Revealing the Li$_2$O$_2$ Nucleation Mechanisms on CeO$_2$ Catalysts for Lithium-Oxygen Batteries

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The addition of ceria (CeO$_2$) nanoparticles to the cathode of a lithium-oxygen battery results in increased capacity, lower overpotentials and better cyclability. To shed light on the mechanisms of this performance enhancement, we have investigated the early stages of Li$_2$O$_2$ nucleation at stoichiometric and reduced ceria surfaces by means of atomistic simulations based on density functional theory. Adsorption energies are stronger on ceria than on graphene, that is, nucleation mainly would take place on the oxide. The adsorption process of O$_2$ is the one that determines the nucleation sites for the Li$_2$O$_2$ formation on the different CeO$_2$ surfaces. The LiO$_2$ intermediate is adsorbed at the O$_2$ reduction sites. On the reduced (100) surface, the LiO$_2$ tends to adsorb dissociatively, opening up the possibility to the formation of other species than the desired end-product, Li$_2$O$_2$. On the contrary, optimal properties are found for the reduced (110) surface, which should therefore be the most active surface for Li$_2$O$_2$ nucleation among all low-index surfaces of ceria. These findings could pave the route to produce better cathodes for Li-oxygen batteries by the addition of carefully designed ceria nanoparticles, which maximizes the exposition of the most favorable facet.

Introduction

Despite the efforts for approaching in practice its high theoretical energy density, the deployment of Li–O$_2$ batteries (LOB) is hindered by many challenges. With reason, it has been suggested that, instead of simply sticking to performance improvements of LOBs, fundamental issues should be considered.[1] Among these issues are the effect of the solvent on the morphology and charge transport properties of the discharge product,[2,3] the use of redox mediators (liquid catalysts),[4–8] modifying the porosity of the carbon cathode,[9,10] the use of noble metals and metal oxide catalysts.[11–13] In this work, we focus on ceria (CeO$_2$), a promising catalyst for LOBs,[14–17] with the aim to shed light on the mechanisms operating in the nucleation of Li$_2$O$_2$ at stoichiometric and reduced ceria surfaces by means of atomistic simulations based on density functional theory.

The growth mechanism of Li$_2$O$_2$ during the discharge of the non-aqueous Li–O$_2$ battery (LOB) varies depending on the donor number (DN) of the solvent.[2] When DN is high, there are more solvated LiO$_2$ species and the solution mechanism prevails, increasing the battery capacity but leading to the formation of large (toroidal shape) Li$_2$O$_2$ particles, whose re-dissolution during the recharge requires high over-potentials. On the other hand, when DN is low, O$_2$ is reduced to superoxide on the cathode surface where it combines with a Li$^+$ ion to form LiO$_2$ (adsorbed at the cathode surface), which reduces again or it disproportionates to form adsorbed Li$_2$O$_2$. Since Li$_2$O$_2$ is a large band gap insulator,[18] the charge transport occurs by tunneling through thin Li$_2$O$_2$ films (up to 10 nm thick), which limits the capacity of the battery, although it exhibits lower over-potential during recharge.[14]

As a way to circumvent this dichotomy, it has been recently shown experimentally that thicker films (non-toroidal) can grow on small CeO$_2$ nanoparticles (NPs) added to carbon nanotubes (CNT), and the solution affinity of the solvent is increased through H$_2$O addition.[14] It was suggested that the nucleation enhancement by the CeO$_2$ NPs precludes the solution mechanism despite the increased donor number, forming a thin Li$_2$O$_2$ film. This is followed by the production of LiO$_2$, from ceria-free areas of the CNT, which disproportionates in solution forming Li$_2$O$_2$ deposits on the existing thin film, maintaining its shape. Also, the strong adsorption of LiO$_2$ at CeO$_2$ microspheres supported on graphene foam has proved to improve the LOB efficiency by avoiding its dissolution in the electrolyte and forming a uniform deposit of Li$_2$O$_2$.[16]

