## Energy & Environmental Science

Cite this: Energy Environ. Sci., 2011, 4, 1268

www.rsc.org/ees

## COMMUNICATION

# Towards active and stable oxygen reduction cathodes: a density functional theory survey on $Pt_2M$ skin alloys<sup>†</sup>

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*Received 11th December 2010, Accepted 2nd February 2011* DOI: 10.1039/c0ee00762e

Pt metal, when used as a cathode for oxygen reduction ( $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ), suffers from high overpotential and catalyst corrosion. Here, first-principles based theoretical methods for electrochemical systems are utilized to identify the critical factors affecting cathode performance. By analyzing a large set of Pt alloys, we show that alloys are in general less stable than Pt at the same O coverage under electrochemical conditions, and that maintaining a zero O coverage at the working potentials (*e.g.* 0.9 V) is key to achieve both high activity and stability. Two quantities, *i.e.* the surface corrosion energy and the free energy barrier to OOH dissociation, are found to be the main descriptors for the stability and activity. A Pt<sub>2</sub>Mo skin alloy is discovered to be a good candidate for an oxygen reduction cathode. The theoretical framework provides a new route for the rational design of oxygen reduction catalysts.

Platinum, as an indispensable electrode material, plays a central role in modern fuel cell applications.<sup>1,2</sup> However, the high overpotential (>300 mV) in oxygen reduction reactions (ORRs) on Pt cathodes significantly limits the energy efficiency of fuel cells.<sup>3,4</sup> Moreover, because of the agglomeration and dissolution of metal particles, the lifetime of Pt cathodes places another severe constraint on the long-term application.<sup>4-6</sup> To date, many alloy materials composed of Pt and other elements, namely PtM alloys, have been tested in experiments (*e.g.* M = Ni,<sup>7-9</sup> Co,<sup>8,10-12</sup> Fe,<sup>8,13</sup> Ti,<sup>8</sup> V,<sup>8</sup> Sc, Y,<sup>14</sup> Cu<sup>15-19</sup>), and it remains highly challenging to find alternative catalysts better than Pt with both high activity and high stability. This is partly because the ORR catalyst is required to activate O<sub>2</sub> under corrosive conditions (oxidative, acidic and high potential (~1 V *vs.* NHE)). Fundamentally, due to the lack of an atomistic picture of the process, no reliable measure for efficiently screening catalysts is available towards the rational selection of the alloying element and the identification of the optimum alloying ratio (Pt : M).

Although a complete microscopic mechanistic picture of the ORR is still under debate, some factors influencing the activity and stability have been outlined recently. By analyzing the morphology of active PtNi skin alloys (a monolayer of Pt over bulk  $Pt_3Ni$  alloy) that were demonstrated to have a higher ORR activity than that of bulk alloys and pure Pt, Stamenkovic *et al.* observed that the active PtNi skin alloy has a lower surface O coverage at 0.8–0.9 V compared to a pure Pt catalyst, which implies a weaker O adsorption on the skin alloy.<sup>7</sup> Norskov and coworkers utilized the computed O atom adsorption energy as a thermodynamic descriptor to select potential ORR alloy catalysts by large-scale first principles calculations,<sup>14</sup> as it was suggested that a good ORR catalyst may possess a lower O binding ability by ~0.2 eV than pure Pt. Experiments were then utilized to identify the best candidate.<sup>14</sup>

### **Broader context**

The identification of active and stable cathode materials for electrocatalytic oxygen reduction (OR) has been a long-standing problem in fuel cell technology. In this contribution, we utilize the first-principles periodic continuum solvation method developed recently to establish a complete theoretic framework for screening potential OR cathode materials. Unlike most previous work in the field focusing mainly on the activity issue, we start from a screening of  $Pt_2M$  skin alloys by assessing their surface stability *via* a quantitative measure, *i.e.* surface corrosion energy. We show that the key difficulty in the design of OR cathodes is in fact not to achieve a high activity, but to maintain a high stability of the metal surface under the corrosive cathode conditions. From more than 20 different  $Pt_2M$  alloys, we identify Mo as a good element, which can alloy with Pt to make a stable surface at high electrochemical potentials. We further show that  $Pt_2M$  opssesses a lower kinetic barrier for OR compared to Pt, and the barrier towards OOH dissociation is a key kinetic parameter for OR activity. With this bottom-up approach, we believe that the development of OR cathodes for fuel cell applications can be greatly facilitated.

