

The forgotten term of the scaling relations in the oxygen electrocatalysis

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To ensure a successful shift to renewable energy sources, hydrogen production through electrocatalytic water splitting must be optimized. So far, this process has been limited by the oxygen evolution reaction (OER), which refers to the anodic part of the electrocatalytic water splitting. One piece of solving that puzzle is finding efficient and sustainable catalyst materials. From a theoretical perspective, the design of such catalysts is thermodynamically restrained by the so-called scaling relations,¹ i.e., linear functions that connect the adsorption energies of reaction intermediates to a descriptor. While the scaling relation between *OH and *OOH intermediates of the OER is well-established and has low variance, only the slope of the relation between *OH and *O has an estimated numerical value.² The intercept of this scaling relation is frequently assumed to be zero.³ In our latest work, we demonstrate how this assumption can lead to incorrect results. We simulate potential-dependent OER volcano plots at different intercepts by utilizing our in-house analysis technique of generalized mechanistic volcano plots.⁴ An example of such a plot is shown in Figure 1.⁵ It turns out that the intercept value of the *OH vs. *O scaling relation has a major impact on the shape of the volcano plot and the prevalent mechanism at the peak of the volcano plot. Our advanced volcano plots shed further light on limiting factors of the oxygen electrocatalysis and may enable further progress in the smart design of OER catalysts.

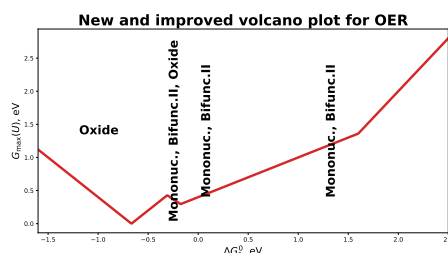


Figure 1. An example of a generalized mechanistic volcano plot at $U = 1.60$ V vs. reversible hydrogen electrode (RHE) applying $G_{\max}(U)$ as a measure for the electrocatalytic activity. Surprisingly, the oxygen evolution reaction volcano consists of a global minimum in which the oxide pathway predominates and a local minimum in which oxygen formation can occur via multiple mechanisms.⁵

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