

Why Is Bulk Thermochemistry a Good Descriptor for the Electrocatalytic Activity of Transition Metal Oxides?

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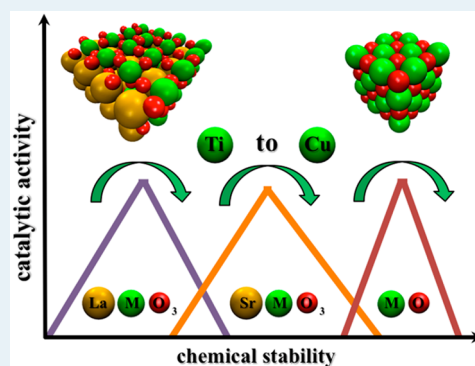
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Supporting Information

ABSTRACT: It is well known that transition metal oxides can efficiently catalyze electrochemical reactions of interest in electrolyzers and fuel cells. The question is how to describe and rationalize the variations in catalytic activity among a given class of oxides, so that known materials can be improved and new active materials be predicted. In this context, descriptor-based analyses are a powerful tool, as they help to rationalize the trends in catalytic activity through correlations with other properties of the material. Particularly, bulk thermochemistry has long been used to describe the trends in catalytic activity of oxide surfaces. Here we explain the reason for the apparent success of this descriptor on the basis of perovskite oxides and monoxides and the oxygen evolution reaction: essentially, bulk thermochemistry and surface adsorption energetics depend similarly on the number of outer electrons of the transition metal in the oxide. This correspondence applies to a wide number of transition metals and is responsible for the linear relationship between bulk and surface properties that enables the construction of volcano-type activity plots.

KEYWORDS: perovskite oxides, monoxides, outer electrons, oxygen evolution reaction, bulk energy of formation, volcano plot

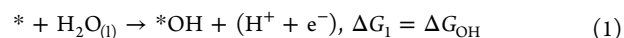


Due to the scarceness of fossil fuels and their related environmental concerns, society needs to trigger and sustainably propel the so-called hydrogen economy.¹ This paradigm requires the widespread use of devices such as electrolyzers and fuel cells. These utilize catalysts for the capture and transformation of solar energy into electricity and fuels with null or reduced carbon footprints. The interconversion between chemical and electrical energy is currently far from being energetically efficient and cost-effective, which hinders the commercialization of these technologies.² Therefore, better catalysts made from earth-abundant elements are required. In this respect, transition metal oxides (and related compounds such as hydroxides and oxy-hydroxides) offer good trade-offs between catalytic activity and total costs, as they are not necessarily made of noble metals.³ Some of these oxides have been thoroughly studied for the past 30 years,⁴ and new materials have been discovered recently through systematic experimental and theoretical routines.^{3a,5} Among those routines, descriptor-based analysis has proved successful in rationalizing the trends in reactivity of transition metal oxides.^{3a,6} This analysis correlates experimental or theoretical estimations of the catalytic activity with a descriptor, in such way that several catalysts can be directly compared and smooth (often linear) trends are observed. The challenge lies in finding the appropriate descriptor for a specific reaction and class of materials. Among the large number of theoretical descriptors for the catalytic activity of oxides, we highlight the binding energies of key intermediates,^{6b,7} the average energies of the p-

band of lattice oxygen atoms at the surface, and the number of outer electrons of the transition metal in the oxide.^{6a} On the other hand, experimental electrocatalysis has traditionally resorted to bulk thermochemistry to describe activity trends,^{4b,c} and only recently, alternative descriptors such as orbital occupations have come into play.^{3a}

In this article, we will show that the simple concept of outer electrons is able to explain why bulk thermochemistry is an excellent descriptor for the electrocatalytic activity of a wide range of transition metal oxides. Thus, we aim to provide a link between theoretical and experimental descriptors by establishing energetic scaling relations between bulk and surface properties. Our case study is the oxygen evolution reaction (OER), which takes place at the anode of electrolyzers. We will analyze the trends for two families of perovskite oxides, namely, AMO_3 , where A is either La or Sr and M is a metal from Sc to Ge. This range includes not only the previous range of oxides from Ti to Cu^{6b,9} but also covers Sc, Zn, Ga, and Ge at the M site. Additionally, we will consider the case of monoxides (MO) in the range between Ca and Cu.

