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Theoretical exploration of novel catalyst support materials for fuel cell applications

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Abstract

In this work, a range of corrosion resistant materials have been assessed for their suitability as Pt catalyst supports using density functional theory. The influence of support material on the catalytic activity has been disentangled into the geometric and electronic effects via a correlation between the d-band centre of the supported Pt film and the interfacial lattice strain (lattice match). Two energetic descriptors, the Pt wetting parameter and the relative oxygen binding energy have been used to describe the catalyst-support adhesion behaviour and the resultant activity. Taking both of the factors into account, some novel candidate materials, e.g. TiC and WC, are recommended as catalyst supports.

1. INTRODUCTION

Fuel cell (FC) technology offers an attractive combination of highly efficient fuel utilisation and environmentally friendly operation.[1]Despite different types of cell design, the electrochemical reaction in low temperature fuel cell generally requires using platinum group metal (PGM) based catalysts and a supporting electrode which provides a physical surface for metal catalyst dispersion. Currently, carbon is the most commonly used supporting material. However, the conductive carbon support is susceptible to corrosion conditions experienced in electrochemical oxidation. [2]Furthermore, at high loading on carbon, Pt and other precious metal catalysts tend to aggregate into large particles with intrinsically low dispersions. Neither the carbon support nor the highly dispersed particles are sufficiently stable in the fuel cell environment. Therefore, finding a corrosion resistant support material to improve the mass activity of PGM catalysts emerges as an important topic in fuel cell research.

In this work, different types of carbon alternative supports including metal oxides [3-5], nitrides [6], carbides [2] and corrosion resistant metals e.g. W and Ta [7] have been considered and accessed by theoretical modelling using density functional theory (DFT). All of these candidate materials exhibit good environmental resistance to the harsh operating conditions within a fuel cell. According to the previous experimental studies, the nitride and carbide supports are chemically inert, also present metallic properties.[2][6]In particular, the transition metal carbide of hexagonal structure WC, exhibits Pt-like electronic density of states around Fermi Level and is expected to have a synergetic effect on the catalytic activity.[8] The sub-stoichiometric oxides [9-12] such as oxygen reduced TiO_x and Nb doped TiO_2,[13] have been considered as catalyst supports due to their experimentally observed promotion of the metal-support interaction as well as elevated electron conductivity compared to undoped TiO_2 substrate. [2]Additionally, some corrosion resisting metals e.g. W and Ta also are of interest for their potential usage as a tie layer to assist Pt adhesion on the support.

Using the first principle, DFT modelling approach, we attempted to develop activity descriptors that would provide quantitative comparison of various support structures for

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their suitability as a catalyst support. The wetting of the support by Pt is considered as a key factor which affects the catalyst dispersion on support surfaces. Several modelling efforts have been undertaken to study the Pt deposition on different substrate surfaces. As suggested by Greeley, [14] the stability of Pt films on the support can be assessed by the Pt dissolution potential $U_{diss,}$ which is converted from the Pt binding energy. In their earlier paper, a thermodynamic formalism combined with DFT calculations has been used to determine the trends in the reversible deposition/dissolution potentials of Pt embedded on the substrate of rutile oxides. [15] However, this descriptor hasn't taken into account the substrate geometry when diverse support structures are involved. Moreover, the ideal support should also improve the catalytic activity, since Pt tend to bond the reaction intermediates over strongly [17].The oxygen binding energy, which has previously been shown by Norskov and co-workers to be an important parameter that governs the ORR activity of transition metal, has been correlated with d-band centre, a quantum electronic property, [16-20] and used as activity descriptor for the supported Pt in this work.

In addition, the structural impact of the support on the Pt film stacking order as well as the catalytic performance is another important aspect that has been probed in the current study. Various support structures of rutile, anastase, perovskite, rock salt and wurtzite have been studied, including their influence on the Pt electronic structure and catalytic activity in terms of geometric strain and electronic bonding effects. The latter are manifest in the relative shifts of the Pt d-band centre for the supported catalyst system. The relations between oxygen binding and d-band centre have been explored for the Pt coated support surfaces.

2. METHODS

All periodic DFT calculations presented here were carried out using CASTEP code. [21] The Revised-Perdew–Burke–Ernzerhof (RPBE) functional within the generalized gradient approximation (GGA) have been employed to describe the exchange and correlation effects. [22] Ionic cores and their interaction with valence electrons for the elements involved are calculated by the use of ultrasoft pseudopotentials with a kinetic energy cut-off of 350

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eV. All systems are sampled with Monkhorst-pack k-point meshes of actual spacing close to 0.04Å.

