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Cerium doped graphene-based materials towards oxygen reduction reaction catalysis

Lanna E. B. Lucchetti^a, Pedro A. S. Autreto^a, Mauro C. Santos^a, James M. de Almeida^b

^a*Centro de Ciências Naturais e Humanas (CCNH) - Universidade Federal do ABC (UFABC), Santo André, SP, Brazil*

^b*Ilum School of Science (CNPEM), Campinas, SP, Brazil*

Abstract

With the global transition towards cleaner energy and sustainable processes, the demand for efficient catalysts, especially for the oxygen reduction reaction, has gained attention from the scientific community. This research work investigates cerium-doped graphene-based materials as catalysts for this process with density functional theory calculations. The electrochemical performance of Ce-doped graphene was assessed within the computation hydrogen electrode framework. Our findings reveal that Ce doping, especially when synergized with an oxygen atom, shows improved catalytic activity and selectivity. For instance, Ce doping in combination with an oxygen atom, located near a border, can be selective for the 2-electron pathway. Overall, the combination of Ce doping with structural defects and oxygenated functions lowers the reaction free energies for the oxygen reduction compared to pure graphene, and consequently, might improve the catalytic activity. This research sheds light from a computational perspective on Ce-doped carbon materials as a sustainable alternative to traditional costly metal-based catalysts, offering promising prospects for green energy technologies and electrochemical applications.

Keywords: Graphene, cerium, oxygen reduction reaction, density functional theory

1. Introduction

As the world shifts toward cleaner and more sustainable energy generation, the development of efficient catalysts is critical (Chu et al., 2017). Electrochemical processes play a pivotal role in a wide range of energy conversion technologies and green chemistry applications, such as fuel cells (Souza et al., 2022) and water treatment (Santos et al., 2022). The oxygen reduction reaction (ORR) is particularly important in that context (Tian et al., 2020). When this reaction follows a 4-electron mechanism, oxygen molecules are electrochemically reduced to water, releasing energy that can be harnessed to generate electricity. On the other hand, hydrogen peroxide is obtained when it follows a 2-electron mechanism, a very attractive alternative to the harmful anthraquinone process (Siahrostami et al., 2013). Regardless, the ORR is central to the operation of many clean energy systems and greener processes, and its efficiency is of paramount importance for the practical viability of these technologies. Traditional catalysts used in these processes, however, are usually based on rare and expensive metals. Therefore, new catalysts based on more abundant and sustainable materials are detrimental to reducing the environmental impact of the new processes and enhancing their sustainability. Furthermore, the novel catalysts also have to promote a good electrochemical performance of ORR both in terms of activity and selectivity.

In this sense, recent progress in materials science and computational modelling techniques has opened up new possibilities for designing catalysts with precisely tailored structures and properties. This design-driven approach allows researchers to optimize catalysts for specific applications, potentially achieving breakthroughs in ORR efficiency. Additionally, metal-doped graphene systems have been exhaustively investigated

with theoretical calculations (Lucchetti et al., 2021; Zhang et al., 2023; Fan et al., 2023). However, because most studies focus on transition metal doping, Ce-doped carbon surfaces remain to be explored. Some studies in that direction have investigated different catalytic reactions on Ce single atoms adsorbed on carbon nanotubes (Zhang et al., 2011), Ce atoms adsorbed on graphene flakes (Lashanizadegan et al., 2020), and Ce-N-coordinated graphene (Li et al., 2021). Other works combine cerium with carbon nitride (Sun et al., 2023; Yang et al., 2023) or boron nitride sheets (Guo et al., 2023). Besides aiming to address a less explored route in metal functionalization for graphene, this work is also motivated by a contemporary issue regarding rare earth metals mining. Ce and La make up for 70% of the mined rare earth metals, and Ce is the predominant element in rare earth ores (Sims et al., 2022; Binnemans and Jones, 2015). However, despite its availability, Ce is still treated as an undesirable and a low-value byproduct. Therefore, investigating and developing novel applications to employ Ce might eventually induce a positive effect on the waste and environmental impacts of the mining industry, while simultaneously providing cheaper and relatively abundant catalysts compared to precious or scarce transition metals.

