

산소발생 촉매분야에서 분자 전자 촉매 설계의 최신 연구동향

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In the recent years, water splitting has attracted substantial interest as a key process in hydrogen production from sunlight and electricity.¹ The conversion from water could indirectly be done by electrolysis using a potential difference obtained from a solar cell or from a wind turbine. In cases, effective catalysis for water oxidation to the oxygen evolution reaction (OER) is needed. There are, however, several challenges that have to be solved for the process to become economically attractive. One of them is associated with the substantial overpotential at the anode, according to the following overall reaction, [Eq. (1)]:²



Substantial effort has been devoted to find more effective catalysts for OER and to explain the reaction mechanism.³

Table 1. Various materials for oxygen electrode.

Rutile-type	$\text{RuO}_2, \text{IrO}_2, \text{MnO}_2, \text{PbO}_2$ $\text{PtO}_2, \text{OsO}_2, \text{ReO}_2$	Mixed oxides with $\text{SnO}_2, \text{TiO}_2, \text{Fe}_2\text{O}_3$ Doped oxides $\text{SnO}_2, \text{MnO}_2, \text{PbO}_2$
Spinel-type	CO_3O_4 MCo_2O_4 M = Ni, Mn, Cr . . . Fe_3O_4 MFe_2O_4 M = Ni, Co, Mn . . .	Doped oxides CO_3O_4
Perovskite-type	NiM_2O_4 M = La, Pr, Nd $\text{M}'_{1-x}\text{Sr}_x\text{MO}_3$ { M = Mn, Co, Fe, Ni M' = La, Nd	{ x = 0; 1 LaCoO ₃ , LaNiO ₃ SrFeO ₃
Other oxides	$\text{NiO}_x, \text{PdO}, \text{M}_x\text{WO}_3, \text{Bi}_2\text{M}_2\text{O}_7$ M = Rh, Ru $\text{Li}_{0.5}\text{Pt}_3\text{O}_4, \text{SrPd}_3\text{O}_4, \text{Ti}_2\text{O}$ ABO_2 { A = Pt, Pd, Ag, Cu B = Co, Cr, Ru, Ir $\text{ABO}_4 \cdot x\text{MO}_2$ { A = Al, Rh B = Sb, Nb, Ta M = Ru, Ir	

To improve upon current electrocatalysts, it is important to develop a fundamental understanding of the reactions on different materials.^{3f-h} The electrocatalytic activity is to a large extent determined by the binding strength of the reaction intermediates to the electrode surface. Plotting the activity as a function of binding energy can give rise to a volcano plot.