The support surfaces were studied by a slab model with vacuum space separation of 25 Å to allow the inclusion of additional platinum layers on the substrate surface. The convergence of the surface energy has been achieved with a slab thickness up to 5 layers, in which the top two layers were allowed to relax, whilst the remaining bottom layers were fixed. The most energetically favourable support surfaces have been chosen for the Pt deposition study, however, different surface terminations need to be considered for the some support structures, e.g. carbides and aluminum nitride, since the surface termination has a significant influence on the interfacial bond formation. The detailed calculation models including bulk, surfaces and surface terminations are discussed in the Supplementary Information. 4 Pt overlayers have been added on each support surface, atom by atom to study the stacking order optimization of the Pt films. The catalytic activity descriptors of oxygen binding energy and d-band centre were calculated for the outmost layer of the supported Pt films, thereby allowing us to quantify the electronic influence of the support on Pt films.

The d-band centre is calculated either as a median of the d-projected PDOS or as a 1st moment (most probable value).[16] The adsorption energies of an oxygen atom on the supported Pt surfaces have been correlated with the d-band centre descriptor. The reference energy used for oxygen adsorption E[O] is taken as half the energy of the O_2 molecule. The most stable adsorption site of oxygen atoms has been identified for different Pt overlayer structures. For the stepped surfaces, the edge sites have been compared with the terrace sites for oxygen adsorption. The data used in the reaction activity analysis are the lowest adsorption energies that have been obtain.

Additionally, the stability of Pt deposition films, which implies the tendency of catalyst sintering, is also of great importance for material selection. The Pt deposition study is carried out in a limited size slab model with the periodic boundary conditions, therefore，the Pt atoms are constrained to form a Pt film on the support surface. However, the sintering tendencies of these overlayer films can be estimated by calculating the binding energy

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increment for each additional Pt atoms. Taking into consideration the stoichiometric effect of complex support-catalyst interfaces, the sum of the binding energy increment for adding N layers of Pt atoms $\sum_{i=1}^{N} dE_i[Pt]$ (i=1, 2, 3, 4) (since the binding energy increment $dE_i[Pt]$ converges to 0 around the 4th layers, i=4) has been normalized with the surface area of the support, and used as the Pt wetting descriptor, $\delta = \sum_{i=1}^{N} dE_i[Pt] / A_{Surf}$ i.e. the average energy cost of Pt binding per unit surface area. When adding Pt atoms on the equilibrium Pt (111) surface, the DFT modelling gives a reference value of δ_0 [Pt] equal to 0.176 eV/A^2 for Pt overlayer growth (calculated in a model of 4 layer depth). Hereby, we can predict Pt wetting ability according to the value of δ, if $\delta<\delta_0$, Pt overlayers are more likely to attach to the support surfaces, conversely if $\delta>\delta_0$, Pt films tend to detach. A calculated overlayer slab model of the metal-support catalyst is sketched in **Figure 1**.

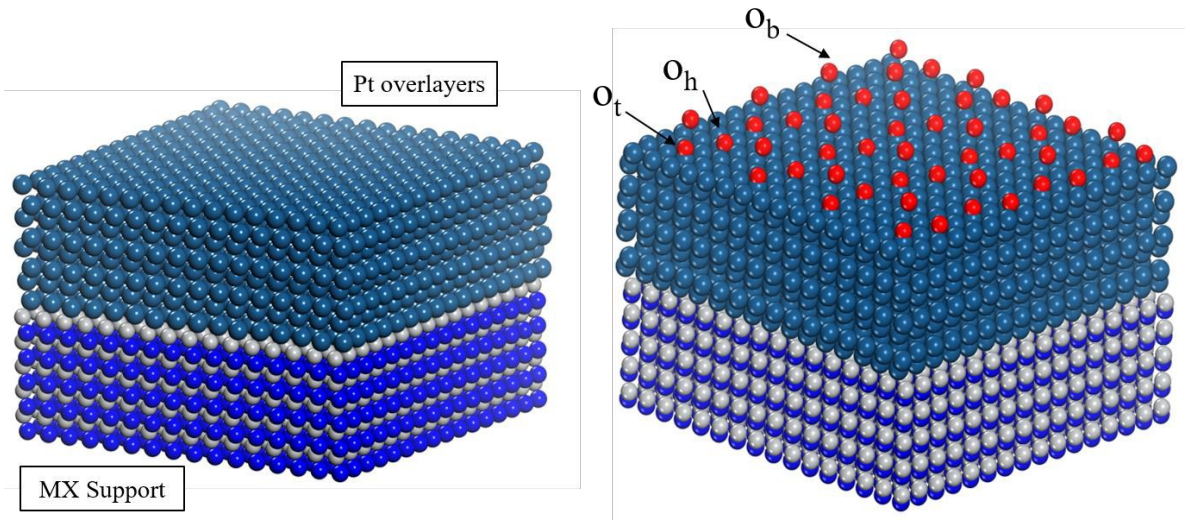

Figure 1. The atomic model of Pt overlayer on MX support (Left). Oxygen adsorption on the MX supported Pt films (Right). O_t, O_b and O_h denote the top, bridge and hcp (or fcc) sites for oxygen adsorption.

