The effect of $\text{SnO}_2(110)$ supports on the geometrical and electronic properties of platinum nanoparticles

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Received: 25 July 2019 / Accepted: 10 October 2019 / Published online: 25 October 2019

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Abstract

While Pt-nanoparticles supported on SnO_2 exhibit improved durability, a substantial detriment is observed on the Pt-nanoparticles' activity toward the oxygen reduction reaction. A density functional theory method is used to calculate isolated, SnO_2 - and graphene-supported Pt-nanoparticles. Work function difference between the Pt-nanoparticles and SnO_2 leads to electron donation from the nanoparticles to the support, making the outer-shell atoms of the supported nanoparticles more positively charged compared to unsupported nanoparticles. From an electrostatic point of view, nucleophilic species tend to interact more stably with less negatively charged Pt atoms blocking the active sites for the reaction to occur, which can explain the low activity of Pt-nanoparticles supported on SnO_2 . Introducing oxygen vacancies and Nb dopants on SnO_2 decreases the support work function, which not only reduces the charge transferred from the Pt-nanoparticles to the support but also reverses the direction of the electrons flow making the surface Pt atoms more negatively charged. A similar effect is observed when using graphene, which has a lower work function than Pt. Thus, the blocking of the active sites by nucleophilic species decreases, hence increasing the activity. These results provide a clue to improve the activity by modifying the support work function and by selecting a support material with an appropriate work function to control the charge of the nanoparticle's surface atoms.

Graphic abstract

Keywords Density functional theory · Platinum nanoparticles · SnO_2 · Support effect · Polymer electrolyte fuel cells

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-1478-0>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2019) 1:1485 | <https://doi.org/10.1007/s42452-019-1478-0>

1 Introduction

Polymer electrolyte fuel cells (PEFCs) have been widely investigated as technologies for the transportation sector [1–6], portable power generation [5], and residential co-generation systems [1, 3, 4, 6] because of their environmentally friendly operation [1, 3, 4, 6], modularity [4], and high energy conversion efficiency [1, 2, 5, 6]. However, some long-standing issues remain, including the high cost of platinum (Pt), unreliable performance, and poor durability, which are major impediments to large-scale commercialization of the PEFC [1, 2, 4, 5, 7–10]. Pt and Pt-based alloys are generally the most used catalysts for PEFC because Pt exhibits the highest catalytic activity for the oxygen reduction reaction (ORR), chemical stability, high exchange current density, and superior work function [10]. However, Pt is a scarce and expensive element. Thus, many researchers have focused on reducing the amount of Pt required in PEFCs [4–8, 10–15]. Currently, Pt-nanoparticles are uniformly dispersed on carbon supports to maximize the active surface area per unit mass of Pt, to stabilize/immobilize the catalyst, to ensure sufficient electronic conductivity, and to decrease cost [6, 8, 10, 14–17]. Carbon blacks are the most commonly used supports for Pt and Pt alloys due to their large surface area, good electronic conductivity, and low cost [8, 10, 16, 18–21]. Nevertheless, carbon blacks are unstable under the operating conditions experienced at the cathode side of PEFCs, i.e., relatively elevated temperature [3, 22], acidic conditions [3, 22], humidity [3], and high electrical potential [3, 6, 22].

Resistance toward corrosion, low cost, and availability of certain metal oxides increase their suitability for the replacement of carbon-based support materials [23]. Among the many different metal oxides, tin oxide has emerged as one of the promising candidates for PEFC applications. In particular, the use of SnO_2 has resulted in a large improvement in durability when used as support for Pt-nanoparticles [22, 24]. However, some mild degradation was observed due to Ostwald ripening, and low electrocatalytic activity was recognized, due to the low electrical conductivity of SnO_2 [23, 25]. Theoretical and experimental results showed the preferential growth of SnO_2 films along the [110] in an oxidizing environment [26], such as the conditions at the cathode side of the PEFC. Additionally, STEM images confirmed that the lattice planes of Pt(111) were parallel to those of Nb-doped SnO_2 (110) [6], and nanostructured Sb-doped SnO_2 (110) [27, 28]. The support morphology also plays an important role in the activity and stability; crystalline SnO_2 showed improved stability and higher electrochemical surface area of Pt catalyst [29]. Compared with carbon

materials, the conductivity of SnO_2 limits its application as an electrode substrate material. To increase the electric conductivity and hence the activity, Pt-nanoparticles were supported on hybrid supports such as SnO_2/C [30], $\text{SnO}_2/\text{N-doped carbon nanotubes}$ [29], Nb- SnO_2 containing graphitized carbon black [6], SnO_2 nanowires grown on carbon fibers [31], etc. Additionally, PtSn bimetallic nanoparticles supported on carbon-based materials promoted the oxidation of methanol [32] and ethanol [33] and exhibited enhanced lifetime [32], which led the PtSn nanoparticles to be selected as a promising catalyst for the ORR. PtSn nanoparticles and nanowires showed an increased performance; however, the decay in the mass activity for the catalysts was considerable [34]. Enhanced electrical conductivity of SnO_2 has been achieved by introducing small percentages of dopant elements [6, 22, 25, 35–39]. Specially, Nb as dopant for SnO_2 leads to increased electronic conductivity [22, 39], increased electrochemical surface area [22, 25], increased hydrophilicity [6], increased/decreased the stability compared to carbon black [3, 6, 22, 25] / SnO_2 [22], increased activity toward the ORR, which was attributed to the increase in the electronic conductivity [22, 25]. Although Ta-doped [38] and Sb-doped [3] SnO_2 have electrical conductivities 40 times higher than Nb-doped SnO_2 , the ORR activities of Sb- and Ta-doped SnO_2 were not correspondingly higher than Nb-doped SnO_2 . As such, no clear correlation between the conductivity of the support and the ORR activity was reached. Similarly, the effect of various dopants with different concentrations on the ORR activity was investigated and concluded that while doping SnO_2 affects the activity directly, the ambiguity between support conductivity and ORR activity still holds, as the highest activity was not obtained for Pt supported on doped SnO_2 with the highest electrical conductivity [39]. Moreover, high Pt loadings on oxidized SnO_2 , reduced SnO_2 , and graphene all showed comparable ORR. Only in the case of oxidized SnO_2 , decreasing the Pt loading led to lower ORR activity, which was attributed to stronger adsorption of oxygenated species [40]. It was shown that electronic metal–support interactions can affect the charge of the catalytically active outer surface of nanoparticles [41]. This long-range charge transfer scales with the work function difference between the support and the catalyst [41] and is also size-dependent [42]. However, theoretically, the charge transferred between the support and Pt-nanoparticles was quantified [42–47]. The effect of the charge transfer based on the work function difference between the SnO_2 supports, and Pt-nanoparticles is scarce. One example is the effect of the work function difference of Sb-doped SnO_2 , Sb-doped $\text{SO}_{2.8}$, and Pt_{55} on the charge transfer [41]. To the best of our knowledge, the size dependence of the charge

