Atomic Scaled Depth Correlation to the Oxygen Reduction Reaction Performance of Single Atom Ni Alloy to the NiO$_2$ Supported Pd Nanocrystal

Li, Haolin; Dai, Sheng; Wu, Yawei; Dong, Qi; Chen, Jianjun; Chen, Hsin-Yi Tiffany; Hu, Alice; Chou, Jyh-Pin; Chen, Tsan-Yao

Published in:
Advanced Science

Published: 14/04/2023

Document Version:
Final Published version, also known as Publisher's PDF, Publisher's Final version or Version of Record

License:
CC BY

Publication record in CityU Scholars:
Go to record

Published version (DOI):
10.1002/advs.202207109

Publication details:
https://doi.org/10.1002/advs.202207109

Citing this paper
Please note that where the full-text provided on CityU Scholars is the Post-print version (also known as Accepted Author Manuscript, Peer-reviewed or Author Final version), it may differ from the Final Published version. When citing, ensure that you check and use the publisher's definitive version for pagination and other details.

General rights
Copyright for the publications made accessible via the CityU Scholars portal is retained by the author(s) and/or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights. Users may not further distribute the material or use it for any profit-making activity or commercial gain.

Publisher permission
Permission for previously published items are in accordance with publisher's copyright policies sourced from the SHERPA RoMEO database. Links to full text versions (either Published or Post-print) are only available if corresponding publishers allow open access.

Take down policy
Contact lbscholars@cityu.edu.hk if you believe that this document breaches copyright and provide us with details. We will remove access to the work immediately and investigate your claim.
Atomic Scaled Depth Correlation to the Oxygen Reduction Reaction Performance of Single Atom Ni Alloy to the NiO₂ Supported Pd Nanocrystal

Haolin Li, Sheng Dai, Yawei Wu, Qi Dong, Jianjun Chen, Hsin-Yi Tiffany Chen, Alice Hu,* Jyh-Pin Chou,* and Tsan-Yao Chen*

This study demonstrates the intercalation of single-atom Ni (NiSA) substantially reduces the reaction activity of Ni oxide supported Pd nanoparticle (NiO₂/Pd) in the oxygen reduction reaction (ORR). The results indicate the transition states kinetically consolidate the adsorption energy for the chemisorbed O and OH⁻ species on the ORR activity. Notably, the NiO₂/Ni³/Pd performs the optimum ORR behavior with the lowest barrier of 0.49 eV and moderate second-step barrier of 0.30 eV consequently confirming its utmost ORR performance. Through the stepwise cross-level demonstrations, a structure–E_{ads}–\Delta E correspondence for the proposed NiO₂/Niⁿ/Pd systems is established. Most importantly, such a correspondence reveals that the electronic structure of heterogeneous catalysts can be significantly differed by the segregation of atomic clusters in different dimensions and locations. Besides, the doping-depth effect exploration of the NiSA in the NiO₂/Pd structure intrinsically elucidates that the Ni atom doping in the subsurface induces the most fruitful NiSA/PdML synergy combining the electronic and strain effects to optimize the ORR, whereas this desired synergy diminishes at high Pd coverages. Overall, the results not only rationalize the variation in the redox properties but most importantly provides a precision evaluation of the process window for optimizing the configuration and composition of bimetallic catalysts in practical experiments.

1. Introduction

Fuel cells (FCs) are widely acknowledged as the most promising renewable energy technologies owing to their cost-efficient, zero-emission, and environment-friendly essences fitting perfectly with the global rising issue of carbon-neutral.[1–3] The heterogeneous catalyst for oxygen reduction reaction (ORR) performance is the key bottleneck that takes the largest overpotential loss, the lowest reaction kinetics and the highest production cost among all components in FCs, hereby attracting intensive resources in academic research.[4–8] The acidic FCs have earlier penetrated into the FCs commercial market due to their relatively matured materials and engineering processes ahead of other kinds.[9] However, the redox dynamics of cathodic catalyst in such type of FC is lower than that of alkaline electrolyte ones (AFCs). In the AFCs, the ORR is inherently more efficient and less passivated than in acidic conditions.[10,11] The corresponding reaction coordinates are proceeding via a four-electron (4e⁻) route that includes two substeps, the “O₂ dissociation” and subsequent “O” (adsorbed atomic
oxygen) hydrogenation. Such a scenario enables the natural advan-
tages of transition metals for facilitating the first O₂ dissociation step (commonly regarded as the rate determine step [i.e.,
RDS])

\[
\text{Substep 1: O}_2 \text{ dissociation}
\]

\[
\text{O}_2 \rightarrow \text{O}^+ + \text{O}^-
\]

\[
\text{Substep 2: O}^\# \text{hydrogenation}
\]

\[
\text{2O}^\# + 2\text{H}_2\text{O} + 4e^- \rightarrow 2\text{OH}^- + 2\text{OH}^-
\]

consequently, shining light on the possibility of a substantially reduced noble metal usage in AFCs cathode.

Until now, precious metal platinum (Pt) is commonly recog-
nized as the second-to-none for AFCs due to its well verified first-class ORR activity compared with other single-crystal met-
als in both theoretical and practical approaches, nonetheless, its persistent earth scarcity as well as the resulting high overall cost, critically limiting the commercial applications of the func-
tional materials with high Pt loading. Hence, the screen for low- or even non-Pt electrocatalyst with high performance is imp-
ervative to access large-scale industrialization for the FCs. 

Palladium (Pd) catalyst, which is an important member of the “Pt clan” transition metals, features the high-performing ORR
that second only to Pt catalyst according to its electrochemical
activity, theoretical volcano-plot position and relatively
more resource-abundant, albeit, the material price is increas-
ing, the recycle technologies and feasibility of Pd are rela-
tively accessible as compared to those of Pt. In addition, some experimental evidences demonstrated that the Pd NCs perform
higher ORR performance than Pt ones in AFCs. Meanwhile,
to further improve the ORR activity and reduce the material cost, effective attempts by alloying with transition metals (e.g., Mo, Ni, Cu) or metal oxides (e.g., TiO₂, MoO₃, or ZrO₂) had been achieved. Nickel oxide (NiO₂), due to its large lattice mismatch and a low cost to the noble metal, is regarded as a prospective candidate for foreign support combined with highly active metal to synergistically explore the electrocatalyst’s commercial potential. Even so, inadequate activity augmentation and unwished structure disintegration is still difficult to be solved due to the inevitable disordered structures of general alloying modification.

