



Boron-doped graphene as active electrocatalyst for oxygen reduction reaction at a fuel-cell cathode



Gianluca Fazio, Lara Ferrighi, Cristiana Di Valentin*

Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 55, 20125 Milano, Italy

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ABSTRACT

Boron-doped graphene was reported to be the best non-metal doped graphene electrocatalyst for the oxygen reduction reaction (ORR) working at an onset potential of 0.035 V (Jiao et al., 2014). In the present DFT study, intermediates and transition structures along the possible reaction pathways are determined. Both Langmuir–Hinschelwood and Eley–Rideal mechanisms are discussed. Molecular oxygen binds the positively charged B atom and forms an open shell end-on dioxygen intermediate. The associative path is favored with respect to the dissociative one. The free energy diagrams along the four-reduction steps are investigated with the methodology by Nørskov and co. (2004) in both acidic and alkaline conditions. The pH effect on the stability of the intermediates of reduction is analyzed in terms of the Pourbaix diagram. At pH = 14, we compute an onset potential value for the electrochemical ORR of $U = 0.05$ V, which compares very well with the experimental value in alkaline conditions.

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1. Introduction

Platinum (Pt) and its alloys are still the most widely used electrocatalysts for the oxygen reduction reaction (ORR) in fuel cells and metal–air batteries. However, the high-cost, scarcity, and large overpotential, are the main reasons for the intensive efforts devoted by the scientific community in finding efficient, metal-free and cheap electrocatalysts for ORR and other redox reactions [1]. Doped graphene systems have been recently proposed in the literature as promising alternatives [2–9], being potentially active catalysts for ORR. Among them, N-doped graphene has attracted most of the attention and research work [2,4,6–8], although, more recently, B-doped graphene systems have also been reported to efficiently catalyzed this reaction [10,11]. Some comparative experimental data [12] have just appeared in the literature showing that B-doped graphene is even slightly better than N-doped one, both definitely surpassing the performance of other non-metal (O-, P-, S-) doped graphene systems. The details of the reaction path are yet not very clear [13,14]. Moreover, they could be different for different doping elements. In the case of N-doped graphene [15–22], the dissociative

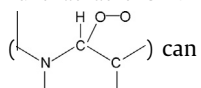
path is generally considered not to be a viable route to products, even though no clear-cut evidence definitely proves that. As regards the associative mechanism, the more efficient direct $4e^-$ pathway is found to compete with the $2e^-$ one.

The molecular oxygen adsorption step, which is the first step for both dissociative and associative mechanisms, is considered to be critical in the ORR process. On pure graphene (G), it goes through the formation of an intermediate side-on bridging dioxygen species ($\begin{matrix} \text{O} \\ | \\ \text{C} \text{---} \text{C} \\ | \\ \text{O} \end{matrix}$) paying a very high-energy cost (about +2.5 eV with respect to $G + O_{2(g)}$) [21,23], which is essentially the reason for the total inertness of graphene toward molecular oxygen. In the case of N-doped graphene (NG), which is the most studied and known case of doped graphene, the analogous species ($\begin{matrix} \text{O} \\ | \\ \text{N} \text{---} \text{C} \\ | \\ \text{O} \end{matrix}$) is still rather high in energy (about +1.6 eV with respect to $NG + O_{2(g)}$) [21]. In most theoretical works [17,19,20], this preliminary and very energetically expensive step is overlooked or neglected, in favor of the much more stable hydroperoxo species ($\begin{matrix} \text{HO} \\ | \\ \text{N} \text{---} \text{C} \\ | \\ \text{O} \end{matrix}$). This oversimplification of the reaction path is a serious issue, primarily because it leads to incorrect conclusions. Some authors [21,22], recognizing the limitations of bulk graphene N species as attractive sites for O_2 adsorption, have proposed a prominent role of the

* Corresponding author.

E-mail address: cristiana.divalentin@mater.unimib.it (C. Di Valentin).

quaternary N atoms at the graphene edges, especially in the case of N-doped graphene nanoribbons (NR). They find that at the NR edges, a stable end-on dioxygen intermediate



can be formed with a much lower adsorption energy barrier (only 0.35 eV) than the side-on one in the NG bulk (). The end-on species was proposed to be the first intermediate for O₂ adsorption in both dissociative and associative paths for ORR.

Other critical issues in the use of doped graphene as electrocatalysts for ORR regard (i) the activation barriers for the proton/electron transfers along the full reduction process, arising at the equilibrium potential, which require a potential bias to be applied to the fuel cell and (ii) the selectivity toward the 4e⁻ associative path. These issues can be addressed and analyzed by applying a methodology which has been first developed by Nørskov and co. [24] for ORR on the paramount case of Pt electrodes. This method in combination with density functional calculations provides a description of the free energy landscape of the electrochemical ORR over the electrocatalyst surface as a function of the applied bias and suggests ways to improve the electrocatalytic properties of fuel-cell cathodes.

