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Carbon Alloy Catalysts: Active Sites for Oxygen Reduction Reaction

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Nitrogen-doped carbon-based catalysts are attracting increased interest as potential Pt-free electrode catalysts for polymer electrolyte fuel cells. In this computational study, we inspect possible oxygen adsorption and reduction processes on various models for the exposed edges of these catalysts. The dynamics of an O₂ molecule solvated in water, which mimicks the cathode environment, shows that O₂ adsorption depends on the morphology and the atomic structure of the system. We show that carbon alloys with N dopants at specific sites can exhibit metal-free catalytic activity.

Introduction

The polymer electrolyte fuel cell (PEFC) is one of the most promising power sources. It is characterized by a rather high efficiency, a low operating temperature, and a low environmental impact. However, its practical use continues to be hindered by the prohibitive cost of Pt-based catalysts that are needed for electrode reactions at operating temperatures of $T < 80$ °C. Alternative Pt-free electrode catalysts are being pioneered by the use of more abundant elements in an attempt to reduce the cost of PEFCs. The rate of oxygen reduction reaction (ORR) at the cathode is significantly lower than that of the counterpart reaction at the anode; for this reason, research efforts mainly target the cathode. Recently, several groups^{1–7} reported surprisingly high ORR activities in carbon-based nanomaterials that were doped with N (and B). These materials include a certain number of heteroatoms and are termed carbon alloys.⁸ The general idea is that a systematic study of C-based alloys could lead to the discovery of high-performance alloys. Some of us undertook investigations in this direction by using carbonization processes of carbon polymers and nitrogen precursors such as phthalocyanine.^{1–3} The materials that were synthesized with these procedures display some remarkable features. First, they are constituted by a substantial number of nanoshells that are mainly composed of sp² carbon. Furthermore, we significantly enhanced the ORR activity by increasing the concentration of N (or by codoping B and N). Moreover, the presence of defects,

which are detected by transmission electron microscopy (but are still unidentified on the atomic scale), is likely to at least partially contribute to the high ORR activities. These findings indicate that carbon alloy catalysts (CACs) are likely to possess catalytic activity that is at least comparable to that of conventional Pt-based catalysts. Yet, a rational design and tuning of their catalytic performance require detailed atomistic insight into the N-dopant arrangement in the carbon network. This information cannot be easily extracted from experiments because CACs have a complex structure and reaction intermediates are generally too short-lived to be detected. Soft X-ray absorption spectroscopy (XAS) measurements, which are aimed at investigating the electronic states that originate from the N doping in CACs, showed three peaks in the π^* region of N 1s XAS.⁹ This suggests that N occupies at least three chemically different sites, which is consistent with the X-ray photoelectron spectroscopy data. The variation of the relative intensity of these three peaks was found to be correlated with the relative ORR activities of the samples that differ in the N-doping method. Namely, high-activity samples contain more graphite-like N than pyridine-like N, which suggests a close relationship between 3-fold N and ORR activity.

Obviously, our present knowledge of CACs is still insufficient to identify both the atomic sites of the doped N and the actual catalytic centers in which ORR occurs. The present computational study is intended to complement the experiments by providing the missing information. Possible adsorption states and subsequent reduction steps of O₂ on CACs have been explored via first-principles molecular dynamics, which shows that specific N sites enhance the catalytic activity without requiring metal catalysts.