Aiming at screening the potential structures or combinations at nano- or atomic-scale for Pd-based catalyst with the superhigh

ORR, a well-ordered core/shell-like structure, which is theoretically derived based on the d-band model theory developed by Nørskov and Hammer et al. and the optimum catalyst idea of the Sabatier principle, is considered to be an effective design strategy to controllably improve the ORR activity as well as the structural stability by introducing the synergy of ligand effect and strain effect into catalysts. Apart from those structure engineering (i.e., size, alloy, bifunctional, ligand, and lattice strain), the geometric configuration and the local confinement of the active atomic clusters in the metal and metal oxide interface raises a quantum leap on the kinetics of redox reaction in the heterogeneous catalyst surface. Such a scenario had been demonstrated in ORR by decorating atomic clusters of various sizes and species in the metallic nanoparticles. 

In these scenarios, the changes in the adsorption energy (E_ads) for the intermediate species (i.e., O₂ and OH), the d-band center (ε_d), projected DOS, and the charge density distribution are intensively studied. These results all revealing the facilitation of ORR performance by the combination effects of electron localization and the gradient distribution for the E_ads around the decorated atomic clusters. However little had been solved on the location and distribution of the atomic catalytic clusters with extreme dimension control from several atoms to a single-atom (SA) level in metal catalysts.

To address all the above-mentioned issues and obtain the NCs with a series of desirable characteristics, meanwhile considering the unavoidable heterotatom intermix occurring during fast wet chemical crystallization experimentally, we propose a NiO₂ supported Pd (NiO₂(core)/Pd(shell)) with different levels of Ni atoms intercalated in the shell Pd layer for evaluating the ORR activity by using density functional theory (DFT) calculations. With the increasing number of Ni atom(s) from few-atom to many-atom, the models are named the “NiO₂/Ni/Pd” catalyst systems. Meanwhile, the NiSA doping depth elucidates the subsurface-doping of NiSA (i.e., the interlayer of three-layer Pd, NiSA/Pd) endowing the NiO₂/Pd structure the maximum improvement in ORR by raising the most remarkable NiSA/Pd synergy combining the electronic influence and strain effect, compared to the bottom-layer and top-layer doping ones. By cross-referencing the results, we establish a structure-E_ads-ΔE correspondence for our proposed NiO₂/Ni/Pd systems concerning the ORR. Corresponding results demonstrate that the electronic structure of heterogeneous catalysts is significantly controlled by the dimension of atomic clusters. In addition, the location is the strongest effective factor among existing structure parameters in the reaction coordinate of the decorated NCs in ORR. For further clarification, the above
2. Computational Details

First-principles calculations are performed within the Vienna ab initio simulation package (VASP)\(^{49-51}\) based on DFT with the projector augmented wave (PAW)\(^{32}\) method. To describe the exchange and correlation interaction, the Perdew–Burke–Ernzerhof (PBE)\(^{33}\) functional under the generalized gradient approximation (GGA)\(^{54}\) is used. The total energy of bulk shows convergence with 20 \(\times\) 20 Monkhorst-Pack k-point sampling in the Brillouin zone and 420 eV cut-off kinetic energy. A 4 \(\times\) 4 supercell with six atomic layers was used to mimic the Pd(111) and the NiO\(_2\)/Ni\(^{\#}\)/Pd catalysts in a close-packed FCC(111) stacking, which is consistent with our earlier work.\(^{55-57}\) The NiO\(_2\)/Ni\(^{\#}\)/Pd (\(n = 1, 2, 3, 4, 7, 10, 13, 1\text{ML, and 2ML}) systems were made up of three layers of Pd(111) on the two trilayers of NiO\(_2\) with nine distinct Ni\(^{\#}\) substitution on Pd atom (superscript \(n\) denotes the number of doped Ni atoms). Herein, a 15 Å vacuum space was used to avoid the interaction between periodic slabs. All the involved adsorbates and the uppermost three (four) layers of the slabs were fully relaxed, while the bottom two layers of the NiO\(_2\) (Pd) were fixed. A grid of 5 \(\times\) 5 \(\times\) 1 k-point sampling was used for the slab supercell geometry optimization and transition-state (TS) calculations, while a refined 7 \(\times\) 7 \(\times\) 1 k-point sampling was implemented for precise electronic calculations (e.g., the DOS and charge analysis). The calculated optimized lattice constant of the Pd(111) and proposed NiO\(_2\)/Ni\(^{\#}\)/Pd surface model are 3.94 and 3.95 Å under PBE functional, respectively. Total energy sensitivity was examined converged for the lattice constant, k-point sampling, kinetic energy cut-off, slab thickness, and vacuum space. In this thesis, the formation energy \(E_f\) is expressed as the following equation

\[ E_f = \left( E_{sys} - \sum n_i \mu_i \right) / N \]  

(2.1)

where, \(n_i\) and \(\mu_i\) are the number of atoms and chemical potential of the species \(i\), respectively; \(E_{sys}\) is the total energy of the system. The chemical potential was calculated using the bulk energy per atom. While \(N\) denotes the total number of atoms that correspond to \(E_{sys}\). The adsorption energy \(E_{ads}\) is used to measure the strength of the bond between the slab and its adsorbate, which is defined by the equation

\[ E_{ads} = E_{sys} - E_s - E_{surf} \]  

(2.2)

here, the energy of the overall system is \(E_{sys}\), the energy of the adsorbed species is \(E_s\), and the energy of the surface is \(E_{surf}\).

The TS was determined using the climbing image nudged elastic band (CI-NEB) calculation through the VTST code,\(^{38,59}\) and the reaction barriers related to the energy difference between the initial state (IS) and the TS. In this work, the reaction barrier \(\Delta E\) is calculated by the following equation

\[ \Delta E_n = TS_n - IS_n \]  

(2.3)

here, \(n = 1\) or 2, which corresponds to the two different ORR sub-stages on different surface models, i.e., “1” means the “O\(^2\)- dissociation” stage, and “2” denotes the “O\(^*\)-hydrogenation” stage. The \(E_f\) and \(E_{ads}\) after optimization were used to determine the IS and final-state (FS) model configurations. Bader charge population was conducted on the basis of the grid-based methodology developed by Henkelman et al., which was primarily utilized to measure the charge around an atom.\(^{60,61}\) The isosurface of the charge density difference was presented to qualitatively study the charge transfer situation around embedded Ni atoms in the NiO\(_2\)/Ni\(^{\#}\)/Pd systems as follows

\[ \Delta \rho = \rho_{\text{total}} - \rho_{\text{slab}} - \rho_{\text{Ni}} \]  

(2.4)

here \(\rho_{\text{total}}\) denotes the entire system’s total charge density; \(\rho_{\text{slab}}\) means the charge density of the slab without decorated Pt; and \(\rho_{\text{Ni}}\) is the charge density of the individual Ni atoms fixed in its original position of the slabs, respectively.

