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Stabilization of Pt monolayer catalysts under harsh conditions of fuel cells

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Abstract

We employed density functional theory (DFT) to explore the stability of core (M = Cu, Ru, Rh, Pd, Ag, Os, Ir, Au)-shell (Pt) catalysts under harsh conditions, including solutions and reaction intermediates involved in the oxygen reduction reaction (ORR) in fuel cells. A pseudomorphic surface alloy (PSA) with a Pt monolayer (Pt_{1ML}) supported on a M surface, Pt_{1ML}/M(111) or (001), was considered as a model system. Different sets of candidate M cores were identified to achieve a stable Pt_{1ML} shell depending on the conditions. In vacuum conditions, the Pt_{1ML} shell can be stabilized on the most of M cores except Cu, Ag and Au. The situation varies under various electrochemical conditions. Depending on the solutions and the operating reaction pathways of the ORR, different M should be considered. Pd and Ir are the only core metals studied, being able to keep the Pt_{ML} shell intact in perchloric acid, sulfuric acid, phosphoric acid and alkaline solutions as well as under the ORR conditions *via* different pathways. Ru and Os cores should also be paid attention, which only fall during the ORR *via* the *OOH intermediate. Rh core works well as long as the ORR does not undergo the pathway via *O intermediate. Our results show that PSAs can behave differently from the near surface alloy (NSA), Pt_{1ML}/M_{1ML}/Pt(111), highlighting the importance of considering both chemical environments and the atomic structures in rational design of highly stable core-shell nanocatalysts. Finally, the roles that d-band center of a core M played in determining the stability of supported Pt_{1ML} shell was also discussed.

1. Introduction

Pt monolayer (Pt_{1ML}) catalysts on metal (M) supports, or M core- Pt shell, have attracted considerable attentions as advanced catalysts, being able to accelerate the slow oxygen reduction reaction (ORR) in fuel cells and reduce the Pt loading.[1-6] To understand the promoting effect, extensive theoretical studies have been carried out;[7-13] however little attention has been paid for the stability of Pt_{ML} shell,[3, 14, 15] which is critical to achieve the durable activity required for commercialization. Systematic theoretical studies were reported on the stability of the Pt_{ML} shell supported on various metal cores;[13, 16-21] yet the harsh operating conditions of fuel cell, in particular the solutions, had been paid little attention, which could induce the segregation of core metals to the surface and the decreased activity and stability.[15, 22, 23]

Here we employed density functional theory (DFT) to estimate the stability of the Pt_{1ML} shell by studying the segregation of core M (M = Cu, Ru, Rh, Pd, Ag, Os, Ir, Au) under various environmental conditions. In principle, the segregation of core M should be prohibited to achieve the stability and activity of Pt_{1ML} shell.[24] To simulate the core-shell conformation, we previously used near surface alloys (NSAs) with $Pt_{1ML}/M_{1ML}/Pt(111)$ sandwich structure.[25] Such model was used to describe the case with Pt core -M shell nanoparticles with size > 4 nm, which displayed the bulk-like properties in term of both activity and stability.[4, 15, 26] Due to the lower surface energy of Pt than M, part of the core Pt atoms segregated to the surface and form a Pt_{1ML} shell, while the M shell atoms were buried in the subsurface. In this case, the surface

strain in the Pt_{1ML} shell due to the mismatch between Pt and M lattice was not considered.[27] In this paper, pseudomorphic surface alloys (PSAs) were considered to model the M core - Pt shell catalysts, where 1 ML of Pt was deposited on the single crystal M surfaces and formed Pt_{1ML}/M(111) for M=Cu, Rh, Pd, Ir, Ag, Au and Pt_{1ML}/M(001) for M=Ru, Os. Different from NSAs, Pt adopted the lattice of M bulk in the case PSAs. In this way, the surface strain within the Pt_{1ML} shell introduced by the core metal was included. Such PSA model has been extensively used to describe the core-shell nanocatalysts in electrochemical applications.[12, 13, 18-20, 28-32]

Our results showed that to achieve a stable Pt_{1ML} shell, different sets of candidate core M were identified depending on the type of solutions, perchloric acid ($HClO_4$), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and alkaline solutions, as well as the undergoing reaction pathways for the ORR, direct or associative mechanisms. In addition, the segregation of a same core M under the same chemical environment can vary depending on the adopted conformation, PSA or NSA. Finally, our study highlights the importance of d-band center of core M(111) or (001) in determining the stability of Pt_{1ML} shell.