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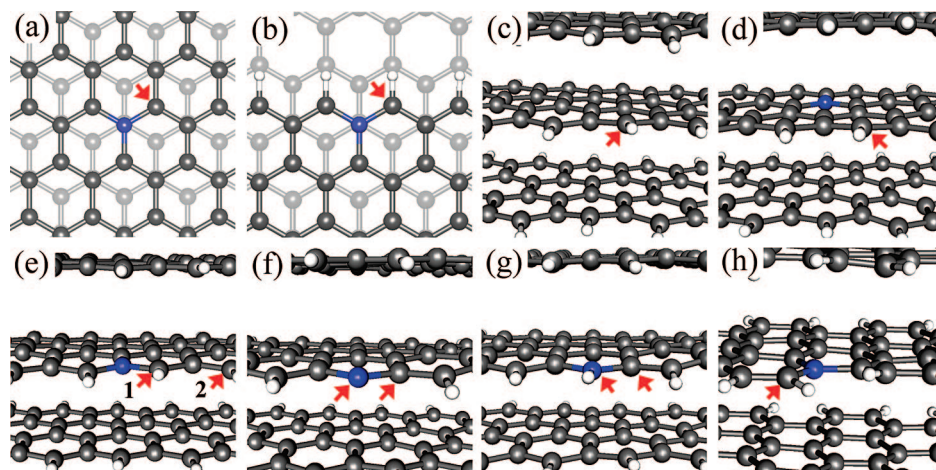


Figure 1. Model structures of carbon alloy catalysts for O_2 adsorption. Graphite-like N atoms are contained in models a, b, d, e, and h, and pyridine-like and pyridinium-like N are included in models f and g, respectively. Model h is for the armchair-edge case, whereas model c is for the undoped zigzag-edge case. H is white, C is gray, N is blue, and O is red. We estimated the free-energy profile for O_2 adsorption by making an O_2 molecule approach the atoms that are marked by arrows in each panel.

Computational Method

We used the Car–Parrinello MD approach^{10,11} within a plane-wave pseudopotential scheme including HCTH gradient corrections¹² on the exchange and correlation functionals in an unrestricted spin scheme. The valence–core interaction was described by Troullier–Martins¹³ pseudopotentials (PP) for C, N, and O and by von Barth–Car¹⁴ PP for H. The sampling of the Brillouin zone was restricted to the Γ point. A systematic set of simulations was performed for various models that were composed of graphene sheets that were doped with N at different positions, one O_2 molecule, and a certain number of H_2O molecules in a simulation box with periodic boundary conditions. This amounts to slab systems of about 200 atoms that consist of 2 (for basal plane) or 4 (for edge plane) graphene sheets with the bottom C fixed to bulk graphite and saturated with H, with borders from the catalytic center restrained to oscillate around the crystal positions by a harmonic potential, and with water (10 Å) plus 1 O_2 molecule initially in a spin triplet state, mimicking the environment around a hypothetical CAC cathode in PEFCs. Free-energy barriers for the adsorption and subsequent reduction of O_2 were estimated by the Blue Moon method,^{15–18} and the temperature was kept at 300 K by velocity rescaling.

Results and Discussion

To examine possible O_2 adsorption sites in CACs, we prepared eight different model structures (Figure 1) in which N replaces sp^2 C atoms (except in Figure 1c). This reproduces three possible configurations on the exposed surface: basal plane, zigzag edge, and armchair edge. These were interfaced with a 10 Å dilute water layer that included a single O_2 molecule that was initially in its ground state (triplet) far from the surface. We computed free-energy barriers for the adsorption of an O_2 molecule for both N and C sites by making this O_2 molecule approach the target sites. We remark that the free-energy barriers were estimated at constant S_z for the whole system, which enabled the spin state of the approaching O_2 to change as a result of the interaction with the adsorbents. We found that not all of the graphite-like N atoms allow for O_2 adsorption. For instance, an infinite basal plane (Figure 1a) displays a monotonic increase in the free-energy difference ΔF up to ~ 80 kcal/mol by decreasing the distance $d_{\text{C}^\#-\text{O}_2}$ between O_2 and the target C