3. Results and Discussion

3.1. Determination of Slab Model Configurations

The multidimensional appearances of the nine NiO\(_2\)/Ni\(^{\#}\)/Pd nanocatalyst models proposed in this work are summarized in Figure 1, these proposed designs refer to and match our prior NiO\(_2\)-Pt nanocatalyst experiments.\(^{57,62}\) (Detailed descriptions and explanations are provided in Note S1, Supporting Information). For brevity, the NiO\(_2\)/Ni\(^{\#}\)/Pd systems are simplistically represented as the “\(N\_g\)” in the follow-up discussions, that is, \(\text{Ni}_1, \text{Ni}_2, \text{Ni}_3, \text{Ni}_4, \text{Ni}_7, \text{Ni}_{10}, \text{Ni}_{11}, \text{Ni}_{13}, \text{Ni}_{1\text{ML}}, \text{and Ni}_{2\text{ML}}\) corresponding to Figure 1b–j.

The calculated system formation energy \(E_f\) is used to assess the structural stability and rationality of the NiO\(_2\)/Ni\(^{\#}\)/Pd surface models. Figure S1 (Supporting Information) provides all the associated \(E_f\) of the proposed model structures. The nine NiO\(_2\)/Ni\(^{\#}\)/Pd structures have extremely comparable negative \(E_f\) values that are in the range from \(-0.37\) to \(-0.40\) eV, which is significantly lower than 0.19 eV of pure Pd(111) benchmark. This suggests that all of the proposed NiO\(_2\)/Ni\(^{\#}\)/Pd nanocatalyst structures are energetically favorable and well-structured, indicating the intruding Ni atoms can freely spread from the basal NiO\(_2\) into the Pd thin layers, which is also consistent with our previous experimental results.\(^{57,61}\) Besides, the “single-atom Ni” doping configuration features the lowest \(E_f\) of \(-0.402\) eV among all the configurations of interest, which means the Ni\(_1\) model is probably the experimentally most attainable structure of the raised designs.

3.2. Adsorbability of Atomic Oxygen and Hydroxyl Radical

On the grounds of the Sabatier principle concerning the ORR,\(^{25}\) the bonding strength (quantified by \(E_{ads}\)) between an ideal catalyst and its adsorbed O\(^*\) (the most critical ORR intermediate) ought to be at a befitting magnitude, i.e., sufficiently strong to easily obtain intermediates O\(^*\) while keeping comparatively weak to let those O\(^*\) break loose efficiently. Therefore, we used the calculated adsorption energy of O\(^*\) (\(E_{ads}-O\(^*\))), which is regarded a
pivotal characteristic for forecasting the ORR activity of multifarious transition metals catalysts \[24, 64–66\] to initially assess the ORR patterns of the nine Ni\# model catalyst. Hereon, a calculated minus $E_{\text{ads}}$ implies a spontaneous binding, i.e., a thermodynamically favorable adsorption behavior, and vice versa (details about the atomic adsorption configurations and descriptions about the site-labels and corresponding landing locations for the O* and OH adsorption sites are supplied in Figure S2 and Note S2, Supporting Information).

From Figure 2a, the Pd(111) benchmark owns the $E_{\text{ads}}$-O* in the range of −1.22 to −1.41 eV, where its Pd-hcp sites with more moderate $E_{\text{ads}}$-O* (−1.22 eV) can be regarded as the more preferable sites for ORR. Whereas, the $E_{\text{ads}}$-O* of the eight Ni\# systems (except Ni\#1) roughly show a tendency of gradually decreasing from Ni\#1 to Ni\#2ML, i.e., for their respective M-h sites, the trend of the O* bonding strength generally follows the sequence: Ni\#1 (−1.29 to −1.30 eV) > Ni\#2 (−1.28 to −1.29 eV) > Ni\#3 (−1.25 to −1.30 eV) > Ni\#4 (−1.24 to −1.30 eV) > Ni\#5 (−1.18 to −1.30 eV) > Ni\#7 (≈ −1.21) > Ni\#10 (≈ −1.14 to −1.27 eV) > Ni\#2ML (≈ −1.02 eV). Compared to shell-component Pd, the $E_{\text{ads}}$-O* observed on these eight Ni\# systems evidently have a wider catalytic selectivity scope, and concurrently exhibit a trend of stepwise diminishing with the bottom two Pd layers (i.e., second and third Pd layer) completely replaced by Ni atoms/layers (i.e., the Ni\#10). More explicitly, the $E_{\text{ads}}$-O* at the proposed optimal hcp sites of the Ni\#1 to Ni\#4 (−1.24 to −1.30 eV) perform slightly stronger adsorbability than that of the benchmark Pd(111) (−1.22 eV), which predicts a more easily O2 dissociation with lower activation barriers to break the tough O–O bond compared to Pd.

In contrast, the rest of the Ni\#7 to Ni\#2ML show the relatively weaker $E_{\text{ads}}$-O* (−1.02 to −1.18 eV) than that of the Pd(111), which assumes a harder O2 splitting but a potential easier O* hydrogenation than the others. It is worth noting that the Ni\#13 significantly features the strongest $E_{\text{ads}}$-O* with the largest range from −1.39 to −2.77 eV, which is mainly attributed to the distinguishing arrangement of its doped thirteen Ni atoms, where its upper three Ni atoms incorporated into the outermost Pd layer exposing outside straightforwardly leading to the undesired metal Ni’s adsorbability with severely excessive $E_{\text{ads}}$-O* nearly −3 eV, rather than to improve the $E_{\text{ads}}$-O* of metal Pd via the synergistic effect between the overlying Pd and the underneath Ni just like the other Ni\# systems (corresponding values of the $E_{\text{ads}}$-O* at various adsorption sites of each surface model are presented in Table S1, Supporting Information).