transfer between Pt-nanoparticles and SnO₂ supports was not carried out, and the activity of the Pt/SnO₂ systems based on the interaction with oxygenated species and its effect on the ORR as a result of the charge transfer has not been discussed.

In this work, the influence of SnO₂ on the physical and electronic properties of Pt-nanoparticles is analyzed after conducting density functional theory (DFT) calculations, showing that the support effect tends to dissipate as the size of the supported nanoparticle increases. However, for nanoparticles up to 2 nm, which is the largest Pt-nanoparticle supported on SnO₂ in this study, the support effect is still quantifiable. Moreover, the nature of the activity of the Pt-nanoparticles of different sizes supported on SnO₂ supports is discussed from an electrostatic point of view generalized by the charge transfer between the Pt-nanoparticles and different supports (reduced SnO₂, Nb-doped SnO₂, and graphene) as a result from their work function (Φ) difference. As the outer-shell atoms of the Pt-nanoparticles become more positively charged (Pt/SnO₂ systems), nucleophilic species will interact strongly, blocking the active sites for the ORR to occur. On the other hand, Pt-nanoparticles on supports with smaller work function than SnO₂, such as reduced SnO₂, Nb-doped SnO₂, and graphene, will exhibit outer-shell Pt atoms less positively charged or even negatively charged, and an increased availability of active sites as the interaction of nucleophilic species with the less positive outer-shell Pt atoms will become weaker. These results can help to explain experimental observations showing the higher activity of Pt-nanoparticles supported on reduced SnO₂, Nb-doped SnO₂, and graphene compared to Pt-nanoparticles supported on SnO₂. Moreover, in this work, the difference in stability of Pt-nanoparticles supported on SnO₂ against Pt-nanoparticles supported on graphene is explained. These results show the importance of the metal–support electronic interactions to control the activity, and stability of catalysts, and at the same time, provide a clue for the tunability of the electronic structure of metal nanoparticles to improve their activity via their interaction with the support material.

2 Computational details

All calculations performed in this study are based on the plane wave DFT method implemented in the Vienna Ab initio Simulation Package (VASP 5.3.5) [48–50]. Perdew–Burke–Ernzerhof parameterization under the generalized gradient approximation (GGA) was employed as exchange–correlation functional together with the projector augmented wave method [51]. Spin-polarized calculations were performed throughout the study with a plane

wave cutoff energy of 400 eV. The convergence criteria for all calculations were set until the difference in total energy between two ionic steps was less than 10^{−4} eV/atom, and 10^{−5} eV/atom for the self-consistent field cycles. The optimization of the face-centered cubic phase of bulk Pt and the rutile-type structure of SnO₂ was performed with 16×16×16 and 8×8×12 Monkhorst–Pack *k*-point meshes, respectively, for the Brillouin zone integration where all the atoms and the whole crystal volume were relaxed. After optimization, the calculated lattice parameters of bulk Pt (*a* = 3.966 Å) and SnO₂ (*a*, *b* = 4.763 Å, and *c* = 3.222 Å) were in good agreement with experimentally reported values for bulk Pt (*a* = 3.916 Å) [52], and SnO₂ (*a*, *b* = 4.737 Å, and *c* = 3.186 Å) [53]. Isolated Pt-nanoparticles (Pt_{*n*}) containing 4 (0.26 nm), 13 (0.53 nm), 55 (1.07 nm), 201 (1.70 nm), 405 (2.23 nm), 711 (2.77 nm), 807 (2.92 nm), and 2406 (4.33 nm) atoms were modeled and optimized until reaching the convergence. To avoid interaction between periodic images, the minimum distance between the boundaries of the cell and the Pt atoms was set to 6 Å, i.e., minimum 12 Å between neighbor image Pt-nanoparticles. After optimization, Pt₄, Pt₁₃, and half-spherical clusters of Pt₃₇, Pt₁₁₉, and Pt₂₃₃ that were truncated from Pt₅₅, Pt₂₀₁, and Pt₄₀₅, respectively, were set to interact with their (111) planes parallel to those of SnO₂(110), as it has been observed experimentally [6]. Two-layered oxygen terminated SnO₂(110) (a single layer consists of top O, middle SnO, and bottom-O planes) was used as support for Pt₄, Pt₁₃, Pt₃₇, Pt₁₁₉, and Pt₂₃₃ nanoparticles. For the Pt_{*n*}/SnO₂ systems, a minimum distance of 7.5 Å was set between the boundaries of the cell and the Pt atoms. Optimization of the isolated Pt_{*n*} and Pt_{*n*}/SnO₂ systems was performed at the Γ point in reciprocal space, due to the significant spatial extent of the systems, where all Pt atoms and the atoms of the top layer of SnO₂ were allowed to relax. The models employed in the calculations are shown in Fig. 1. To corroborate the difference in stability of Pt-nanoparticles on SnO₂ and directly compare the effect of graphene as support material, a single Pt atom, Pt₄, Pt₁₃, and Pt₃₇ nanoparticles supported on graphene were also modeled and optimized with the same conditions as the Pt-nanoparticles on SnO₂.

