Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Information for:

Towards Active and Stable Oxygen Reduction Cathode: A Density Functional Theory Survey on Pt_2M skin alloys

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Computational Methods

All density functional theory calculations were performed using the Vienna ab initio simulation program (VASP)[1-3] with a plane-wave basis and ultrasoft pseudo-potentials.[3] Exchange and correlation functional utilized was PW91 functional proposed by Perdew and Wang.[4] A planewave energy cutoff of 400 eV was used and the Monkhorst-Pack k-point mesh was utilized for first Brillouin zone integrations. In this work, $(2\times4\times1)$ and $(2\times2\times1)$ k points were used for the calculations of $(3\times\sqrt{3})$ and $(3\times2\sqrt{3})$ unit cell, respectively. The smaller unit cell was mainly used for the catalyst screening and the larger unit cell was used to obtain more realistic energetics for tthe reaction pathway on Pt and Pt_2Mo surfaces. The Quasi-Newton Broyden method was employed for geometry relaxation until the maximal forces on each relaxed atom were less than 0.05 eV/Å. Transition states of the catalytic reaction were searched using the Constrained-Broyden-Minimization[5] and dimer method.[6] All the surfaces were modelled by a six-layer symmetric slab with adsorbates adsorption on both sides of the slab. The middle two layers were fixed at the bulk-truncation position while the other layers were allowed to relax.

To derive the free energy reaction profile, we first obtain the reaction energy of each elementary step (strictly, ΔF at 0 K, 0 bar*)*, which is directly available from DFT total energy (ΔE) after the ZPE correction. For elementary surface reactions without involving the adsorption/desorption of gaseous or liquid molecules, ΔF at 0 K, 0 bar is a good approximation to the Gibbs free energy (ΔG) as the temperature T and pressure p contributions at solid phase are small. To compute the free energy change ΔG of elementary reactions involving gaseous or liquid molecules, such as oxygen, hydrogen and water, the large entropy term at 298 K is essential to take into account. We utilize the standard thermodynamic data[7] to obtain the temperature and pressure contributions for the *G* of the aqueous H_2O and gaseous H_2, which are -0.57 eV (the entropy contribution is -0.22 eV in solution) and -0.31 eV compared to the total energy of the corresponding free molecule (*E*, 0 K), respectively.[8] The G of O_2 is derived as $G[O_2] = 4.92\ (eV) + 2G[H_2O] - 2G[H_2]$ by utilizing OER equilibrium at the standard conditions. For reactions involving the releasing of proton and electron, the reaction free energy can be computed by referencing to NHE as suggested by Bockris[9] and Nørskov[10] group. This is governed by $G_{proton+electron} = G_{1/2H2(g)} - neU$ where e presents the transfer electron and U is electrochemical potential.

Detailed calculation setups for constructing the surface phase diagram have been described in our recent study.[11] The effect of the water environment on the phase diagram and on the reaction kinetics has been examined through a continuum solvation model with a smooth dielectric function by solving the Poisson-Boltzmann equation numerically in the periodic slab as implemented recently.[12,13] We found that the solvation effect on the phase diagram is small (<0.05 eV), while the solvation can help to stabilize adsorbed O_2 and OOH intermediates (see Table S1 below).