The well known catalytic activity of CeO$_2$ due to the formation of oxygen vacancies that result in the partial reduction of lattice cerium ions from Ce$^{4+}$ to Ce$^{3+}$, together

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with reversibility of this process, facilitates both, the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) during the discharge and charge of the LOB.\textsuperscript{[19]}

It has been shown that the catalytic performance of ceria nanoparticles depends on its morphology and that the redox activity varies on the different exposed CeO$_2$ facets.\textsuperscript{[20–22]} Even in the context of the LOB, it has been reported that NPs with film-like morphology exhibits higher capacity than octahedral and spherical ones.\textsuperscript{[23]} However, no details are given regarding the different crystalline facets that are exposed in the reported NPs, and the higher capacity is explained in terms of higher surface area.

The energetic of the intermediates and precursors of the ORR at the reduced surfaces of CeO$_2$ (111) was recently studied.\textsuperscript{[24]} It was concluded that the reaction path with the lithium adsorption as the first step was the most probable one, a fact that has not been experimentally confirmed yet.

Here we study, by resorting to DFT calculations, the first step of the surface Li$_2$O$_2$ formation analyzing the adsorption of O$_2$ and LiO$_2$ intermediates on both, stoichiometric and reduced (111), (110), and (100) surfaces, to evaluate the different catalytic activity in all the low index surfaces of CeO$_2$. In the context of this work, and from the technical point of view of chemical processes that imply charged ions approaching insulating substrates. Our aim is to assess the nucleation power for Li$_2$O$_2$ of the different ceria facets, in order to suggest new routes to improve the catalytic efficiency of this catalyst in a LOB.

Details on the DFT calculations are described in the Computational methods section.

Results and Discussion

Recently, a volcano correlation was found between the discharge/charge voltage of the LOB and the LiO$_2$ adsorption on different metals.\textsuperscript{[25]} It was shown that those metals with calculated adsorption energies for LiO$_2$ close to ~2.6 eV present a better performance, that is, a smaller discharge/charge overpotential. It was linked to smaller Li$_2$O$_2$ particle size of the discharge product. In the following, we will use these optimal values as a reference.\textsuperscript{[25,26]}

In our DFT+$U$ calculations, several adsorption sites were considered for each of the species. Along this work we will use the following notation: ST = stoichiometric, SOV = surface oxygen vacancy, and SSOV = subsurface oxygen vacancy.

In the Supplementary Information we report the calculated surface energies (Table S1) and oxygen vacancy formation energies (Table S4) for the most stable configurations of the three surface orientation considered for CeO$_2$.

### Oxygen/lithium superoxo adsorption on the stoichiometric CeO$_2$ surfaces

In Figure 1, the most energetically stable configurations of O$_2$ and LiO$_2$ upon the ST (111), (110) and (100) facets are shown. Table 1 summarizes the corresponding adsorption energies ($E_{\text{ads}}$) and geometrical parameters for O$_2$ and LiO$_2$. The results for all the studied configurations are shown in the Supplementary Information (Tables and Figures S1–S3).

The valence state of the adsorbed oxygen molecule is assessed through the resulting O–O bonding length, d$_{O–O}$, upon reduction. That is, for the peroxide valence state O$_2^{2–}$, the superoxide O$_2^{–}$ and the neutral oxygen molecule, the expected d$_{O–O}$ are ~1.5 Å, ~1.3 Å and ~1.2 Å, respectively. It is worth to mention that the charged state of the molecules was confirmed by the calculated Bader charges as we show in the Supplementary Information (Table S8).

As it is known, the O$_2$ molecule adsorption on the ST facets is always a physical adsorption, with a weak adsorption energy and an adsorbed height between 2.49 and 2.80 Å. The O$_2$ molecule does not dissociate in any of the three ST facets and the oxygen bond-length is close to that of the neutral molecule ~1.2 Å. The O$_2$ adsorption orientation is similar in the ST (111) and ST (110) facets, where it remains in a lying position while it is perpendicular to the ST (100) surface. These results confirm previous studies,\textsuperscript{[21]} indicating that superoxo and peroxo species of O$_2$ do not form in the low index facets of ST CeO$_2$.

