Catalytic Reaction on FeN₄/C Site of Nitrogen Functionalized Carbon Nanotubes as Cathode Catalyst for Hydrogen Fuel Cells

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ABSTRACT:

We utilized first-principles spin-polarized density functional theory (DFT) calculations to study the electrocatalytic reaction steps on FeN₄/C site of carbon nanotubes. O₂ molecule can be adsorbed and partially reduced on FeN₄/C site without any activation energy barrier. The partially reduced O₂ further reacts with H⁺ and e⁻ through a direct pathway (DPW) and forms two water molecules without any activation energy barrier. Through an indirect pathway (IDPW), there is an activation energy barrier of ~0.15 eV for the formation of the first H₂O molecule. The formation of the second H₂O molecule through IDPW does not have any activation energy barrier.

KEYWORDS

First-principles calculations, Electrocatalytic reactions, Carbon nanotubes, Catalyst, Fuel cells

I. Introduction

Developing non-precious-metal (NPM) catalysts to substitute for platinum is one of the major targets in the current research for commercializing hydrogen fuel cells (HFCs). Materials based on transitional metal-nitrogen-carbon (M-N-C) networks show high electrocatalytic activity towards oxygen reduction reaction (ORR)[1-6]. Recently, several groups demonstrated significant enhancement in ORR activity over FeN₄-macrocyclic compounds embedded in carbon nanomaterials [7-10]. Dodelet et al. attributed ORR activity to FeN₂₊₂/C and FeN₄/C sites in nitrogen-functionalized carbon structures [11-15]. Liu et al demonstrated that FeN_x ($x = 2,4$) are the active sites towards ORR in N-CNTs [16,17]. Liang et al. and Kattel et al. investigated the electrocatalytic activity of FeN₄ site in doped graphene for ORR by DFT calculations, and found that FeN₄ is an active site toward ORR [18,19]. Some experimental reports have proposed that pyridinic-type sites on the open edges of CNTs may contribute to the high ORR activity over N-CNTs. Previously, we examined the catalytic reaction steps for ORR and water formation reaction (WFR) on open edges of N-CNTs [20]. Here, we report our recent studies on the electrocatalytic properties of another possible catalytic site in N-CNTs: the FeN₄/C site embedded into the wall of short CNTs (FeN₄/CNTs).

2. Theoretical and computational methods

We performed first-principles spin-polarized DFT calculations using VASP [21-23], which implemented the projector augmented plane wave (PAW) potentials [24,25]. The exchange-correlation interaction potentials and energies were described by electron density functional formalism in local density approximation (LDA). For comparisons, we also performed first-principles DFT calculations using generalized gradient approximation (GGA) for the exchange-

correlation interactions. An energy cutoff of 400 eV was employed. A supercell with cell lattice parameters of $15 \text{ \AA} \times 15 \text{ \AA} \times 16 \text{ \AA}$ was used. In the self-consistent DFT computations, the total energy converged to $< 1 \times 10^{-5}$ eV. Atomic positions were fully relaxed until the residual forces were $< 0.05 \text{ eV/\AA}$ on atoms. Short pieces of (10,0) CNTs with 10 carbon atomic rings were used as the carbon support. We mainly focus on the catalytic properties of FeN₄/CNT site. The open-edges of the CNTs were saturated by H atoms to stabilize the structure. Six C atom sites on the CNT wall were substituted by four N atoms and a single Fe atom. The Fe atom locates in the center of the N₄ rectangle, forming a FeN₄ structure on the wall of CNT.

3. Results and discussion

We studied the formation of the FeN₄ defect site embedded into the wall of CNT. The calculated formation energy of FeN₄ defect in the CNT is -5.04 eV, indicating that the FeN₄/C catalytic site is energetically stabilized. Experimentally, Liu et al. at Argonne National Laboratory have demonstrated the stability of the FeN₄ defect incorporated into aligned CNTs prepared through a chemical vapor deposition method [16,17].

We also calculated the charge transfer (CT) of Fe and N atoms through the Bader charge analysis using the code developed by Henkelman *et al* [26]. The results show that there are substantial charge transfers at the FeN₄/C site. The Fe and four N atoms become Fe^{+1.22}, N^{-2.57}, N^{-2.58}, N^{-2.57} and N^{-2.56}, respectively. Part of the charge transfers to N atoms are from the surrounding C atoms on the CNT, which become C^{+1.06}, C^{+1.07}, C^{+1.08}, C^{+1.07}, C^{+1.13}, C^{+1.09}, C^{+1.03}, and C^{+1.18}, respectively. These results show that there are large transfers between N and Fe and between N and C; and consequently, N atoms play a role to stabilize the FeN₄/C site.