3. RESULTS AND DISCUSSION

1) Pt stacking order on the supports

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The growth of Pt films has been investigated with respect to different support geometries using the overlayer slab model. The calculation results suggest the stacking order of Pt for all the optimized overlayer structures can be related to the three energetically favourable surfaces of Pt (211), (111) and (100) as a result of the surface compression or expansion (**Figure 2)**. The equilibrium structure of the three most stable Pt surfaces from theoretical calculations and the corresponding structures are given in the Supplementary Information (Table S1 and S2).

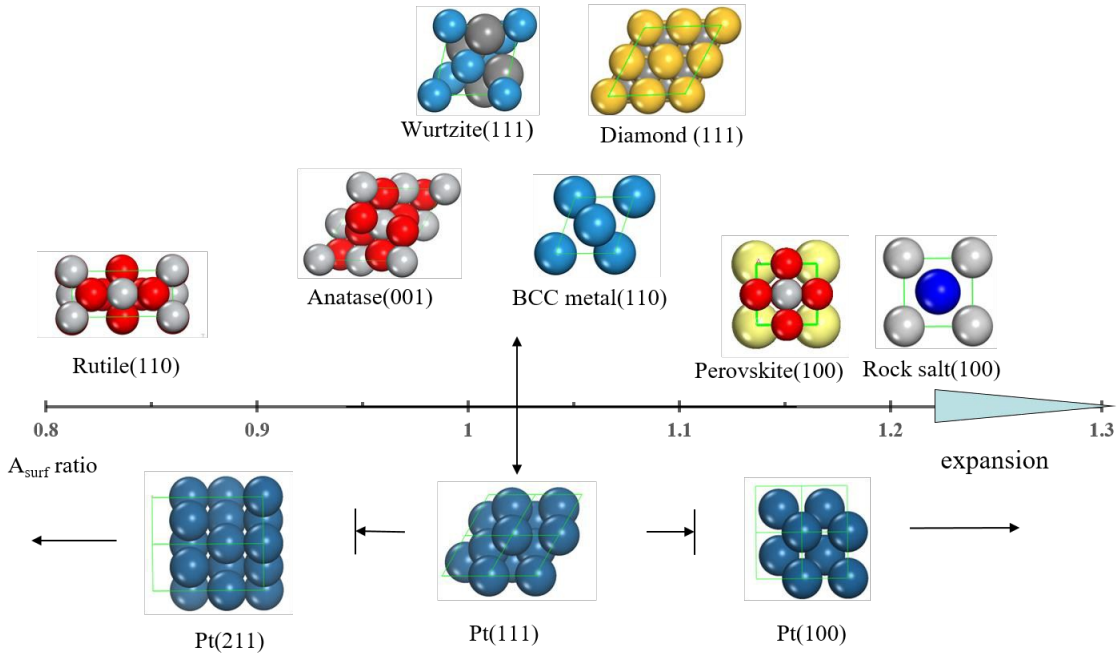

Figure 2. The stacking order of Pt overlayers in relation to the support surface geometries of Pt (111), (100) and Pt (211).

The support material can affect the stacking order of Pt overlayers. In particular, the rutile MO_2 (110) tends to constrain the growth of the most stable Pt (111) surface. A stepped Pt (211) surface, which can be viewed as a contracted form of Pt (111), has been adopted for the Pt overlayers due to the strains induced by the interfacial lattice mismatch. For the anatase TiO_2(001) substrate, since it has a larger surface area than rutile (110) and gives a better match with Pt(111), a slightly compressed hcp overlayer of Pt(111) can be formed. These (111) type overlayer structures have also been found for other hcp support surfaces such as WC(111), SiC(100) and AlN(100), but with expansions on the equilibrium

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structure of Pt(111). In addition, when expanding the Pt lattice in a cubic array, the Pt(100) type overlayer structures are generated on the support surfaces due to the better symmetry match (4-fold vs. 3-fold). However, we have to note that such a size effect of the support surface can be reduced by employing large supercell models, which minimize the interfacial strain for Pt overlayers growth and the most stable Pt(111) surface may become more energetically favorable to form. In order to compare the geometric effect of different supports, the surface areas calculated from DFT modelling were normalized by the number of Pt in a monolayer coverage i.e. the unit of support surface area occupied by a Pt atom.

2) The influence of support lattice

As suggested in the previous study of Pt layer deposition,[23] a Pt film of 4 overlayer thickness (or 12 atoms in the case of rutile MO_2 [15]) screens the influence of the support regardless of the support structure. In our calculations this was confirmed by observing that the binding energy increment for adding the 4^{th} layer of Pt has converged towards the Pt bulk value. However, a small d-band shift compared to Pt bulk has been noticed and this minima shift of d-band centre can predominantly be attributed to a combination of the slight expansion or contraction of the Pt lattice, relative to its idealized position and an electronic contribution from the support material.

