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A multi-scale model of the oxygen reduction reaction on highly active graphene nanosheets in alkaline conditions

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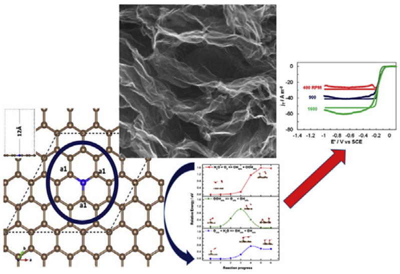
HIGHLIGHTS

- Multi-scale model to account for ORR on N-GN catalysts in alkaline media.
- Density functional theory and continuum model at the atomistic and mesoscale levels.
- Sensitivity to evaluate each elementary step unlike single-scale models.
- O_{2ads} to form OOH_{ads} is rate-determining step due to highest barrier and sensitivity.

GRAPHICAL ABSTRACT



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ABSTRACT

A multi-scale model based on a mean field approach, is proposed to describe the ORR mechanism on N-GN catalysts in alkaline media. The model implements activation energies calculated with Density Functional Theory (DFT) at the atomistic level, and scales up them into a continuum framework describing the cathode/electrolyte interface at the mesoscale level. The model also considers mass and momentum transports arising in the region next to the rotating electrode for all ionic species and O_2; correction of potential drop and electrochemical double-layer capacitance. Most fitted parameters describing the kinetics of ORR elementary reactions are sensitive in the multi-scale model, which results from the incorporation of activation energies using the mean field method, unlike single-scale modelling Errors in the deviations from activation energies are found to be moderate, except for the elementary step (2) related to the formation of O_{2ads}, which can be assigned to the inherent DFT limitations. The consumption of O_{2ads} to form OOH_{ads} is determined as the rate-determining step as a result of its highest energy barrier (163.10 kJ mol^{-1}) in the system, the largest error obtained for the deviation from activation energy (28.15%), and high sensitivity. This finding is confirmed with the calculated surface concentration and coverage of electroactive species.

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1. Introduction

Nitrogen-doped graphene nanosheets (N-GN) have become a viable alternative as non-noble electrocatalysts in low-temperature fuel cells (e.g. hydrogen or methanol-feed) since the more

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electronegative nitrogen removes electrons from adjacent carbons, which enhance their positive charge and act as active sites for the Oxygen Reduction Reaction (ORR) high kinetics [1]. In addition, the simplicity of N-GN synthesis, and exceptional mechanical and electronic properties of graphene nanosheets (GN) spur even more their potential for commercialization [2–4]. N-GN catalysts typically contain five types of nitrogen bonding: pyridinic (sp^2 hybridization), pyrrolic (sp^3 hybridization), graphitic (sp^3 hybridization), and oxidized pyridinic which electrocatalytic activity has not been assigned whatsoever [5–7].

Recent DFT calculations have determined that from all possible adsorption sites for the intermediates including nitrogen on a N-GN structure, the adsorption on any carbon adjacent to a graphitic (also known as quaternary) nitrogen represents a considerable decrease in the energy barrier for ORR in alkaline electrolytes, and the removal of ^3O species to form OH_{ads} on the electrode surface is the rate-controlling step [8,9]. Theoretical and experimental studies support this finding [10,11], although it is worthwhile mentioning that other analyses [12,13] suggest that pyridinic N is responsible for the electrocatalysis of these materials towards ORR. This wide diversity of observed results could be due to remarkable differences in structure (e.g. HOPG, Carbon Nanotubes), pH electrolyte (acid), method for synthesis, among other parameters. However, there exists a consensus that graphitic N is the most active site to perform ORR on N-GN structures in alkaline media [8,9]. Although this information is overriding to reveal the electronic structure and other quantum interactions arising at atomistic level, it does not offer access to mesoscopic and macroscopic phenomena describing the output of instruments characterizing cell components and the overall fuel cell performance. Mathematical models describing catalyst layer (CLM) and transport phenomena through different approaches (e.g. interface, agglomerate, thin film) have been shown as suitable for these purposes [14–19]. As the best of our knowledge, only very few continuum models have been reported describing the electrochemical behavior of N-GN catalysts. These models are mainly based on the physics description of the catalyst surface/electrolyte interface where the electrode kinetics is typically simulated as coupled to mass and charge transfers. However, the majority of CL models reported so far presents a drawback since they rely to Butler-Volmer theory to describe the electrochemistry, i.e. they do not directly rely on the electronic structure and atomistic interactions of catalyst (i.e. N-GN) as in *ab initio* studies [20–22]. These models do not reflect the relationship structure-reactivity, but only an overall step of electrochemical response. This might not be appropriate to account for multi-step mechanisms such as the ORR, which extensively depends on the chemical and nanostructural properties of the catalyst material.