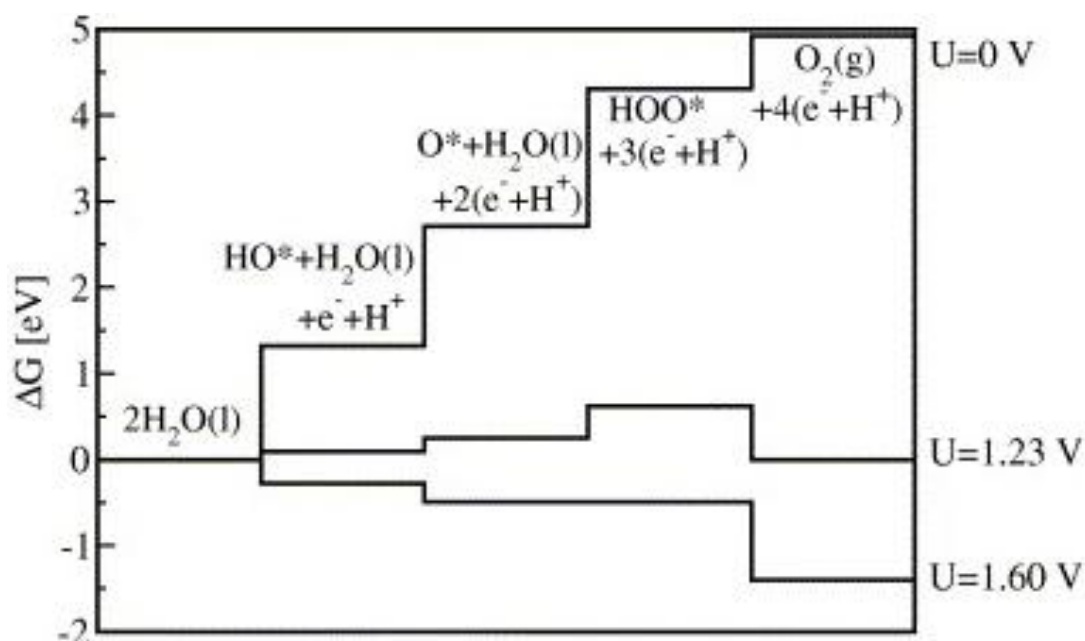


Figure 1. The free energies of the intermediates on O-terminated RuO₂ at three different potentials (U = 0, U = 1.23, and U = 1.60 V) are depicted. At the equilibrium potential (U = 1.23 V) the reaction steps are uphill in free energy. At 1.60 V all reaction steps are downhill in free energy

This concept has been successfully applied to the oxygen evolution reaction.^{3a,c,h} As the binding energies are difficult to measure, other descriptors believed to correlate with the reactivity, have been used. An example is the use of the standard enthalpy of lower to higher oxide transformation ($\text{MO}_x \rightarrow \text{MO}_{x+1}$).^{3b, d-g}

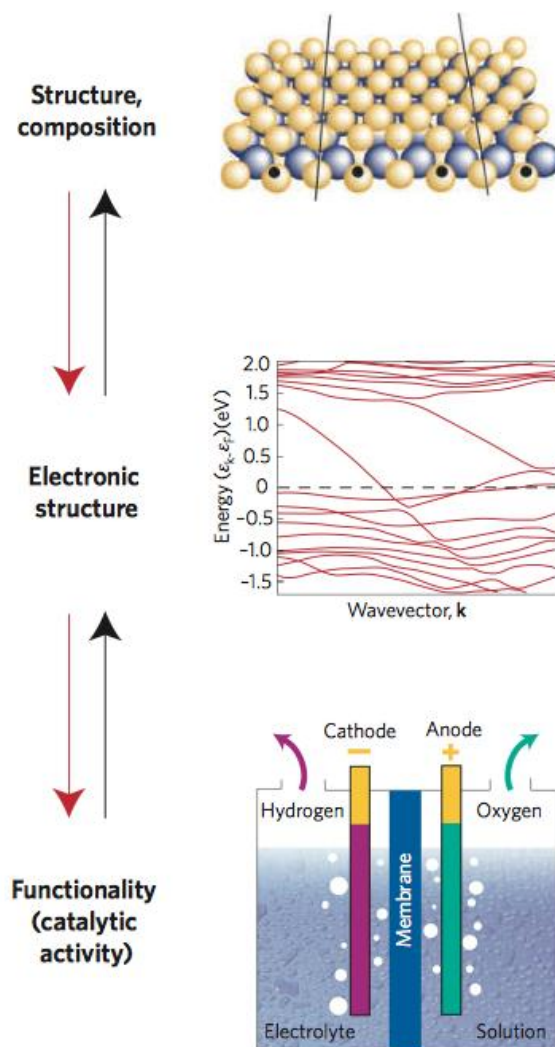


Figure 2. Illustration of the way the electronic structure is the link between the structure and composition of a material and its functionality.

Advances in density functional theory (DFT) calculations make it possible to accurately determine surface binding energies that can hence be used as activity descriptors.^{3h} The reverse reaction, the oxygen reduction reaction (ORR) in which molecular oxygen is reduced to water, involves the same general reaction intermediates as the OER. Recently, new alloy electrocatalysts for the ORR have been suggested on the basis of computational studies, in which the values of the activity descriptor are calculated, followed by identification of promising candidates.^{4,5}