#### Table 1. $E_{\text{ads}}$, adsorbed height ($h_{\text{ads}}$) and the distance d$_{O–O}$ between oxygens for the adsorbed O$_2$ and LiO$_2$ molecules on the ST (111), (110) and (100) facets.

| Orientation | $O_2$ $E_{\text{ads}}$ [eV] | $h_{\text{ads}}$ [Å] | d$_{O–O}$ [Å] | LiO$_2$ $E_{\text{ads}}$ [eV] | $h_{\text{ads}}$ [Å] | d$_{O–O}$ [Å] |
|-------------|--------------------------|---------------------|----------------|---------------------------|---------------------|------------------|
| ST(111)     | –0.10                    | 2.69                | 1.23           | –1.41                     | 1.63                | 1.35             |
| ST(110)     | –0.16                    | 2.80                | 1.24           | –2.50                     | 1.08                | 1.33             |
| ST(100)     | –0.08                    | 2.49                | 1.23           | –1.97                     | 1.03                | 1.25             |

![Figure 1](www.chemcatchem.org)
It can also be observed in Figure 1 and Table 1, that in the ST (111) surface, the most stable adsorption energy of LiO$_2$ is $-1.41 \text{ eV}$ with an adsorption height of 1.63 Å, being this one, the weakest adsorption among the three facets. On the other hand, the ST (110) and ST (100) cases have adsorption energies of $-2.50 \text{ eV}$ and $-1.97 \text{ eV}$, with similar adsorption heights. Resorting to the volcano behavior, the ST (110) facet presents an adsorption energy that is very close to the one of the top of the volcano ($-2.6 \text{ eV}$), indicating that it could have a good performance in the formation and decomposition of Li$_2$O$_2$.

Each facet shows a different adsorption orientation of the LiO$_2$ molecule, as depicted in Figure 1. For both, ST (111) and ST (110) facets, the LiO$_2$ is slightly tilted and the O$_2$ bond length is 1.35 Å, that corresponds to the superoxo species. On the other hand, at the ST (100) surface, the LiO$_2$ is basically dissociated, leading to adsorbed Li and the formation of one surface Ce$^{+3}$, meanwhile, the O$_2$ moves away with $d_{o_{2}-0}=1.25$ Å, that is close to that of the neutral species.

These results show that the LiO$_2$ molecule can be adsorbed at the ST CeO$_2$ (111) and (110) surfaces, the last case presenting an adsorption energy which is very close to the optimal value of the volcano plot. However, taking into account that O$_2$ does not get reduced at the stoichiometric CeO$_2$ surface, it should find alternatives paths to get reduced in order to form Li$_2$O$_2$, for instance through the solution mechanism at unpassivated areas of the carbon cathode close to the NPs.

**Oxygen/lithium superoxo adsorption on the reduced CeO$_2$ surfaces**

In this section, we will describe the adsorption of these intermediate species at the reduced CeO$_2$ surfaces.

Recently, a controversy has aroused on the stability of the SOV configuration in the (111) surface. On one hand, Sauer and coworkers provided evidence for the formation of various superoxo and peroxo species at single crystal O-vacancy sites on reduced CeO$_2$ (100) and (110) surfaces, but not on the reduced (111) one, which is the more stable surface orientation. Since the calculated formation energy of the oxygen vacancy in the subsurface is $\sim 0.28 \text{ eV}$ lower than the surface one, the absence of superoxo and peroxo formation at this particular facet is assigned to a subsurface diffusion of O vacancies. However, Schilling et al. show through in situ Raman spectroscopy that in contrast to single crystals, the (111), truncated nanoparticles possess both surface and subsurface oxygen vacancies, and peroxides species do form at $35^\circ C$. Therefore, both vacancy configurations should be considered in the (111) facet if aiming to describe the effect of CeO$_2$ nanoparticles in the context of the LOB.