2. Methods and models

Similar to our previous study,[25] spin-polarized DFT calculations were performed using the CASTEP code.[33, 34] The generalized gradient approximation (GGA)[35] with the revised Perdew–Burke–Ernzerhof functional (RPBE)[36] was used to describe the

exchange and correlation potential. The cutoff energy for the plane-wave basis set was set to 520 eV in all calculations. The Monkhorst-Pack[37] mesh k-points ($9 \times 9 \times 9$) and ($5 \times 5 \times 1$) were used for the bulk and slab calculations, respectively. A convergence accuracy of 1.0×10^{-6} eV/atom was set for the self-consistent field (SCF) calculation. In DFT calculations, the core shell alloys, Pt_{ML}/M(111) (M= Cu, Ru, Rh, Pd, Ag, Os, Ir, Au) were modeled using a five-layer slab and a 2×2 array in each layer (Figure 1a). In addition, the gradual segregation of core M from the second layer in the subsurface to the surface layer by exchanging position with nearby Pt atoms in the surface, via Pt_{1ML}/M(111) [or (001) for Os and Ru] to $Pt_{0.75ML}M_{0.25ML}/Pt_{0.25ML}M_{0.75ML}$/M(111) or (001), $Pt_{0.5ML}M_{0.5ML}/Pt_{0.5ML}M_{0.5ML}$ /M(111) or (001), $Pt_{0.25ML}M_{0.75ML}/Pt_{0.75ML}M_{0.25ML}$/M(111) or (001) and eventually M_{1ML}/Pt_{1ML}/M(111) or (001), was considered for both surfaces with and without adsorbates (Figure 1). A vacuum gap of 15 Å in the z-direction was introduced to separate two subsequent slabs. The atoms in the top three layers were allowed to relax, while the atoms on the remaining two layers were fixed at their ideal bulk positions.

The adsorption energies of *O, *OH, *OOH, $*ClO_4$, $*SO_4$ and $*PO_4$ at different adsorption sites were examined at the coverage of 0.25 ML. The effect of coverage was not considered assuming that the difference from one system to the next under the same conditions was similar. This is our interest in the present study. The segregation energy under vacuum conditions is calculated according to :

$$\Delta E_{segr}(i) = E_{Pt_{(1-i)ML}M_{iML}/Pt_{iML}M_{(1-i)ML}/M(111)} - E_{Pt_{1ML}/M_{1ML}/M(111)}. \quad \text{(eq. 1)}$$

The segregation energy under the ORR conditions is calculated as

$$\Delta E_{segr}(i) = E_{ads+Pt_{(1-i)ML}M_{iML}/Pt_{iML}M_{(1-i)ML}/M(111)} - E_{ads+Pt_{1ML}/M(111)}, \quad \text{(eq. 2)}$$

where E is the total energy of the slabs, and "*ads*" represents an adsorbed species on the surface. "i" is the coverage (ML) of M atom in the surface layer ($0 \leq i \leq 1$). $\Delta E_{segr}(i)$ stands for the energy cost for core M atoms segregating from subsurface to surface. The binding energy of surface M_4 layer (ΔE_b) on a $M_4/Pt_4/M$ surface is defined as

$$\Delta E_b = E_{M_{1ML}/Pt_{1ML}/M(111)} - E_{Pt_{1ML}/M(111)} - nE_M, \quad \text{(eq. 3)}$$

where $E_{M_{1ML}/Pt_{1ML}/M(111)}$, $E_{Pt_{1ML}/M(111)}$ and E_M represents the total energy of a $M_{1ML}/Pt_{1ML}/M(111)$ surface, the $Pt_{1ML}/M(111)$ surface formed by removing the surface M layer, and a free M atom in gas-phase, respectively. n is the number of M atoms in the surface.

3. Results and discussions

3.1 Stability under vacuum conditions

According to the calculated segregation energy, ΔE_{segr}, under vacuum conditions $Pt_{1ML}/M(111)$ or (001) (M = Ru, Rh, Os, Ir) in a PSA conformation is the most stable conformation, followed by $Pt_{0.75ML}M_{0.25ML}/Pt_{0.25ML}M_{0.75ML}/M(111)$ or (001) > $Pt_{0.5ML}M_{0.5ML}/Pt_{0.5ML}M_{0.5ML}/M(111)$ or (001) > $Pt_{0.25ML}M_{0.75ML}/Pt_{0.75ML}M_{0.25ML}/M(111)$ or (001) > $M_{1ML}/Pt_{1ML}/M(111)$ or (001) in a decreasing sequence (Figure 2 and Table

S1[38]). That is, Pt energetically prefers to form a Pt_{1ML} shell, while core M favors to stay in the core. The segregation of core M to the shell is endothermic, which increases with the increasing amount of M in the shell. The opposite trend is observed for M = Ag, Au (Figure 2) as observed for the corresponding NSAs, which is attributed to the lower surface energy of Ag or Au than that with a Pt (Table S2[38]).[25] In addition, the magnitude of ΔE_{segr} depends on the electronic difference between core M and Pt. In general, the core M that locates further away from Pt (e.g. Ru) in a periodic table affect ΔE_{segr} or the stability of the Pt_{1ML} shell more strongly than those that is near Pt (e.g. Pd).