Analogically, from Figure 2b, compared to the adsorption energy of adsorbed OH radical (i.e., $E_{\text{ads}}$-OH) of the referential
atomic oxygen ($O^\bullet$) through the calculated $E_{\text{ads}}-O^\bullet$. Specifically, when the surface metallic atoms are compressed/stretching, the overlap of $d$ orbitals between neighboring metal atoms increases/decreases, causing the broadened/narrowed bandwidth and the downshift/upshift of the $\epsilon_d$ versus the Fermi level ($E_{\text{Fermi}}$) to keep the $d$-band filling, thus leading to the more/less occupied states of $d$ orbitals and the resulting weaker/stronger chemisorption for the intermediate $O^\bullet$. Figure 3 depicts the calculated correspondence relationship between the calculated $\epsilon_d$ of the selected three-fold hcp site and the value of its $E_{\text{ads}}-O^\bullet$. For comparison, the selected triatomic hcp site for all models correspond to the same central locus on outermost surfaces (details about the selected M-hcps and corresponding values of the $\epsilon_d$ and $E_{\text{ads}}-O^\bullet$ are listed in Tables S2 and S1, Supporting Information). From Ni$_1$ to Ni$_{\text{NiML}}$, the $E_{\text{ads}}-O^\bullet$ (the black line) varies upward (weaken) progressively from $-1.30$ to $-1.02$ eV, and then abruptly go down (strengthen) to Ni$_{13}$ ($-2.23$ eV) due to its hcp site replaced by Ni atoms. On the other side, the $\epsilon_d$ values fluctuate in a tendency completely reverse to the $E_{\text{ads}}-O^\bullet$, i.e., gradually drift downward from $-2.32$ to $-2.46$ eV (from Ni$_{1}$ to Ni$_{\text{NiML}}$), and then rise steeply to $-1.90$ eV of Ni$_{13}$. Hence, there is an almost exactly opposite correspondence between the calculated $E_{\text{ads}}-O^\bullet$ and $\epsilon_d$, which also validates well the deduction mentioned above that the farther the locus of $\epsilon_d$ is from $E_{\text{Fermi}}$, the weaker the obtained $E_{\text{ads}}-O^\bullet$. As for the pure Pd(111) benchmark, its calculated $\epsilon_d$ is around $-1.77$ eV, which is in accordance with the literature as well as our previous works (see in Table S2, Supporting Information). Therefore, based on the $d$-band model corollary, the calculated $\epsilon_d$ of the Ni$_n$ systems ($-1.90$ to $-2.46$ eV) at the involved hcp sites lie below the benchmark Pd ($-1.77$ eV), which suggests that our proposed Ni$_n$ catalysts are highly anticipated to outweigh the noble metal Pd(111) in terms of the ORR activity.

To better understand the physical mechanism behind this dependency between $\epsilon_d$ and $E_{\text{ads}}-O^\bullet$, the density of state (DOS) as well as the charge migration calculations are conducted to evaluate how the synergistic effect of the NiO$_2$-Pd structure and the interfacial Ni$^\rr$ doping influence the surface electronic structures of the proposed NiO$_2$/Ni$^\rr$/Pd systems. Figure 4a shows the total and projected DOS of the pure Pd(111) model, which is well

![Figure 2](https://www.advancedsciencenews.com/content/2207109/fig/fig2.png)

**Figure 2.** a,b) Adsorption-energy diagrams of absorbed atomic O ($E_{\text{ads}}-O^\bullet$) and OH radical ($E_{\text{ads}}-\text{OH}$) at various threefold hollow sites of different models.

![Figure 3](https://www.advancedsciencenews.com/content/2207109/fig/fig3.png)

**Figure 3.** Calculated adsorption energies of atomic oxygen ($E_{\text{ads}}-O^\bullet$, eV) as a function of the $d$-band centers ($\epsilon_d$, eV) at the involved surface atoms (M-hcp sites) of the proposed model catalysts.
consistent with the literature. The projected DOS of the Ni₁ model in Figure 4b exhibits that as the main states contributor around the Fermi level, the Pd 4d orbitals of Ni₁’s three Pd layers (the purple line) have a significant shift toward lower energy levels compared to the corresponding Pd orbitals of benchmark Pd(111), which indicates that more occupied state electrons are obtained to broaden its surface integral d-bandwidth and to sink the corresponding εₜ. Meanwhile, the doped NiSA is also observed to contribute its major Ni 3d orbitals (the green line) to its occupied states, which is favorable to the εₜ migration to the deep levels. Figure 4e highlights the overwhelming majority of NiSA 3d states in Ni₁, accompanied with the strongest orbital peak are located just below the $E_{\text{Fermi}}$ (−1 to 0 eV), which confirms important role of NiSA in Ni₁ for facilitating surface electron exchange and d-band sinking. As the number of doped Ni atoms increases to two monolayers’ substitution (i.e., Ni₃ML) in Figure 4c, the major contribution to the occupied states is strongly hybridized Ni 3d and Pd 4d orbitals, where both of the two orbitals feature a tendency to shift toward lower levels compared to Ni₁ and Pd(111), which results in the lowest εₜ position (see Figure 3). As for Ni₁₃ from Figure 4d, its Pd 4d orbitals still feature an analogical distribution to that of the Ni₁. However, its Ni 3d orbitals exhibit a distinct trend to move towards higher levels with a narrower bandwidth due to its exclusive exposed Ni atoms on outermost Pd surface, thereby causing a εₜ elevation (corresponding projected DOS results for all proposed NiO₂/NiSA/Pd model catalysts are provided in Figure S5, Supporting Information). As a result, the calculated DOS results trace out the significant synergistic effect triggered by the NiO₂/Pd heterostructure and the interfacial Ni heteroatomic doping on the regulation of the surface electronic structures of the proposed NiO₂/NiSA/Pd systems, which not only reveal the underlying factors for the εₜ shift, but also solidifies our theoretical prediction for the adsorption properties and ORR activity.