Cohesive energies of isolated Pt_{*n*}, E_{coh} , adsorption energies of Pt_{*n*} on support, E_{ads} , and formation energies of supported Pt clusters, E_{form} , were defined as:

$$E_{\text{coh}} = E_{\text{Pt}_n} - nE_{\text{Pt}} \quad (1)$$

$$E_{\text{ads}} = E_{\text{Pt}_n/\text{Support}} - (E_{\text{Support}} + E_{\text{Pt}_n}) \quad (2)$$

$$E_{\text{form}} = E_{\text{Pt}_n/\text{Support}} - (E_{\text{Support}} + nE_{\text{Pt}}) \quad (3)$$

where *n* is the number of atoms in the nanoparticle, E_{Pt} is the energy of a single Pt atom, E_{Pt_n} is the energy of the

Fig. 1 Models employed in the calculations: **a** isolated and **b** supported Pt-nanoparticles

Pt-nanoparticle (the energies of Pt_{37} , Pt_{119} , and Pt_{233} were obtained by a single point self-consistent field calculation after the corresponding Pt-nanoparticles were optimized and cleaved in the (111) direction), E_{support} is the energy of the SnO_2 or graphene slabs, and $E_{\text{Pt}_n/\text{Support}}$ is the energy of the Pt-nanoparticle interacting with SnO_2 or graphene. From the definition of the cohesive, adsorption, and formation energies, negative values denote a stable Pt–Pt interaction in the unsupported Pt-nanoparticles, a stable interaction between the Pt-nanoparticles and the support, and a stable Pt–Pt interaction in the supported Pt-nanoparticles, respectively. Although a more stable interaction between Pt-nanoparticles and graphene support was reported by including dispersion corrections, a possibility of overestimation of the interaction energy was pointed out [15]. In this study, the stability of Pt-nanoparticles supported on graphene and SnO_2 was approximated without considering van der Waals interactions. Our results and conclusions about the stronger interaction of Pt-nanoparticles with SnO_2 than with graphene support agree with a previous experimental/theoretical study [6].

Reduced and Nb-doped SnO_2 supports were modeled to examine the effect of crystallographic defects such as oxygen vacancies ($V_{\text{O}}^{\bullet}$) and dopants on the SnO_2 work function. These supports contain 5 SnO_2 layers, symmetrically terminated to avoid artificial dipole induced between the top and bottom terminated sides of the slabs, where the atoms of the middle SnO_2 layer were kept fixed. The vacuum slab was kept to 15 Å. Reduced

SnO_2 was modeled after removing an O atom from the top and the bottom layers of the stoichiometric SnO_2 slab. Once the most stable position for the $V_{\text{O}}^{\bullet}$ was obtained a new O atom was subtracted from the previously reduced SnO_2 and the most stable position of the new $V_{\text{O}}^{\bullet}$ was obtained. This process was repeated 6 times to obtain $\text{SnO}_{2-\delta}$, where the value of δ depends on the number of $V_{\text{O}}^{\bullet}$. For the case of Nb-doped SnO_2 , it was shown that $\text{Pt}/\text{Sn}_{0.98}\text{Nb}_{0.02}\text{O}_2$ exhibits an improved ORR activity than Pt/SnO_2 [22]. Based on the size of the slab, 2% Nb doping corresponds to the symmetric substitution of one Sn atom from the top and bottom layers of stoichiometric SnO_2 . The geometry structures of SnO_2 , $\text{SnO}_{2-\delta}$, and $\text{Sn}_{0.98}\text{Nb}_{0.02}\text{O}_2$ slabs are shown in Figure S1.

Work functions were determined as the difference between the plateau value of the electrostatic potential in the vacuum region and the Fermi level of the supports (stoichiometric, reduced, and Nb-doped SnO_2). The work function of platinum was reported to be 5.65 eV, which corresponds to the experimental value obtain photoelectrically [54]. Pt atom and Pt_4 were set to interact with the reduced and Nb-doped SnO_2 to estimate the effect of modifying the support work function on the Pt_n charge. Because the work function influences the relative alignment of electronic adsorbates states and metallic surface states, substantial implications for the catalytic properties can be expected. The different work function values corresponding to SnO_2 , $\text{SnO}_{2-\delta}$, and $\text{Sn}_{0.98}\text{Nb}_{0.02}\text{O}_2$ slabs are summarized in Table 1.

Table 1 Calculated work function (Φ) values of SnO_2 , $\text{SnO}_{2-\delta}$, and $\text{Sn}_{0.98}\text{Nb}_{0.02}\text{O}_2$. Unit is eV

Support	V_0	Φ
SnO_2	0	7.08
$\text{SnO}_{1.98}$	2	6.14
$\text{SnO}_{1.95}$	4	5.27
$\text{SnO}_{1.93}$	6	5.13
$\text{SnO}_{1.90}$	8	5.03
$\text{SnO}_{1.88}$	10	4.83
$\text{SnO}_{1.85}$	12	4.58
$\text{Sn}_{0.98}\text{Nb}_{0.02}\text{O}_2$		6.39

3 Results and discussion

3.1 Isolated Pt-nanoparticles

3.1.1 Geometrical features

In this section, the structural aspects of isolated Pt-nanoparticles and their dependence on size are explored. Figure 2a shows the ratio of surface sites in the outer-shell atoms of the isolated Pt-nanoparticles. All outer-shell atoms of Pt_4 and Pt_{13} are located at the vertices of the nanoparticles. As the size increases, the ratio of atoms at the vertices decreases. Similarly, from Pt_{55} to Pt_{2406} , the percentage of edge atoms also decreases with increasing the nanoparticle size. The ratio dependency of the {100} sites on nanoparticle size is less clear. The fraction of {100} sites increases in the order $\text{Pt}_{201} < \text{Pt}_{807} < \text{Pt}_{405} < \text{Pt}_{2406} < \text{Pt}_{711}$. Increasing the size of the nanoparticle leads to an increase in the fraction of {111} sites, which become predominant in Pt_{201} or larger. Atoms at edges and vertices are of higher energy (i.e., more reactive) as they are chemically unsaturated, with a lower coordination number. The ratio of atoms with coordination numbers of 5, 6, and 7 decreases with

increasing size, while the ratio of atoms with a coordination number of 12 increases.

