Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2015

First principles investigation of the activity of thin film Pt, Pd and Au surface alloys for oxygen reduction

Vladimir Tripkovic[1,2,3*], Heine Anton Hansen[1], Jan Rossmeisl[2,3], Tejs Vegge[1]

[1]Department of Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark

[2]Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark.

[3]Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Note 1: Linear scaling relationships

Figure S1 shows the OOH vs. OH and O vs OH linear scaling relations for the binary and ternary thin films. For comparison we also denote the linear scaling relations between the OOH and OH calculated for metals in ref. 1. As seen, there is a small difference in the slopes and intercepts between the thin film and metal data. The energy differences cancel to a large extent after adding a water stabilization effect, which is necessary for getting the free energy differences that can be related to the activities. In ref. 1 this effect is found to be approximately 0.30 eV for OOH, whereas in this work it is calculated to be 0.16 eV for OOH on Pt(111) and 0.22 eV for OOH on Pd(111). The difference in the water stabilization effect in the two studies is probably due to different DFT codes (presumably pseudopotentials) employed for calculating the binding energies.

It is also noteworthy that the O vs. OH scaling relations for Au containing thin films form different subsets. Every subset is for a fixed concentration of Au in the surface layer. A high change in the O binding energy between different subsets is because Au is not an oxophilic element, thus when oxygen adsorbs e.g. in a face-centered-cubic (fcc) site between one Au and two Pt atoms, the O lies in the position that is in between the fcc and a bridge site between the two platinum atoms. This causes jumps in the oxygen binding energy. Nevertheless, the large change in the oxygen binding energy does not affect the potential determining step because the reduction of OOH to O is the most exergonic step in the free energy path. Even, if the oxygen binding energy was 3 eV, the OOH reduction step would still be downhill in free energy by more than 1 eV.