Furthermore, the underlying charge relocation between the interfacial intercalation of NiSA and its surrounding atoms in the Ni₁ system was evaluated by charge density difference and Bader charge calculations on behalf of the NiO₂/NiSA/Pd series. From Figure 4f-h, the 3D plots of charge density difference exhibit a significant tendency of charge agglomeration over the doped NiSA. More explicitly, extra available charge injected to the Ni-fcc site is believed can enhance the capture capacity of the electroneutral O₂ and H₂O to promote their chemisorption, simultaneously, introduce the repulsive force for the electronegative O* and OH to facilitate their desorption, therefore, synergistically boost the two ORR steps moving forward in the positive direction. Bader charge population was then calculated to quantify the charge transfer of the specific atoms/elements, as shown in Figure 4g,h, which demonstrates that the additional available charge obtained to the NiSA and its above Pd atoms due to the synergistic effect (strain, ligand, and geometric effects) significantly enables the surface Ni-fcc site a superior redox activity for Ni₁ system compared to pure Pd. Meanwhile, a large increase in the excess charge of the O atom coordinated with the NiSA means a much stronger Ni–O electrovalent bond, i.e., a thermodynamically more stable core–shell doping structure. (More detailed discussions about the charge transfer/relocation scenarios (around NiSA) and their impact on the ORR activity of Ni₁ systems are provided in Note S3, Supporting Information.)
3.4. ORR Mechanisms on the NiO₂/Ni⁰/Pd Systems

To ascertain the ORR mechanism of our proposed NiO₂/Ni⁰/Pd systems under base conditions, the simulated kinetic CI-NEB approach is used to seek the reaction activation barriers of the respective O₂ dissociation step (i.e., ΔE₁) and O* hydrogenation step (i.e., ΔE₂), which can directly characterize the catalytic dynamic behaviors for the cathode catalysts. The results are also compared with the benchmarking Pd(111) (Details about the atomic adsorption structure and descriptions for the stable IS and FS of the two substeps on the proposed Niₐ surface models are provided in Figures S3 and S4 and Note S4, Supporting Information, respectively). The calculated reaction coordinates of the two ORR subroutes and the corresponding values of ΔE₁ and ΔE₂ corresponding to the TS of each reaction route are presented in the lower right of Figure 5. Table S3 and Figure S6 (Supporting Information), respectively. First, for the rate-determining step (RDS), the O₂ dissociation path on each catalyst is thermodynamically spontaneous (endothermic) judged by the energy relation between IS1 and FS1. Ni₁ reveals the lowest ΔE₁ of only 0.49 eV among all (0.49–0.67 eV) except for Ni₁₃. In comparison with the benchmark Pd(111)’s 0.62 eV, the proposed Ni₁ with minimal Ni doping (Ni⁰SA) reduces the O–O bond cleavage obstacle by 0.13 eV (over 20% decline), which contributes to the improved efficiency of initial O₂ splitting and the intermediates O* acquisition of the catalyst, but less noble Pd usage. As the number of doped Ni atoms increases (Ni₃ to Ni₂ML), their computed ΔE₁ for O₂ splitting are observed to augment progressively from 0.50 to 0.67 eV, but only Ni₂ML with maximal Ni doping shows ΔE₁ (0.67 eV) softly exceeding that of pure Pd (0.62 eV) by less than 0.05 eV due to its weakest EₜS₁/O*. In addition, Ni₁₃ is observed to have a sharply dropped ΔE₁ to about 0.1 eV compared with the others (0.49–0.67 eV), which is evidently attributed to its considerably enhanced O* bonding strength (EₜS₁/O*, −1.39 to −2.77 eV) that almost erases its O–O breakage barriers. Subsequent is the “O* hydrogenation,” where the obtained O* will be reduced by H₂O into absorbed OH. Contrary to the preceding O₂ splitting, O* hydrogenation for all proposed Niₐ systems and pure Pd are thermodynamically nonspontaneous reactions (endothermic). As the benchmark one in the alkaline, Pd(111) features a low ΔE₂ of 0.21 eV (corresponding to the TS2). By comparison, Ni₁ shows a slightly higher ΔE₂ (0.30 eV) than that of pure Pd due to its moderately stronger EₜS₂/O*, which results in a little harder than Pd but still quite easy O* desorption. The same holds true for the rest Niₐ systems that own a relatively low ΔE₂ range of 0.24–0.34 eV. Another point of concern is Ni₁₃, its dramatically increased EₜS₂/OH balances the abnormal increase of ΔE₂ (to just 0.40 eV) caused by its excessively increased EₜS₁/O*, yet, the too strong OH binding may impede OH* desorption away from surface sites. This unusual ORR kinetic behavior observed on the Ni₁₃ still needs further investigation. These results verified that our proposed NiO₂/Ni⁰/Pd systems with low Pd loading can exhibit superb ORR activity outperforming the benchmarking Pd(111) via interfacially doping Ni. Specifically, the NiO₂/Ni⁰/Pd with Ni₃ML intercalating in overlying Pd layer performs the optimal kinetic behavior in the two key ORR substeps (i.e., ΔE₁, 0.49 eV and ΔE₂, 0.30 eV).

Moreover, for ease of understanding the improvement mechanism in ORR, the charge transfer scenarios behind the two kinetic stages between the doped Ni⁰SA surface atoms and the relevant absorbates for the representative optimal Ni₁ system were investigated, as shown in the upper right of Figure 5. During the four key stages IS₁ (O₂*), IS₂ (O* + O*), FS₁ (H₂O* + O*), and FS₂ (HO* + HO*), though buried at the bottom of the three-layer
Pd shell, the Ni\textsuperscript{SA} still has a significant charge interaction with the surface adsorbates through the Pd atoms sandwiched in the middle. In more vivid words, the interfacially intercalated Ni element seems to act more like an “electron-regulation hub” in the NiO\textsubscript{2}/Ni\textsuperscript{n}/Pd system, whose catalytic activity is mainly featured by its outward Pd shell and a Ni\textsuperscript{SA} interior, eventually achieve: 1) activity improvement of outermost layer Pd atoms within a local domain via the electronic structure adjustment, 2) cover-up the disadvantage of less activity and easier passivation of cheap Ni compared to Pd, and 3) stability enhancement of the core-shell-type NiO\textsubscript{2}/Pd structure via stronger ionic bonding between interfacially doped Ni\textsuperscript{SA} and core-part O atom. Since the atoms in subsurface or deeper layers of catalysts usually play an inferior role in the ORR, the partial replacement of expensive Pd in subsurface-layer(s) with much cheaper Ni is believed not only greatly reduce the cost of nanocatalysts, more notably, the local synergistic effect introduced by the interior Ni\textsuperscript{SA} triggers a prominent reactivity and selectivity on catalyst surface, which realize the bi-functionality of the ORR improvement as well as the cost control. The schematic of charge transfer process inside the optimized NiO\textsubscript{2}/Ni\textsuperscript{n}/Pd system and the chemical interactions between the catalyst and ORR species is illustrated in the left of Figure 5.