The size dependence of the average interatomic Pt–Pt distance for different nanoparticles is shown in Fig. 2b. The average Pt–Pt distance has been studied as a function of nanoparticle size, approximated by $n^{-1/3}$, and proved to be proportional to the effective radius of the nanoparticle and its surface-to-volume ratio [55–58]. Here, the interatomic distance increased linearly with increasing the nanoparticle size approaching the bulk Pt value of 2.823 Å, which is in good agreement with our calculated bulk value of 2.805 Å and with the experimentally reported value of 2.775 Å [59]. The overestimation of the predicted value for the interatomic Pt–Pt distance in bulk Pt compared to the experimental value (by 0.048 Å) is typically observed in DFT calculations employing GGA functionals [55], which agrees well with previous theoretical works on scaling the properties of palladium nanoparticles [45, 46], copper, gold, and silver nanoparticles [57]. Although the interatomic distance averaged over all atoms scales to the bulk values, the outer-shell atoms do not exhibit a clear tendency.

Another size-dependent property is the cohesive energy of the nanoparticle. The cohesive energy is equal to the energy to divide the metal nanoparticle into isolated atoms [56, 60, 61]. The cohesive energy shows a linear relation with $n^{-1/3}$, gradually approaching the corresponding bulk energy as the nanoparticle size increases, as shown in Figure S2. The extrapolated Pt bulk value of the cohesive energy is -5.66 eV/atom, in agreement with the calculated value using a bulk model consisting of 4 atoms (-5.49 eV/atom), as well as the experimentally reported value of -5.84 eV/atom [62]. Underestimation of the cohesive energy with respect to the experimental bulk Pt-value is attributed to the GGA functionals because similar behavior has been observed for the cohesive energy of palladium [56] and ruthenium [63] nanoparticles. It should be noted

Fig. 2 Size dependence of the isolated Pt-nanoparticles geometrical features: **a** ratio of surface sites: vertices (red diamonds), edge (purple squares), {100} (orange stars), and {111} atoms (blue circles), and **b** average Pt–Pt distances in the nanoparticles (gray circles),

and only the outer-shell atoms (blue squares). The linear regression line (dashed green) and the coefficient of determination are also shown. The linear regression intercept, 2.823 Å, corresponds to the extrapolated Pt bulk value

that these values are averaged over all atoms, while different stabilities are expected to be observed for atoms in the outer-shell of each nanoparticle, depending on their degree of coordination. This is because chemically unsaturated atoms with a lower coordination number are more prone to dissolution and bond weakening induced by adsorbates than highly coordinated atoms [2, 12, 64].

3.1.2 Electronic properties

The electronic structure analysis of the isolated platinum nanoparticles is presented based on the DOS profiles in Fig. 3. This analysis can provide relevant information regarding the catalytic activity because possible changes and other features in the DOS profiles will lead to different

reactivity of the nanoparticles. Figure 3a shows the size dependency of the DOS profiles of the entire Pt-nanoparticles. As the Pt-nanoparticles become smaller, a decrease in the confinement dimensions results in the energy levels becoming more discrete. The decrease in the overlapping of energy levels increases the energy separation between adjacent levels. The energy level spacings are large for Pt₄ and Pt₁₃, indicating their more molecular-type character. Increasing the number of atoms in the nanoparticle results in a continuous DOS due to the overlapping of orbitals, as in the cases of Pt₅₅ or larger. The same behavior has also been previously reported for copper [58], silver [58], gold [58], and Pt-nanoparticles [65]. In addition, as the Pt-nanoparticles become larger, the difference in their DOS profiles became less pronounced, as shown in Fig. 3b. Because

Fig. 3 Electronic properties of isolated Pt-nanoparticles: **a** partial DOS profiles of the Pt-nanoparticles, **b** partial DOS difference between contiguous nanoparticles, **c** partial DOS profiles of the outer-shell atoms of the Pt-nanoparticles

the interaction of adsorbates is directly on the outer-shell atoms, the DOS profiles of only the outer-shell atoms are also shown in Fig. 3c. For smaller nanoparticles, the DOS profiles are similar for both the whole nanoparticle and the outer-shell atoms, due to a maximized surface-to-volume ratio. As the size of the Pt-nanoparticles increases, the DOS profile of the outer-shell starts to resemble that of Pt(111), correlating well with the dominance of {111} sites for the larger nanoparticles, as shown in Fig. 2a. In the Hammer–Nørskov model [66–68], the adsorption energy correlates with the position of the *d*-band center relative to the Fermi level. A downshift of the *d*-states relative to the Fermi level decreases the binding energies as the antibonding states are filled. When the *d*-band center is too close to the Fermi level, as in the case of Pt, the metal surface binds oxygen, oxides, or anions too strongly, limiting the rate of the ORR [69]. For the ORR, the electrocatalyst should be active enough to dissociate the O₂ and noble enough to release the bound oxygen in the form of H₂O [70]. The activation of O₂ involves the transfer of a proton and electron to form OOH before the dissociation of the O–O bond. After the dissociation, the electrocatalyst should bind O atom and OH moderately for the H₂O desorption to be fast. An endergonic reduction reaction by the transfer of a proton and electron of adsorbed O atom or OH to form OH and H₂O, respectively, will lead to the surface of the electrocatalyst to be covered by these species blocking the active sites for the O₂ adsorption. From experimental, and DFT results, it was concluded that a surface that binds O atom 0.0 to 0.4 eV more weakly than Pt(111) should exhibit an enhanced ORR activity compared to Pt [70, 71]. Following this line, an increased ORR activity was reported for Pt₃M (M = Co, Ni, Fe, V, Ti) bimetallic alloy surfaces with Pt skin configuration, from which Pt₃Co exhibited ca. 3 times enhanced activity compared to polycrystalline Pt [69]. This enhancement was because the active sites were less blocked due to a decrease in the adsorption and coverage of oxygenated species compared to Pt, as a result of the *d*-band center of the Pt₃Co surface, –2.86 eV, being more distant from the Fermi level compared to –2.55 eV of the polycrystalline Pt [69]. Figure S3(a) shows the *d*-band center relative to the Fermi level for the isolated platinum nanoparticles. The *d*-band centers of the nanoparticles and their outer-shell atoms are downshifted as the nanoparticle size increases. The *d*-band center of –2.54 eV calculated for Pt(111) is close to the experimental value of the polycrystalline Pt [69]. The *d*-band centers of the outer-shell atoms approach the value of Pt(111) as the nanoparticle size increases. Only Pt₂₀₁ and Pt₄₀₅ showed slightly downshifted *d*-band center values compared to Pt(111). Thus, following the *d*-band center model, these nanoparticles should exhibit an increased activity than Pt(111); however, it should be noted that the *d*-band center model showed