We first studied the ORR process on the FeN₄/CNT site. The adsorption energy (E_{ads}) of the ORR process is determined by:

$$E_{ads} = E_{FeN_4O_2} - E_{FeN_4} - E_{O_2} \quad (1)$$

where E_{FeN_4} and $E_{FeN_4O_2}$ represent the total energies of FeN₄/CNT before and after O₂ adsorption, respectively; E_{O_2} is the total energy of a free O₂. The minimum energy pathways (MEPs) of the reaction processes were calculated using nudged elastic band (NEB) method [27-29] implemented in VASP. Using this method, we have successfully calculated the MEPs for ORR and WFR on nitrogen-doped fullerenes and on open-edge sites of N-CNTs [20,30].

3.1. Oxygen reduction reaction (ORR) on FeN₄/CNT site

Fig. 1 (a) shows the relative potential energy of O₂ adsorption and reduction on the FeN₄/CNT site from LDA calculations. Initially, an O₂ molecule is 4.0 Å away from the Fe-N bridge site. O₂ is then adsorbed/reduced onto the FeN₄/CNT site by forming Fe-O bond. In the following discussion, O(1) refers to the one atop nitrogen atom, and O(2) refers to the second O atom bonded with Fe after reduction. After adsorption, O(1) tilted upon the Fe-N-C-C-N pentagon. This is in agreement with the calculated results from Liang et al. and Kattel et al. [18,19]. Previously, Tanaka et al. suggested a similar bridge interaction for plane graphene sheets [31]. Recently, theoretical calculations for FeN₂₊₂/C sites by Szakacs suggested that a side-on binding of oxygen on FeN₂₊₂/C might be favorable during ORR in comparison to end-on [32]. We also performed first-principles calculations for side-on coordination of O₂ towards iron. The total energy of end-on adsorption of O₂ onto the FeN₄/CNT site is lower than that of side-on O₂ adsorption by 0.30 eV. These results show that an end-on coordination of O₂ is more favorable.

The calculated O(1)-N bond length is 3.11 Å and the O(2)-Fe bond length is 1.71 Å (listed in Table 1). There is no activation energy barrier (E_a) for this ORR. The calculated E_{ads} of O₂ is -1.92 eV. The reduction of O₂ can be measured by three major physical quantities: the first one is the extension of O-O bond length, which is increased to 1.27 Å after reduction, from 1.22 Å in a free O₂. The second quantity is the calculated charge transfers, wherein two O atoms become O(1)^{-0.18} and O(2)^{-0.30}, respectively. The third one is the change of magnetic moment of O₂ molecule, which is reduced to 0.14 μ_B from 2.0 μ_B (for a free O₂ molecule).

After ORR, Fe becomes more positive (~Fe^{+1.51}), i.e., Fe atom is more oxidized. The effective charges on the four N atoms remain nearly the same, within the calculation error for the charge transfer. It indicates that the major part of charge transfer to the adsorbed O₂ is from Fe. In addition, the calculated charge transfers of the Fe atom before and after ORR (Fe^{+1.22}/ Fe^{+1.51}) imply that the ORR is more likely processed on a ferrous state instead of a ferric state, that agrees with the previous experimental [10] and theoretical reports [33].

The spin states of the Fe atom before and after ORR can be described by the change of its calculated magnetic moments, which are 0.112 μ_B, and 0 μ_B, respectively. The decrease of magnetic moment of Fe after ORR also indicates the Fe atom is more oxidized during the ORR process.

Fig. 1(b) shows the 3-D iso-surfaces (with iso-density value of 0.1 e/Å³) of the electron density (spin-up plus spin-down) map of FeN₄/CNT after O₂ adsorption. The overlap between the electron densities of Fe and O(2) indicates the formation of Fe-O bond. Fig. 1(c) displays the 3-D iso-surfaces (with an iso-density value of 0.01e/Å³) of magnetization density (defined as spin-up density minus spin-down density) maps of free O₂ and reduced O₂. The magnetization

density between two O atoms is substantially reduced after adsorption. The calculated magnetic moments of O(1) and O(2) for the reduced O₂ are 0.067 μ_B and 0.077 μ_B , respectively, which are much smaller than 1.0 μ_B /O in a free O₂.