In this paper, the support influence has been discussed in terms of geometric (lattice strain) and electronic (interfacial binding) factors. The d-band centre and oxygen binding energy calculation are based on the periodic slab model of 4 Pt overlayers supported on a range of metal and ceramic substrate surfaces. To investigate the support influences on the reactivity, we have plotted the d-band centre of Pt film as a function of Pt-support lattice mismatch. The lattice mismatch is calculated here as:

$$x = A_1[support]/A_2[Pt(111)] * n_2[Pt(111)]/ n_1[support],$$

in which, A_1 and A_2 are the calculated surface area of supports and the most stable Pt surface(111) from DFT calculations (as listed in Supplementary Information **Table S1** and **S2**); n_1 is the number of Pt in a monolayer coverage on the support surface, and n_2 is the Pt

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atom contains in one layer of Pt(111) surface. Therefore, the lattice mismatch of Pt and different support materials are given regardless of the size of the calculation models. Here x=1 means there is an exact surface area match between the support and Pt(111), whilst x <1 suggests the surface is compressed by the support and x>1 indicates an expansion effect on the Pt overlayers.

Figure 3 illustrates the geometric and electronic influence of the support material on Pt overlayer growth through the d-band centre shifts, with lattice match x of Pt and support surfaces. Three data series can be identified corresponding to the three stacking orders of Pt (211), (111) and (100). When x is in the range of 0.7 to 0.90, the (211) type Pt overlayer forms on the rutile support surfaces. A linear decrease of d-band centre with increase of lattice match can be observed. For 0.9< x <1.2, Pt (111) type films tend to grow on the hcp support structures. The d-band centre moves towards the Fermi level with increasing lattice match. However, when further expanding the lattice for x>1.1, the Pt overlayers also tend to convert to a lower coordination number. Pt (100) type overlayers, in which Pt is 8 fold rather than 9 fold in Pt (111) can be formed on the TiX (100) surfaces. The d-band centre also shifts up with lattice expansion.

Therefore, the trend of d-band centre change with lattice match can be concluded to be the geometric influence of the support materials. The supported (solid lines) and unsupported Pt films (dash lines) also have been compared to illustrate the electronic effects arising from the interfacial bonding of Pt-support. The d-bands of unsupported Pt films are calculated by removing the underneath support layers but keeping the bottom lattice of the Pt film fixed, i.e. the geometric lattice strain remains. The relative offsets between the supported Pt overlayer and unsupported Pt films can be seen as the electronic influence from support-Pt interfacial binding. Thereby, we can disentangle the electronic effects of the substrate from those originating from the compression of the platinum lattice through the geometric and electrons terms as shown in **Figure 3**.

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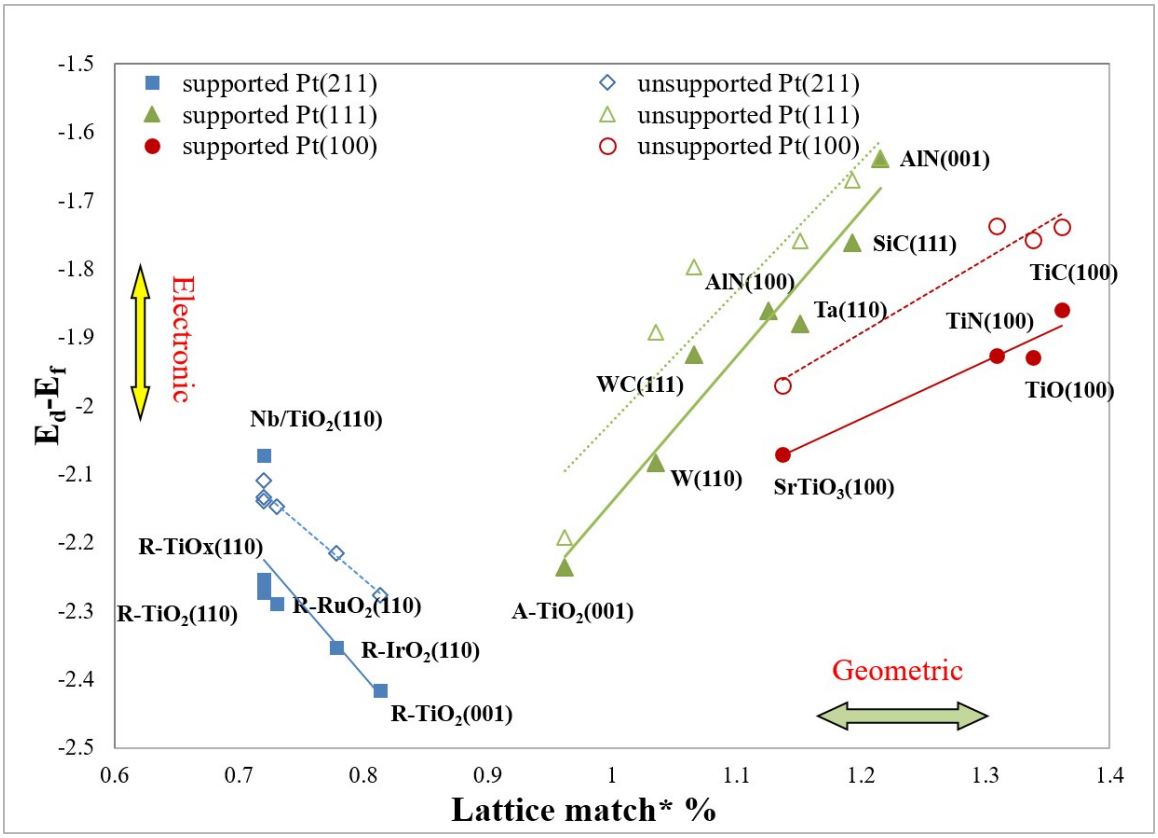