Using Cu(111) as core is the only case in our study, where the segregation energy can be both positive and negative depending on the number of Cu atoms in the shell (Figure 2, Table S1[38]). Balbuena, et al. also predicted the segregation of Cu to the Pt/Cu(111) surface both under vacuum and in interaction with oxygen.[13] This is different from the case of NSAs, where only positive segregation energy is observed.[25] Indeed, Chorkendoff and coworkers found that only Pt_{1ML}/Cu_{1ML}/Pt(111) conformation displayed an 8-fold improvement in the ORR activity of Pt(111).[39] Although the partial segregation of Cu is thermodynamically favorable, the corresponding reaction energy is less than 0.4 eV. Given that, such small driving force for core Cu segregating to the shell may not be feasible under the operating temperature of fuel cells due to the kinetic obstacles, which may only take place via the surface defects.[15]

To achieve both the activity and stability of core-shell catalysts for the ORR in fuel cells, the formation of Pt_{1ML} shell is preferred. Following the method employed to describe the NSAs,[25] we scaled the stability of PSAs using the lowest segregation energy, which represents the lowest energy cost to allow core M to segregate and therefore destabilize the Pt_{1ML} shell. As shown in Figure 3, under vacuum conditions Ru, Rh, Pd, Os, and Ir can be considered as good candidates for the core, where the color index (blue to white) indicates that the formation of Pt_{1ML} shell is either exothermic or at least thermoneutral. For M = Ag, Au, the Pt_{1ML}/M(111) has been found active for the ORR.[24] However, it is not as stable as the formation of M_{1ML}/Pt_{1ML}/M(111), which destabilizes the Pt_{1ML} shell and leads to the decrease in activity.[40] Therefore, Ag and Au cores will not be considered for our further study in the following. Similar results were observed in the case of NSAs.[25] The only difference between PSAs and NSAs is for M=Cu. Pt_{1ML}/Cu_{1ML}/Pt(111) in the NSA conformation displays higher stability under vacuum conditions than those with Cu partially or fully segregated to the shell; however in the form of PSA, the partial segregation of Cu is more favorable than that of Pt_{1ML}/Cu(111) (Figure 3). Since Pt partially stays on the surface, Cu core will be considered for the further study.

3.2 Understanding the trend

The variation trend of segregation energy, ΔE_{segr}, with the species of core M (Figure 2) can be well described by d-band center (E_d)[8, 32, 41] of core M. In the case that core M segregates to form a M_{1ML}/Pt_{1ML}/M(111) or (001), for example, the

corresponding segregation energy, ΔE_{segr}, increases exponentially with the E_d of M_{1ML} shell shifts toward the Fermi-level (Figure 4a). When the E_d of M shifts upwards and approaches to that of Pt (M= Au, Ag), ΔE_{segr} becomes less negative (Figure 4a, Table S3[38]). That is, thermodynamically it is favorable for core M to segregate under vacuum conditions. In the case that the E_d of M is close to that of Pt, the formation of $M_{1ML}/Pt_{1ML}/M(111)$ (M= Pd) shows the least variation in ΔE_{segr} ($\leq$ 0.05 eV), which is greatly increased by using core M (M= Ru, Rh, Ir, Os) with the E_d lying higher than that of Pt. In both cases, the segregation of core M is likely to be hindered and the formation of the Pt_{1ML} shell should be preferred.

The d-band center of M(111) or M(001) determines the stability of Pt_{1ML} shell via the interplay between the surface energy of M and binding property of M with Pt or the core-shell interaction, which can vary depending on the strain introduced by the lattice mismatch between Pt and M. Upon the full segregation of core M (Figure 4a), there is no strain on the surface of $M_{1ML}/Pt_{1ML}/M(111)$ or (001). For M = Ru, Rh, Pd, Ag, Os, Ir, Au, the control of E_d to the variation in segregation can be simply estimated according to the E_d of M(111) or (001) bulk surface. With the strain in the Pt-Pt bond is less than 5% (Table S2[38]), the d-band of segregated M_{ML} shell and therefore the corresponding surface energy is close to that of M(111) or (001) bulk surfaces (Table S3[38]). The higher the d-band center and surface energy of M(111) or (001), the higher the segregation energy for the core M and therefore the more stable the P_{1ML} shell is. In this case, the shell-core interaction does not play a major role. As

shown in Figure 4b, the interaction between M_{1ML} shell and Pt_{1ML}/M(111) or (001) core shows a decreasing with the increasing in E_d of M, which is opposite to that seen for the corresponding segregation energy (Figure 4a).

