Identifying active surface phases for metal oxide electrocatalysts: A study of manganese oxide bi-functional catalysts for oxygen reduction and water oxidation catalysis

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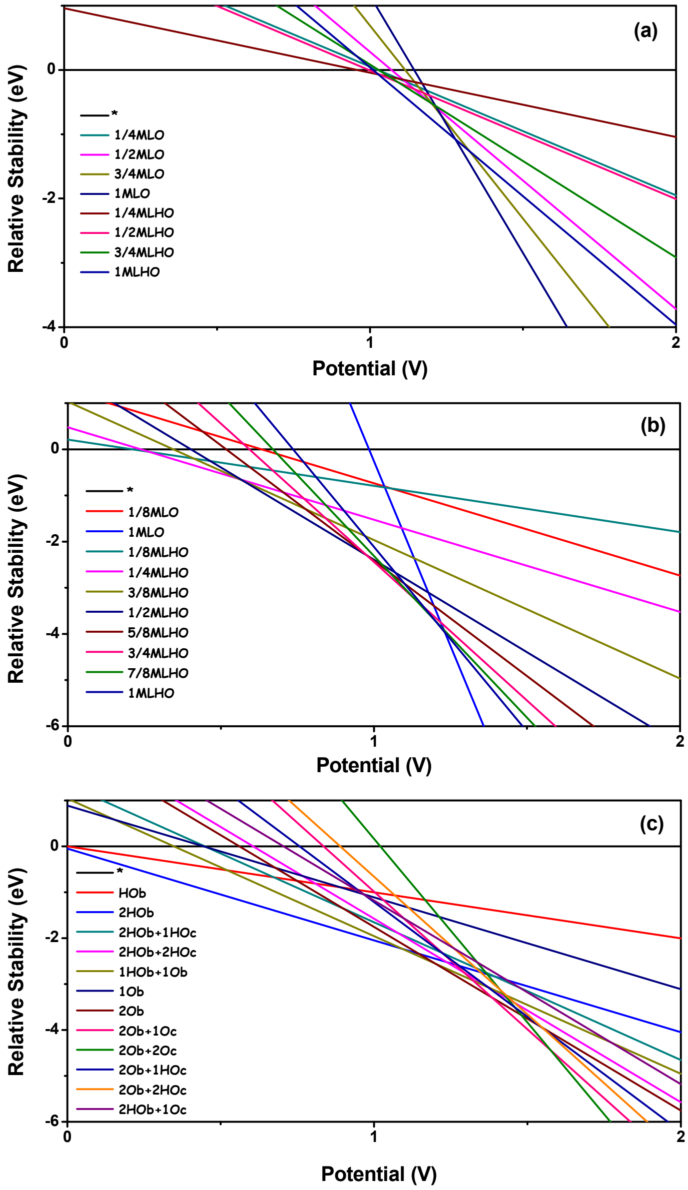

Figure S1. The phase-diagram of the (a) Mn_3O_4 (001), (b) Mn_2O_3 (110), and (c) MnO_2 (110) surfaces calculated as function of the potential at pH=0. The notations *, b and c within the figure legends represent the stoichiometric surfaces (Mn_3O_4 (001) and Mn_2O_3 (110)) or reduced surface (MnO_2 (110)), the adsorbates at the bridge sites and coordinated unsaturated sites, respectively. The dissolution process is not included here.