Herein, the catalytic activity of different graphene-based materials doped with Ce in combination with structural defects, oxygenated functions, and borders, is assessed with density functional theory (DFT) calculations. Our results show that Ce doping can improve the catalytic activity of the carbon sheets. Particularly, the combination of cerium doping with an oxygen atom has the best performance, indicated by the lowest theoretical overpotential values for both 4-electron and 2-electron ORR. When this functionalization is close to a border, the 2-

electron ORR overpotential becomes significantly lower, indicating a promising site to promote H_2O_2 electrogeneration selectively. This investigation has been carried out to fill in a gap in the theoretical literature and to shed light on the role of Ce doping in the catalytic activity of graphene towards the ORR.

2. Methods

We have investigated different combinations of Ce functionalization with 1) defects on the carbon network — double vacancy, 555-6-777 and 555-777; 2) oxygenated functions — Ce coordinated with one, two, or three oxygen atoms; and 3) finite clusters containing either a double-vacancy or its combination with one oxygen atom. Atomically dispersed cerium atoms on graphene have been previously reported and investigated by (Hwang et al., 2018) and by (Lashanizadegan et al., 2020). Furthermore, 5-9 nm wide CeO_2 nanoparticles, which is very close to a single Ce coordinated with O atoms on graphene, have been synthesized by (Zhao et al., 2018), combined with Cu and graphene with great catalyst stability being reported by the authors. Furthermore, cerium incorporated to graphene was obtained by Li et al. (2022). These experimental works illustrate the stability of similar structures, even though the exact nature of the catalytically active Ce site coordination remains to be determined. The different functionalizations proposed in our work have been based on experimental findings, like the aforementioned ones and by similar computational investigations carried out for different single metal doping graphene, such as single atom Fe-doped graphene (Jiang et al., 2019). We reckon that there are numerous possibilities of vacancies, defects and oxygenated functions combined with single-atom catalysts, making it impossible to address all at once. We approached this issue by selecting different combinations that have not yet been reported in the literature for Ce, but have shown good catalytic activity with other metals (Lucchetti et al., 2021; Jiang et al., 2019). Figure 1 illustrates the structural models considered in this work and these structures will be referred to as D1, D2, D3 (defects); O1, O2, O3 (oxygenated functions), C1 and C2 (clusters).

To optimize the selected structures and access their catalytic activity towards the ORR, plane-wave DFT calculations were performed with the Quantum ESPRESSO package (Giannozzi et al., 2009). Standard solid-state efficiency pseudopotentials (SSSP) were employed to describe core electrons (Prandini et al., 2018), and plane-wave basis functions with a 50 Ry kinetic energy cutoff to describe valence electrons. The exchange-correlation energy was treated with generalized gradient approximation functionals (GGA-PBE) (Perdew et al., 1996). A Hubbard-like parameter of $U_{\text{eff}} = 5\text{eV}$ was applied to correct the on-site Coulomb interaction of localized Ce-4f states (Zacherle et al., 2013). The ORR was modelled to address the two possible reaction mechanisms, according to the following equations (Nørskov et al., 2004):

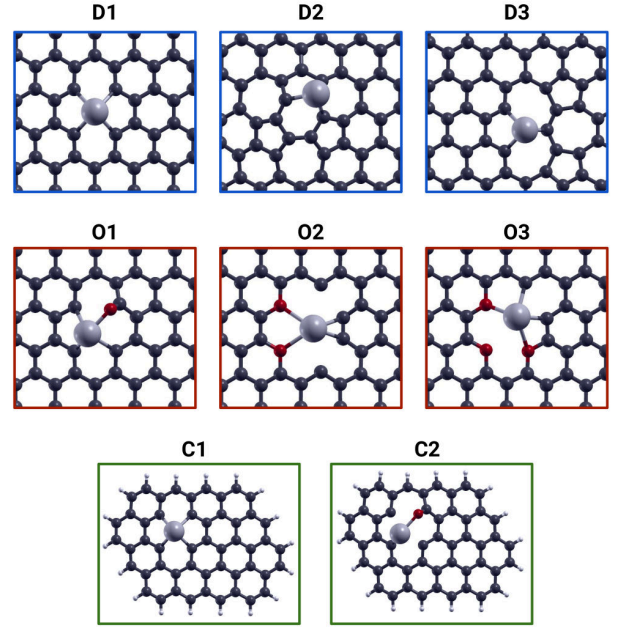
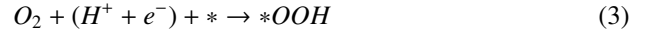
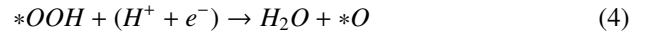


Figure 1: Selected structural models of Ce doping combined with different defects (blue framed), oxygenated functions (red framed), and clusters (green framed). The defects are, respectively: a carbon double vacancy (D1), a 555-6-777 defect (D2), and a 555-777 defect (D3); Ce coordinated with one (O1), two (O2) and three (O3) oxygen atoms; a carbon double vacancy (C1) and Ce coordinated with one oxygen atom (C2) clusters.

