

# Rational Design of Oxide Catalyst for Oxygen Evolution Reaction

Tuğçe Kutlusoy

## Electrocatalysis of the transition metal oxides for the oxygen evolution reaction

Substantial effort has been devoted to find more effective catalysts for the oxygen evolution reaction and to elucidate the reaction mechanism. 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 and thereby energy losses at the anode, where oxygen is evolved, according to the following overall reaction, involving four electron transfers. Here, rational design of transition metal oxides for oxygen evolution reaction, is presented.

### Oxygen evolution reaction (OER)

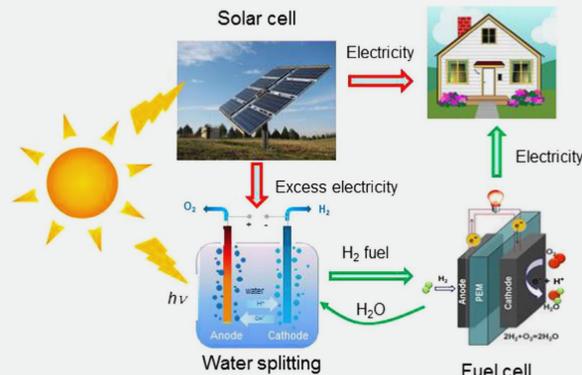
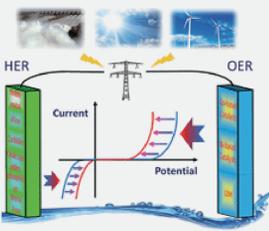
The splitting of water into hydrogen and oxygen is a vital component of a promising renewable energy infrastructure.

The overall process of water splitting comprises two half reactions.

- The evolution of O<sub>2</sub> (in the anode)
- The evolution of H<sub>2</sub> (in the cathode)

The water oxidation ( $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$ ) step has been considered the bottleneck of this process due to the necessary overpotential in the anod.

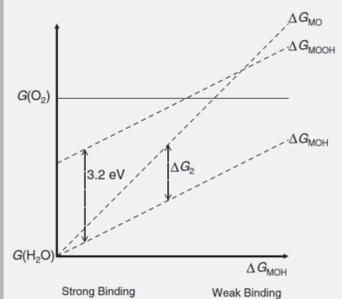
OER mechanism consists of four consecutive proton and electron transfer steps via 3 intermediates (\*OH, \*O, \*OOH).



Schematic representation of the energy cycle using water electrolysis to store excess solar electrical energy and fuel cells to provide the electricity during the low peak or night period. Adapted from Cheng et al. (2015)

### Modelling the Electrocatalyst

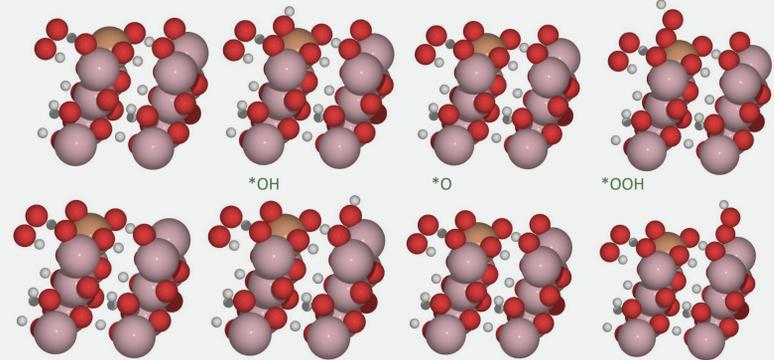
The overall process itself, however, is limited by the kinetically sluggish oxygen evolution reaction (OER) at the anode. Finding a stable and affordable catalyst with good OER activity is therefore a critical bottleneck in any future electrochemical energy storage device. The task of the rational design is to prepare catalysts nearing the apex of the volcano curve.



of the volcano curve.

