

## The forgotten mechanism in electrocatalysis: On the importance of Walden steps for the modelling of energy conversion processes

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Since the birth of the computational hydrogen electrode approach,<sup>1</sup> it is considered that the activity trends of electrocatalysts in a homologous series can be quantified by the construction of volcano plots.<sup>2</sup> This method aims to steer materials discovery by the identification of catalysts with improved reaction kinetics, though evaluated by means of thermodynamic descriptors.<sup>3,4</sup> While the conventional volcano approach in the oxygen evolution reaction (OER) relies on the assumption of the mononuclear mechanism, consisting of the \*OH, \*O, and \*OOH intermediates,<sup>1,2</sup> in this contribution we report new mechanistic pathways comprising the idea of the Walden inversion in that bond-breaking and bond-making occurs simultaneously.<sup>5</sup>

In a recent communication, it was reported by our group that Walden-type mechanisms, in which the release of the product O<sub>2</sub> and the adsorption of the reactant H<sub>2</sub>O occur concurrently, govern the apex of the OER activity volcano plot.<sup>5</sup> Applying electronic structure calculations in the density functional theory (DFT) approximation, we have gained insight into the importance of Walden steps to the mechanistic description of various OER catalysts. While IrO<sub>2</sub> belongs to the golden standard in acid, cobalt oxide-based materials are superb electrocatalysts in alkaline media. Pentlandites, a class of iron-nickel sulfides, are also discussed as a promising material class for the alkaline OER. Taking representative surface facets for these three materials, it is demonstrated that the neglect of Walden steps to the OER mechanism leads to erroneous conclusions in terms of activity predictions or the identification of limiting reaction steps.<sup>6</sup> We conclude that the mechanistic motif of Walden inversion steps has far-reaching implications beyond the oxygen electrocatalysis by referring to other electrocatalytic processes such as the electrochemical nitrogen reduction reaction.

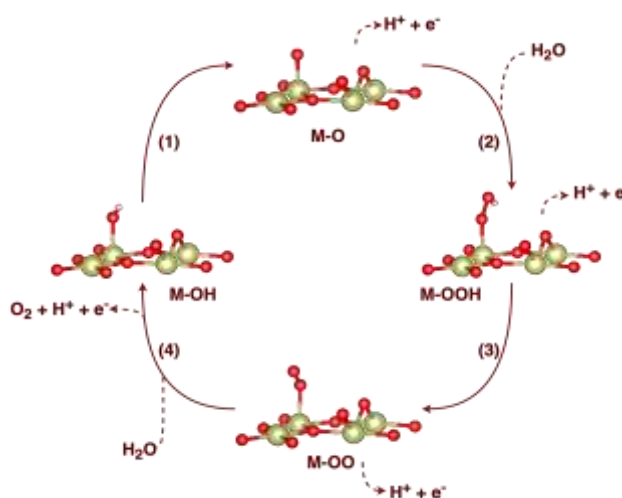


Figure 1. Example of a Walden-type OER mechanism, in which the release of the product O<sub>2</sub> and the adsorption of the reactant H<sub>2</sub>O takes place concurrently in step (4).

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### References

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