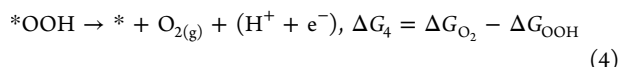
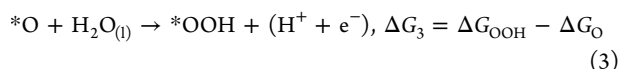
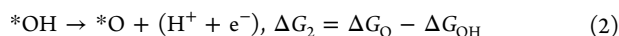
We will start by assuming that the OER proceeds in acid media through the following series of reaction steps:^{6b,10}



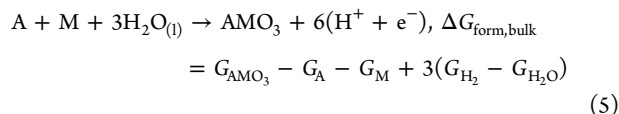
Received: October 28, 2014

Revised: December 19, 2014

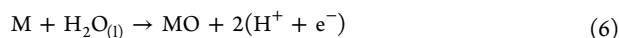
Published: December 19, 2014



Where * denotes an active M site at a(001)MO₂-terminated surface in AMO₃, or an M site at the (001) surface of MO. According to these equations, the adsorbed intermediates of the OER are *O, *OH and *OOH, the adsorption energies of which are ΔG_O , ΔG_{OH} , and ΔG_{OOH} , respectively. The energetics of proton–electron pairs in solution is estimated through the computational hydrogen electrode (CHE, see further details in the Supporting Information).¹¹ Within this scale, the formation energy of O₂(ΔG_{O_2}) is 4.92 eV (that is 1.23 V \times 4 e⁻), whereas that of H₂O is zero. On the other hand, the free energies of formation of the bulk perovskites were calculated at 298.15 K from the A and M components and water, protons and electrons (making use of the CHE), in the following way:



The formation energies of MO were calculated analogously through CHE approach:



In Figures 1 and 2, we summarize the trends in bulk formation energies and in the adsorption energies of *O, *OH, and *OOH for LaMO₃, SrMO₃, and MO.

In Figures 1 and 2, the trends in bulk thermochemistry and surface adsorption energies are smoothly described by the number of outer electrons of the transition metal at the M site in AMO₃ in the ranges from 0 to 7 for SrMO₃, 0 to 8 for LaMO₃, and 0 to 9 for MO. The number of outer electrons is equivalent to the number of valence electrons for a pure element, and in ionic compounds, it is calculated as the resulting number of valence electrons in an ion upon oxidation or reduction.^{6a} For instance, Cr possesses six valence electrons, as its electronic distribution ends in 4s¹ 3d⁵. Hence, Cr²⁺, as in CrO, has four outer electrons; Cr³⁺, as in LaCrO₃, has three outer electrons; while Cr⁴⁺, as in SrCrO₃, has two outer electrons.

The trends in Figures 1c and 2b have been observed both experimentally and theoretically (see ref 9 and references therein) and have also been extended to other families of perovskite oxides.¹² Besides, the trends in formation energies of other classes of oxides such as rutiles are also known to follow similar electron-counting rules.¹³ It is important to note that although the trends in formation energies are well captured for LaMO₃, SrMO₃, and MO by RPBE, a constant shift exists between theoretical predictions and experimental values of the formation energies.⁹ Such error is largely or totally suppressed when only oxides take part in the chemical reactions, and the GGA + U method is known to improve the overall description of oxides.¹⁴

The linear trends in the range of outer electrons between 1 to 7–8–9 (depending on the oxide family) in Figures 1a,b and 2a are extensible to pure metals (M), and adsorption energy grids can be created, as the slopes of the lines are nearly the