Schematic representation of the scaling relations for  $\Delta G_{\text{MOH}}$ ,  $\Delta G_{\text{MO}}$  and  $\Delta G_{\text{MOOH}}$  as functions of  $\Delta G_{\text{MOH}}$ . The constant difference between  $\Delta G_{\text{MOH}}$  and  $\Delta G_{\text{MOOH}}$  of 3.2 eV and the universal activity descriptor  $\Delta G_2$  are also shown. Adapted from Rossmeisl (2013). OER activity trends for rutile, anatase,  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3$  oxides. The negative values of the theoretical overpotential are plotted against the standard free energy difference of  $\Delta G_{\text{MO}} - \Delta G_{\text{MOH}}$ . Adapted from Man et al. (2011)

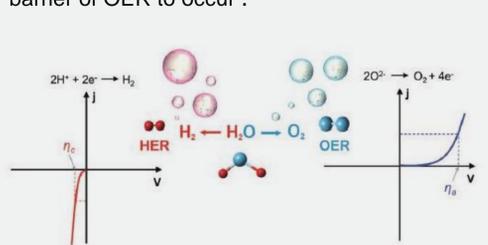
Previous studies have shown that cobalt surface can lead to significant decreases in the theoretical overpotential for OER. We carried out similar calculations in order to determine the extent to which the overpotential for  $\beta\text{-CoOOH}$  could be reduced by substitutional doping of a Co active site by another transition metal cation. The evolution of O<sub>2</sub> is assumed to occur not only at the dopant site but also at the cobalt active site with neighboring dopant atom. The binding energies of the intermediates O\*, HO\*, and HOO\* was obtained using DFT with RPBE exchange-correlation functional.



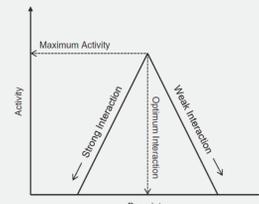
Fe doped CoOOH (01-12) and intermediates

### Overpotential and Volcano Plot

One of the important reasons that keeps these systems from being of practical use to date is the sluggish kinetics (high overpotential ( $\eta$ ),  $\eta_a > \eta_c$ ) of the oxygen evolution reaction. OER is a four electron-proton coupled reaction while HER is only a two electron-transfer reaction, and hence it can be easily expected that OER requires a higher energy (higher overpotential) to overcome the kinetic barrier of OER to occur.



Polarization curves for HER (left) and OER (right). The  $\eta_c$  and  $\eta_a$  are the overpotentials for cathode and anode at the same current ( $j$ ), respectively

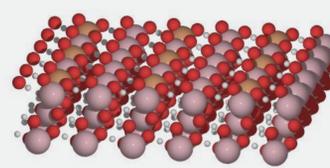


Schematic representation of a volcano plot which shows the variation in catalytic activity as a function of a reactivity descriptor. Maximum activity is achieved at an optimum descriptor value where the interaction of a key intermediate with the surface is neither too strong nor too weak

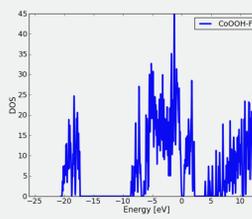
The (density functional theory) DFT-based computer screening of prospective catalysts constructs a "volcano" curve linking the predicted catalytic activity with a suitable reaction descriptor, typically the binding energy of a key intermediate. The apex of the volcano represents the optimal catalyst.

### Future Work

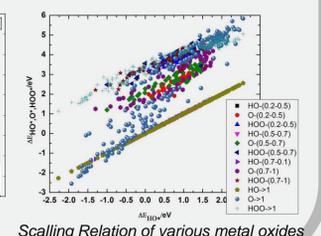
- Investigate the catalytic activity of the special sites on the selected surfaces (metal oxides).
- Focus on regarding trends of oxygen binding energy changes on the various metal oxides
- Assert a rational new mechanism for OER intermediates on the metal oxides (cobalt, nickel, ruthenium etc.)



CoOOH (01-12) (doped with Fe)



DOS of CoOOH (01-12) (doped with Fe)



Scalping Relation of various metal oxides