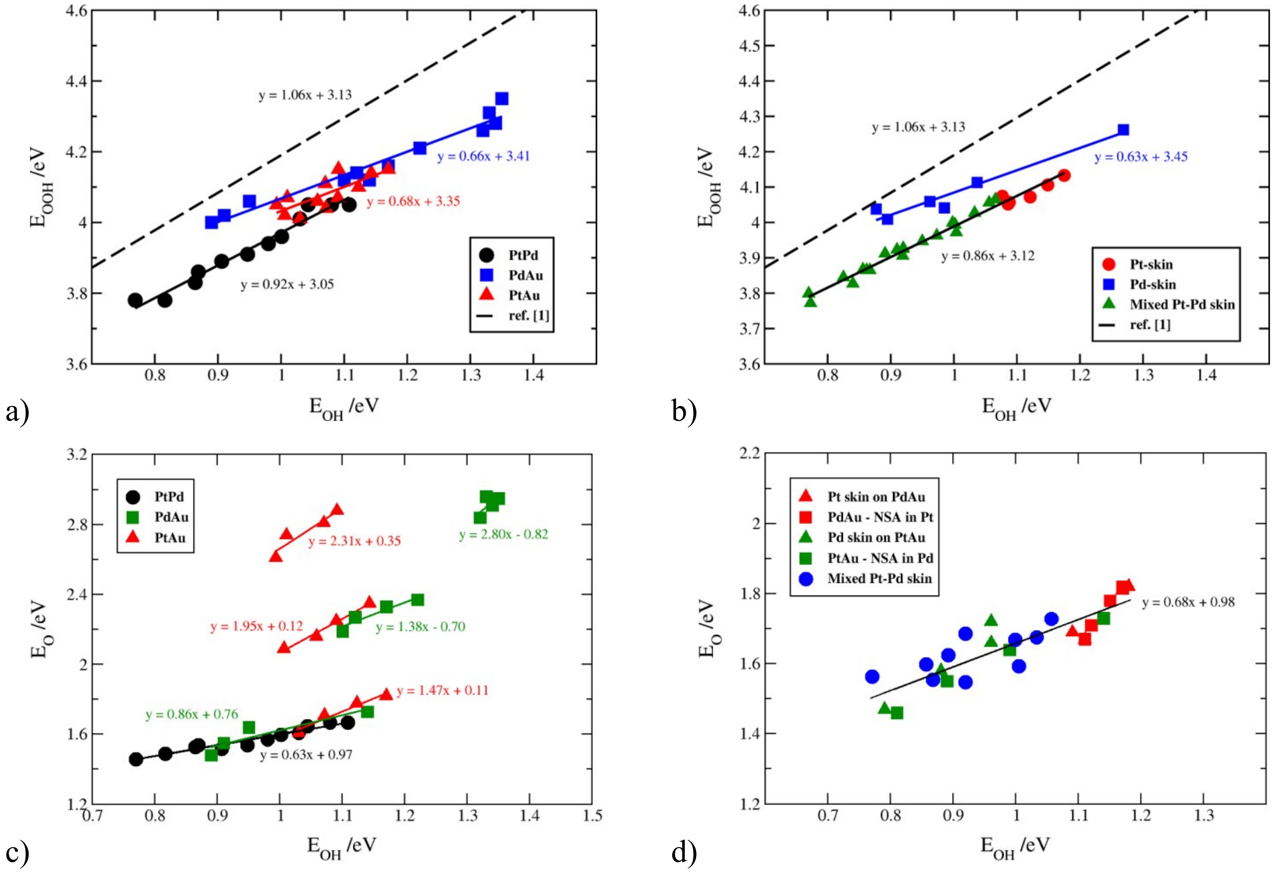

Figure 1 Linear scaling relations OOH vs. OH (a and b) and O vs. OH (c and d) for the binary (a and c) and ternary thin films (b and d).

<u>Note 2: Convergence with respect to the slab thickness</u>

The convergence with respect to the number of layers for Pt(111), and selected binary (111) catalysts is shown in Table S1. As can be seen the relative differences depend on the slab thickness as well as on the thin film composition. In particular, the OH binding energy on Pt(111) is changing significantly between the odd and even number of layers. We choose an even number of layers (4) because the Pt(111) skin on Au(111) has been experimentally shown to be slightly less active than Pt(111), whereas the Pt(111) skin on Pt(111) is slightly more active than Pt(111).[2]

Table S1: OH binding energies on selected catalysts. Values are in eVs.

Number of slab layers	Pt	$Pt_3/Au_3/Pt$	$Pt_3/Pd_3/Pd$
3	0.88	1.02	0.96
4	1.03	1.00	1.07
5	0.91	0.99	1.03
6	0.98	1.03	-

Note 3: Values for the activity and stability descriptors

Table 2 Binary thin films. Formulations more active than Pt are colored in red.