The strain effect can play an important role when the contraction or stretch in the lattice is significant. For the systems studied, this is only the case for Pt_{1ML}/Cu(111), where the biggest difference in lattice between Pt and Cu (Table S2[38]) introduces the highest contraction in Pt-Pt bond ($d_{Cu-Cu}/d_{Pt-Pt} - 1$, -8.8%).[38] As a consequence, Pt is deactivated due to the down-shifted d-band center (E_d = -2.69 eV) (Table S3[38]). Consequently, the interaction between Pt and Cu is too weak to hold the Pt_{1ML} shell. The stability of Pt_{1ML} shell can be promoted by intermixing Pt with Cu, which releases the surface stress to -6.4%, -4.3% and -2.1% respectively with the increasing number of Cu in the shell going from 1 to 3 (Table S1[38]); yet the stabilization is less significant. Eventually, with the complete release of the stress in the shell, Cu_{1ML}/Pt_{1ML}/Cu(111) is less stable than Pt_{1ML}/Cu(111) (Figure 2), though Cu(111) displays lower surface energy than Pt(111) (Figure S2).[38] That is, E_d and surface energy for Cu(111) in this case cannot explain the trend in segregation energy; instead the core-shell interaction is found to play a dominant role. Due to strongly stressed Pt-Pt bond, the core-shell interaction for Cu_{1ML}/Pt_{1ML}/Cu(111) is significantly weakened. It shifts the E_d of Cu_{1ML} shell towards the Fermi level (E_d= 1.96 eV), which is higher than that of Pt(111). Therefore, the higher surface energy for Cu_{1ML}/Pt_{1ML}/Cu(111) is observed (Figure 4), while the E_d of Cu(111)[8, 32, 41] and therefore the surface energy

(Table S2[38]) is lower than Pt(111) (Table S2[38]). Decreasing the amount of Cu in the shell effectively reduces the surface energy and ΔE_{segr} increases negatively (Figure 2).

Overall, the stability of Pt_{1ML} shell is associated with the E_d of core M. When the shell strain introduced by the core is relatively small, one can simply use the E_d of M(111) or (001) bulk surface to estimate the stability of Pt_{1ML} shell. To assure the stability of Pt_{1ML} shell in vacuum, the core metals should be chosen among those with the E_d and therefore the surface energy higher than Pt, e.g. Ru, Rh, Pd, Os, and Ir. When the strain is strong, e.g. Pt_{1ML}/Cu(111) and Cu_{1ML}/Pt_{1ML}/Cu(111), the E_d of Pt or the Cu_{1ML} shell can be very different from the bulk surfaces. In this case, the stability of Pt_{1ML} shell likely depends on the core-shell interaction.

3.3 Stability under acidic and alkaline solutions.

The electrochemical reaction occurs at the electrodes under solutions, which is typically either acidic or alkaline. According to our previous study of NSAs, [25] we estimate the solution effect by recalculating ΔE_{segr} in presence of anions from the solution adsorbed on the surface (Figure 5). Accordingly, to describe the effect of acid solution, $HClO_4$, H_2SO_4 and H_3PO_4 , the adsorbed $*ClO_4$, $*SO_4$ and $*PO_4$ were considered. The effect of alkaline was simulated by *OH adsorbed on the surfaces. The adsorption of anions on metal electrodes has been one of the major topics in surface electrochemistry. It has been realized for a long time that these specifically adsorbing anions have an important effect in a number of electrochemical reactions, including the stability of catalysts.[42, 43] Our calculations started with the most stable

surface conformation, and the possibility of sequentially pulling core M to the shell and forming strong bonds with the adsorbates was also included (Figure 5).