A more thorough approach would be the integration of both types of modelling: continuum approaches enabling to analyze mass and charge transport of electroactive species along with atomistic models capturing the structural and consequent electronic properties of the catalysts. Nevertheless, there is a lack of information regarding the connection between *ab initio* methods accounting for the physics of ORR on carbon materials at atomistic levels, and electrode kinetics at larger scales. In addition, few efforts have been oriented to evaluate the ORR mechanism in alkaline electrolytes, whereby the kinetic rates of multiple chemical and electrochemical processes arising on the electrocatalyst and transport influence remain unknown. Thus, this study aims to develop a multi-scale model (bottom-up approach), in order to account for the multiple reactions involved in the ORR occurring on active N-GN under alkaline conditions. Details of experimental characterization (chemical and electrochemical) for these catalysts, and method of synthesis have been described in a previous publication [9]. *Ab initio* calculations (DFT) are initially used to determine the activation energies for each step of the ORR mechanism occurring on N-GN. These inputs are injected into an electrode kinetics model described trough a modified Butler-Volmer approach, which also considers mass, momentum and charge transport of electroactive species stemmed by long-range diffusion, convection and migration phenomena within a boundary layer. The model is subsequently fitted to in-house experimental data collected with a rotating disk electrode (RDE) to estimate kinetic parameters (e.g. charge-transfer coefficients, rate constants) that have not been determined using computational *ab initio* methods (DFT), and the deviations (ΔE_{act}) associated with the activation energies (i.e. fraction of total activation energies not accounted by DFT). A multiparametric sensitivity analysis is performed to determine the significance of each elementary step of the reaction mechanism and its rate-controlling step.

2. Materials and methods

2.1. Synthesis of N-GN catalysts and electrochemical study

An extremely rapid heating rate was utilized to synthesize N-GN having a highly opened structure, combining thermal reduction and ammonia treatment into a one-step process without using a substrate. The graphene oxide (GO) used for N-GN preparation was based on a modification of Hummer's method using natural graphite [23]. Further details of the synthesis and characterization of the N-GN catalysts used in the present work can be consulted in Ref. [9].

The ORR electroactivity of N-GN was tested in 100 mol m^{-3} KOH using a three-electrode one-compartment cell: a glassy carbon electrode (diameter: 0.5 cm, geometric area: 0.196 cm^2) coated with a suspension of 20 mL of 4 mg mL^{-1} N-GN (0.5 wt% Nafion in ethanol) was used as the working electrode (catalytic loading of ca. 0.4 mg cm^{-2}). The electroactivity of this material was compared with that of a 20 wt% Pt/C coated working electrode prepared on glassy carbon with the same loading. A saturated calomel electrode (SCE) and a platinum wire were utilized as reference and counter electrodes, respectively. All the electrochemical measurements were conducted using a RDE at room temperature, using a potentiostat Pine Instrument Co., AFCBP-1.

2.2. Density functional theory calculations

Full geometry optimizations and activation energy calculations of selected steps during the ORR were performed using the Vienna ab Initio Simulation Package (VASP) [24,25]; for all models spin polarized calculations were employed. The Projector Augmented wave (PAW) potentials were employed to describe the interactions between ions and electrons. Exchange-correlation was described using the parametrization of Perdew-Burke-Ernzerhof [26] within the generalized gradient approximation. The wave functions were expanded in the plane wave basis up to a kinetic energy of 600 eV, k-point sampling was done by 5 × 5 × 1 Gamma centered k-point grids within the Monkhorst-Pack scheme, both wave function expansion and k-point sampling were tested for convergence. The model used for the calculations (Fig. 1) consisted of a 4 × 4 graphene layer in which doping was performed by substitution of a carbon atom in the center of the unit cell (i.e. graphitic N doping), to construct the slab model and enabling adsorption, a 12 Å vacuum space was allowed in the z direction. All atoms were allowed to relax until the forces became lower than 0.05 eV/Å while the criteria for electronic loop convergence was set to a difference of 1×10^{-4} eV between successive steps.

The Climbing-image Nudged Elastic Band (CNEB) method [27] was used to find the saddle point along the path formed by the

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