Usually, LDA tends to under-predict bond lengths and overestimate binding energies. For comparisons, we also performed GGA calculations. The calculated MEP for ORR from GGA method is similar to that of the LDA (shown in Fig. 1), except for the calculated adsorption energy from GGA (-1.16 eV), which is noticeably lower than that from LDA calculations (-1.92 eV). Similarly, Zhang et al. performed first-principles GGA calculations for the adsorption of O₂ onto the FeN₄/CNT catalytic site, by using the Dmol³ code [34]. The calculated adsorption energy of O₂ onto the FeN₄/CNT site is -1.13 eV, which is close to the value we obtained by GGA calculations. The bond lengths of Fe-O, O-O, O(1)-N, and the charge transfer from GGA are slightly larger than those from LDA calculations (see Table 1). The magnetic moment for reduced O₂ from GGA is smaller than that from LDA calculations.

In order to test the tubule curvature effect of CNT on the ORR, we also performed first-principles calculations for the ORR process on the FeN₄/C site of planar graphene. The results indicate that the tubule curvature characteristics of CNT do not have substantial effect on the ORR on the FeN₄/C site (see the details in Supporting Information (SI)).

3.2. Water formation reaction (WFR) on FeN₄/CNT site

We further investigated the WFR processes after ORR on the FeN₄/CNT site. We found two possible pathways through which the reduced O₂ reacts with H⁺ and e⁻, forming H₂O molecules. The first one is the direct pathway (DPW), in which two H⁺ nearly simultaneously approach a reduced O with two e⁻, forming a H₂O that desorbs from the catalytic site. The second one is the indirect pathway (IDPW) through which H⁺ approaches reduced O sequentially.

Fig. 2(a) shows the relative potential energies for the reaction of O(1) with two H^+ and two e^- through DPW. In the initial state, two H are 4.0 Å away from O(1). As long as the two H atoms reach a distance of 1.5 Å from O(1) (an intermediate state), they react with O(1), forming a $H_2O(1)$ molecule. The as-formed $H_2O(1)$ is trapped to the catalytic site due to a weak interaction between O(2) and one of the H atom in $H_2O(1)$. The O(2)-H bond length is 1.62 Å. The O(1)-O(2) distance is 2.61 Å. The $H_2O(1)$ molecule needs to overcome a desorption energy (E_d) of 0.29 eV to be completely desorbed from the catalytic site. In the final state, the O(1)-O(2) distance is 3.98 Å. As shown in Fig. 2(a), the relative potential energy of the formed $H_2O(1)$ molecule is much lower than that of the initial state of the system by 7.87 eV. Part of the energy can drive $H_2O(1)$ to desorb from the catalytic site before an equilibrium state of the system can be reached.

O(1) can also react with two H^+ and two e^- through IDPW (Fig. 2(b)). A H atom moves toward O(1) first and forms O-H in the intermediate state, with an O-H bond length of about 0.99 Å. A second H needs to overcome an energy barrier E_a of 0.16 eV to cross a transition state (TS), move close to O-H and form a H_2O molecule. To confirm the TS in the MEP for WFR, we calculated the vibrational frequencies of the H^+ at the TS. In a harmonic approximation, the calculated vibrational frequencies of H^+ are 403 cm^{-1} , 296 cm^{-1} , and 669i cm^{-1} . There is only one imaginary frequency related to the vibration of H^+ along the MEP. This demonstrates that the TS derived from NEB calculation is a saddle point. The calculated effective charges show that O(1) becomes $O(1)^{-0.99}$ in the intermediate state. When the second H^+ moves close to O(1)-H, from the intermediate state to the TS, there is a potential energy change of about 0.84 eV due to Coulomb electric interaction. Part of the potential energy change can transfer to the kinetic energy of H^+ , that is not included in the first-principles DFT calculation, which was done essentially at $T = 0$ K.

When H^+ reaches the TS, its instantaneous kinetic energy could easily overcome the activation energy barrier (0.16 eV). $H_2O(1)$ is weakly adsorbed to the catalytic site, due to the interaction of O(2) with one of the H in the formed $H_2O(1)$ molecule. The O(2)-H bond length is 1.62 Å. The O(1)-O(2) distance becomes 2.61 Å. The calculated E_d for $H_2O(1)$ is 0.37 eV. After desorption, the O(1)-O(2) distance is 3.99 Å.

We further studied the WFR process on O(2). Fig. 2(c) shows the relative potential energy for H_2O formation on O(2) through a DPW. Two H move close to O(2) simultaneously, forming $H_2O(2)$ which then moves away from the catalytic site. There is no activation energy barrier for this reaction process. However, $H_2O(2)$ stabilizes at a position with a Fe-O distance of 2.12 Å, indicating that H_2O is still weakly trapped. To desorb $H_2O(2)$ from the catalytic site, Fe-O bond needs to be broken. The calculated E_d for $H_2O(2)$ is 0.92 eV. After desorption, the Fe-O distance is 4.0 Å. The relative potential energy of the formed $H_2O(2)$ molecule is substantially lower than that of the initial state by 6.81 eV (Fig. 2(c)). Part of the energy can drive the $H_2O(2)$ to desorb from the catalytic site before an equilibrium state of the system can be reached. After the desorption of the second H_2O , the system recovers back to its original structure and can serve for next catalysis reaction cycle.

