ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

DFT study of stabilization effects on N-doped graphene for ORR catalysis

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ARTICLE INFO

Keywords:
Oxygen reduction reaction
Density functional theory
N-doped graphene
Explicit solvation

ABSTRACT

Noble metal free catalysts, such as N-doped graphene, have drawn a lot of attention as a promising replacement for platinum in low temperature fuel cells. Computational prediction of catalytic activity requires accurate description of the oxygen reduction reaction (ORR) intermediates adsorption energies. Two stabilizing effects, immanently present in experimental ORR setups with basal plane N-doped graphene catalyst, are studied systematically by means of density functional theory. Distant nitrogen with no adsorbates on neighboring carbon atoms selectively stabilizes *O and $*O_2$ adsorbates. Water solvation stabilizes all ORR intermediates, having a greater impact on *O and $*O_2$, than on *OH and *OOH, in contrast to metal and oxide catalysts. Synergistic stabilization of *O caused by both effects reaches remarkably a high value of 1.5 eV for nitrogen concentrations above 4.2% N. Such a strong effect is explained by a high reactivity of *O and $*O_2$, which possess empty O(sp) states. At 6.25% N, the reaction environment is found to comprise *O and free nitrogen spectators. Finally, strong *O solvation is found to be present in a broader class of systems, comprising all materials where the ORR occurs on a 2nd row element. Including at least a single explicit water layer is paramount to achieve the correct description of the ORR intermediates adsorption energies on these materials.

1. Introduction

Low temperature fuel cells have been recognized as one of the most attractive alternatives to combustion engines for automotive applications [1]. The promise of higher energy efficiency, independence from limited resources of fossil fuels and reduction in air pollution drives the research to overcome the obstacles to commercialization of this technology. Some of the difficulties are related to the development of auxiliary technologies, such as hydrogen production *via* water splitting and effective hydrogen storage [2], but the most troublesome issue directly related to the fuel cell stack is finding a durable material, which would efficiently catalyze the sluggish oxygen reduction reaction (ORR) [3].

Most commonly utilized cathodic materials for fuel cells are currently based on platinum [3,4]. However, due to its price and scarcity, methods of decreasing Pt loading, or completely replacing it with earth-abundant alternatives, are intensively explored [3,5,6,7–9]. The latter possibility is particularly attractive, as it may allow to further reduce the cost of the technology.

Setting aside arguably the most promising non-precious ORR catalysts containing a FeN_4 moiety [10,11], we draw attention to metal-free materials. This class of ORR catalysts is dominated by conductive carbon nanostructures, modified by various types of doping, especially nitrogen doping [7,9]. In recent years, N-doped carbon nanotubes and graphene have been extensively studied both experimentally and computationally. Theoretical approaches investigated, among other things, effects such as: the type of nitrogen doping (graphitic, pyridinic, pyrrolic) [12], morphology and concentration of N-dopants [13], structural defects [14,15], curvature effect [14], solvation of $*O_2$ [16] and other ORR intermediates [17] by water, and the influence of additional nitrogen dopants on $*O_2$ [16] and *O [18] stability (where * is an active site on the catalyst's surface).

In the present paper, the latter two effects are revisited and reassessed. An unoccupied nitrogen dopant in the cell, referred to as “free nitrogen”, is a nitrogen atom, where neighboring carbon atoms are empty adsorption sites. Such nitrogen is particularly interesting due to its selective stabilization of *O over *OH and *OOH [18]. Similarly, the presence of water was found to stabilize $*O_2$ adsorbate by a uniquely high value of 0.83 eV, twice as much as *OH [17]. In what follows, the influence of these two effects on all ORR intermediates is systematically studied as a function of nitrogen concentrations, number of nitrogen atoms per adsorbate and number of water molecules per adsorbate. We employ Bader charge analysis [19] and projected density of states (PDOS) calculations to gain insight into the underlying phenomena and explain why different ORR intermediates respond differently to both effects. Finally, we include a case study of the oxygen reduction process on a selected catalytic system to show how our findings are applicable to the ORR modeling.