Figure 3 d band centre of Pt overlayer as a function of Pt-support lattice match. The offset between the dash and solid trend lines gives the electronic influence of the support and the slope shows the geometric lattice expansion.

The d-band centre of Pt film is a function of lattice strain caused by the lattice mismatch between support and Pt surfaces. It is through this mechanism that support materials can control the growth of deposited Pt and control the ORR activity of Pt films. This influence also reflects on the oxygen adsorption energy. A similar linear relationship can be found for the oxygen binding energy of supported Pt films varying with the lattice match between the support and Pt surfaces. However, since different oxygen adsorption sites are involved, more significant deviations can be expected, especially for the oxygen adsorption on the stepped surfaces related to Pt (211). The stepped Pt surfaces, which are compressed by the lattice strains arising from the rutile oxide supports, tend to bind oxygen atoms more strongly and thus would be predicted to reduce the ORR activity.

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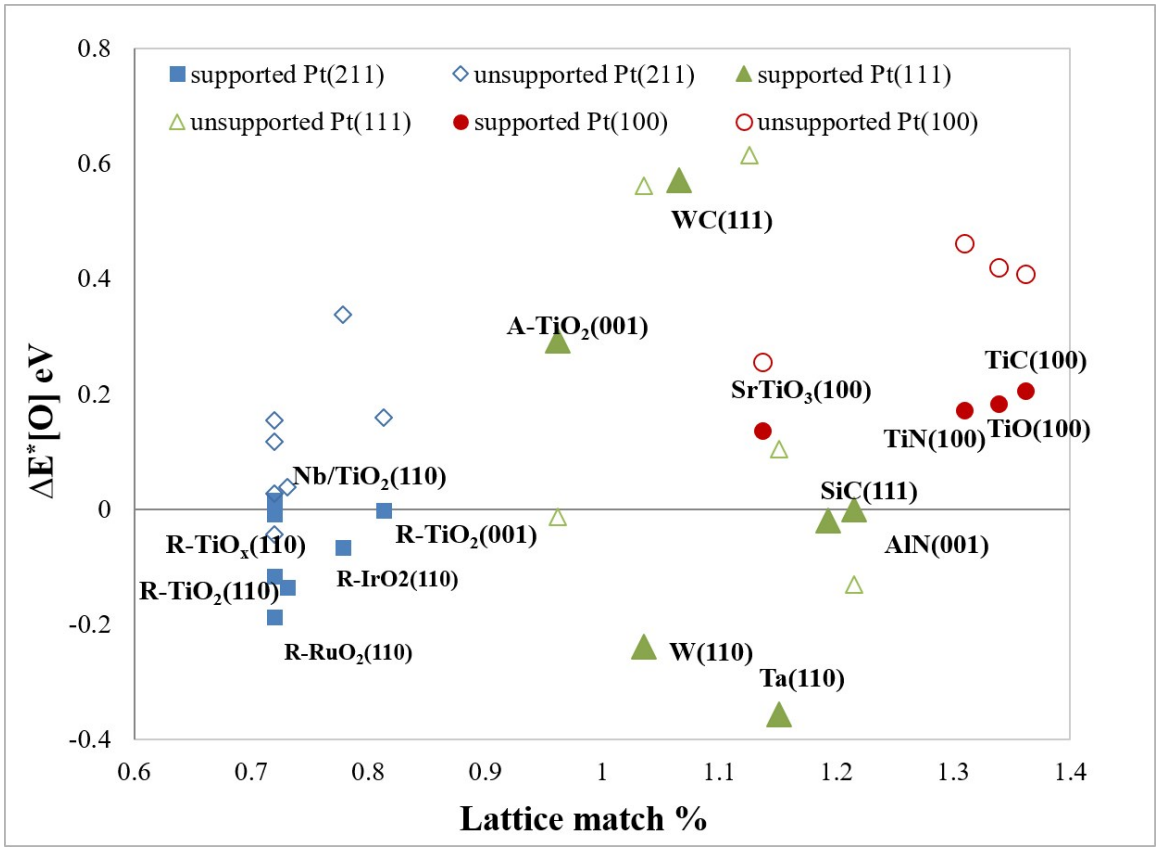

Figure 4 the relative oxygen binding energy E*[O] on the Pt overlayer changes with Pt-support lattice match.