The calculated formation energies of the vacancies at each surface are presented in the Supplementary Information (see Table S4). It is important to remark, that despite the (111) orientation is the more stable one, the formation energy of the oxygen vacancy is lower in the (110) one, so that a higher concentration of Ce$^{+3}$ is expected at this surface.

In Figure 2 we show the optimized adsorption configurations of O$_2$ and LiO$_2$ for the more stable situations in the SSOV (111), SOV (111), SOV (110) and SOV (100) facets. Table 2 summarizes the corresponding adsorption energies and geometrical parameters. Again, the results of the rest of the studied configurations are given in the Supplementary Information (Tables and Figures S5–S7).

In the SOV (110) and SOV (100) cases, the O$_2$ prefers to fill the oxygen vacancy site and the bond length is increased from 1.23 Å to 1.44 and 1.47 Å, close to the characteristic bond length of the peroxo species. The O$_2$ reduction leads to the oxidation of a Ce$^{+3}$ to Ce$^{+4}$ (see Figure 2), in agreement with previous reported calculations. The adsorption energies of the more stable situations in the (110) and (100) surfaces are $-1.30$ and $-2.03 \text{ eV}$, respectively, in contrast to the SSOV (111) one where O$_2$ presents a physical adsorption with a bond height of 1.83 Å and a $d_{o_{2}-0}$ bond length of 1.26 Å, close to the one of the neutral O$_2$, 1.23 Å. Furthermore, in this last case, the two Ce$^{+3}$ remains at the surface, and the O$_2$ is not reduced, confirming previous results by Sauer and coworkers.

Even when the SOV (111) surface orientation is not the more stable defect situation, we have also studied the O$_2$ and LiO$_2$ adsorption on the SOV (111) case because, as mentioned before, in truncated NPs is a plausible one. The most stable adsorption structures of O$_2$ upon the SOV (111) surface are

![Figure 2. The most stable adsorbed configuration of O$_2$ and LiO$_2$ onto SSOV (111), SOV (111), SOV (110) and SOV (100) facets, top and side view.](image-url)

| Orientation | $E_{ads}$ (eV) | $h_{ads}$ (Å) | $d_{o_{2}-0}$ (Å) | $E_{ads}$ (eV) | $h_{ads}$ (Å) | $d_{o_{2}-0}$ (Å) |
|------------|---------------|-------------|-------------|---------------|-------------|-------------|
| SSOV(111)  | $-0.25$       | 1.83        | 1.26        | $-3.12$       | -           | 1.46        |
| SOV(111)   | $-2.03$       | -           | 1.44        | $-2.77$       | 0.47        | 1.47        |
| SOV(110)   | $-1.30$       | -           | 1.44        | $-2.98$       | 1.37        | 1.47        |
| SOV(100)   | $-2.03$       | -           | 1.47        | $-4.02$       | 0.12        | 1.46        |
shown in Figure 2 and Table 2. In this surface, the O\textsubscript{2} also prefers to fill the SOV site increasing the d\textsubscript{o-\textsubscript{O}} bond-length up to 1.44 Å (the peroxo bond-length), while two Ce\textsuperscript{3+} are oxidized to Ce\textsuperscript{4+} (see Figure 2).

In the SSOV (111), SOV (110) and SOV (100) facets the final d\textsubscript{o-\textsubscript{O}} bond lengths of the more stable adsorbed LiO\textsubscript{2} molecules are 1.46 and 1.47 Å, close to the corresponding bond length of the peroxo species. The LiO\textsubscript{2} is reduced leaving only one Ce\textsuperscript{3+} at the surface (see Figure 2).\[27\]

In the SSOV (111), the LiO\textsubscript{2} is slightly tilt, and one of the oxygen’s surface moves towards the subsurface vacancy site to fill it. In the SOV (110), the LiO\textsubscript{2} is in a flat-lying position with an adsorption height of 1.37 Å to the SOV site. On the other hand, in the SOV (100) case, the LiO\textsubscript{2} dissociates and the O\textsubscript{2} stays close to the vacancy site with an adsorption height of 0.12 Å and the Li is adsorbed farther from the O\textsubscript{2}.