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https://doi.org/10.1016/j.cattod.2018.02.015
Received 18 December 2017; Received in revised form 2 February 2018; Accepted 9 February 2018
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Please cite this article as: Reda, M., Catalysis Today (2018), https://doi.org/10.1016/j.cattod.2018.02.015

2. Computational methods

All density functional theory (DFT) calculations are done using Atomic Simulation Environment (ASE) [20] coupled with the Vienna *Ab Initio* Simulation Package (VASP) [21–24]. The core electrons are described with the projector augmented wave method [25,26], and the basis set for the electronic wavefunctions are plane waves below a 400 eV energy cutoff. We use a Fermi smearing of electronic occupations with a width of 0.1 eV and Monkhorst-Pack [27] mesh for the Brillouin zone sampling of $(k_1, k_2, 1)$, with k_i such that $k_i v_i > 40$ for v_i being the corresponding lattice vector. The structure relaxation is performed until the maximum force on each atom drops below 0.01 eV/Å.

In this study, we consider systems in which water molecules interact with one another and with the hydrophobic surface of the catalyst. In such systems, dispersion forces can play a significant role, and semi-local exchange-correlation functionals like PBE [28] or RPBE [29] do not account for non-local van der Waals interactions. Here, we employ the BEEF-vdW [30] functional in which vdW-DF2 [31] non-local correlation is used. This approach proved to be successful in predicting adsorption bond energies both to transition metal surfaces [32] and carbon-based materials [30], as well as adsorption energy error estimation [33].

Solvation of the surface and adsorbates is taken into account by including water implicitly or explicitly. For implicit solvent calculations we use the continuum solvation model implemented in VASPsol [34,35] with a 600 eV plane wave cutoff. Explicit water layer structures are determined by the minima hopping algorithm implemented in ASE [36,37]. This global optimization method was accompanied by additional sampling of minimas, achieved by manual change of orientations of those H_2O molecules, which hydrogen atoms can point either towards or away from the surface. The vacuum layer region between periodic images of the system is about 10 Å. The dipole correction is used to decouple electrostatic potentials on the two sides of the two-dimensional structure.

The free energy corrections for adsorbed species are based on the quantum mechanical harmonic approximation and calculated vibrational frequencies. For calculations of the free energy diagrams, the total energy of the gas phase O_2 is corrected based on the formation Gibbs free energy of liquid H_2O as described previously [38], and the total energies of the systems with adsorbates are corrected according to the Christensen's correction scheme [39,40]: $\Delta E(O\text{–}O) = 0.2$ eV, $\Delta E(H_2O) = -0.03$ eV, and $\Delta E(H_2) = 0.09$ eV.

3. Results

All considered N-doped graphene models consist of graphitic nitrogen atoms uniformly dispersed in the graphene sheet. When a nitrogen atom is introduced into the system preserving its unit cell, it is placed in a position that maximizes the distance between nitrogen atoms. In that case, uniformity of N distribution cannot be strictly preserved. However, all the studied properties of the system are found to be insensitive to such deviations from uniformity. Non-uniform dopant distribution, such as nitrogen clustering, introduces another degree of freedom and is beyond the scope of this study.

The studied NG model systems are referred to in the following format:

$NGxyN/ads/zH_2O$,

where x – nitrogen concentration (atomic ratio), y – N/*ads ratio, ads – considered adsorbate (O, OH, OOH or O_2 for a specific adsorbate, or “ads” for general considerations), z – H_2O/*ads ratio. For example, NG_4.2%_2N/O/11H_2O denotes nitrogen-doped graphene with 4.2% of nitrogen, atomic oxygen adsorbate, N/*O ratio of 2 and H_2O/*O ratio of 11.