Similar to the case of NSAs,[25] the tetrahedral $*ClO_4$ adopts a η^3 conformation via three oxygen atoms at Pt atop sites (Figure 5). Compared to the results under vacuum conditions, $*ClO_4$ induces the decreasing of ΔE_{segr} (Figure 6a, Table S4[38]). Again, big changes in ΔE_{segr} are observed when the E_d of core M(111) or (001) (M=Ru, Os, Ir) is away from that of Pt(111), while the variation is relatively small for M(111) (M=Rh, Pd) with the E_d close to that of Pt (Figure 6a). Among the systems studied, the case with Ru(001) core shows the most significant changes in ΔE_{segr} going from 2.76 eV under the vacuum conditions to 1.49 eV due to the presence of $*ClO_4$. This is due to the fact that Ru has the highest-lying E_d than the other core M studied (Figure 3, Table S3[38]), which allows Ru to provide a high binding to the cation and therefore a big driving force for Ru segregating to the surface. However, it is not strong enough to compensate the overall cost for Ru segregation and ΔE_{segr} remains positive. Similar situation is also observed for PtOs and PtIr. In contrast, for Pt_{1ML}/M(111) (M = Cu, Rh, Pd) such driving force is capable to overcome the endothermicity and ΔE_{segr} decreases to negative values (Figure 6a, Table S4[38]). Yet, the magnitude is very small (> -0.4 eV) with M = Rh, Pd due to the close E_d and therefore the binding activity among Rh, Pd and Pt (Figure 4, Table S3[38]). Therefore, the driving force induced by the difference in binding energy between Pt-ClO_4 and M-ClO_4 (M=Rh, Pd) is not as strong as the cases with M=Ru, Os, Ir. Pt_{1ML}/Cu(111) is

an exceptional case, where the Cu atoms are distorted from the lattice position on interacting with $*\mathrm{ClO_4}$ more significantly than the other systems (Figure 5). It results in the activation of Cu and the decreased ΔE_{segr} to around -1 eV (Figure 6a, Table S4[38]). Here, we note that increasing the size of unit cell can help in alleviating the distortion. Even though, the results using 2×2 unit cell on the different behavior of PtCu from PtM (M=Ru, Rh, Pd, Os, Ir) are still valid, which is the interest of our current study.

The tetrahedral $*\mathrm{SO_4}$ and $*\mathrm{PO_4}$ adopt the same conformation as $*\mathrm{ClO_4}$ on metal surfaces (Figure S1, Figure S2)[38] in consistent with the previous observations on the NSAs. [25] In addition, ΔE_{segr} is decreased further more when changing the solution from $H\mathrm{ClO_4}$ to $H_2\mathrm{SO_4}$ and $H_3\mathrm{PO_4}$ (Figure 6a-c). The considerable effects of $H_2\mathrm{SO_4}$ [44] and $H_3\mathrm{PO_4}$ on the crystal structure of Pt catalysts has been observed experimentally in contrast to $\mathrm{HClO_4}$.[45] The difference depends on the binding activity of the anions. Although in $H_2\mathrm{SO_4}$ ΔE_{segr} stays positive for Pt_{1ML}/Ru(001), Pt_{1ML}/Os(001) and Pt_{1ML}/Ir(111) as that in $H\mathrm{ClO_4}$, the magnitude is decreased significantly due to the stronger $*\mathrm{SO_4}$ species than $*\mathrm{ClO_4}$ (Figure 6b, Table S5[38]). On the contrary, for Pt_{1ML}/Pd(111) and Pt_{1ML}/Rh(111) ΔE_{segr} stays more or less the same as that in either solutions (> -0.4 eV) due to the close binding properties of core M to Pt, as addressed above based on the d-band center (Figure 3). The decreased ΔE_{segr} is also observed for Pt_{1ML}/Cu(111) in $H_2\mathrm{SO_4}$ compared with that in $H\mathrm{ClO_4}$ (Figure 6a,b). Again this is attributed to the structural changes of Cu interacted with $*\mathrm{SO_4}$

(Figure S1[38]), which is more significant than the other systems. Therefore, to stabilize the Pt_{1ML} shell in H_2SO_4 , the core M should be chosen among Ru, Os, Ir, Rh, and Pd.

$*PO_4$ promotes the segregation of core M more strongly than $*SO_4$ and $*ClO_4$. As shown in Figure 6c and Table S6[38] only Pt_{1ML}/Os(001) and Pt_{1ML}/Ir(111) are able to keep ΔE_{segr} positive and maintain the Pt_{1ML} shell. For Pt_{1ML}/Ru(001), ΔE_{segr} is negative, though the magnitude is small (> -0.25 eV). Again ΔE_{segr} for Pt_{1ML}/Pd(111) and Pt_{1ML}/Rh(111) is not sensitive to the changing of the solutions and stays as slightly negative (> -0.4 eV). On Pt_{1ML}/Cu(111), $*PO_4$ shows stronger effects than $*SO_4$ and $*ClO_4$ on decreasing ΔE_{segr} via the structural distortion of Cu on the surface (Figure S2 [38]), which enables the segregation of Cu more thermodynamically favorable (Figure 6c, Table S6[38]). Accordingly, in H_3PO_4 solution Os, Ir as well as Ru, Rh and Pd can be considered as the cores to stabilize the Pt_{1ML} shell.