In this work, we present a detailed study of the possible reaction paths for ORR as catalyzed by B-doped graphene, through the identification of all the intermediates and transition structures for both dissociative and associative mechanisms. Additionally, the methodology by Nørskov and co. [24], which is generally applied to metal electrodes, is presently used to analyze the B-doped graphene catalyst. This approach allows to determine the critical reduction steps along the overall process and to make a comparison with the analogous quantities for Pt electrodes. Finally, we also present the Pourbaix diagram [25] to identify the dependence of the potential for each step of reduction [4 × (H⁺ + e⁻)] with the pH value of the electrolytic solution.

We find that the O₂ adsorption on B-doped graphene goes through an end-on dioxygen intermediate, never observed for both G and NG, involving the bulk graphene B atom (), which is preliminary to the formation of the high-energy side-on () intermediate for the dissociative mechanism and of the hydroperoxo () species for the associative one. The existence of this end-on adsorbed O₂ species is crucial to trigger the associative ORR path which we consider to be the reason for the excellent performance of B-doped graphene as an electrocatalyst for this reaction [10–12].

2. Computational details

All the calculations were performed with the Gaussian09 [26] (G09) suite of programs and the B3LYP [27,28] functional. Spin polarization is taken into account in the case of open shell systems. The model for pure graphene is a circumcoronene molecule (C₅₄H₁₈). In a previous work, we have shown through a detailed comparison of molecular calculations with periodic systems that the energetics of oxygen reactivity with graphene and B-doped graphene obtained with the different approaches is fully consistent [23]. The orbitals were described with Gaussian basis functions [6-311+G* for the inner five C atoms, the B atom, and the O and H atoms involved in the water formation; 6-31G* for the rest of the model]. All atoms were allowed to relax during the geometry optimization without any symmetry constraint.

Critical points on the potential energy surface have been characterized by diagonalizing the Hessian matrices. The transition-

state structures were searched by numerically estimating the matrix of the second-order energy derivatives at every optimization step and by requiring only one eigenvalue of this matrix to be negative.

Vibrational frequencies in the harmonic approximation were calculated for all optimized structures and used, unscaled, to compute zero point energies, enthalpies and Gibbs free energies.

The reference electrode is the standard hydrogen electrode SHE [24]. At pH = 0 and at potential $U = 0$ V vs. SHE, the reaction $H^+ + e^- \leftrightarrow \frac{1}{2}H_2$ is in equilibrium at 1 bar H_{2(g)} at 298 K, thus $G(H^+ + e^-) = G(\frac{1}{2}H_2)$ in these conditions. The free energy difference for the full ORR with the present setup is -4.64 eV, which we consider in more than satisfactory agreement with the experimental value of -4.92 eV. The free energy of OH⁻ is derived as $G(OH^-) = G(H_2O_{(l)}) - G(H^+)$, where $G(H^+)$ is corrected by $-kT \times \ln 10 \times \text{pH}$, to account for the pH conditions.

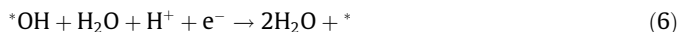
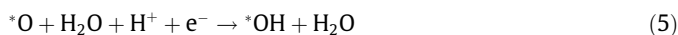
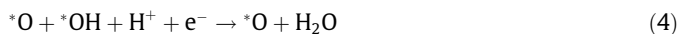
The contribution of bulk solvent (water) effects to the Gibbs free energy (G_{sol}) was computed using the polarizable continuum model (PCM) in the SMD version [29,30] implemented in the Gaussian09 package. Small structural modifications are observed as a consequence of the relaxation in the solvent. The effect of dispersion forces, estimated with the Grimme D3 method [31,32] as implemented in the Gaussian09 code, was found to be analogous for the intermediates of the ORR and therefore negligible on the ΔG values.

3. Results and discussion

3.1. Oxygen reduction reaction paths

The pathways for the oxygen reduction reaction may be a) dissociative or b) associative.

The dissociative pathway is generally considered to go through the following steps (* = surface):



We have investigated this reaction path on the BG surface as described in detail in Fig. 1 (Eqs. (1)–(4)) and 3 (Eqs. (5) and (6)), where the free energy variation (ΔG_{sol}) for the various intermediates and transition structures is reported along the reaction coordinate, with the reference free energy set at the value of the starting reagents, i.e. $G_{\text{sol}}[BG + O_2(g) + 4H^+ + 4e^-]$. Molecular oxygen in its triplet state binds to the positively charged B atom (according to NBO charges: 0.7) on the BG surface, forming an end-on dioxygen species in a doublet spin configuration state (which will be called BG_{OO} or species **2**), without any spin crossing issues. The residual spin density is localized entirely on the two oxygen atoms (see Fig. S1 in the Supplementary Material). This intermediate can evolve to a less stable side-on dioxygen species (**3**) through a transition state (**2TS**) with a 1.04 eV activation free energy. This step is required in order to proceed to the O–O bond breaking (Eq. (2)), which is the most energetically expensive (rate determining) step, with an activation free energy of 1.13 eV, to form a very

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