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<sup>†</sup> Electronic supplementary information (ESI) available: Computational methods; illustration of the structures for the surface adsorption phase and their corresponding surface vacancy phase; surface phase diagram for Pt(111) and Pt<sub>x</sub>Mo skin alloys; free energy profile for the direct O<sub>2</sub> dissociation channel; the calculated free energies of elementary steps in ORR. See DOI: 10.1039/c0ee00762e

In addition to the activity issue, the long-term stability of ORR cathodes against dissolution in acidic media is another major concern.<sup>20–25</sup> It was observed that PtM (M = Co, Fe) bulk alloy catalysts do not provide long-term improvements in catalytic activity and electrochemical durability, due to the leaching of the alloying M element under intensive potential cycling.11,24,25 For instance, PtCo nanoparticles will slowly evolve towards Pt-skin alloy structures in the long-term PEMFC test.<sup>26,27</sup> The higher stability of clean Pt covered skin alloys under vacuum were also confirmed by theoretical calculations.28,29 Recently, we studied the atomic-level mechanism of Pt cathode dissolution using first principles calculations, by taking into account the effect of the electrochemical environment explicitly.<sup>32c</sup> We showed that the corrosion of Pt under electrochemical conditions occurs only above a certain surface O coverage, as controlled by electrochemical potential: on the Pt(111) surface, Pt atoms start to dissolve above 0.5 monolayer (ML) O coverage, corresponding to 1.05 V vs. NHE. The surface O coverage on Pt surfaces increases rapidly upon increase of the electrochemical potential, according to the surface phase diagram.

While the atomic O adsorption energy (data often available only for clean surfaces) is believed to be important for the activity of the ORR catalyst, this descriptor alone appears not to be sensitive enough to predict a good ORR catalyst.<sup>14,30</sup> Especially since, based on knowledge recently gained for electrocatalytic reactions, the *in situ* O coverage of the cathode at the working potentials (0.8–0.9 V) could be high and the presence of the lateral interaction might significantly affect the stability and activity. Obviously, the electrochemical conditions, including the electrochemical potential, the surface coverage and the solvation effects, must play important roles in catalytic kinetics and thus should be taken into account to identify the key descriptors towards the rational design of ORR catalysts.

To establish a complete theoretical framework for understanding the ORR activity and stability, here we first analyze a set of  $Pt_2M$  skin alloys by focusing on their surface stability with and without the presence of adsorbed O. Next, by evaluating the surface stability at ~1.05 V under electrochemical conditions and computing the reaction profile of ORR, we show that  $Pt_2Mo$  skin alloy is a good candidate for an ORR cathode operating at a potential of 0.9 V. All calculations were performed using the plane-wave density functional theory slab method, as implemented in the Vienna *ab initio* simulation program (VASP).<sup>31</sup> The methods for calculating electrochemical systems and the detailed setup are provided in the ESI† along with our recent work.<sup>32</sup>

We started with the investigation of the surface stability of a set of Pt<sub>2</sub>M skin alloys (Pt<sub>2</sub>M alloy covered by a monolayer of Pt) under high O coverage conditions, with M being mainly 3d and 4d metals. These skin alloys were created by replacing 1/3 Pt atoms from two to five layers in a six-layer Pt(111) slab (e.g. 2 Pt atoms replaced by M per layer in a  $(3 \times \sqrt{3})$  unit cell). Initially, the O coverage was fixed at 0.5 ML for all surfaces for the purpose of comparing with Pt, since Pt(111) starts to dissolve above this coverage.<sup>32c</sup> The skin alloys investigated included the 3d metals: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and the 4d metals: Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag and Cd. It is worth mentioning that the corrosion of Pt metal is kinetically self-accelerated under electrochemical conditions once a defect site on the close-packed (111) surface is created, since the kinetic barrier to surface oxidation is lower at the defect sites.<sup>32c</sup> While a low density of intrinsic defect sites may be preferentially terminated by specific initial treatment (such as via doping), the close-packed (111), forming the

majority of the surface sites, largely dictates the stability of ORR cathode. It is therefore critical to examine the stability of the close-packed (111) surface, as will be addressed below.