Compared to the acid solutions, the effect of alkaline solutions on the surface segregation is less effective. The preferential adsorption sites vary from atop, bridge to hollow depend on the amount of M on the surface (Figure 7). Figure 6d and Table S7[38] show that *OH also leads to the lowered ΔE_{segr}; yet the effect is not as strong as that of $*SO_4$ $*PO_4$, but rather as weakly as that of $*ClO_4$ (Figure 6). Therefore, in alkaline solutions, the same core metals (Ru, Rh, Pd, Os, and Ir) as those in $HClO_4$ are predicated to stabilize the Pt_{1ML} shell.

As shown in Figure 3, using Ru, Os, Ir, Pd, and Rh as core is able to stabilize the Pt_{1ML} shell in acid and alkaline solutions. Depending on the binding strength of anions

with the surface, the stability of Pt_{1ML}/M(111) or (001) (M=Ru, Os, Ir) varies significantly. The strong $*PO_4$, are likely to decrease $\Delta E_{segr}(i)$ and destabilize the Pt_{ML} shell more strongly than the weak $*ClO_4$ and *OH (Figure 3). In contrast, Pt_{1ML}/Rh(111) and Pt_{1ML}/Pd(111) show less sensitivity to the variation in solution and the corresponding ΔE_{segr} under all environments stays roughly thermoneutral (Figure 3). Thus, the segregation may not be feasible under operating temperature of fuel cells due to the kinetics obstacles.

Combining with our previous study of NSAs, [25] we predict that Ru, Os, Ir, Rh, and Pd can be considered as alloying metals with Pt to stabilize the Pt_{1ML} shell in $HClO_4$, H_2SO_4 and alkaline solutions, no matter whether the PSA or NSA conformations are adopted (Figure 3). However, one has to be careful with H_3PO_4 solution, where in a NSA conformation only Rh, Pd and Ir can be selected for alloying with Pt. This is associated with the surface strain introduced by M segregation in the case of NSAs. Cu is another case, where the structure makes big difference. By adopting a NSA conformation, the Pt_{1ML}/Cu_{1ML}/Pt(111) is stabile in $HClO_4$ and alkaline solutions; however, in a PSA conformation, Pt_{1ML}/Cu(111) cannot survive under any environment, where the huge contraction is introduced in the Pt-Pt bond by the Cu core.

3.4 Stability under the ORR condition.

It has been shown that the slow kinetics of the ORR on the cathode hinders the overall performance of low-temperature fuel cell. Therefore, we also studied the

catalyst stability during the ORR. Following our previous study of the NSAs, [25] we estimated the effect by considering the adsorption of reaction intermediates involved in the ORR, where the adsorptions of *O, *OH and *OOH were considered as the key intermediates involved in direct and/or associative pathways of the ORR. Since the ORR occurs by exposing to the air, the stability under the ORR can also be applied to that under air exposure.

*O interacts strongly with the surfaces by occupying the three-fold hollow sites. As shown in Figure 8a and Table S8[38], *O has a strong effect on the surface segregation as that of $*PO_4$, where ΔE_{segr} is decreased effectively compared to the case in vacuum. Positive ΔE_{segr} is only observed for Pt_{1ML}/Os(001) and Pt_{1ML}/Ir(111), and the slightly negative values are obtained for Pt_{1ML}/Rh(001) and Pt_{1ML}/Pd(111). Pt_{1ML}/Cu(111) corresponds to a highly negative ΔE_{segr}. It means that under the ORR via *O intermediate the Cu core segregation is thermodynamically favorable and the formation of Cu oxides on the surface is likely to occur, in agreement with experiment.[46]

In contrast to *O, the effect introduced by *OH is much less. For all the systems studied, ΔE_{segr} is either positive or close to zero except Pt_{1ML}/Cu(111) (Figure 6d, Table S7[38]). In the case of *OOH, the situation is complicated (Figure 8b and Table S9[38]). Depending on the surface composition, it can be adsorbed either molecularly on a top position (Figure 9) or dissociatively (Figure S3 [38]), where the *OH and *O fragments sit atop and hollow sites respectively. Our results show that the dissociative

adsorption is energetically much more favorable than the molecular adsorption, which drives ΔE_{segr} highly negative (Figure 8b). This is the case when using Ru and Os as core. Cu core also prefers to segregate and interact with *OOH; however the adsorbate stays in a molecular form, but leads to a more significant surface distortion than the other cases (Figure 9). In the cases of using Pd and Rh cores, *OOH stays molecularly and ΔE_{segr} remains close to zero. Ir is the only core, which displays highly positive ΔE_{segr} and therefore highly stable Pt_{1ML} shell.