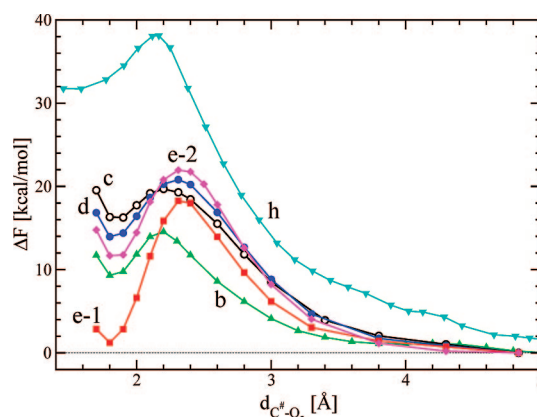


Figure 2. Free-energy profiles for O_2 adsorption on atoms marked by arrows in Figure 1b–d,e-1,e-2,h. The reaction coordinate is the distance between the center of mass of the O_2 molecule and the target adsorption site.

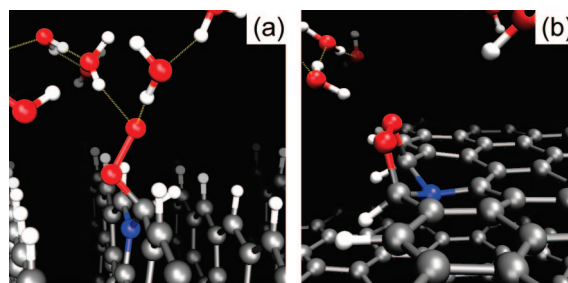


Figure 3. Structures of adsorbed O_2 on the (a) zigzag-edged surface and the (b) zigzag-shaped step edge. Hydrogen bonds are indicated as dashed lines. H is white, C is gray, N is blue, and O is red.

(labeled as $\text{C}^\#$ and marked with arrows in Figure 1). For the other sites, ΔF has a maximum between 14 and 38 kcal/mol in the $2.2 < d_{\text{C}^\#-\text{O}_2} < 2.4$ Å range of distances (Figure 2), which depends on the structure of the exposed graphene edges and on the position of the substitutional N. In contrast with the basal plane, C atoms that are located at zigzag edges (Figure 1c) tend to adsorb O_2 even in the absence of N dopants. The high chemical reactivity of zigzag edges of graphene was already suggested in a former work.¹⁹ In the present cases, we note that upon adsorption O_2 molecules become tightly bound to C atoms in the outermost layer of the zigzag edge if substitutional N atoms are located next to the adsorption sites, as in Figure 1e–

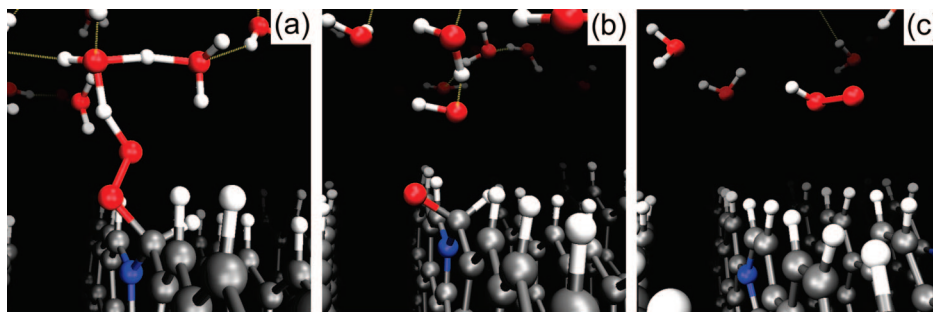


Figure 4. Bifurcation of the ORR pathway upon the first proton transfer to the associatively adsorbed O_2 (panel a). Panel b shows the formation of OH^- (and subsequent H_2O), whereas in panel c, an undesired hydroperoxide radical OOH^- is formed. The former path also holds for the associative adsorption of O_2 on armchair edges. Panels a and b are for the zigzag-edge case, and panel c is for the armchair-edge case. H is white, C is gray, N is blue, and O is red.