In this work, the stability of the surface is measured by the free energy change ( $\Delta G_c$ ) of reaction (1), which describes the dissolution/ corrosion process of a surface Pt atom, corresponding to the initial step in surface corrosion.<sup>32c</sup>

$$O_x/Pt_s/Pt_2M \rightarrow O_x/\Box -Pt_s/Pt_2M + Pt^{2+} + 2e^{-}$$
(1)

During the process, a surface Pt (O<sub>2</sub>/Pt<sub>2</sub>M) dissolves under the electrochemical conditions, and ends up with a surface vacancy  $(O_x/$ □-Pt/Pt<sub>2</sub>M) (structure illustrated in ESI Fig. S1<sup>†</sup>). The adsorbates, such as O atoms, if present, will help to stabilize the surface vacancy. It should be mentioned that the standard half-cell potential,  $E^{\odot} = 1.2$ V for the Pt  $\rightarrow$  Pt<sup>2+</sup> + 2e<sup>-</sup> equilibrium (this means that below 1.2 V the Pt<sup>2+</sup> in solution tends to adsorb and segregate as pure Pt metal at the standard condition), is utilized in calculating  $\Delta G_{c}$ , as introduced in our previous work.<sup>32c</sup> Since the exact value of  $\Delta G_c$  depends on the unit cell applied, because the concentration of the final vacancy state is pinned by the unit cell size, a relative value of  $\Delta G_c$ , namely  $\Delta G_c^*(X)$  $= \Delta G_{\rm c}({\rm X}) - \Delta G_{\rm c}|_{0.5 {\rm MLO/Pt}}$ , is utilized here for comparison in the catalyst screening, which is defined by comparing  $\Delta G_c$  of X to that of Pt(111) at 0.5 ML O coverage in the same unit cell. A positive  $\Delta G_c^*$ would imply a better anti-segregation and anti-corrosion ability of the material than Pt. The computed  $\Delta G_c^*(X)$  (in a  $(3 \times \sqrt{3})$  unit cell) is listed in Fig. 1, together with those of the clean surfaces (at zero O coverage).

Fig. 1 clearly shows the relative order of the stabilities of the skin alloys, and demonstrates that the corrosion of alloy metals is significantly facilitated by the presence of O. The trend of  $\Delta G_c^*$  across the periodic table for the O covered surfaces is just opposite to that for the clean surfaces. On going from left to right across the periodic table,  $\Delta G_c^*$  has a minimum for the Pt<sub>2</sub>V/Pt<sub>2</sub>Nb skin alloys for the 0.5 ML O covered surfaces, but it has a maximum for the Pt<sub>2</sub>Ti/Pt<sub>2</sub>Nb alloys for the clean surfaces. On clean surfaces,  $\Delta G_c^*$  are all positive and it is pure Pt(111) that has the lowest  $\Delta G_c^*$ . On the 0.5 ML O covered surface,  $\Delta G_c^*$  are all negative, indicating a poorer surface stability for all of the alloying materials compared to Pt at a high O coverage. The results imply that the stability of even skin alloys under electrochemical conditions could be a severe problem for the long-term operation of cathodes, without even mentioning the activity.