The reaction mechanism is given by:



where (*) indicates a surface site. The $* \text{OOH}$ is a key intermediate after which a H_2O_2 molecule can be formed on the 2-electron pathway, or it can undergo further reduction along with the O-O bond break, following the 4-electron pathway. This reaction can be modeled within the computational hydrogen electrode (CHE) framework proposed by Nørskov *et al.* (Nørskov et al., 2004). In this case, the intermediate reaction steps, namely $* \text{OOH}$, $* \text{O}$, and $* \text{OH}$ are simulated with DFT adsorption calculations. The adsorption energies are calculated taking gaseous H_2 and H_2O molecules as references, considering the system to be in equilibrium and at $\text{pH} = 0$. Under these assumptions, the energy of a proton/electron pair can be given by:

$$(\text{H}^+ + \text{e}^-) = \frac{1}{2} \text{H}_2 \quad (7)$$

The experimental reduction potential values are also considered, to determine the total reaction Gibbs free energy change

- $E^0 = 1.23V$, for the 4-electron and $E^0 = 0.70V$ for the 2-electron ORR. Finally, the theoretical overpotential (η), used to describe the catalytic activity is calculated according to the following equation :

$$\eta = \frac{\max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]}{e} \quad (8)$$

The limiting potential (U_{lim}) is derived from Equation 8 as follows:

$$U_{lim} = E^0 - \eta \quad (9)$$

3. Results and Discussion

The stability of the proposed functionalizations in this work has been investigated in terms of formation energies. The formation energy was determined by taking the obtained surface and subtracting the total energy of its isolated compounds - the graphene sheet, without the functionalization, and the O and Ce atoms, taking the O_2 molecule, when applicable, and the cubic Ce Fm3m structure as a reference Jain et al. (2013). This is summarized by the following equation:

$$E_{form} = E_{structure} - E_{graphene} - E_{Ce} \quad (10)$$

Employing this equation, negative formation energy values will indicate that the obtained structure is energetically favourable in comparison with its isolated compounds. Table 1 shows the obtained formation energies and it can be seen that the adsorption of the Ce functionalization to the defected graphene sheets is favourable in all cases proposed in this work.

Surface	$E_{form}(eV)$
D1	-4.45
D2	-3.72
D3	-4.80
O1	-6.20
O2	-10.13
O3	-10.82
C1	-4.94
C2	-7.67

Table 1: Calculated formation energies of the different functionalizations proposed in this work.

Figure 2 shows top and side views of all ORR intermediate reaction steps ($*OOH$, $*O$, and $*OH$) on the different structures after relaxation. The Gibbs free energy diagrams in Figure 3 and the calculated theoretical overpotential values in Table 3 show that Ce-doping lowers the adsorption energy of all ORR intermediates compared to pristine graphene. When Ce is combined with a double vacancy or a 555-777 defect (D1 and D3), as shown in Figure 3a, the $*OOH$ adsorption free energy values become closer to the ideal. However, the interaction with the $*O$ intermediate is too strong and that could lead to surface poisoning or hinder the catalytic activity altogether. On D2, the adsorption energy of all intermediate species is below the acceptable range for a catalytic material. This can be attributed

Surface	$\eta(4e^-)$	$\eta(2e^-)$
pristine	2.03	1.50
D1	1.73	0.64
D2	3.28	2.96
D3	1.94	1.75
O1	0.87	0.64
O2	2.15	1.82
O3	1.15	1.51
C1*	n/a	n/a
C2	3.00	0.12

Table 2: Calculated theoretical overpotentials for the 4-electron and 2-electron oxygen reduction reaction on different Ce-functionalized graphene.