moderate linear correlations between the heats of adsorption of small molecules or atoms such as CO, H₂, O₂, and C_xH_y on various metal surfaces [66–68]. It was proved that the relationships between adsorption energy and *d*-band center do not account for the effect of less coordinated atoms, such as the ones located at the vertices and edges of nanoparticles, on the adsorption, especially for small cluster particles that do not expose well-defined planes [72–74]. Considering the experimental value of –2.86 eV of Pt₃Co surfaces, the calculated values of the *d*-band centers of the outer-shell atoms of the Pt-nanoparticles considered in this study point out to a stronger adsorption of oxygenated species; O^{2–}, OH[–], H₂O, H₂O₂, etc. (i.e., species found at the cathode environment of a PEFC), which will lead to more active sites being blocked than for the Pt₃Co, and to a lower activity for the ORR. In Figure S3(b), the relationship between the average charge distribution at the outer-shell atoms of the Pt-nanoparticles and their average *d*-band center is shown. By taking into consideration this “linear” relationship, the charge per atom corresponding to the *d*-band center of Pt₃Co (–2.86 eV) can be extrapolated, i.e., –0.0529 e/atom. Thus, as the outer-shell atoms become more negatively charged, electrostatic repulsion with oxygenated species (nucleophilic) found at the cathode environment of the PEFC will arise, decreasing their stable adsorption and their coverage, which will lead to an increase in the ORR kinetics. It should be noted that the charge distribution for the Pt₃Co outer-shell atoms could be even more negative than the estimated value of –0.0529 e/atom as a result of electron donation from Co atoms in the core region to Pt atoms in the surface because of the work function difference. Nevertheless, this estimated value for the charge per atom and *d*-band center of –2.86 eV can be used as a “guide” for Pt-nanoparticles.

3.2 Effect of SnO₂ as support material

In this section, the influence of using a SnO₂(110) support on the geometrical features and electronic properties of Pt-nanoparticles is discussed.

3.2.1 Effect of SnO₂ on nanoparticle geometry

Figure 4a shows the frequency distribution of Pt–Pt interatomic distances of isolated Pt-nanoparticles compared to those supported on SnO₂. SnO₂-supported nanoparticles consisting of 4, 13, and 37 atoms exhibit significant differences in Pt–Pt distance compared to larger nanoparticles (i.e., SnO₂-supported Pt₁₁₉ and Pt₂₃₃). The average interatomic Pt–Pt distance is plotted against the size of the nanoparticle in Fig. 4b. The interaction between Pt-nanoparticles and SnO₂ leads to an increase in the Pt–Pt distance

Fig. 4 Effect of SnO_2 on the Pt-Pt distance: **a** frequency distribution of the Pt-Pt distance of the isolated (gray bars) and supported (dark red bars) Pt-nanoparticles, **b** size dependence of the Pt-Pt distance of isolated Pt-nanoparticles (gray circles) and supported

Pt-nanoparticles (dark red triangles), and **c** variation in the Pt-Pt distance of the outer-shell atoms of isolated (blue squares) and supported (red diamonds) Pt-nanoparticles

compared to isolated nanoparticles. As the nanoparticle size increases, this effect decreases, showing that the support effect tends to dissipate with increasing the size of the nanoparticle. The most substantial elongation of the interatomic distance was 0.044 Å for Pt_{37/SnO_2} , which also exhibited the highest amount of atomic rearrangement. Moreover, the variations in the interparticle distance due to the interaction with SnO_2 were analyzed for the outer-shell atoms of the SnO_2 supported nanoparticles. Figure 4c

shows the average interatomic Pt-Pt distances from the top facet to the Pt/ SnO_2 interface. The most considerable variations are observed for atoms located at the triple phase boundary (TPB), i.e., the outer-shell atoms situated at the interface between Pt and SnO_2 . As the size of the nanoparticle increases, the average interatomic distance at the interface decreases, except for the case of Pt_4 , ranging from an expanded Pt-Pt distance of 2.800 Å at the Pt_{13}/SnO_2 interface to a compressed Pt-Pt distance of 2.725 Å

at the $\text{Pt}_{233}/\text{SnO}_2$ interface. Moreover, for the atoms at the top facets, the variations in the interatomic distance become smaller compared to the interface atoms (except for Pt_4), especially for the larger nanoparticles. The exception of Pt_4 can be explained by its small size and the lack of a core atom to behave as a bulk-like atom. These results show that the support effect weakens with increasing nanoparticle size and that it is localized at the metal/support interface. Similar behavior has been previously reported for spherical cuboctahedral platinum nanoparticles supported on graphene [15].