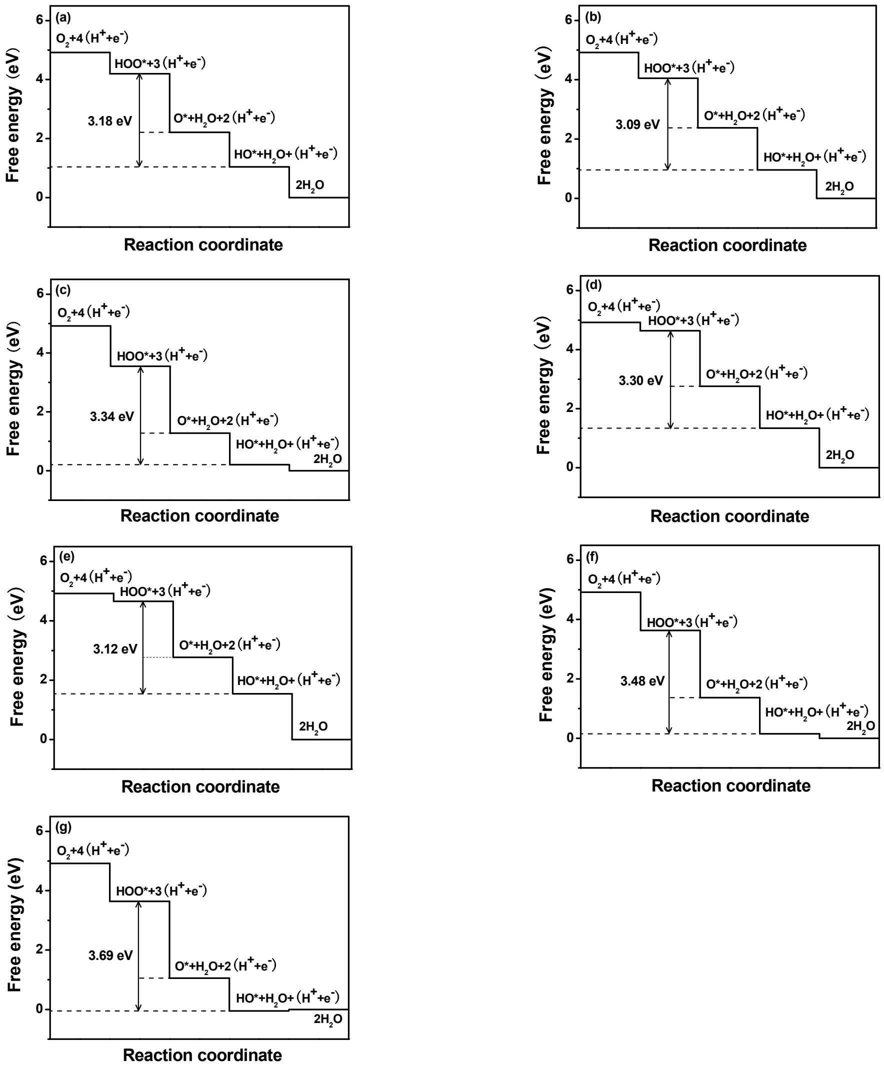

Figure S2. Free-energy diagram for oxygen reduction on (a) Mn_3O_4 (001) with 1/4 ML HO* as spectator species, (b) Mn_3O_4 (001) with 1 ML HO* as spectator species, (c) Mn_2O_3 (110), (d) MnO_2 (110) with O* and HO* as spectator species at the bridge sites, (e) MnO_2 (110) with O* as spectator species at the bridge sites, (f) MnO_2 (110) with O* as spectator species at the bridge site, (g) MnO_2 (110) with HO* as spectator species at the bridge site.

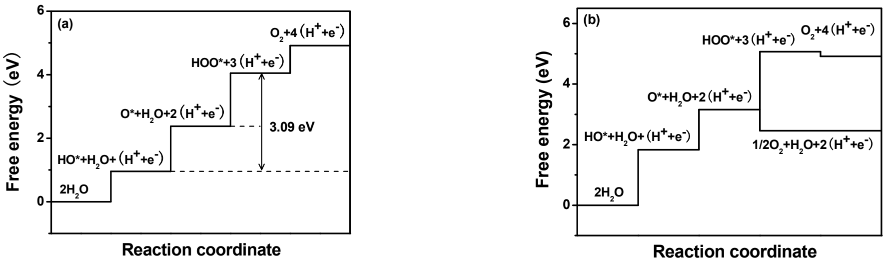

Figure S3. Free-energy diagram for oxygen evolution on (a) Mn_3O_4 (001) with 1ML HO* as spectator species by associative mechanism and (b) MnO_2 (110) with O as spectator species at the bridge sites and coordinated unsaturated site by associative mechanism and direct mechanism at U = 0, pH = 0 and T = 298 K.

Calculation of O (N_O):

The method to calculate the number of O (N_O) coordinated with Mn on various manganese oxide surfaces Mn_3O_4 (001), Mn_2O_3 (110), and MnO_2 (110) is shown using Mn_3O_4 (001) as an example (see Figure 8). Every Mn in Mn_3O_4 (001) coordinates with five O atoms: four O atoms in the top layer and one O atom in the second layer. Each of the four O atoms is coordinated with three Mn atoms and the O in the second layer coordinates with four Mn atoms. The number of O (N_O) coordinated with Mn is: $4\times 1/3+1/4=1.58$

Constructing the Pourbaix diagrams:

The method to construct the Pourbaix diagram including bulk and surface is shown here. The free energy of an oxide particle with N metal atoms in equilibrium with H_2O, H^+ and electrons is (assuming negligible contributions from steps and kinks):

$$\Delta G = N\Delta G_{MOx} + \sum_{i,x} \gamma_i^x A_i^x \quad (1)$$

where ΔG_{MOx} is the formation energy of bulk MO_x per metal atom (here we use the experimental values), γ_i^x is the surface free energy of the facet 'i' with the adsorbate phase (or termination) 'x' (for example, γ_{110}^x could be the surface free energy for the stoichiometric MnO_2(110) facet and γ_{110}^O could be the surface free energy of the (110) facet with O at the surface), and A_i^x is the surface area (A_i^x should be chosen to minimize ΔG, which should lead to the Wulff construction). We can rewrite (1) as

$$\Delta G = N\Delta G_{MOx} + \sum_{i,x} (\gamma_i^x - \gamma_i^*) A_i^x + \sum_{i,x} \gamma_i^*) A_i^x \quad (2)$$

where γ_i^* is the surface energy of the stoichiometric termination of the facet i.