3) Oxygen binding energy vs d band centre

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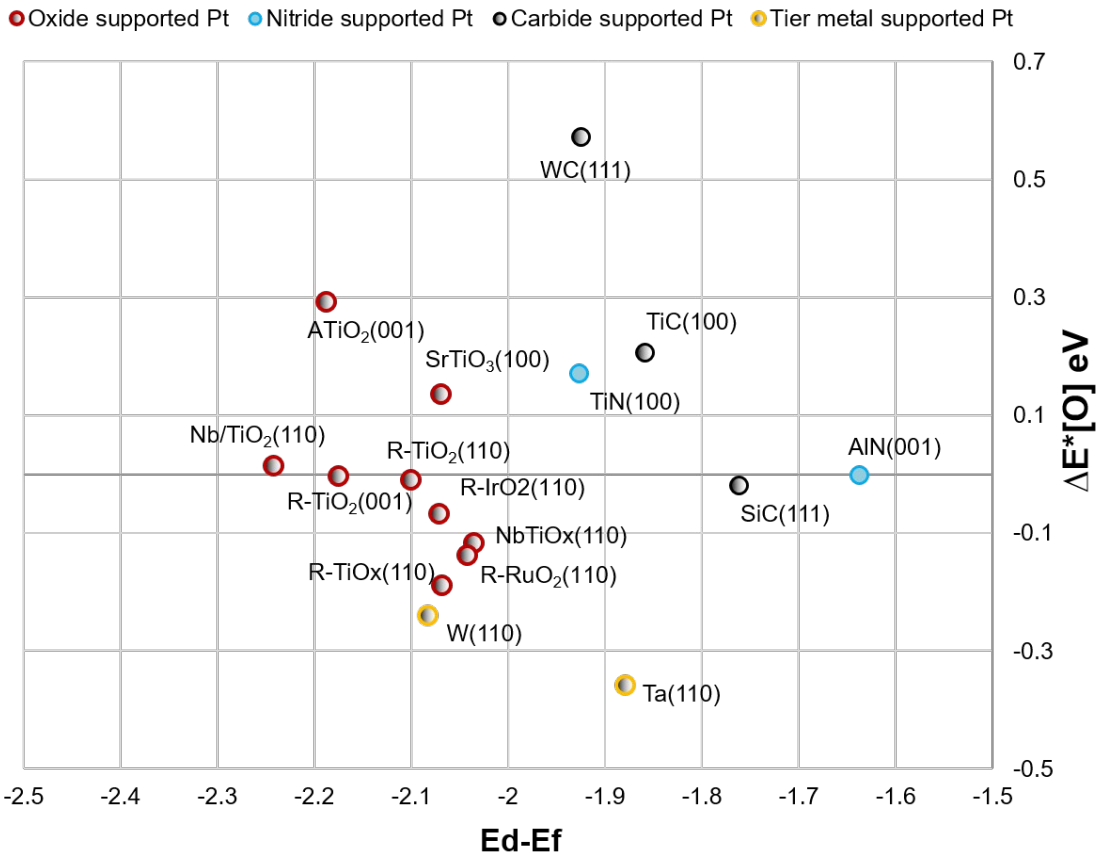

Figure 5 oxygen binding energy vs d band centre of Pt overlayer. The relative adsorption energy, denoted as ΔE*[O] has been normalised with respect to Pt(111), i.e. the oxygen binding energy differences for the supported Pt films and unsupported Pt(111) surface.

Nørskov's earlier work demonstrated the linear relationship between two catalytic activity descriptors of d-band centre and oxygen binding energy for a variety of metals [17] and alloys[18] using a first-principles computational approaches. In this paper, this linear relationship has been further explored for the Pt films on different types of support structure. The calculated relative oxygen adsorption energies, ΔE*[O], for oxygen atoms at the most stable sites have been plotted against the d-band centre of the supported Pt films as presented in **Figure 5**.

According to previous studies of transition metal catalysts, observation of the d-band centre moving towards the Fermi level leads to stronger oxygen binding on the metal surfaces. [17] [20] This trend becomes less distinctive for the transition metal alloys [24] and supported catalysts due to the complicated structure resulting in a loss of sensitivity in the descriptor.

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However, a pronounced trend that a lower d-band centre corresponding to higher oxygen adsorption energy can still be concluded for the supported Pt films. For the oxides, nitrides and carbides supports, the oxygen binding energy on the surfaces is roughly proportional to the d-band centre within each support type. There are significant outliers in the oxides series such as TiO, the oxygen binding energy on the TiO supported Pt film is more close to the data series of TiN and TiC due to the structural effect of the support.

However, the d-band centre and the oxygen binding energy for the supported Pt films can only be adjusted within a small range around the value of pure Pt metal. Since the d-band centre is a descriptor of catalyst electronic structure, while the relative oxygen binding energy can be directly linked to the intermediate's reactivity. Therefore, the relative oxygen binding energy $\Delta E^*[O]$ is used as a criterion in the latter section for the theoretical selection of support materials.

