

Report on the Max Buchner research project

Identifying the optimum hydrogen binding energy of hydrogenases

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Motivation

Hydrogenases are metalloenzymes with an outstanding activity for the conversion of molecular hydrogen into protons or electrons and its reverse reaction. Without any ado, hydrogenases are highly efficient bifunctional catalysts for the hydrogen evolution (HER) and hydrogen oxidation (HOR) reactions. The bifunctional hydrogen electrocatalysis takes place in unitized regenerative proton exchange membrane fuel cells (UR-PEMFC) when switching between the electrolyzer (HER) and fuel cell (HOR) modes.

In chemical industry, solid-state electrodes rather than molecular entities are used for the energy conversion of chemical and electrical forms of energy such as encountered in UR-PEMFC. Despite this, solid-state electrodes commonly reveal lower intrinsic activities than hydrogenases. To better understand the difference in intrinsic activity between solid-state electrodes and metalloenzymes, we have designed a microkinetic study based on a dedicated modeling approach using the Python software.

Results

We have performed microkinetic simulations by steady-state analysis for the two-electron HER and HOR following the Volmer-Heyrovsky or Volmer-Tafel mechanisms and evaluated their bifunctional performance by means of Tafel-slope analysis. The code of our microkinetic simulations is freely accessible on Zenodo.^[1]

Based on our data-driven framework, we identify a general criterion for efficient bifunctional performance of solid-state materials in the hydrogen electrocatalysis, which refers to a change in the reaction mechanism when switching from cathodic to anodic working conditions. Only if a change in the reaction mechanism is observed, a solid-state material reveals excellent intrinsic activity for the HER and HOR both. Our modeling study has been published in a special issue of the journal *iScience*, and we refer to our recent publication for further details.^[2]

Implications of the results

Our microkinetic simulations rely on the adoption of proton-coupled electron transfer steps as this is the common assumption for solid-state electrodes under applied bias. On the contrary, it has been experimentally demonstrated in various works that the elementary steps of the HER and HOR over hydrogenases follow decoupled proton-electron transfer due to separate proton and electron channels in the active site environment.

Therefore, we conclude that the main difference in intrinsic activity between solid-state electrodes and metalloenzymes can be related to the transfer of proton and electrons in the mechanistic pathways by referring to coupled and decoupled steps, respectively. Consequently, there is *not an optimum hydrogen binding energy* of hydrogenases as these metalloenzymes largely rely on hydrogen in various forms, ranging from negatively charged hydride to positively charged hydrogen species. This contrasts with solid-state electrodes where adsorbed hydrogen, *H , is reconciled with the key intermediate in the HER and HOR. To enhance the intrinsic activity of solid-state materials for the bifunctional hydrogen electrocatalysis, we suggest decoupling the proton-electron transfer, thus mimicking the mode of operation of the metalloenzyme.

References

- [1] Razzaq, S.; Exner, K. S. DOI: 10.5281/zenodo.10368516
- [2] Razzaq, S.; Exner, K. S. Why efficient bifunctional hydrogen electrocatalysis requires a change in the reaction mechanism. *iScience* **2024**, *in press*, DOI: 10.1016/j.isci.2024.108848.