The higher stability of clean alloy surfaces can indeed be inferred by the calculated Pt d-band structure, which shows that the alloying



Fig. 1 The calculated relative surface stability ( $\Delta G_c^*$ ) of Pt<sub>2</sub>M skin alloys (M as *x*-axis). By definition,  $\Delta G_c^*$  of Pt(111) surface at 0.5 ML O coverage is zero.

generally leads to the stabilization of the Pt d-band,<sup>8b,33,34</sup> and therefore the surface Pt atoms are more difficult to segregate or dissolve. By contrast, in the presence of adsorbed O atoms the Pt removal is facilitated, because the surface vacancy can be more strongly stabilized by O atoms compared to the initial perfect surface. This can be understood as follows. Firstly, the Pt atoms at the surface vacancy are less coordinated and possess more active d-states, which can more strongly bond with O atoms, compared to terrace Pt atoms, Secondly, with the exposure of the second layer atoms at the surface vacancy, it is possible to form a much stronger O-M bond compared to the O-Pt bond. This is indeed observed in our search for the optimum structure after a Pt removal, which shows that the surface vacancy is preferentially terminated by O atoms that sink to bond with the solute M atoms at the second layer. For example, in Pt<sub>2</sub>Ti skin alloys, the surface vacancies with a configuration containing O-Ti bonding are much more stable (by 1.44 eV) than those with only O-Pt bonding. This is consistent with the fact that the atomic O on metals is anion-like, with a strong tendency to accept electrons, and prefers to form ionic-bonds.

Since the stability of alloys is sensitive to both the alloying element and the coverage of O, it is naturally expected that a considerably lower O coverage at the concerned electrochemical potentials (0.8-1.2 V) than that on Pt is a prerequisite for a stable ORR catalyst. Theoretically, the thermodynamic equilibrium O coverage under electrochemical potentials can be determined by constructing the surface phase diagram.35,36,32c Therefore, our next step is to select seven representative  $Pt_2M$  skin alloys (M = 3d: Sc, Ti; 4d: Zr, Nb, Mo, Ag, Pd) to determine their O coverage at around 1 V and examine their stability. At this time, 4d metals are taken as the major candidates because their  $\Delta G_{c}^{*}$  are generally larger than those of 3d metal alloys in the presence of O (Fig. 1). In this work, only the adsorbed O species is considered in constructing the surface phase diagram since we are mainly concerned with the high potential regimes (e.g. > 1 V) of relevance to surface corrosion, when it is the adsorbed O atoms not hydroxyls that dominate.32c It was noticed that at  $\sim 0.8$  V the coexistence of hydroxyls with atomic O is likely on Pt(111).35,36

Our calculated phase diagrams for the seven alloys are shown in Fig. 2. In general, the surface O coverage increases with the increase in potential. At the same potential, the O coverage of the skin alloys is lower than or equal to that of pure Pt. At 1.05 V (dotted line in Fig. 2), Pt<sub>2</sub>Ti, Pt<sub>2</sub>Zr, Pt<sub>2</sub>Mo, Pt<sub>2</sub>Nb and Pt<sub>2</sub>Sc have 0.17 ML O coverage, much lower than the 0.5 ML in Pt, and Pt<sub>2</sub>Pd and Pt<sub>2</sub>Ag have a 0.33 ML O coverage. The  $\Delta G_c^*$  of these alloys at ~1.05 V, with the O coverage obtained from Fig. 2, can therefore be computed using the same theoretical approach as above. The  $\Delta G_c^*$  of these alloys (in a (3 ×  $\sqrt{3}$ ) unit cell) are found to be -0.25 (Pt<sub>2</sub>Sc), -0.21 (Pt<sub>2</sub>Ti), -0.48 (Pt<sub>2</sub>Zr), -0.15 (Pt<sub>2</sub>Nb), 0.22 (Pt<sub>2</sub>Mo), -0.07 (Pt<sub>2</sub>Ag) and -0.08 (Pt<sub>2</sub>Pd) eV, respectively. This shows that the stability of the surfaces follows the order Pt<sub>2</sub>Mo > Pt > Pt<sub>2</sub>Ag > Pt<sub>2</sub>Pd > Pt<sub>2</sub>Nb > Pt<sub>2</sub>Ti > Pt<sub>2</sub>Sc > Pt<sub>2</sub>Zr. It reveals that up to the high potential 1.05 V, only Pt<sub>2</sub>Mo exhibits a higher stability than pure Pt.