4) Theoretical material selection: activity versus stability

Two important properties of catalyst supports, Pt wetting ability and ORR catalytic activity have been considered for the material selection via two modelling descriptors of wetting parameter δ and relative oxygen binding energy $\Delta E^*[O]$, respectively. A good support material should satisfy both criteria in addition to the requirements of corrosion resistance and adequate conductivity.

Figure 6 summaries the calculation results of relative oxygen adsorption energy and support wetting parameter, a suitable support material which can be expected to improve both catalytic activity and wetting property of Pt should therefore lie below and to the right of Pt (111) on this graph. With regards to Pt overlayer stability, the reference value δ_0 denotes the data calculated for adding Pt atoms on the equilibrium Pt (111) surface. A higher δ value than δ_0 means Pt are more likely to detach from the support substrate, while a lower δ value suggests a stronger tendency for Pt wetting. From **Figure 6**, the high energetic cost of adding platinum to the MO_2 surface could be expected to favour clustering of the platinum atoms over the formation of a thin film. In contrast, Pt sintering is very unlikely to occur on W and Ta substrates indicated by the negative values of δ. Therefore,

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Ta and W metals could potentially be used as tie layers for Pt dispersion to increase the mass activity. The carbides and reduced/doped oxides are also promising support materials for Pt deposition since they all give δ values lower than δ_0. These results are in agreement with various experiment studies that suggest the using of carbide [25][26] and oxygen reduced metal oxides [27][28] can alleviate Pt sintering.

Turning our attention to the predicted catalyst ORR activity, Pt metal tends to bond oxygen too strongly thereby leading to a reduction in ORR activity. Therefore, we are looking for a support material that can tune the oxygen binding energy to a slightly lower level. The predicted apex of the activity volcano lies to the right of the oxygen binding energy on platinum at a small number (close to 0.2 eV in the case of oxides [14]) as represented by the red line in **Figure 6**. Through use of a combination of the two descriptors, Pt wetting and ORR activity, candidate materials can be compared and identified for application as Pt supports, from each class of material considered herein the most promising are:

i. Reduced or Nb doped TiOx and TiO,

ii. Wurtzite AlN,

iii. TiC, SiC and WC.

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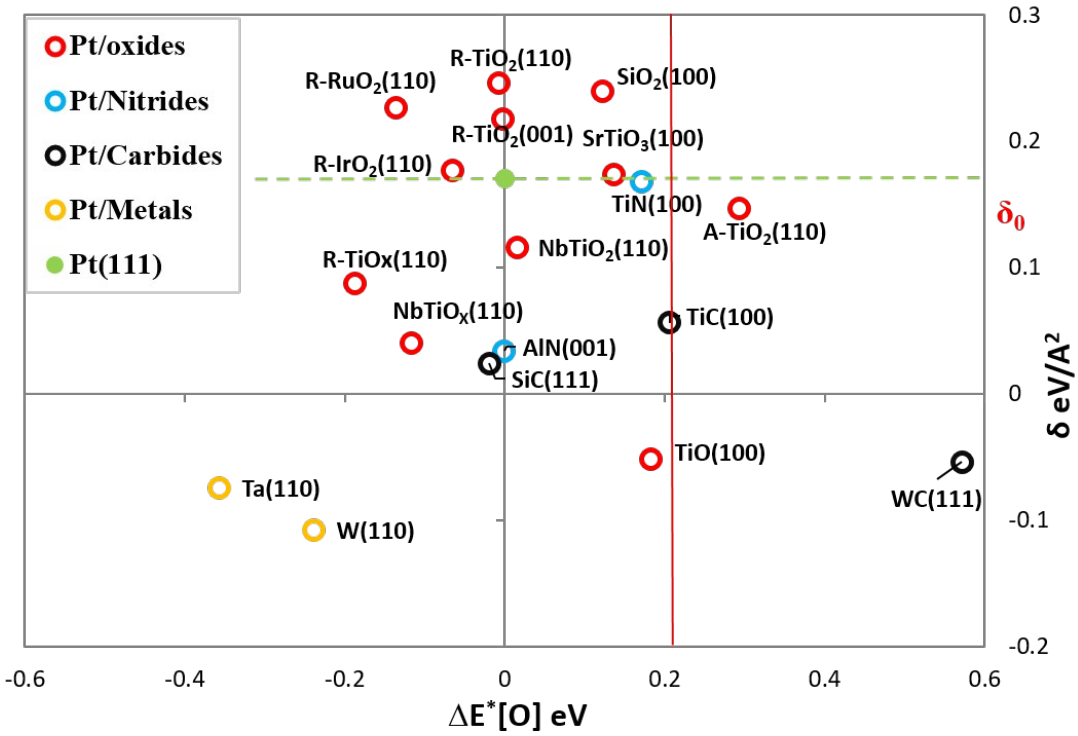

Figure 6. Support material selection through Pt wetting ability parameter δ and oxygen binding energy, ΔE*[O]. The dash line is corresponding to the wetting parameter δ_0 of unsupported Pt (111) surface. The red line denotes the apex of ORR activity.