Thin film	OH binding energy /eV	Surface energy eV/Atom	Thin film	OH binding energy /eV	Surface energy eV/Atom
PtPd thin films (Pt-host)			PtPd thin films (Pd-host)		
$Pt_3/Pt_3/Pt$	1.030	0.530	$Pt_3/Pt_3/Pd$	1.011	0.486
$Pt_2Pd/Pt_3/Pt$	0.906	0.515	$Pt_2Pd/Pt_3/Pd$	0.887	0.472
$PtPd_2/Pt_3/Pt$	0.769	0.498	$PtPd_2/Pt_3/Pd$	0.748	0.447
$Pd_3/Pt_3/Pt$	0.791	0.474	$Pd_3/Pt_3/Pd$	0.812	0.426
$Pt_3/Pt_2Pd/Pt$	1.043	0.495	$Pt_3/Pt_2Pd/Pd$	1.034	0.471
$Pt_2Pd/Pt_2Pd/Pt$	0.947	0.487	$Pt_2Pd/Pt_2Pd/Pd$	0.921	0.464
$PtPd_2/Pt_2Pd/Pt$	0.816	0.477	$PtPd_2/Pt_2Pd/Pd$	0.780	0.448
$Pd_3/Pt_2Pd/Pt$	0.851	0.461	$Pd_3/Pt_2Pd/Pd$	0.779	0.436
$Pt_3/PtPd_2/Pt$	1.080	0.466	$Pt_3/PtPd_2/Pd$	1.057	0.452
$Pt_2Pd/PtPd_2/Pt$	0.980	0.466	$Pt_2Pd/PtPd_2/Pd$	0.944	0.454
$PtPd_2/PtPd_2/Pt$	0.864	0.462	$PtPd_2/PtPd_2/Pd$	0.815	0.455
$Pd_3/PtPd_2/Pt$	0.934	0.451	$Pd_3/PtPd_2/Pd$	0.828	0.451
$Pt_3/Pd_3/Pt$	1.108	0.447	$Pt_3/Pd_3/Pd$	1.072	0.448
$Pt_2Pd/Pd_3/Pt$	1.001	0.452	$Pt_2Pd/Pd_3/Pd$	0.956	0.459
$PtPd_2/Pd_3/Pt$	0.869	0.454	$PtPd_2/Pd_3/Pd$	0.821	0.466
$Pd_3/Pd_3/Pt$	0.903	0.451	$Pd_3/Pd_3/Pd$	0.888	0.469
PtAu thin films (Pt-host)			PdAu thin films (Pd-host)		
$Pt_3/Pt_3/Pt$	1.030	0.530	$Pd_3/Pd_3/Pd$	0.889	0.478
$Pt_2Au/Pt_3/Pt$	1.006	0.469	$Pd_2Au/Pd_3/Pd$	1.102	0.310
$PtAu_2/Pt_3/Pt$	0.993	0.375	$PdAu_2/Pd_3/Pd$	1.322	0.178
$Au_3/Pt_3/Pt$	1.582	0.272	$Au_3/Pd_3/Pd$	1.662	0.117
$Pt_3/Pt_2Au/Pt$	1.071	0.616	$Pd_3/Pd_2Au/Pd$	0.913	0.425
$Pt_2Au/Pt_2Au/Pt$	1.058	0.535	$Pd_2Au/Pd_2Au/Pd$	1.124	0.257
$PtAu_2/Pt_2Au/Pt$	1.010	0.419	$PdAu_2/Pd_2Au/Pd$	1.338	0.125
$Au_3/Pt_2Au/Pt$	1.481	0.315	$Au_3/Pd_2Au/Pd$	1.624	0.080
$Pt_3/PtAu_2/Pt$	1.123	0.634	$Pd_3/PdAu_2/Pd$	0.920	0.387
$Pt_2Au/PtAu_2/Pt$	1.090	0.544	$Pd_2Au/PdAu_2/Pd$	1.173	0.220
$PtAu_2/PtAu_2/Pt$	1.070	0.414	$PdAu_2/PdAu_2/Pd$	1.334	0.090
$Au_3/PtAu_2/Pt$	1.534	0.317	$Au_3/PdAu_2/Pd$	1.598	0.082
$Pt_3/Au_3/Pt$	1.170	0.604	$Pd_3/Au_3/Pd$	1.140	0.384
$Pt_2Au/Au_3/Pt$	1.143	0.505	$Pd_2Au/Au_3/Pd$	1.224	0.230
$PtAu_2/Au_3/Pt$	1.091	0.382	$PdAu_2/Au_3/Pd$	1.346	0.133
$Au_3/Au_3/Pt$	1.627	0.278	$Au_3/Au_3/Pd$	1.603	0.139

Table 3 Ternary thin films.[1] Formulations more active than Pt are colored in red.