3.5. Correspondence between Adsorption Energies and Reaction Barriers for the NiO\textsubscript{2}/Ni\textsuperscript{n}/Pd Systems

Based on the above results involving the adsorption energies of O\textsuperscript{*} ($E_{\text{ads}}$-O\textsuperscript{*}) and OH ($E_{\text{ads}}$-OH), the ORR activation barriers of the O\textsuperscript{*} dissociation ($\Delta E1$) and O\textsuperscript{*} hydrogenation ($\Delta E2$) reactions, we found an underlying relationship between these four key factors and the corresponding model configurations. In a word, the very analogical fitting crescent-shaped trendline for the distributions of $E_{\text{ads}}$-O\textsuperscript{*}, $E_{\text{ads}}$-OH, $\Delta E1$, and $\Delta E2$ are observed from the pure Pd to Ni\textsubscript{SA}, as shown in Figure 6a–d, respectively, which well proves our predicted dependency as well as the reciprocal action between adsorption energy versus reaction barrier for the proposed Ni\textsubscript{n} systems mentioned above (Detailed descriptions and discussions involving the variation relations between calculated $E_{\text{ads}}$, $\Delta E$ and proposed structures are supplied in Note S5, Supporting Information). As a result, the calculated variations of the $E_{\text{ads}}$-O\textsuperscript{*} and $E_{\text{ads}}$-OH, together with their respective $\Delta E1$ and $\Delta E2$ revealed a structure–$E_{\text{ads}}$–$\Delta E$ correspondence between the adsorption strength (O\textsuperscript{*} and OH), two-step’s barriers, and the corresponding NiO\textsubscript{2}/Ni\textsuperscript{n}/Pd structures with the gradual infiltration of Ni atom(s) from the NiO\textsubscript{2}/Pd interface to the subsurface. In brief, the ORR activity basically continuously improves with the decreasing number of doped Ni atoms, where the optimal ORR activity is achieved at the doping level being minimized to the single-atom scale. This conclusion is considered can be applied as a guideline in future theoretical and experimental research.

Comprehensively, concerning the proposed core/shell structured NiO\textsubscript{2}/Ni\textsuperscript{n}/Pd with surface geometry identical to Pd(111) (i.e., Ni\textsubscript{1} to Ni\textsubscript{3ML}), the gradual infiltration of Ni atom(s) from the NiO\textsubscript{2}/Pd interface (i.e., third Pd layer) to the subsurface (i.e., second Pd layer) is believed can 1) lead to the weakening of the $E_{\text{ads}}$-O\textsuperscript{*}, which synchronously increase the $\Delta E1$ of the first O\textsubscript{2}
Based on the foregoing, we have proved that the Ni₁ system, with only single-atom Ni doping in its Pd-shell featuring the optimum ORR performance via cross-referencing the result of the surface adsorption properties, electronic structures, charge relocation, and the ORR kinetics behavior. However, theoretical and experimental studies had also indicated that the electronic influence and strain effect of the substrate on the topmost surface of transition-metal catalysts would begin to vanish gradually for the coverages of n > 3 ML. Therefore, to screen the optimal intercalation scheme of NiSA and to achieve a deepgoing understanding regarding the architectural feature and catalytic property of the optimal NiO₂/Pd system in atomic level, herein, the doping effect of NiSA in Pd layer of the NiO₂/Pd structure on ORR is further explored.

Figure 7a–c illustrated the proposed three NiO₂/Pd₁/Pd systems corresponding to a NiSA intermixed in the third Pd layer, second Pd layer, and first Pd layer in the NiO₂/Pd core/shell configuration, which are denoted as the "NiSA-3rd", "NiSA-2nd", and "NiSA-1st", respectively. The calculated Eᵣ of the three model slabs listed in Figure 7 show that the three proposed Ni systems (Pd-NiSA solid-solution structures) are energetically reasonable due to their almost identical Eᵣ values within less than 0.01 eV/atom. Meanwhile, the NiSA is thermodynamically slightly easier to replace the Pd atom in the or second or third Pd layer compared to in outermost Pd layer (first), which is also consistent with our previous experimental observations.[37,63] Figure 5a shows a very similar variation range of E_ads-O* on the Ni₁₃-3rd and Ni₁₃-2nd systems due to their identical outermost-layer appearance to Pd₁₁₁. Nevertheless, the NiSA doping depth still leads to a slight difference on the E_ads-O*, specifically, the second-layer doping of NiSA has a more significant impact on the electronic structure of the topmost Pd layer compared to the third-layer doping. Specifically, the doped-Ni atom in the second Pd layer with smaller Wigner radius can introduce a salient compressed lattice zone into the outermost Pd surface above it, which triggers a stronger eᵣ downhill of the involving Pd surface atoms and the attenuation of the corresponding E_ads-O* (i.e., the calculated average Pd–Pd bond length of the surface triatomic Pd-hcp site above the NiSA of the Ni₁₃-2nd (2.75 Å) is ≈0.04 Å shorter than that of the Ni₁₃-3rd (2.79 Å), which means the Pd-hcp site of Ni₁₃-2nd is subjected to 14% more compressive strain than that of the Ni₁₃-3rd, as shown in Figure S7, Supporting Information). For another, the NiSA-1st shows a remarkably increased E_ads-O* from ~1.33 to ~1.97 eV mainly due to its doped NiSA exposed on the topmost Pd layer that is similar to the aforementioned Ni₁₃ (detailed E_ads-O* values of the three Ni₁ systems see Table S4, Supporting Information). Qualitatively, the NiSA-2nd and NiSA-3rd further improve the surface O* binding strength for the robust Pd (i.e., quasi-Pd level), while the NiSA-3rd exibit an E_ads-O* range within a large fluctuation between metal Pd and Ni. Figure 8b also verifies the linear relation between the eᵣ at the involved surface atoms and their corresponding E_ads-O* (the selected hollow sites are marked in Figures 3 and 7). It indicates that the NiO₂/Pd systems with the identical surface appearance (including NiSA-2nd and NiSA-3rd) tend to land in the superior coordinate range (left bottom) appropriate for the ORR than those of the Ni₁₃-1st and Ni₁₃ systems with the Pd/Ni hybrid surfaces, according to the general trend of the classical eᵣ-E_ads correlation on the ORR.[37] Meanwhile, the Pd-hcp site of NiSA-2nd features a catalytically more preferable coordinate to NiSA-3rd, which is due primarily to the more significant synergistic effect (electronic and strain) on the surface triggered by the doped NiSA in the second Pd layer than that in the lower third Pd layer. Thus, the ORR activity trend described from our calculated eᵣ-E_ads correlation and the E_ads-O* plot basically follows the sequence: NiSA-2nd > NiSA-3rd > NiSA-1st.