3.2.2 Effect of SnO_2 on the nanoparticles' electronic properties

Electron transfer is rationalized in terms of electronic equilibration between the support material and the catalyst nanoparticle. Upon contact, and in line with the work function difference, electrons are withdrawn from Pt to SnO_2 . The charge transfer ranges from 0.76 electrons for Pt_4 , to 4.10 electrons for Pt_{233} , leading to average charges from 0.19 e/Pt atom to 0.02 e/Pt atom, respectively. In our calculations, the electron density redistribution showed to be localized mainly at the nanoparticle-support interface. For all the supported Pt-nanoparticles, the average charge of the Pt atoms at the TPB was positive, decreasing with the size of the nanoparticle from +0.27 e/atom for the TPB of Pt_4 to +0.154 e/atom for the atoms at the TPB of Pt_{13} , to +0.029 e/atom for the TPB atoms of Pt_{37} , then increased to +0.094 e/atom for the Pt_{119} 's TPB, and lastly decreasing again to +0.075 e/atom for the atoms at the TPB of Pt_{233} . As the size of the nanoparticle increases, more atoms from the nanoparticle are in contact with the support donating electrons to reach the electronic equilibrium. For this reason, as the size of the nanoparticle increases, the outer-shell atoms at the top layers were less affected by the support. Except for the top layer of Pt_{13} , from Pt_4 to

Pt_{233} , the top layer atoms were charged negatively, and for Pt_{119} and Pt_{233} , all the outer-shell atoms were charged negatively except the TPB atoms. The average charge per atom of the outer-shell atoms decreased from 0.19 e/atom for Pt_4 to −0.008 e/atom for Pt_{233} . These results show the size dependency of the Pt-nanoparticles supported on SnO_2 ; with increasing the diameter of the nanoparticle, more Pt atoms will be in contact with the support. These Pt atoms will be the main ones to donate electrons “shielding” the surface atoms located at the top and intermediate layers. It should be noted that even though the outer-shell atoms of the supported nanoparticles became more negatively charged with increasing the size of the nanoparticle, their charge is less negative than the outer-shell atoms of the isolated Pt-nanoparticles, as shown in Fig. 5. Thus, a stronger interaction with nucleophilic species is to be expected, which should result in blocking of the catalyst active sites, retarding the reaction kinetics.

Regarding the nanoparticle size effect, it has been reported that the oxophilicity of metal nanoparticles increases with decreasing size [75–77], which results in the formation PtO_x [76] that have been known to be prone to dissolution during the electroreduction of O_2 [78]. In this work, the largest supported Pt-nanoparticle, $\text{Pt}_{233}/\text{SnO}_2$, has a size of ca. 2.11 nm. From the charge transfer analysis, $\text{Pt}_{233}/\text{SnO}_2$ is expected to be a suitable adsorbent for oxygenated species, which will block the active sites for the ORR to occur. Our results agree and explain the low activity exhibited by Pt-nanoparticles of ca. 2 nm supported on SnO_2 [40]. Experimentally, the strong interaction of oxygenated species on Pt-nanoparticles with diameters of 2 nm supported on SnO_2 is responsible for the low ORR activity compared to those supported on glassy carbon [40]. The ORR activity increased only after extended Pt regions were formed on oxidized SnO_2 due to the large Pt loadings, where the effect of the support is minimal. Our results show a similar tendency with experimental

Fig. 5 Color coding of the charge of Pt atoms, and charge distribution on the outer-shell atoms of isolated (blue squares) and supported (red diamonds) Pt-nanoparticles

observations, where SnO_2 as an alternative to carbon will help to stabilize the interaction of oxygenated species on Pt-nanoparticles, blocking the active sites, and lowering ORR activity. Considering the size of the Pt-nanoparticles in this study, as the nanoparticle becomes larger, our results show that the effect of SnO_2 tends to dissipate. This tendency agrees well with previous observations from cyclic voltammograms of Pt-nanoparticles supported on Nb-doped SnO_2 , where decreasing the size of the nanoparticle led to a negative shift in the oxygen desorption peak potential indicating stronger adsorption of oxygenated species [25]. However, in the previous study [25], the Pt-nanoparticles were supported on Nb-doped SnO_2 ; thus, the interplay between the dopant and the particle size effect may have made the oxygenated species less prone to interact with Pt-nanoparticles > 2.6 nm.

Variations in the d -band centers of supported nanoparticles arising from the interaction with SnO_2 are shown in Figure S4. Because the interaction of Pt-nanoparticles with gaseous species and adsorbates will be directly on the outer-shell atoms, only the d -band centers of the outer-shell atoms were analyzed in this study. Only for the $\text{Pt}_{13}/\text{SnO}_2$, all the outer-shell Pt atoms underwent a significant downshift in their d -band centers of ca. 0.305 eV. As the size of the nanoparticle increased, the downshift in the d -band center decreased to 0.056 eV for $\text{Pt}_{37}/\text{SnO}_2$. Conversely, an upshift of 0.01 eV was observed for the surface atoms of $\text{Pt}_{119}/\text{SnO}_2$. And the outer-shell atoms of $\text{Pt}_{233}/\text{SnO}_2$ experienced a downshift of 0.007 eV with respect to the outer-shell atoms of the isolated Pt-nanoparticles. The d -band center of the TPB atoms of $\text{Pt}_{13}/\text{SnO}_2$ was largely downshifted by 0.672 eV. For the $\text{Pt}_{37}/\text{SnO}_2$, the TPB atoms' d -band center downshifted 0.098 eV. Contrarily, Pt_{119} and Pt_{233} experienced an upshift of 0.083 eV. It is interesting to note that the change from a downshift in the d -band center to an upshift is for nanoparticles between 37 and 119 atoms. The atoms at the top facet of the supported nanoparticles (except for the case of $\text{Pt}_{13}/\text{SnO}_2$) exhibited an upshift in their d -band centers, which increases with the nanoparticle size. Additionally, the d -band centers of the layers between the TPB and the top facet became more downshifted. This downshift decreased as the size of the nanoparticle increased. According to the Hammer-Nørskov model [66–68], the upshift/downshift of the d -band centers will lead to stronger/weaker adsorption of oxygenated species. This effect tends to decrease with increasing the nanoparticle size on the support. A contradicting correlation is observed between the different values of the electron density distribution and the changes in the d -band centers. From the d -band center results, the large downshift of the outer-shell atoms of Pt_{13} (weaker adsorption of gaseous species) is opposite to the results from the charge analysis, where the Pt_{13} atoms were positively

charge compared to the isolated Pt-nanoparticles. Similarly, the downshift in the d -band center experienced by the surface atoms at the layers between the top and TPB of Pt_{37} , Pt_{119} , and Pt_{233} indicate a weaker adsorption than on the isolated Pt-nanoparticles, which is in contradiction of the results obtained from the charge analysis showing that a stronger adsorption of nucleophilic species is to be expected.