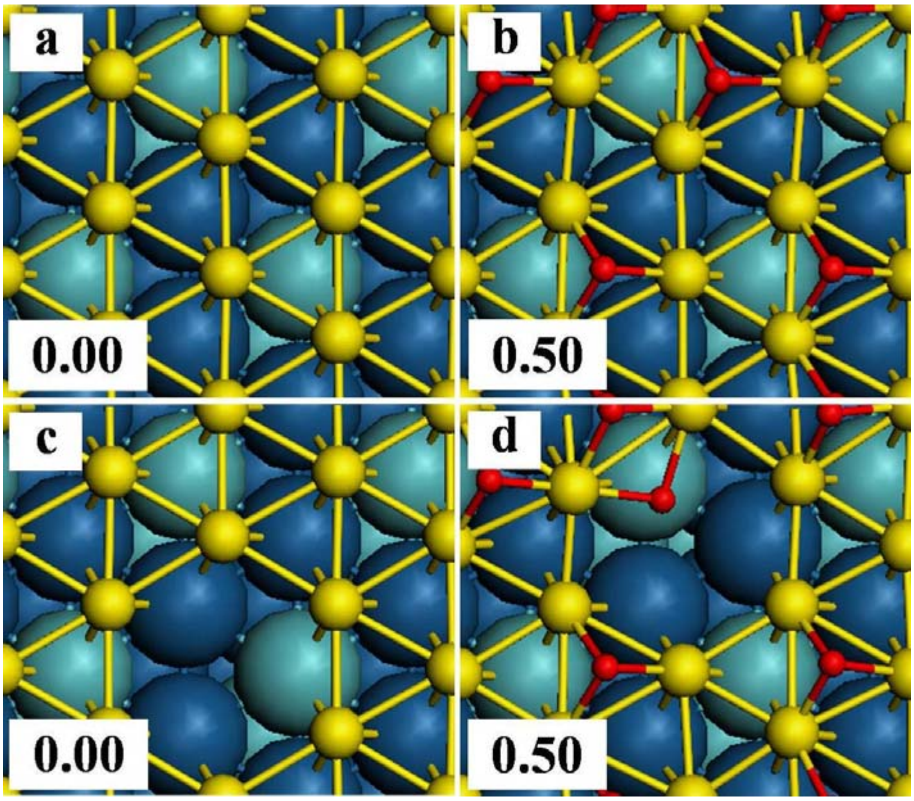


Figure S1. Illustrustion of the structures for the surface adsorption phase (a and b) and their corresponding surface vacancy phases (c and d) at zero and 0.5 ML O coverages for Pt_2Mo skin alloy. Large blue ball: subsurface: Pt atoms; large cyan ball: subsurface M atoms; small yellow ball: top layer Pt atoms; small red ball: O atoms.

