

The Oxygen Reduction Reaction on Nitrogen-doped Graphene

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ABSTRACT

The oxygen reduction reaction on a graphene sheet with 6.3% doping of nitrogen is analyzed using density functional theory calculations. It is found that all intermediates involved in the oxygen reduction reaction bind on the carbon atom next to the nitrogen dopant. The first reduction step to produce the OOH* intermediate is only moderately downhill in free energy while further reduction to O* and OH* are more exothermic. **The reduction from step from O* to OH* is found responsible for the experimentally observed overpotential.**

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MAIN TEXT

The development of catalytic materials for the oxygen reduction reaction (ORR) that are efficient, cost-effective and stable is one of the greatest challenges in a sustainable society.^[1] Up to now, the most efficient catalysts are based on platinum, often alloyed with one or more non-precious metals, like Ni, Fe or Co.^[2-6] Yet, even for the best materials, the overpotential necessary to drive the reaction is still substantial and they still incorporate significant amounts of platinum.^[7] Recently, a new class of materials, nitrogen-doped carbon has been discovered to act as metal-free catalysts for the ORR.^[2,8-12] These materials reduce oxygen to water at an overpotential similar to that of platinum. So far, there is still a lot of discussion about the active site of the material and the function of the nitrogen,^[12] and there have only been few theoretical studies on this subject.^[13,14,15]

Herein, density functional theory (DFT) calculations on the mechanism of the ORR on nitrogen-doped graphene are presented. The computational hydrogen electrode (CHE) model is used in order to analyze the electro-chemical reduction of oxygen to water. **Within this model, zero voltage is defined based on the reversible hydrogen electrode where protons and electrons are in equilibrium with gas phase hydrogen. The chemical potential of a proton-electron pair is therefore equal to half of the potential of H₂ gas and can hence be calculated using dft. The influence of the applied potential is adjusted by the standard relation between chemical and electrical potential, $\Delta G = -eU$.** This model has proven successful in describing the ORR on transition-metals^[16] and transition-metal oxides^[17] as well as the electro-chemical reduction of N₂ and CO₂.^[18,19] A 16 atom graphene slab is used for the calculations. One of the carbon atoms of the slab is exchanged with nitrogen resulting in a 6.3 % doping of the material (see Figure 1).

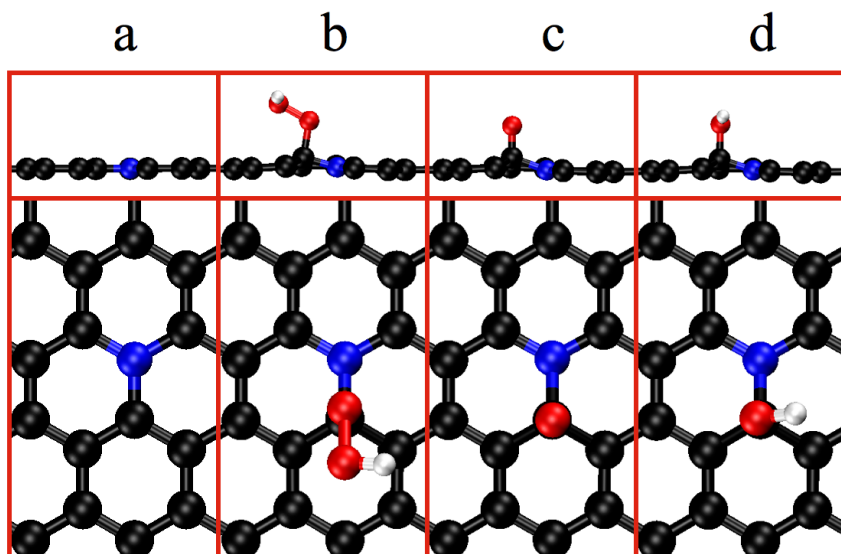


Figure 1. Super cell used as a model of nitrogen-doped graphene (a), and optimized structures of adsorbed intermediates OOH* (b), O* (c) and OH* (d) shown in their most stable adsorption site. Carbon is black, nitrogen is blue, oxygen is red and hydrogen is white.

