O\(_2\) electroreduction to H\(_2\)O\(_2\) in acid electrolyte, and this may explain the catalytic effect observed for nitried carbon. Furthermore, the weak catalytic effect of untreated carbon can be attributed to the weaker bonding of the OOH(ads) reaction intermediate to H atom-terminated graphite edge sites. Substitutional N atoms that are far from the graphite sheet edges will be active, and those that are close to the edges will be less active.

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References and Notes

(11) For a recent review, see Muhl, S.; Medez, J. M. Diamond Relat. Mater. 1999, 8, 1809.