Fig. 2(d) shows that O(2) can also react with two H^+ and e^- through IDPW, forming $H_2O(2)$. A H moves close to O(2) first, forming O-H with a bond length of 1.0 Å. A second H then approaches to O(2)-H forming $H_2O(2)$ without any activation energy barrier. The calculated E_d for $H_2O(2)$ is 0.91 eV. After desorption, the Fe-O distance is 4.0 Å. The relative potential energy of $H_2O(2)$ is lower than that of its initial state by about 6.77 eV (Fig. 2(d)), part of which will overcome the desorption energy of $H_2O(2)$ from the catalytic site.

We also studied the WFR steps using GGA calculations. The calculated MEPs are similar to those from LDA calculations (Fig. 2), except that the relative potential energies from GGA differ slightly from those of LDA. For the DPW, both the GGA and LDA calculations found no activation energy barrier. E_d for the two water molecules from GGA calculations are 0.17 and 0.70 eV, respectively, which are lower than those from the LDA calculations (0.29 and 0.92 eV). For the IDPW, the activation energy barrier for the formation of the first H₂O(1) from GGA is 0.14 eV; it is smaller than that from LDA calculation (0.16 eV). GGA also found no activation energy barrier for the formation of the second water molecule H₂O(2). In addition, the E_d of the two water molecules from GGA (0.14~0.75 eV) are smaller than those from LDA results (0.37~0.91 eV). These numbers confirm that LDA calculation tends to overestimate binding energies of molecules, as discussed above.

4. Conclusions

In summary, by using first-principles spin-polarized LDA and GGA calculations, we calculated the electrocatalytic reaction steps, minimum energy pathways, and activation energy barriers of ORR and WFR on FeN₄/CNT, which was identified as a potential electrocatalytic site for the cathode electrode of hydrogen fuel cell. O₂ can be chemisorbed and partially reduced on the FeN₄/CNT site. Through direct and indirect pathways, the partially reduced O₂ can further react with H⁺ and e⁻, forming H₂O molecules. This work provides detailed results of the electrocatalytic reaction steps at microscopic level that may help to understand experimental results on ORR activities over FeN₄/CNT catalytic site.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests for this work.

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Figure captions:

Fig. 1. (a) Relative potential energy for ORR on the FeN₄/CNT site from the LDA calculations. Embedded are relaxed structures of FeN₄/CNT before and after ORR; (b) Three-dimensional charge density distribution of FeN₄/CNT with O₂ adsorption; and (c) Three-dimensional magnetization density of free O₂ and FeN₄/CNT with O₂ adsorption. Purple, red, gray, blue and white spheres represent Fe, O, C, N and H atoms, respectively.

Fig. 2. Relative potential energies from LDA calculations for the H₂O formation processes on O(1) through a direct pathway (a) and an indirect pathway (b) on FeN₄/CNT; and WFR for O(2) through a direct pathway (c) and an indirect pathway (d), respectively. Embedded images show the atomic structures of the initial, intermediate, and final states of the reaction processes, respectively.

Fig. 1

Fig. 2

Table 1. Bond lengths (d), charge transfer, magnetic moment (MM) of O_2 , and adsorption energies (E_{ads}) for ORR at the FeN_4/CNT site, from LDA and GGA calculations.

	d_{Fe-O} (Å)	d_{O-O} (Å)	$d_{O(1)-N}$ (Å)	Charge Transfer	MM (μ_B)	E_{ads} (eV)
LDA	1.71	1.27	3.11	$O(1)^{-0.18}$, $O(2)^{-0.30}$	0.14	-1.92
GGA	1.75	1.30	3.16	$O(1)^{-0.19}$, $O(2)^{-0.32}$	0.12	-1.16

Table 2. Activation energy barriers (E_a) for the WFR steps at the FeN_4/CNT site through DPW and IDPW and the desorption energies (E_d) of the H_2O molecules, from LDA and GGA calculations.

	DPW				IDPW			
	E_a (eV)		E_d (eV)		E_a (eV)		E_d (eV)	
	$H_2O(1)$	$H_2O(2)$	$H_2O(1)$	$H_2O(2)$	$H_2O(1)$	$H_2O(2)$	$H_2O(1)$	$H_2O(2)$
LDA	0	0	0.29	0.92	0.16	0	0.37	0.91
GGA	0	0	0.17	0.70	0.14	0	0.14	0.75

Graphical abstract