Regarding the LiO\textsubscript{2} adsorption energy and resorting to the volcano plot,\[25\] the closest value to the top of the volcano plot obtained is for the SOV (110) surface with E\textsubscript{ads}(LiO\textsubscript{2}) = −2.98 eV, followed by the SSOV (111) with the E\textsubscript{ads}(LiO\textsubscript{2}) = −3.12 eV, and then by the SOV (100) case with E\textsubscript{ads}(LiO\textsubscript{2}) = −4.02 eV. Again, as with the stoichiometric surfaces, it should be remarked that O\textsubscript{2} does not get reduced at the SSOV (111) configuration. Therefore, in order to form LiO\textsubscript{2}, the O\textsubscript{2} molecules should first find alternatives places to get reduced.

For the SOV (111) case, as in the previous ones, the LiO\textsubscript{2} is reduced in a peroxo situation and prefers to fill the SOV site while the adsorbed LiO\textsubscript{2} remains slightly tilt over the surface (see Figure 2). Despite the final LiO\textsubscript{2} adsorption configuration is similar for both, the SOV and SOV defects of the (111) orientation, there is a difference of 0.35 eV in the adsorption energy, being the LiO\textsubscript{2} adsorption stronger on the SSOV than on the SOV surface. The LiO\textsubscript{2} adsorption in the SOV (111) facet is close to the optimal value of the volcano plot;\[25\] although the energetic indicates that the SOV vacancy site is expected to be scarcer.

It is worth to mention that either, in the stoichiometric or in the reduced CeO\textsubscript{2}, after the molecular adsorptions, the bond O–O of the O\textsubscript{2} and LiO\textsubscript{2} intermediates never breaks. The stability of this bond in the different facets is a necessary condition for Li\textsubscript{2}O\textsubscript{4} formation, and an indication that non desired side reactions are unlikely.

Another important remark is that the calculated adsorption sites of the O\textsubscript{2} molecule are the same as for the adsorbed LiO\textsubscript{2}. In all the cases the adsorbed O\textsubscript{2} fills an oxygen vacancy and gets anchored there. This fact indicates that the initial O\textsubscript{2} reduction will determine the nucleation sites for Li\textsubscript{2}O\textsubscript{4} formation within the surface mechanism at the ceria facet. This conclusion is at variance with the one by Li et al.;\[26\] that claim that Li\textsuperscript{+} adsorption is the first step of the reaction path. In that work, the calculated adsorption energy of neutral Li was stronger than that of the oxygen molecule. However, we believe that the adsorption energy of neutral Li does not account for the electrochemical process in which a charged Li is adsorbed at the surface.

Summarizing, the oxygen vacancy formation energy is lowest at the (110) surface, so that this orientation is expected to be more easily reduced than the others. This is important because, without vacancy sites at the surface, the O\textsubscript{2} molecule does not form peroxo nor superoxo species. On the other hand, the LiO\textsubscript{2} adsorption energy at the (110) facet is very close to the optimal value of the volcano plot;\[25\] Then, although the O\textsubscript{2} adsorption energy is stronger for the (100) facet, the LiO\textsubscript{2} dissociates there, so that no Li\textsubscript{2}O\textsubscript{4} nucleation is expected at this particular orientation. Finally, the more stable reduced condition for the (111) surface is not reactive towards O\textsubscript{2} reduction because the vacancy sites are at the subsurface layer. That is why we conclude this (111) exposed plane is not the more reactive one. However, as reported by Schilling et al.;\[22\] surface vacancy sites can be present for non-single crystal truncated particles, and considering the calculated LiO\textsubscript{2} adsorption energies, the Li\textsubscript{2}O\textsubscript{4} nucleation cannot be completely disregarded in this case. In view of all the above results we conclude that the (110) facet is the more suitable for the Li\textsubscript{2}O\textsubscript{4} nucleation.