With Mo being identified as a promising alloying candidate, we are now in the position to examine the ORR reaction kinetics at 0.8–0.9 V potentials to ensure that ORR can also occur efficiently on Pt<sub>2</sub>Mo. To map out the ORR reaction pathway and the free energy profile, we utilized a larger unit cell ( $3 \times 2\sqrt{3}$ ) to avoid the lateral interaction between reaction intermediates, and the solvation free energy of the reaction intermediates is included by using our recently-developed



**Fig. 2** A surface phase diagram of Pt (111) and Pt<sub>2</sub>M (M = Sc, Ti, Zr, Nb, Mo, Pd, Ag) alloys. To illustrate each curve clearly, a constant spacing in the *y*-axis is applied for the  $\Delta G$  of the clean surfaces (defined as energy zero for each curve).

periodic continuum solvation model.<sup>32</sup> For comparison, the ORR on Pt was also studied with the same theoretical approach. According to the refined surface phase diagram in the large unit cell (ESI Fig. S2†), the Pt(111) surface is covered by 0.25 ML O at 0.8 V and 0.33 ML at 0.9 V, whilst the O coverage is no more than 0.08 ML for the Pt<sub>2</sub>Mo skin alloy surface below 0.93 V. Therefore, we took the clean Pt<sub>2</sub>Mo skin alloy surface (0.8 and 0.9 V), and the 0.25 ML (0.8 V) and 0.33 ML (0.9 V) O-covered Pt(111) surfaces as the model surfaces for investigating ORR kinetics.

In general, the ORR initiates by molecular  $O_2$  adsorption on the surfaces. It is noted that in the presence of adsorbed O (*e.g.* Pt at 0.9 V), the surface O may need to rearrange to free sites for  $O_2$  adsorption (see  $\Delta G_0$  in Fig. 3) because an  $O_2$  molecule adsorption requires at least two Pt atoms. Next, the adsorbed  $O_2$  can either hydrogenate to OOH ( $O_2 + H^+ + e^- \rightarrow OOH$ ), that can later dissociate into adsorbed O and OH, or undergo direct O–O bond



**Fig. 3** A schematic free energy profile for the OOH reaction channel of ORR on a Pt(111) surface and a Pt<sub>2</sub>Mo skin alloy surface at 0.8 V and 0.9 V. The calculated values (eV) of  $\Delta G_0$ ,  $\Delta G_1$ ,  $\Delta G_2$ ,  $\Delta G^{\ddagger}$ ,  $\Delta G_3$  and  $\Delta G_4$  are listed in the inserted table. The solvation free energy of all of the states has been corrected using a periodic continuum solvation model. To allow O<sub>2</sub> adsorption, surface oxygen atoms may undergo rearrangement to free two atop sites (Sur  $\rightarrow$  Sur\*).

splitting into adsorbed atomic O. No matter which reaction channel is followed, the final steps are the hydrogenation of O and OH into H<sub>2</sub>O.<sup>37-39</sup> Here, both reaction pathways were investigated and the transition states (TSs) for the OOH dissociation and O2 dissociation have been located. We found that these TSs dictate the highest free energy positions in the reaction pathways. The reaction free energy profiles for the OOH pathway on Pt2Mo and Pt surfaces are shown in Fig. 3 and the data is detailed in Table S1 in the ESI<sup>+</sup>. The free energy profile of the direct O-O dissociation channel is similar to the OOH channel at 0.8 V (ESI Fig. S3<sup>†</sup>) and thus not discussed here. It should be mentioned that the exact surface phase at  $\sim 0.8$  V, particularly on Pt(111), might be quite complex due to the possible coexistence of surface hydroxyl groups and atomic O from theory35,36,39b (this is also not clear from experiments). The reaction barriers reported here are therefore mainly utilized for the purpose of the activity comparison of Pt and PtMo alloys under the same theoretical framework.