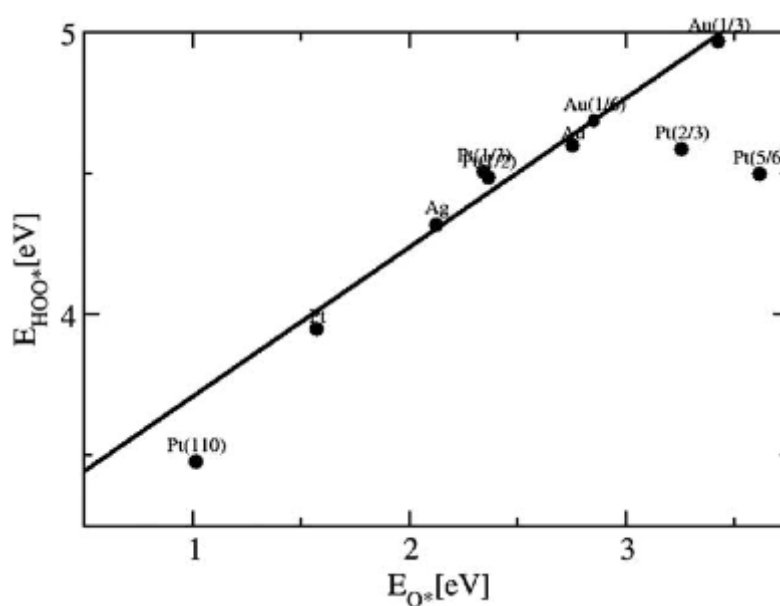


Figure 3. The DFT-binding energy of HOO^* as a function of the O^* binding energy. The two binding energies are related with the function $E_{HOO^*} = 0.53E_{O^*} + 3.18$. The numbers in parentheses are the coverage of pre-adsorbed oxygen.

The OER has been studied using computational methods on two classes of materials: metals⁶ and rutile oxides.⁷ A similar computational approach has been used for the OER which is in competition with chlorine evolution on rutile oxides. In these studies, the proposed reaction mechanism consists of four consecutive proton and electron transfer steps. Considering the OER intermediates to be HO^* , O^* , and HOO^* , free energy diagrams have been constructed and the oxygen evolving activity has been estimated using O^* binding energies as a descriptor. The studies^{6,7} have shown that scaling relationships can be established between the binding energies of HO^* , HOO^* , and O^* species on oxide surfaces. The scaling relations suggest that there is only one free parameter that determines the free energy diagram and thereby the activity. In other words, the activity can be plotted as a function of only one parameter, for example, the oxygen binding energy.

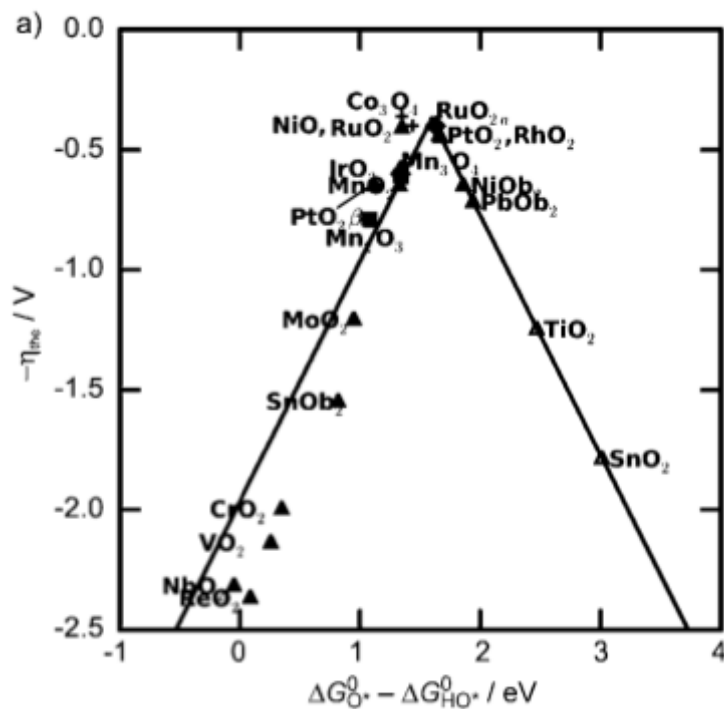


Figure 4. Activity trends towards oxygen evolution, for rutile, anatase, Co_3O_4 , Mn_xO_y oxides.

The result is a volcano-shaped relationship between catalytic activity and the calculated oxygen adsorption energy. Prof. J.K. Norskov found that on the surfaces that bind oxygen too strongly, the potential is limited by the formation of HOO^* species, whereas for surfaces that bind oxygen too weakly, the potential is limited by the oxidation of HO^* .^{6,7}

Reference

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