Lithium peroxide adsorption on the reduced (110) CeO\textsubscript{2} surface

In this section, we focus on the (110) facet and we study in detail the adsorption of the LiO\textsubscript{2} molecule on the SOV (110) surface at the more stable nucleation sites determined before by the O\textsubscript{2} and LiO\textsubscript{2} intermediates. In Figure 3, the final adsorbed Li\textsubscript{2}O\textsubscript{4} molecule, with calculated adsorption energy −3.38 eV, is shown.

In order to assess the nucleation power of ceria, we also calculate the adsorption of the LiO\textsubscript{2} molecule onto the (1-100) Li\textsubscript{2}O\textsubscript{4} surface and graphene. We chose these particular cases firstly because the (1-100) Li\textsubscript{2}O\textsubscript{4} surface is the more stable one, as we show in the Supplementary Information (Table S9 and Figure S9), so that it is expected to be the more abundant exposed facet of the already formed discharge product. Secondly, graphene is usually used as a reference cathode in several theoretical and experimental works.\[14,15,28\]

We obtained E\textsubscript{ads} = −2.68 and −1.00 eV, for (1-100) Li\textsubscript{2}O\textsubscript{4} surface and graphene, respectively. The adsorption is clearly strongest at the SOV (110) CeO\textsubscript{2} surface. These results suggest, on one hand, that the LiO\textsubscript{2} prefers to be adsorbed onto ceria than on unpassivated regions of graphene, or on top of the existent Li\textsubscript{2}O\textsubscript{4}. On the other hand, this last fact implies that the amount of Li\textsubscript{2}O\textsubscript{4} deposited in the form of large particles is not expected if ceria is present at the cathode.

![Figure 3. Optimized structure of Li\textsubscript{2}O\textsubscript{4} on SOV (110) facet, top and side view.](image-url)
There are other indications that support this conjecture. First, there are several sites where LiO₂ can be adsorbed on SOV (110) with similar adsorption energies (see Tables and Figures S6–S7). Second, the adsorption energy of a LiO₂ molecule on the SOV (110) surface is larger than the cohesive energy of bulk LiO₂ (\(E_{\text{coh}} = -3.27 \text{ eV}\)). Finally, when we adsorb a second LiO₂ molecule, we observe that the less favorable configuration is that in which the second molecule is on top the first one. In view of all these facts, we conclude that LiO₂ might be prone to cover homogeneously the ceria surface rather than form large particles on it.

We also calculated the misfit factor \(\eta = \frac{|1 - 2 \Omega/(\Omega + A)|}{100\%}\), as defined by Wang et al.\(^{[29]}\) where \(\Omega\) is the surface area of (110) CeO₂ surface and \(A\) is the surface area of the more stables (1-100) and (0001) LiO₂ facets. We found a relative large \(\eta\) of 7.55 and 9.41, respectively, as compared with other works, where the misfit between LiO₂ and TiC has been studied.\(^{[29,30]}\) Therefore, we do not expect a high crystallinity of the LiO₂ deposited onto ceria.

**Conclusions**

We have studied the adsorption of O₂, LiO₂ and Li₂O at the low index surfaces of CeO₂, both in stoichiometric and reduced conditions, by DFT. The adsorption process of O₂ will determine the nucleation sites for the LiO₂ formation on the different CeO₂ surfaces. In this respect, the SOV (100) surface exhibits a strongest adsorption energy for O₂ but our results indicate that the LiO₂ bond breaks, in such a way that LiO₂ formation is not expected at this exposed plane.

On the other hand, the more stable configuration of the reduced CeO₂ (111) surface, is not reactive towards O₂ because the oxygen vacancy is at a subsurface site and, consequently, the nucleation power of this orientation is not expected to be high. However, the formation of O₂⁻ and O₂²⁻ species were reported in truncated nanoparticles\(^{[22]}\) and they exhibit rather strong calculated O₂ adsorption energies, implying that the reactivity of this plane is not null.