The ORR on a Pt<sub>2</sub>Mo alloy surface follows a similar reaction profile as that on Pt, as shown in Fig. 3. The TS for OOH dissociation dictates the height of the potential profile, and in all systems the overall barrier,  $\Delta G^{\ddagger}$  (the free energy difference between the adsorbed O<sub>2</sub> and the TS for OOH dissociation), determines the activity. With an increase in potential (0.8 V to 0.9 V), the ORR is retarded due to the increased  $\Delta G^{\ddagger}$ . By comparing Pt<sub>2</sub>Mo with Pt, we can see that the O/OH ( $\Delta G_1 + \Delta G_3$  in Fig. 3) and molecular O<sub>2</sub> ( $\Delta G_1$ ) bind more strongly on the O-covered Pt surface, while the free energy of the OOH state ( $\Delta G_1 + \Delta G_2$ ) and the TS for OOH dissociation ( $\Delta G^{\ddagger}$  +  $\Delta G_1$ ) are similar for Pt<sub>2</sub>Mo and Pt. As a result, the overall barrier  $\Delta G^{\ddagger}$ is about 0.2 eV lower on Pt<sub>2</sub>Mo than that on Pt, due to the reduced  $O_2$  adsorption on the skin alloy surface. For example, at 0.9 V, the  $\Delta G^{\ddagger}$  on Pt is 0.63 V, while it is only 0.43 eV on Pt<sub>2</sub>Mo. From microkinetics, it can be deduced that the overall rate at 0.9 V (under the standard conditions) on the Pt<sub>2</sub>Mo surface is three orders of magnitude faster than that on Pt provided with the same preexpoential factor.

To understand why  $Pt_2Mo$  has a lower barrier, we first examined the optimized structure for  $O_2$  adsorption, and the OOH dissociation TS on  $Pt_2Mo$  and on Pt, as shown in Fig. 4. The key structural parameters are labelled. These identified structures are similar except that there are precovered O atoms near to the adsorbed  $O_2$  and OOH TS on Pt. Due to the lateral interaction, the adsorbed  $O_2$  molecule on

Pt prefers two atop sites, while it sits over three Pt atoms (bridge-toatop) on Pt<sub>2</sub>Mo. We noticed that the O-Pt bond lengths are generally longer on Pt<sub>2</sub>Mo compared to those on Pt(111), which is consistent with the fact that the adsorption of O-involved species is always weaker on Pt<sub>2</sub>Mo under vacuum. Secondly, by analyzing the energetics with and without the solvation effect, we found that the adsorption of the OOH fragment, being close to saturation, is less sensitive to the change of substrate in vacuum, and at the mean time the TS of OOH dissociation experiences a larger solvation on Pt<sub>2</sub>Mo compared to on Pt (ESI Table S1<sup>†</sup>), which overall yields the similar free energy height in two systems. In fact, the solvation energy contribution to the reaction intermediates (O<sub>2</sub> and OOH) on Pt<sub>2</sub>Mo is generally larger (up to 0.16 eV) than to those on Pt. This is apparently due to the lack of coadsorbed O on the Pt<sub>2</sub>Mo skin alloy, where the aqueous surroundings can have a stronger electrostatic interaction with the adsorbed intermediates. These results demonstrate that the aqueous environment, together with the *in situ* O coverage, plays an important role in facilitating the ORR on alloy surfaces.