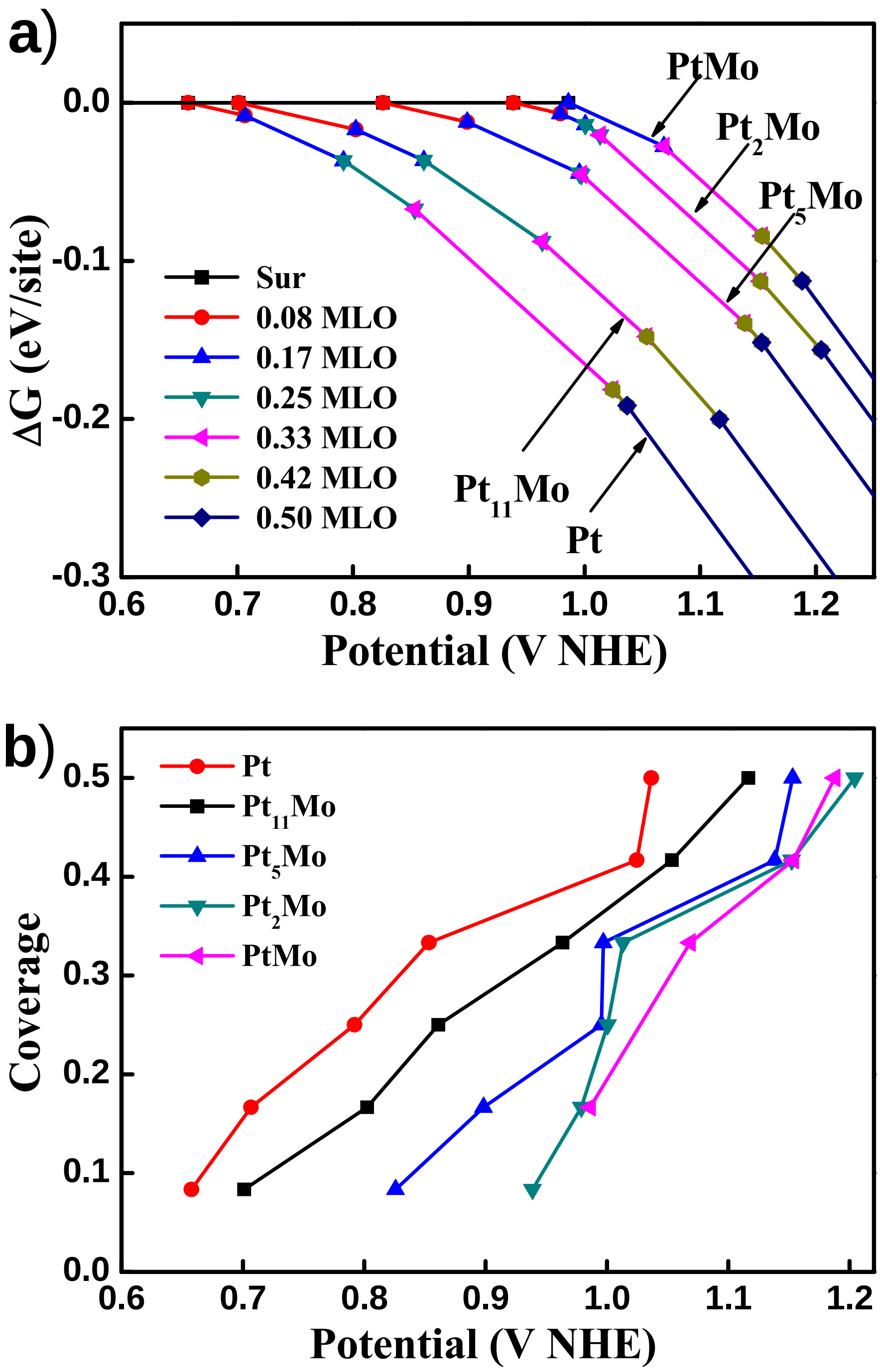
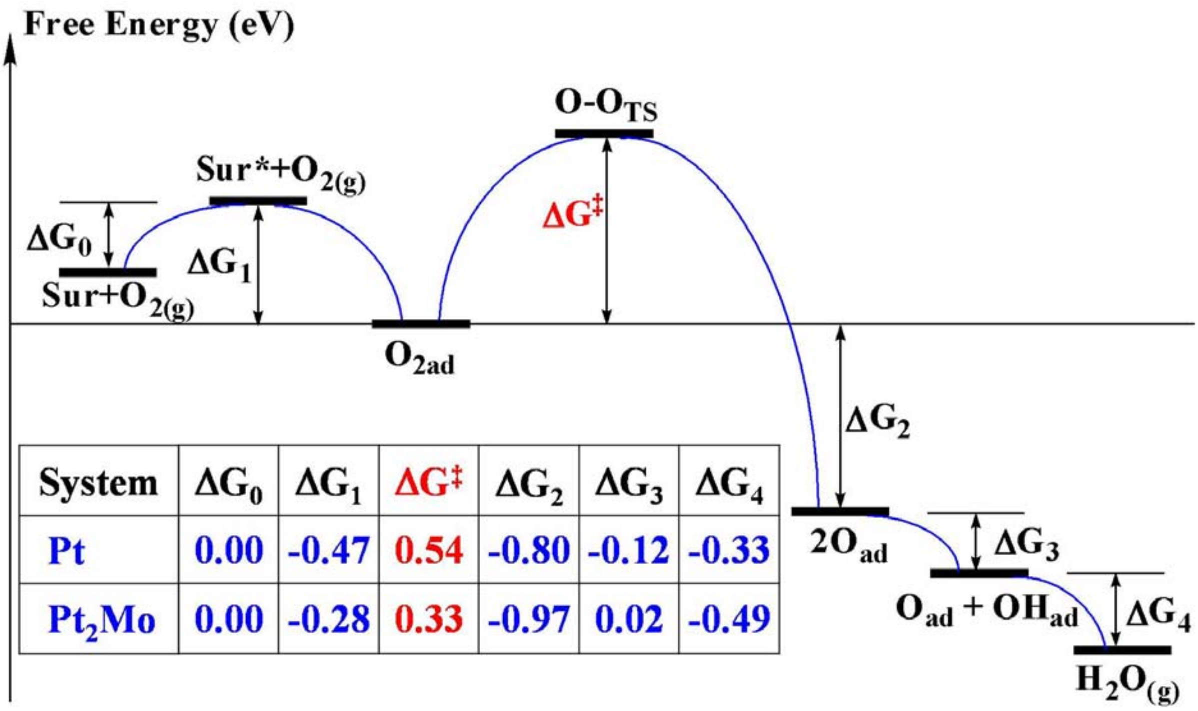