The adsorption of LiO₂ molecule is the key intermediate step in the LiO₂ formation, and it is considered as a descriptor for the performance of a LOB. The adsorption of LiO₂ on the different CeO₂ surfaces studied is, in general, rather strong as compared to graphene. This behavior is in line with the experimental observation of a high nucleation power of ceria NPs deposited on graphene based cathodes.\(^{[14–17]}\) In the adsorption process, the surface oxygen vacancy is filled, and the oxidation of Ce⁻³ to Ce⁺⁴ takes place.

Considering the optimal adsorption energy obtained of the LiO₂ molecule on the SOV (110) surface, together with a good reactivity for O₂, we conclude that this particular exposed plane presents better conditions as a catalyst for the LOB.

We propose that, in order to improve the efficiency of the catalyst, the exposure of the (110) NP facets should be maximized while the (100) one avoided. One possible route is the use of rod-shaped NPs (nanorods), which have been shown to expose mainly the face (110).\(^{[31–33]}\)

These discoveries are crucial not only for enriching our understanding of the mechanism of the ceria catalyst in the cathode of a LOB, but also provide direction for future promising research activities aimed at further enhancing the catalytic effect.

**Computational details**

Calculations were performed using density functional theory (DFT) with the projector augmented wave method (PAW) as implemented in the Vienna Ab initio Simulation Package (VASP).\(^{[34–36]}\) The Coulomb interaction of occupied \(f\) orbitals is corrected via the DFT + U\(^{[37]}\) approach employing the GGA-PBE\(^{[38]}\) functional and an effective Hubbard-type U parameter of 5 eV. The DFT + U approach is necessary to account for the localized nature of the Ce-4f electrons.\(^{[39–41]}\) A plane wave kinetic energy cutoff of 400 eV was used, and structures were optimized until forces acting on relaxed atoms were below 0.02 eVÅ⁻¹. Spurious interactions induced by dipole moments perpendicular to the surface are corrected with the dipolar correction.

The p(3×3), p(2×3) and c(2×2) surface unit cells studied in this work were generated by cutting bulk CeO₂ (lattice parameter \(a = 5.435 \text{ Å}\) obtained with DFT + U) without Van der Waals corrections, in reasonable agreement with the experimental value of 5.411 Å\(^{[42]}\) in the (111), (110), and (100) orientations. The resulting slab models consist of 9, 7, and 11 atomic layers separated by a vacuum layer of 12 Å\(^{[21,22]}\).

The semi-empirical C/\(\eta\)\(_{\text{e}}\) term parametrized by Grimme (DFT + D2)\(^{[43,44]}\) was added to total energies and gradients, to correct for missing long-range dispersion-type interactions that might become relevant for some adsorbed species. Van der Waals parameters for Ce were previously derived and tested.\(^{[45]}\)

The adsorption energies were calculated as:

\[
\Delta E = E_{\text{slab} + x} - (E_{\text{slab}} + E_{x})
\]

where \(E_{\text{slab} + x}\) is the total energy of the system, \(E_{\text{slab}}\) and \(E_{x}\) are the substrate and adsorbed species energies, separately.

To correct the known oxygen over-binding error, we employed the same approach as Cortes \textit{et al.}\(^{[46]}\), obtaining a correction of 14 meV using DFT + D2.

The surface energies were calculated as:

\[
\gamma_{\text{slab}} = \frac{E_{\text{slab} - nE_{\text{bulk}}}}{2A}
\]

where \(E_{\text{slab}}\) is the total energy of the slab containing \(n\) formula units, \(E_{\text{bulk}}\) is the total energy per formula unit of bulk and \(A\) is the surface area of one of the two symmetric surfaces.

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Conflict of Interest

The authors declare no conflict of interest.

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