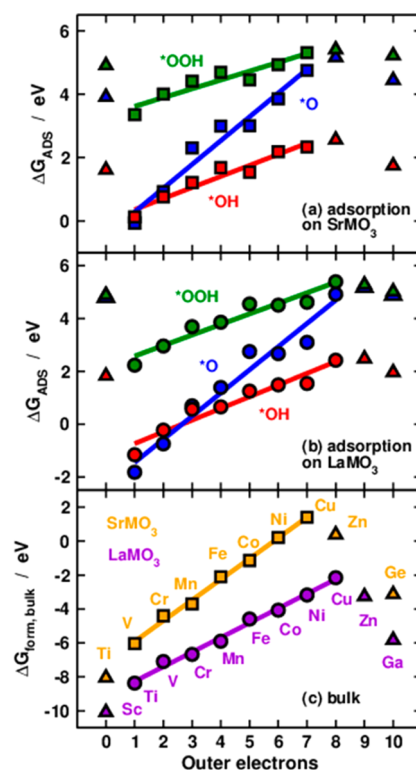


Figure 1. Trends in surface adsorption and bulk thermochemistry of SrMO₃ (squares) and LaMO₃ (circles) as a function of the number of outer electrons of M. The adsorption energies of *O (blue), *OH (red), and *OOH (green) are given for (a) SrMO₃ and (b) LaMO₃. (c) Formation energies of LaMO₃ (violet) and SrMO₃ (orange) from La/Sr, M, and H₂O. The metal at the M site is given in each case. The parameters of the linear fits are provided in the Supporting Information. Data in (a) and (b) was taken from ref 6; data in (c) was adapted from ref 9. Triangles correspond to the materials for which the bulk-surface correlation does not apply.

same and the separation between them is also a constant.^{6a} This demonstrates the wide range of applicability of outer electrons as descriptors in adsorption processes. Moreover, the theoretical activity predictions for the OER based on those trends reproduce the experimental ones,^{4d,6b} and the catalytic activity of transition metal hydroxides has also been shown to follow similar trends.¹⁵

Clearly, for the range of outer electrons between 1 and 7–8–9 because both bulk and surface energetics depend linearly on the same parameter (the number of outer electrons), it is expected that, by transitivity, bulk and surface energetics will also scale linearly with each other, as shown in Figure 3. The similar dependence on the number of outer electrons of both surface and bulk properties allows for the use of the latter to describe trends in surface reactivity. This apparently simple result is the underlying chemical justification for the use of bulk data to rationalize surface catalytic activity not only in electrocatalysis^{4b,c} but also in heterogeneous catalysis.¹⁶ It is also important to note that the energetics of materials with zero outer electrons, namely, CaO, LaScO₃, and SrTiO₃, deviate significantly from the main trends in Figure 3.^{6a} This is because the electronic structure of these compounds is optimal, as all of their components possess noble gas configurations. This implies that the bulk exhibits the most stable energies of formation possible within a given family of compounds, while the surface is quite noble, as the binding of adsorbates implies

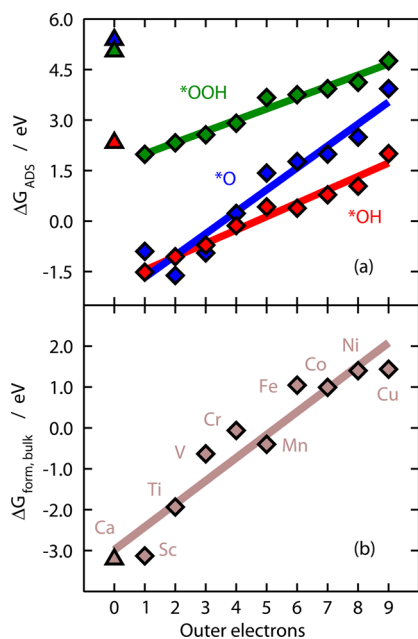


Figure 2. Trends in surface adsorption and bulk thermochemistry of MO as a function of the number of outer electrons of M, with M ranging between Ca and Cu. (a) Adsorption energies of *O (blue), *OH (red), and *OOH (green), taken from ref 6. (b) Formation energies of bulk MO from M and H_2O , adapted from ref 9. The parameters of the linear fits are provided in the Supporting Information. Triangles correspond to the materials for which the bulk-surface correlation does not apply.

electron covalence with already filled bands. Similar arguments justify the existence of the observed minima at 10 outer electrons in Figure 1 for SrGeO_3 and LaGaO_3 , as this value implies a full d-band for M and noble gas configurations for A and O. Clearly, the deviations from the linear trends in Figure 3 originate from the mismatch between the bulk and surface energetics in Figures 1 and 2. This kind of mismatch is well known to cause deviations in energetic scaling relationships and is most prominent for the adsorption energies of *O in Figure 3.¹⁷