Adsorption energies are defined as the DFT energies of the following reactions:

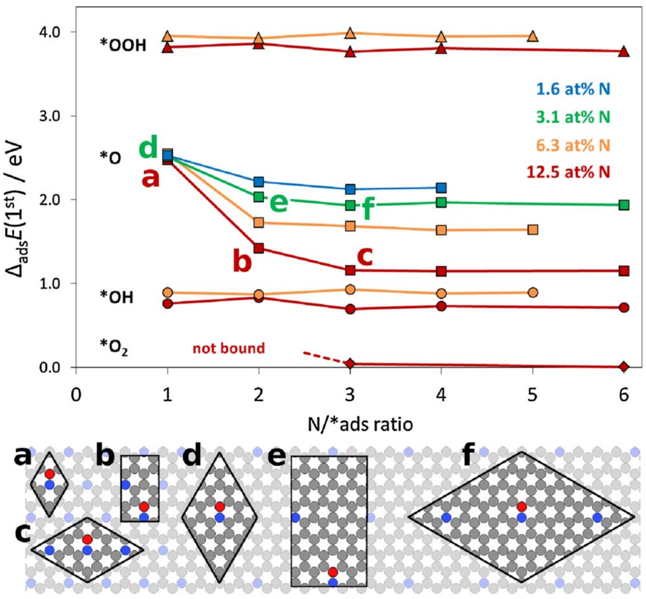

Fig. 1. First adsorption energy, $\Delta_{ads}E$(1st), vs. N/*ads ratio at different nitrogen concentrations; ads = {O, OH, OOH, O_2}. Sample unit cell structures are marked on the figure with letters (a)–(f). Color code for atoms: gray – carbon, blue – nitrogen, red – oxygen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$*+H_2O \rightarrow *O + H_2, \quad \Delta_{ads}E(O) \tag{1}$$

$$*+H_2O \rightarrow *OH + \frac{1}{2}H_2, \quad \Delta_{ads}E(OH) \tag{2}$$

$$*+2H_2O \rightarrow *OOH + \frac{3}{2}H_2, \quad \Delta_{ads}E(OOH) \tag{3}$$

$$*+O_2 \rightarrow *O_2, \quad \Delta_{ads}E(O_2) \tag{4}$$

Superscripts are added when considering adsorption energies in the presence of free nitrogen [$\Delta^{N}_{ads}E(O)$], water [$\Delta^{W}_{ads}E(O)$] or both [$\Delta^{N+W}_{ads}E(O)$].

Stabilization by free nitrogen is the difference between the adsorption energy in the 1N/*ads system (no free nitrogen, *e.g.* Fig. 1a or d) and > 1N/*ads systems:

$$\Delta^{N}_{stab}E(X) = \Delta_{ads}E(X) - \Delta^{N}_{ads}E(X) \tag{5}$$

The energy of stabilization *via* solvation is the difference between ORR adsorption energies in vacuum and in water, and equals the negative solvation energy:

$$\Delta^{W}_{stab}E(X) = -\Delta_{solv}E(X) = \Delta_{ads}E(X) - \Delta^{W}_{ads}E(X) \tag{6}$$

To calculate the adsorption energy in the presence of water, one H_2O molecule from the water layer is replaced with adsorbate. The energy of that water molecule is assumed to be the average energy of H_2O in the water layer.

3.1. *Stabilization by free nitrogen*

It is well known that a nitrogen dopant embedded in a graphene structure creates net positive charge on adjacent carbon atoms, making them more favorable for O_2 adsorption and facilitating the oxygen reduction reaction [41]. More recently, it was found that free nitrogen atoms which are located far away from the active site stabilize certain ORR adsorbates as well [18].

The effect of up to five free nitrogen atoms on the adsorption energy of ORR intermediates at different N concentrations is shown in Fig. 1. The OH and OOH adsorption energies are essentially independent of the N/*ads ratio, only fluctuations of ± 0.05 eV are observed. By contrast,

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