According to our calculations, if the ORR follows the direct pathway via *O and *OH, Os, Ir, Ru and Pd can be considered as core (Figure 4) to stabilize the Pt_{1ML} shell in a PSA conformation. Only Pd and Ir cores work well if the reaction undergoes the associative pathway via *O, *OH and *OOH. When changing the structure to the NSA conformation, the candidate M can be very different depending on the reaction mechanism.[25] In that case, Pd, Rh and Cu are predicted as good candidates for the ORR via both pathways. Ir is only selected for the ORR via the direct pathway. Os and Ru are ruled out,

Overall, our calculations show that Pd and Ir are the only core metals among the systems studied here to keep the Pt_{1ML} shell intact as well as activity under vacuum, acid ($HClO_4$, H_2SO_4 , H_3PO_4), alkaline solutions and the ORR *via* different pathways (Figure 3). This agrees well with the previous experiments, showing an increased stability of Pt shell when using Pd or Ir rather than Pt as core during the ORR in acid.[15, 47] Ir is one of the most stable metals and its activity towards the ORR

is slightly enhanced by alloying with other transition metals.[1, 48] In addition, our calculations also show that Ru and Os should also be paid attention, which only fall during the ORR *via* the *OOH intermediate. Rh also works as long as the ORR does not undergo the pathway via *O intermediate. The destabilization of the Pt_{ML} shell by core Cu under all conditions studied was observed.

The d-band center of M(111) or (001) bulk surface is found as an effective descriptor to explain the variation trend in ΔE_{segr} for all Pt_{ML}/M(111) or (001) alloy surfaces studied. According to our results, the stability can be estimated simply according to the E_d. To stabilize the Pt_{1ML} shell under various conditions of the ORR, the core metal should adopt a E_d close to that Pt. Compared to Pt, the M (Au, Ag) cores with lower-lying E_d display a lower surface energy and are likely to destabilize the Pt shell via preferential segregation in vacuum. Under various solutions and the ORR, similar segregation is likely to occur by using the active core M (Ru, Rh, Os), which adopt a higher-lying E_d than Pt and therefore bind the adsorbates more strongly. By adopting a E_d slightly higher than Pt, Pd and Ir cores display a superior performance in stabilizing the Pt_{1ML} shell than the cores studied here, being able to provide a moderate property, active enough to hinder the segregation in vacuum and inert enough to prevent the segregation in interacting with an adsorbate under reaction conditions. Such general role cannot be applied to the case with huge strain introduced by the core, e.g. Cu. On interacting with an adsorbate, the structural distortion occurs, which is more significant than the other systems. In this case, Cu E_d

for bare surfaces cannot be used to describe the behavior of the alloy under the reaction conditions. According to the previous studies, the stability of Pt shell can be improved by using PtCu alloy as core to release the contraction, increasing the thickness of Pt shell from one monolayer to multiple layers, or varying Pt:Cu ratio to form NSAs which can survive all the environments except H_2SO_4 and H_3PO_4 solutions.[25, 46] In addition, a recent study show that for a variety of Pt-based core-shell catalysts, the stability of Pt shell supported on a Pt alloy core can be promoted by introducing a subsurface Au layer.[49]

4. Conclusion

DFT was employed to study the stabilization of Pt_{1ML} shell by using various M cores (M = Cu, Ru, Rh, Pd, Ag; Os, Ir, Au) under harsh ORR conditions in fuel cells on the basis of a PSA conformation, Pt_{1ML}/M(111) or (001). To achieve a stable Pt_{1ML} shell, different sets of candidate M cores were identified depending on the conditions. Pd and Ir are the only two cores studied, being able to stabilize the Pt_{1ML} shell under vacuum conditions including acid ($HClO_4$, H_2SO_4 , H_3PO_4)/alkaline solutions and the ORR *via* different pathways. In addition, Ru and Os should also be paid attention, which only fall during the ORR *via* the *OOH intermediate. Rh also works as long as the ORR does not undergo the pathway via *O intermediate.

Depending on the binding strength of anions from solution with the surface, the stability of Pt_{1ML} shell varies significantly when using Ru, Os, and Ir as core; in

contrast Rh and Pd cores show less sensitivity and the corresponding segregation energy under all studied environments is roughly thermoneutral. Thus the segregation may not be feasible under operating conditions of lower-temperature fuel cells due to the kinetics obstacles. The Pt_{1ML} shell is not stable under all environments with Cu core. The interaction of Cu with the anions from solutions and the reaction intermediates involved in the ORR can lead to more significant distortion of Cu than the other systems, which accelerates the dissolution of Cu on the surface and therefore deactivates the catalyst.