DFT calculations were performed with the all-electron code GPAW^[20,21] using the **BEEF-vdW functional as defined in ref[22]**. Nitrogen-doped graphene is modeled by a slab consisting of 15 carbon and 1 nitrogen atoms that are repeated periodically in all directions and separated by 20 Å of vacuum. **Convergence of adsorption energies was found after doubling of the unit cell to 32 atoms (30 carbons, 2 nitrogen, and 1 adsorbate). A 8x4x1 and 4x4x1 k -point sampling is applied in order to sample the Brillouin zone, for the small and doubled unit cell, respectively.**^[23] Gas-phase oxygen was corrected relative to the energy of gas-phase water and hydrogen in the same way as described elsewhere.^[24] The vibrational frequencies that were used to determine the zero point energy corrections and the entropy contributions to the free energy were calculated in the harmonic normal-mode approximation (see supporting information for a list of vibrational modes of the different intermediates).

All intermediates bind strongest to the carbon atom next to the nitrogen as seen in Figure 1 (see supporting information for energies of intermediates on other adsorption sites). This can most likely be attributed to the breaking of the conjugated system by the nitrogen dopant, which leads to an activated carbon atom close to the nitrogen. Carbon atoms further away from the nitrogen will feel this effect to a lesser extent and therefore bind intermediates weaker. Figure 2 shows the free energy diagram of the ORR on nitrogen-doped graphene. Each reduction step involves the transfer of one proton-electron pair. For the overall reduction of O₂ to water 4 proton-electron pairs are needed. The free energy of the reaction will change as a function of the applied potential with the number of proton-electron pairs transferred according to:^[16]

$$\Delta G_n(U) = \Delta G^0 + neU \quad (1)$$

where ΔG^0 is the free energy at zero potential, U is the applied potential, e is the elementary charge and n is the number of proton-electron pairs transferred relative to O₂. The free energy diagram shown in Figure 2 is constructed at standard conditions, that is 298K, 1 bar of H₂ and at pH=0.

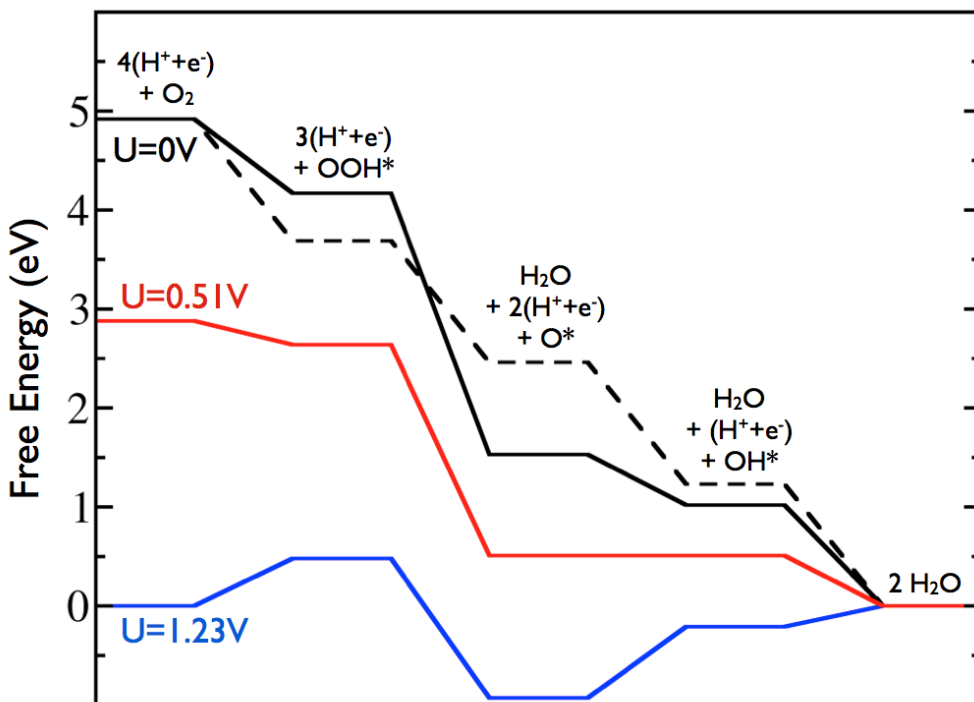


Figure 2. Free energy diagram for ORR on nitrogen-doped graphite at $U=0V$ (black line), $U=1.23V$ (blue line) and $U=0.51V$ (red line) (using equation 1). The optimal ORR catalyst at $U=0V$ is shown for comparison (dashed line).