Simulated ORR reaction coordinates of the two ORR subroutes with the corresponding energy barrier (TS/ΔE) for the three "Ni₁₃" are presented in Figure 8c. NiSA-2nd catalyst reveals a quite low ΔE in the RDS “O–O dissociation” (0.45 eV), which is even 0.04 eV smaller than that of NiSA-3rd (0.49 eV). Not only that, the ΔE in the subsequent “O* hydrogenation” of NiSA-2nd is also the smallest (0.26 eV) among the three, which remains lower than that of NiSA-3rd (0.30 eV) by 0.04 eV. Besides, although the NiSA-1st shows a fairly small ΔE of 0.17 eV compared with the other two, its dramatically reduced activation barrier of O* adsorption is mainly derived from the stronger oxidation capacity of its NiSA embedded in the outermost surface, which undesirably leads to an elevated obstacle in the following O* desorption and...
affects the ORR efficiency like aforementioned Ni13. Therefore, the transition-state calculations kinetically verify the Ni5A doping in the Pd subsurface contributing the most to catalytic synergy on the improvement of both O2 dissociation and O* desorption stages. As a comparison with another benchmark platinum catalyst in alkaline FCs, the key RDS barriers of the NiO2/Ni5A/Pd systems (ΔE1, 0.50–0.67 eV) are quite lower than that of the precious Pt(111) benchmark (1.04 eV).[56,79] where the ΔE1 further descends dramatically by 84% to 53% since the Ni atom(s) are intercalated as a single atom on the Pd layer (ΔE1, 0.17–0.49 eV from Ni5A-1st to Ni5A-3rd, as shown in Figure S8, Supporting Information).

Besides, from a thermodynamic point of view in Figure S9a (Supporting Information), the calculated potential energy surface (ΔE = IS – FS) of O2 dissociation (ΔE1) and hydrogenation (ΔE2) thermodynamically shows that the first O2 dissociation reactions for all three Ni1 models are thermodynamically spontaneous (i.e., ΔE1 > 0, 1.42–1.67 eV). On the contrary, the second O* hydrogenation reactions are all thermodynamically non-spontaneous processes (i.e., ΔE2 < 0, −0.21 to −0.42 eV), which means that there is a far greater risk of a reverse O* hydrogenation for the three catalysts compared to their preceding O2 dissociation. Notably, Ni5A-2nd features the ΔE2 (−0.21 eV) closest to zero along the positive direction of the second step, indicating that the O* hydrogenation on Ni5A-2nd is thermodynamically more stable to proceed among the three models, especially much more positive than −0.42 eV of Ni5A-1st catalyst. From another kinetic point of view in Figure S9b (Supporting Information), the calculated reverse reaction barriers (ΔE<sub>R1</sub> = TS – FS) of O2 dissociation (ΔE<sub>R1</sub>) and hydrogenation (ΔE<sub>R2</sub>) kinetically quantify the difficulty of unwanted backward reactions of the two ORR steps. The ΔE<sub>R1</sub> of the three catalysts (1.85–1.86 eV) is much higher than their corresponding forward ΔE1 (0.17–0.49 eV), indicating that the forward process of O2 dissociation is kinetically pretty stable. While for the subsequent O* hydrogenation, the ΔE<sub>R2</sub> of all three Ni1 catalysts (0.03–0.05 eV) shows a similar but slightly small magnitude to the corresponding forward ΔE2 (0.26–0.45 eV), which suggests the possible risk of reverse OH* de-hydrogenation causing the intermediate O* blocking. In vivid words, O* hydrogenation is more like a free two-way highway. Likewise, Ni5A-2nd is observed to have the highest ΔE<sub>R2</sub> (0.05 eV) than Ni5A-1st (0.03 eV) and Ni5A-3rd (0.04 eV), meaning that the O* hydrogenation on Ni5A-2nd is kinetically more difficult to proceed backward than the other two. As a result, the Ni5A-2nd system is believed to feature a more reasonable and efficient ORR behavior from both thermodynamic and kinetic perspectives, especially in avoiding the blockage of intermediates O* between the two ORR substeps (caused by reverse reaction) and the desorption of final products OH* (caused by the strong E<sub>ads</sub>-O* and E<sub>ads</sub>-OH), which should be the severe issues faced by the Ni5A-1st system.

Bader charge analysis in Figure 8d deeply uncovers that the excess charge (n<sup>−</sup>) obtained from the surface triatomic sites right above the doped Ni5A of the three systems is roughly in this sequence: Ni5A-2nd (0.118 e<sup>−</sup>) > Ni5A-3rd (0.074 e<sup>−</sup>) > Ni5A-1st (−0.166 e<sup>−</sup>), where the hcp-site of Ni5A-2nd features the most available (excess) charge among the three that proving its potential highest activity in the ORR. For another, the hcp-site of
Ni\textsuperscript{5+} - 1st exhibits a negative value of the excess charge (−0.166 e\textsuperscript−) is due to the exposure of smaller electronegative Ni\textsuperscript{5+} (χ = 1.91) in the hcp-site, resulting in the electrons extraction to its surrounding higher electronegative Pd atoms (χ = 2.20). Since the charge-deficient hcp-site would tend to extract electrons from O atoms to compensate for its d electrons loss, which in turn causes the key intermediates O\textsuperscript0 the metastable state due to the valence charges balance of octet rule, eventually giving rise to the prone surface-site passivation and inadequate ORR efficiency.

By cross-referencing the energetics adsorption properties, the corollaries of d-band model, kinetics simulation verification, and the in-depth charge transfer scenario, we intrinsically elucidate the influence of Ni\textsuperscript{5+}-doping depth in the Pd shell (from first to third layer) on the ORR performance, that is, the Ni\textsuperscript{5+} intercalated in the subsurface (Ni\textsuperscript{5+}-2nd) is believed to trigger the most fruitful Ni\textsuperscript{5+}/Pd\textsuperscript{3+} synergy combining the electronic influence and strain effect that significantly alter the surface electronic structure and synchronously optimize the redox properties of the NiO\textsubscript2/Pd structure, followed by the Ni atom infiltrating into the third layer of Pd-shell (Ni\textsuperscript{5+}-3rd), where the introduced synergistic effect between Ni\textsuperscript{5+} and Pd atoms begins to whittle for more than one Pd layer coverage. While, the Ni\textsuperscript{5+} incorporated into the outermost layer (Ni\textsuperscript{5+}-1st) exhibits an abnormal ORR behavior, which is considered unfavorable for the enhancement of ORR performance compared to the other two. Overall, the potential ORR activity of three NiO\textsubscript2/Ni\textsuperscript1/Pd systems generally follows the sequence: Ni\textsuperscript{5+}-2nd > Ni\textsuperscript{5+}-3rd > Ni\textsuperscript{5+}-1st.