Figure S2. a) Surface phase diagram for Pt(111) and Pt$_x$Mo skin alloys as calculated in the $(3\times2\sqrt{3})$ unit cell. b) The coverage of adsorbed O at varied electrochemical potentials for Pt(111) and Pt$_x$Mo skin alloys.



System	ΔG_0	ΔG_1	$\Delta G^‡$	ΔG_2	ΔG_3	ΔG_4
Pt	0.00	-0.47	0.54	-0.80	-0.12	-0.33
Pt_2Mo	0.00	-0.28	0.33	-0.97	0.02	-0.49

Figure S3. Schematic free energy profile for the direct O_2 dissociation channel of ORR on Pt(111) surface and Pt_2Mo skin alloy surface at 0.8 V. The calculated values (eV) of ΔG_0, ΔG_1, $\Delta G^‡$, ΔG_2, ΔG_3, ΔG_4 are listed in the inserted table. The solvation free energy is corrected by using periodic continuum solvation model.

Table S1. Calculated free energies of elementary steps in ORR on the O-terminated phase of Pt(111) and Pt_2Mo skin alloy surface. ΔH(0→298K) is deduced from reference 7. All ZPE were corrected using the computed values on Pt(111) surface. The solvation free energy contribution (**ΔG_{solv}**) is computed by using periodic continuum solvation model.