1. Therefore, O_2 adsorption is enhanced by N in zigzag edges. Interestingly, if an analogous situation is realized at armchair edges, then the O_2 adsorption does not give rise to stable structures, which suggests that the edge-localized states near the Fermi level that are specific to zigzag edges play a critical role in the reduction of the free-energy barrier for O_2 adsorption. More details will be discussed in a forthcoming publication.

According to XAS experiments,⁹ pyridine-like (and pyridinium-like) N does not induce ORR catalytic activities. This observation is supported by our simulations in which pyridine-like (Figure 1f) and pyridinium-like (Figure 1g) models show free-energy curves that increase monotonically beyond 80 kcal/mol when O_2 approaches any edge site. Therefore, the catalytic activity for ORR in CACs is likely to be related to the presence of graphite-like N at exposed zigzag edges. Figure 3 shows the two adsorption structures, $-C-O-O^{\bullet}$ and $-C-O-O-C-$, that were observed in our simulations for the zigzag and the zigzag-shaped step edges. We found that O_2 molecules are mostly adsorbed on C atoms in a nondissociated form, which is in contrast with Pt-based catalysts, and they convert the double bond $O=O$ to a single bond $-O-O-$ (Figure 3a). However, a bridgelike $-C-O-O-C-$ configuration (Figure 3b) can break apart and become a double $-C=O$ structure. Analogously, the dissociative adsorption (not shown) of O_2 could occur depending on some peculiar local structure of the CAC.

We investigated the subsequent steps of O_2 reduction by assuming that additional e^- and H^+ are supplied separately and consecutively by the anode through an external circuit and by a polymer electrolyte, respectively, in which the lowest-possible spin state of the system was used whenever necessary. In the case of radicals, a check within the self-interaction correction (SIC) that was proposed in refs 20 and 21 did not display any significant change with respect to SIC-uncorrected energetics. The ORR depends on the active site. For configuration e-1 in Figures 1 and 2, when the associative O_2 adsorption is stable, a selective H^+ attack of the terminal O occurs that is driven by the hydrophobicity of $-CH$ of the substrate (Figure 4a). The breaking of the $O-O$ bond in the $-C-O-O$ adduct leads to the formation of OH^- (Figure 4b) and then to the formation of the first H_2O molecule without any appreciable activation energy. The subsequent reduction of the remaining O atom on the adsorption site, which leads to the formation of a second H_2O , is characterized by a free-energy barrier of ~ 5 kcal/mol because of the relatively strong $C-O$ bond to be cleaved, which was formed in the reaction $O^* + H^+ + e^- \rightarrow ^*OH$. (Here * indicates that the associated species remains on the adsorption site.) A complete reduction of O_2 is thus expected for the e-1 site. In contrast, the reaction site of Figure 1h has two alternative ORR pathways. Upon H^+ attack of the terminal O, the $C-O$

bond in the $-C-O-O^{\bullet}$ adduct breaks because of the weak associative adsorption of O_2 , and OOH^- is formed (Figure 4c). This leads to an undesired H_2O_2 final product, which was formally summarized as $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$. However, a second pathway that is similar to that of e-1 is also possible. As for the bridgelike adsorption (Figure 3b), the $O-O$ bond of the adsorbed O_2 is cleaved if an additional electron occupies the low-lying $O-O$ antibonding orbital. Therefore, the formation of H_2O_2 can be avoided, and two $-C=O$ sites are left behind in which the O_2 reduction can be completed via a pathway that is analogous to the one that is described above.

Conclusions

Our first-principles simulations suggest that CACs possess potential ORR catalytic activity that is enhanced by N atoms that are doped at specific sites. An O_2 molecule is preferentially adsorbed associatively at C sites on graphene-like zigzag edges if a graphite-like N is located nearby. The subsequent reaction mainly takes the path that leads to the formation of two H_2O molecules with free-energy barriers of ~ 5 kcal/mol. Despite the absence of a bias voltage and the intrinsic DFT limitations, the insight that our study offers into ORR active sites represents the first step toward a rational design of Pt-free cathode catalysts.

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