Finally, it is interesting to ask whether there is an optimum Pt : Mo ratio in the Pt<sub>x</sub>Mo skin alloys. To identify the best ratio, we further considered three skin alloys with varied Pt : Mo ratios (x = 11, 5 and 1), and their activity and stability were then evaluated and compared with those of the Pt<sub>2</sub>Mo skin alloy. Firstly, the surface diagrams of these Pt<sub>x</sub>Mo alloys were constructed to determine the surface coverage of O under the electrochemical conditions (see ESI Fig. S2<sup>†</sup>). Not surprisingly, we found that the increase in Mo content suppresses the coverage of surface O. For example, the O atoms (0.08 ML) start to emerge on Pt(111) at 0.65 V, but do not start to emerge until 0.99 V on the PtMo surface. At  $\sim$ 1.05 V, when the O coverage reaches 0.5 ML on Pt, all Pt<sub>x</sub>Mo alloys manage to maintain an O coverage below  $\sim 0.3$  ML. Next, with the O coverage determined, we computed the relative surface stability ( $\Delta G_c^*$ ) at 0.9 and 1.1 V, and also calculated the O<sub>2</sub> adsorption state and the TS of OOH dissociation to obtain the key ORR kinetic parameters,  $\Delta G^{\ddagger}$ , at 0.9 V. These results are plotted in Fig. 5.

Fig. 5 reveals that the optimum content of Mo in  $Pt_xMo$  skin alloy is ~30%. With  $\Delta G_c^*$  being always positive, all PtMo alloys are more stable than pure Pt at both 0.9 V and 1.1 V, but  $Pt_2Mo$  has the highest  $\Delta G_c^*$  at 0.9 V and  $Pt_5Mo$  has the highest  $\Delta G_c^*$  at 1.1 V. The stability



**Fig. 4** Side (upper panel) and top (lower panel) views of the O<sub>2</sub> adsorption and located TS structures for O–OH dissociation at 0.9 V. (a) and (b): O<sub>2</sub> adsorption and TS for OOH dissociation on  $Pt_2Mo$ ; (c) and (d): O<sub>2</sub> adsorption and TS for OOH dissociation on 0.33 ML O covered Pt(111). Large blue ball: subsurface Pt; large Cyan ball: subsurface Mo; small yellow ball: top layer Pt; small red ball: O; small white ball: H. The bond distances labelled are in Å.



**Fig. 5** Calculated stability  $\Delta G_c^*$  of Pt and Pt<sub>x</sub>Mo skin alloys at 0.9 V and 1.1 V together with the calculated overall free energy barrier  $\Delta G^{\ddagger}$  at 0.9 V.

of the  $Pt_xMo$  alloys drops quickly with increasing potential, which is in line with the rapid increase of surface O coverage for  $Pt_xMo$ surfaces above 0.9 V. As for the activity, the  $\Delta G^{\ddagger}$  of  $Pt_2Mo$  is the lowest (0.43 eV), whilst the  $\Delta G^{\ddagger}$  of  $Pt_{11}Mo$ ,  $Pt_5Mo$  and PtMo alloys are close to that of Pt (difference within 0.1 eV). We notice that due to the too weak adsorption of O<sub>2</sub> and O on PtMo, the dissociation of OOH on PtMo becomes kinetically difficult, which leads to the high overall barrier on PtMo. Therefore, we can conclude that the  $Pt_2Mo$ skin alloy achieves the best balance of stability and activity. A low Mo content (below 30% *e.g.*  $Pt_5Mo$ ) may achieve a higher stability at high potentials but the activity is not better than Pt at 0.9 V, whilst a high Mo content (above 30%, *e.g.* PtMo) will start to destabilize the alloy and also reduce the activity.

In summary, this work outlines the key quantities affecting the stability and activity of Pt-based ORR catalysts from theory. By analyzing a group of  $Pt_2M$  skin alloys, we show that the surface stability at high electrochemical potentials is a sensitive measure for a first screening of materials, owing to the fact that the dissolution of surface atoms in alloys is significantly facilitated with the increase of O coverage. The free energy barrier to OOH dissociation, an activity quantity, can serve for the fine tuning of catalyst composition because of the similarity of the ORR mechanisms for Pt-based alloys and Pt. Based on the current theoretical framework, we show that a  $Pt_2Mo$  skin alloy is a good candidate for a stable and active ORR cathode.

#### Acknowledgements

This work is supported by NSF of China (20825311), 973 program (2011CB808500), Science and Technology Commission of Shanghai Municipality (08DZ2270500) and Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institute of Higher Learning.

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