In order to have no overpotential for the ORR, all reaction steps need to be downhill by the equilibrium potential, 1.23 eV (dashed line in Figure 2).^[16] The first step, formation of the OOH* intermediate, however, is only downhill by -0.64 eV for nitrogen-doped graphene. **On the other hand, reduction of OOH* to O* is downhill by -2.64 eV, resulting in an overbinding of O* with respect to the optimal electro-catalyst. The breaking of the O-O in OOH* upon the transfer of one proton-electron pair has been calculated to occur spontaneous. Transfers of protons from solution to adsorbates have usually very low barriers (far below 0.5 eV) and are thus facile at room temperature.**^[24,25]

Figure 2 also shows the free energy diagrams for several electrode potentials using Equation 1. For a potential of 1.23 V, the equilibrium potential of the ORR, reduction of O₂ to OOH* becomes uphill in energy, while the next reduction step is strongly downhill. The next two reduction steps of O* and OH* are uphill again. The third reduction is identified as the step that determines the onset potential of the reaction. At a potential of 0.51V, all reduction steps become downhill in free energy. We can hence correlate this potential to an overpotential of 0.72V for this reaction. These values are higher compared to the theoretical overpotential found for platinum,^[16] and in fair agreement with experimental data for ORR on nitrogen-doped grapheme. ORR on nitrogen-doped grapheme is often carried out at higher pH values. In order to address these, a correction to the free energy is needed (see Figure S2 for free energy diagrams at a pH of 7 and 14).^[8,9,19]

Solvation effects by the water layer at the water-solid interface have been neglected in this study. These effects can be significant as shown for adsorbates on the Pt(111) surface that were found to be stabilized by 0.5 and 0.25 eV for OH* and OOH*, respectively.^[16,26,27] Applying corrections of similar size to the current system will reduce the theoretical overpotential for the first reduction step by 0.25 eV due to the stabilization of OOH*. On the other hand, stabilization of OH* will make its reduction uphill in free energy. This might shift the potential limiting step from the reduction of O* to the reduction of OH*. In addition the overpotential will likely be smaller than calculated here, since the reaction step O* → OH* becomes more downhill in energy. Further studies of solvation effects are needed in order to establish corrections for nitrogen-doped graphene in more quantitative numbers.

An interesting question related to the use of nitrogen-doped graphene as a fuel cell material concerns its stability. In the electrochemical environment one could imagine reduction of the

nitrogen-doped graphene sheet to graphene with a vacancy and gas-phase ammonia. The first transfer of a proton-electron pair to the nitrogen is calculated to be uphill by 1.73 eV in free energy; total reduction to ammonia is calculated to be uphill by 6.01 eV. Nitrogen-doped graphene should hence be thermodynamically stable at potentials up to -2 V under standard conditions. The picture may be quite different at the edges and corners of the graphene sheet and may bring down the potential upon which nitrogen-doped graphene is stable substantially.

The ORR on nitrogen doped carbon has been investigated and it has been found that intermediates bind strongest on the carbon next to the nitrogen dopend. The energetics are quite favourable for the ORR apart from the first reduction step to form OOH*, which is binding to weakly to the nitrogen-doped carbon, and the reduction of O* to OH*, where O* is bound very strongly to the surface. So far the focus was on nitrogen-doped graphite as a material in the ORR. It should be mentioned that other carbo-nitrides like g-C₃N₄ with a higher content of nitrogen also work as ORR catalysts.^[10] Doping of graphene with other elements than nitrogen also offers the possibility to further fine-tune the adsorption energy of the intermediates involved in the ORR and hence bring down the overpotential of this reaction. It has been shown for example that boron or sulfur incorporate into other carbo-nitrides like g-C₃N₄.^[28-30] This provides a promising route towards non-precious metal ORR catalysts with a low overpotential.

ASSOCIATED CONTENT

Supporting Information. Supporting information contains total energies, vibrations, zero point energies and entropies of all adsorbates on the different sites of the nitrogen-doped grapheme sheet. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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