(*)The ORR species are not stable and desorb from the structure forming a defect in this case.

to the considerable surface distortion that happens along with the reaction steps in this case. Interestingly, D1 has a theoretical overpotential of $\eta = 0.64 V$ for the 2-electron pathway and $\eta = 1.73 V$ for the 4-electron pathway. While ΔG_{*OOH} is ideal on this surface, ΔG_{*O} is too negative, making the O-O bond break the potential determining step. The strong interaction between the Ce and the O atom also results in a bond stretching to the point that the Ce atom moves away from the carbon network, indicating that further stabilizing would be required in this case. This could be achieved by surrounding the Ce atom with more electronegative species, such as oxygen itself, or nitrogen. The overpotential value $\eta = 0.64 V$ is still higher than ideal, but it indicates that this structure could be selective for the 2-electron ORR.

On the other hand, when Ce is combined with oxygenated functions, the catalytic activity can be tuned accordingly. The O1 structure particularly approaches the ideal catalytic behavior (Figure 3b), lowering the reaction free energy values. It can also be noted that the oxygen coordination indeed promotes additional stabilization of the Ce atom, which does not move away from the carbon support in this case (Figure 2). The 2-electron overpotential is similar to the D1 structure, and the 4-electron ORR has an overpotential of $\eta = 0.87 V$. As the number of oxygen atoms increases, however, the interaction between the Ce atom and the ORR intermediates becomes too strong, which worsens the catalytic performance. Among the three structures considered in this case, O1 is the most promising for ORR applications via either 2-electron or 4-electron pathways.

The catalytic profile of Ce-doped graphene combined with either structural defects or oxygen atoms is overall very similar to what has been observed by Liu *et al.* (Li et al., 2021). The authors noted that cerium-doped graphene coordinated by nitrogen atoms had better catalytic activity than pristine graphene, with negative Gibbs free energy following the reaction steps. However, the calculated theoretical overpotential values were still too high for most Ce-N-doped graphene structures due to the considerably strong absorption of ORR intermediate species. The only exception among the investigated structures in this work was Ce(OH)-N₄-C, where the Ce atom was also coordinated with an -OH axial ligand, with comparable catalytic performance to Fe-N₄ doped graphene. In fact, other works in