3.2.3 Effect of SnO_2 on nanoparticle stability

Pt-nanoparticles with small diameter supported on carbon have reduced lifetime under the operating conditions of a PEFC. The weak interaction between platinum and carbon leads to nanoparticle aggregation and detachment from the support [11]. On the other hand, Pt-nanoparticles supported on SnO_2 exhibited stronger interaction and thus greater stability, although some degradation due to Ostwald ripening has been observed [22]. In this section, the interaction strength between Pt-nanoparticles and SnO_2 is approximated by the adsorption energy. Additionally, the adsorption energy of Pt-nanoparticles on graphene is calculated and compared to SnO_2 . Figure 6a displays the Pt clusters supported on graphene. The adsorption energies for all the Pt_n/SnO_2 systems are more negative; stronger interaction between the Pt_n and SnO_2 , than for the $\text{Pt}_n/\text{graphene}$ systems. For both systems, increasing the size of the nanoparticle increased the total interaction with the support, as shown in Fig. 6b. On the other hand, the adsorption energy per atom in the nanoparticle decreases with increasing nanoparticle size, in agreement with a previous theoretical study [15]. The effect of the support material on the Pt–Pt interaction was estimated from their formation energies, as shown in Fig. 6c. The formation energies of all the Pt_n/SnO_2 systems are more negative, and hence, they are more stable than the $\text{Pt}_n/\text{graphene}$ systems. These results are relevant because they show a destabilizing effect of graphene in Pt–Pt interaction compared to SnO_2 support. Although a previous DFT work showed the influence of the shape of isolated and carbon-supported Pt-nanoparticles against dissolution [12], the effect of graphene in the Pt–Pt interaction was not taken into consideration. While other effects such as carbon corrosion are also considered in experimental observations showing the faster degradation of Pt/graphene systems, the stronger interaction between the Pt clusters and the SnO_2 support, and the effect of SnO_2 on the Pt–Pt interaction go a long way to explaining the suppressed Pt atom dissolution, nanoparticle aggregation, and detachment. The size dependence of the formation energies shows that with increasing the nanoparticle size, more stable Pt–Pt interaction is to be expected, which is opposite to the adsorption energy per atom trend. Therefore, as the size of

Fig. 6 Effect of the support on the stability of Pt-nanoparticles: **a** models of the calculated Pt_n/graphene structures, **b** adsorption energies and **c** formation energies of Pt-nanoparticles supported on SnO₂ (red circles) and graphene (brown asterisks)

the nanoparticle increases, the increased Pt–Pt interaction improves nanoparticle stability. Sixth-generation density derived electrostatic, and chemical (DDEC6) atomic population analysis was conducted to compute the bond orders [79]. Individual bond orders and the sum of bond orders can help provide valuable information regarding stability and activity trends. To single out the effect of SnO₂ on the Pt–Pt interaction of the outer-shell atoms, the bond order values were computed for the isolated Pt₄ and Pt₁₃ nanoparticles, for the hemispherical Pt clusters, and then compared to the respective outer-shell atoms of the supported nanoparticles. The bond order values for the outer-shell atoms of the isolated nanoparticles become larger with increasing the size, as shown in Figure S5. Similarly, larger bond orders were observed with increasing the nanoparticle size of the supported Pt-nanoparticles. The bond order values of the outer-shell atoms of Pt₄, Pt₁₃, and Pt₃₇ supported on SnO₂ were smaller than the values of the outer-shell atoms of isolated Pt-nanoparticles, revealing a detrimental effect of SnO₂ in the Pt–Pt interaction. The detrimental impact dissipates for supported Pt-nanoparticles containing more than 37 atoms, i.e., Pt₁₁₉ and Pt₂₃₃. Weakening the Pt–Pt interaction can explain the Pt mass loss due to the dissolution of PtO_x as a consequence of the strong adsorption of oxygenated species [75, 76].

3.2.4 Effect of the support work function on the charge of Pt-nanoparticles

Pt-nanoparticles supported on reduced SnO₂ [40] and Nb-doped SnO₂ [22] showed improved ORR activity compared to Pt/SnO₂. This improved activity, in some part, can be explained in terms of perturbation of the electronic structure of the Pt catalyst driven by the new electronic equilibrium between the Pt and the reduced or doped SnO₂ affecting the charge transfer compared to SnO₂. The formation of V_O[•] and doping SnO₂ with Nb leads to the

formation of electrons, as shown in Eqs. (4) and (5). These electrons will decrease the work function of the support material (Table 1); hence, the charge redistribution on Pt/SnO_{2-δ} and Pt/Sn_{0.98}Nb_{0.02}O₂ will be different from that on Pt/SnO₂.

The perturbation on the work function values as a result of V_O[•] and Nb doping led to a decrease in the charge withdrawn from the Pt atom and Pt₄ supported on SnO_{2-δ} and Pt/Sn_{0.98}Nb_{0.02}O₂. As the number of V_O[•] increased the work function decreased becoming lower than the Pt's work function; thus, electrons were donated to Pt atom and Pt₄ in line with the difference in work function, as shown in Fig. 7a. To corroborate this statement, the effect of graphene support on the charge of Pt₃₇ was calculated. The calculated value of graphene's work function is 4.46 eV, which is in good agreement with the experimental value of 4.60 eV [80]. The comparison between the charge of the outer-shell atoms of Pt₃₇/SnO₂, Pt₃₇/graphene, and the isolated Pt-nanoparticle is shown in Fig. 7b. Upon contact, electrons will flow from the graphene support to the Pt-nanoparticle in line with the work function difference between these two materials. Our results indicate that graphene is donating 0.261 electrons to the Pt₃₇, which is opposite to the Pt-nanoparticles supported on SnO₂. The charge transfer to the nanoparticle led that the outer-shell atoms of Pt₃₇/graphene to exhibit a charge of −0.039 e/atom, which is more negative than the outer-shell atoms of Pt₃₇/SnO₂ and the isolated Pt-nanoparticle, 0.007 and −0.037 e/atom, respectively. Thus, based on electrostatic interactions, nucleophilic species will be more affine to the outer-shell atoms of the nanoparticle supported on SnO₂.