4. Conclusions

In this study, the non-Pt nanocatalyst composed of NiO\textsubscript2 supported Pd surface configurations with various degrees of Ni atoms interfacially intercalated in the Pd layer, i.e., the NiO\textsubscript2/Ni\textsuperscript{n}/Pd systems (where n denotes 1, 2, 3, 4, 7, 1ML, 10, 2ML, and 13), are constructed and their physical and chemical properties and the corresponding dimension and depth effects of doped-Ni on the ORR performance are systematically cross-assessed by using the DFT calculations.

Our results demonstrate that the crucial $E_{\text{ads}}$−O\textsuperscript− index of the NiO\textsubscript2/Ni\textsuperscript{n}/Pd systems shows an evident tendency of gradually decreasing from Ni\textsuperscript{n} to Ni\textsubscript{2ML} (−1.02 to −1.30 eV) as the bottom two Pd layers substituted by Ni atoms. Together, the slightly enhanced adsorption energy of OH radical ($E_{\text{ads},\text{OH}}$) observed in Ni\textsuperscript{1}, is forecasted to contribute to the O\textsuperscript{2−} hydrogenation compared to pure Pd. The subsequent $E_{\text{ads}}$ projected DOS and physical charge transfer calculations respectively describe the well coincidence relation between the calculated $E_{\text{ads}}$ of the threefold site and its $E_{\text{ads}}$−O\textsuperscript− value as well as the state’s contribution of the adjusted Pd layer and the doped-Ni, which confirm the significant synergy on the surface electronic-structure regulation for the NiO\textsubscript2/Ni\textsuperscript{n}/Pd system, indicating a superior level of ORR performance to the costly benchmark Pd. TS calculations of the reaction pathway kinetically verify the above prediction of $E_{\text{ads}}$−O\textsuperscript−/OH on the ORR activity. Especially, the optimized Ni\textsuperscript{1} system performs the optimum ORR behavior with the lowest $\Delta E1$ (0.49 eV) and very moderate $\Delta E2$ (0.30 eV) compared with benchmark Pd (0.62 and 0.21 eV). The charge transfer scenarios behind the two key ORR stages uncover the focal role of interfacially intercalated Ni\textsuperscript{5+} the “electron-regulation hub” in the NiO\textsubscript2/Ni\textsuperscript{n}/Pd system, which tunes the electronic structure of the Pd-shell layers and concurrently increases the heterogeneous interface bonding via stronger ionic bonding. Through stepwise cross-level demonstration between the outcomes of the $E_{\text{ads}}$ d-band model, projected DOS and reaction coordinates simulation, a noteworthy Structure−$E_{\text{ads},\text{ads}}$−$\Delta E$ relationship is excavated for our proposed Ni\textsuperscript{n} systems, which reveals the important correspondence between the four key ORR factors and related catalyst structures. Furthermore, we explore the influence of the Ni\textsuperscript{5+} doping depth for the NiO\textsubscript2/Ni\textsuperscript{n}/Pd system on ORR, which intrinsically elucidates that the Ni\textsuperscript{5+} incorporated into the subsurface of Pd (Ni\textsuperscript{5+}-2nd) raises the remarkable Ni\textsuperscript{5+}/Pd\textsuperscript{3+} synergy combining the electronic influence and strain effect to improve the ORR activity, whereas this uplifting synergy begins to vanish for more than one Pd coverages (i.e., Ni\textsuperscript{5+}-3rd). Ni\textsuperscript{5+}-1st performs an unusual low $\Delta E1$ and a relatively higher $\Delta E1$ due to its several Ni atom exposed on the catalyst surface, the same applies to the Ni\textsuperscript{1}.

In conclusion, interfacial doping few inexpensive Ni in costly subsurface-Pd-layer in the NiO\textsubscript2/Ni\textsuperscript{n}/Pd systems can motivate a unique local synergy accompanied by a remarkably improved reactivity and selectivity to the catalysts compared with benchmark Pd(111), particularly, the NiO\textsubscript2/Ni\textsuperscript{n}/Pd model with Ni\textsuperscript{5+} intercalated in the subsurface has been proven to be optimal configuration design, which realizes the anticipated bifunctionality of activity enhancement and cost control. By means, the use of precious platinum in generally conceived “good commercial electrocatalysts” can be sharply cut down to “non-Pt level” but with a superior overall performance. The concepts and findings presented in this work provide a precision evaluation of the process window for optimizing the composition and structure of multimetallic catalysts in practical experiments regarding the novel Pt-free, high-performance, long-lasting, and environmentally-friendly techniques.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

H.L. acknowledges the funding support by Zhejiang Provincial Natural Science Foundation of China, China (Grant No. LQ23E0200008) and Science Foundation of Zhejiang Sci-Tech University (ZSTU), China (Grant No. 22212153-Y). J-P.C. gratefully acknowledges the financial support from the National Science and Technology Council, Taiwan (NSCT 109-2112-M-018-008-MY3). A.H. acknowledges the financial support from the City University of Hong Kong (Grant No. 9610336). T-Y.C. acknowledges the financial support from the National Science and Technology Council, Taiwan (NSCT 109-2112-M-007-030-MY3, NSCT 109-2923-E-007-005-, NSCT 109-3116-F-007-001-) and MA-tek (022-T-010). The authors thank the National Center for High-performance Computing (NCHC) for providing computational and storage resources.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

T-Y.C. and J-P.C. conceived the overall project. H.L.L. and J-P.C. proposed and refined the model design. H.L.L. carried out all the DFT
calculations. H.L.L., J.-P.C., and T.Y.C. performed the corresponding data analysis. H.L.L., J.-P.C., and T.Y.C. interpreted the results and wrote the manuscript. H.Y.T.C. provided ideas and suggestions on the DOS calculations and analysis. S.D. and J.C. offered auxiliary ideas about the nanocatalysts from the aspect of their previous experimental observations concerning nanomaterials and heterogeneous doped structures. A.H., Y.W.W., and Q.D. assisted in further discussions and proofreading.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

bimetallic catalysts, DFT calculations, fuel cell, oxygen reduction reaction

Received: December 2, 2022
Revised: January 11, 2023
Published online: February 8, 2023