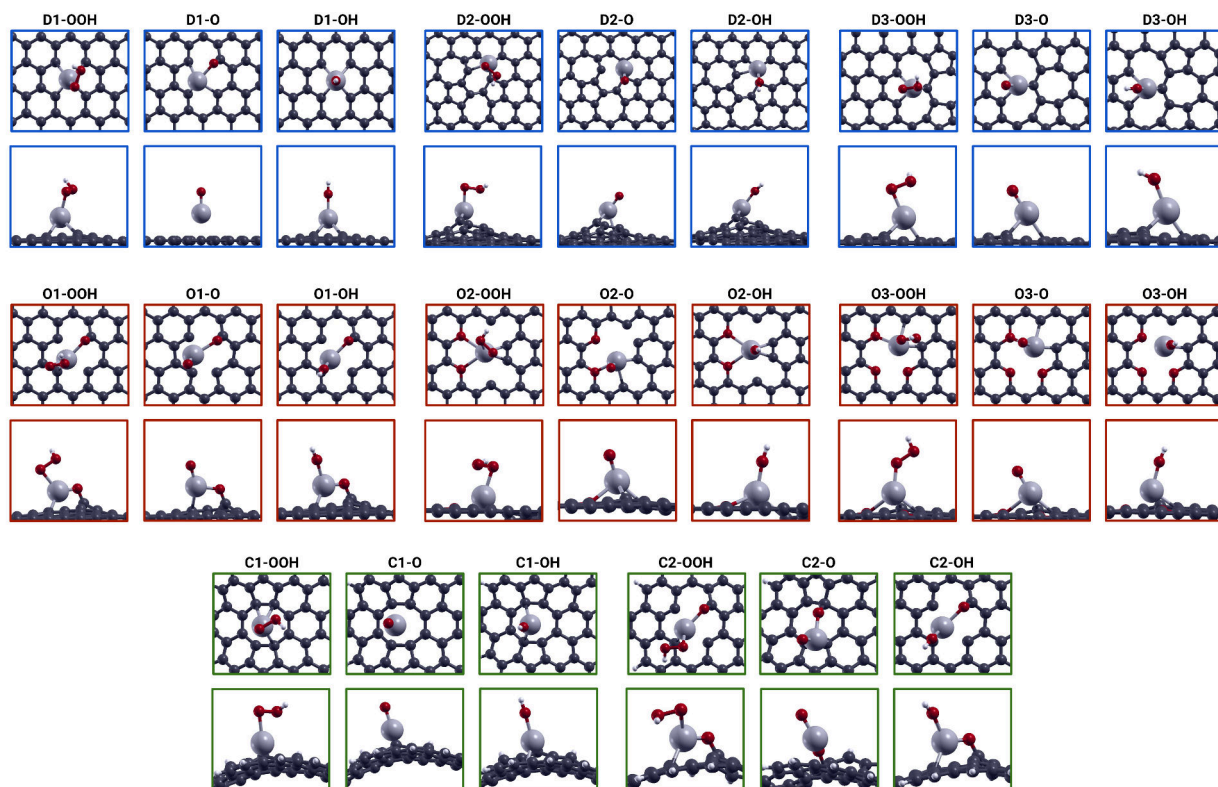


Figure 2: Optimized coordinates of oxygen reduction reaction steps on different Ce-functionalized graphene.

the literature suggest that not only the -OH axial ligand can improve the catalytic activity, but it can also shift the preferred pathway (Wang et al., 2020; Zhang et al., 2017), which can be a promising direction for future studies of Ce-doped carbon materials.

On the other hand, when the ORR intermediates are adsorbed on the double-vacancy Ce-doped cluster (C1) the oxygen atom forms a strong bond with the cerium atom and it desorbed from the surface. The strong bonds yield very negative adsorption free energy values, and as the species desorbed, Stone-Wales defects are formed in all cases (Figure 2). This means the ORR is not favorable and this would be a poor catalytic site for this reaction. However, it can be seen that when a Ce atom is close to a border and interacts with oxygenated species forming a Stone-Wales defect, the carbon network reactivity can change. This is aligned with experimental works in the literature, where carbon-based catalysts had more defects and oxygenated groups after their modification with ceria nanostructures (Pinheiro et al., 2018; Assumpção et al., 2012).

Furthermore, (Lashanizadegan et al., 2020) have shown that Ce/Cd nanocatalysts exhibited excellent performance and stability towards the 4-nitrophenol reduction and olefin oxidation reactions. Additionally, a work from (Zhao et al., 2018) presented a synthesized Cu-Ce graphene catalysts for CO oxidation where the experimental characterization via XRD, XPS, and Raman spectra indicated that the well dispersed Ce could be found in combination with oxygenated species. The authors

state that the interaction with dispersed Ce and graphene is very significant, stronger than that of Cu, providing experimental evidence of the stability of these structures. Their results indicate that the catalysts prepared in this work would perform poorly for the CO oxidation reaction when those were single metal-supported catalysts, namely Cu/graphene and Ce/graphene, whereas the bimetallic catalysts had a better performance, attributed to the relative number of active species and oxygenated groups on the catalytic surface, which were determined by the Cu/Ce molar ratio. These experimental findings can be correlated with what has been observed in this work, since our DFT calculations show that different proposed sites yielded very different catalytic profiles, and the combination of Ce with a second metallic atom might have induced changes in the catalyst structure and its specific sites, therefore shifting the catalytic activity, as the authors indicate.

Similar to what was observed for the periodic system, a neighboring oxygen added to the C2 model can stabilize the Ce atom and the cluster retains its structure when the *OOH intermediate is adsorbed on this site. A high theoretical overpotential for the 4-electron pathway is observed, nonetheless, due to a strong interaction with the *O intermediate species and a different carbon defect formed in this case. The ΔG_{*OOH} value, however, is ideal for the 2-electron pathway, yielding a very low overpotential value of $\eta = 0.12$ V. If *OOH is taken as a descriptor, a volcano plot can be built, so the catalytic activity can be evaluated in terms of the limiting potential, as shown in

Figure 3d. Pristine graphene, indicated by the gray data point, is also plotted for comparison. It can be seen that most of the selected structures have poor catalytic activity with unfeasible limiting potentials, like D2, D3, O2, and O3. Three configurations are promising – D1 and O1, where the reaction might occur at higher onset potentials in the experimental setting, and C2, with the lowest overpotential among all structures considered in this study, and therefore lying on the top of the volcano.