Finally, the d-band center of M(111) or (001) bulk surface is found as an effective descriptor for the shell stability of Pt_{1ML}/M(111) or (001) alloy surfaces studied, when the strain introduced by the lattice mismatch between Pt and M is not significant. The superior performance of Pd and Ir in stabilizing the Pt_{1ML} shell is associated with by the adopted E_d slightly higher than Pt. As a result, Pd and Ir are able to provide a moderate property, active enough to hinder the segregation in vacuum and inert enough to prevent the segregation in interacting with an adsorbate under reaction conditions. Our results not only provide the guidance to design core-shell catalysts with reasonable stability and activity, but also highlight the importance of interplay between the reaction environment and the catalysts structure in catalyst design.

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Figure captions

Figure 1 Optimized structures of core shell alloys surfaces: (a) Pt_{1ML}/M(111); (b) $Pt_{0.75ML}M_{0.25ML}/Pt_{0.25ML}M_{0.75ML}$/M(111); (c) $Pt_{0.5ML}M_{0.5ML}/Pt_{0.5ML}M_{0.5ML}$/M(111); (d) $Pt_{0.25ML}M_{0.75ML}/Pt_{0.75ML}M_{0.25ML}$/M(111); (e) M_{1ML}/Pt_{1ML}/M(111); Blue: Pt; Brown: M.

Figure 2 Calculated segregation energy, ΔE_{segr}, as a funcation of number of M on the surface, $Pt_{(1-i)ML}M_{iML}/Pt_{iML}M_{(1-i)ML}$/M (111) or (001).

Figure 3 Color-labeled stability of the Pt_{1ML} shell on various cores M(111) (or M(001) for hcp) surfaces under various conditions. Color index scales the stability from high (dark blue) to low (dark red) according to the lowest ΔE_{segr} calculated using DFT.

Figure 4 Correlation between the calculated $\Delta E_{segr}(1ML)$ (Upper panel) or ΔE_b (lower panel) under vacuum conditions and the d band center with respect to Pt(111), E_d- $E_{d\text{-}Pt}$, of M on the surfaces of M_{1ML}/Pt_{1ML}/M(111) or (001).

Figure 5 Optimized structures of *ClO_4 on the core-shell alloy surfaces: (a) Pt_{1ML}/Cu(111), (b) $Pt_{0.75ML}Cu_{0.25ML}/Pt_{0.25ML}Cu_{0.75ML}$/Cu(111), (c) $Pt_{0.5ML}Cu_{0.5ML}/Pt_{0.5ML}Cu_{0.5ML}$/Cu(111), (d) $Pt_{0.25ML}Cu_{0.75ML}/Pt_{0.75ML}Cu_{0.25ML}$/Cu(111). Blue: Pt; Brown: Cu; Red: O; Purple: Cl.

Figure 6 Calculated segregation energy, ΔE_{segr}, as a funcation of number of core M

segregated to the surface, $Pt_{(1-i)ML}M_{iML}/Pt_{iML}M_{(1-i)ML}/M$ (111) or (001), in $HClO_4$, (a) H_2SO_4 , (b) H_3PO_4 (c) and alkaline (d) solutions.

Figure 7 The optimized structures of *OH on the Pt/M(111) alloy surfaces: (a,b) $Pt_{1ML}/Cu(111)$, (c) $Pt_{0.75ML}Cu_{0.25ML}/Pt_{0.25ML}Cu_{0.75ML}/Cu(111)$, (d) $Pt_{0.5ML}Cu_{0.5ML}/Pt_{0.5ML}Cu_{0.5ML}/Cu(111)$, (e) $Pt_{0.25ML}Cu_{0.75ML}/Pt_{0.75ML}Cu_{0.25ML}/Cu(111)$. Blue: Pt; Brown: Cu; Red: O; White: H.

Figure 8 Calculated segregation energy, ΔE_{segr}, as a funcation of number of core M segregated to the surface, $Pt_{(1-i)ML}M_{iML}/Pt_{iML}M_{(1-i)ML}/M$ (111) or (001), under the ORR condition: (a) *O; (b) *OOH.

Figure 9 The optimized structures of *OOH molecularly and dissociatively to *O and *OH on the core-shell alloy surfaces: (a) $Pt_{1ML}/Cu(111)$, (b) $Pt_{0.75ML}Cu_{0.25ML}/Pt_{0.25ML}Cu_{0.75ML}/Cu(111)$, (c) $Pt_{0.5ML}Cu_{0.5ML}/Pt_{0.5ML}Cu_{0.5ML}/Cu(111)$, (d) $Pt_{0.25ML}Cu_{0.75ML}/Pt_{0.75ML}Cu_{0.25ML}/Cu(111)$. Blue: Pt; Brown: Cu; Red: O; White: H.