Note in the linear regions in Figure 3 that for a given M, the binding energies of OER adsorbates on MO are typically stronger than those of LaMO_3 and those are, in turn, stronger

than those of SrMO_3 . This is because M^{2+} is less oxidized than M^{3+} and M^{4+} , and increasing oxidation states correspond to weaker adsorption energies.^{6a} With the bulk-surface scaling relationships in Figure 3, one can generate activity plots for the OER. To do so, we follow Rossmeisl and co-workers,^{6b,10} who found that, generally, steps 2 (with ΔG_2) and 3 (with ΔG_3) are the possible potential-limiting steps of the OER. In Figure 4, we have taken the highest energies among ΔG_1 , ΔG_2 , ΔG_3 , and ΔG_4 for each perovskite and monoxide and subtracted them from 1.23 V, in order to obtain a first estimation of the OER overpotential in identical conditions for all oxides. The volcano plots in Figure 4 resemble previous activity plots that used surface adsorption energies as descriptors.^{6b,10} Note, however, that volcano plots based on scaling relationships are more robust than the one in Figure 4, as only they only require two lines to represent the activity trends (see Figure S1 in the Supporting Information, where the scaling relations between the adsorption energies of the OER intermediates are provided for all oxides in this study). Conversely, the activity plot in Figure 4 needs two lines per family of oxide compounds. Volcano plots exclusively based on adsorptive scaling relations are also advantageous because they tend to have little deviations from the main trends. However, the kind of volcano plot in Figure 4 possesses a unique feature: it simultaneously provides an estimation of the catalytic activity and the chemical stability of materials. This is because the formation energy of the bulk as defined in eqs 5 and 6 is a measure of the stability of the oxide in aqueous solution. Evidently, these initial stability estimations for MO and AMO_3 require further analysis of other (electro)chemical reactions, such as oxide-phase changes and dissolution of A and/or M, in order to provide a thorough estimation of the stability of the oxide under OER conditions.^{9,18} Note that an additional advantage of the volcano plot in Figure 4 is the large availability of bulk energetics data for most oxides.

In any case, it is possible to say that, according to the volcano plots in Figure 4, the most active compounds tend to be the least stable ones, as the majority of the oxides on the volcano curves lie on their left legs (that is, on the lines with positive slopes in Figure 4). As activity and stability follow opposite trends, high pH values are recommended to enhance the chemical stability of perovskite oxides. Note that LaMO_3 perovskites are always more stable than their SrMO_3 and MO

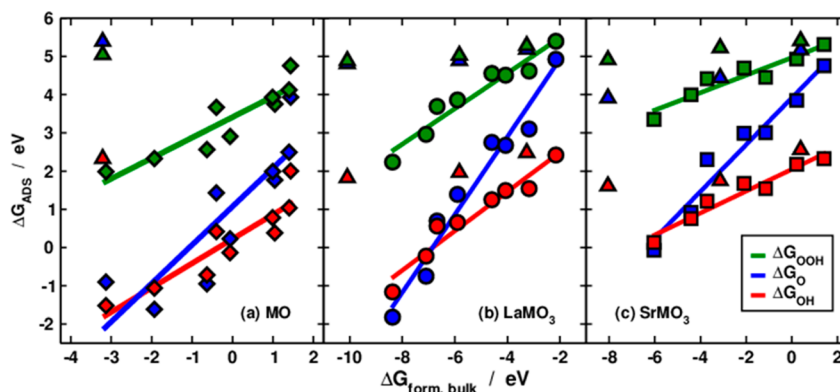


Figure 3. Scaling relationships between the energies of formation of the bulk and the adsorption energies of *O (blue), *OH (red) and *OOH (green) for (a) MO, (b) LaMO_3 , and (c) SrMO_3 . The figure shows that for the range between Ti to Cu, bulk thermochemistry is an excellent descriptor of surface adsorption energies. The parameters of the linear fits are provided in the Supporting Information. Triangles represent the data for which the linear relationships do not apply.

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