4. Conclusions

This research has demonstrated that cerium (Ce) doped graphene-based materials can provide a promising avenue for catalyst design. The study's theoretical findings using DFT calculations reveal that Ce doping shows improved catalytic activity towards the ORR, enhancing the potential for clean electricity generation and hydrogen peroxide electrogeneration. Our results are in agreement with previous experimental works in the literature, where the functionalization with cerium and oxygen resulted in carbon-based materials with better performance for the ORR in comparison with their non-functionalized counterparts. Moreover, when considering different structural models of Ce-doped carbon, it was found that certain combinations are more effective in promoting the desired reactions, such as Ce doping when combined with an oxygen atom and located near a border has the potential to be selective for the 2-electron pathway. These results shed light on Ce-doped carbon catalysts and show that understanding the catalytic activity at an atomic level is paramount for the development of novel materials.

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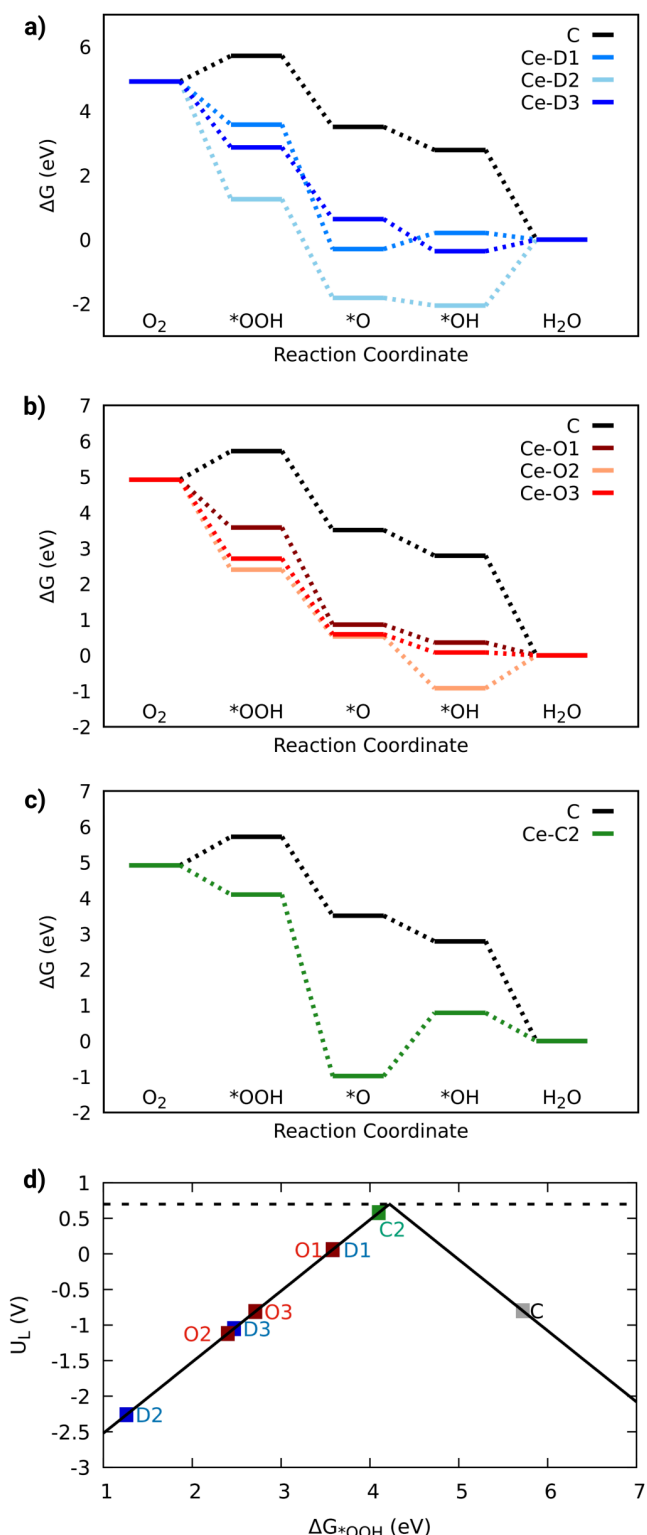


Figure 3: Gibbs free energy diagrams on different Ce-functionalized graphene (a-c) and volcano plot of the catalytic activity in terms of $*OOH$ Gibbs free energy and limiting potential for the 2-electron pathway (d).

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