Next, let us assume the particle is spherical, and has a single type of facet. Then we can drop the index i, and rewrite (2) as

$$\Delta G = N\Delta G_{MOx} + \sum_{x}(\gamma^{x} - \gamma^{*})A^{x} + \sum_{x}\gamma^{*})A^{x} \qquad (3)$$

The free energy of the particle with a particular termination 'X' is then

$$\Delta G = N\Delta G_{MOx} + (\gamma^{x} - \gamma^{*})A + \gamma^{*}A \qquad (4)$$

$$(\gamma^{x} - \gamma^{*})A = \Delta G_{ads} \qquad (5)$$

Here ΔG_{MOx} depends on pH and potential in the usual way. γ^{*} is independent of potential and pH. If the particle is large enough, it is closer to bulk and the contribution from surface i.e., $\gamma^{*}A$ can be neglected.

Then, we can rewrite (4) as

$$\Delta G = N\Delta G_{MOx} + (\gamma^{x} - \gamma^{*})A \qquad (6)$$

A and N may be determined from the assumption that the particle is spherical, knowing the volume per formula unit of the oxide. The stability of particles of different oxides may then be compared for particles with a fixed number of metal atoms N. In this paper, N is chosen to be 1000000, at this value the results are converged using bulk phase diagram as a reference. (Pourbaix, M. Atlas of Electrochemical Equilibria in Aqueous Solutions, 1st English edition, Pergamon Press: New York, 1966)

Then we calculate the formation energies from experimental data taken from Pourbaix Atlas of Electrochemical Equilibria using the standard dissolution potential of pure manganese and the respective oxide:

$$xMn^{2+} + 2xe^{-} \leftrightarrow xMn \quad \text{with} \quad U^{0}_{M^{2+}/Mn} \qquad (7)$$

$$Mn_xO_y(bulk) + 2yH^+ + x\left(\frac{2y}{x} - 2\right)e^- \leftrightarrow xMn^{2+} + yH_2O(l) \text{ with } U^0_{Mn_xO_y/Mn^{2+}} \tag{8}$$

If we sum the two reactions, we can calculate the standard free energy of formation for an oxide:

$$\Delta G^{0,\exp}_{form,MO_x} = e\left(2xU^0_{Mn^{2+}/Mn} + x\left(\frac{2y}{x} - 2\right)U^0_{Mn_xO_y/Mn^{2+}}\right) \tag{9}$$

The change in the formation energy with the pH or with the potential varies in the following manner:

$$\Delta G^{\exp}_{form,MO_x} = 2yk_BT\ln a_{H^+} - 2ex\left(U_{Mn^{2+}/Mn} - U^0_{Mn^{2+}/Mn}\right) - ex\left(\frac{2y}{x} - 2\right)\left(U_{Mn_xO_y/Mn^{2+}} - U^0_{Mn^{2+}/Mn}\right) \tag{10}$$

Table S1. Standard reduction potentials for Mn_yO_x oxides relative to Mn^{2+}. In our calculation concentration of Mn^{2+} is considered to be 1.

Mn_xO_y	$U^0_{Mn^{2+}/Mn_xO_y}$
MnO	*-0.727-0.0591pH* [1]
Mn_3O_4	*1.824-0.2364pH-0.0886log(Mn^{2+})*
Mn_2O_3	*1.443-0.1773pH-0.0591log(Mn^{2+})*
MnO_2	*1.228-0.1182pH-0.0295log(Mn^{2+})*

Table S2. Standard reduction potentials for the soluble products, which we take into consideration. Their concentration is considered to be 1.

$U^0_{Mn^{2+}/Mn}$	$-1.179 + 0.0295*\log[Mn^{2+}]$
$U^0_{MnO_4^{2-}/Mn^{2+}}$	$1.742 - 0.1182pH + 0.0148\frac{(MnO_4^{2-})}{(Mn^{2+})}$
$U^0_{MnO_4^-/Mn^{2+}}$	$1.507 - 0.0945pH + 0.0148\frac{(MnO_4^-)}{(Mn^{2+})}$
$U^0_{HMnO_2^-/Mn^{2+}}$	$\log\frac{(HMnO_2^-)}{(Mn^{2+})} = -34.39 + 3pH$

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[1] For MnO it was considered standard reduction potential for the reaction Mn + $H_2O(l) \leftrightarrow$ MnO + $2H^+ + 2e^-$