elementary steps	**ΔE**	**ΔH(0→298K)**	**ΔZPE**	**-TΔS**	**$-\lvert e\rvert U$**	**ΔG_{solv}**	**ΔG**
Pt(111) at 0.8V (0.25 ML O)							
$Sur+O_{2(g)} \rightarrow O_{2ad}$	-1.02	-0.09	0.05	0.64	0.00	-0.05	-0.47
$O_{2ad}+H^++e^- \rightarrow OOH_{ad}$	-0.60	-0.04	0.19	0.21	0.80	-0.07	0.48
$OOH_{ad} \rightarrow OOH\text{-}TS$	0.10	0.00	-0.05	0.00	0.00	0.00	0.05
$OOH\text{-}TS \rightarrow O_{ad}+OH_{ad}$	-1.35	0.00	-0.05	0.00	0.00	-0.04	-1.45
$O_{ad}+OH_{ad}+H^++e^- \rightarrow O_{ad}+H_2O_{(g)}$	-0.93	0.06	0.13	-0.47	0.80	0.18	-0.24
$O_{ad}+H_2O_{(g)}+H^++e^- \rightarrow OH_{ad}+H_2O_{(g)}$	-0.75	-0.04	0.10	0.21	0.80	-0.06	0.25
$OH_{ad}+H_2O_{(g)}+H^++e^- \rightarrow 2H_2O_{(g)}$	-0.90	0.06	0.13	-0.47	0.80	0.04	-0.34
Pt(111) at 0.9V (0.33 ML O)							
$Sur+O_{2(g)} \rightarrow Sur^*+O_{2(g)}$	0.34	0.00	0.00	0.00	0.00	0.01	0.35
$Sur^*+O_{2(g)} \rightarrow O_{2ad}$	-0.94	-0.09	0.05	0.64	0.00	-0.08	-0.43
$O_{2ad}+H^++e^- \rightarrow OOH_{ad}$	-0.60	-0.04	0.19	0.21	0.90	-0.09	0.57
$OOH_{ad} \rightarrow OOH\text{-}TS$	0.11	0.00	-0.05	0.00	0.00	0.01	0.07
$OOH\text{-}TS \rightarrow O_{ad}+OH_{ad}$	-1.37	0.00	-0.05	0.00	0.00	-0.07	-1.48
$O_{ad}+OH_{ad}+H^++e^- \rightarrow O_{ad}+H_2O_{(g)}$	-1.00	0.06	0.13	-0.47	0.90	0.14	-0.24
$O_{ad}+H_2O_{(g)}+H^++e^- \rightarrow OH_{ad}+H_2O_{(g)}$	-1.07	-0.04	0.10	0.21	0.90	-0.11	-0.02
$OH_{ad}+H_2O_{(g)}+H^++e^- \rightarrow 2H_2O_{(g)}$	-0.94	0.06	0.13	-0.47	0.90	0.18	-0.14
Pt_2Mo at 0.8V (zero O coverage)							
$Sur+O_{2(g)} \rightarrow O_{2ad}$	-0.75	-0.09	0.05	0.64	0.00	-0.13	-0.28
$O_{2ad}+H^++e^- \rightarrow OOH_{ad}$	-0.80	-0.04	0.19	0.21	0.80	-0.06	0.30
$OOH_{ad} \rightarrow OOH\text{-}TS$	0.18	0.00	-0.05	0.00	0.00	-0.09	0.03
$OOH\text{-}TS \rightarrow O_{ad}+OH_{ad}$	-1.30	0.00	-0.05	0.00	0.00	0.06	-1.28
$O_{ad}+OH_{ad}+H^++e^- \rightarrow O_{ad}+H_2O_{(g)}$	-0.97	0.06	0.13	-0.47	0.80	0.15	-0.30
$O_{ad}+H_2O_{(g)}+H^++e^- \rightarrow OH_{ad}+H_2O_{(g)}$	-0.86	-0.04	0.10	0.21	0.80	-0.06	0.13
$OH_{ad}+H_2O_{(g)}+H^++e^- \rightarrow 2H_2O_{(g)}$	-0.97	0.06	0.13	-0.47	0.80	0.14	-0.31
Pt_2Mo at 0.9V (zero O coverage)							
$Sur+O_{2(g)} \rightarrow O_{2ad}$	-0.75	-0.09	0.05	0.64	0.00	-0.13	-0.28
$O_{2ad}+H^++e^- \rightarrow OOH_{ad}$	-0.80	-0.04	0.19	0.21	0.90	-0.06	0.40
$OOH_{ad} \rightarrow OOH\text{-}TS$	0.18	0.00	-0.05	0.00	0.00	-0.09	0.03
$OOH\text{-}TS \rightarrow O_{ad}+OH_{ad}$	-1.30	0.00	-0.05	0.00	0.00	0.06	-1.28
$O_{ad}+OH_{ad}+H^++e^- \rightarrow O_{ad}+H_2O_{(g)}$	-0.97	0.06	0.13	-0.47	0.90	0.15	-0.20
$O_{ad}+H_2O_{(g)}+H^++e^- \rightarrow OH_{ad}+H_2O_{(g)}$	-0.86	-0.04	0.10	0.21	0.90	-0.06	0.23
$OH_{ad}+H_2O_{(g)}+H^++e^- \rightarrow 2H_2O_{(g)}$	-0.97	0.06	0.13	-0.47	0.90	0.14	-0.21

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