Fig. 7 **a** Charge variation of Pt atom (circles) and Pt₄ (squares) as a function of the support work function (SnO₂ in blue, SnO_{2-δ} in purple and Sn_{0.98}Nb_{0.02}O₂ in cyan). Negative values indicate that elec-

trons are being withdrawn from the support. **b** Charge distribution of the outer-shell atoms of isolated (blue squares), SnO₂ supported (red diamonds), and graphene-supported (gray circles) Pt₃₇

than the surface atoms of Pt₃₇/graphene. Our results can be used to explain the higher activity of Pt-nanoparticles supported on reduced SnO₂ and glassy carbon compared to Pt-nanoparticles supported on SnO₂. As the support work function decreases (effect of $V_O^\bullet$) below the value of the work function of Pt, electrons, upon contact, will flow from the support (graphene and SnO_{2-δ}) to the nanoparticle to reach a new electronic equilibrium. Thus, the electronic donation will make the surface atoms of the nanoparticle more negatively charged, which will tend to decrease the interaction of nucleophilic species. Similarly, the effect of Nb dopant showed to decrease the work function of SnO₂. However, compared to SnO_{2-δ}, the influence was not as considerable; hence, there is a possibility that on the Nb-doped SnO₂ may also exist a certain percentage of $V_O^\bullet$ helping to decrease the support work function. This explanation agrees with DFT calculations showing that charge transfer occurs from Pt₅₅ to Sb_{0.035}Sn_{0.965}O₂ and due to the presence of $V_O^\bullet$, electrons were donated to Pt₅₅ from Sb_{0.035}Sn_{0.965}O_{2-δ} [41]. Additionally, our results can also be used to explain the suppressed charge transfer from Pt-nanoparticles to reduced CeO₂ compared to the stoichiometric CeO₂ [42]. The lower propensity of the partially reduced ceria to accept additional electrons [42] is due to a decreased work function of the reduced support compared to the stoichiometric CeO₂, and not just to the nucleation of Pt-nanoparticles at the defects of the reduced CeO₂ as it was stated [42]. Thus, the difference between the work function of the Pt-nanoparticles and the reduced CeO₂ support is smaller than when the Pt-nanoparticles are supported on the stoichiometric CeO₂ support. Hence, a decrease in the charge withdrawn from the nanoparticles to CeO_{2-δ} was observed as a result of the new electronic equilibrium between the Pt and the reduced CeO₂.

Our results match different experimental observations/tendencies; our results show that as the size of the

nanoparticle decreases, there is a tendency for the nucleophilic species to interact more stably on Pt-nanoparticles supported. A similar tendency was observed for Pt-nanoparticles supported on carbon [40], glassy carbon [81], and Nb-doped SnO₂ [25]. The low activity of Pt-nanoparticles of ca. 2.0 nm supported on SnO₂ is due to the strong interaction of OH species [40], and that the OH interaction on reduced SnO₂ is weaker than on Pt/SnO₂ [40]. Additionally, our results can explain the fact that nanoparticles supported on reduced SnO₂ and Nb-doped SnO₂ exhibited increased ORR activity, which so far was related to the increased electronic conductivity due to Nb doping than the Pt/SnO₂ systems [22, 25]. The experimental observations are summarized in Table S1.

4 Conclusions

The geometrical features and electronic properties of isolated and SnO₂ supported Pt-nanoparticles of different sizes are analyzed after conducting DFT calculations. Although for isolated Pt-nanoparticles, their electronic properties tend to converge as their size increases, the outer-shell atoms do not show such tendencies. After contact, a new equilibrium is reached between the Pt-nanoparticles and SnO₂ support, where electrons are donated from the nanoparticles to the support making the outer-shell atoms more oxidized than the isolated nanoparticles. On the other hand, reducing the SnO₂ work function by the presence of Nb dopant and $V_O^\bullet$, charge transfer occurs from the support to the Pt-nanoparticles. A similar effect is observed when Pt₃₇ is supported on graphene resulting in the outer-shell atoms to be more negatively charged than the isolated nanoparticles. From an electrostatic point of view, the interaction with nucleophilic species is expected to be stronger/weaker on less/more negatively charged Pt atoms, which leads to a change in the activity.

It is observed that as the nanoparticle size increases, the support effect tends to mitigate. However, the effect of SnO_2 support is not negligible, even for Pt-nanoparticles of ca. 2.00 nm. Moreover, Pt-nanoparticles supported on SnO_2 are more stable compared to the Pt-nanoparticles supported on graphene, in agreement with experimental results. Nevertheless, the Pt–Pt interaction of the outer-shell atoms of Pt_4 , Pt_{13} , and Pt_{37} nanoparticles is weaker compared to isolated nanoparticles, while the interatomic interaction of larger size nanoparticles is slightly stronger, exhibiting a size dependence stability for nanoparticles supported on SnO_2 . This study not only highlights the importance of the metal–support electronic interactions to control the stability and activity of catalysts but also provides a clue for the tunability of the electronic structure of metal nanoparticles to improve their activity via their interaction with the support material. These results have important implications for the use of supports in catalysis, electrocatalysts, sensing devices, etc.

Acknowledgements Activities of INAMORI Frontier Research Center are supported by KYOCERA Corporation. Part of the research is supported by ACCEL, Japan Science and Technology Agency (Grant No. JPMJAC1501). This work was supported by “Advanced Computational Scientific Program” of Research Institute for Information Technology, Kyushu University.

Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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