Of the materials identified in our optimal region, SiC and WC have been extensively studied as catalyst supports. A good mass activity of Pt can be expected for using SiC support as demonstrated by the experiments,[29][30] but the oxygen binding on the SiC supported Pt films is as strong as on the pure Pt(111) surface. WC when used a support material, shows a significant positive shift of the relative binding energy E*[O] and therefore is also expected to have a direct influence on the ORR activity through a synergic effect with Pt catalyst. [31-40] In **Figure 6**, this effect is evident by a remarkable change of both wetting parameter δ and oxygen binding energy for Pt overlayers supported on WC (111). However, such a weakening effect of oxygen binding on Pt films might be too great, in which case, other platinum group metals e.g. Pd or Ir, could be potentially used in conjunction with the WC support to further prompt the ORR performance. Recent experimental studies provide a comparison between WC supported Pt and Pd catalysts, the results suggest WC support does not enhance the Pt intrinsic catalytic activity (corresponding to the weak oxygen binding effect in this work), but Pd [41] or Pd based

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bimetallic catalyst (eg. Pd-Au) [42] can offer superior catalytic activity for oxygen reduction reaction. The improvement of Pt dispersion on WC support also have been reported by other modelling works, which considered different surface models of WC support and draw to the conclusion that Pt tends to bond H too weak in the HER/HOR process. [43][44] Moreover, as plotted in **Figure 6**, TiO and TiC supports are also predicted to improve both stability and catalytic activity of Pt films. The DOS to TiO(001) suggests a good match between the Pt d-band centre and the d-band gap a low energy cost for the interfacial bond formation and enhanced Pt wetting behaviour[23](as indicated by the negative value of δ). In contrast, the low δ value of TiC(001) is due to the increasing covalent character of the Ti-C bond. [23] The novel support materials of TiO and TiC have been synthesized and reported in a wide range of applications exploiting their electrical and mechanical properties. Based on the results presented herein, we are of the opinion these materials could be very competitive candidates for catalyst support. The theoretical modelling approach described in this work is considered as a preliminary step for developing new catalyst support that works in real operating conditions.

4. CONCLUSIONS

DFT has been used to explore various ceramic materials as Pt catalyst support for application in a fuel cell. The influence of support surfaces has been analysed and rationalized in terms of both geometric and electronic effects. The modelling results suggest that the support material can control the growth of Pt deposition layer and contribute to the stability of Pt films. The d-band centre of the supported Pt layer is investigated as a function of lattice strain. Two modelling descriptors of relative oxygen binding energy and Pt wetting parameter δ have been developed to estimate the ORR activity and stability of the supported Pt films, respectively. From the screening study presented herein, the most promising candidates for use as Pt supports are: WC, TiC and TiO.

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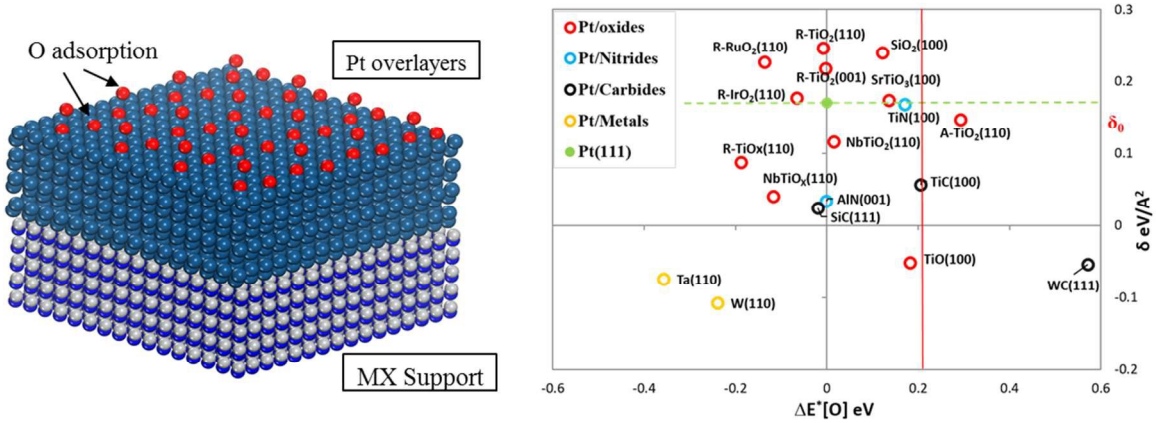

(Left) The atomic model of oxygen adsorption on the MX supported Pt overlayer film. (Right) Support material selection through Pt wetting ability parameter δ and oxygen binding energy, ΔE*[O]. The dash line is corresponding to the wetting parameter δ_0 of unsupported Pt (111) surface. The red line denotes the apex of ORR activity.

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