Thin film pure skin	OH binding energy /eV	Surface energy eV/Atom	Thin film mixed skin	OH binding energy /eV	Surface energy eV/Atom
Pure metal skins (Pt-host)			Mixed metal skins (Pt-host)		
$Pd_3/Pt_3/Pt$	0.793	0.474	$PtPd_2/Au_3/Pt$	0.919	0.549
$Pd_2Au/Pt_3/Pt$	1.037	0.366	$Pt_2Pd/Au_3/Pt$	1.056	0.581
$PdAu_2/Pt_3/Pt$	1.269	0.288	$PtPd_2/PtAu_2/Pt$	0.856	0.586
$Au_3/Pt_3/Pt$	1.582	0.272	$Pt_2Pd/PtAu_2/Pt$	0.998	0.613
$Pt_3/Pd_3/Pt$	1.108	0.447	$PtPd_2/Pt_2Au/Pt$	0.770	0.573
$Pt_3/Pd_2Au/Pt$	1.121	0.483	$Pt_2Pd/Pt_2Au/Pt$	0.919	0.597
$Pt_3/PdAu_2/Pt$	1.149	0.526	$PtPd_2/PdAu_2/Pt$	0.891	0.495
$Pt_3/Au_3/Pt$	1.170	0.604	$Pt_2Pd/PdAu_2/Pt$	1.033	0.514
$Pd_3/Pt/Pt$	0.791	0.474	$PtPd_2/Pd_2Au/Pt$	0.867	0.471
$Pd_3/Pt_2Au/Pt$	0.877	0.540	$Pt_2Pd/Pd_2Au/Pt$	1.004	0.480
$Pd_3/PtAu_2/Pt$	0.962	0.546	$PtPd_2/Au_3/Pt$	0.919	0.549
$Pd_3/Au_3/Pt$	0.961	0.502	$Pt_2Pd/Au_3/Pt$	1.056	0.581
Pure metal skins (Pd-host)			Mixed metal skins (Pd-host)		
$Pt_3/Pd_3/Pd$	1.072	0.457	$PtPd_2/Au_3/Pd$	0.920	0.430
$Pt_2Au/Pd_3/Pd$	1.086	0.375	$Pt_2Pd/Au_3/Pd$	1.066	0.459
$PtAu_2/Pd_3/Pd$	1.077	0.257	$PtPd_2/PtAu_2/Pd$	0.825	0.502
$Au_3/Pd_3/Pd$	1.662	0.117	$Pt_2Pd/PtAu_2/Pd$	0.950	0.529
$Pd_3/Pt_3/Pd$	0.812	0.434	$PtPd_2/Pt_2Au/Pd$	0.773	0.513
$Pd_3/Pt_2Au/Pd$	0.895	0.483	$Pt_2Pd/Pt_2Au/Pd$	0.910	0.536
$Pd_3/PtAu_2/Pd$	0.985	0.464	$PtPd_2/PdAu_2/Pd$	0.862	0.418
$Pd_3/Au_3/Pd$	1.140	0.384	$Pt_2Pd/PdAu_2/Pd$	1.002	0.436
$Pt_3/Pd_3/Pd$	1.072	0.457	$PtPd_2/Pd_2Au/Pd$	0.841	0.440
$Pt_3/Pd_2Au/Pd$	1.088	0.448	$Pt_2Pd/Pd_2Au/Pd$	0.973	0.446
$Pt_3/PdAu_2/Pd$	1.175	0.432	$PtPd_2/Au_3/Pd$	0.920	0.430
$Pt_3/Au_3/Pd$	1.176	0.480	$Pt_2Pd/Au_3/Pd$	1.066	0.459

(1) Rossmeisl, J.; Logadottir, A.; Nørskov, J. K. *Chem. Phys.* **2005**, *319*, 178–184.

(2) Nilekar, A. U.; Xu, Y.; Zhang, J.; Vukmirovic, M. B.; Sasaki, K.; Adzic, R. R.; Mavrikakis, M. *Top. Catal.* **2007**, *46*, 276–284.

[1] For completeness of data Table 3 contains also some binary thin films from Table 2.